2009 spring

Advanced Physical Metallurgy

"Amorphous Materials"

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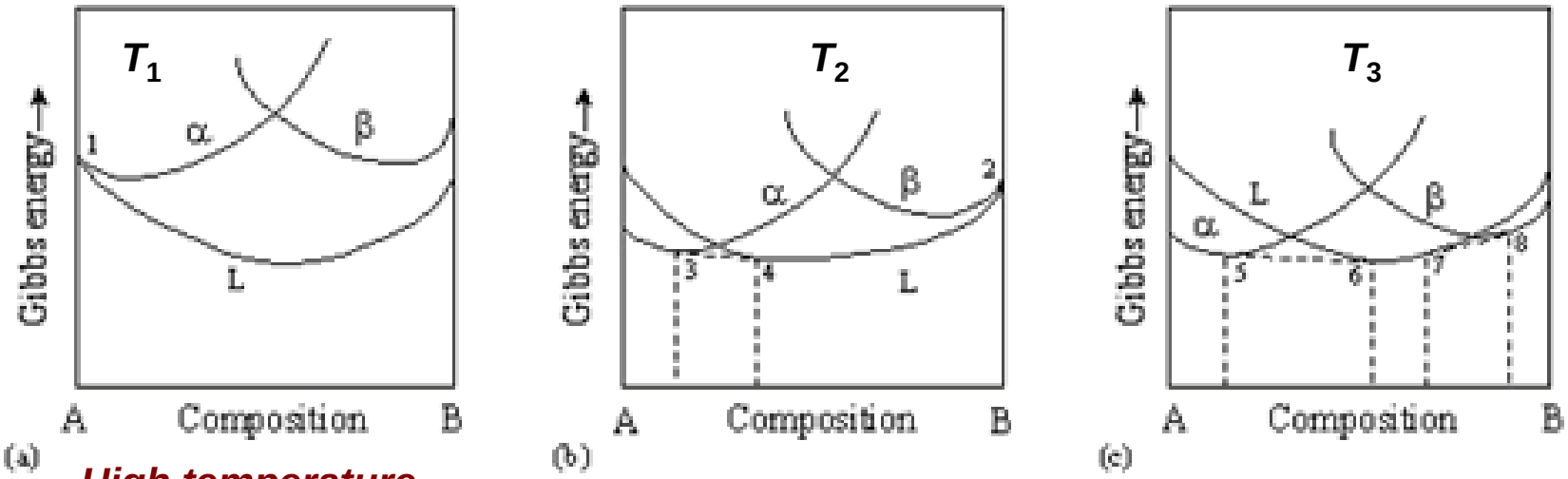
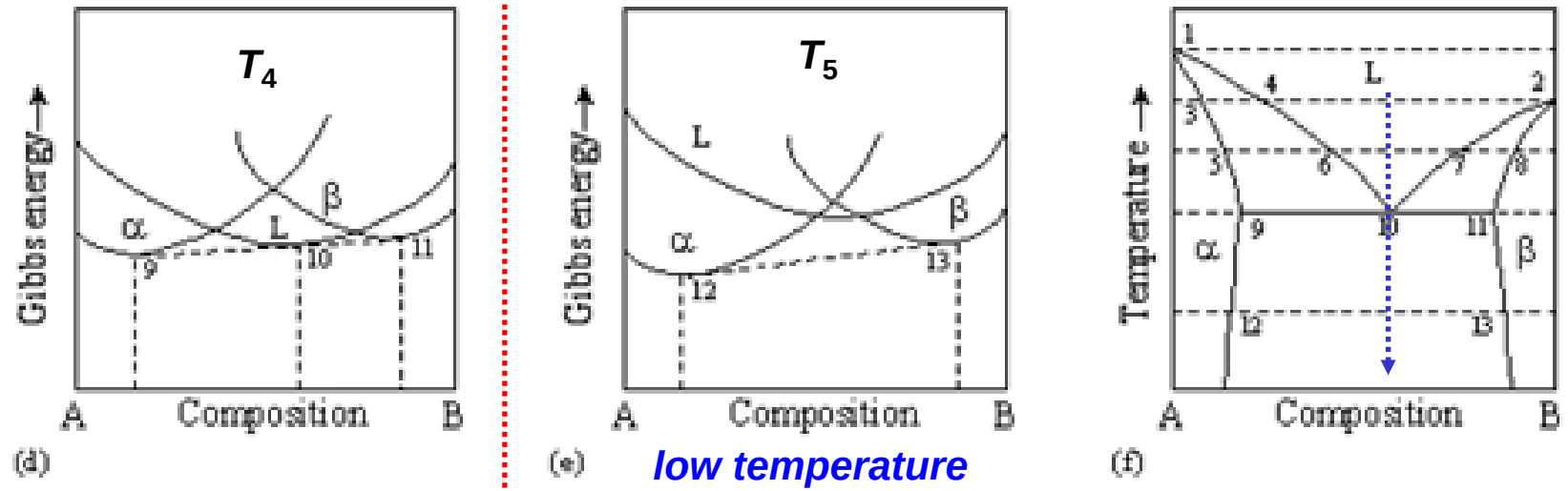
Use of Gibbs energy curves to construct a binary phase diagram of the eutectic type.



