재 료 상 변 태

Phase Transformation of Materials

2008.09.04.

박 은 수

서울대학교 재료공학부

Contents in Phase Transformation

상변태를 이해하는데 필요한 배경

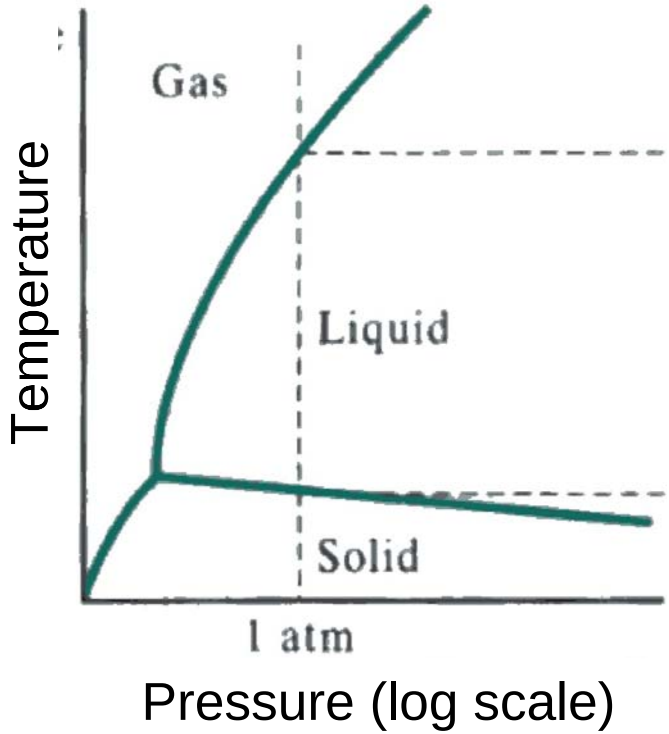
- **(Ch1) 열역학과 상태도: Thermodynamics**
- **(Ch2) 확 산 론: Kinetics**
- **(Ch3) 결정계면과 미세조직**

대표적인 상변태

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

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

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

➡ **Thermodynamics & Kinetics**

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!!!

동질이상(同質異像): 화학성분 같고 결정구조 다름

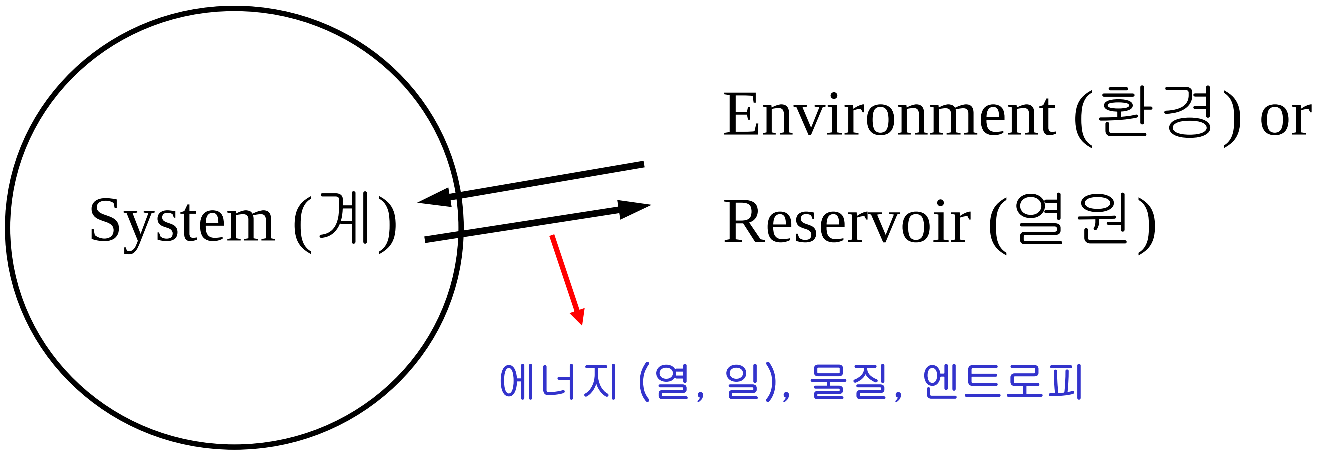
There is a driving force for diamond to convert to graphite

but there is (huge) nucleation barrier.

How long it will take is the problem of kinetics.

The time variable is a key parameter.

Thermodynamic system



* **Isolated system** : physical system that does not interact with its surroundings.

It obeys a number of conservation laws its total energy and mass stay constant.

They cannot enter or exit, but can only move around inside.

* **Closed system** : Can interchange energy and mechanical work with other outside systems but not matter. Ex. mass conservation

* **Open system** : Can be influenced by events outside of the actual or conceptual boundaries.

Thermodynamic system

Isolated system (고립계) : 환경과 열, 물질, 일 모두 교환하지 않는 계이다.

