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## KINETICS OF GLASS FORMATION AND DEVITRIFICATION BEHAVIOR

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**Résumé.**- La formation du verre est considérée sous un aspect cinétique. La cinétique de nucléation, aussi bien homogène qu'hétérogène, ainsi que la croissance du cristal sont initialement suivies. Les informations obtenues dans ces domaines sont réunies avec des traitements de cristallisation pendant un refroidissement constant afin d'évaluer des vitesses critiques de refroidissement nécessaires à la formation de verres de différents matériaux. Les paramètres du matériau contribuant à la formation et au procédé de cristallisation à chaud du verre sont considérés. Le traitement cinétique est aussi utilisé pour décrire d'autres phénomènes comme les effets d'hétérogénéités de nucléation sur la formation du verre et l'utilisation d'expériences de DTA pour évaluer les barrières de la nucléation du cristal.

**Abstract.**- The process of glass formation is viewed from a kinetic perspective. Initial attention is directed to the kinetics of nucleation, both homogeneous and heterogeneous, and of crystal growth. Information obtained in these areas is combined with treatments of crystallization during continuous cooling to evaluate the critical cooling rates required to form glasses of various materials. Consideration is given to the material parameters which are conducive to glass formation, and to the process of crystallization on reheating of glass. The kinetic treatment is also used to describe other phenomena such as the effects of nucleating heterogeneities on glass formation and the use of DTA experiments to evaluate the barriers to crystal nucleation.

1. **Introduction.**- A liquid may solidify in either of two ways: it may form a crystalline solid, in which the molecules are regularly arranged on a lattice; or it can form an amorphous solid, called a glass, in which the molecular array is characterized by the absence of long-range order. It is generally believed (although not proven, to the author's knowledge) that crystalline solids represent the thermodynamically stable state of matter at low temperatures; but the formation of such solids requires the nucleation and growth of a new phase, and these processes do not take place with infinite rapidity. If the cooling rate is sufficiently rapid, relative to the kinetics of crystallization, the liquid phase can be cooled indefinitely without the occurrence of detectable crystallinity and a glass will be formed.

Once formed, amorphous solids can persist for long periods of time in their thermodynamically unstable state: recall the billion-year-old glasses returned from the surface of the moon, where they had been preserved at temperatures near ambient in the absence of mineralizing agents such as water. The very existence of amorphous solids provides a *prima facie* violation of the third law of thermodynamics in the form originally advanced by Nernst, and seems to require its restriction to systems

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in internal thermodynamic equilibrium, as suggested by Simon (1). Further, glasses are subject to the paradox noted by Kauzmann (2), viz., that if sufficient time were allowed for the amorphous system to reach equilibrium, extrapolation of the equilibrium properties (from above the glass transition) would suggest the existence of amorphous phases having smaller specific volumes and entropies than the corresponding crystals.

In addition to providing us with such intriguing fundamental problems, glasses are also of considerable technological importance. The past two decades have seen impressive progress across a broad front, ranging from the effective completion of the float glass revolution and the extensive exploration of semiconducting glasses and amorphous solar collectors, to the introduction of glass optical waveguides as essential parts of optical communications systems and glassy passivation layers in integrated circuit devices.

It is now widely recognized that glass formation is not restricted to the familiar silicates, or even to oxide materials more generally. Glassy polymers such as polycarbonate and polymethyl methacrylate are important articles of commerce; metal alloy glasses are receiving wide attention; and simple organic glasses, fused salt glasses, and aqueous solution glasses have all been extensively investigated.

While glasses can be formed in a wide variety of ways, ranging from flame hydrolysis and vacuum vapor deposition to shock wave treatment of crystals and electrolytic deposition (see Ref. 3 for extensive discussion), the cooling of a melt is by far the most important. Since a cooling melt can crystallize at temperatures below the liquidus, the process of glass formation seems best viewed from the perspective of whether detectable crystallinity will develop at a given cooling rate. This, in turn, directs attention to the processes of crystal nucleation and growth, whose kinetics establish a time scale for the cooling process.

The present paper will be concerned with the kinetic conditions required to form glasses of various materials, and in particular with kinetic treatments which consider both nucleation and crystal growth. Other approaches to the issue of glass formation have been discussed elsewhere (4, e.g.). Specific attention will be directed to recent applications of the kinetic analysis to areas such as crystallization on reheating a glass, the role of nucleation transients in glass formation, and the measurement of nucleation rates.

2. Nucleation and Crystal Growth.- The steady state rate of homogeneous nucleation  $I_V^{Ho}$  displays a complex temperature dependence:

$$I_V^{Ho} \approx N_V^0 \nu \exp\left(-\frac{K_1 \sigma^3}{kT\Delta G_V}\right) \quad (1)$$

Here  $N_V^0$  is the number of molecules per unit volume in the liquid;  $\nu$  is the frequency of atom transport at the nucleus-matrix interface;  $K_1$  is a geometric factor

( $K_1 = \frac{16\pi}{3}$  for spherical nuclei);  $\sigma$  is the crystal-liquid surface free energy;  $\Delta G_V$  is the difference in Gibbs free energy per unit volume between liquid and crystal; and  $k$  is Boltzmann's constant.