High temperature



low temperature

Liquid: metastable ⟶ glass

Theories for the glass transition

A. Thermodynamic phase transition

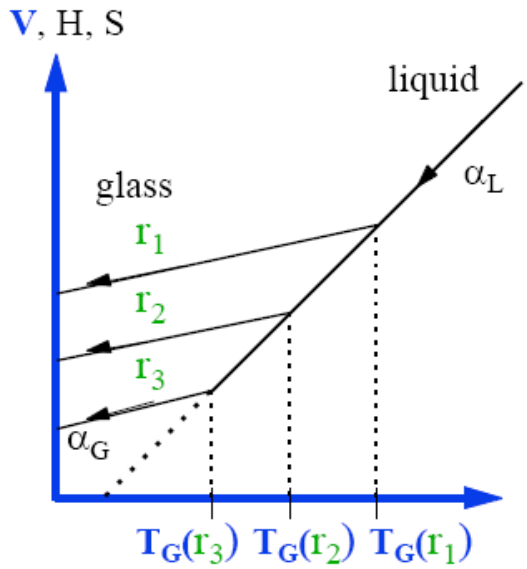
- **Glass transition**

  H , V , S : continuous C_p α_T K_T : discontinuous

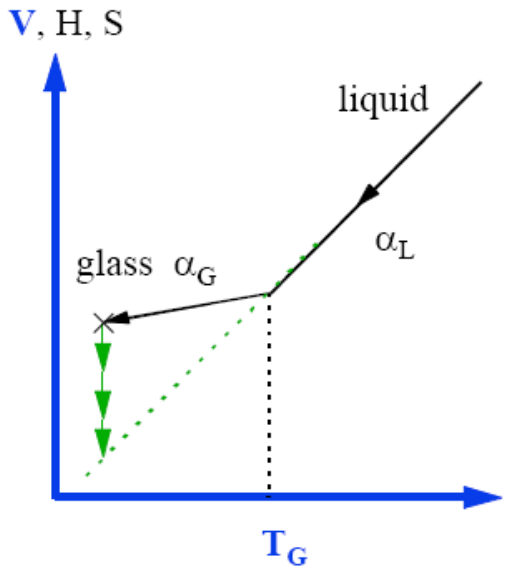
→ by thermodynamic origin, 2nd order transition

But, *1) Tg is dependent on thermal history of sample.*

→ If GT is 2nd order transition, Tg is not changed by kinetic factor.



Tg depends on the rate at which the liquid is cooled. $T_G(r_3) < T_G(r_2) < T_G(r_1)$ if $r_3 < r_2 < r_1$



Specific Volume (density) of the glass depends on the time at a given $T < T_g$

But, ***2) Thermodynamic consideration*** ***S , V : continuous***

(a) continuity of S

$$\therefore \frac{dT_g}{dP} = \frac{TV(\alpha_{T_2} - \alpha_{T_1})}{(C_{P_2} - C_{P_1})} = \frac{TV\Delta\alpha_T}{\Delta C_P} \qquad (1)$$

(b) continuity of V

$$\therefore \frac{dT_g}{dP} = \frac{\Delta\kappa_T}{\Delta\alpha_T} \qquad (2)$$

measureable

→ **Eq. (1) & (2) should be proved experimentally.**

It is found by measuring the discontinuities $\Delta\alpha_T$, ΔC_P, $\Delta\kappa_T$ at the glass transition that Eq. (1) is almost always obeyed within experimental error, but that values for $\Delta\kappa_T/\Delta\alpha_T$ are generally appreciably higher than those of dT_g/dP (Eq. (2)).

