

Kinetics of Heterogeneous Nucleation

D. TURNBULL

Research Laboratories, General Electric Company, Schenectady, New York

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Consider a phase transition $\alpha \rightleftharpoons \beta$. Stable β -embryos can be retained in the temperature range of α -stability in cavities of suitable extraneous solids present in the system. Retained β -embryos may nucleate the $\alpha \rightarrow \beta$ -transformation in the range of β -stability.

Using these concepts a theory for the effect of thermal history upon the kinetics of phase transformations is proposed. The kinetics of heterogeneous nucleation in the absence of retained embryos is discussed.

INTRODUCTION

MOST of the theories for the kinetics of nucleation that have been advanced apply to "homogeneous nucleation" which is initiated in the interior of a single phase. The nucleation theory of Becker and Doring¹ was successful semiquantitatively in accounting for the experimental results of Volmer and Flood² on the rate of nucleation of liquids in supersaturated vapors.

Although theories of homogeneous nucleation have had some qualitative success in explaining certain features of the kinetics of nucleation in condensed systems, many investigations have indicated that nucleation in these systems is "heterogeneous," that is nuclei form preferentially at some interface in the system. Particularly for liquid-solid transformations in relatively large volumes of liquid the evidence seems decisive that at least the first few nuclei that appear originate by a heterogeneous mechanism at the surfaces of the containing vessel or of colloidal inclusions in the system. If the growth rate is rapid these few nuclei may transform the entire sample without the formation of homogeneous nuclei.

An important characteristic of liquid-solid transformations in relatively large samples is the very marked effect of thermal history upon the rate of the process first observed by Othmer.³ Richards and co-workers^{4,5} have made comprehensive studies of the phenomenon and obtained convincing evidence that it must be explained in terms of extraneous structures present in the system. Webster⁶ has shown that the effect also is important in the solidification of certain bulk metals. Similarly, the author has observed that the solidification of gallium is very thermal history dependent. Gallium is advantageous for study because of the very rapid growth rate (at least 1 cm/sec. at 0°C) of the crystal so that the kinetics of the transformation are generally controlled by the nucleation rate alone.

The effect of thermal history upon the kinetics of many liquid-solid bulk transformations is illustrated

schematically in Fig. 1. ΔT_+ is the number of degrees above the melting point, T_m , to which the liquid is heated after melting. ΔT_- is the number of degrees that the liquid must be subsequently sub-cooled in order for nucleation to occur during some specified holding time at the lower temperature. In the region of the curve ab which usually extends only a few degrees above the melting temperature, ΔT_- is strongly dependent upon ΔT_+ while in the region bc ΔT_- is virtually independent of ΔT_+ . For example, in gallium samples the region ab extended to about 20° above the melting point but for a given sample ΔT_- was found to be independent of ΔT_+ , within experimental error, for values of the latter ranging between 50 and 1050°.

The following are a number of other important features of the thermal history effect.

1. The length of time in the sub-cooled range does not alter the relation between ΔT_- and ΔT_+ significantly. In experiments with gallium the whole curve was shifted only 1-2° toward higher temperatures when the holding time was shifted from the order of a few minutes to one day.

2. Increasing the time at temperature above the melting point, after a certain minimal period—usually of the order of a few minutes, does not significantly affect the value of ΔT_- subsequently observed.

3. ΔT_- is generally characteristic of the highest temperature attained in the ΔT_+ region.

4. When a sample is solidified after having been heated in the bc -region the ΔT_- vs. ΔT_+ relation originally obtained is usually not changed significantly. Certainly this is true for gallium. However, there are exceptions to this behavior. Hinshelwood and Hartley⁷ observed that after sulfur samples are heated into the bc -region and then solidified the ΔT_- vs. ΔT_+ relation is altered so that the ΔT_+ coordinate of b is only an insignificant fraction of its former value.