At small undercoolings,  $\Delta T$ , below the melting point,  $T_E$ ,  $\Delta G_V$  increases linearly with undercooling, as

$$\Delta G_V \approx \Delta H_V \frac{\Delta T}{T_E} \quad (2)$$

where  $\Delta H_V$  is the heat of fusion per unit volume. For metals, this expression provides a good approximation over a wide range of undercooling (5); but for most oxides and simple organics, the expression due to Hoffman (6) - which considers the difference in heat capacity between crystal and liquid - represents a better approximation:

$$\Delta G_V \approx \Delta H_V \frac{\Delta T}{T_E} \frac{T}{T_E} \quad (3)$$

It is often assumed that the temperature dependence of the frequency factor,  $\nu$ , is the same as that of the viscosity,  $\eta$  :

$$\nu = b / \eta \quad (4)$$

For simple organics, the coefficient  $b$  may well be taken as the Stokes-Einstein value:

$$b = \frac{kT}{3\pi a_0^3} \quad (5)$$

where  $a_0$  is a molecular diameter. For complex oxides, such as the familiar silicates, recent work (7) has suggested a proportionality factor larger by about a factor of 40:

$$b \approx \frac{40 kT}{3\pi a_0^3} \quad (6)$$

The overall variation of nucleation rate with temperature reflects both the variation of viscosity with temperature - itself rather complex save for the classic network liquids ( $\text{SiO}_2$ ,  $\text{GeO}_2$ ,  $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{SiO}_2$ ), which exhibit Arrhenian behavior - and the variation of  $\exp(-K/T\Delta G_V^*)$ . It would therefore be remarkable to observe, over any extensive range of temperature, an Arrhenian temperature dependence of  $I_V$ .

When nucleating heterogeneities are present in a sample, one must also consider their effect on the nucleation rate. This is usually effected using the familiar spherical cap model of the nucleus, with result :

$$I_V^{\text{HET}} = n_V^0 N_V^{2/3} A \nu \exp - \frac{K_1 \sigma^3 \phi}{kT\Delta G_V^2} \quad (7)$$

where  $n_V^0$  is the number of heterogeneities per unit volume,  $A$  is the area per heterogeneity, and  $\phi$  can be expressed :

$$\phi = \frac{(2+\cos\theta)(1-\cos\theta)^2}{4} \quad (8)$$

Here  $\theta$  is the contact angle between nucleating substrate and crystal nucleus.

In treating the process of heterogeneous nucleation, it should be noted that the number of active heterogeneities is depleted as such nucleation occurs. This depletion can be approximated in terms of its effect on  $n_V$  (8) :

$$n_V^t \approx n_V^0 (1 - I_V^{\text{HET}} V t) \quad (9)$$

where  $n_V^t$  and  $n_V^0$  are the concentrations of nucleating heterogeneities at time  $t$  and initially; and  $V$  is the volume of the sample. This equation assumes that each heterogeneity can provide a single nucleation event.

With one notable exception (9, 10), experimental data on homogeneous nucleation are generally in good accord with classical nucleation theory, Eqn. (1) above (11, 12, e.g.). Both the temperature dependence and the pre-exponential constant are in reasonable accord with predictions of the theory. This is illustrated by the data on anorthite ( $\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ ) in Fig. 1. As predicted by Eqns(1) + (3) + (4), the  $\ln I_V$  vs  $(\Delta T_r T_r)^{-1}$  relation is a straight line of negative slope. Here  $\Delta T_r = \Delta T/T_E$  and  $T_r = T/T_E$ . The intercept in Fig. 1 yields a pre-exponential factor of  $10^{27} \text{ cm}^{-3} \text{ sec}^{-1}$  poise, while theory predicts  $10^{29} - 10^{30} \text{ cm}^{-3} \text{ sec}^{-1}$  poise.

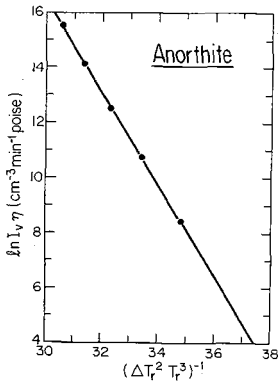


Fig. 1. Logarithm ( $I_v \eta$ ) vs.

$(\Delta T_r^2 T_r^3)^{-1}$  relation for anorthite.  
After Ref. 11.

