
Relaxation in Glass: Review of Thermodynamics

Lecture 11: Thermodynamics in the Glass Transition Region

Thermodynamic Functions... 1st Derivatives

- Temperature Dependence of the Entropy

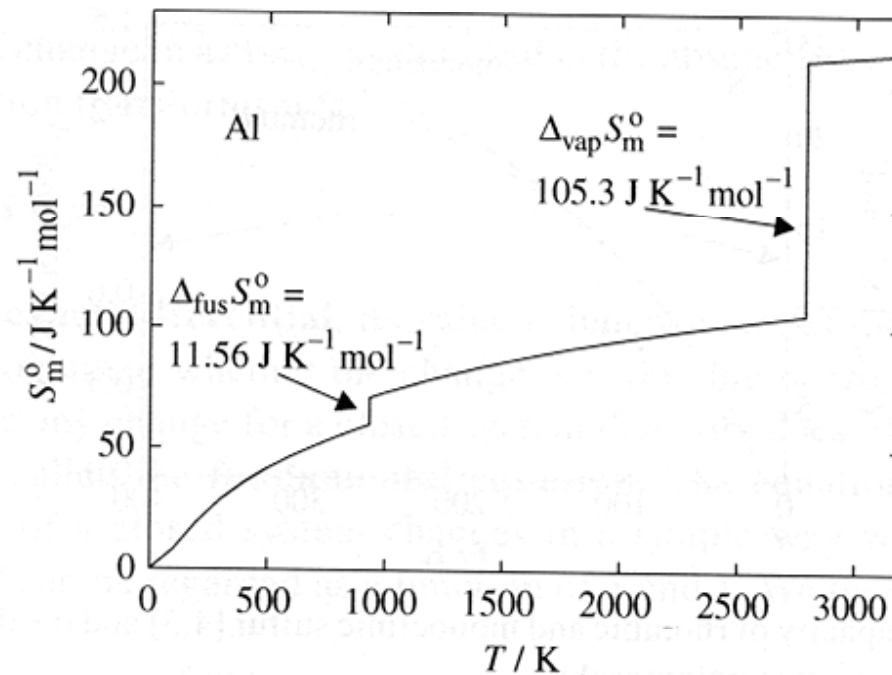


Figure 1.5 Standard entropy of aluminium relative to 0 K. The standard entropy of fusion ($\Delta_{\text{fus}} S_m^0$) is significantly smaller than the standard entropy of boiling ($\Delta_{\text{vap}} S_m^0$).

Thermodynamic Functions... 1st Derivatives

- Temperature dependence of the Gibbs Free-Energy

$$\left(\frac{\partial G^s}{\partial T}\right)_P = -S^s$$

$$< \left(\frac{\partial G^l}{\partial T}\right)_P = -S^l$$

$$\ll \left(\frac{\partial G^g}{\partial T}\right)_P = -S^g$$

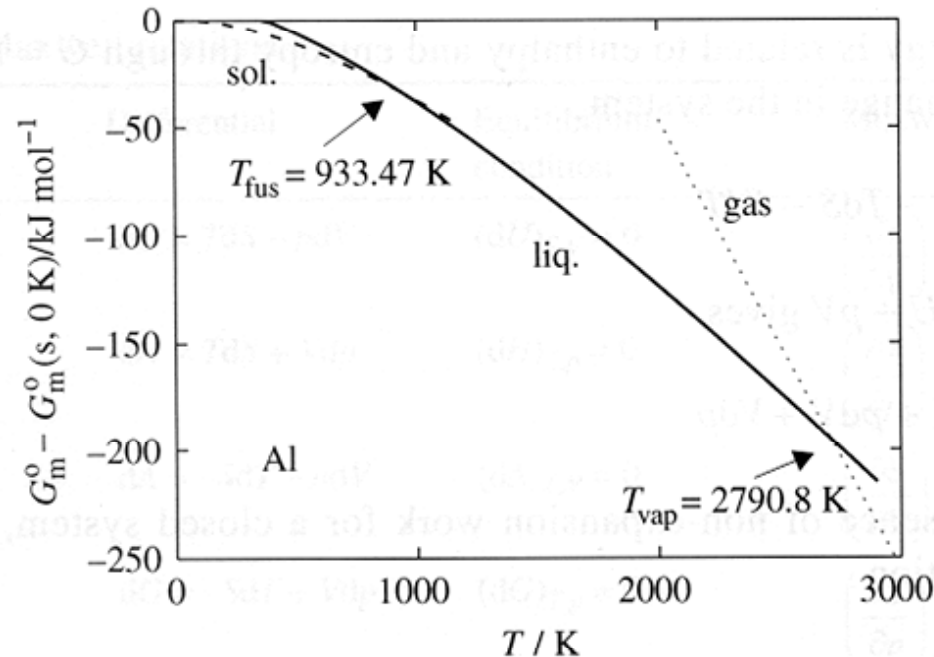


Figure 1.8 Standard Gibbs energy of solid, liquid and gaseous aluminium relative to the standard Gibbs energy of solid aluminium at $T = 0 \text{ K}$ as a function of temperature (at $p = 1 \text{ bar}$).