→ **Eq. (1) = satisfy** **Eq. (2) = dissatisfy :** $\frac{dT_g}{dP} < \frac{\Delta\kappa_T}{\Delta\alpha_T}$

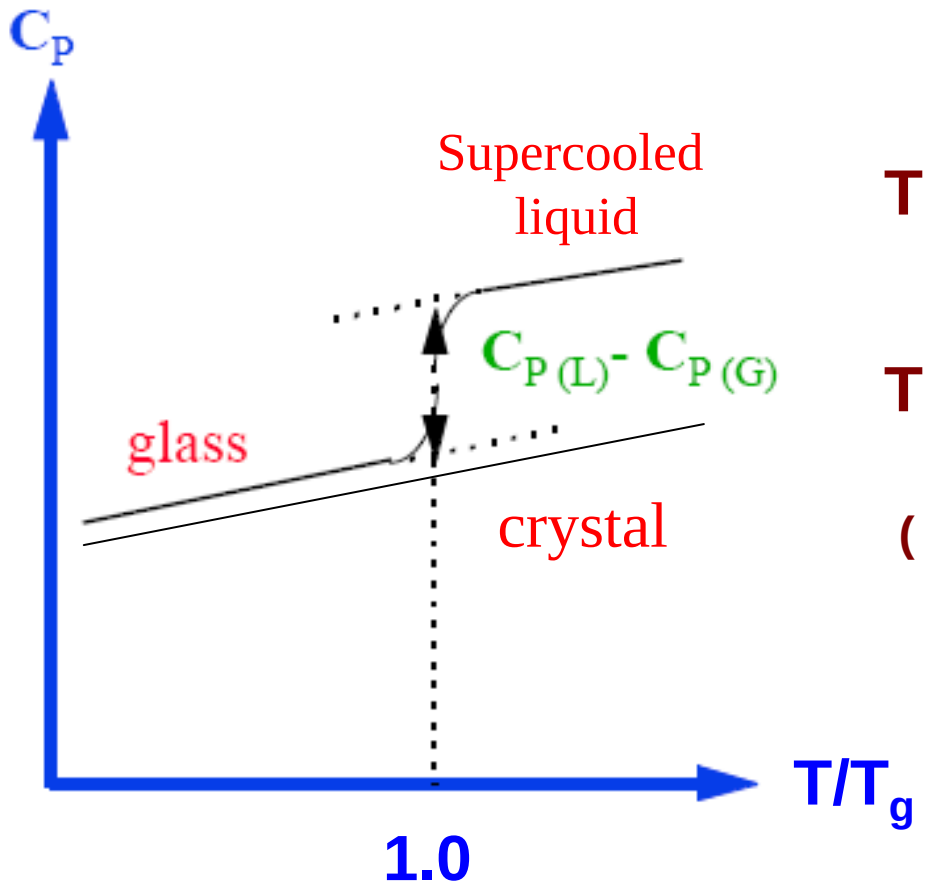
→ **Therefore, it appears on this evidence that the glass transition is not a simple second-order phase transition.**

Theories for the glass transition

B. Entropy

1) Heat capacity → **dramatic change at Tg**

$$S = \int C_P \, d \ln T$$



T < Tg $\quad C_{P_{glass}} \approx C_{P_{crystal}}$

T > Tg $\quad C_{P_{SCL}} > C_{P_{crystal}}$

(∵ configurational degree of freedom in S.C.L.)