In contrast to the agreement between experiment and classical theory shown in Fig.1, as well as that found for a variety of other materials, the results on  $Li_2O \cdot 2SiO_2$  are inconsistent - in the magnitude of the nucleation rate as well as in its temperature dependence - with the predictions of classical theory (9, 10). The origin of this discrepancy is not clear at the present writing. Experiments by Yinnon and Uhlmann on the heating rate dependence of the crystallization temperature of  $Li_2O \cdot 2SiO_2$  glass indicate "normal" behavior (i.e. behavior in accord with classical nucleation theory employed in the analysis), with a reasonable nucleation barrier. While studies of homogeneous nucleation in glass - forming systems are few in number, detailed studies of the kinetics of heterogeneous nucleation are almost non-existent. It is known that heterogeneities which provide a good match in lattice parameter with the crystal being nucleated (within perhaps 5 pct.) serve as potent nucleating catalysts. The situation seems less clear-cut, however, for heterogeneities which provide intermediate matches in lattice parameter (perhaps 10-15 %). In such cases, nucleation on adventitious heterogeneities (characterized by smaller contact angles ?) can still play a significant role. More interesting, and potentially more important, than such observations on second-phase impurities is the role of dissolved impurities in promoting crystal nucleation. There are scattered reports in the literature of various transition metal and rare earth ions having a significant effect in this regard; but much additional work, theoretical as well as experimental, is needed to provide the requisite insight.

For short crystallization times, the steady-state concentrations of sub-critical embryos may not be developed, and the nucleation rate may be time-dependent. Such time-dependent nucleation rates are often approximated by the expression of Zeldovich (13), which should be good for short times :

$$I_v^t \approx I_v^{SS} \exp(-\tau/t) \tag{10}$$

Here  $I_v^t$  and  $I_v^{SS}$  are the nucleation rates per unit volume at time  $t$  and in steady-state, the latter given by Eqn. (1); and the transient time  $\tau$  is given, to order - of - magnitude accuracy, as :

$$\tau \approx (n^*)^2 / \eta_s v \tag{11}$$

where  $n^*$  and  $\eta_s$  are the number of molecules in the critical nucleus and on the surface of the critical nucleus. The transient time,  $\tau$ , like the time for overall crystallization of a sample, should thus scale with the viscosity.

Turning now to the growth of crystals once nucleated, it should be noted that this process was discussed at length by the present author in a recent review (4). As noted there, the nature of the crystal-liquid interface on an atomic scale is expected to have a decisive influence on the morphology and kinetics of growth. According to

Jackson's criteria (15, 16), materials with small entropies of fusion ( $\Delta S_M < 2R$ ) should have crystal-liquid interfaces which are rough on an atomic scale, while those with large entropies of fusion ( $\Delta S_M > 4R$ ) should have smooth interfaces.

For small  $\Delta S$  materials, the macroscopic interfaces should be non-faceted in both crystallization and melting; the growth rate anisotropy should be small; the kinetics of melting and crystallization, corrected for the variation of viscosity with temperature, should be equal at equal departures from equilibrium; and the growth rate should be described by the normal growth relation :

$$u = v a_0 [1 - \exp(-\Delta H_M \Delta T / RTT_E)] \quad (12)$$

For large  $\Delta S$  materials, the macroscopic interfaces should be faceted in crystallization and non-faceted in melting; the growth rate anisotropy should be large; at equal departure from equilibrium, melting should take place more rapidly than crystallization; and the fraction of growth sites on the interface should increase significantly with increasing undercooling.

To describe crystal growth in such smooth-interface materials, two simple models have been proposed. They represent limiting cases which focus attention on growth at different types of sites.

(a) Growth at step sites provided by screw dislocations : Here the fraction of growth sites increases linearly with undercooling, reflecting the dislocations winding into tighter spirals. The growth rate is expressed :

$$u = f a_0 v [1 - \exp(-\Delta H_M \Delta T / RTT_E)] \quad (13)$$

where  $f$ , the fraction of growth sites on the interface, can be approximated :

$$f \approx \frac{\Delta T}{2\pi T_E} \quad (14)$$

(b) Growth at step sites at the perimeters of two-dimensional nuclei formed on the interface : Here the formation of surface nuclei represents the critical factor in growth, although the lateral growth of the nuclei across the interface should also be included in the analysis. The growth rate can be expressed :

$$u = Av \exp\left(-\frac{B}{T\Delta T}\right) \quad (15)$$

where  $A$  and  $B$  are constants, whose values depend on the detailed model used to describe growth (14).

These two models are based on two different views of the interface and step sites thereon. One considers a smooth but imperfect interface, the other an interface which is both smooth and perfect. Both neglect any roughness on the interface in regions other than the identified sources of steps. The latter represents a considerable assumption, which should be most in error for materials with  $\Delta S_M = 4R - 5R$  crystallizing at large undercoolings.

More realistic treatments of crystal growth have been provided by computer simulation techniques (for discussion and references, see Ref. 14). These techniques, employed by workers such as Jackson, Gilmer and Leamy, have yielded important new insights into the crystallization process, and have provided strong support for the views of Jackson concerning the nature of the crystal-liquid interface. They have indicated that the simple models should be most appropriate (1) for materials with small entropies of fusion and hence rough interfaces; and (2) for materials with very large entropies of fusion (as  $\Delta S_M > 10R - 15R$ ) crystallizing at modest undercoolings.