Thermodynamic Functions... 1st Derivatives

■ $V^s < V^l < V^g$ $\left(\frac{\partial G^s}{\partial P}\right)_T = V^s < \left(\frac{\partial G^l}{\partial P}\right)_T = V^l < \left(\frac{\partial G^g}{\partial P}\right)_T = V^g$

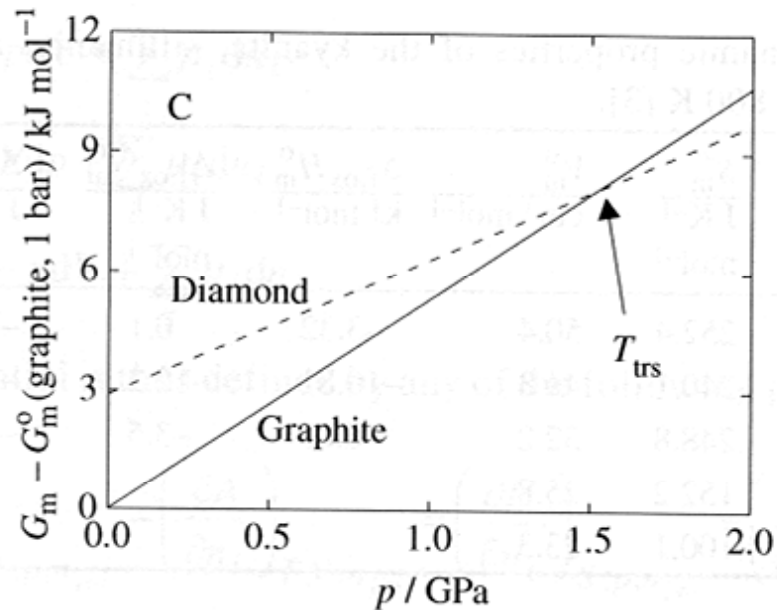


Figure 1.9 Standard Gibbs energy of graphite and diamond at $T = 298$ K relative to the standard Gibbs energy of graphite at 1 bar as a function of pressure.

Homework Exercise for next time:

- Derive an expression for the following quantity in terms of easily measured quantities and apply it to liquid B_2O_3 slightly above its melting point and crystalline B_2O_3 slightly below its melting point

$$\left(\frac{\partial S}{\partial V}\right)_P = \frac{1}{\left(\frac{\partial V}{\partial S}\right)_P} = \frac{1}{\left(\frac{\partial T}{\partial P}\right)_S} = \frac{1}{-\left(\frac{\partial S}{\partial P}\right)_T} \frac{1}{\left(\frac{\partial S}{\partial T}\right)_P}$$

$$= -\frac{\left(\frac{\partial S}{\partial T}\right)_P}{\left(\frac{\partial S}{\partial P}\right)_T} = -\frac{C_p}{-T\left(\frac{\partial V}{\partial T}\right)_P} = \frac{C_p}{T\alpha V}$$

The Enthalpy as a function of temperature, $H(T)$

- The heat capacity C_p measures how much heat it takes to raise the temperature of the system by one degree

$$\left(\frac{\partial q}{\partial T}\right)_P = \left(\frac{\partial H}{\partial T}\right)_P \equiv C_P(T)$$

- ◆ The enthalpy can be calculated from the heat capacity for a large change in temperature

$$H(T_2) - H(T_1) = \int_{T_1}^{T_2} \left(\frac{\partial H(T)}{\partial T}\right)_P dT = \int_{T_1}^{T_2} C_P dT$$

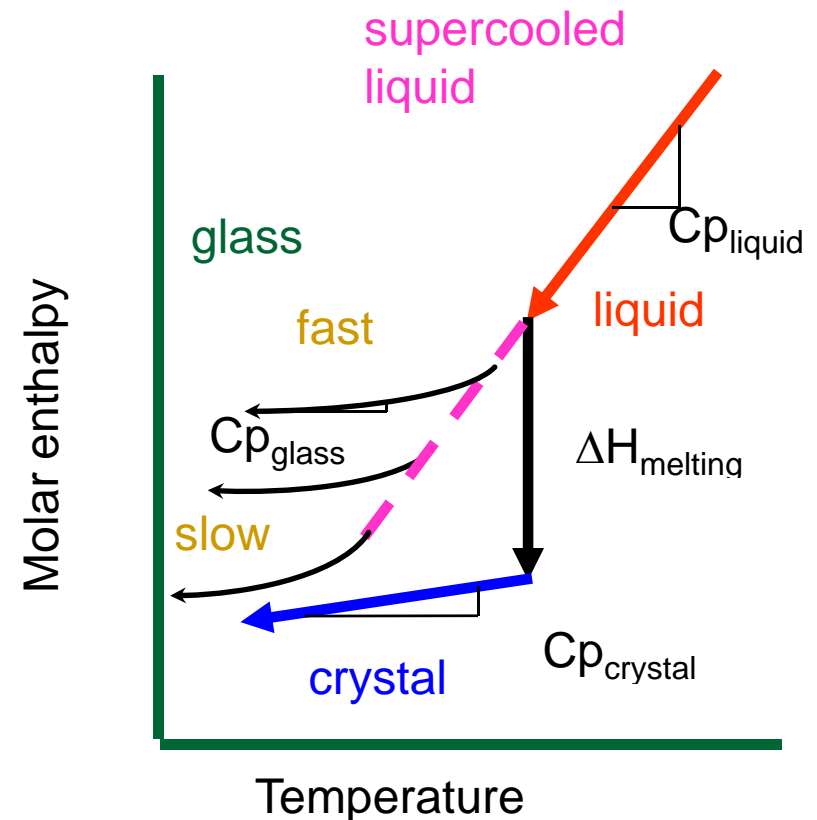
- ◆ If the $C_p(T)$ of solid TiO_2 is $17.97 + 0.28 \times 10^{-3}T - 4.35 \times 10^{-5}/T^2$ cal/mole-K, the ΔH_{melt} is 16 kcal/mole, and the $C_p(T)$ for the liquid is 21.4 cal/mole-K, plot the $C_p(T)$, $H(T)$ and calculate how much heat is required to heat 10 lbs. TiO_2 from room temperature up to 2500 K?

Enthalpy function for glass forming liquids

- Now consider the temperature dependence of the Enthalpy for a liquid cooled from above its melting point to room temperature along two cooling paths:
 - First assume thermodynamic equilibrium holds and the liquid readily crystallizes at its melting (freezing) point to form the equilibrium crystalline phase and then continues to cool to room temperature
 - Second, assume kinetics holds and the liquid bypasses the equilibrium crystallization and super-cools to the glassy state.