5. Richards demonstrated that the phenomenon was highly sensitive to added inclusions such as activated charcoal or powdered quartz. These inclusions greatly increased the temperature (by as much as 100-150° in some cases) in the ΔT_+ region that it was necessary to reach before ΔT_- became independent of ΔT_+ .

6. According to Richards the maximum sub-cooling

¹ R. Becker and W. Doring, *Ann. d. Physik* (5) **24**, 719 (1935).

² M. Volmer and H. Flood, *Zeits. f. physik. Chemie* **170A**, 273 (1934).

³ P. Othmer, *Zeits. f. anorg. allgem. Chemie* **91**, 235 (1915).

⁴ W. T. Richards, *J. Am. Chem. Soc.* **54**, 479 (1932).

⁵ Richards, Kirkpatrick, and Hutz, *J. Am. Chem. Soc.* **58**, 2243 (1936).

⁶ W. L. Webster, *Proc. Roy. Soc.* **140A**, 653 (1933).

⁷ C. N. Hinshelwood and H. Hartley, *Phil. Mag.* **43**, 78 (1922).

obtainable for bulk specimens is independent of added inclusions. However, the author observed that this value was specific for particular gallium specimens and ranged from 35 to 55°. The specificity was not significantly changed by heating to ΔT_+ values of 1050°.

Richards proposed a qualitative theory for the effect of thermal history upon the transformation kinetics based on the concept that extraneous structures retain a "crystalline adsorbate" above the melting temperature. This adsorbate is stabilized in the region of liquid stability by a negative heat of adsorption on the extraneous structures. As the temperature of the liquid is increased the crystalline adsorbate becomes less stable and finally disappears altogether at some elevated temperature. He supposes that its rate of reformation is very slow so that the process of heating into the bc -region is essentially irreversible, as observed.

Other investigations that demonstrated the role of extraneous surfaces in promoting the nucleation of solid phases in liquids are those of Goetz,⁸ Hammer⁹ and Meyer and Pfaff.¹⁰

Although it has been recognized (see Johnson and Mehl¹¹) that a large number of solid-solid transformations are nucleated preferentially at grain boundaries, there seems to be little systematic information regarding the role of extraneous particles of other phases located either at the grain boundary or within the grain in promoting nucleation in solid-solid transformations. In view of the evidence on liquid-solid transformations it is expected that such influences may prove to be very important in many reactions involving only solid phases. Avrami¹² has developed a theory for the kinetics of such transformations in which it is supposed that all nuclei originate from pre-existing embryos, some of which presumably might be stabilized by extraneous particles of other phases.

It is the purpose of this paper to develop further the theory of the kinetics of heterogeneous nucleation. An

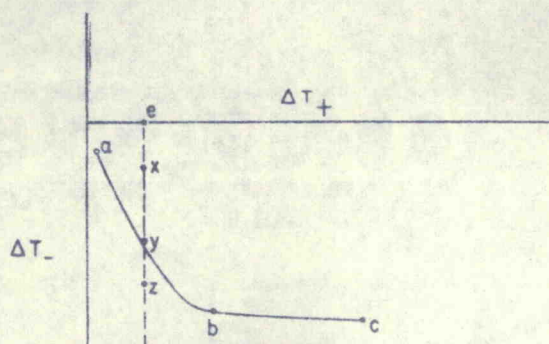


FIG. 1. Effect of thermal history on temperature of rapid nucleation in liquid-solid transformations.

⁸ A. Goetz, Phys. Rev. **35**, 193 (1930).

⁹ C. Hammer, Ann. d. Physik **33**, 445 (1938).

¹⁰ J. Meyer and W. Pfaff, Zeits. f. anorg. allgem. Chemie **217**, 257 (1934).

¹¹ W. A. Johnson and R. F. Mehl, Trans. A.I.M.E. **135**, 416 (1939).