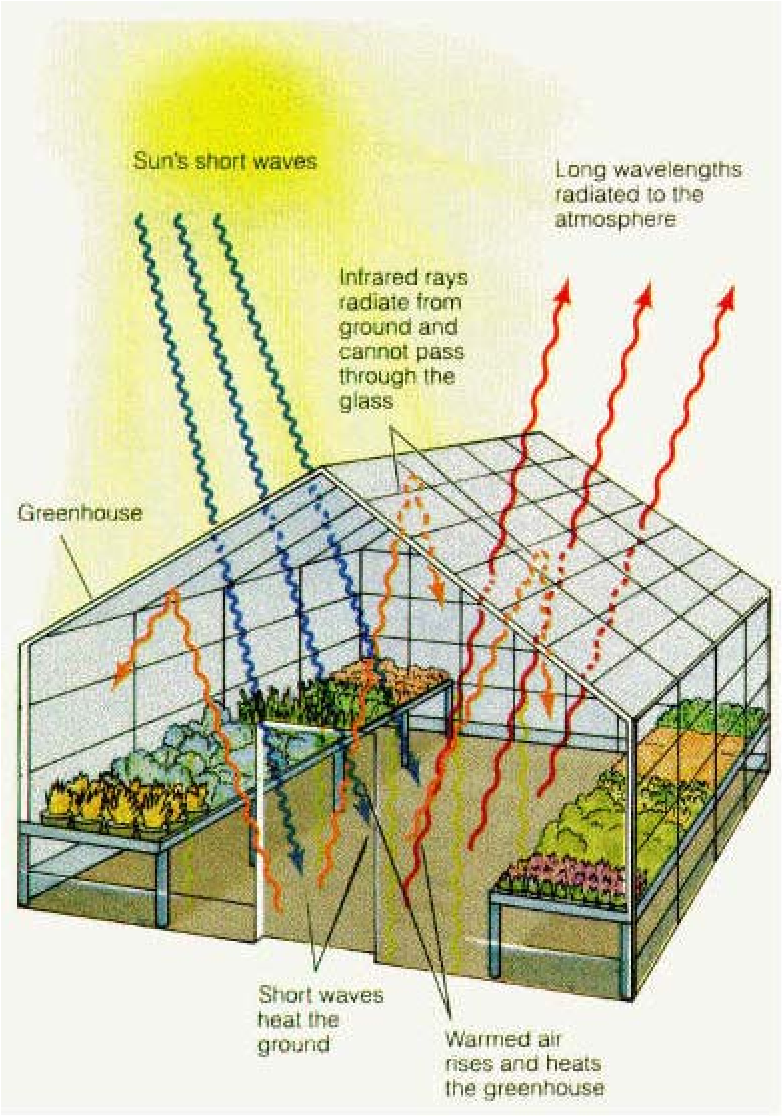
이 말은 수학적으로 $TdS = 0, dN = 0, pdV = 0$를 의미하며, 따라서 $dE = 0$를 의미한다.

Thermodynamic system

Closed system (닫힌계) :

환경과 에너지**(**열과 일**)**는 교환하지만 물질은 교환하지 않는 계를 말한다**.**

- 단열 경계**(adiabatic boundary) :**
  열교환이 일어나지 않는다**,** $TdS = 0$
- 단단한 경계**(rigid boundary) :**
  일**(work)** 교환이 일어나지 않는다**,** $pdV = 0$



Thermodynamic system

Open system (열린계**)** : 에너지**(**열과 일**),** 물질 모두 환경과 교환하는 계이다**.**

이런 경계는 투과성 있는**(permeable)** 경계라 한다**.**

The four laws in thermodynamics

- **Zeroth law : 열역학적 평형**

  – *만약 계 A와 계 B를 접촉하여 열역학적 평형상태를 이루고 있고 계 B와 계 C를 접촉하여 열역학적 평형상태를 이루고 있다면, 계 A와 계 C를 접촉하여도 열역학적 평형을 이룬다.*

  – *열역학적 평형은 열적 평형(열교환과 온도와 관계)과 역학적 평형(일교환과 압력 같은 일반화된 힘과 관계)과 화학적 평형(물질교환과 화학퍼텐셜과 관계)을 포함한다*

- **First law: : 에너지 보존 법칙**

$$dE = \delta Q - \delta w + d(\sum \mu_i N_i)$$

The change in the internal energy of a closed thermodynamic system is equal to the sum of the amount of heat energy supplied to the system and the work done on the system.

- **Second law : 엔트로피**

$$S = \frac{q}{T}$$

The total entropy of any isolated thermodynamic system tends to increase over time, approaching a maximum value.

- **Third law of thermodynamics : 절대 0 도**

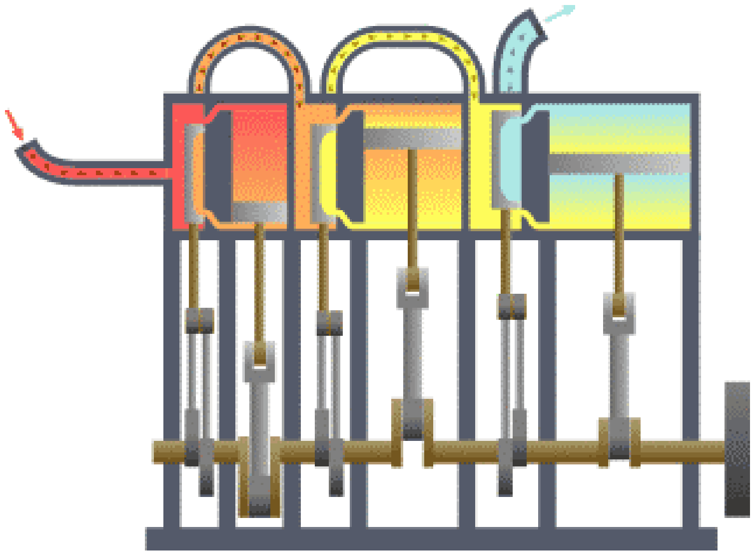
The entropy of all system and of all states of a system is zero at absolute zero or

It is impossible to reach the absolute zero of temperature by any finite number of processes.

1st law **: conservation of energy**

$$dU = \delta q - \delta w$$

Change in the internal energy is equal to the amount added by heating minus the amount lost by doing work on the environment.



U : exact differential

(경로에 관계 x = 상태 함수)

δq, δw → not exact differential

(경로에 관계 O = 상태함수 아님)

- 2nd law ; Entropy (S) ; irreversibility, disorder

- In an isolated system, a process can occur only if it increases the total entropy of the system. If a system is at equilibrium, by definition no spontaneous processes occur, and therefore the system is at maximum entropy.
- Heat cannot spontaneously flow from a material at lower temperature to a material at higher temperature.
- It is impossible to convert heat completely into work.

