2009 fall

Phase Transformation of Materials

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Contents for previous class

Contents in Phase Transformation

상변태를
이해하는데
필요한 배경

- **(Ch1)** 열역학과 상태도: **Thermodynamics**
- **(Ch2)** 확 산 론: **Kinetics**
- **(Ch3)** 결정계면과 미세조직

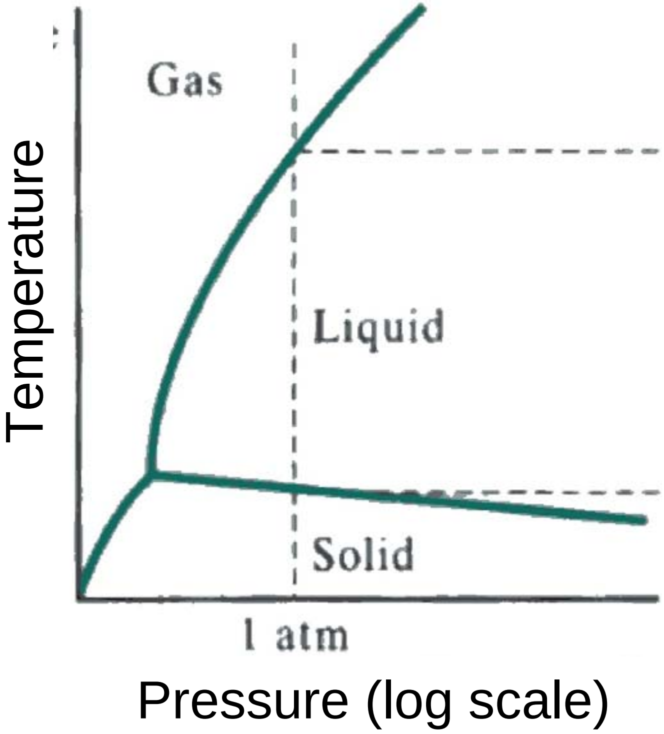
대표적인 상변태

- **(Ch4)** 응 고: **Liquid → Solid**
- **(Ch5)** 고체에서의 확산 변태: **Solid → Solid (Diffusional)**
- **(Ch6)** 고체에서의 무확산 변태: **Solid → Solid (Diffusionless)**

Contents for previous class

Basic Ideas

Phase 균일한 물리적 • 화학적 특성을 갖는 계의 한 부분



Phase diagram

일반적으로 평형상태에서의 환경제약 인자 (예:온도 또는 압력), 조성 및 안정된 상 구역 사이의 관계를 도식적으로 나타냄

→ ***Thermodynamics***

Phase Transformation

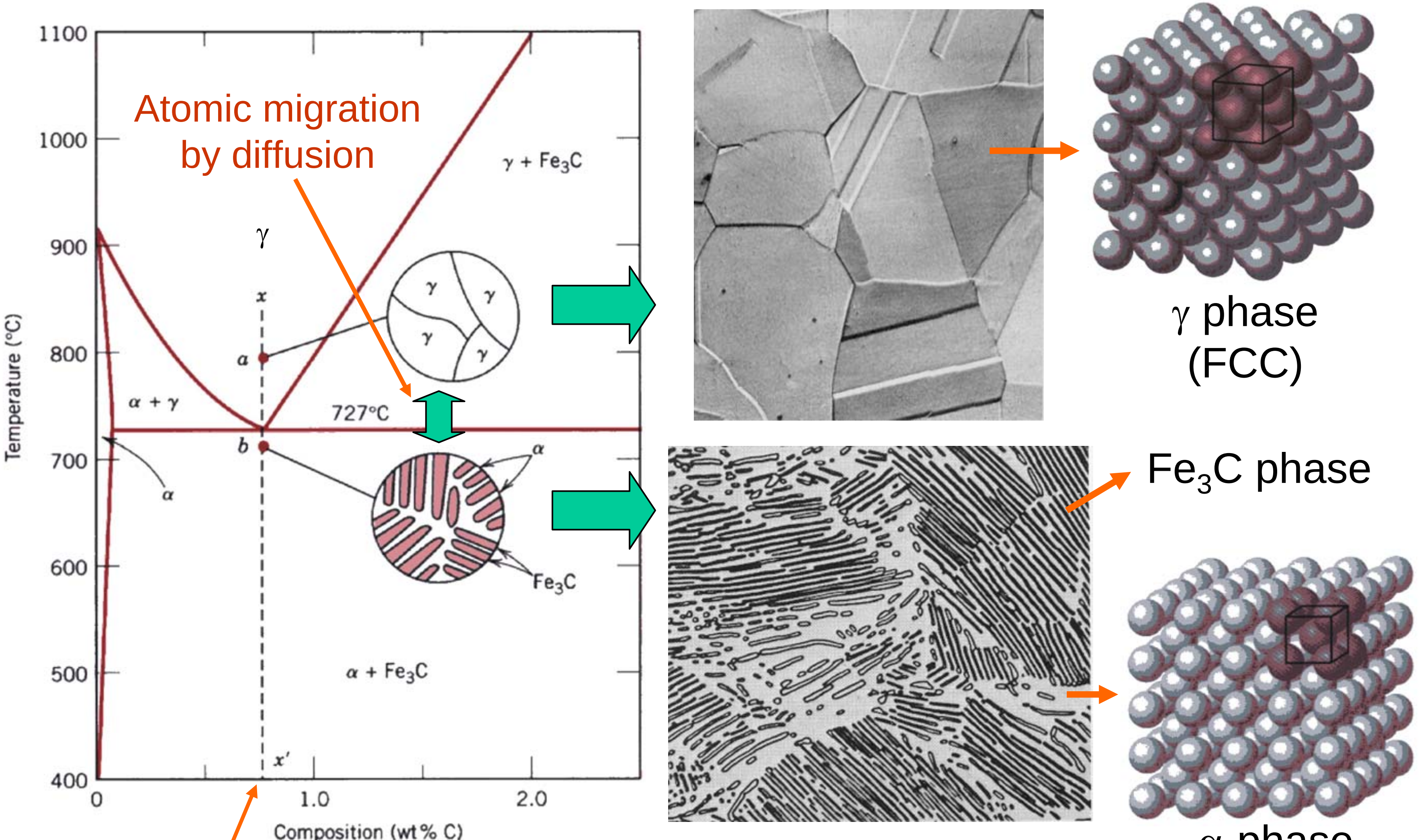
하나의 상에서 다른 상으로 변화 → 비평형 상태 동반

structure or **composition** or **order**

→ ***Thermodynamics & Kinetics***

Contents for previous class

Equilibrium Phases of Iron-Carbon Alloy



Atomic migration by diffusion

γ phase (FCC)

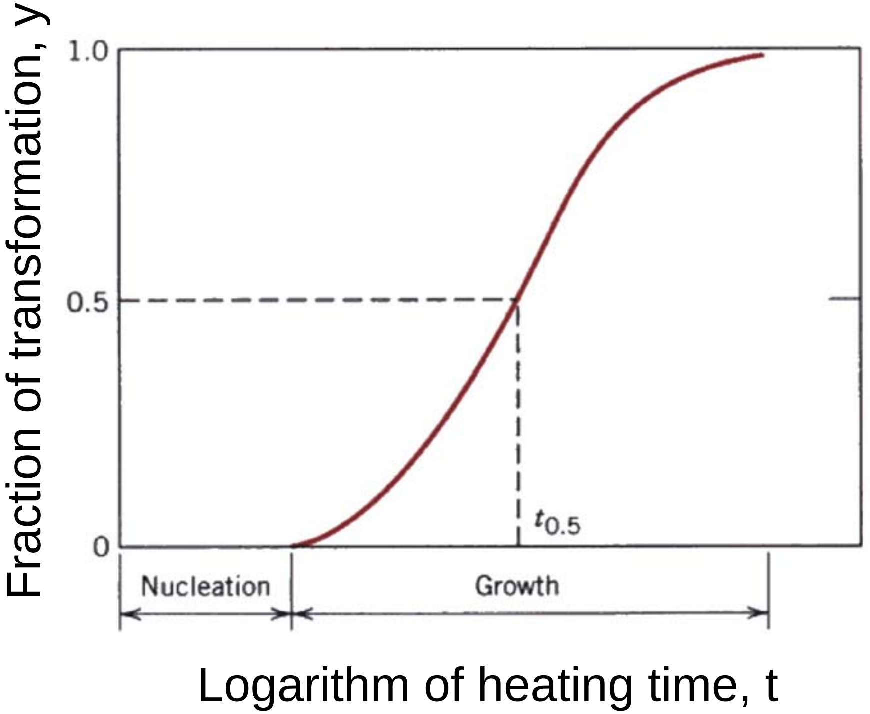
Fe_3C phase

α phase (BCC)