¹² M. Avrami, J. Chem. Phys. **7**, 1103 (1939).

explanation for the effect of thermal history upon transformation kinetics will be offered along the lines of the basic concepts suggested by Richards, but in more explicit terms containing the interfacial energies involved rather than heats of adsorption. A more

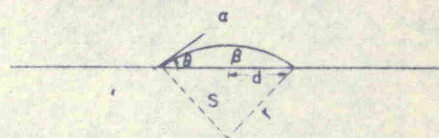


FIG. 2. β =embryo on a flat surface, θ =equilibrium contact angle.

mechanistic explanation will be offered for the irreversibility of the phenomena with respect to temperature.

THEORY

Volmer¹³ has calculated the work of nucleating a phase β in the transformation $\alpha \rightarrow \beta$, where β is considered to be the low temperature modification, on a flat solid substrate denoted by S . Let the contact angle between the β -embryo and S be θ as shown in Fig. 2. Then for $180^\circ > \theta > 0$

$$\sigma_{\alpha-S} = \sigma_{\beta-S} + \sigma_{\beta-\alpha} \cos \theta, \quad (1)$$

where σ denotes interfacial energy. If it is assumed that the σ 's are isotropic the free energy ΔF required to form an embryo having the shape of a spherical sector is,¹³

$$\Delta F = [\pi r^3 (f_\beta - f_\alpha) / 3v_\beta + \pi r^2 \sigma_{\beta-\alpha}] \times [2 - 3 \cos \theta + \cos^3 \theta], \quad (2)$$

where f is the free energy per-atom, v =volume per atom, and r is the radius of the sphere. In the region of α -stability there is no possibility of retaining β -embryos on flat surfaces for which the condition $\theta > 0$ holds since the term involving surface energy in (2) is always positive for this condition. Volmer¹³ shows that the work of forming a nucleus of critical size is,

$$[16\pi\sigma_{\beta-\alpha}^3 v_\beta^2 / 3(f_\beta - f_\alpha)^2] [(2 + \cos \theta)(1 - \cos \theta)^2 / 4] \quad (3)$$

which differs from the work of forming a nucleus in the interior of α by the factor $[(2 + \cos \theta)(1 - \cos \theta)^2 / 4]$.

When $\sigma_{\alpha-S} > \sigma_{\beta-S} + \sigma_{\beta-\alpha}$ some β -adsorbate can be retained on S at temperatures not greatly exceeding the equilibrium temperature, T_0 . If this β -adsorbate is removed by heating to a temperature greatly exceeding T_0 the only positive work of subsequently nucleating β on S at $T < T_0$ is that of forming the periphery of the β -embryo.

Volmer¹⁴ has pointed out that stable embryos of phase β can be retained in cavities of various types in the substrate S at temperatures in excess of T_0 under the proper conditions which may include values of θ considerably greater than zero such that no β -adsorbate

¹³ M. Volmer, Zeits. f. Elektrochemie **35**, 555 (1929).

¹⁴ M. Volmer, *Kinetik der Phasenbildung* (Steinkopf, Leipzig, 1939), p. 103.

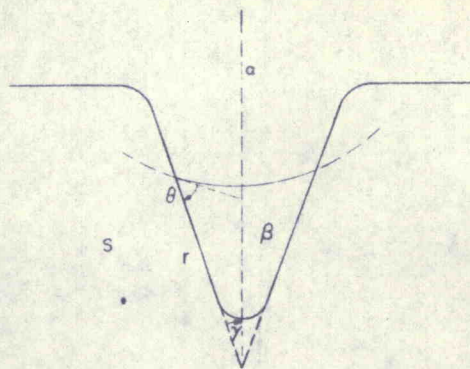


FIG. 3. Nucleation in a conical cavity.

is stable on a perfectly flat surface. This concept will form the basis of our theory for the effect of thermal history upon the kinetics of the $\alpha \rightarrow \beta$ -transition. In our treatment the retention of embryos in conical and cylindrical cavities will be considered.