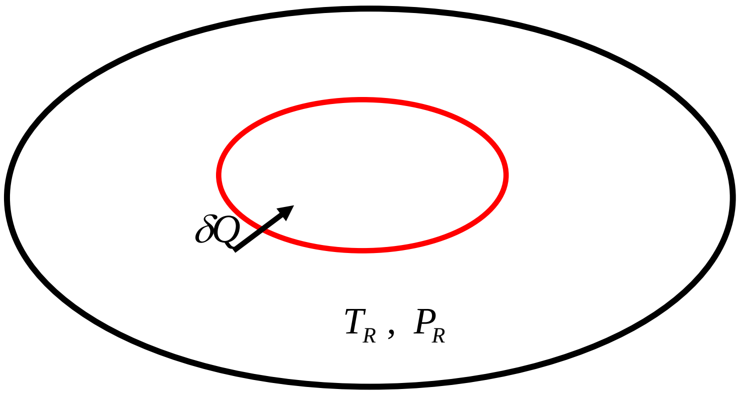
$$\text{Enropy} \quad : \quad S = \frac{q}{T}$$

Ex) A+B → C+D
; toward an equil. state
Spontaneous >> increase in entropy

; degree of irreversibility
→평형에 가까울수록 줄어든다
→ degradation
Ex) mixing of gases

What is reversible process?
→ Continuous maintenance of equil. state
→ 무한히 느리다
→ Degree of irrevesibility가 최소 (≈0)
→ Imaginary process

- Applying the Second Law to an isolated system (called the total system or universe), a sub-system of interest, and the sub-system's surroundings. These surroundings are imagined to be so large that they can be considered as an *unlimited* heat reservoir at temperature T_R and pressure P_R .



$$S_{tot} = S + S_R$$

$$dS_{tot} = dS + dS_R \geq 0 \qquad : \text{2nd law}$$

$$dE = \delta Q - \delta w + d(\sum \mu_i N_i) \qquad : \text{1st law}$$

$$\delta Q = -T_R dS_R \leq T_R dS$$

$$\delta w \leq -dE + T_R dS + \sum \mu_{iR} dN_i$$

$$\delta w_u \leq -dE + T_R dS - P_R dV + \sum \mu_{iR} dN_i = -d(E - T_R S + P_R V - \sum \mu_{iR} N_i)$$

$$X = E - T_R S + P_R V - \sum \mu_{iR} N_i$$

$$\boxed{dX + dw_u \leq 0}$$

The change in the subsystem's energy plus the useful work done *by* the subsystem must be less than or equal to zero.

Gibbs and Helmholtz free energies

When no useful work is being extracted from the sub-system, $dX \leq 0$

The energy X reaching a minimum at equilibrium, when $dX=0$.

If no chemical species can enter or leave the sub-system, then $\sum \mu_{iR} N_i$ can be ignored.

If furthermore the temperature of the sub-system is such that T is always equal to T_R,

then $X = E - TS + P_R V + const$

If the volume V is constrained to be constant, then $X = E - TS + const' = A + const'$

where A is the thermodynamic potential called Helmholtz free energy, $A=E-TS$.

Under constant volume conditions therefore, $dA < 0$ if a process is to go forward;

and $dA=0$ is the condition for equilibrium.

Helmholtz free energy **: $\boldsymbol{A=E-TS}$.**

Useful when V is constrained during thermodynamic process.

If the sub-system pressure P is constrained to be equal to the external reservoir pressure P_R,

$$X = E - TS + PV + const = G + const$$

,where G is the Gibbs free energy, $G=E-TS+PV$. Therefore under constant pressure conditions, if $dG \leq 0$, then the process can occur spontaneously, because the change in system energy exceeds the energy lost to entropy. $dG=0$ is the condition for equilibrium. This is also commonly written in terms of enthalpy, where H=E+PV.   G=H-TS

Gibbs free energy **:** $\boldsymbol{G=E+PV-TS=H-TS}$

Useful when P is constrained during thermodynamic process.

Intensive property: 계의 크기와 무관한 성질, T, P

Extensive property: 계의 크기**(**몰수**)**와 관계되는 성질**, V, E, H, S, G** 등

Gibbs Free Energy : Relative Stability of a System

$$G = H - TS$$

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

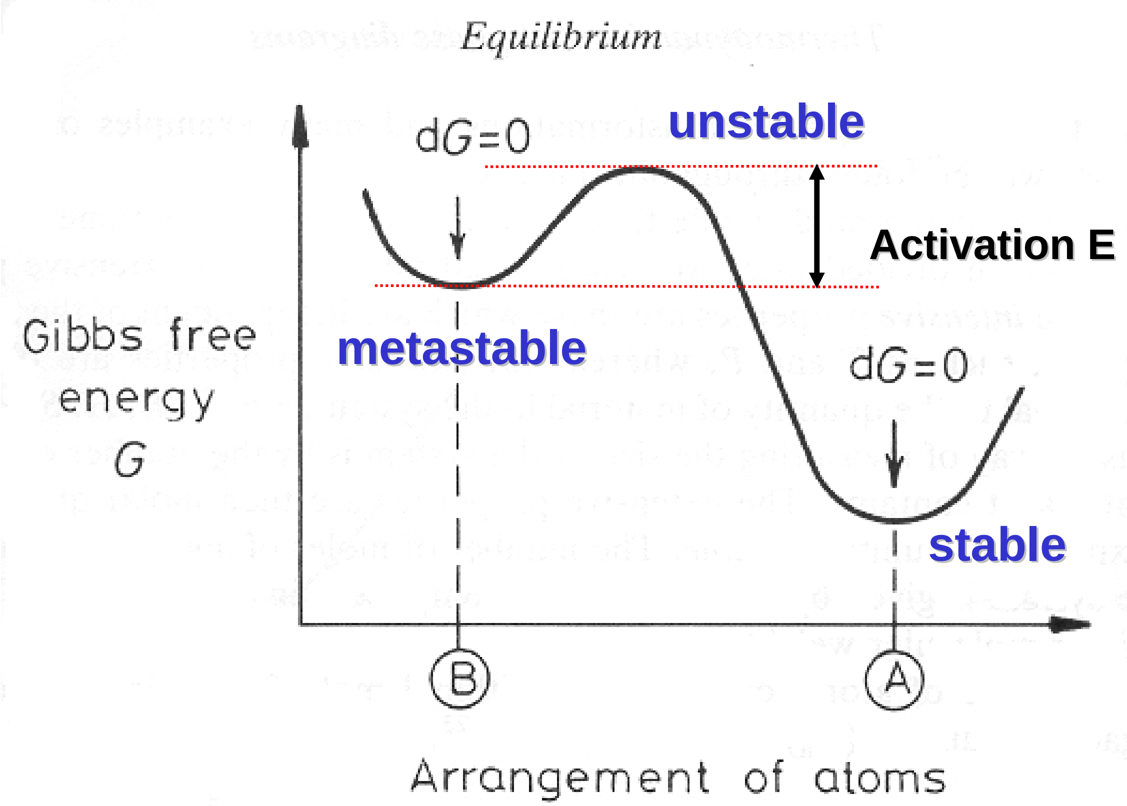
S : Entropy, The Randomness of the System

