Chapter 1.

Thermodynamics and Phase Diagrams

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1.1. Equilibrium

- **System**
  - An alloy that can exist as a mixture of one or more phase
- **Phase**
  - A portion of the system whose properties and composition are homogeneous
- **Component**
  - Different elements or chemical compounds which make up the system

1.1. Equilibrium

Phase Transformation :

how one or more phase is an alloy(system) change into a new or mixture of phase

Why? Initial state is **unstable**

1.1. Equilibrium

❖ **Gibbs free energy, *G***

$$G = H - TS$$

Internal energy (=kinetic energy + potential energy)

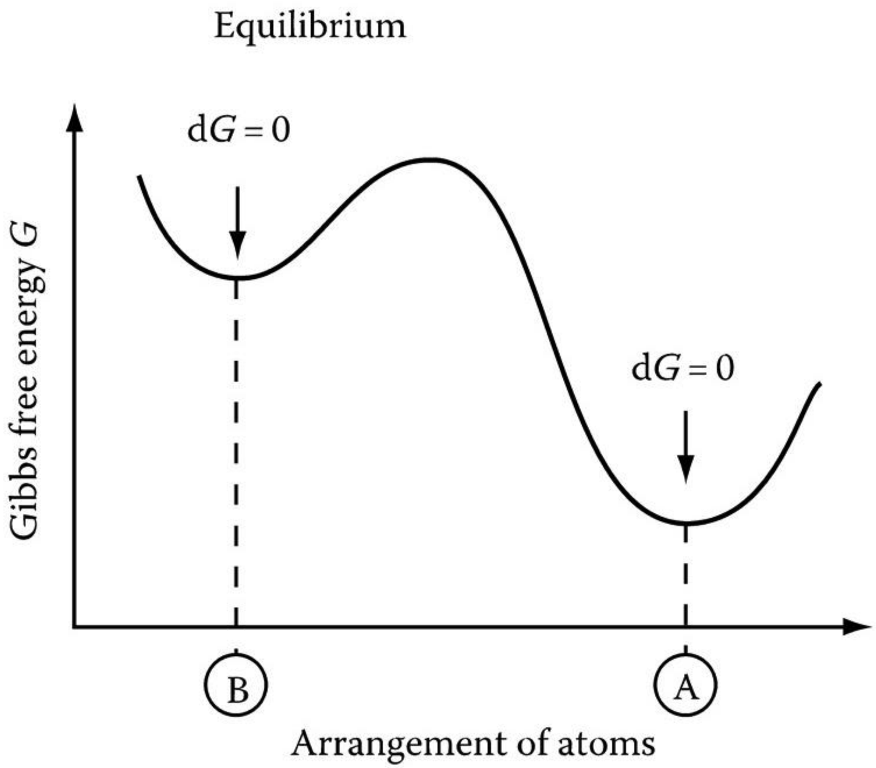
H (enthalpy) = E + PV

For condensed phase (liquid or solid), usually small

S (entropy)

1.1. Equilibrium

❖ Gibbs free energy, G



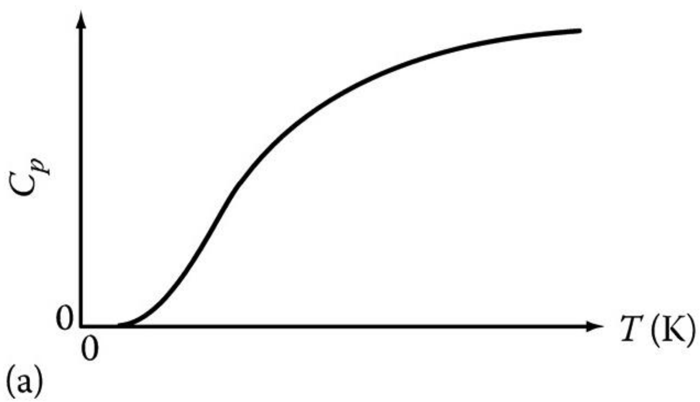
dG = 0 — Stable equil. / Metastable equil.