In considering any of the growth models - whether computer models or the expressions of Eqns (12), (13) or (15) - it is necessary to relate the frequency of transport at the interface,  $v$ , to some measurable quantity. It is suggested that Eqn. (4), together with Eqn. (5) or (6), be used for this purpose. For simple organic materials, it can readily be visualized that the reorientation of the molecules required for crystallization involves motions similar to those in viscous flow. For complex oxides such as the silicates, it seems reasonable that transport at the interface involves the breaking of directional bonds and reorganization of the network processes which again are similar to those in viscous flow. Support for this view is provided by the results of crystallization studies on  $\text{SiO}_2$ ,  $\text{GeO}_2$  and  $\text{Na}_2\text{O}\cdot 3\text{SiO}_2$ . For each of these materials, the growth rates are well described by theoretical models, provided Eqns (4) and (6) are used to represent  $v$ . The quality of the agreement between theory and experiment, and the wide range of temperature over which this agreement is observed (hundreds of Centigrade degrees in each case), is almost inconceivable without the suggested  $v$ - $\eta$  relation being applicable.

The discussion to here has been concerned exclusively with materials whose rates of crystallization are limited by interface attachment kinetics. For materials which melt to fluid liquids and materials which crystallize with sizable changes in composition, the crystal growth process is limited by diffusional processes (heat flow or mass diffusion) over much if not all of the range where crystallization takes place. The morphology of such crystallization often takes the form of dendrites, frequently parallel arrays of dendrites. Faceted crystals are sometimes observed as well, particularly at small undercoolings (21, 22).

The dendritic morphologies observed at sizable undercoolings represent the most common form of diffusion-controlled growth. Such growth typically takes place at rates which are independent of time, reflecting the scale of the diffusion field being independent of time (17). Theoretical descriptions are available for the growth of isolated dendrites (18) or parallel arrays of dendrites (19, 20). The growth rate in the latter case is determined by the interdiffusion coefficient in the melt (which is apparently inversely related to the viscosity), the size and spacing of the dendrites, and the differences between the concentration at the interface and those in bulk liquid and in the crystal.

The central problems at the present writing in this area are : (1) The determination of an independent relation between the radius of curvature of the dendrite tips and the undercooling; and (2) the determination of whether the faceted crystals observed at small undercoolings reflect interface-controlled growth of diffusion-controlled growth. The faceting in the latter case clearly indicates anisotropy in growth; but it remains to be established whether this represents local anisotropy with crystals whose overall growth rate is determined by diffusional processes (analogous to the growth of bismuth hopper crystals), or whether it represents interface-controlled growth at small undercoolings (with a transition to diffusion-controlled growth at larger undercoolings). Experiments to resolve this issue are present underway at Saint Gobain and at MIT.

### 3. Kinetic Treatments of Glass Formation

As should be clear from the discussion in Section 1 above, the critical question in discussing glass formation is not WHETHER a material is a glass-former with respect to cooling from the liquid state, but HOW FAST must the liquid be cooled to avoid detectable crystallization. In answering this question, our attention will therefore be directed to the kinetics of crystallization and to the cooling rates achievable with bodies of various sizes and material characteristics.

In addressing the question of glass formation, Turnbull (23) adopted the criterion of avoiding a single crystal nucleation event during cooling. This approach has justification for fluid melts where a single nucleation event can result in complete

crystallization of a sample. An alternative view was adopted by Dietzel and Wickert (24), who correlated glass-forming ability ("glassiness") with low crystal growth rates. This approach has some justification for viscous melts where a sensibly glassy body can be produced even with copious nucleation.

While each of these views directs attention to an important kinetic process, neither can provide a sufficient answer to the question of how fast must a liquid be cooled to form a glass. To provide the requisite predictive capability, it is necessary to consider both nucleation and crystal growth. Such an approach was adopted by the present author about a decade ago (25), and has been used with considerable success to describe the process of glass formation.

With this approach, one adopts the formal theory of transformation kinetics (26-29) to relate the volume fraction crystallized,  $V_C/V$ , to the nucleation rate per unit volume,  $I_V$ , and the crystal growth rate,  $u$  :

$$\frac{V_C}{V} = 1 - \exp \left[ - \int_0^t I_V \left( \int_0^{t'} u dt' \right)^3 dt' \right] \quad (16)$$

Both  $I_V$  and  $u$  must be considered as functions of time through their dependences on temperature in continuous cooling situations.

By measuring or calculating the nucleation rate and crystal growth rate at a given temperature, the degree of crystallinity can be evaluated as a function of time. By repeating the calculations for a series of temperatures, the locus of times at various temperatures required to form a given fraction crystallized can be determined. Such loci are called time-temperature-transformation or TTT curves. A representative TTT curve is presented in Fig. 2 for anorthite for a volume fraction crystallized of  $10^{-6}$ . This fraction crystallized has been suggested (25) to represent a just-detectable degree of crystallinity - i.e., a  $V_C/V$  which must be avoided in order to form a glass.

