A SIMPLIFIED MODEL FOR GLASS FORMATION, D.R. Uhlmann, Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Mass. 02139 and P.I.K. Onorato, GTE Laboratories, Waltham, Mass. 02154.

The critical cooling rate for glass formation has been determined for many materials using the formal theory of transformation kinetics. In order to apply this theory to a particular material, it is necessary to know the viscosity and the crystal growth rate over a wide range of temperature. It is also important to know the magnitude of the nucleation barrier in the material. Unfortunately, such information is not available for many materials; and measurements of this type are time consuming. It would therefore be useful to have a simple model which could be applied with limited data to determine the critical cooling rate necessary to form a glass. This is particularly important for lunar glasses whose thermal histories are of considerable interest.

When determining the critical cooling rate from a time-temperature-transformation (TTT) diagram, the only part of the curve which is ultimately required is the nose of the curve. If the time and temperature of the nose could be predicted, the critical cooling rate could also be predicted. According to transformation kinetics, the volume fraction crystallized in a time t at a given temperature is:

$$\frac{V_c}{V} \approx \frac{\pi}{3} I_v u^3 t^4 \tag{1}$$

where I_v is the nucleation frequency per unit volume and u is the growth rate.

If the temperature of the nose of the TTT diagram is known, the critical cooling rate can be estimated:

$$\left(\frac{dT}{dt}\right)_{crit} \approx \frac{T_E - T_{nose}}{t_{nose}} \tag{2}$$

where T_E is the melting point or liquidus temperature.

The application of the theory of transformation kinetics to a wide range of materials has produced many TTT and continuous cooling (CT) curves. The temperatures at the nose are shown in Table 1 for several classes of materials. If the temperature of the nose is compared with the liquidus temperature, it can be seen that the ratio of these temperatures is approximately constant: $T_{nose}/T_E \approx 0.77$. Changing the barrier to homogeneous nucleation changes the temperatures of the nose only slightly.

Making the approximation that for all materials

$$T_{nose} = 0.77\ T_E \tag{3}$$

and using the formal theory of transformation kinetics, we obtain the critical cooling rate for glass formation:

$$\left(\frac{dT}{dt}\right)_{crit} = \frac{0.177\ T_E^2}{C\eta\ (.77T_E)} \exp\ (-0.2117B)\left(1-\exp - \frac{0.3\Delta H^{3/4}}{RT_E}\right) \tag{4}$$

Here $(dT/dt)_{crit}$ is the critical cooling rate; η is the viscosity; T_E is the melting point or liquidus temperature; the barrier to crystal nucleation is bkT at a relative undercooling of 0.2, ΔH is the heat of fusion, and

$$C = \frac{x^{1/4}(243)^{1/4}\ \pi^{3/4}\ a_o^{9/4}}{(N^\circ_v)^{1/4}\ k} \tag{5}$$

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Table 1: Temperature of Nose of TTT Curve Compared with Melting Point or Liquidus Temperature

Material	T_{melt} (K)	T_{nose} (K) (ΔG^* at $\Delta T/T_E$=0.2)	T_{nose}/T_E
Apollo 15 Green Glass	1543	1140 (60kT)	.739
Lunar comp. 15286	1483	1129 (60kT)	.761
Lunar comp. 15498	1543	1176 (60kT)	.762
Lunar comp. 60095	1543	1165 (60kT)	.755
Lunar comp. 65016	1633	1207 (60kT)	.739
Lunar comp. 70019	1453	1132 (55kT)	.779
Lunar comp. 79155	1523	1176 (60kT)	.772
$Na_2O.2SiO_2$	1146	894 (50kT)	.78
GeO_2	1389	1040 (50kT)	.749
Salol	316.6	240 (70kT)	.757
H_2O	273	202 (50kT)	.74
SiO_2	1996	1540 (50kT)	.772
Anorthite	1823	1389 (60kT)	.762
O-terphenyl	328	269 (50kT)	.82

To predict the critical cooling rate for a material of unknown glass-forming ability, all that remains is to determine or estimate the heat of fusion, the nucleation barrier, and the viscosity at 0.77 T_E.

Available data on nucleation behavior for a wide variety of materials were collated; the crystal-liquid surface energies were calculated from the range of undercooling at which homogeneous nucleation was observed; and these surface energies were related to the molar heats of fusion. The results indicate a typical nucleation barrier of about 12.6 $(\Delta S_M/R)kT$ at a relative undercooling of 0.2.

Using the glass transition temperature, T_g, as a corresponding states parameter, we obtained a least-squares fit of the Vogel-Fulcher relation

$$\log_{10}\eta = A + \frac{B}{T/T_g - \alpha} \qquad (5)$$

to the flow data on 13 lunar compositions. Values of A and B were determined for all compositions with α varying from 0.8 to 1.2 at intervals of 0.01. The mean and the standard deviation of both A and B were determined at each value of α. It was found that the best overall fit to the viscosity data for the lunar compositions was

$$\log_{10}\eta = -1.60 + \frac{3.12}{T/T_g - .83} \qquad (6)$$

This relation describes the viscosity at the temperature of interest (0.77 T_m) within about an order of magnitude of that interpolated from measurements.

Using these results together with Eqn. (4), and taking ΔS_M=5R for all lunar compositions and ΔS_M=6R for anorthite, the critical cooling rates were calculated, with the results shown in Table 2. These results are quite encouraging. The predictions of the simplified model agree within about an order of magnitude with those obtained from the detailed CT analysis (which requires considerable information about the materials). The results also agree well with experience. The Apollo 15 Green Glass is in fact the most difficult composition to form as a glass among all the lunar compositions tested. Composition 79155 is a relatively poor glass former, and 70019 is a good glass former.

Table 2: Critical Cooling Rates for Glass Formation Calculated from Curves and Using Simplified Method

Material	Critical Cooling Rate (°C/sec) CT	Simplified Method
Apollo 15 Green Glass	89	600
Lunar comp. 15286	2	23
Lunar comp. 15498	1.8	19
Lunar comp. 60095	7.5	27
Lunar comp. 65016	16	8.4
Lunar comp. 70019	3.8	1.8
Lunar comp. 79155	8	10^2
Anorthite	14	2.3

The differences between the simplified method and the complete method using TTT and CT diagrams are derived from two sources: the viscosity and the temperature at the nose of the TTT diagram. Of these, the difference due to the temperature at the nose is not significant.

The determination of a critical cooling rate for glass formation has now been reduced to three measurable quantities: the glass transition temperature, the melting temperature and the molar heat of fusion. For ease of glass formation, the heat of fusion should be high, so that the nucleation frequency is low; the liquidus temperature or melting point should be low and the glass transition temperature should be high. The melting temperature may be high if the glass transition temperature is also high; but a high melting temperature and a low glass transition temperature indicate a poor glass-former (Apollo 15 green glass). This is in accord with the previous findings.