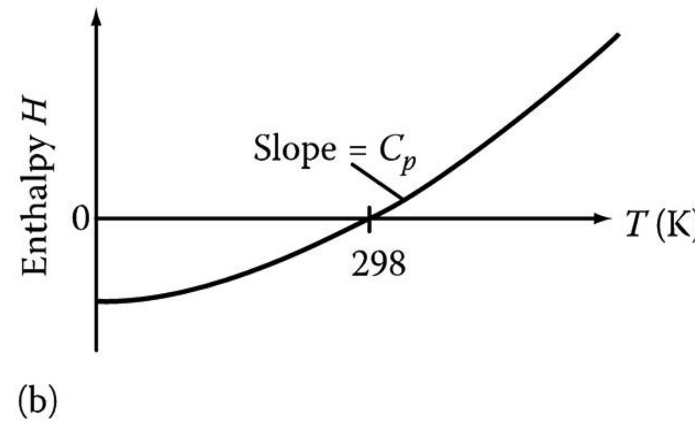
dG ≠ 0 — Unstable

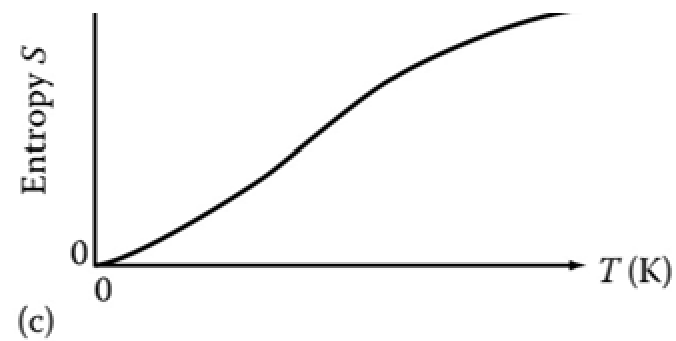
- Kinetics : How fast does a phase transformation occurs

1.2.1. Gibbs free E. as a function of temperature

❖ Enthalpy, Entropy vs. Temperature







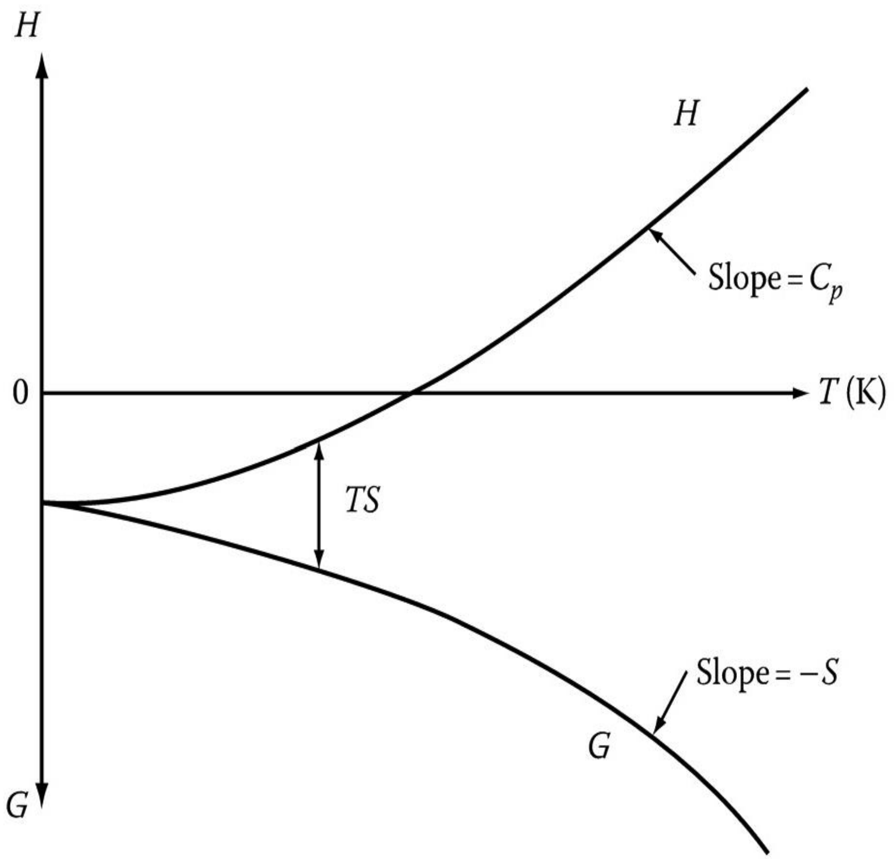
$$C_p = \left(\frac{\partial H}{\partial T}\right)_p \longrightarrow H = \int_{298}^{T} C_p \, dT$$