Eutectoid composition

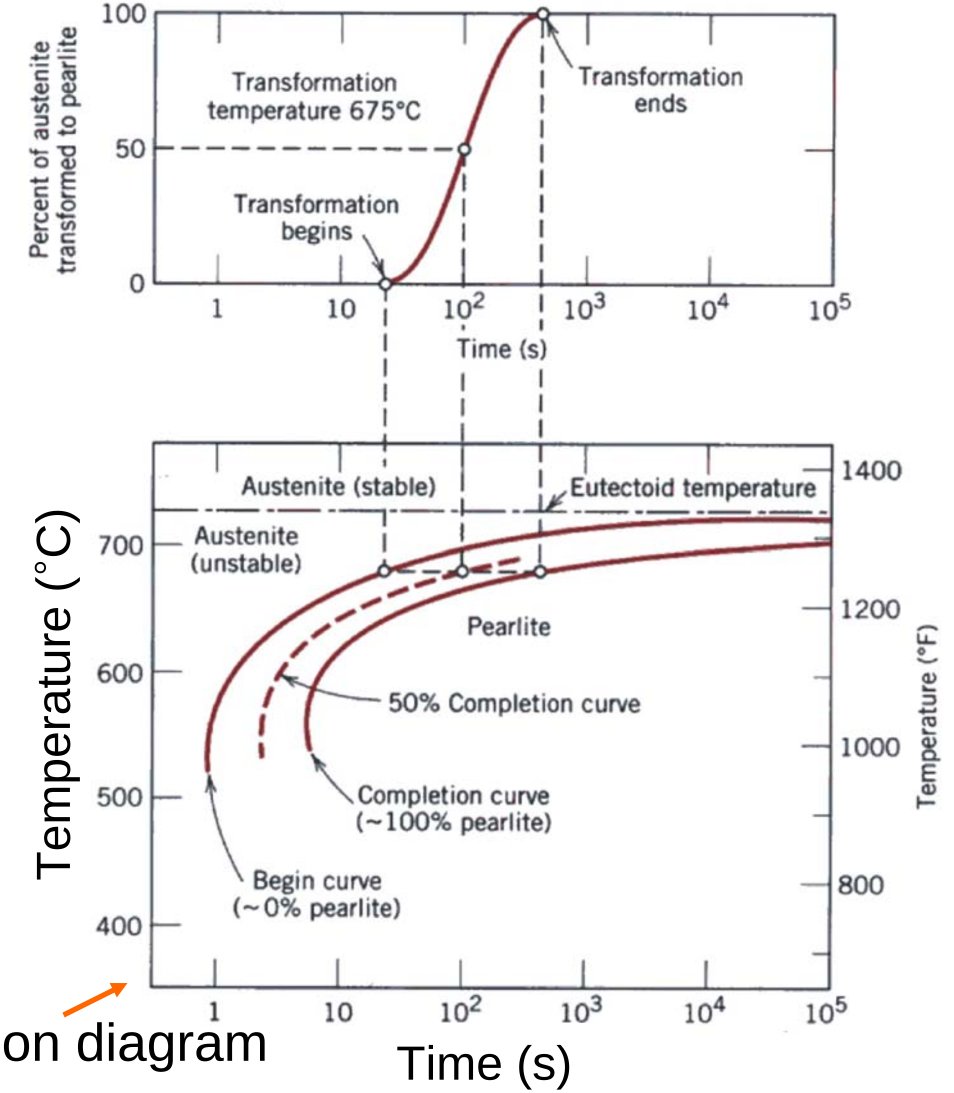
Contents for previous class

Transformation Kinetics and Isothermal Transformation Diagram



$$y = \exp(-kt^n)$$

Kinetics of diffusion-controlled solid-state transformation



Isothermal transformation diagram

Contents for today's class

Chapter 1

Thermondynamics and Phase Diagrams

- Equilibrium
- Single component system

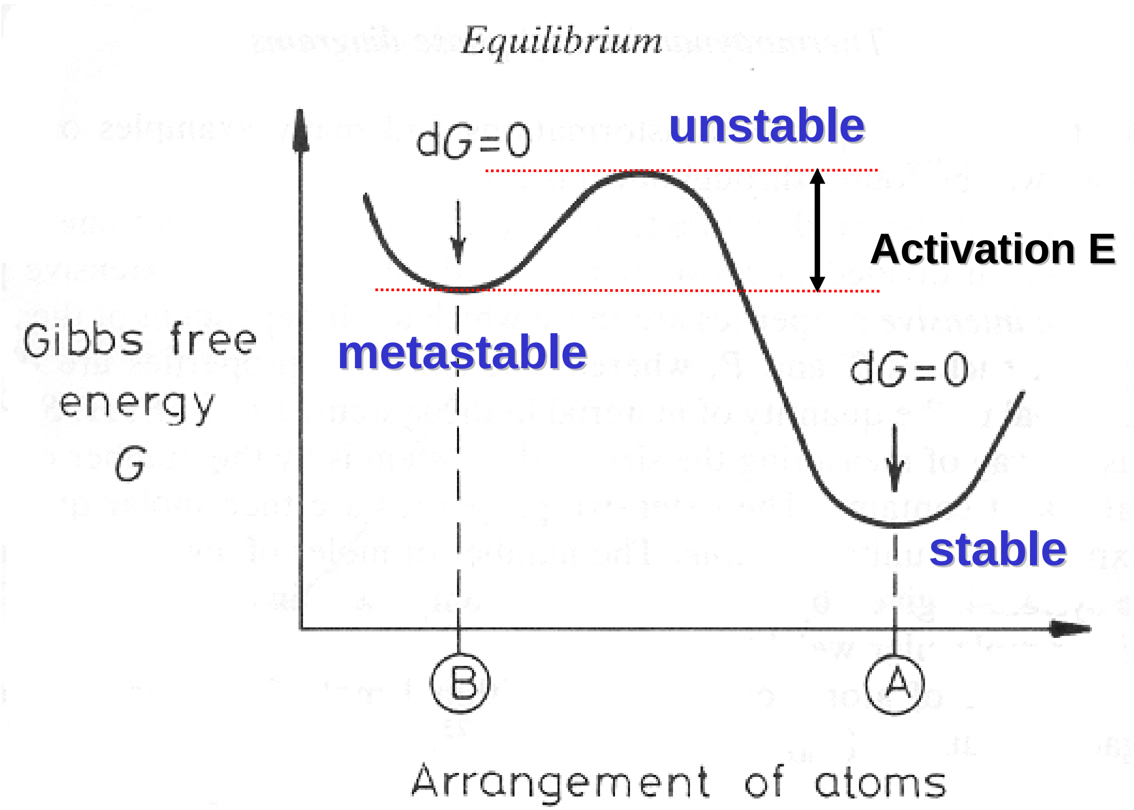
  Gibbs Free Energy
  as a Function of Temp. and Pressure
- Driving force for solidification
- Classification of phase transition

Equilibrium

$$\boxed{dG = 0}$$

Lowest possible value of Gibb's Free Energy

No desire to change ad infinitum



Phase Transformation

$$\boxed{\Delta G = G_2 - G_1 < 0}$$

Relative Stability of a System → Gibbs Free Energy

$$\boxed{G = H - TS}$$

H : Enthalpy ; Measure of the heat content of the system

$$H = E + PV$$

$$H \cong E \quad \textit{for Condensed System}$$

E : Internal Energy, Kinetic + Potential Energy of a atom within the system

Kinetic Energy :

Atomic Vibration (Solid, Liquid)

Translational and Rotational Energy in liquid and gas.