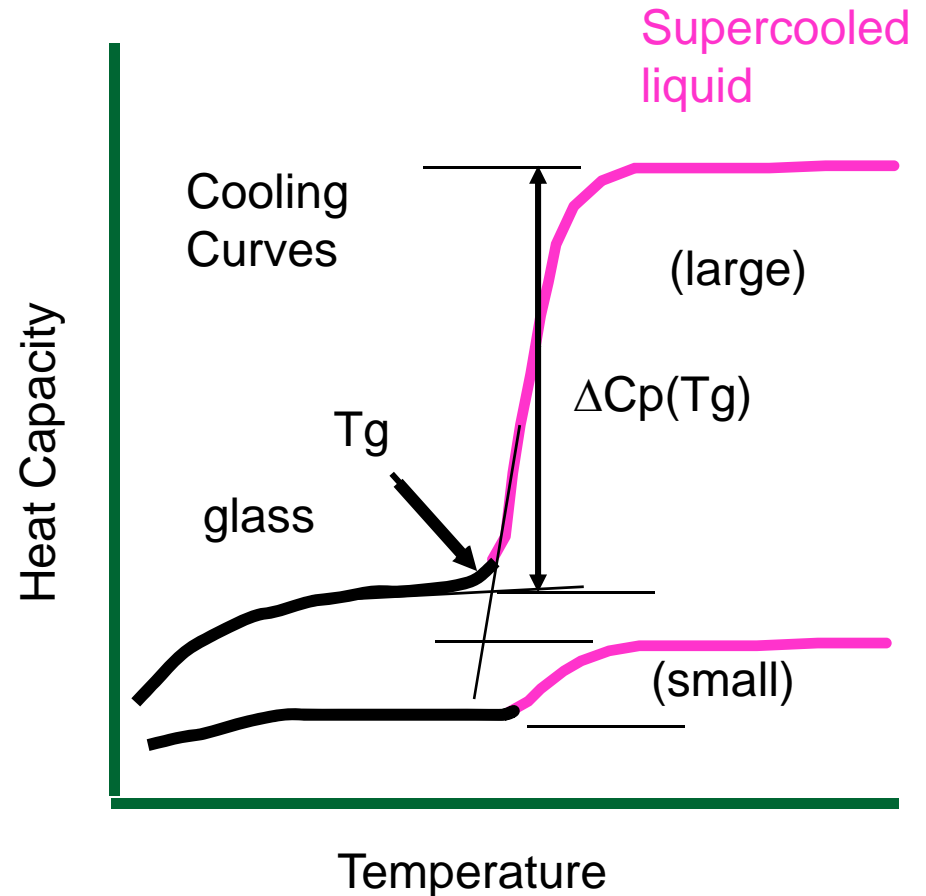
Enthalpy Changes in the Glass Transition Region

- $H(T)$ decreases continuously with cooling
- Slope of the $H(T)$ curve is the heat capacity which changes from liquid-like to solid-like values in the transition region
- Change in heat capacity at the glass transition $\Delta C_p(T_g)$ measures the differences between the liquid and solid (glassy) C_p values
- Sub- T_g annealing and relaxation can occur if liquid is given sufficient time to relax to lower enthalpy state



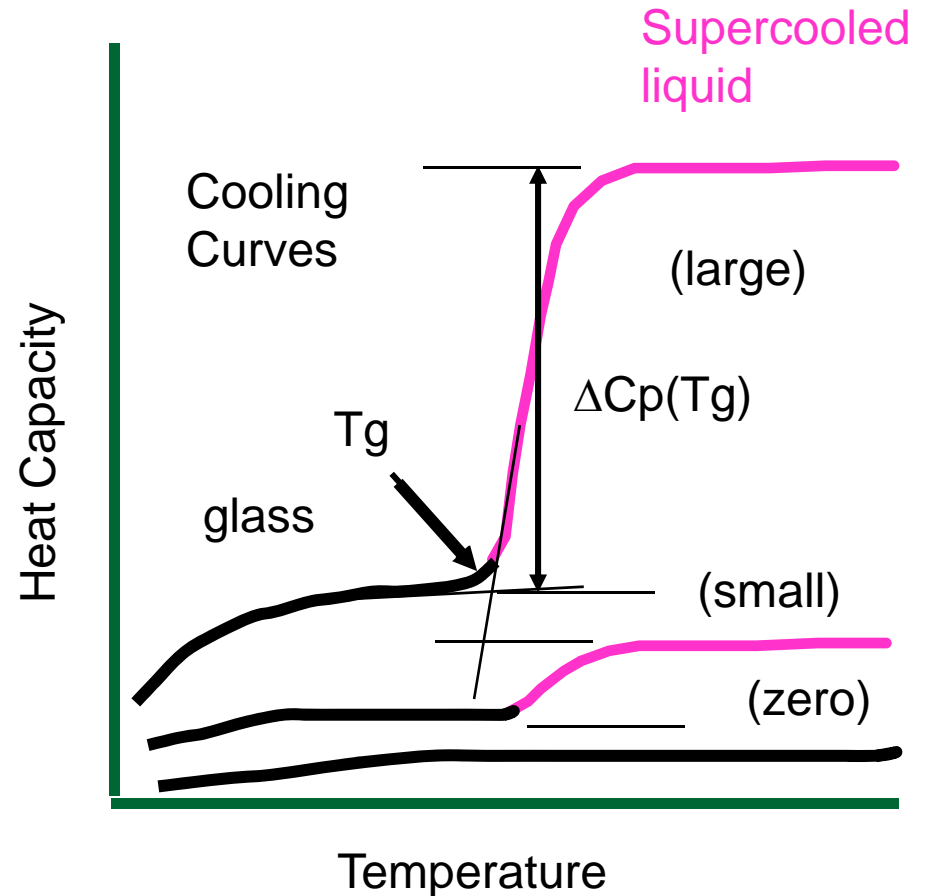
Heat Capacity changes at T_g : $\Delta C_p(T_g)$