<u>Equilibrium</u>

$$dG = 0$$

Lowest possible value of Gibb's Free Energy

No desire to change *ad infinitum*



Phase Transformation

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

$$dE = \delta Q - P \cdot dV$$

When V is constant

$$\frac{\delta Q}{dT} = \frac{dE}{dT} + P\frac{dV}{dT} \quad (\frac{dV}{dT} \rightarrow 0)$$

$$C_V = (\frac{\partial Q}{\partial T})_V = (\frac{\partial E}{\partial T})_V$$

$$C_V = (\frac{\partial E}{\partial T})_V \quad \text{or} \quad E = \int C_V dT$$

실험적으로 V 를 일정하게 하는 것이 어렵기 때문에 V 보다 P를 일정하게 유지하는 것이 편함 → pressure ex)1 atm,

When pressure is const.

$$H \equiv E + PV$$

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

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

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

$$(\frac{dH}{dT})_P = (\frac{\delta Q}{dT})_P = C_P$$

$$H = \int C_p dT$$

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

Single component system
(단일 성분계)

One element (Al, Fe)
One type of molecule (H_2O)

How is C_p related with H and S?

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

H = ?

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

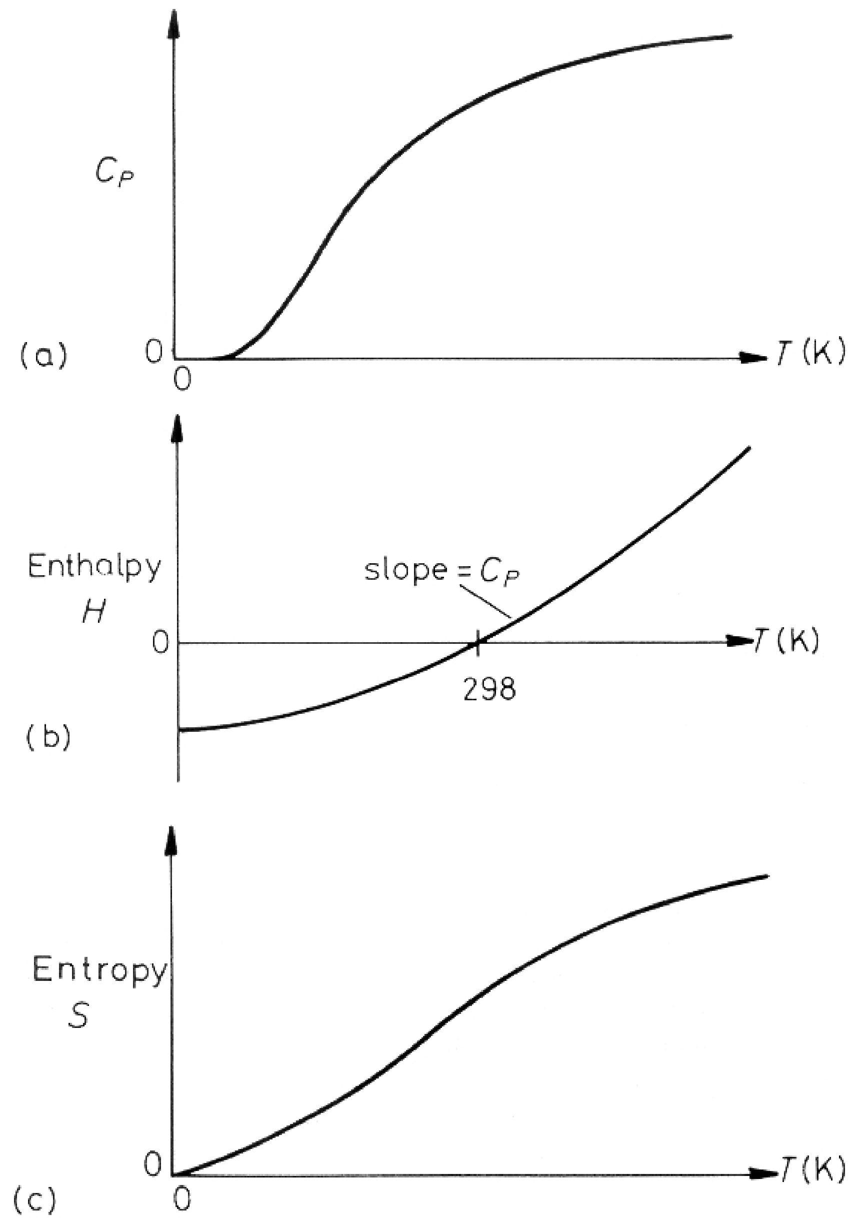
H = 0 at 298K for a pure element in its most stable state.

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

S = ?