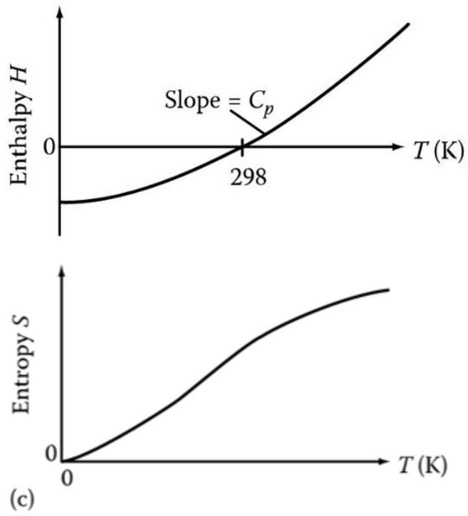
$$\frac{C_p}{T} = \left(\frac{\partial S}{\partial T}\right)_p \longrightarrow S = \int_{0}^{T} \frac{C_p}{T} dT$$

1.2.1 Single component system

❖ **Variation of Gibbs free energy with temperature**

$$G = H - TS$$





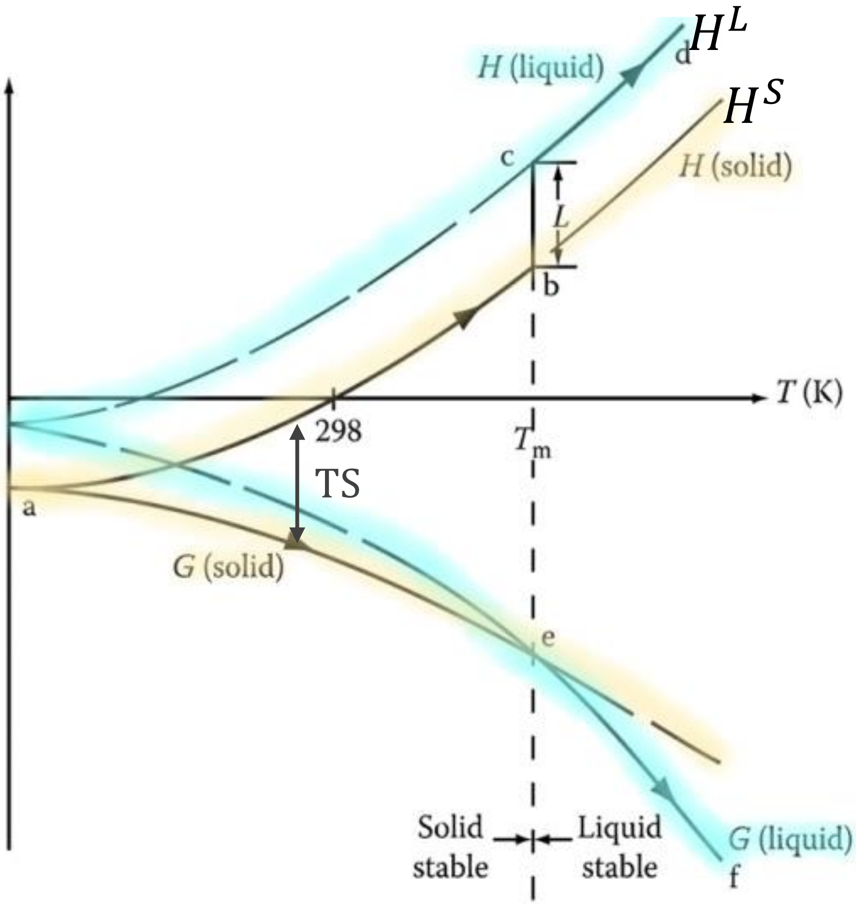
$$dG = -SdT + VdP$$

as pressure const. dP=0

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

1.2 Liquid and Solid Phase

$$G = H - TS$$

