2010 Spring

"Amorphous Materials"

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Eun Soo Park

Office: 33-316
Telephone: 880-7221
Email: espark@snu.ac.kr
Office hours: by an appointment

Fragility

~ extensively use to figure out liquid dynamics and glass properties corresponding to "frozen" liquid state

< Quantification of Fragility >

$$m = \left.\frac{d\log\eta(T)}{d(T_{g,n}/T)}\right|_{T=T_{g,n}} = \left.\frac{d\log\tau(T)}{d(T_g/T)}\right|_{T=T_g}$$

Slope of the logarithm of viscosity, η (or structural relaxation time, τ) at T_g

- ***Strong liquid vs. Fragile liquid***

  - ***Strong glass forming liquid***

→ **covalent bond of SiO_2**

→ **small difference of C_p between SCL and glass at T_g** *(small difference of structu*

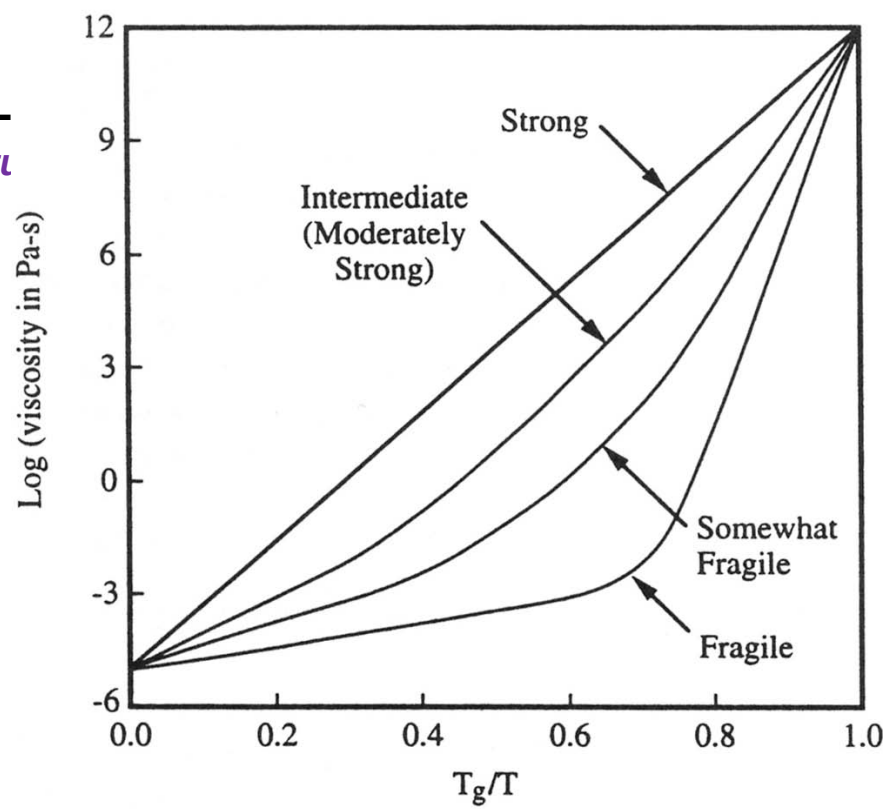
→ **SCL: relatively low entropy**

  - ***Fragile glass forming liquid***

→ **non-directional bonding** *(Van der waals bonding)*

→ **large difference of C_p at T_g** *(relatively large free volume)*

→ **SCL: relatively high entropy**

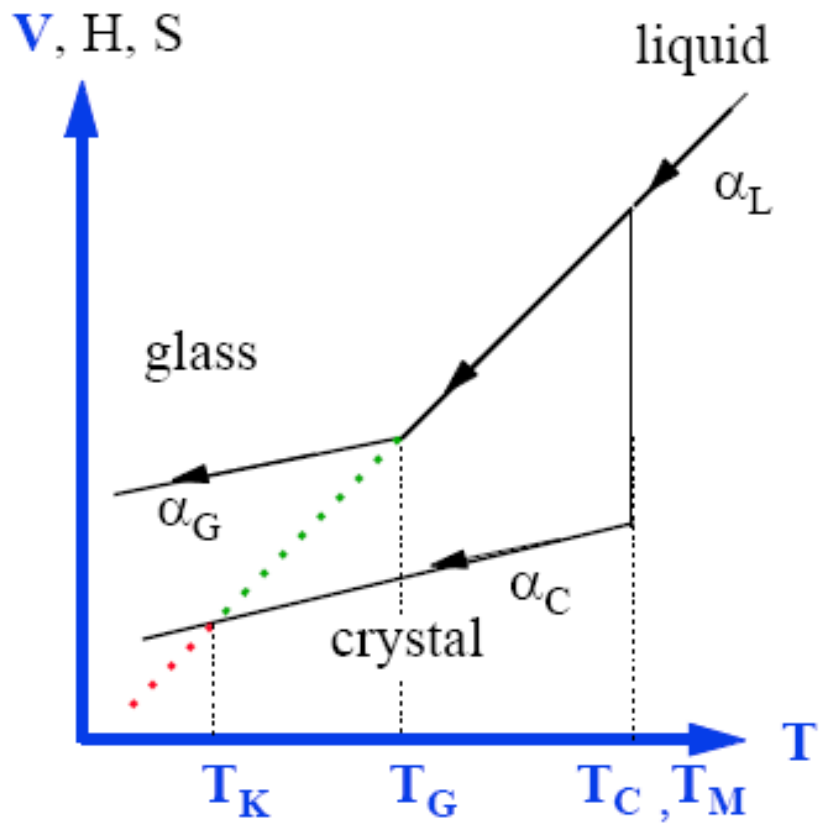


Controversies in amorphous solids: The Kauzmann Paradox

Kauzmann paradox is not possible, two solutions are possible:

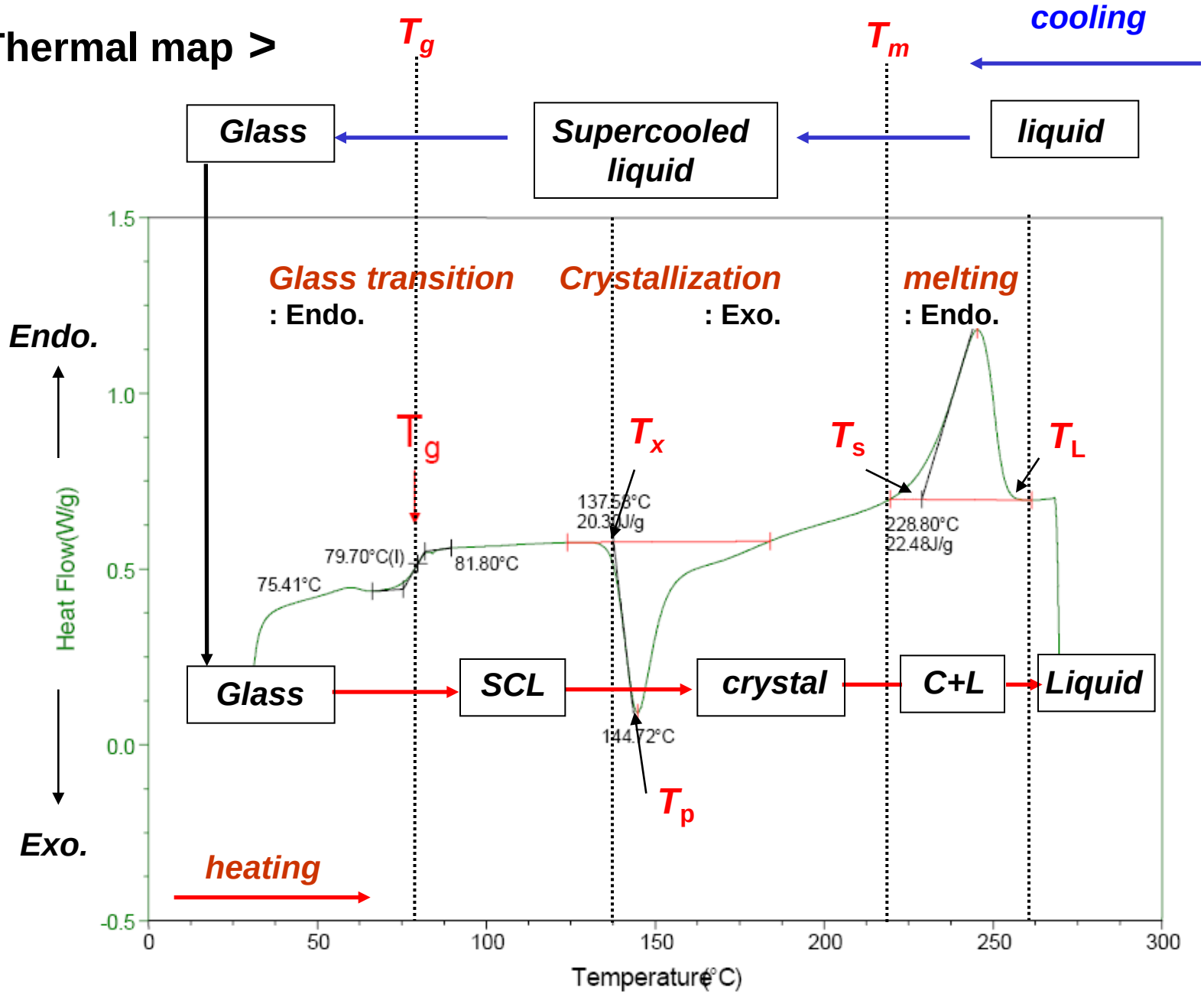
1) At T_K, there is a true 2nd order phase transition between the liq. and the glass.