- The change in slope in enthalpy at T_g is a measure of the difference between heat capacity of the liquid and the glass
- Heat capacity of *glasses* arises mostly from vibrational contributions
 - rotational and translational degrees of freedom have been “frozen” out
- Heat capacities of *liquids* arise from all three contributions
 - rotational, translational, and vibrational



Heat Capacity changes at T_g : $\Delta C_p(T_g)$

- Exercise: What would the enthalpy curve look like in the region of T_g if the change in heat capacity at T_g for some reason vanished, that is $\Delta C_p(T_g) \rightarrow 0$?



Heat Capacity changes at T_g : $\Delta C_p(T_g)$

- Glass transition occurs when:
 - Thermal energy, heat, being input into the glass has filled all the available thermal degrees of freedom, vibrations, in the glass
 - The vibrational states are essentially filled and at maximum amplitude
 - Additional heat supplied to the glass must be accommodated by other degrees of freedom
 - Rotational and translational degrees of freedom now become available and as such, $C_{p_{\text{liquid}}} \gg C_{p_{\text{glass}}}$

Heat Capacity Changes at T_g : $\Delta C_p(T_g)$

- Covalently bonded liquids exhibit “strong” rigidly held structures (SiO_2 , for example)
 - Generally exhibit higher glass transition temperatures and smaller $\Delta C_p(T_g)$ values
- Molecular, or ionic salt liquids exhibit “fragile”, weakly held structures (sucrose, for example)
 - Generally exhibit lower glass transition temperatures and larger $\Delta C_p(T_g)$ values
- Behaviors can be interchanged by chemically changing the liquid
 - Depolymerizing covalent liquids through non-bridging oxygens

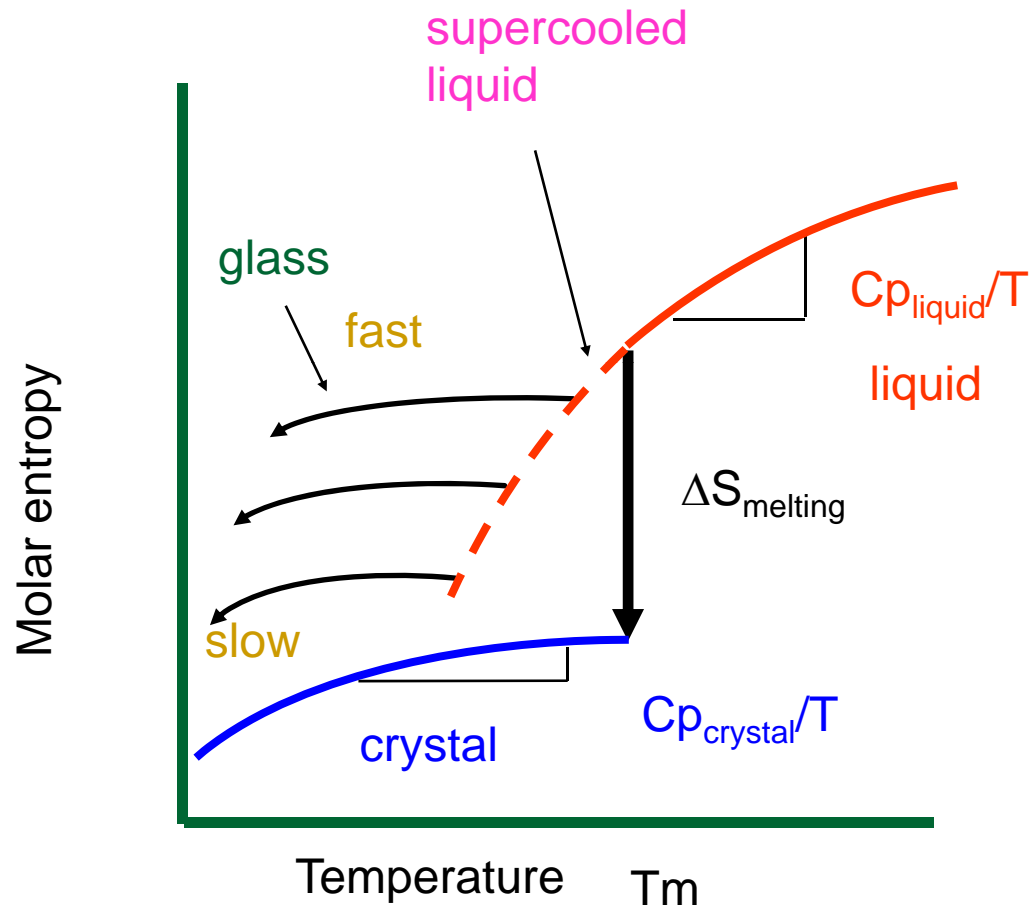
Temperature dependence of the Entropy, $S(T)$

- Entropy measures the disorder in the system
 - It is always positive, and always increases with temperature
 - Hot things are always more disordered than cool things
 - Entropy can go to zero at 0 K

$$S(T_2) - S(T_1) = \int_{T_1}^{T_2} \left(\frac{\partial S(T)}{\partial T} \right)_P dT = \int_{T_1}^{T_2} \frac{C_P}{T} dT$$