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

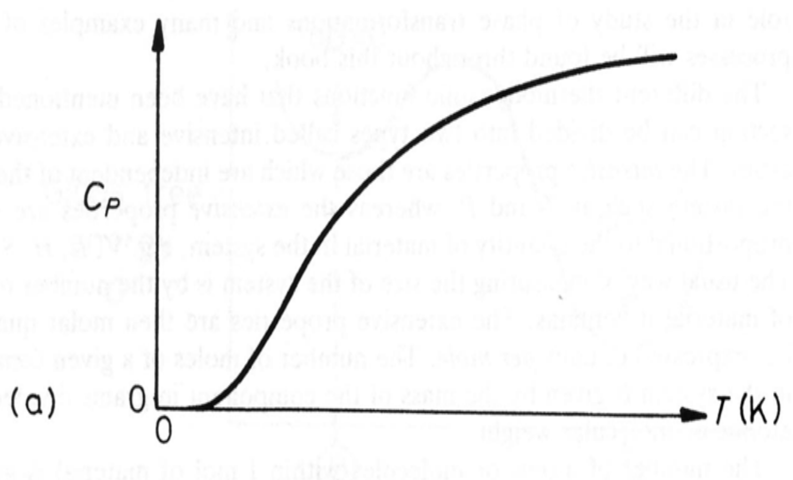
$$S = \int_0^T \frac{C_P}{T} dT$$

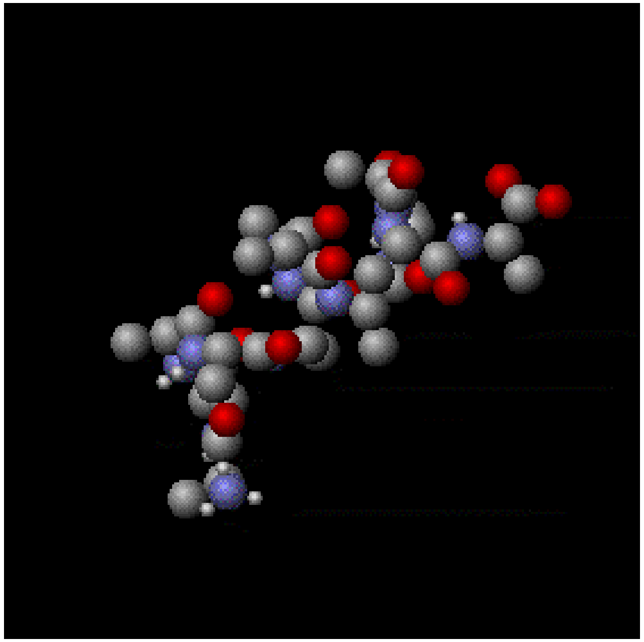


C_P; 온도에 따라 변함 (온도의 함수)

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

(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^{-1} K^{-1}	C_p J mol^{-1} K^{-1}	C_v J mol^{-1} K^{-1}	Volumetric heat capacity J cm^{-3} K^{-1}
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.

Single component system
(단일 성분계)

One element (Al, Fe)
One type of molecule (H_2O)

How is C_p related with H and S?

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

H = ?

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

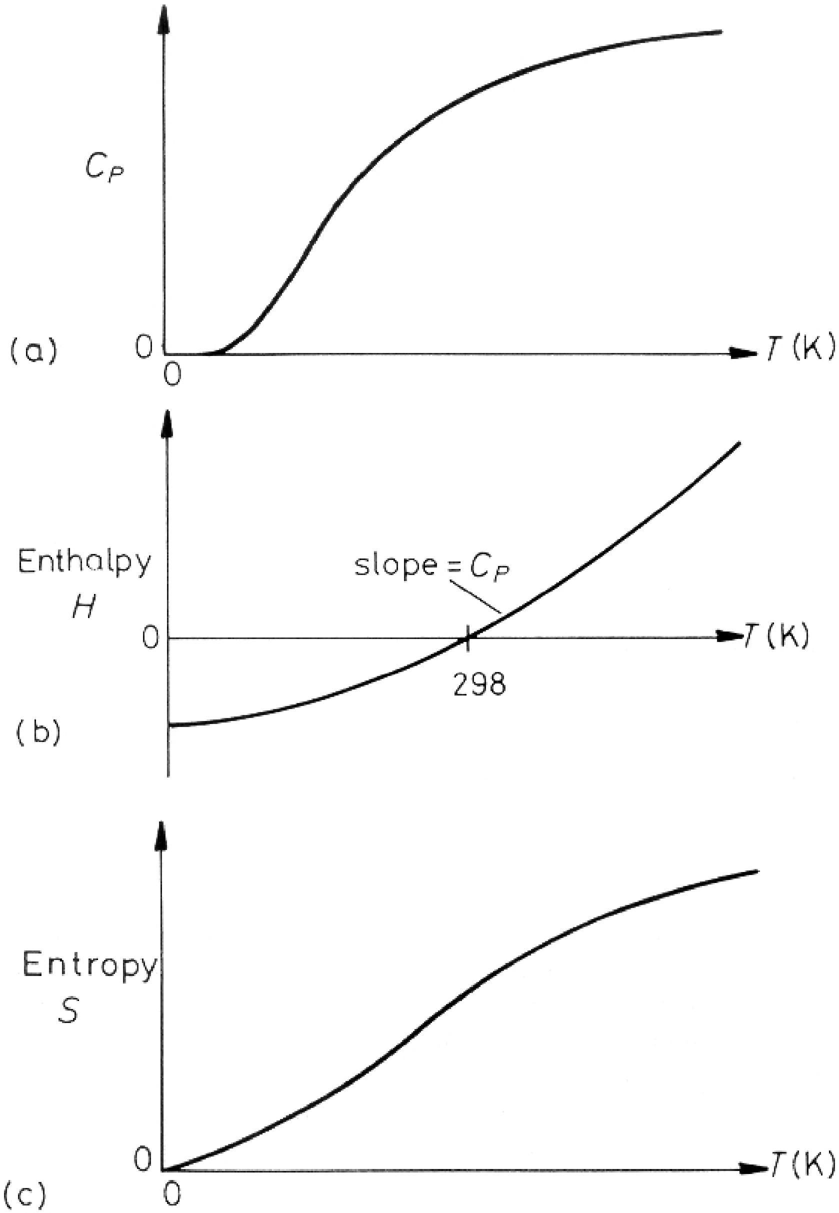
H = 0 at 298K for a pure element in its most stable state.