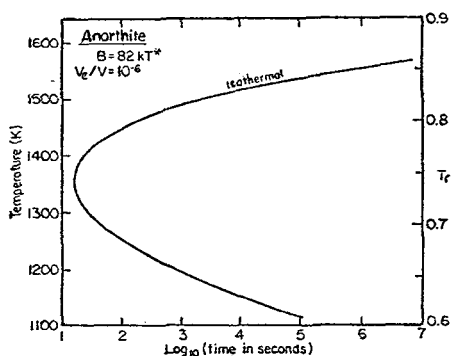


Fig. 2. Time-temperature transformation curve for anorthite.

$$V_C/V = 10^{-6}.$$

The nose of each TTT curve denotes the least time required at any temperature to form the particular fraction crystallized. If one assumes that the kinetics of crystallization over the full range of temperature between the melting point  $T_E$ , and the nose,  $T_N$ , are as rapid as at the nose temperature, one may obtain a useful estimate (overestimate) of the critical cooling rate required to form a glass :

$$\dot{T}_C \approx \Delta T_N / t_N \quad (17)$$

where  $\Delta T_N = T_E - T_N$ ; and  $t_N$  is the time at the nose of the TTT curve.



The thickness of material obtainable as a glass can correspondingly be approximated :

$$y_c \approx (D_{TH} t_N)^{\frac{1}{2}} \tag{18}$$

where  $D_{TH}$  is the thermal diffusivity of the sample.

More accurate estimates of the critical cooling rates for glass formation can be obtained by constructing continuous cooling or CT curves. This approach was introduced by Grange and Kiefer (30) and applied to the treatment of glass formation by Onorato and Uhlmann (31). Representative CT curves are shown in Fig. 3 for constant-rate and logarithmic cooling. As expected, the critical cooling rates estimated from CT curves are lower than those obtained from Eqn. (17), typically by a factor of 5-10.

While the CT analysis provides more accurate estimates of critical cooling rates than those obtained with Eqn. (17), it still involves some notable approximations (see discussion in Ref. 4). An exact description of the numbers and size distributions of crystals in a body subject to an arbitrary thermal history was provided by Hopper et al. (32). The treatment, whose application involves numerical techniques, can be used to describe complex phenomena such as crystallization on reheating a glass (a topic to be discussed explicitly below). With this approach,

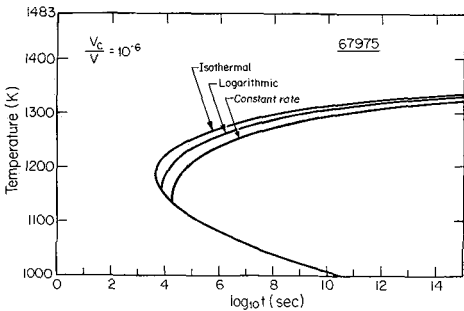


Fig. 3. Continuous cooling curves for constant-rate and logarithmic cooling for lunar composition 67975.  $V_c/V = 10^{-6}$ . After Ref. 40.

the volume fraction crystallized is represented :

$$\frac{V_c}{V}(t_j) = 1 - \exp \left\{ - \sum_{i=1}^j \frac{4\pi}{3} R_i^3(t_j, t_i) I_{V_i}(t_i) \Delta t \right\} \tag{19}$$

where  $V_c/V(t_j)$  is the fraction crystallized at time  $t_j$ ;  $I_{V_i}$  is the steady state nucleation frequency at time  $t_i$ ; and  $R_i(t_i, t_j)$ , the radii at time  $t_j$  of crystals nucleated at time  $t_i$ , is expressed :

$$R_i = R_i^* + \sum_{k=1}^j U_k(t_k) \Delta t \tag{20}$$

where  $R_i^*$  is the size of the critical nucleus at time  $t_i$ ; and  $U_k$  is the crystal growth rate at time  $t_k$ .

While this analysis, termed crystallization statistics, can provide an exact description of crystallization during cooling of a liquid, it requires detailed kinetic data on the material. In cases where such data are not available, a simplified model can be used to obtain order-of-magnitude estimates of critical cooling rates. This model is based on the observation that the noses of TTT curves generally occur at temperatures in the range of  $0.77 T_E$ , and on a relation between the barrier to crystal nucleation at a temperature of  $0.8 T_E$ ,  $\Delta G^{**}$ , and the molar entropy of fusion,  $\Delta S_M$  :

$$\Delta G^{**} \approx 12.6 \frac{\Delta S_M}{R} kT^* \quad (21)$$

where  $T^* = 0.8 T_E$ . This relation is applicable for high- $\Delta S_M$  materials (in Jackson's sense). A corresponding relation between  $\Delta G^{**}$  and  $\Delta S_M$  holds for low- $\Delta S_M$  materials, but with a larger proportionality coefficient.

In using this approach, it is necessary to estimate the viscosity at  $T_N = 0.77 T_E$ . For oxide materials, this can be accomplished by combining high temperature viscosities obtained from the models of Shaw (33) or Bottinga and Weill (34) together with measured values of the glass transition temperatures. Using a polynomial fit to the combined "data", the overall viscosity-temperature relation can be obtained. For other classes of materials, the viscosity at  $0.77 T_E$  can be estimated from the free volume model.

