Phase Transformation

Dr.K. Santhy
Associate Professor
Department of Materials and Metallurgical Engineering

Content

- **Review of Thermodynamics:**
  - Equilibrium
  - Single Component Systems
  - Binary Solutions
  - Equilibrium in Heterogeneous Systems
  - Binary Phase Diagrams
  - Kinetics of Phase Transformations.

- **Review of Diffusion:**
  - Atomics Mechanisms of Diffusion
  - Interstitial diffusion
  - Substitutional diffusion
    - Self-Diffusion
    - Vacancy Diffusion
  - Diffusion in Substitutional Alloys

Thermodynamics

- The study of the flow of heat or any other form of energy into or out of a system as it undergoes a physical or chemical transformation is called thermodynamics.
- The study of transformation of energy is called thermodynamics.
- Thermodynamics: all about "if"
  - tells whether or not a process or a reaction can occur
  - applicable to systems in stable or metastable equilibrium
  - sufficient driving force is needed to enforce a favorable transformation

Limitations of Thermodynamics

(1) Thermodynamics is applicable to macroscopic systems and not to microscopic systems

(2) Thermodynamics does not bother about the time factor. It is concerned only with the initial and the final states of the system.

Kinetics

- The study of rate of transformation of energy is called as Kinetics.
- Kinetics: all about "how"
  - how fast or slow a process can occur, i.e., determining the rate
  - applicable to systems in transition from nonequilibrium to equilibrium, or between two equilibrium states
  - kinetics of a process is generally about how to overcome the energy barrier to finish the transformation from the starting (reactant) state to the final (product) state.

Phase Transformation

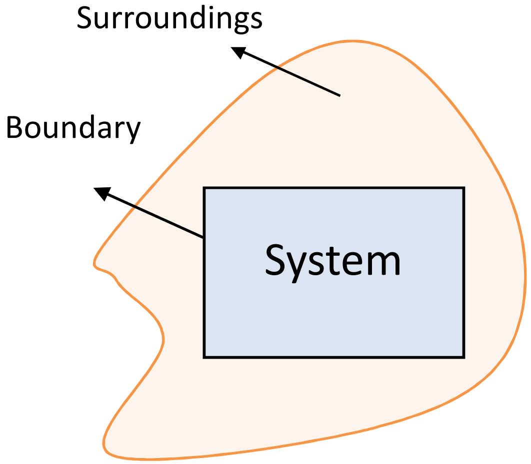
- Relative stability of any system is determined by its Gibbs energy (G).
- Gibbs energy – Useful energy to do work
- Gibbs energy of a system is defined by the equation,

$$G = H - TS$$

H – Enthalpy   T- Temperature S – Entropy

- *System:* System is the part of the universe which is under thermodynamic study.

Example: It may be a reaction vessel, an electrochemical cell, a biological cell and so on.



The phase transformation always deals with the changes occur within a given system. Ex.: alloy – mixture of ore or more phases.

- *Components (C)* : chemical compounds that make up a system

STATE OF A SYSTEM

- State of a System: A thermodynamic system is said to be in a certain state when all its properties are fixed.
- The fundamental properties which determine the state of a system are pressure (*P*), *temperature* (*T*), *volume (V), mass(n) and composition.* *T*hese are referred to as State variables or State functions or Thermodynamic parameters.
- The state variables *P, V, T are interrelated in the form of an algebraic relationship called the Equation of State***.**

$$PV=RT$$

- It is not necessary to state all the properties (state variables) to define a system completely. Since variables classified as dependent variable and independent variable

The macroscopic or bulk properties (variables) of a system (Volume, pressure, mass, etc) can be divided into two classes:

- Intensive properties
- Extensive properties

Properties depend on the quantity of the system is called as *extensive variable/properties*. ex: V, m. (H, U, S and G)

Properties which does not depend on the quantity of the system is called as intensive variable/properties. ex: P, T

Extensive expressed per unit volume or unit mass of the system are called as *specific intensive property*. ex: specific volume, density. (H_m, U_m, S_m and G_m)

Homogeneous and Heterogeneous Systems

- When a system is uniform throughout, it is called a Homogeneous System. A homogeneous system is made of one phase only.