Consider a conical cavity in surface S as shown in Fig. 3. It is assumed that the bottom and edges of the cavity are rounded. Neglecting the volume change due to the rounding of the bottom of the cavity the work of forming the embryo in the cavity is:

$$\Delta F = \pi r^2 (f_\beta - f_\alpha) \varphi / v_\beta + \pi r^2 \sigma_{\beta-\alpha} [2\mu - \sin \gamma \cos \theta], \quad (4)$$

where φ and μ are trigonometric functions given by:

$$\varphi = [\sin^2 \gamma \cos \gamma / 3 - 2 \sin^3 \gamma / 3 \cos^3 (\gamma + \theta) + \sin^3 \gamma \tan (\gamma + \theta) / \cos^2 (\gamma + \theta) - \sin^3 \gamma \tan^3 (\gamma + \theta) / 3]$$

$$\mu = [\sin^2 \gamma / \cos^2 (\gamma + \theta) - \sin^2 \gamma \tan (\gamma + \theta) / \cos (\gamma + \theta)].$$

In Eq. (4) the surface energy term can be negative for values of γ and θ such that $\cos \theta > [2 \sin \gamma / \cos^2 (\gamma + \theta)] \times [1 - \sin (\gamma + \theta)]$. Figure 4 shows the free energy relations involved in forming β -embryos in cavities for $T > T_0$ for this situation.

At each temperature above T_0 there is a stable position of the α - β -interface specified by r_0 . As the temperature increases r_0 becomes less and the embryos will disappear altogether when r_0 becomes of the order of the dimensions of the bottom of the cavity. After the embryos have been destroyed by the high temperature treatment a positive free energy at a lower temperature must be expended (see Fig. 4b) to reform them because this process must begin on surfaces which are approximately flat (i.e., on the rounded bottom of the cavity).

In cylindrical cavities (see Fig. 5) the work of embryo formation is given by:

$$\Delta F = \pi r^2 h (f_\beta - f_\alpha) / v_\beta + 2 \pi r \sigma_{\alpha-\beta} \times [r(1 - \cos \theta) / \sin^2 \theta - h \cos \theta]. \quad (5)$$

For values of h sufficiently large the surface energy term in Eq. (5) will be negative. However, the factor that determines whether or not β -embryos will be retained in the pores above the transformation tem-

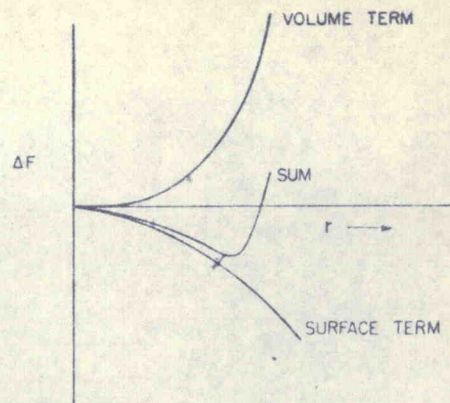


FIG. 4a. Free energy of embryo formation in conical cavity above transformation temperature.

perature is the coefficient p , of h in (5)

$$p = \pi r^2 (f_\beta - f_\alpha) / v_\beta - 2 \pi r \sigma_{\alpha-\beta} \cos \theta.$$

If p is negative β -embryos are retained. This condition is fulfilled when

$$m = 2 \sigma_{\alpha-\beta} \cos \theta (v_\beta) / (f_\beta - f_\alpha) > r. \quad (6)$$

The work of embryo formation as a function of h and r is shown schematically in Fig. 6. Again it is noted that after retained β -embryos are destroyed by heating to high temperatures their reformation at a lower temperature involves an increase in free energy. For each temperature there is a critical value of $r = m$ such that no β -embryos are retained in pores exceeding this size. m decreases sharply as the temperature increases.

The existence of retained embryos in cavities on the container wall or in extraneous particles explains satisfactorily the effect of thermal history on the rate of nucleation. Suppose that the β -phase is heated above T_0 by varying amounts $= \Delta T_+$. The maximum values of γ and r for conical and cylindrical cavities in which embryos are retained are shown as functions of ΔT_+ in Fig. 7.