Potential Energy : Interactions or Bonds between the atoms within the system

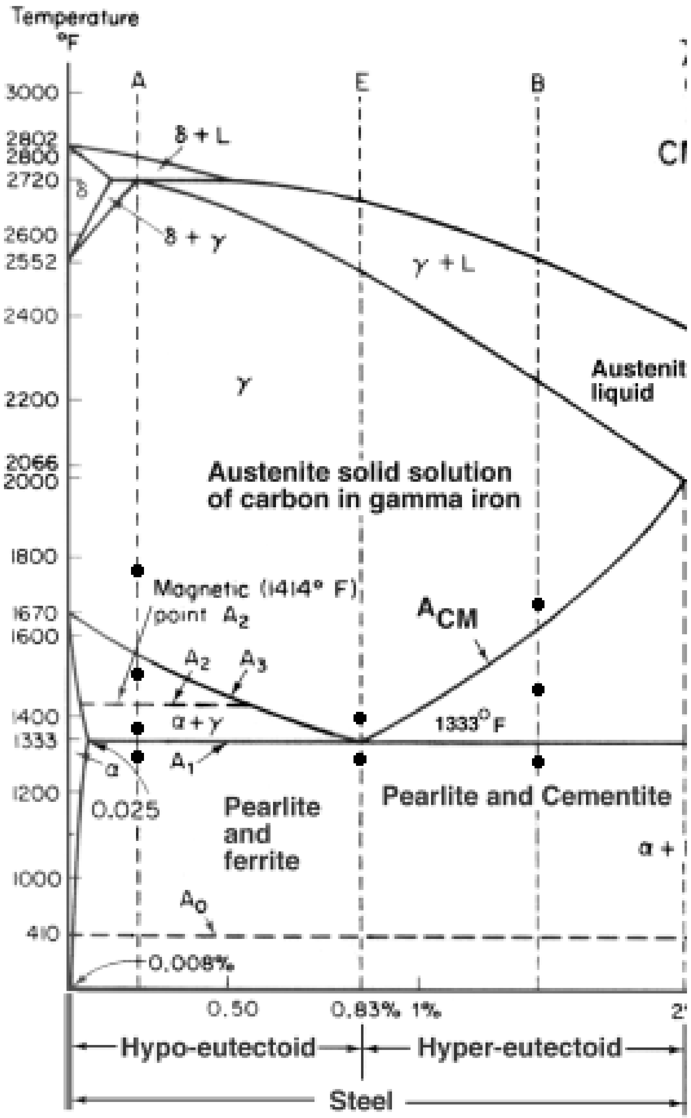
T : *The Absolute Temperature*

S : Entropy, The *Randomness* of the System

1.2 Single component system (단일성분계)

One element (Al, Fe)

One type of molecule (H_2O)



Fe ⟶ **C**

$$G = H - TS$$

⇨ 1.2.1 Gibbs Free Energy as a Function of Temp.

$$H = E + PV \longrightarrow \boxed{dE = \delta Q - P \cdot dV}$$

When V is constant

$$\frac{\delta Q}{dT} = \frac{dE}{dT} + P\,\cancelto{0}{\frac{dV}{dT}} \qquad C_V = \left(\frac{\partial Q}{\partial T}\right)_V = \left(\frac{\partial E}{\partial T}\right)_V \qquad \boxed{C_V = \left(\frac{\partial E}{\partial T}\right)_V \quad \text{or} \quad E = \int C_V\, dT}$$

실험적으로 V 를 일정하게 하는 것 (Cv)이 어렵기 때문에 V 보다 P를 일정하게 유지하는 것 (Cp)이 편함 → pressure ex)1 atm,

When pressure is const.

$$H \equiv E + PV$$

$$\begin{aligned} dH &= dE + PdV + VdP \\ &= \delta Q - \delta w + PdV + VdP \\ &= \delta Q - PdV + PdV + VdP \\ &= \delta Q + VdP \end{aligned}$$

$$\frac{dH}{dT} = \frac{\delta Q}{dT} + V\frac{dP}{dT}$$

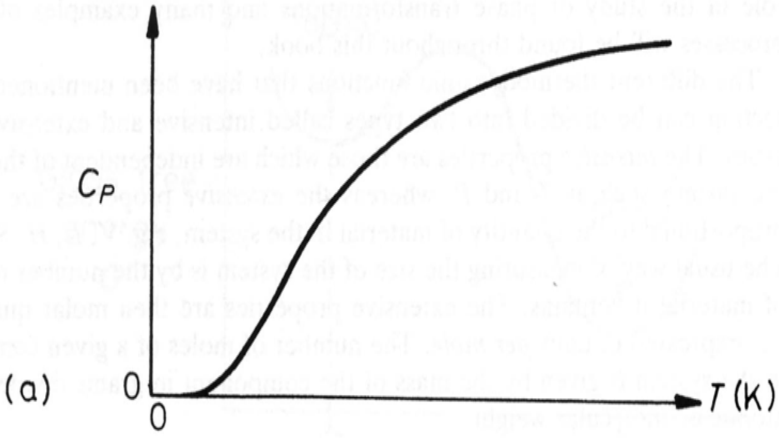
$$\frac{dP}{dT} = 0 \quad \text{when} \quad P \text{ is constant}$$

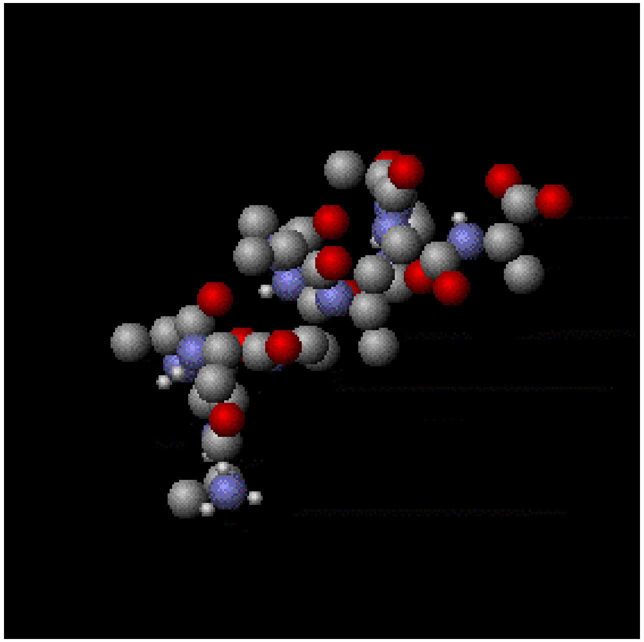
$$\boxed{\left(\frac{dH}{dT}\right)_P = \left(\frac{\delta Q}{dT}\right)_P = C_P} \qquad \boxed{H = \int C_p\, dT}$$

C_P ; 온도에 따라 변함 (온도의 함수)

$$C_P = a + bT + CT^{-2}$$

(경험식 above room temp)





Molecules have internal structure because they are composed of atoms that have different ways of moving within molecules. Kinetic energy stored in these *internal degrees of freedom* contributes to a substance’s specific heat capacity and not to its temperature.

Table of specific heat capacities

Substance	Phase	C_p J / g·K	C_p J / *mol*·K	C_v J / *mol*·K	Volumetric heat capacity J / cm^3·K
Aluminium	Solid	0.897	24.2		2.422
Copper	solid	0.385	24.47		3.45
Diamond	solid	0.5091	6.115		1.782
Gold	solid	0.1291	25.42		2.492
Graphite	solid	0.710	8.53		1.534
Iron	solid	0.450	25.1		3.537
Lithium	solid	3.58	24.8		1.912
Magnesium	solid	1.02	24.9		1.773
Silver	solid	0.233	24.9		
Water	liquid (25 °C)	4.1813	75.327	74.53	4.184
Zinc	solid	0.387	25.2		

All measurements are at 25 °C unless otherwise noted.

Draw the plots of (a) C_p vs. T, (b) H vs. T and (c) S vs. T.

How is C_p related with H and S?