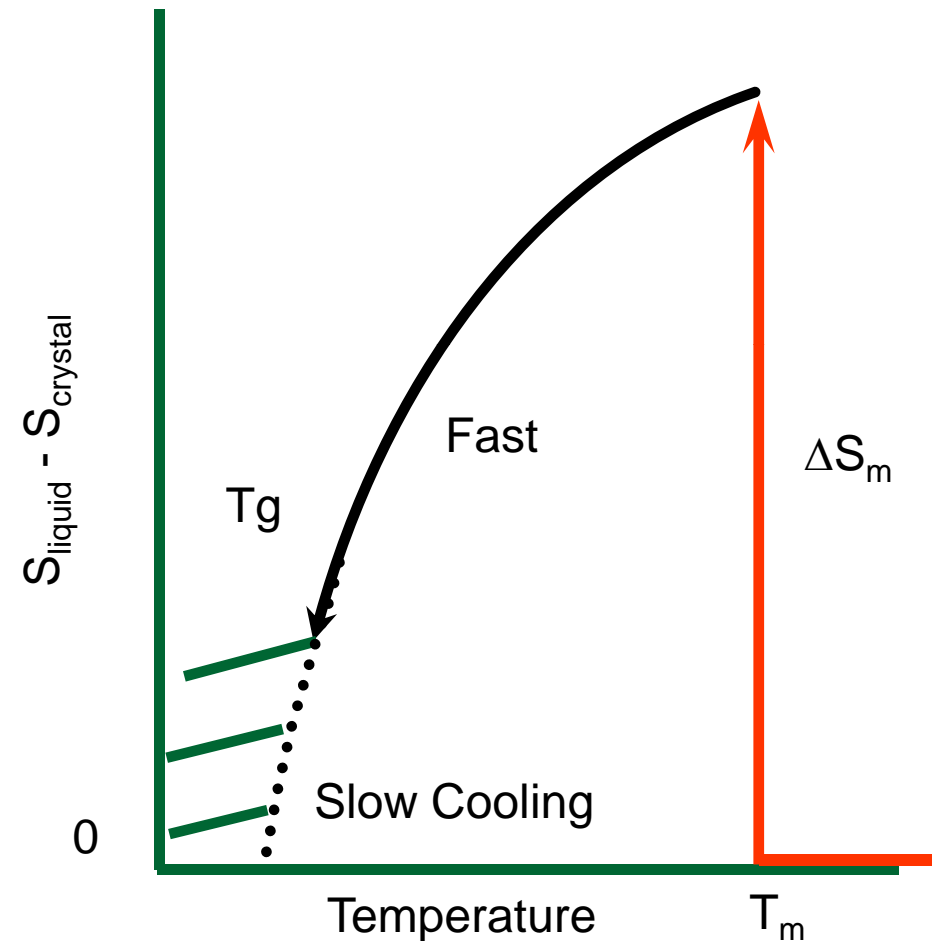
- If the $C_p(T)$ of solid TiO_2 is $17.97 + 0.28 \times 10^{-3}T - 4.35 \times 10^{-5}/T^2$ cal/mole-K, the ΔH_{melt} is 16kcal/mole, and the $C_p(T)$ for the liquid is 21.4 cal/mole-K plot the $S(T)$ and calculate the change in entropy when 10 lbs. TiO_2 is cooled from 2000 K to room temperature?

Temperature Dependence of the Entropy $S(T)$



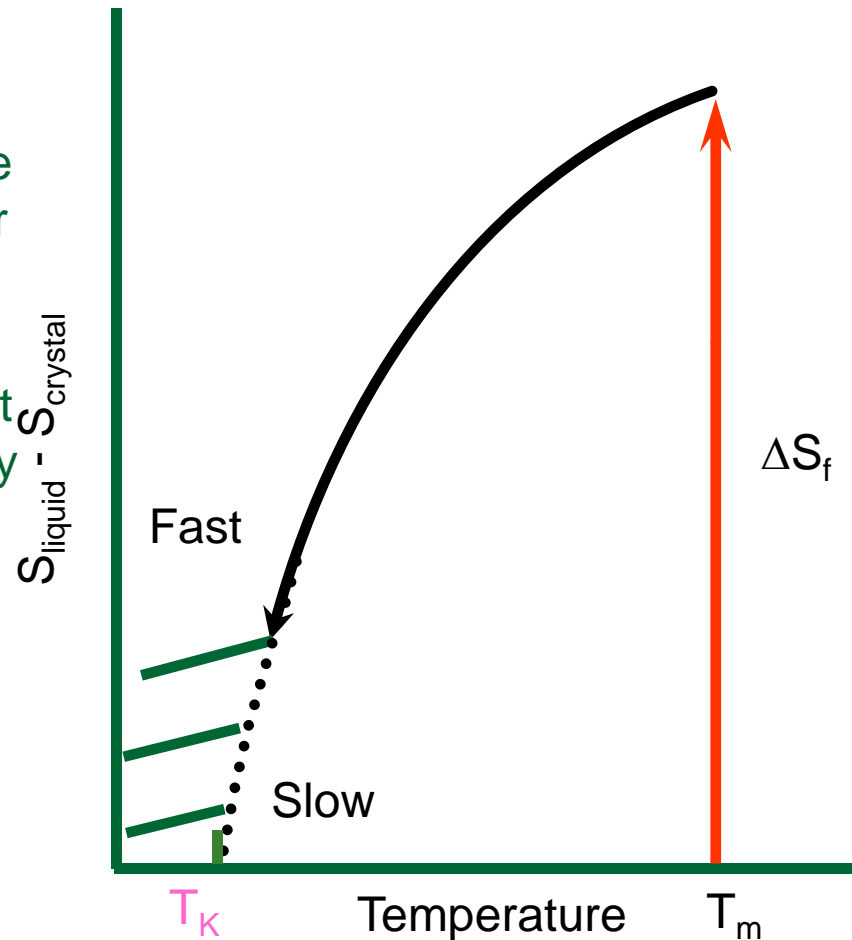
Entropy Changes below T_m

- Entropy is intimately linked to liquid state behavior
 - Highly disordered liquid being reversibly ordered at the freezing point to the crystalline phases
 - Corresponding reversible change in entropy, $\Delta H(T_m)/T_m$
- Glass forming liquids exhibit continuously changing entropy that shows no discontinuities
 - Entropy decreases with temperatures
 - At T_g , continuously changes from liquid-like values to solid like values