  Examples: a pure single solid, liquid or gas, salt solution

- A heterogeneous system is one which consists of two or more phases. In other words it is not uniform throughout.

  Examples : ice in contact with water, soil in water

A phase is defined as a chemically homogeneous, physically distinct and mechanically separable portion of a system.

- Total heat content of the system is called as enthalpy (H)

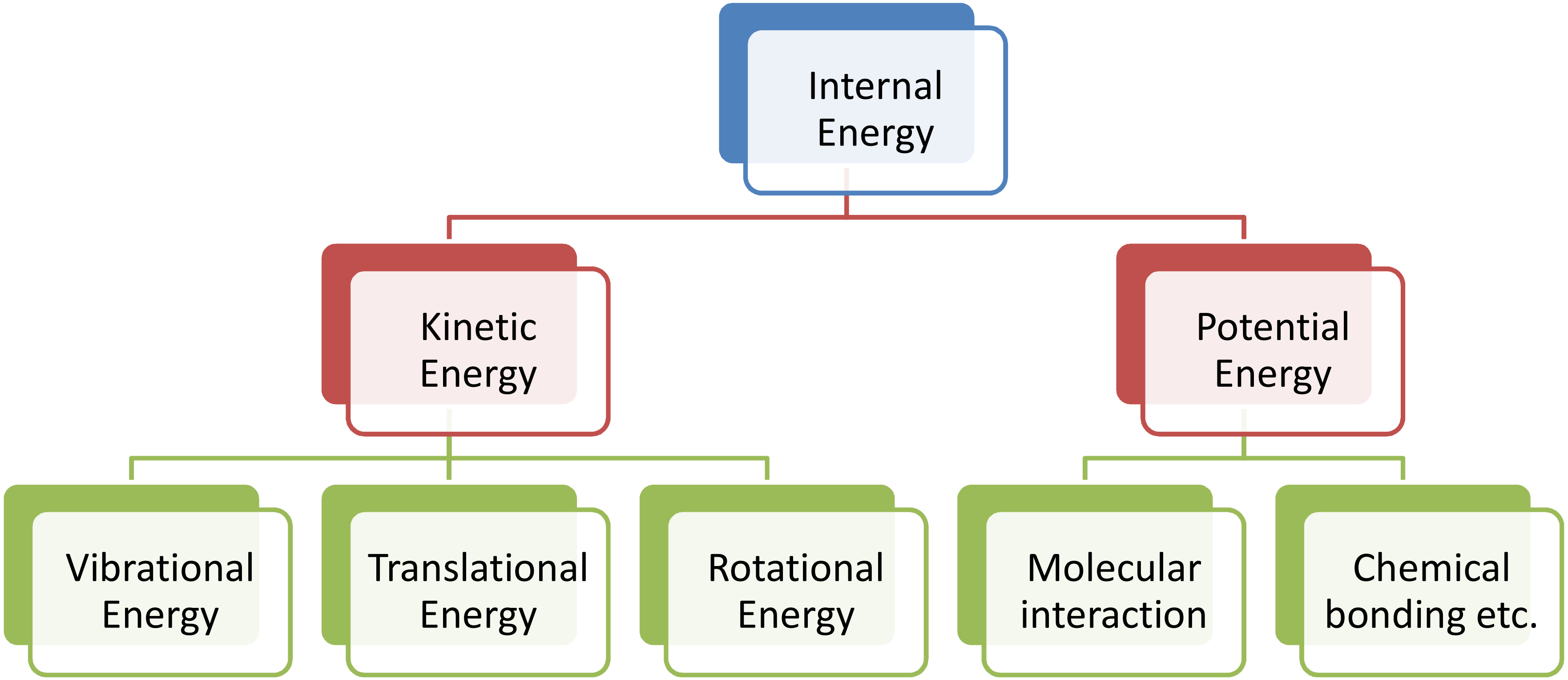
$$H = E+PV$$

E – internal energy P- Pressure V – Volume

- At constant P, PV→0, Hence

$$H \sim E$$

Note: $H \sim E$ is applicable for solids and liquids



Internal Energy

Kinetic Energy

Potential Energy

Vibrational Energy

Translational Energy

Rotational Energy

Molecular interaction

Chemical bonding etc.

Internal energy is a state function and an extensive property.

A system is said to be in equilibrium ,

$$dG=0$$

The state with the highest stability with the combination of low enthalpy and high entropy.

At low temperature, enthalpy dominates

At high temperature, entropy dominates

Heat Capacity: Amount of heat energy required to raise 1˚C of the system

$$C = \frac{q}{m.(T_2 - T_1)}$$

Specific heat capacity: Amount of heat energy required to raise 1˚C of one mole of the system

$$C = \frac{q}{(T_2 - T_1)}$$

Heat capacity varies with temperature,

$$C = \frac{dq}{dT}$$

Unit: $JK^{-1}mol^{-1}$

Classification of heat capacity:

- At constant volume C_V
- At constant pressure C_P

According to 1st law of thermodynamics,

$$dE=dq-dw$$

Rearrange the above equation,

$$dq=dE+dw=dE+P\Delta V$$

Dividing both sides by dT,

$$\frac{dq}{dT}=\frac{dE+PdV}{dT}$$

At constant volume dV=0,

$$\frac{dq}{dT}=\frac{dE}{dT} \qquad \boxed{C_V=\left(\frac{dE}{dT}\right)_V}$$

Thus the heat capacity at constant volume is defined as the rate of change of internal energy with temperature .

$$C = \frac{dq}{dT} = \frac{dE + PdV}{dT}$$

w.k.t, H=E+PV

Differentiate the above equation w.r.t T, at constant P, then

$$\left(\frac{dH}{dT}\right)_P = \left(\frac{dE}{dT}\right)_P + P\left(\frac{dV}{dT}\right)_P$$