With these assumptions as a basis, one can obtain an estimate of the critical cooling rate for glass formation (for details of the model, see Ref. 35) :

$$\dot{T}_c \approx \frac{AT_E^2}{\eta_{0.77T_E}} \exp(-0.212B) \left| 1 - \exp\left(-\frac{0.3\Delta H_M}{RT_E}\right) \right|^{3/4} \quad (22)$$

where the nucleation barrier is  $BkT$  at  $\Delta T/T_E = 0.2$

It is seen that prediction of critical cooling rates using Eqn. (22) requires only minimal information about the material. In light of the considerable approximations used in obtaining Eqn. (22), it is remarkable how useful it seems to be in predicting critical cooling rates (see discussion below).

The discussion to here has considered only homogeneous nucleation, and has thus directed attention to the minimum cooling rates required to form glasses of various materials. To explore the effects of nucleating heterogeneities on critical cooling rates, the spherical cap model of the heterogeneous nucleus (36) has been adopted. The effects of various contact angles, concentrations of nucleating heterogeneities and distributions of heterogeneities have been investigated (31, 37). It was found that heterogeneities with contact angles less than about  $100^\circ$  have a negligible effect on the critical cooling rate for glass formation, at least for concentrations in the range of  $10^7 \text{ cm}^{-3}$ , but that for heterogeneities with smaller contact angles, the critical cooling rate increases appreciably with decreasing contact angle. This is illustrated by the results shown in Fig. 4, which compares continuous cooling curves for anorthite for homogeneous nucleation only with those for homogeneous nucleation +  $10^7$  heterogeneities with contact angles between  $100^\circ$  and  $40^\circ$ . The crowding of the CT curves for small contact angles reflects depletion of the supply of nucleating heterogeneities.

For liquids containing distributions of heterogeneities, the CT curves are dominated by even small concentrations of heterogeneities having small contact angles. As the heterogeneities with small contact angles are depleted (as they nucleate crystals), heterogeneities with larger contact angle become effective, albeit at progressively larger undercoolings. This is illustrated by the plot of  $\log(I_V \eta)$  vs.

$(\Delta T_r^2 T_r^3)^{-1}$  shown in Fig. 5. Pronounced curvature in such relations reflects the presence of nucleating heterogeneities, likely characterized by a range of contact angles. The observation of straight-line  $\log(I_V \eta)$  vs.  $(\Delta T_r^2 T_r^3)^{-1}$  relations, such as that shown in Fig. 1 above for anorthite, suggest that the nucleation being observed is homogeneous.

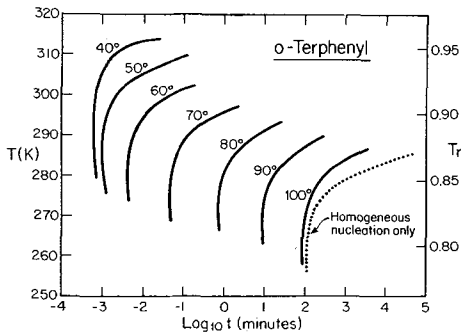


Fig. 4. Continuous cooling curves for anorthite for homogeneous nucleation + bulk heterogeneous nucleation with contact angles as indicated ( $10^7$  heterogeneities  $\text{cm}^{-3}$ ). After Ref. 37.

In all of the above discussion of glass formation, steady-state nucleation has been assumed. It is recognized, however, that steady-state conditions are reached only after some transient time (see discussion of Eqn. (10) above). In evaluating the effects of transients on the critical cooling rates for glass formation, the analysis of crystallization statistics has been modified to include transient nucleation,

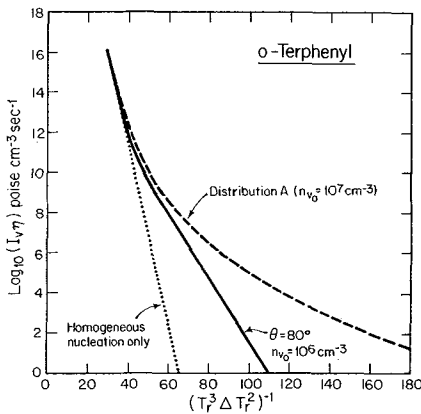


Fig. 5. Logarithm  $(I_V \eta)$  vs  $(\Delta T_r T_r^3)^{-1}$  relation for o-terphenyl. After Ref. 37.

as represented by Eqns. (10) and (11). It was found (8) that in the case of homogeneous nucleation, the critical cooling rates for most materials are sufficiently low that the transient times are much smaller than the time intervals relevant in assessing the kinetics of crystallization; and hence steady-state conditions are effectively maintained during cooling. The effects of transients on the overall crystallization process should be important only for cooling rates which are notably faster than those required to form glasses.