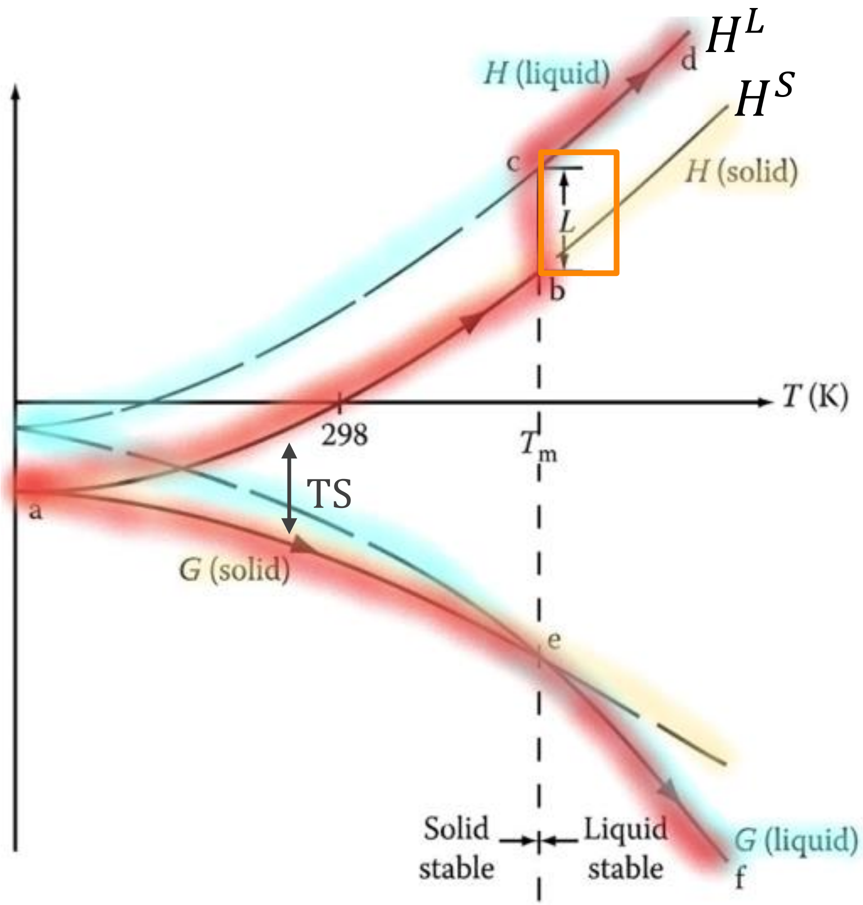


$\boldsymbol{H}$: liquid > solid

$\boldsymbol{S}$: liquid > solid

1.2 Liquid and Solid Phase

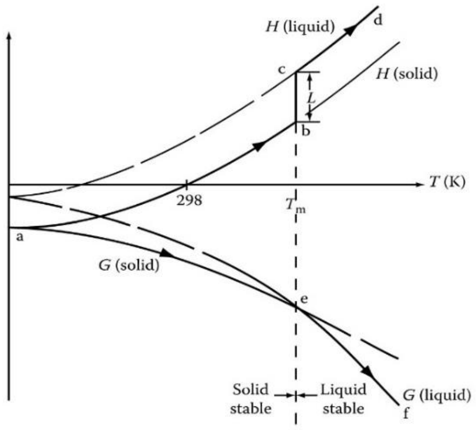
upon heating (heat supplies) …

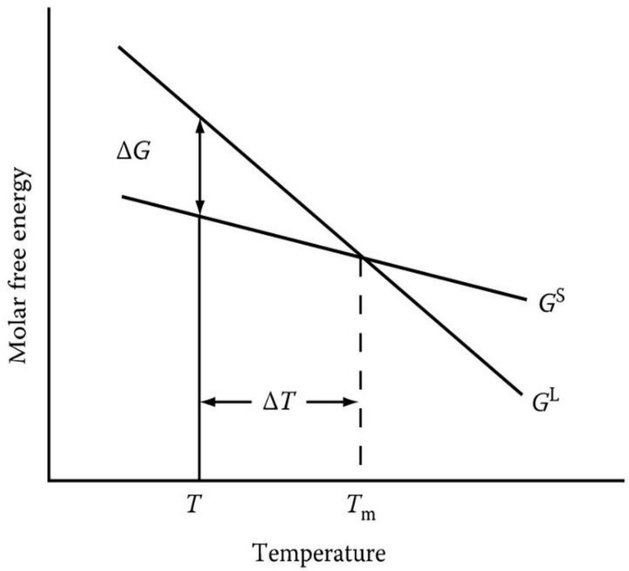


1.2.2 Driving Force for Solidification

❖ Phase transformation deals with ΔG of two phase of interest at temp away from T_e

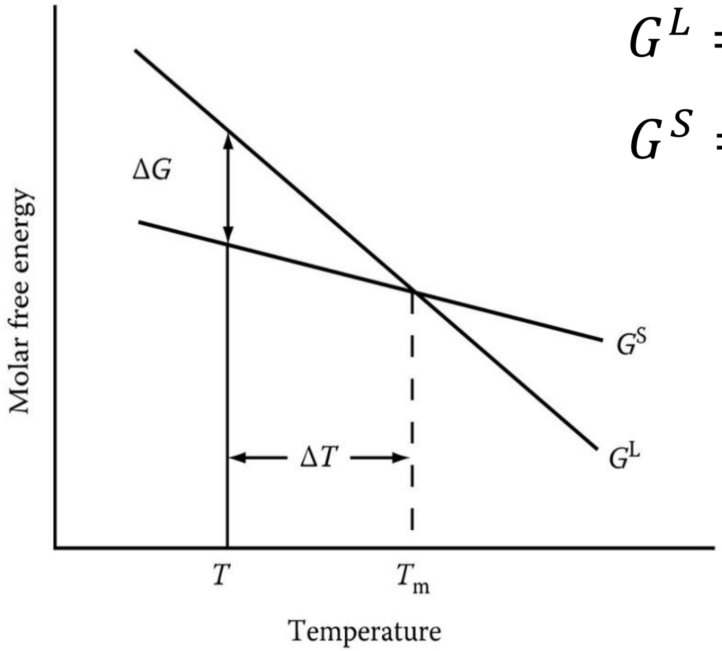
Ex) liquid metal under cooled by ΔT below T_m