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

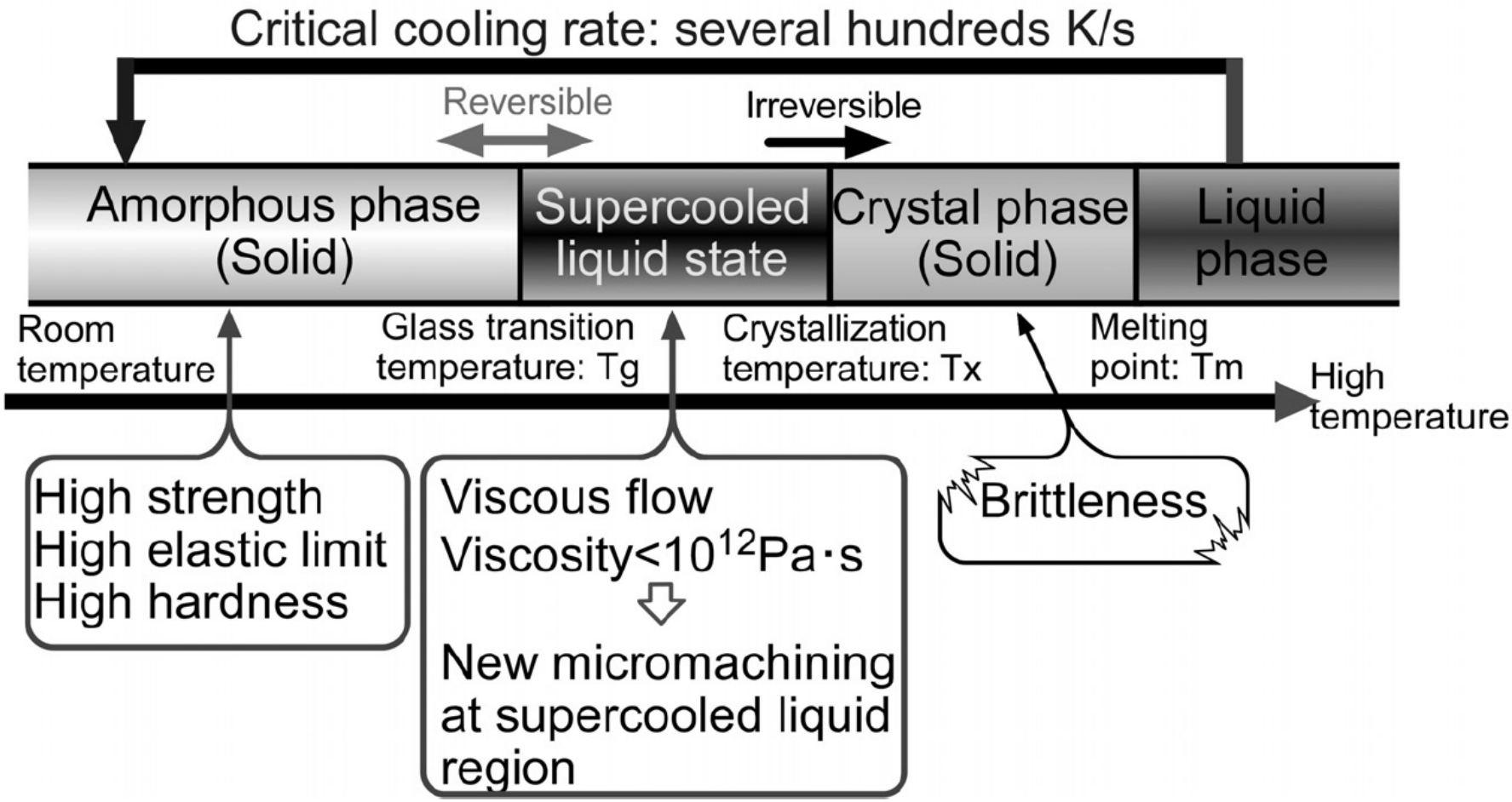


* Measurement of T_g : DSC, DTA, TMA & DMA

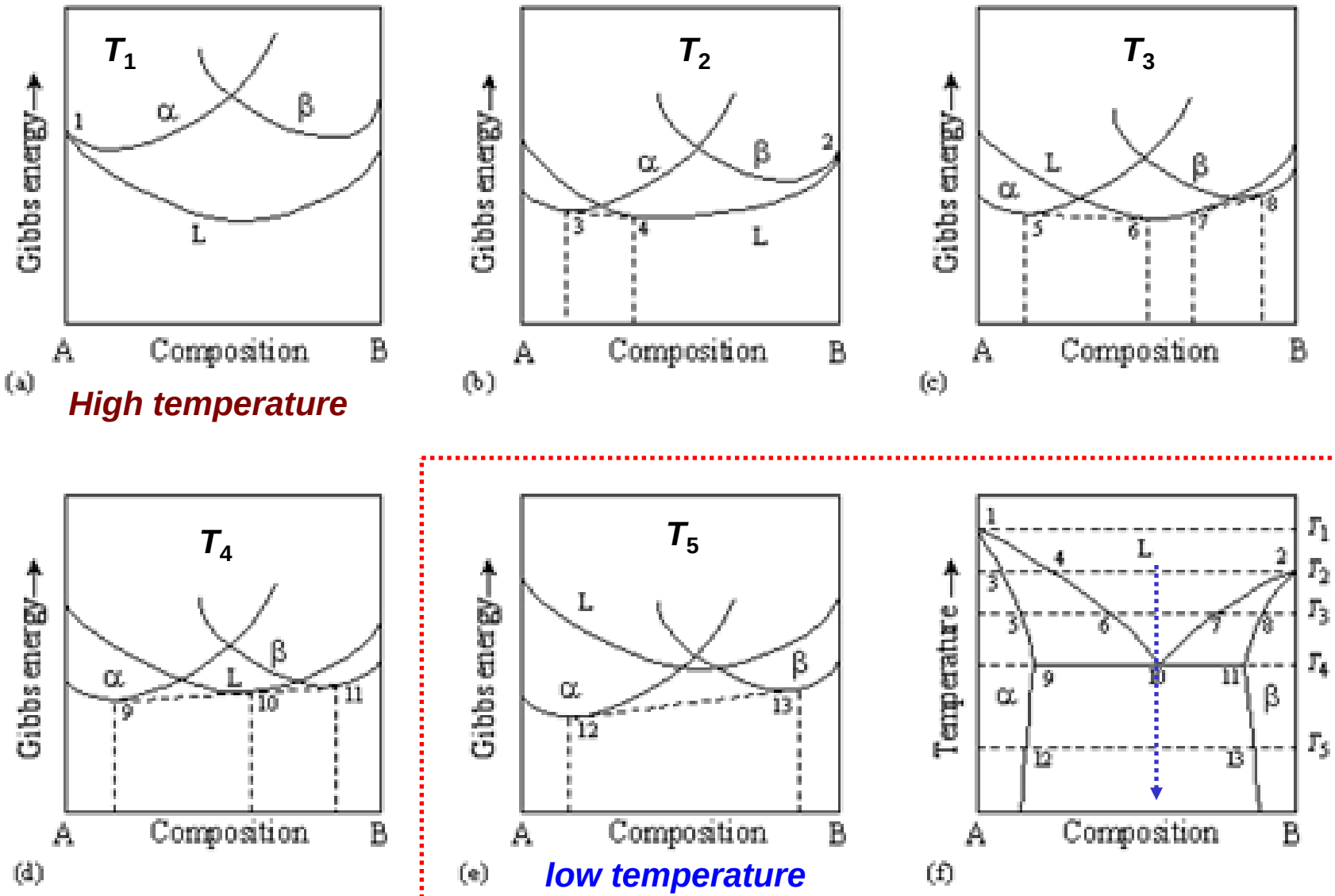
< Thermal map >



< Characteristics of metallic glass >



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