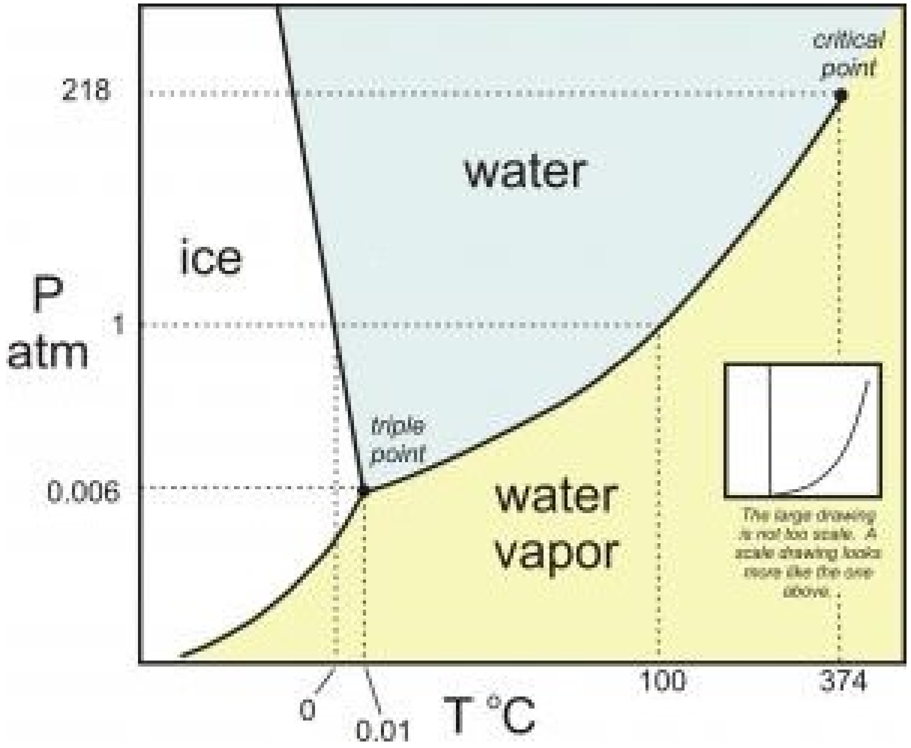
Comparing the above two equation,

$$\left(\frac{dH}{dT}\right)_P = \left(\frac{dE}{dT}\right)_P + P\left(\frac{dV}{dT}\right)_P = \frac{dq}{dT} = C_P$$

$$\boxed{\left(\frac{dH}{dT}\right)_P = C_P}$$

Thus heat capacity at constant pressure is defined as the rate of change of enthalpy with temperature.

Single Component Systems



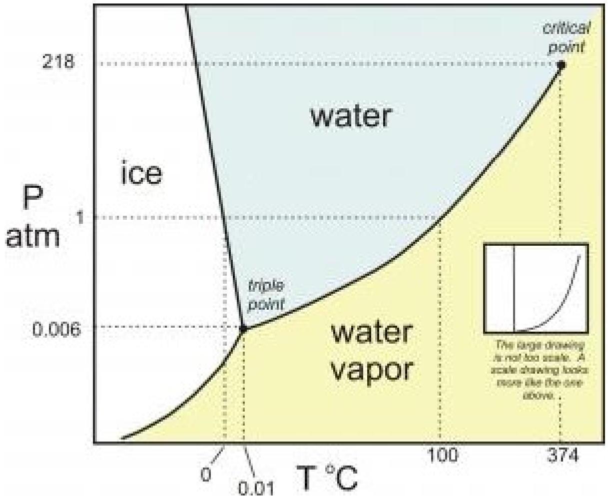