$$\Delta G : Driving\ force\ for\ solidification$$

1.2.2 Driving Force for Solidification



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

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

❖ at *T*, $\Delta G = \Delta H - T\Delta S$

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

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

❖ at T_m $\quad G^L = G^S \quad \therefore\ \Delta G = 0$

$$\Delta H = T_m \Delta S$$

$$\Delta S = \frac{\Delta H}{T_m} = \frac{L}{T_m} = R$$

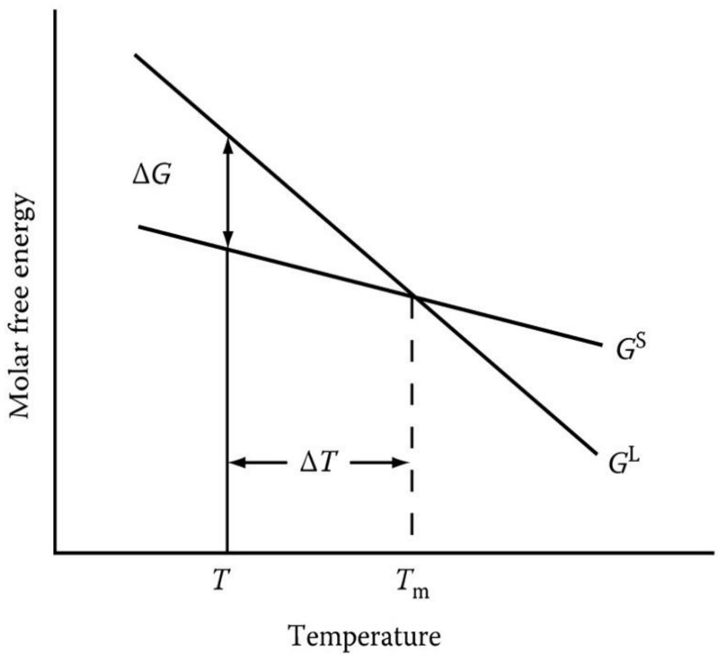
$(\approx 8.3\ Jmol^{-1}K^{-1})$

Entropy of fusion

For most metals →Richard's rule
(*L* 과 T_m은 bonding strength와 같은 경향성!!!)

$$\therefore L \propto T_m$$

1.2.2 Driving Force for Solidification



- at T, $\boxed{\Delta G = \Delta H - T\Delta S}$

$$\begin{cases} \Delta H = H^L - H^S \\ \Delta S = S^L - S^S \end{cases}$$

- For small ΔT, $\Delta C_p (= C_p^L - C_p^S) \sim$ small

$$\Delta H, \Delta S \neq f_n(T) \quad (= \text{const.})$$

$$\Delta G = \Delta H - T\Delta S \quad \Rightarrow \quad \boxed{\Delta G = \frac{L\Delta T}{T_m}}$$