When nucleating heterogeneities are present, faster cooling rates are required to form glasses (at least for heterogeneities with contact angles less than  $100^\circ$ ). In such cases, the nucleation rate at large undercoolings can be significantly time-dependent; and one might be concerned about the effects of this time dependence on the cooling rates required to form glasses. It turns out, however, that in the presence of good nucleating catalysts, the crystallization process is dominated by heterogeneous nucleation taking place at smaller undercoolings. At such undercoolings, the viscosities are lower, the transient times correspondingly smaller, and the steady-state rate (of heterogeneous nucleation) is applicable. Hence the critical cooling rates for glass formation, even in the presence of potent heterogeneous nuclei, do not seem to be strongly affected by transients.

As indicated above, the analysis of crystallization statistics can be used to describe crystallization, not only on cooling a liquid but also on reheating a glass. In

the latter application, detailed consideration is given to the number and size distributions of small crystallites in the body, and to the thermodynamic stability of such crystallites. Since the size of the critical nucleus decreases with increasing undercooling, small crystallites which are stable at low temperatures can become unstable and melt out as the sample is heated (if they do not grow sufficiently during heating). These effects have been considered in the analysis. It has been found that small crystallites generally grow to a stable size on reheating a glass at reasonable rates (only at very fast heating rates is the remelting of crystallites significant). The treatment is presented at length in Ref. 40.

The calculated variation of crystallization temperature (temperature of maximum crystallization rate) with heating rate agrees well with experimental data. This is illustrated by the results for anorthite shown in Fig. 6. Both the absolute crystallization temperature and its dependence on heating rate are well predicted by the analysis. The results can also be used to determine the magnitude of the barrier to crystal nucleation within about  $\pm 3\text{kT}^*$ . For example, the value estimated from the DTA results shown in Fig. 6 -  $80\text{kT}^*$  - agrees quite favorably with that obtained from the direct measurements shown in Fig. 1 ( $82\text{kT}^*$ ). The approach offers considerable promise, therefore, for obtaining useful estimates of nucleation barriers - and hence of crystal - liquid surface energies - from simple DTA experiments.

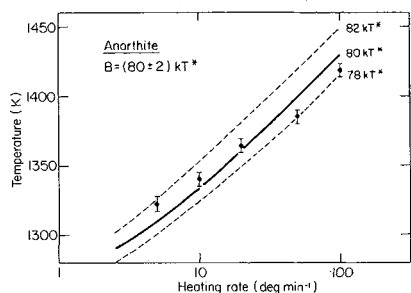


Fig. 6. Variation of crystallization temperature with heating rate for anorthite. After Ref. 11.

When the analysis is applied to a variety of materials, it is found that the crystallization temperature depends strongly on heating rate (a dependence which provides the basis for estimating nucleation barriers) and less strongly but significantly on the cooling rate used to form the glass. The dependence of the crystallization temperature on heating rate and cooling rate had been found experimentally by Thornburg (38) and Lasocka (39). For volume fractions crystallized at  $T_g$  of  $10^{-9}$  to  $10^{-10}$  or less, the calculated crystallization temperature becomes independent of cooling rate; and this has been suggested to provide a definition for a glass whose thermal stability is independent of thermal history.

The predictions of the kinetic treatments of glass formation are in good accord with experimental measurements. Comparisons between model predictions and experiment have been effected in two principal ways. First, the maximum size of body obtainable as a glass can be determined and the heat flow problem solved for the geometry of concern. As examples of this approach, three studies may be cited: (1) for lunar composition 60095 (40), the critical cooling rate estimated from the analysis of crystallization statistics was  $2-3\text{K sec}^{-1}$ , while that obtained from experiment + heat flow analysis was about  $5\text{K sec}^{-1}$ ; (2) for a gold-silicon-germanium metal glass (41), a critical cooling rate of about  $3 \times 10^7\text{K sec}^{-1}$  was estimated (roughly) from kinetic analysis, while the value indicated by heat flow analysis was  $0.2-1 \times 10^7\text{K sec}^{-1}$ ; and (3) for Zr-Be and Ti-Be glasses (42), good agreement was obtained between predicted and experimental critical cooling rates, but the agreement required assumed (albeit reasonable) values of the nucleation barrier.

The second approach involves the direct determination of critical cooling rates in programmed cooling experiments. As one example of this approach, the critical cooling rates were determined (43, 44) for a series of lunar compositions. In several cases, the nucleation barriers were determined from the heating rate dependence of the crystallization temperature. Comparisons were made between experimental data and the predictions of both the exact analysis of crystallization statistics and the simplified model. The results indicate close agreement between experimental data and predictions of the exact analysis. They also indicate good agreement, typically within about an order of magnitude, between experimental data and critical cooling rates predicted using the simplified model. Considering the simplicity of the model and the approximations used in its derivation, this agreement is remarkable.