When α is now sub-cooled into the β -region, the embryos retained in the conical or cylindrical cavities will immediately grow to the mouth of the cavity. However, they are not nuclei for the α - β -transformation unless the radius at the cavity opening equals or exceeds the critical radius for nucleation of a spherical

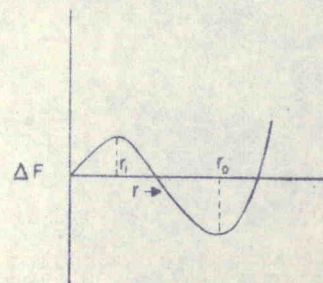


FIG. 4b. Free energy of embryo formation in conical cavity with a rounded bottom.

sector of β on the flat surface

$$d^* = -2\sigma_{\alpha-\beta}r\beta \sin\theta / (f_\beta - f_\alpha). \quad (7)$$

For simplicity it is assumed that the edges of the cavity openings are curved but that the radii of curvature are negligible in comparison with the radii of the openings. Thus, for cylindrical cavities m decreases with ΔT_+ and since d^* decreases with increasing ΔT_- it is evident that the degree of sub-cooling required to cause a β -embryo retained in a cylindrical cavity to become a nucleus will increase as ΔT_+ increases. Similar arguments hold for the promotion of β -embryos in conical cavities to nuclei since the dimensions of the mouths of the cavities will be proportional roughly to γ .

Reformation of β -embryos in cavities at low temperatures after they have been destroyed by a high temperature treatment will be a sluggish process because of the free energy barrier (Figs. 4b and 6) to be surmounted. In some instances the extraneous particles that carry the cavities catalyzing nucleation may dissolve in the α -phase at high temperature. When this occurs, the α - β -transition may be no longer thermal history sensitive for the particular sample.

It is interesting to inquire how the observed nucleation rate of the α - β -transformation changes with time and temperature when embryos are retained. Suppose (see Fig. 1) that samples are heated into the α -range to a ΔT_+ value indicated by e and then quenched to the various values shown. Specimens quenched to z will have retained β -embryos which are supercritical, and these will nucleate immediately. If the growth rate is very slow, some embryos which were only slightly subcritical may nucleate and grow. In any event, the nucleation rate will be a maximum at zero time and will fall off sharply thereafter.

When the sample is quenched to a ΔT_- value of x , all retained β -embryos are sub-critical with respect to nucleation at this temperature. The additional free energy necessary to nucleate them may be so large that no nuclei will form in a reasonable period of time.

At a ΔT_- indicated by y there are a number of retained embryos which are very close to the critical size for nucleation. These retained embryos may nucleate in

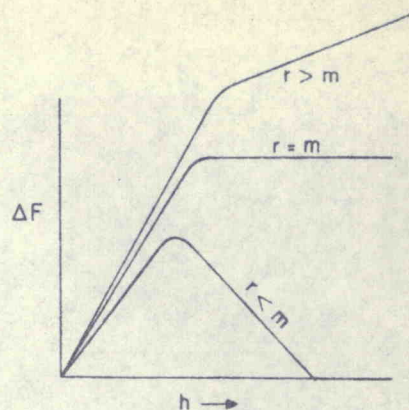


FIG. 6. Free energy of embryo formation in a cylindrical cavity as a function of h .

time, but still later the nucleation rate will decrease as the retained embryos are used up. In general, the rate of nucleation, I , for this case will go through a maximum with time as shown in Fig. 8. If y is very close to the curve ΔT_- vs. ΔT_+ or if the rate of transport across the interface is very rapid, the initial increase, $0x$, may not be observed at all.

For example, Hammer⁹ has published curves showing the variation in I with time for some liquid-solid transitions which resemble the curve in Fig. 8 excepting that the initial increase is absent. The way in which the total number of nuclei appearing isothermally in the range y changes with temperature will be governed by the size distribution curve for cavities in which embryos are retained. Since the number of cavities generally will increase with decreasing cavity size, the nucleation number will increase as the temperature is lowered.