- ***4 viewpoints for Glass transition***

Viscosity

Entropy

Free volume

Relaxation behavior

Kinetic variables depending on time

→ **glass transition can be realized by evaluating one of factors.**

➡ **by thermodynamic origin, 2nd order transition**

H , V , S* : *continuous

C_p α_T K_T* : *discontinuous

Theories for the glass transition

A. Thermodynamic phase transition

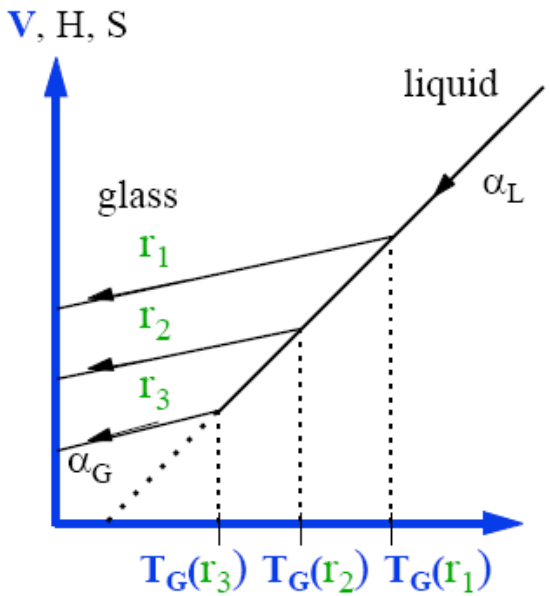
- ***Glass transition***

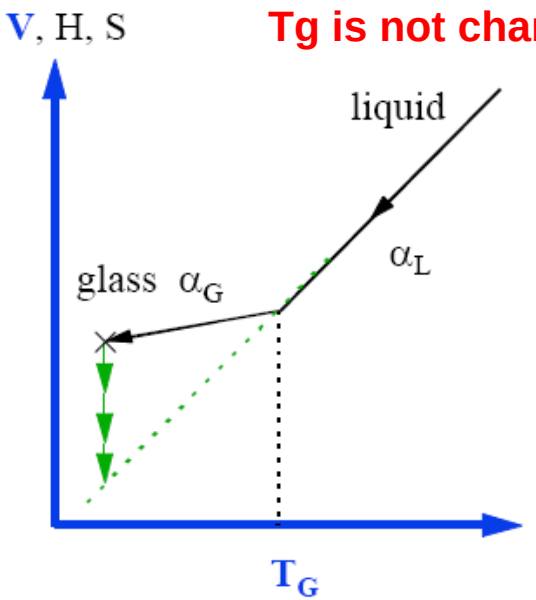
H , V , S : continuous ***C_p α_T K_T : discontinuous***