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

H = ?

$$H = \int_{298}^{T} C_P dT$$

H = 0 at 298K for a pure element

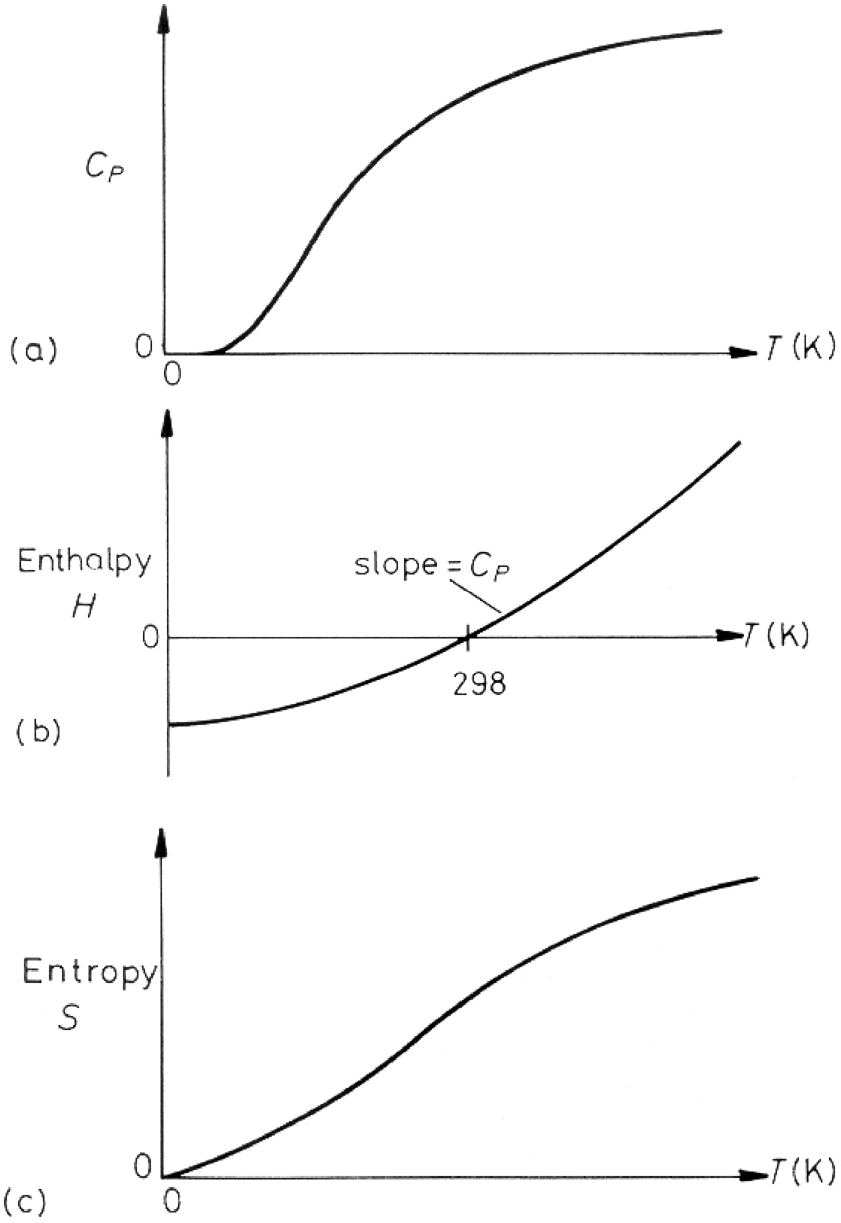
in its most stable state.

$$\text{Enropy}\ :\quad S = \frac{q}{T}$$

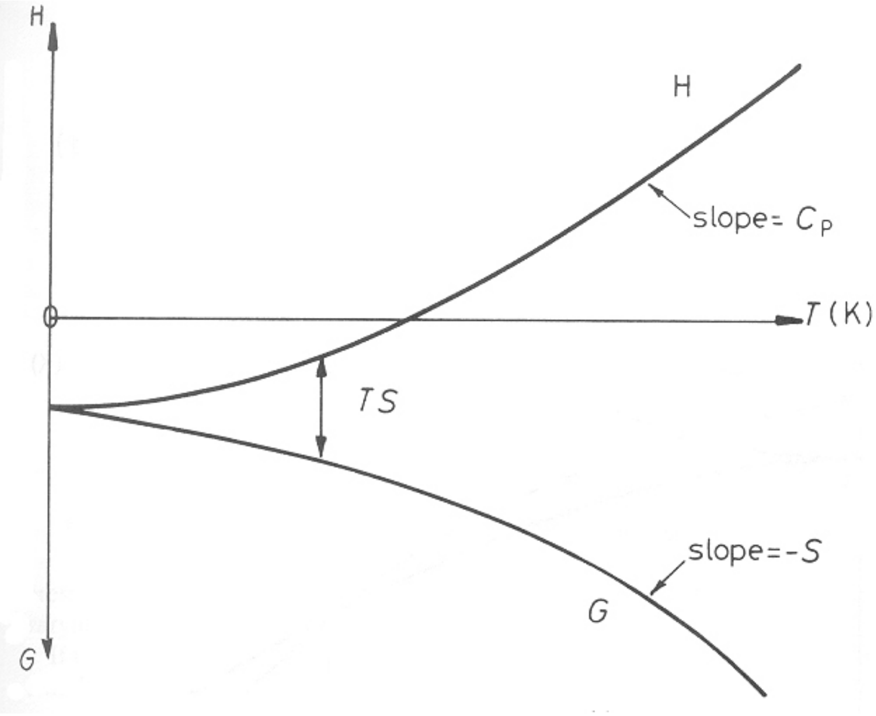
S = ?

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

$$S = \int_{0}^{T} \frac{C_P}{T} dT$$



Compare the plots of H vs.T and G vs. T.



$$G = G(T, P)$$

$$dG = \left(\frac{\partial G}{\partial T}\right)_P dT + \left(\frac{\partial G}{\partial P}\right)_T dP$$

$$G = H - TS$$

$$dG = dH - d(TS) = dE + d(PV) - d(TS)$$

$$dG = TdS - PdV + PdV + VdP - TdS - SdT$$

$$= VdP - SdT$$

$$\left(\frac{\partial G}{\partial T}\right)_P = -S\,, \qquad \left(\frac{\partial G}{\partial P}\right)_T = V$$

$$dG = VdP - SdT$$

$$G(P,T) = G(P_0,T_0) + \int_{P_0}^{P_1} V(T_0,P)dP - \int_{T_0}^{T_1} S(P,T)dT$$

1.2.1 Gibbs Free Energy as a Function of Temp.

- **Which is larger, H^L or H^S?**
- **$H^L > H^S$ at all temp.**

- **Which is larger, S^L or S^S?**
- **$S^L > S^S$ at all temp.**

→ Gibbs free energy of the liquid decreases more rapidly with increasing temperature than that of the solid.

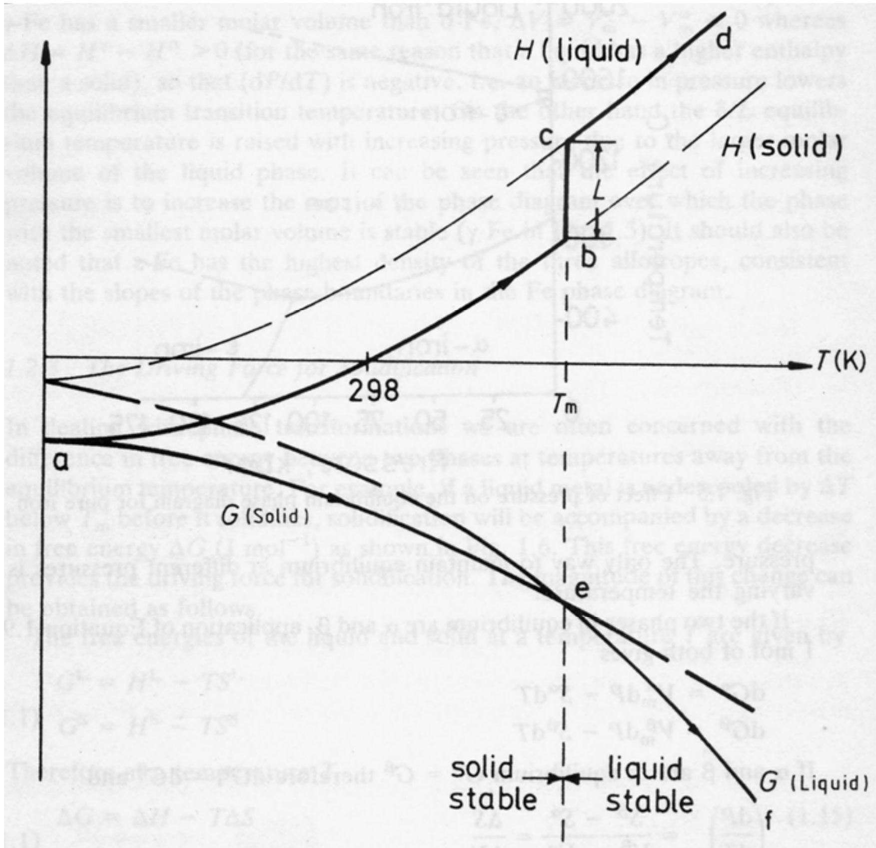


Fig. 1.4 Variation of enthalpy (H) and free energy (G) with temperature for the solid and liquid phases of a pure metal. L is the latent heat of melting, T_m the equilibrium melting temperature.