Single Component Systems

Phase – Ice, water and vapour

Phase boundary – the line which separate phases

Triple point – the point at which three phases coexists

Critical point – the point at which water and vapour phase boundary disappear



Gibbs Energy as a Function of Temperature

- At constant P, the heat capacity is represented by,

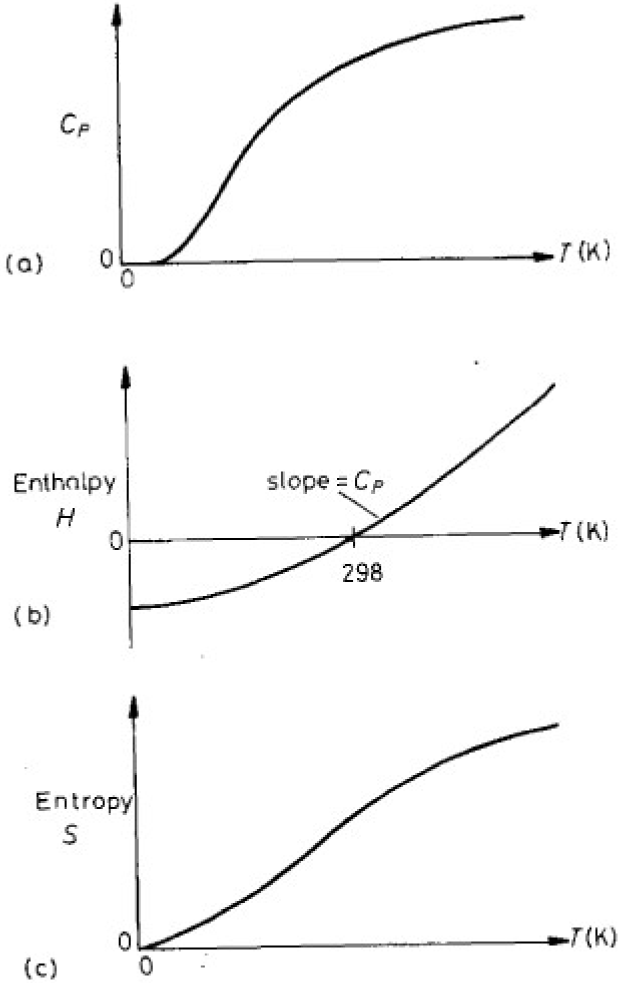
$$\boxed{\left(\frac{dH}{dT}\right)_P = C_P}$$