As a second example, Fang et al. (45) determined the critical cooling rates for forming glasses of various  $\text{Na}_2\text{O}-\text{SiO}_2$  and  $\text{K}_2\text{O}-\text{SiO}_2$  compositions. Nucleation barriers for limiting compositions in the  $\text{Na}_2\text{O}-\text{SiO}_2$  system were determined as about 60 kT\*, and this value was used for all. Typical results are shown in Fig. 7. A pronounced minimum in critical cooling rate is seen in the vicinity of the eutectic. This

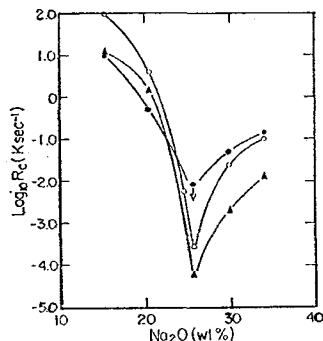


Fig. 7. Variation of critical cooling rate with composition in the  $\text{Na}_2\text{O} - \text{SiO}_2$  system. ● = experimental data; ▲ = predictions of simplified model; ○ = predictions of exact analysis. After Ref. 45

minimum is predicted by the simplified model as well as the exact analysis, and reflects the minimum in crystal growth rate observed in this range of composition.

By applying the kinetic analysis to a variety of materials, it has been found that case of glass formation is favored by a number of material characteristics. These include :

1. A high viscosity at the nose of the TTT or CT curve. This implies a high viscosity at the melting point and /or a viscosity which increases rapidly with falling temperature below the melting point. It also suggests that high ratios of  $T_g/T_E$  would be favorable for glass formation.
2. The absence of potent nucleating heterogeneities. This is favored by compositions which are good solvents, such as  $\text{PbO}$ -containing silicates and metal alloys with large concentrations of Fe and Ni. It is also favored by superheating the melt well above  $T_E$  before cooling.
3. A large barrier to crystal nucleation. This implies a large crystal-liquid surface energy, and for materials within a given class in Jackson's sense, a large heat of fusion.
4. The necessity of extensive solute redistribution during crystallization. This directs attention to compositions which differ appreciably from the crystallizing phases, and in particular to regions of eutectics (especially deep eutectics) in the respective phase diagrams. The effect of compositional ordering on melt stabili-

ty is of importance here. This condition also suggests, where possible, the formulation of multicomponent compositions, and suggests a principle of maximum melt confusion.

4. Concluding Discussion. Kinetic treatments of glass formation have made it possible to predict with confidence the critical cooling rates required to form glasses of various materials. They have also provided a description of complicated kinetic processes, such as crystallization on reheating a glass, and have permitted the evaluation of nucleation barriers from simple DTA experiments.

The success of these treatments depends on the ability to describe the individual processes of crystal nucleation and growth. In these areas, several issues remain to be clarified in satisfactory detail. These include :

1. Detailed determination of the relation between interdiffusion coefficient  $\tilde{D}$ , and viscosity (or between  $\nu$  and  $\eta$ ) for oxide melts. This is essential for quantitative treatments of both nucleation and growth. Available evidence suggests that a modified Stokes-Einstein relation can be used (7); but more experimental data on  $\tilde{D}$  are needed (and are presently being obtained at MIT).

2. Experimental determinations of the kinetics of heterogeneous nucleation and the role of dissolved impurities (such as transition metal and rare earth ions) in promoting crystal nucleation. Available evidence suggests that homogeneous nucleation represents the dominant contribution to the formation of crystal nuclei in the region of large undercoolings which are critical in glass formation; but calculations based on the spherical cap model and classical nucleation theory suggest that even small concentrations of heterogeneities with small contact angles can have a large effect in increasing the critical cooling rates required to form glasses. Elimination of heterogeneities, as by dividing a liquid sample into many small droplets (46) so that most are free of heterogeneities, should favor glass formation; but it remains unclear why the effects of nucleating heterogeneities are not more often observed.

3. Experimental and theoretical studies of transient nucleation. The present author is unaware of any detailed data in this area. This agreement between experimental data and critical cooling rates calculated using steady state nucleation frequencies is encouraging and in accord with theoretical expectations. But agreement is also obtained between theoretical and experimental variations of crystallization temperature with heating rate; yet preliminary calculations indicate that transients are significant during the reheating of a glass.

4. Determination of the rate-limiting process for crystal growth at modest undercoolings in systems crystallizing with sizable changes in composition. If such growth is limited by interface kinetics, these systems would provide attractive vehicles for studying the transition from interface-controlled to diffusion-controlled growth; if not, their study should provide significant insight into diffusion-controlled growth morphologies with anisotropic growth features.

5. Experimental and theoretical studies of coupled diffusion-controlled growth. The establishment of a relation between undercooling and crystal radius seems essential, as do more extensive determinations of growth rates, radii of and spacings between crystals as functions of undercooling. Also needed here is understanding of the origin of spherulitic growth morphologies.

Improved knowledge in areas such as these would add considerably to our understanding of crystallization and glass formation. It seems clear, however, that the ultimate treatments of glass formation will depend on establishing relations bet-

ween crystallization and transport on the one hand and structure and inter-atomic interactions on the other. This presents a formidable challenge, which the present author expects to be taken up during the coming decade.

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