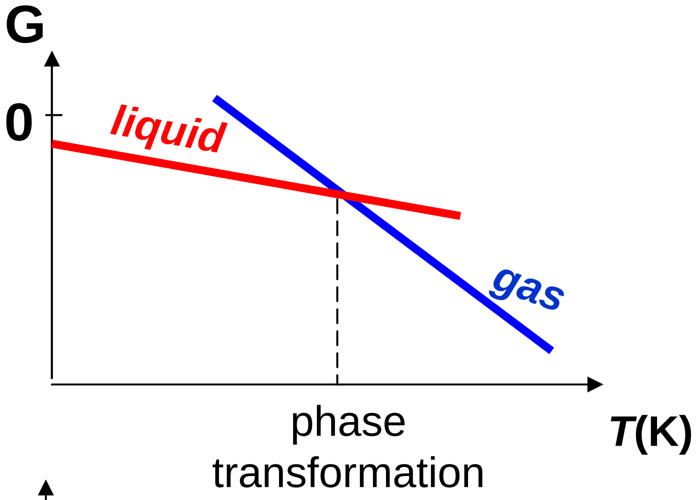
- **Which is larger, G^L or G^S at low T?**
- **$G^L > G^S$ (at low Temp) and $G^S > G^L$ (at high Temp)**

Considering P, T

$$G = G(T,P)$$

$$dG = VdP - SdT$$

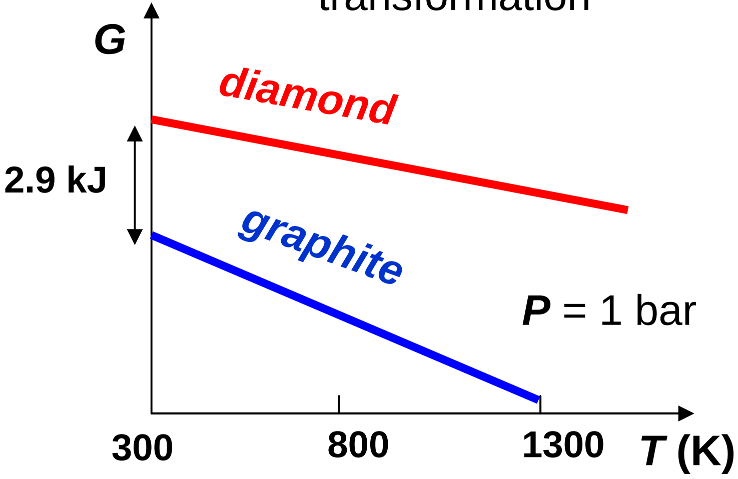
$$G(P,T) = G(P_0,T_0) + \int_{P0}^{P1} V(T_0,P)dP - \int_{T0}^{T1} S(P,T)dT$$



S(water) = 70 J/K

S(vapor) = 189 J/K

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



S(graphite) = 5.74 J/K,
S(diamond) = 2.38 J/K,

1.2.2 Pressure Effects

Different molar volume 을 가진 두 상이 평형을 이룰 때 만일 압력이 변한다면 평형온도 **T** 또한 압력에 따라 변해야 한다.

α,β 상이 평형이라면

$$dG^{\alpha} = V^{\alpha}dP - S^{\alpha}dT$$

$$dG^{\beta} = V^{\beta}dP - S^{\beta}dT$$

At equilibrium,

$$dG^{\alpha} = dG^{\beta}$$

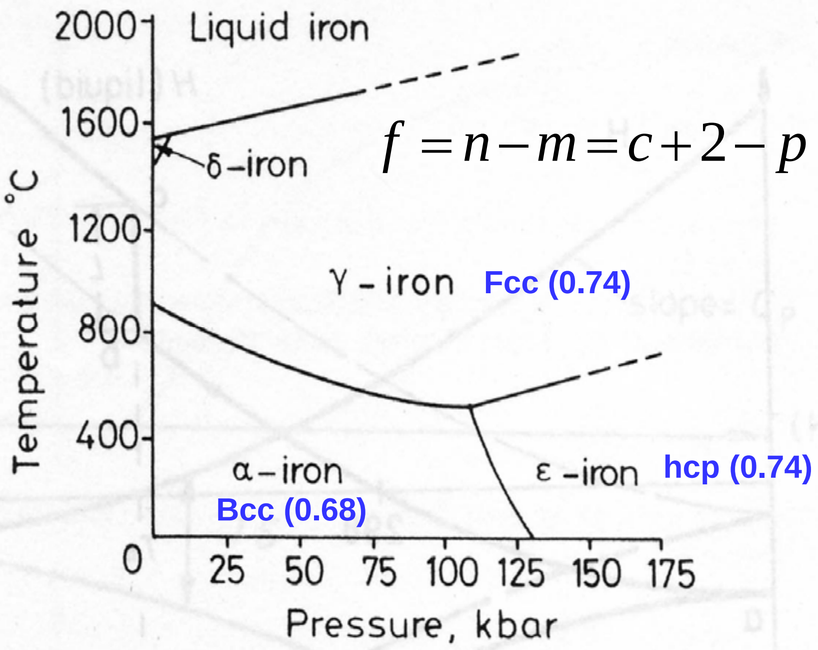
$$\left(\frac{dP}{dT}\right)_{eq} = \frac{S^{\beta}-S^{\alpha}}{V^{\beta}-V^{\alpha}} = \frac{\Delta S}{\Delta V}$$

여기서 $\Delta S = \frac{\Delta H}{T_{eq}}$ 이므로

- *Clausius-Clapeyron Relation* : $\left(\frac{dP}{dT}\right)_{eq} = \frac{\Delta H}{T_{eq}\Delta V}$

(applies to all coexistence curves)

Single component systems



$$f = n - m = c + 2 - p$$

Fig. 1.5 Effect of pressure on the equilibrium phase diagram for pure iron.

ɣ →liquid 의 경우; ΔV (+), ΔH(+)

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

α→ɣ 의 경우 ; ΔV (-), ΔH(+)

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

1.2.3 Driving force for solidification

$G^L = H^L - TS^L$

$G^S = H^S - TS^S$

$\Delta G = \Delta H - T\Delta S$

L : $\Delta H = H^L - H^S$

(Latent heat)