- The variation of H with T is calculated by integrating the above equation,

$$H = \int_{298}^{T} C_p \mathrm{d}T$$

- The variation of entropy with temperature,

$$\frac{C_p}{T} = \left(\frac{\partial S}{\partial T}\right)_P \qquad S = \int_0^T \frac{C_p}{T} \mathrm{d}T$$



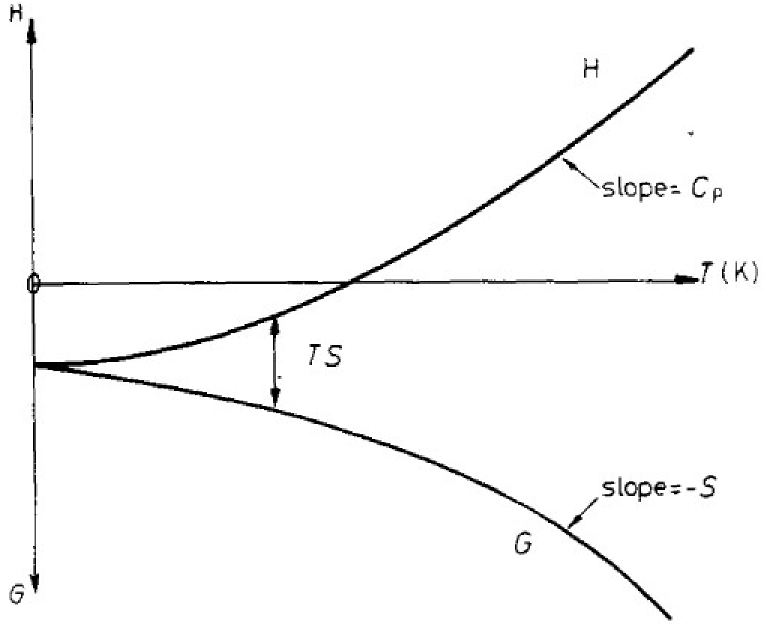
When temperature and pressure vary the changes in G can be obtained by,