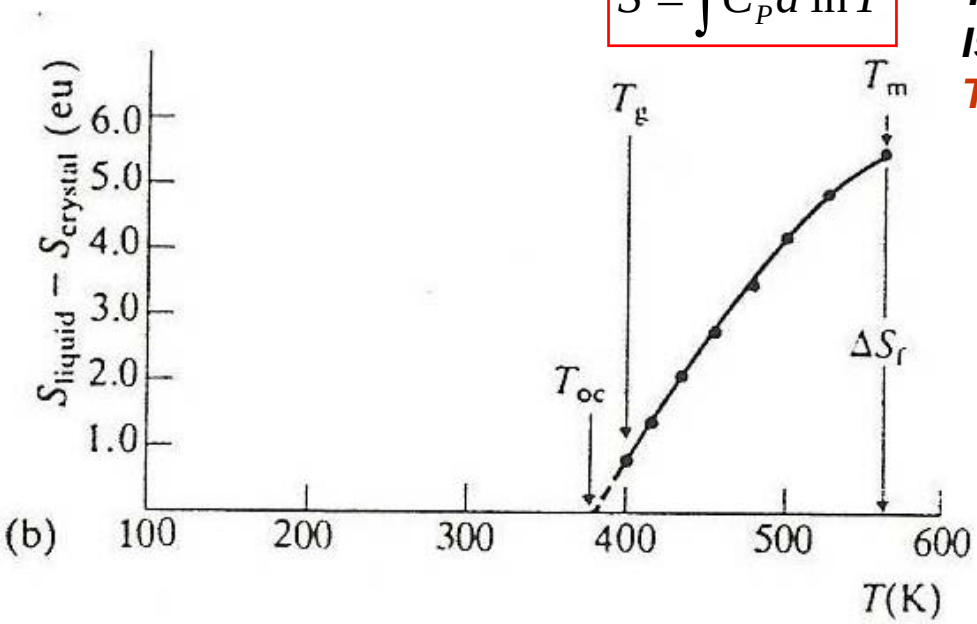
Theories for the glass transition

B. Entropy

- **Description of glass transition by entropy (Kauzmann)**

2) The slow cooling rate, the lower Tg

$$S = \int C_P d \ln T$$



The difference in entropy between liquid and crystalline phases as a function of temperature

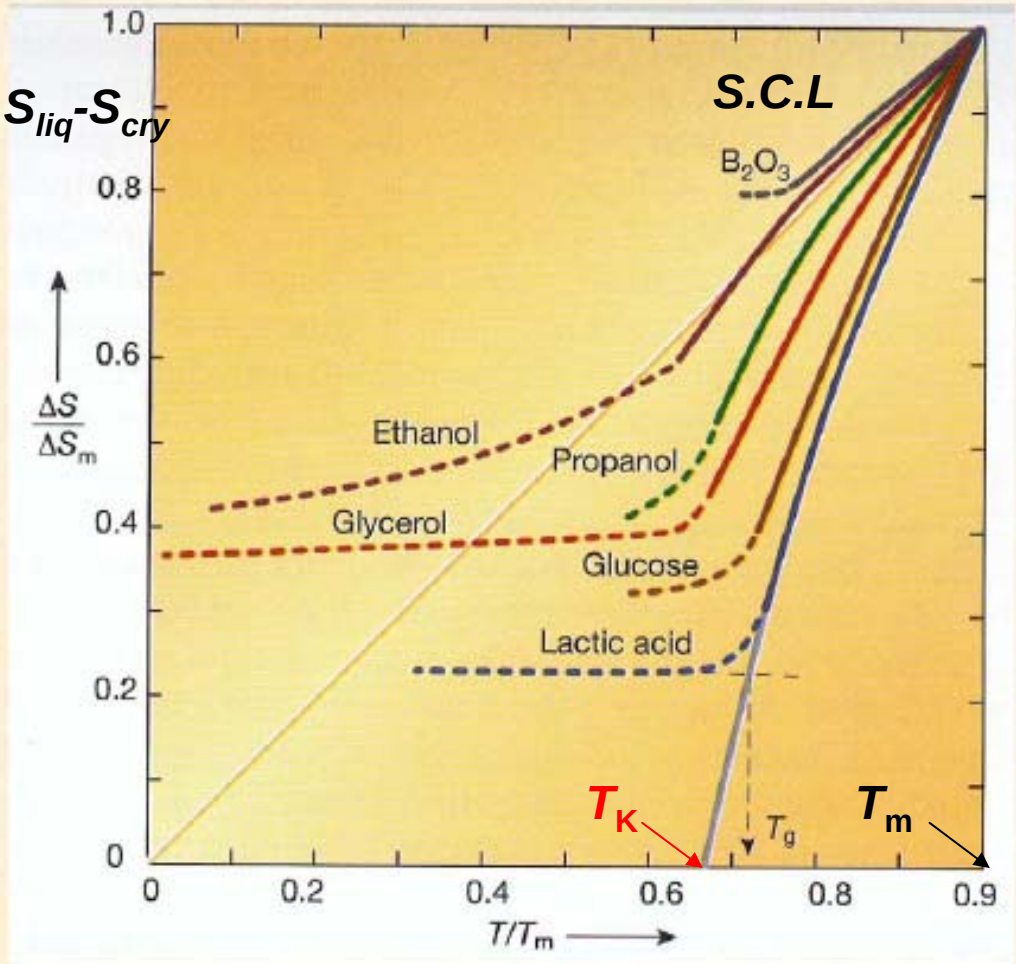
The temperature vanishing excess entropy Is termed the "ideal' glass transition temp. T_{oc} (Wong and Angell 1976)