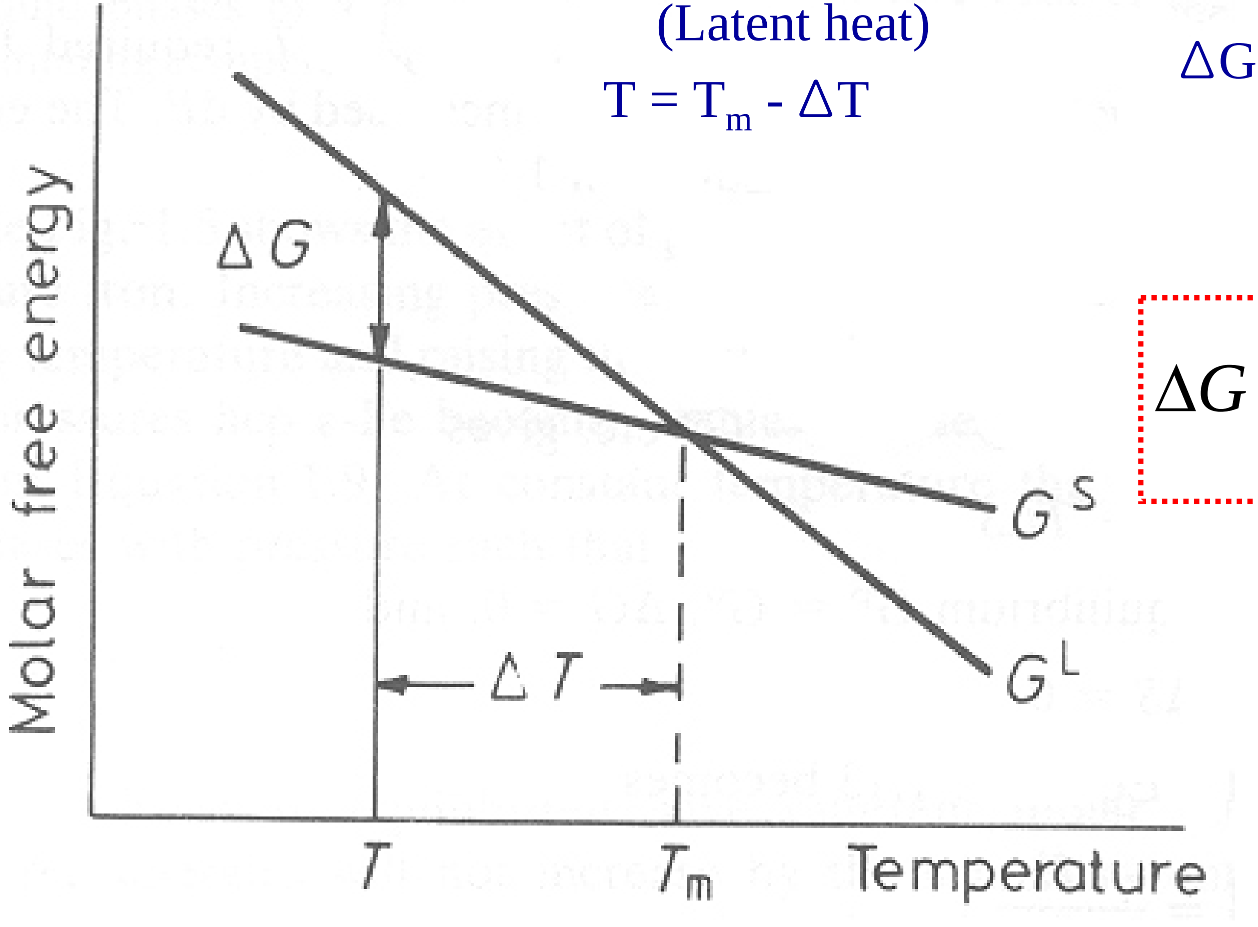
$T = T_m - \Delta T$

$\Delta G = 0 = \Delta H - T_m \Delta S$

$\Delta S = \Delta H / T_m = L / T_m$

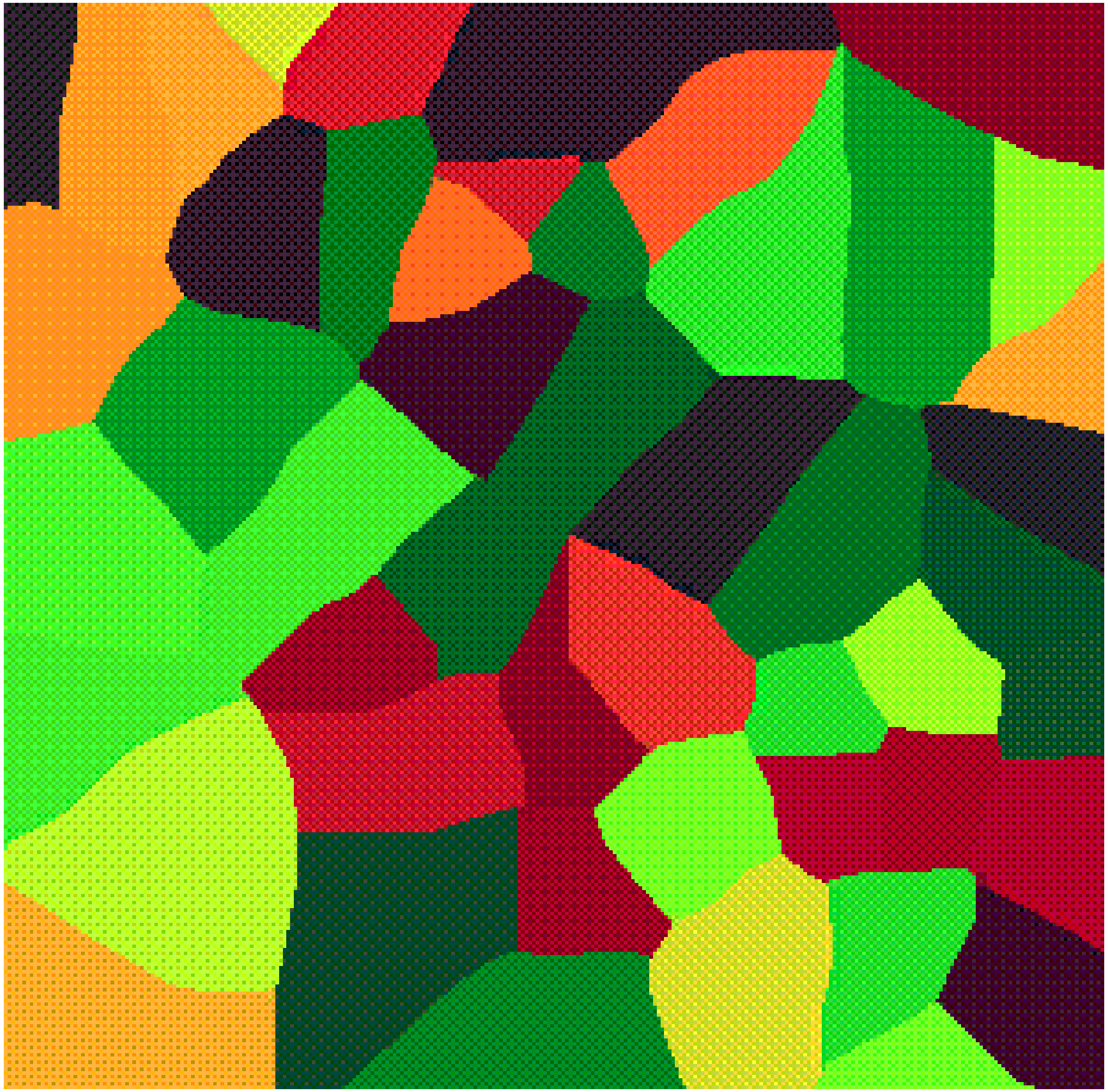
$\Delta G = L - T(L/T_m) \approx (L\Delta T)/T_m$

(eq. 1.17)



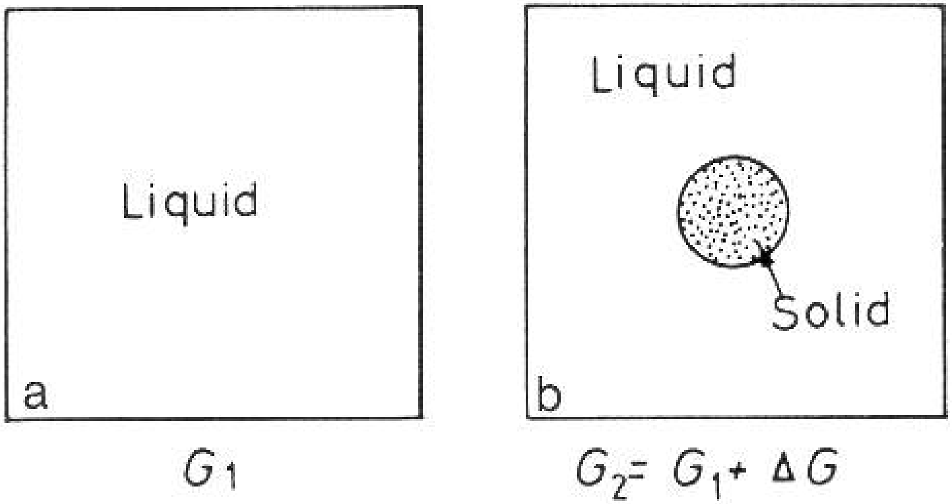
$$\boxed{\Delta G = \frac{L\Delta T}{T_m}}$$

4. Solidification: Liquid → Solid



4 Fold Anisotropic Surface Energy/2 Fold Kinetics, Many Seeds

4.1.1. Homogeneous Nucleation



$$G_1 = (V_S + V_L)G_V^L \qquad G_2 = V_S G_V^S + V_L G_V^L + A_{SL}\gamma_{SL}$$