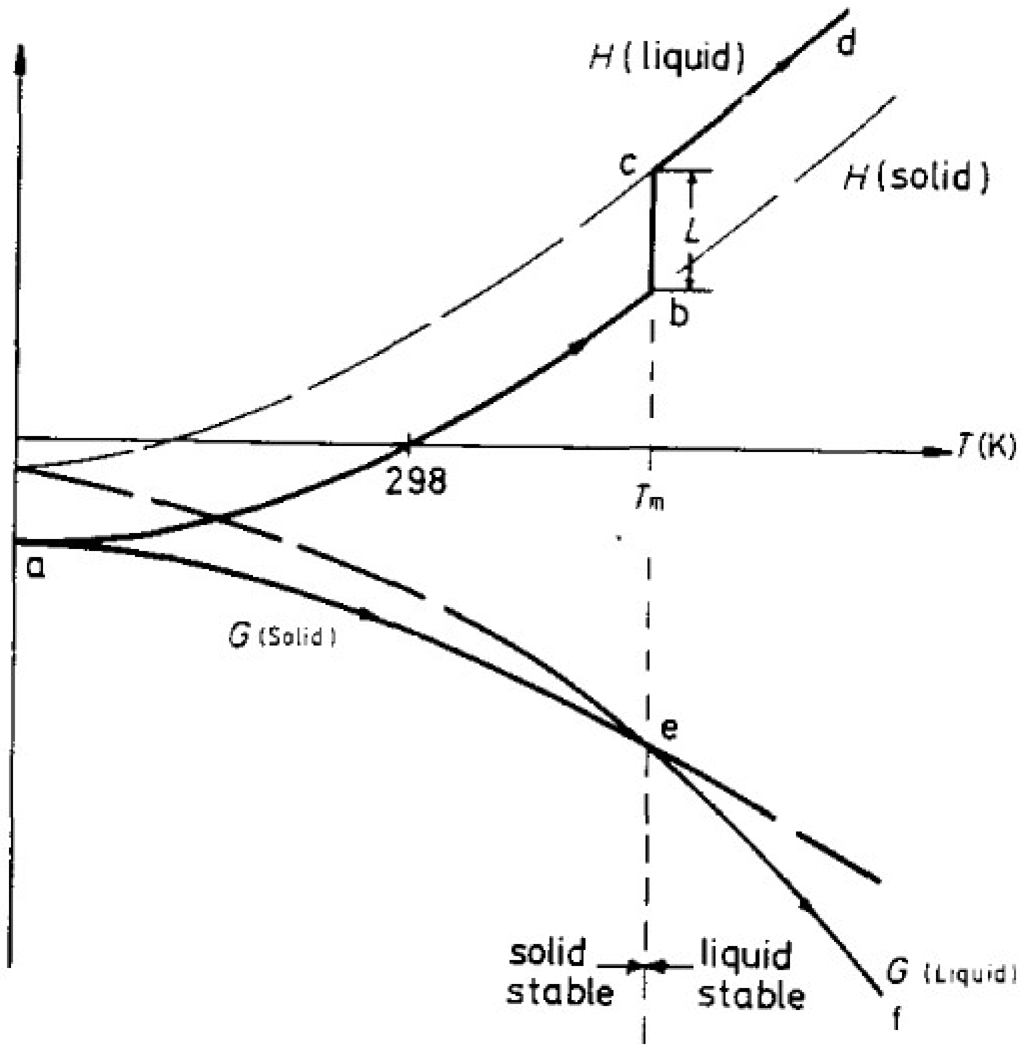
$$dG = -SdT + VdP$$

At constant P, dP=0

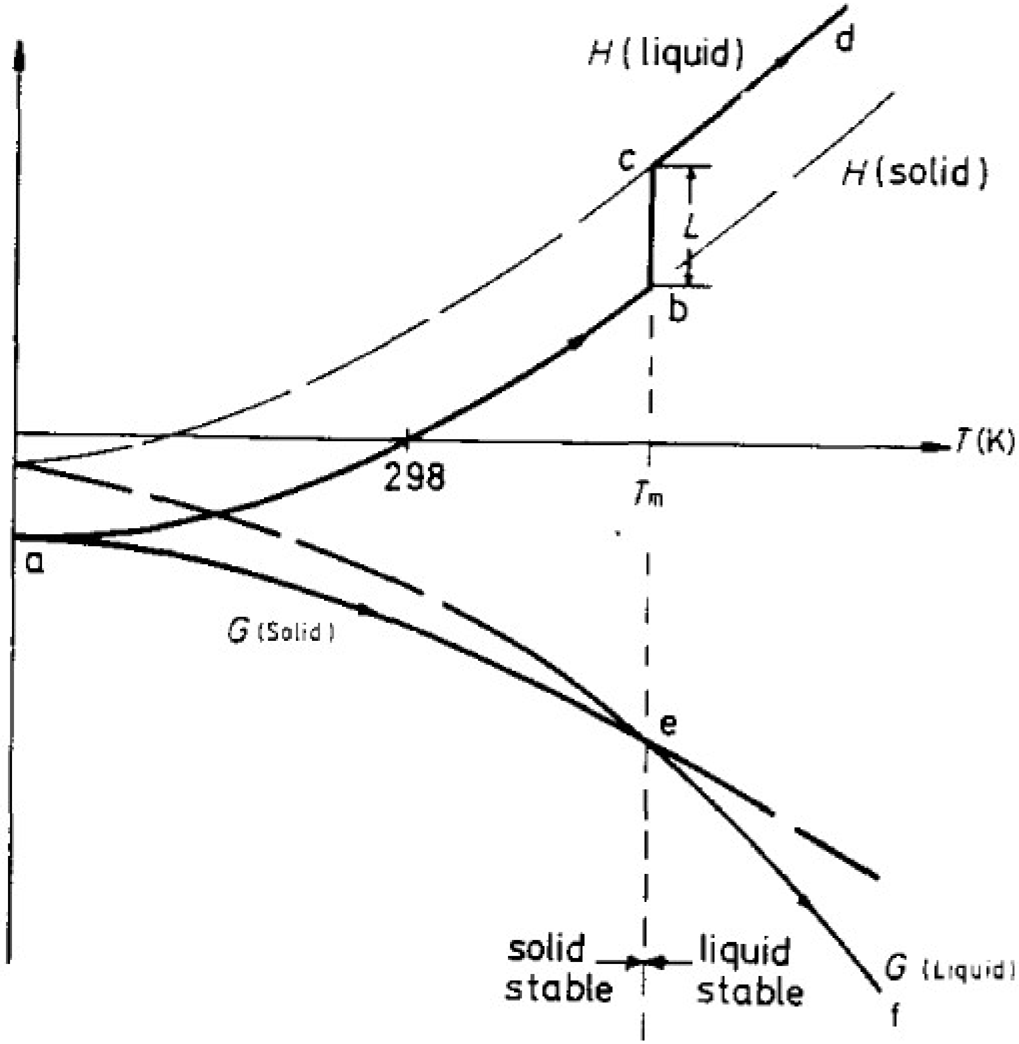
$$\left(\frac{\partial G}{\partial T}\right)_P = -S$$

As T ↑es,   G↓es.



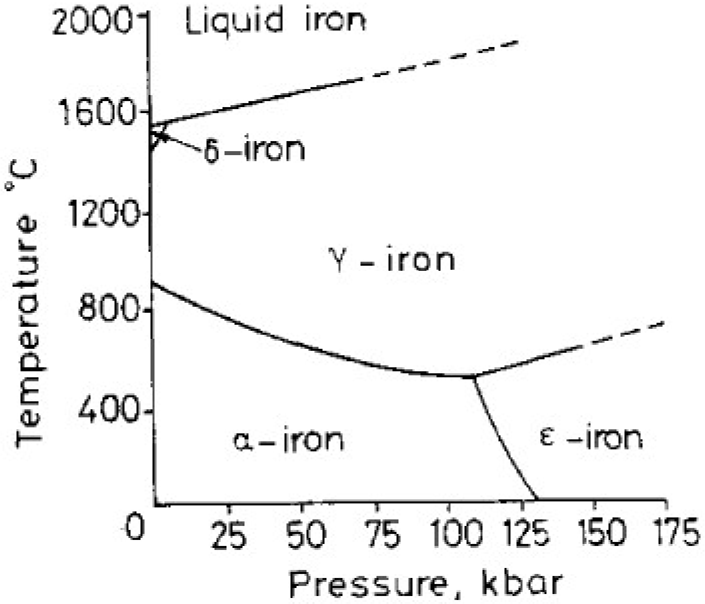

H (liquid)
d
c
H (solid)
L
b
T (K)
298
T_m
a
G (Solid)
e
solid stable
liquid stable
G (Liquid)
f

- As T ↑es, G↓es.
- At all T, $H^L > H^S$.
- At low T, $G^L > G^s$.
- $S^L > S^S$, hence G^L decreases more rapidly with increasing temperature.
- when $T < T_m$, $G^S < G^L$. Hence solid phase is stable.
- when $T > T_m$, $G^L < G^S$. Hence liquid phase is stable.
- At $T=T_m$, $G^L=G^S$, hence both phases are stable.