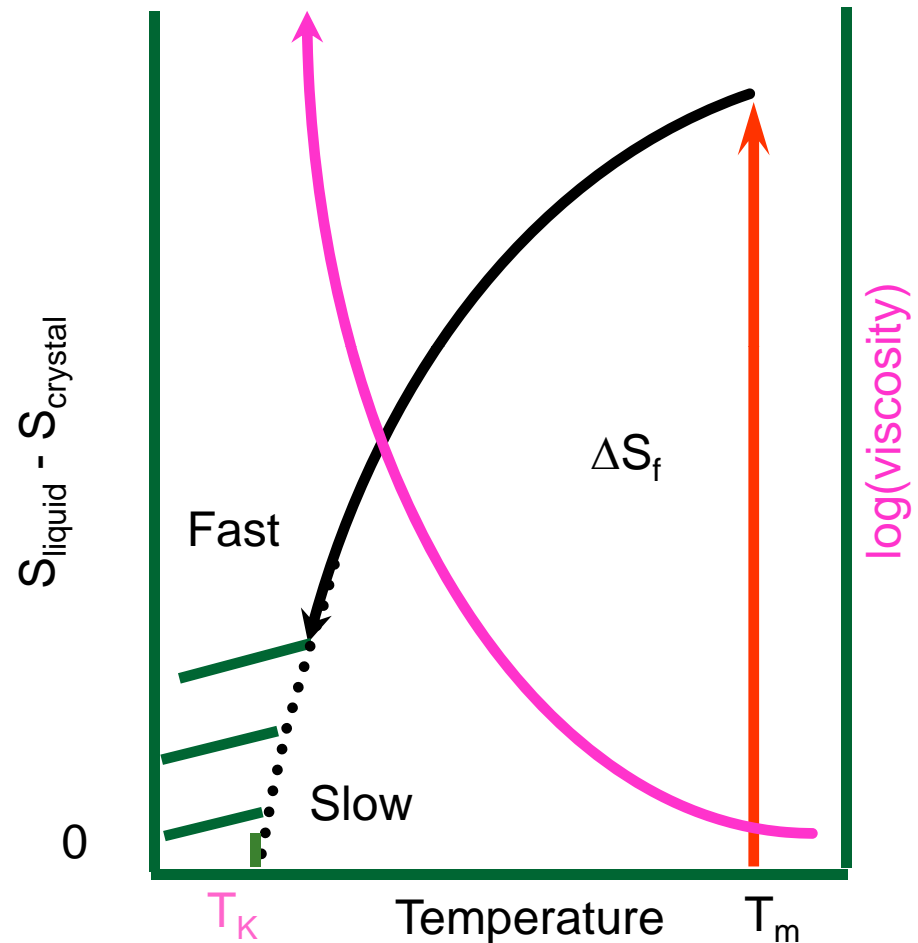
Kauzmann Paradox

- If entropy curve continued along meta-stable equilibrium liquid line
 - At some temperature below T_g , the entropy of the liquids would appear to decrease below that of the crystal
 - How could a liquid, with its inherent structural disorder, have an entropy lower than that of the corresponding crystal
 - The Kauzmann temperature, T_K , is the temperature where the entropy of the liquid would intersect that of the equilibrium crystal
 - Glass at this temperature is often called an “*ideal glass*”