Enropy : $S = \dfrac{q}{T}$

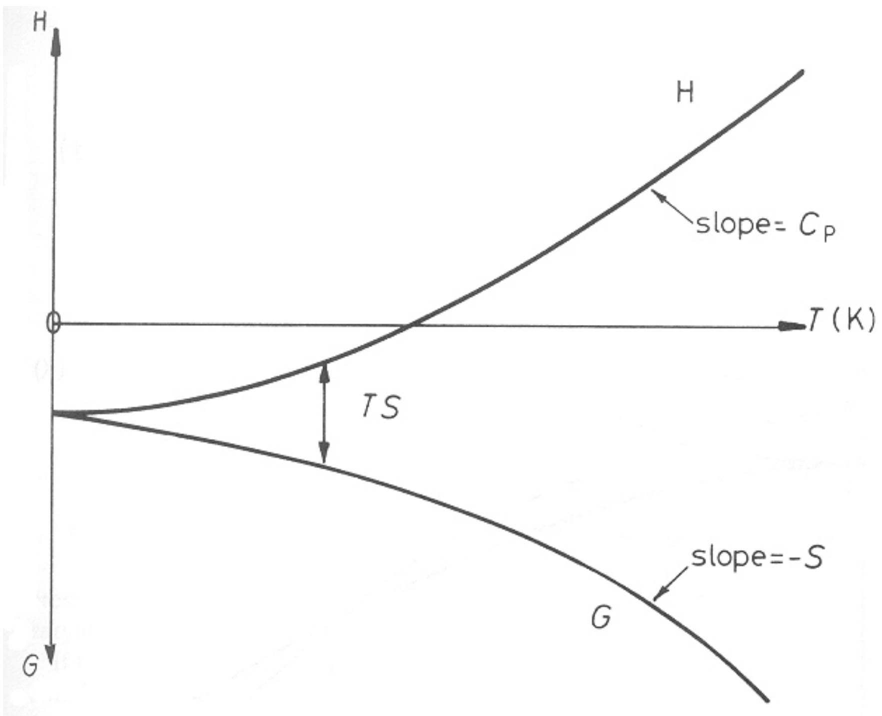
S = ?

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

$$S = \int_0^T \frac{C_P}{T} dT$$



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



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

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

$$G = H - TS$$

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

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

$$= VdP - SdT$$

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

$$dG = VdP - SdT$$

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

Gibbs Free Energy as a Function of Temperature

- **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.

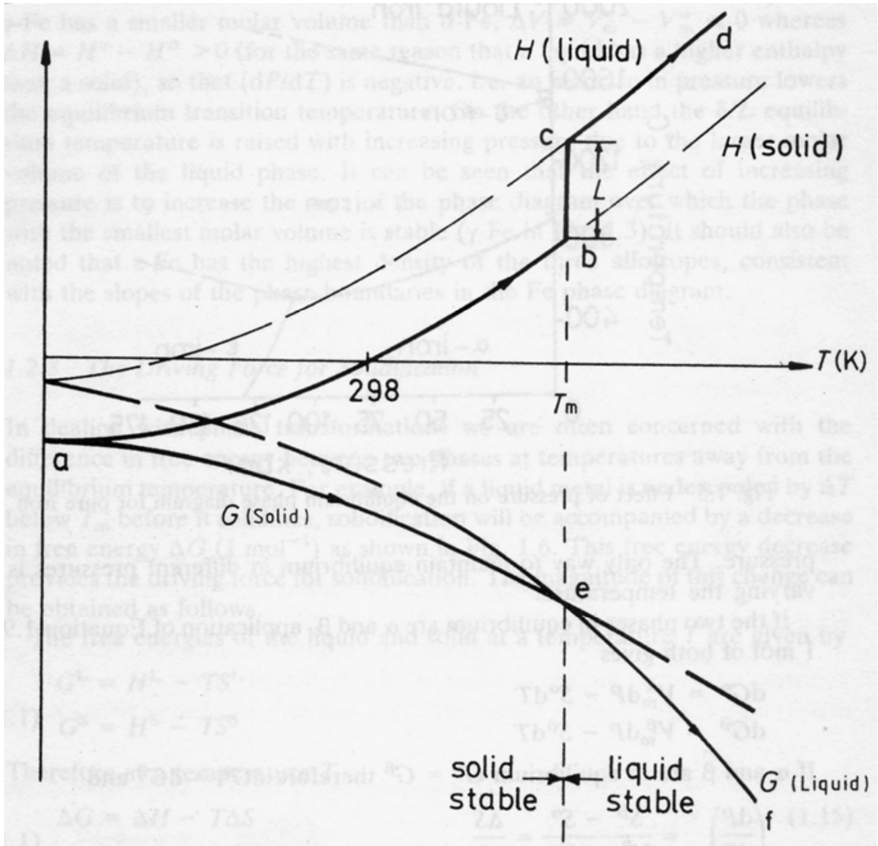


Fig. 1.4 Variation of enthalpy (H) and free energy (G) with temperature for the solid and liquid phases of a pure metal. L is the latent heat of melting, T_m the equilibrium melting temperature.

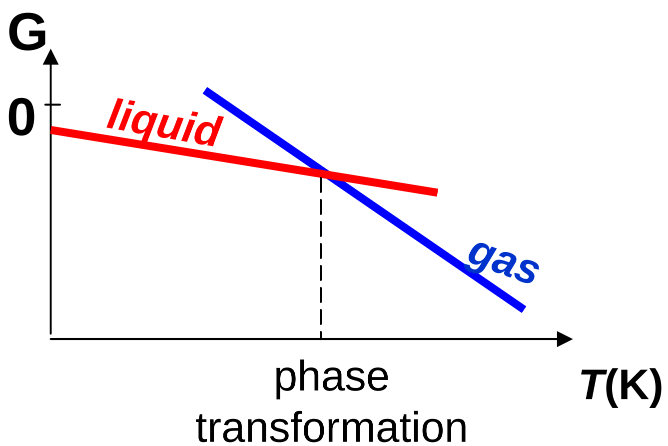
- **Which is larger, G^L or G^S at low T?**
- **$G^L > G^S$ (at low Temp) and $G^S > G^L$ (at high Temp)**

Considering P, T

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

$$dG = VdP - SdT$$

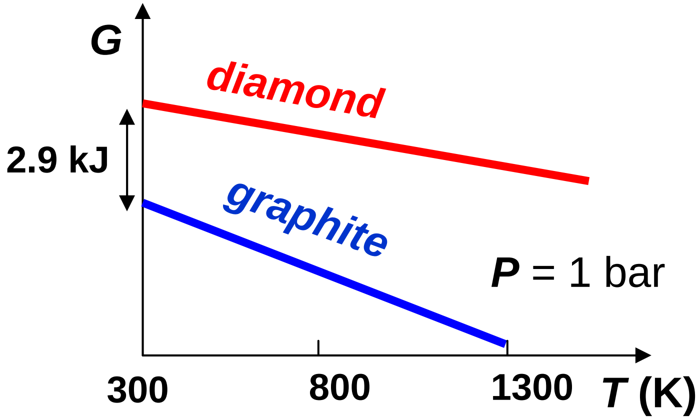
$$G(P,T) = G(P_0, T_0) + \int_{P0}^{P1} V(T_0, P)dP - \int_{T0}^{T1} S(P,T)dT$$