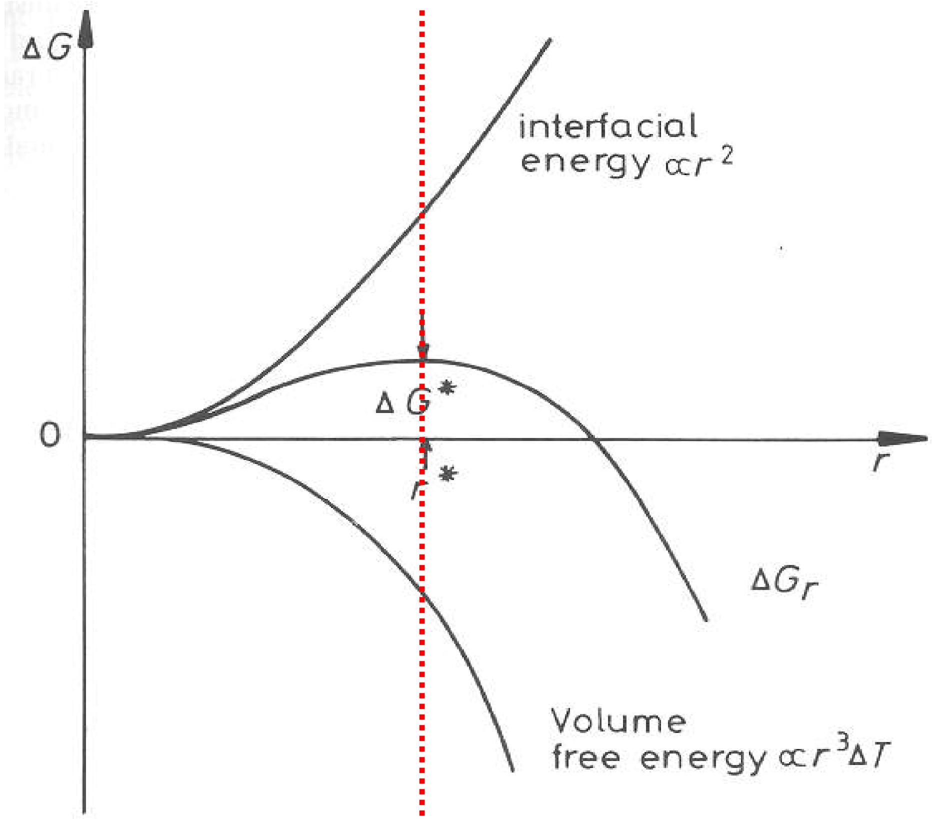
$G_V^S,\ G_V^L$ **: free energies per unit volume**

$$\Delta G = G_2 - G_1 = -V_S(G_V^L - G_V^S) + A_{SL}\gamma_{SL}$$

for spherical nuclei (isotropic) of radius : r

$$\boxed{\Delta G_r = -\frac{4}{3}\pi r^3 \Delta G_V + 4\pi r^2 \gamma_{SL}}$$

4.1.1. Homogeneous Nucleation



Unstable equilibrium

Fig. 4.2 The free energy change associated with homogeneous nucleation of a sphere of radius r.

Why r^* is not defined by $\Delta G_r = 0$?

r < r* : unstable **(lower free E by reduce size)**

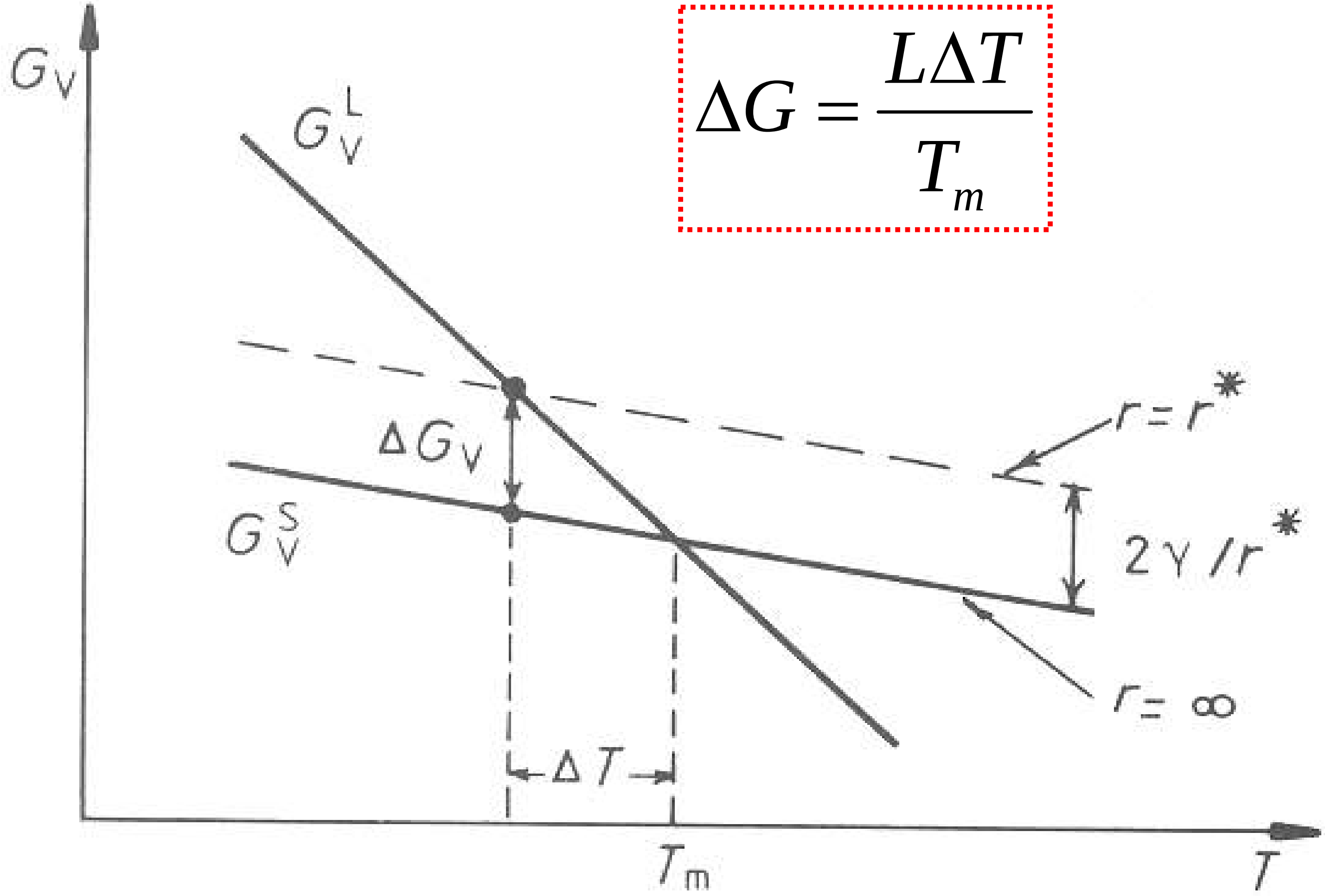
r > r* : stable **(lower free E by increase size)**

r* **: critical nucleus size**

r* ⇒ **dG=0**

1.2.3 Driving force for solidification

$$\boxed{\Delta G = \frac{L\Delta T}{T_m}}$$



Classification of phase transition

- First Order Phase Transition at T_T:
  - G is continuous at T_T
  - First derivatives of G (V, S, H) are discontinuous at T_T

$$V = \left(\frac{\partial G}{\partial P}\right)_T \qquad S = -\left(\frac{\partial G}{\partial T}\right)_P \qquad H = G - T\left(\frac{\partial G}{\partial T}\right)_P$$

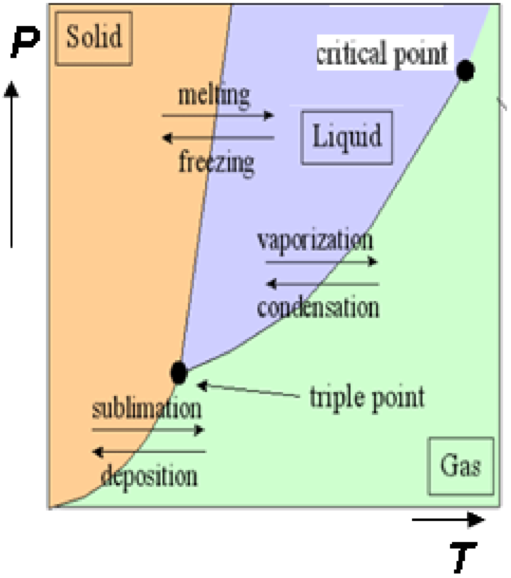
  - Second derivatives of G (α, β, C_p) are discontinuous at T_T

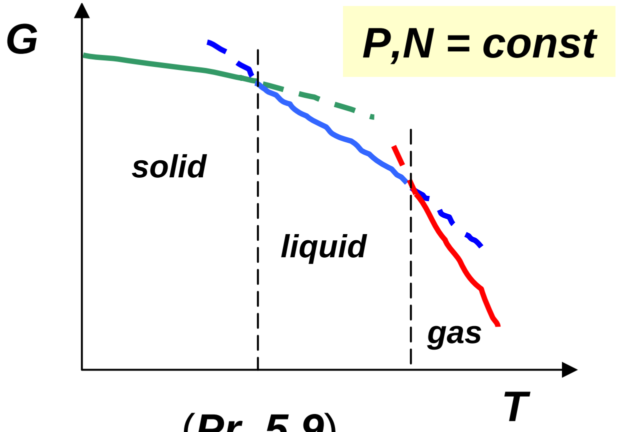
$$C_P = \left(\frac{\partial H}{\partial T}\right)_P \qquad \alpha = \frac{1}{\mathrm{V}}\left(\frac{\partial V}{\partial T}\right)_P \qquad \beta = \frac{-1}{V}\left(\frac{\partial V}{\partial P}\right)_T$$

  - Examples: Vaporization, Condensation, Fusion, Crystallization, Sublimation.