From Eqs. (6) and (7) and setting

$$f_\beta - f_\alpha \approx \lambda(T_0 - T)/T_0,$$

where λ = heat of transformation per atom, a simple equation relating ΔT_- and ΔT_+ can be derived for cylindrical cavities,

$$\Delta T_- / \Delta T_+ = \tan\theta. \quad (8)$$

This equation holds only for one type of catalyst and

FIG. 5. Nucleation in cylindrical cavity.

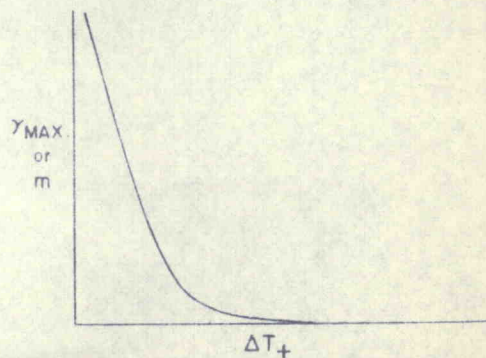
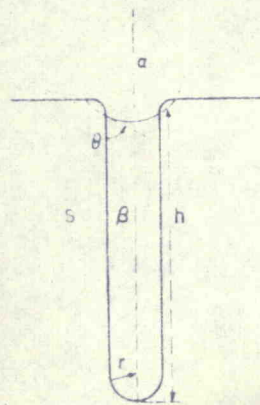


FIG. 7. Effect of thermal history on dimensions of cavities in which embryos can be retained.

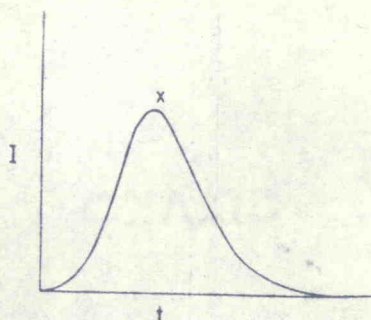


FIG. 8. Nucleation rate as function of time for a limited number of nucleation sites.

where the rate of production of nuclei on flat surfaces or in the interior of α by thermal fluctuations is practically nil. This will be so for relatively small values of ΔT_- . For larger values of ΔT_- the number of nuclei produced by thermal fluctuations becomes very large in comparison with the number originating from embryos retained in cavities; under these conditions, ΔT_- is constant with respect to ΔT_+ as shown by the *bc* portion of Fig. 1.

In order to find the order of magnitude of cavity sizes necessary to explain the observed effects in terms of the theory developed, some calculations were made for the gallium liquid-solid transformation catalyzed by a substrate such that θ between the solid gallium (in equilibrium with the liquid) and the substrate was 60° ; thus, $\Delta T_- \approx 1.7\Delta T_+$. It was assumed that the interfacial energy between liquid and solid gallium¹⁸ is 55 ergs/cm². For $\Delta T_+ = 5$ embryos of solid gallium are retained in cylindrical cavities having diameters $\approx 140\text{\AA}$. These embryos are capable of growing at $\Delta T_- \approx 8.5$, and the number of gallium atoms contained in the spherical sector at the mouth of the cavity is of the order of 6000. It is evident that nucleation by thermal fluctuations at this value of ΔT_- in the absence of retained embryos is impossible. For $\Delta T_+ = 20^\circ$ the maximum diameter of cavities in which embryos are retained is $\approx 35\text{\AA}$ and $\Delta T_- \approx 34^\circ$. However, the number of atoms contained in the spherical sector at the cavity mouth is only about 100, so that nucleation by thermal fluctuations must become predominant at this temperature or slightly below it for the conditions assumed in the calculation.

When a specimen is cooled into the β -region from a temperature in the α -range where retained embryos have been destroyed the nucleation problem becomes one of forming nuclei on catalytic surfaces which are essentially flat. At steady state the number, n , of embryos of critical size per unit area of a given surface is

$$n \approx n_s \exp(-\Delta F^*/kT), \quad (9)$$

where n_s is the number of α -surface atoms per unit area and ΔF^* is given by Eq. (4).