S(water) = 70 J/K

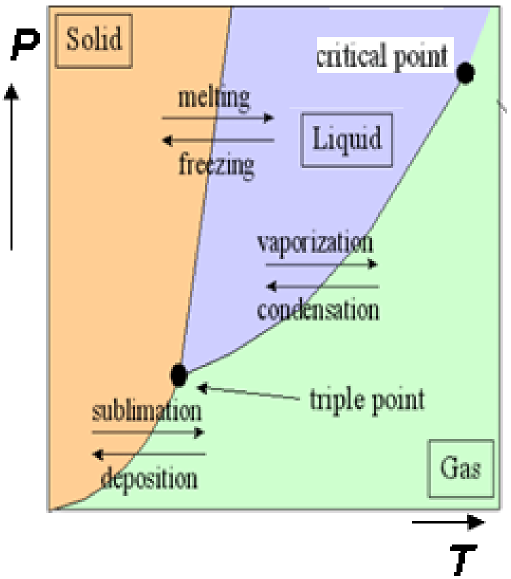
S(vapor) = 189 J/K

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

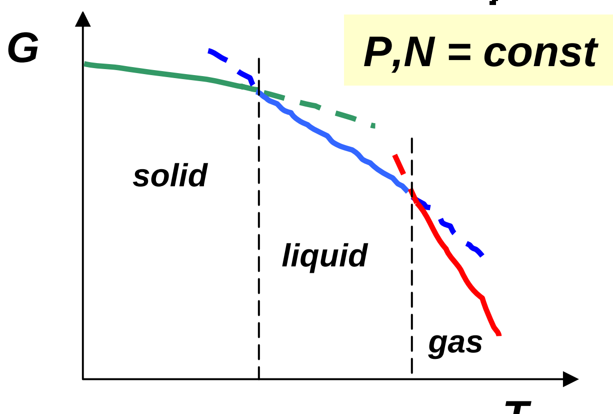


S(graphite) = 5.74 J/K,
S(diamond) = 2.38 J/K,

The First-Order Transitions



Latent heat
Energy barrier
Discontinuous entropy, heat capacity



(*Pr. 5.9*).

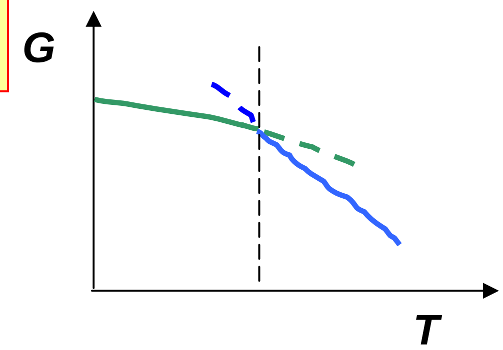
On the graph ***G*(*T*)** at ***P,N*** = const, the slope ***dG*/*dT*** is always negative:

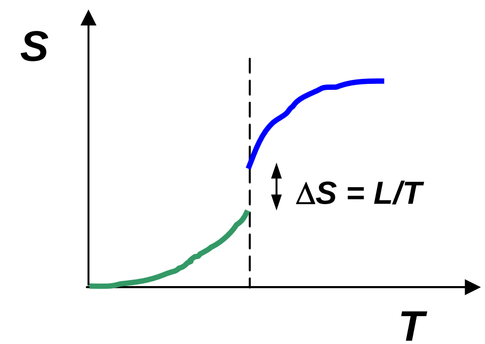
$$S = -\left(\frac{\partial G}{\partial T}\right)_{P,N}$$

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

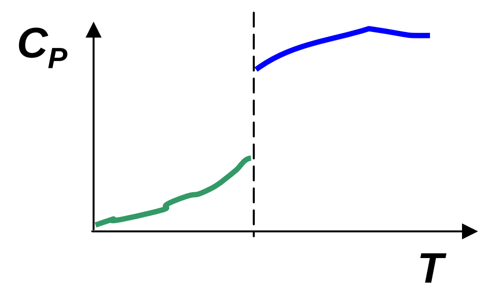
An energy barrier that prevents a transition from the higher μ to the lower μ phase. (e.g., gas, being cooled below $\boldsymbol{T_{tr}}$ does not immediately condense, since surface energy makes the formation of very small droplets energetically unfavorable).

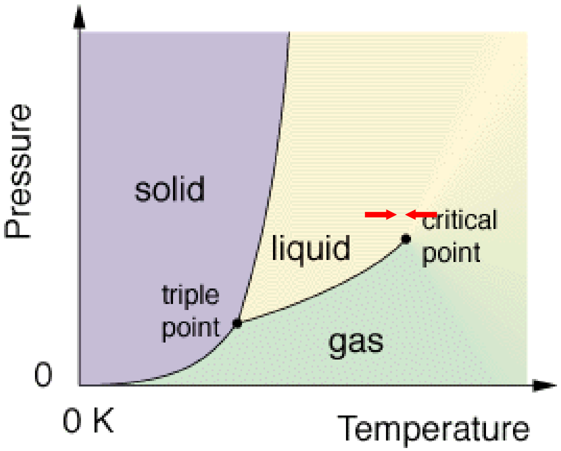
Water in organic cells can avoid freezing down to –20^{0}C in insects and down to –47^{0}C in plants.