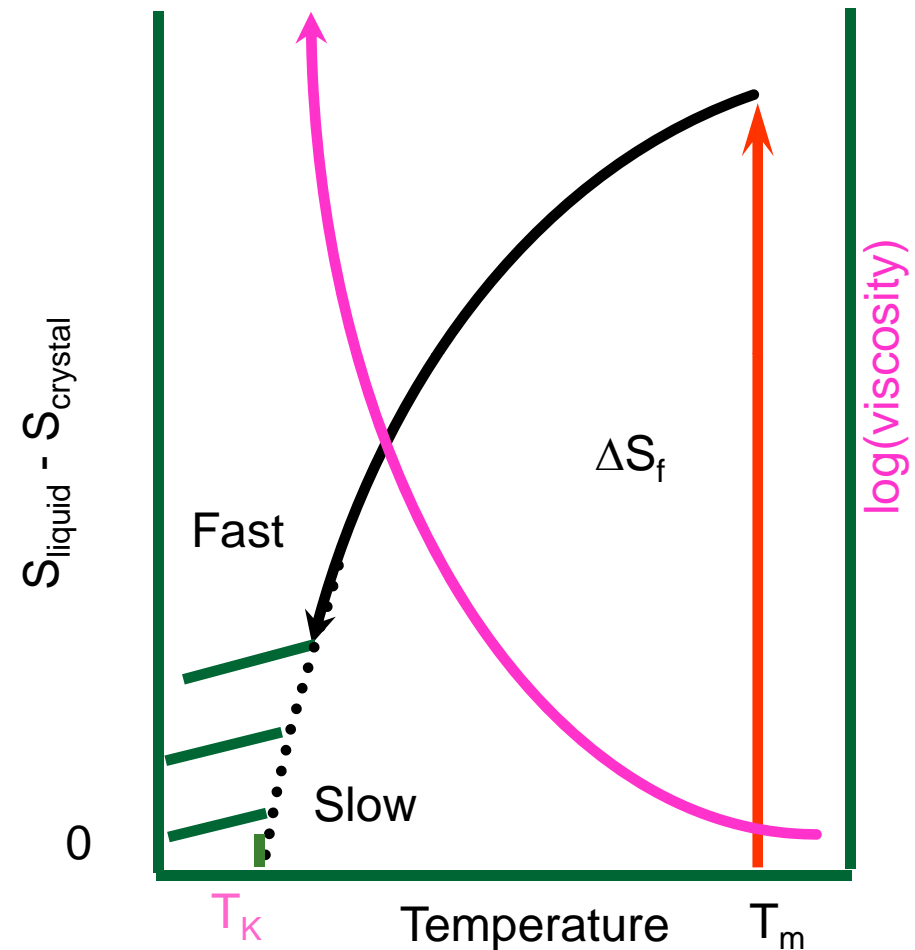
Kauzmann Paradox

- Simultaneous to rapidly decreasing entropy
 - Viscosity is increasing
 - Structural relaxation time is rapidly increasing
 - Time required for the liquid to continue to follow the equilibrium line becomes dramatically longer
- Liquid falls out of equilibrium at a temperature above the Kauzmann temperature because the time required for it to remain in equilibrium simply becomes much longer than the experimental time scale



Excess Entropy ΔS_{excess} of the Supercooled Liquid

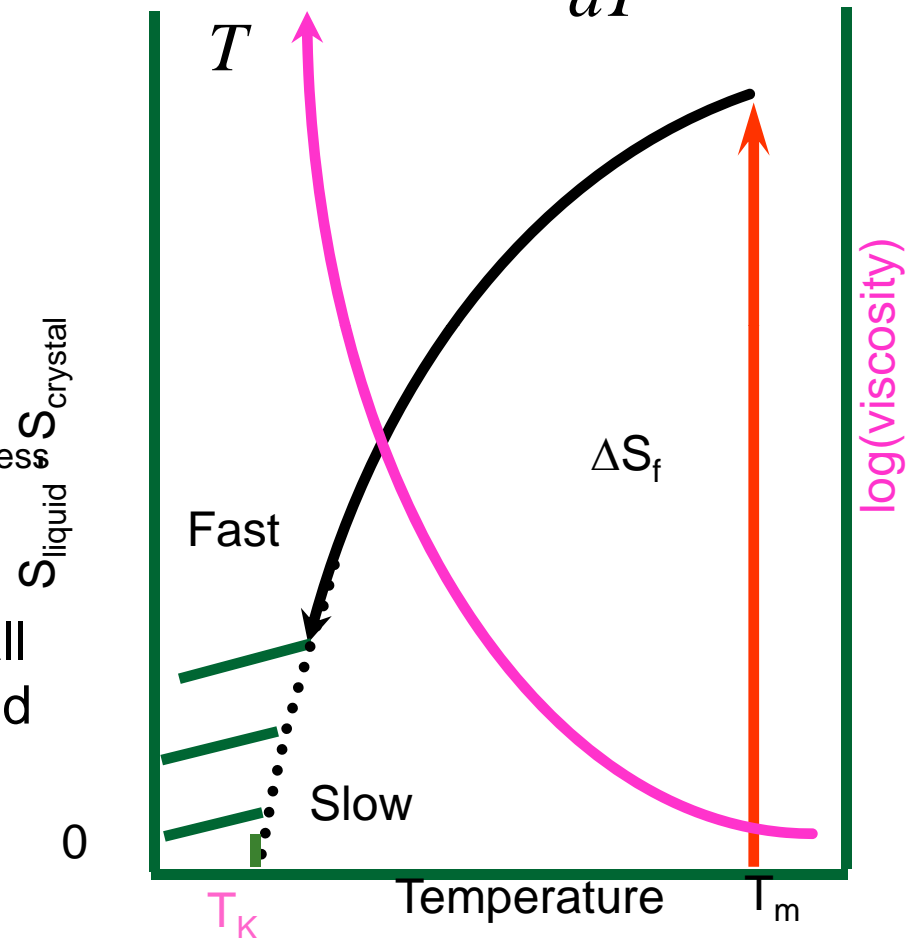
- The important quantity is the extra entropy the liquid has above that of the crystal at the same supercooled temperature
 - Equilibrium liquids above the melting point have no excess entropy
 - Supercooled liquids have excess entropy because they have not “lost” the entropy of melting given to the liquid on melting
 - A supercooled liquid, at maximum has the entropy of melting to lose below T_m
 - At T_K the liquid has lost all of this entropy



Excess Entropy ΔS_{excess} of the Supercooled Liquid

$$\Delta S_{\text{excess}}(T) = \Delta S_{\text{melting}} + \int_{T_m}^T (Cp_{\text{liquid}}(T) - Cp_{\text{crystal}}(T)) dT$$