$$\downarrow \qquad \downarrow$$

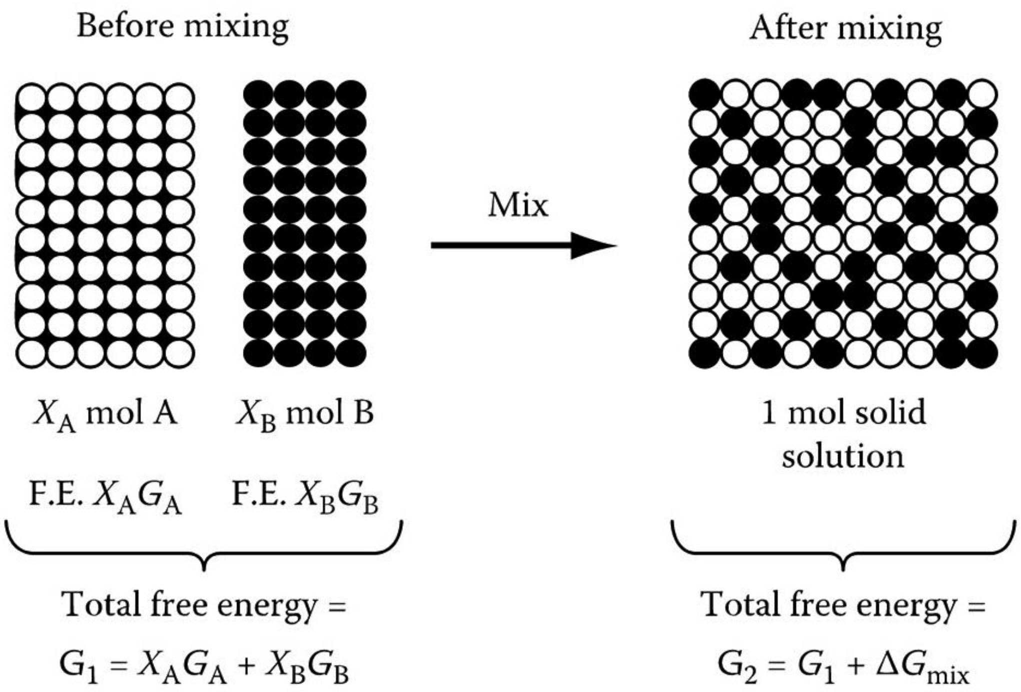
$$L \qquad \frac{L}{T_m}$$

$$= R\Delta T$$

$$\propto \Delta T$$

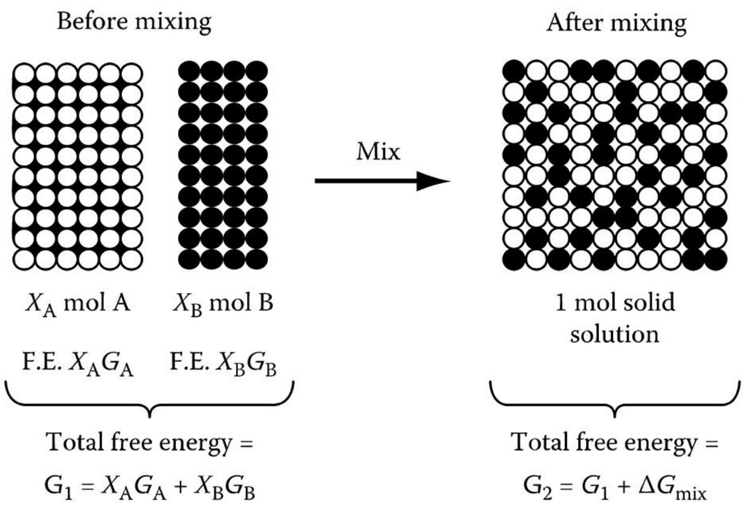
1.3 Binary solution

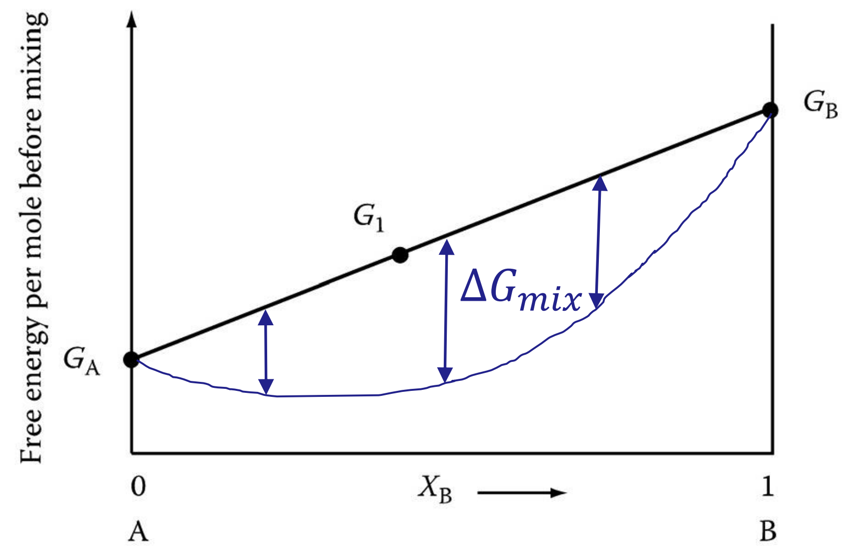
❖ Gibbs free E changes as T, P & composition



X_A, X_B: Mole fraction ($X_A + X_B = 1$)

1.3.1 Gibbs Free Energy of Binary solution





$$G_1 = H_1 - TS_1$$

$$G_2 = H_2 - TS_2$$

$$\Rightarrow \begin{cases} \Delta H_{mix} = H_2 - H_1 \\ \Delta S_{mix} = S_2 - S_1 \end{cases}$$

Heat absorbed or evolved during step 2

$$\boxed{\Delta G^M = \Delta H^M - T\Delta S^M}$$

Difference in entropy between mixed & unmixed state

1.3 Binary solutions

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

- **Ideal solution:** $\boldsymbol{\Delta H_{mix} = 0}$

$$\boldsymbol{\Delta G_{mix} = -T\Delta S_{mix}}$$

- **Regular solution:** $\boldsymbol{\Delta H_{mix} \neq 0, \Delta G_{mix} = \text{ideal sol}}$

  Quasi-chemical approach

- **Real solution**