$$T_g \rightarrow T_{0C} \quad as \quad \frac{dT}{dt} \rightarrow 0$$

➡ ***Not satisfied with third law of thermodynamics***

T_{OC}: lower temperature limit to occur glass transition thermodynamically

- ***Kauzmann's paradox*** **Thermodynamics: The configurational entropy apparently extrapolates to zero at low temperatures.**



T_K defined by an extrapolation of equilibrium properties. Not really justified. If point defects with finite formation energy are present in a reference configuration, the extrapolation is incorrect (Stillinger).

→ **Measurement of Kauzmann temp. is almost impossible.**

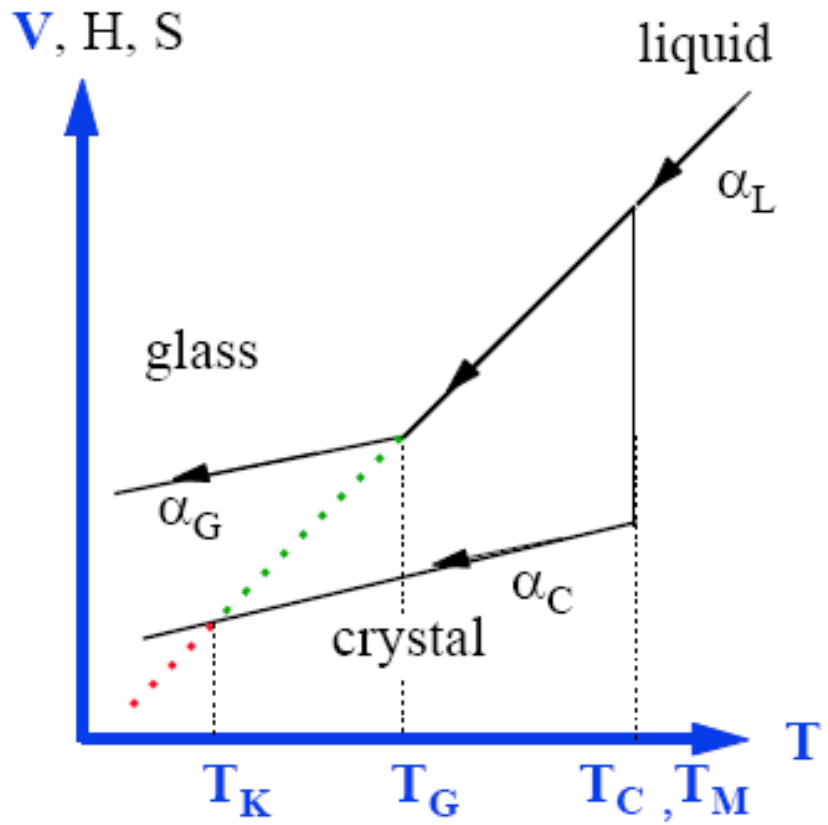
(∵ very slow cooling rate → longer relaxation time → crystallization

Controversies in Amorphous Solids: The Kauzmann Paradox

Kauzmann paradox is not possible, two solutions are possible:

1) At T_K, there is a true 2nd order phase transition between the liq. and the glass.

2) The extrapolation to temperatures far below T_G is not valid.



How does thermodynamics different from kinetics?

Thermodynamics ➡ **There is no time variable.**

says which process is possible or not and never says how long it will take.

The existence of a thermodynamic driving force does not mean that the reaction will necessarily occur!!!

There is a driving force for diamond to convert to graphite but there is (huge) nucleation barrier.

How long it will take is the problem of kinetics.

The time variable is a key parameter.

- **The laws of thermodynamics**

1) Zeroth law: thermal equilibrim
   Objects in thermodynamic equilibrium have the same temperature.

2) First law: conservation of energy
   Energy can be neither created nor destroyed but only transformed.

3) Second law: entropy, $S > 0$
   The entropy of an isolated system not in equilibrium will tend to increase over time, approaching a maximum value at equilibrium.

3) Third law: absolute zero
   As a system approaches absolute zero of temperature, all processes cease and the entropy of the system approaches a minimum value.