The steady state rate of nucleation per unit surface, I_s , is $I_s = K \exp[-(\Delta F^* + q)/kT]$; where q is the activa-

tion energy required to move an atom across the α - β interface. ΔF^* differs from the free energy required for interior nucleation, ΔF_i^* , only by a factor involving the contact angle. Therefore, ΔF^* will vary with temperature in approximately the same way as ΔF_i^* while q remains essentially constant. Consequently I_s will generally pass through a maximum as the temperature is lowered from T_0 just as does I for interior nucleation. Also before the establishment of a steady state of surface nucleation a transient in which I_s accelerates with time should be observed as pointed out earlier.¹⁵ These features of heterogeneous nucleation in the absence of retained embryos are very similar qualitatively to those predicted by the theories of homogeneous nucleation. However, since ΔF^* is much smaller, the rate of heterogeneous nucleation will generally be much greater at a given temperature than the rate of homogeneous nucleation.

In some reactions there may be only a limited number of sites that promote nucleation. In this case the observed rate of nucleation may fall off with time after the rising transient in a way similar to that shown in Fig. 8. In the absence of a transient the rate of nucleation will change with time according to the equation given by Avrami¹² providing that all of the preferred nucleation sites are equivalent.

In order to test the theories of homogeneous nucleation rigorously it is important to devise experiments in which nucleation catalysts are eliminated or localized. Experiments are usually performed on bulk samples where one or more nuclei originating from catalytic sites are able to transform the entire sample under observation. In order to prevent this from occurring, it is desirable that the sample be broken into a large number of small isolated parts. This is accomplished in the well-known experiments of V. Schaefer¹⁶ on the nucleation of snow crystals in a fog of water droplets. B. Vonnegut¹⁷ has used a somewhat similar technique in his study of the liquid-solid transition in tin particles. Also, the author¹⁸ has applied this procedure to mercury and gallium. In these investigations a much larger degree of sub-cooling was obtained than can generally be obtained when bulk samples are sub-cooled.

Observations of the kinetics of transformations on fine dispersions have the following advantages to the study of nucleation:

1. Since the linear growth rate in transformations is approximately constant and the rate of nucleation is proportional to the volume, it is highly probable that in very small droplets one nucleus transforms the whole mass of the droplet. Therefore, observations on the rate of transformation constitute a direct measure of the nucleation rate.
2. Only a negligible number of droplets contact the container walls at any point, so that any points on these walls which promote nucleation are no longer effective.

¹⁵ D. Turnbull, *Metals Tech.* 15, T.P. 2365 (1948).

¹⁶ V. J. Schaefer, *Bull. Am. Meteorolog. Soc.* 29, 175 (1948).

¹⁷ B. Vonnegut, *J. Colloid Science* 3, 563 (1948).

¹⁸ D. Turnbull, *J. App. Phys.* 20, 817 (1949).

3. Extraneous particles promoting nucleation, if their number is not large, may be localized on a negligible proportion of the droplets.

4. If the interfaces are properly chosen, nucleation takes place at the interior of the droplet rather than at the surface. This requires that the material at the interface "wet" the parent phase better than the phase which is forming.

Thus, the technique of observing transformation kinetics on finely dispersed droplets of the mother phase covered by a good wetting agent appears to offer the most promise in measuring rates of homogeneous nucleation in condensed systems. For this purpose it is highly desirable to have dispersions in which the droplet size is very uniform, and accurately known. Under

these conditions a simple kinetic expression may be written for the rate at which volume is transformed per unit time as follows:

$$dV/dt = I\tau(V_0 - V), \quad (10)$$

where V = total volume transformed in time, t , V_0 = total volume at $t=0$, I = rate of nucleation per unit volume, and τ = volume of the droplet. This expression assumes that the transient in the nucleation rate is over and a steady state obtains. Equation (10) may be integrated to give:

$$V = V_0[1 - \exp(-I\tau t)]$$

for the volume transformed in time t .