→ **by thermodynamic origin, 2nd order transition**

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

→ **If 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 $T < T_g$

Value of the Prigogine Defay Ratio: R

- Continuity conditions for G or μ at a first order phase transition allowed us to derive the Clapeyron equation $\left(\frac{dP}{dT}\right) = \frac{\Delta S}{\Delta V} = \frac{\Delta H}{T\Delta V}$

- If T_G is a second order transition, continuity of V and S at T_G leads to two similar relations between materials parameters and state variables.

$$V_G = V_L \qquad dV_G = dV_L$$
$$dV_G = \alpha_G V_G\, dT - \kappa_G V_G\, dP$$
$$dV_L = \alpha_L V_L\, dT - \kappa_L V_L\, dP$$

$$\Rightarrow \quad \left(\frac{dP}{dT}\right) = \frac{\Delta C_p}{VT\Delta\alpha}$$

$$S_G = S_L \qquad dS_G = dS_L$$
$$dS_G = (C_P^G / T)dT - \alpha_G V_G\, dP$$
$$dS_L = (C_P^L / T)dT - \alpha_L V_L\, dP$$

$$\Rightarrow \quad \left(\frac{dP}{dT}\right) = \frac{\Delta\alpha}{\Delta\kappa}$$

By combining both Ehrenfest equations without invoking a second-order thermodynamic transition,

$$R = \frac{\Delta C_p \Delta\kappa}{VT(\Delta\alpha)^2}$$

→ Prigogine Defay Ratio:R

Application of Clausius-Clapeyron relation in the real world

$$\left(\frac{dP}{dT}\right)_{eq} = \frac{\Delta H}{T_{eq}\Delta V}$$

→ applies to all coexistence curves

↓

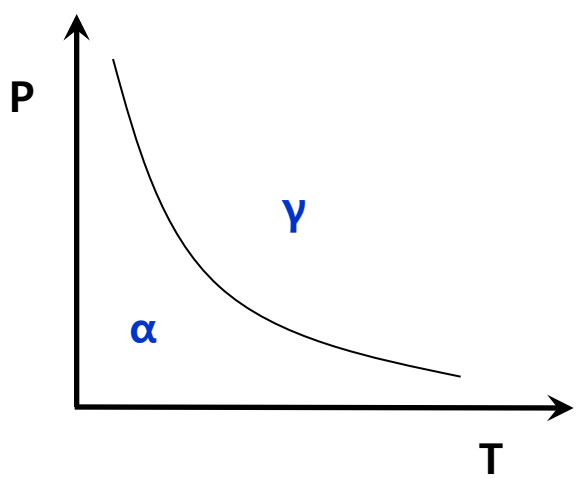
applies to all phase transformation

For example, γ phase transformed to α phase at eq. temperature in Fe.

If applies $\left(\frac{dP}{dT}\right)_{eq} = \frac{\Delta H}{T_{eq}\Delta V}$

volume change : $\Delta V = V_\alpha - V_\gamma > 0$

enthalpy change : $\Delta H = H_\alpha - H_\gamma < 0$



$$\left(\frac{dP}{dT}\right)_{eq} = \frac{\Delta H}{T_{eq}\Delta V} < 0$$

If T increases, |slope| decreases.

적용 사례 1 : 산에서 밥이 설익는 현상

$$\left(\frac{dP}{dT}\right)_{eq} = \frac{\Delta H}{T_{eq}\Delta V}$$

산에서는 기압이 지상에서의 기압보다 낮아지므로,

물분자의 증발이 더 쉬워진다.