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

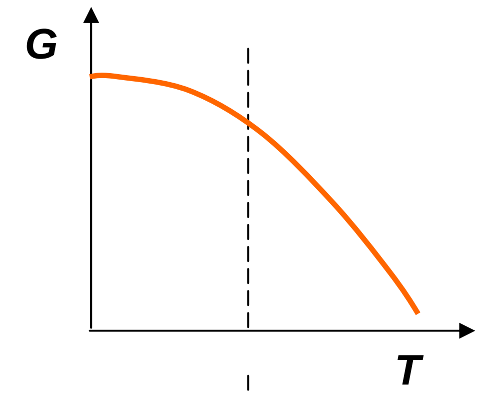


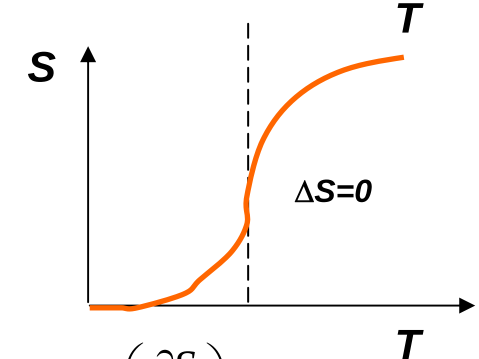


The Second Order Transition

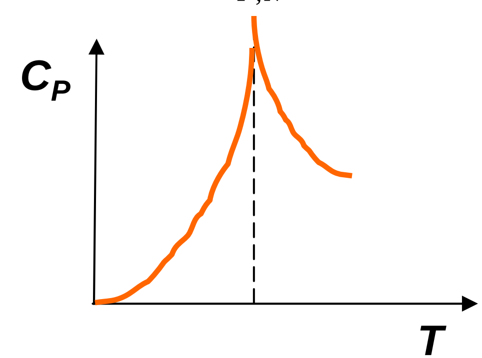
No Latent heat
Continuous entropy

Second-order transition





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



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 1^{st}-order transitions, the 2^{nd}-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 1^{st}-order transitions the $G(T)$ curves have a real meaning even beyond the intersection point, nothing of the sort can occur for a 2^{nd}-order transition – the Gibbs free energy is a continuous function around the critical temperature.

Pressure effect

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

α,β 상이 equil 이라면

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

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

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 $\Delta S = \dfrac{\Delta H}{T_{eq}}$ 이므로

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

(applies to all coexistence curves)

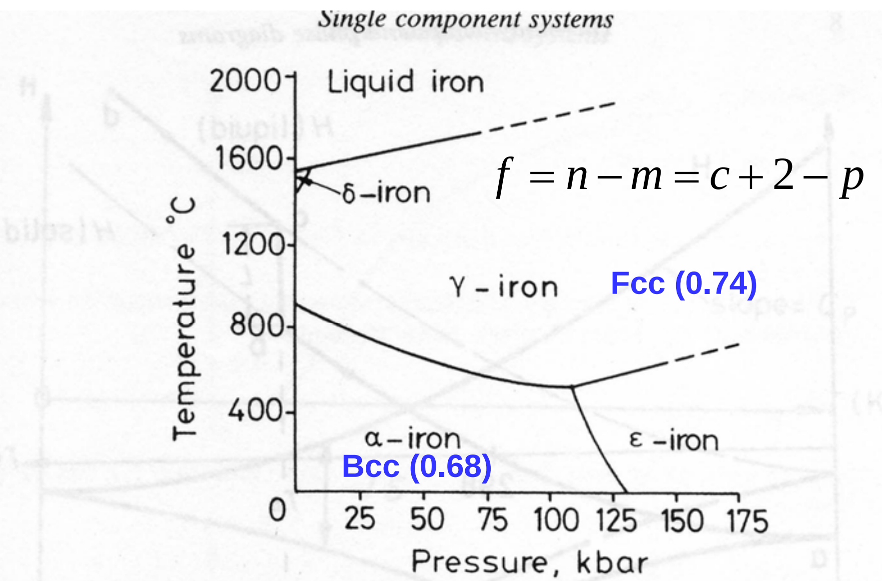


Fig. 1.5 Effect of pressure on the equilibrium phase diagram for pure iron.

ɣ →liquid 의 경우; ΔV (+), ΔH(+)

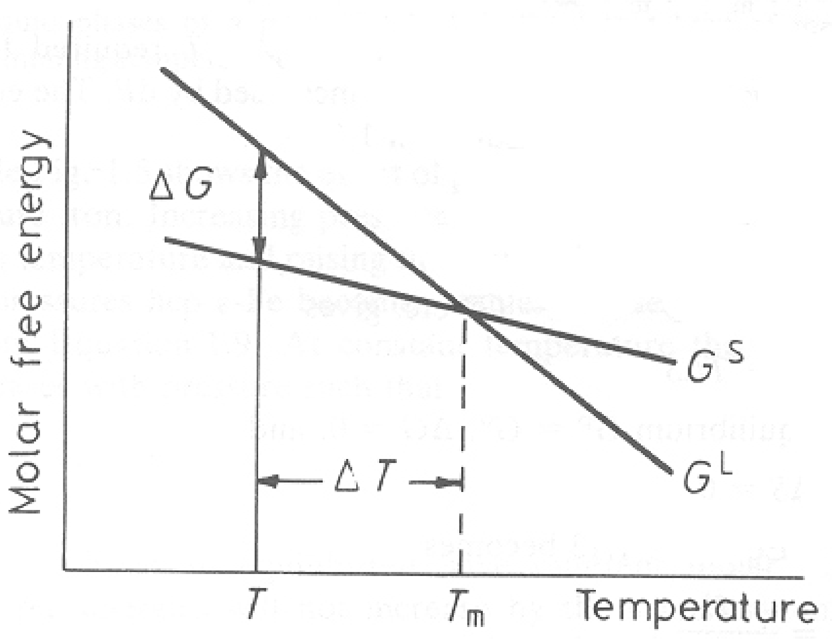
$$\left(\frac{dP}{dT}\right) = \frac{\Delta H}{T_{eq}\Delta V} > 0$$

α→ɣ 의 경우 ; ΔV (-), ΔH(+)

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

The Driving Force for Solidification

$$G^L = H^L - TS^L \qquad G^S = H^S - TS^S$$



at temperature T

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

at equilibrium melting temperature

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

$$\Delta S = \frac{\Delta H}{T_m} = \frac{L}{T_m} \qquad \textit{Entropy of Fusion}$$

and

$$\Delta G \cong L - T\frac{L}{T_m} \qquad i.e. \quad \Delta G \cong \frac{L\Delta T}{T_m}$$

2008년 9월

일	월	화	수	목	금	토
	1	2	3	4	5	6
7	8	9	10	11	12	13
14	15	16	17	18	19	20
21	22	23	24	25	26	27
28	29	30				