The First-Order Transitions

Latent heat
Energy barrier
Discontinuous entropy, heat capacity





(**Pr. 5.9**).

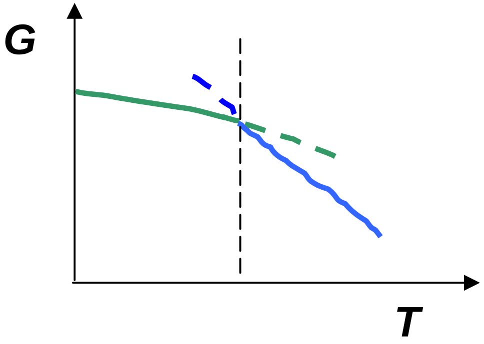
On the graph ***G*(*T*)** at ***P*,*N*** = const, the slope **d*G*/d*T*** is always negative:

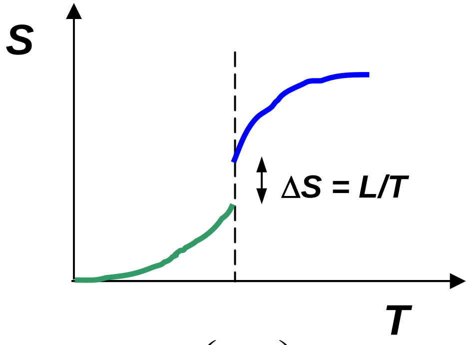
$$S = -\left(\frac{\partial G}{\partial T}\right)_{P,N}$$

In the first-order transitions, the ***G(T)*** curves have a real meaning even beyond the intersection point, this results in ***metastability*** and ***hysteresis***.

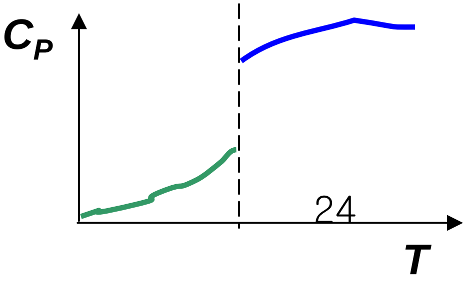
An energy barrier that prevents a transition from the higher μ to the lower μ phase. (e.g., gas, being cooled below T_{tr} does not immediately condense, since surface energy makes the formation of very small droplets energetically unfavorable).

Water in organic cells can avoid freezing down to -20^0C in insects and down to -47^0C in plants.





$$C_P = T\left(\frac{\partial S}{\partial T}\right)_{P,N}$$



- Second Order Phase Transition at T_T:
  - G is continuous at T_T
  - First derivatives of G (V, S, H) are continuous at T_T

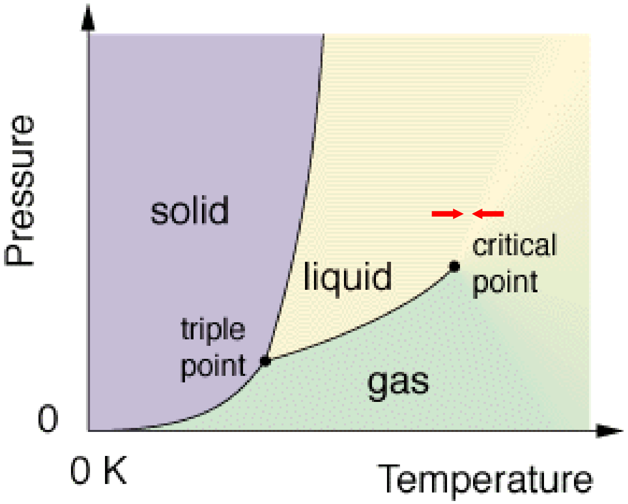
$$V = \left(\frac{\partial G}{\partial P}\right)_T \qquad S = -\left(\frac{\partial G}{\partial T}\right)_P \qquad H = G - T\left(\frac{\partial G}{\partial T}\right)_P$$

  - Second derivatives of G (α, β, C_p) are discontinuous at T_T

$$C_P = \left(\frac{\partial H}{\partial T}\right)_P \qquad \alpha = \frac{1}{\mathrm{V}}\left(\frac{\partial V}{\partial T}\right)_P \qquad \beta = \frac{-1}{V}\left(\frac{\partial V}{\partial P}\right)_T$$

  - Examples: Order-Disorder Transitions in Metal Alloys, Onset of Ferromagnetism, Ferroelectricity, Superconductivity.

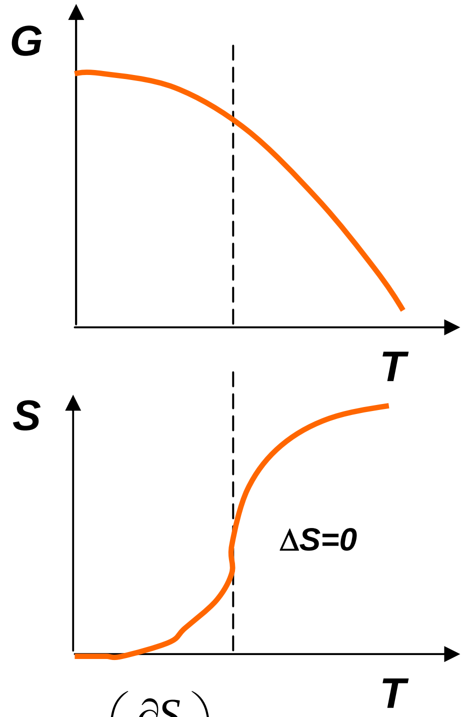
The Second Order Transition



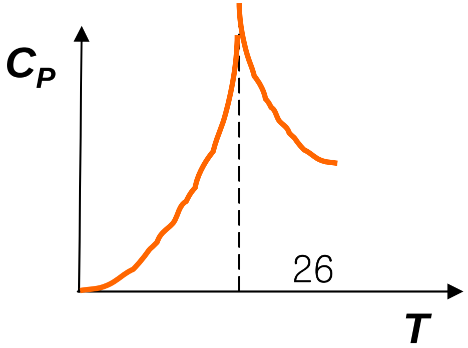
No Latent heat
Continuous entropy

As one moves along the coexistence curve toward the critical point, the distinction between the liquid phase on one side and the gas phase on the other gradually decreases and finally disappears at (T_C, P_C). The T-driven phase transition that occurs *exactly* at the critical point is called a second-order phase transition. Unlike the 1st-order transitions, the 2nd-order transition does not require any latent heat (L=0). In the *second-order transitions* (*order-disorder transitions* or *critical phenomena*) the entropy is continuous across the transition. The specific heat $C_P = T(\delta S/\delta T)_P$ diverges at the transition.
Whereas in the 1st-order transitions the $G(T)$ curves have a real meaning even beyond the intersection point, nothing of the sort can occur for a 2nd-order transition – the Gibbs free energy is a continuous function around the critical temperature.

Second-order transition



$$C_P = T\left(\frac{\partial S}{\partial T}\right)_{P,N} \to \infty$$



Contents for today's class

Chapter 1

Thermondynamics and Phase Diagrams

- **Equilibrium** $dG = 0$

Phase Transformation

$$\Delta G = G_2 - G_1 < 0$$

- **Single component system**

Gibbs Free Energy
as a Function of Temp. and Pressure

$$\left(\frac{\partial G}{\partial T}\right)_P = -S\,, \qquad \left(\frac{\partial G}{\partial P}\right)_T = V$$

- **Driving force for solidification**

$$\Delta G = \frac{L\Delta T}{T_m}$$

- **Classification of phase transition**

First order transition: CDD/Second order transition: CCD