즉, Δ V 가 증가하게 된다.

따라서 물의 끓는점(T_{eq})은 100 °C 보다 낮아지게 되고,

100 °C 보다 낮은 온도에서 끓는 밥은 설익게 되는 것이다.

적용 사례 2 : 냉장고에서 음식이 수분을 잃는 현상

냉장고에서는 온도가 항상 낮게 유지된다. 따라서 증기압도 낮게 유지된다.

그러므로 음식 안에 있는 수분들이 냉장고 공기 중으로 쉽게 증발한다.

이는 우리가 밥이나 빵을 냉장고에 넣은 후에 먹을 때 음식이 딱딱해지는 현상과 밀접한 관련이 있다.

Application of Clausius-Clayperon Relation in the real world

Ice skating

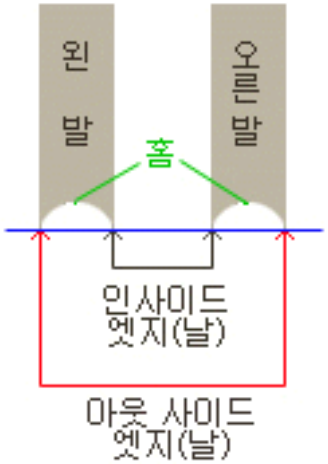
물의 경우, 고체-액체 경계 곡선은 음의 기울기를 가지며,

∴ 외부압력이 증가 → 녹는점 하강

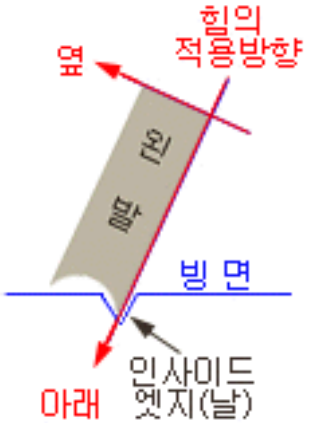
스케이트는 매우 날카로운 칼날을 갖고 있기 때문에
약 60 kg의 체중을 갖는 사람이 스케이트를 신고 서있을 때 얼음에 약 500 기압을 가하는 효과
→ **스케이트 밑의 얼음은 0℃이하에서도 녹게 되고** 스케이트 밑에는 얇은 막이 형성해 얼음 위를 부드럽게 미끄러지게 한다.

수치적으로 계산해 보면, 1 기압이 증가할 때마다 0.0074℃ 씩 내려가서
60 kg의 체중으로 인하여 물이 실제로 녹는점은 -3.7 ℃까지 하강

[1] 날의 구성



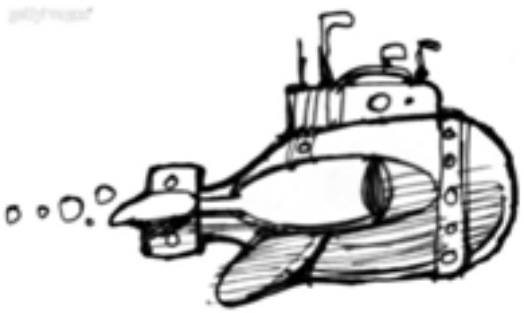
[2] 빙면과 날의 접촉



Clausius-Clapeyron Equation in Real Life

❖ Why the bubbles form near the screw of the boat

- When riding a boat, bubbles formed near the screw are seen. Mechanism of bubble formation is closely related to Clausius-Clapeyron equation.



High speed of the screw
→ Velocity of fluid increases $v \uparrow$

↓

Pressure of water near screw decreases $p \downarrow$

↓

Boiling temperature of water decreases $\Delta T < 0$

↓

Water turns into vapor even at low temperature

Bernoulli's Equation

$$\frac{v^2}{2} + gh + \frac{p}{\rho} = \text{constant}$$

Clausius-Clapeyron Equation

$$\frac{\mathrm{d}P}{\mathrm{d}T} = \frac{L}{T\Delta V}$$

Ref.
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