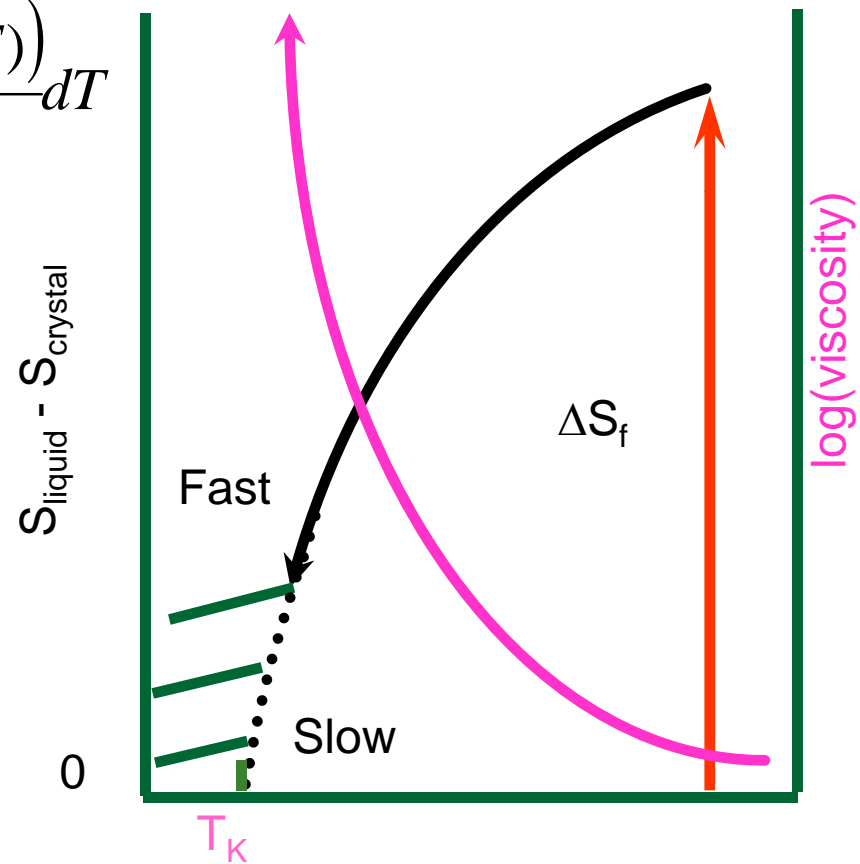
- ◆ At just above the melting point, $\Delta S_{\text{excess}}(\geq T_m) = 0$
- ◆ At just below the melting point, $\Delta S_{\text{excess}}(\leq T_m) = \Delta S_m$
- ◆ As T decreases below T_m , ΔS_{excess} decreases due to the loss of entropy through cooling.
- ◆ At the Kauzmann temperature, all of the entropy gained by the liquid by not crystallizing has been lost through cooling



Vanishing Excess Entropy ΔS_{excess} at T_K

$$\Delta S_{\text{excess}}(T_K) = 0 = \Delta S_{\text{melting}} + \int_{T_m}^{T_K} \frac{(Cp_{\text{liquid}}(T) - Cp_{\text{crystal}}(T))}{T} dT$$

$$\Delta S_{\text{melting}}(T_m) = - \int_{T_m}^{T_K} \frac{(Cp_{\text{liquid}}(T) - Cp_{\text{crystal}}(T))}{T} dT$$



Gibb's Free-Energy Change at T_g

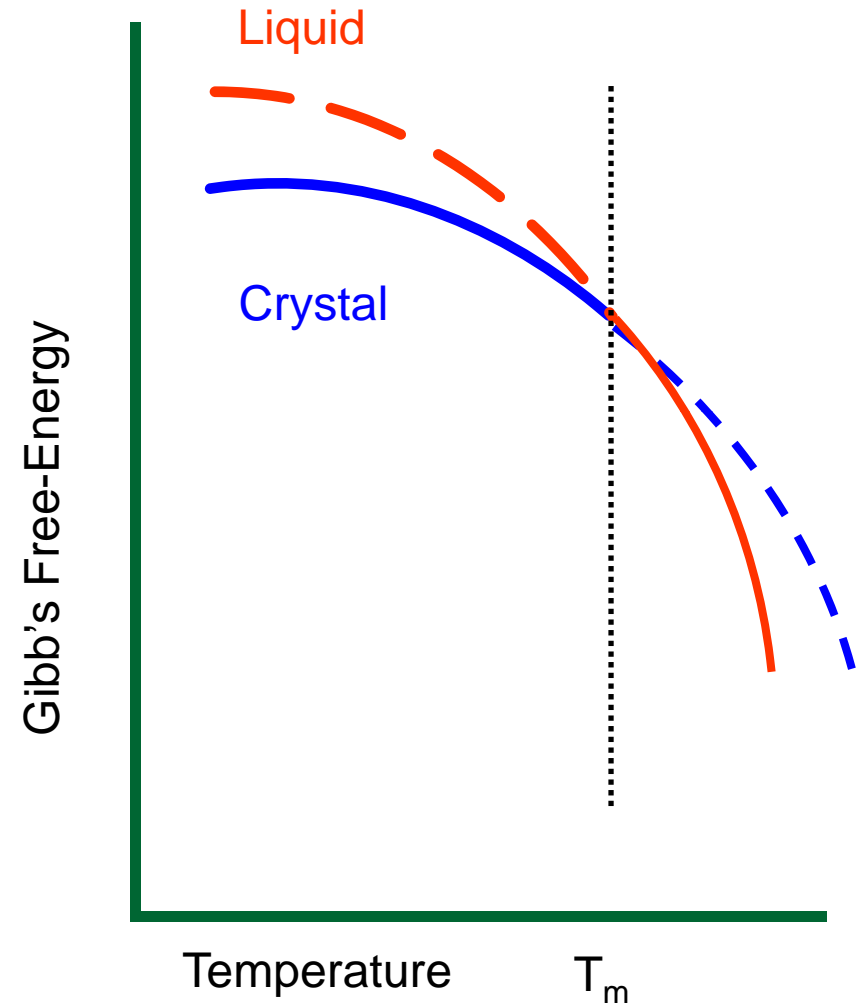
- $G = H - TS$
- Gibbs' Free-Energy change at T_m is continuous, there is no "Latent Free-Energy Change" as is the case for the enthalpy and entropy
- At the melting point

$$G_{\text{liquid}} = G_{\text{crystal}}$$
- Below the melting point

$$G_{\text{liquid}} > G_{\text{crystal}} \text{ and } \Delta G_{\text{crystallization}} < 0$$
- Above the melting point

$$G_{\text{liquid}} > G_{\text{crystal}}$$
- At any point

$$\left(\frac{\partial G(T)}{\partial T} \right)_P = -S(T)$$



Gibb's Free-Energy Change at T_g

- Glasses then “fall off” the liquid line at progressively lower temperatures the slower the cooling rate
- Gibbs' Free-Energy of the glass behaves more like the crystal than the liquid
- Glass transition range is the range of T where the Gibb's Free-Energy changes from “liquid-like” values to “solid-like” values