- At T=Tm, the heat energy supplied will be used convert the phase Instead of raising the temperature of the system (latent heat of melting)

Pressure Effect



Gibbs energy of a system is represented as,

$$dG = -SdT + VdP \qquad \text{--- 1}$$

At constant T, dT=0

$$\left(\frac{\partial G}{\partial P}\right)_T = V \qquad \text{--- 2}$$

Consider two phases such as α and β are in equilibrium,

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

If α and β are in equilibrium, $G^{\alpha} = G^{\beta}$ therefore $dG^{\alpha} = dG^{\beta}$

$$\left(\frac{dP}{dT}\right)_{eq} = \frac{S^{\beta} - S^{\alpha}}{V_m^{\beta} - V_m^{\alpha}} = \frac{\Delta S}{\Delta V} \qquad \text{---- 3}$$

The above equation is simplified as,

$$G^{\alpha} = H^{\alpha} - TS^{\alpha}$$
$$G^{\beta} = H^{\beta} - TS^{\beta}$$

Therefore, $\Delta G = G^{\beta} - G^{\alpha}$

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

At equilibrium, $\Delta G = 0$,

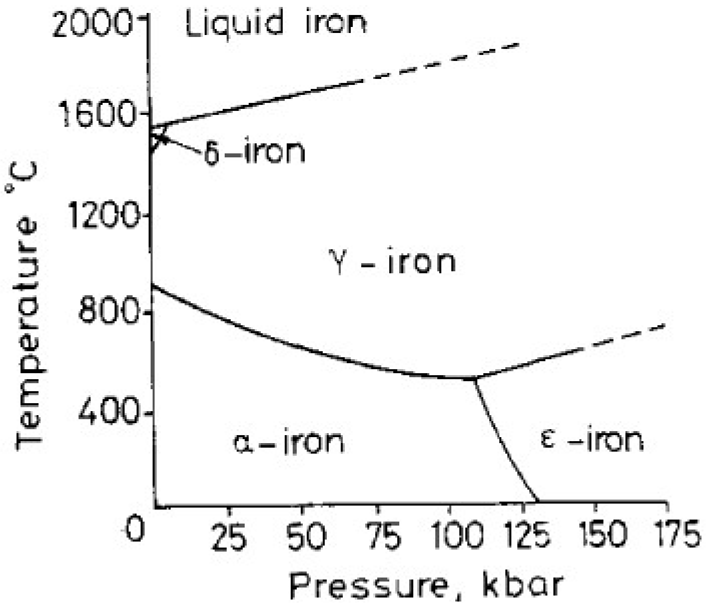
$$\Delta H - T\Delta S = 0$$

$$\Delta S = \Delta H / T$$

Substitute the above equation in 3,

$$\boxed{\left(\frac{dP}{dT_{eq}}\right) = \frac{\Delta H}{T_{eq}\Delta V}}$$ Clausius – Clapeyron equation

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



Consider α and γ phase,

$\Delta V = V^{\gamma} - V^{\alpha} < 0$

$\Delta H = H^{\gamma} - H^{\alpha} > 0$

Hence when P ↑es, equilibrium transition temperature decreases.

Consider γ and L phase,

$\Delta V = V^{L} - V^{\gamma} > 0$

$\Delta H = H^{L} - H^{\gamma} > 0$

Hence when P ↑es, equilibrium transition temperature increases.

Driving Force for Solidification

Gibbs energy of L and S at temp. T is given by,

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

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

At temperature T,

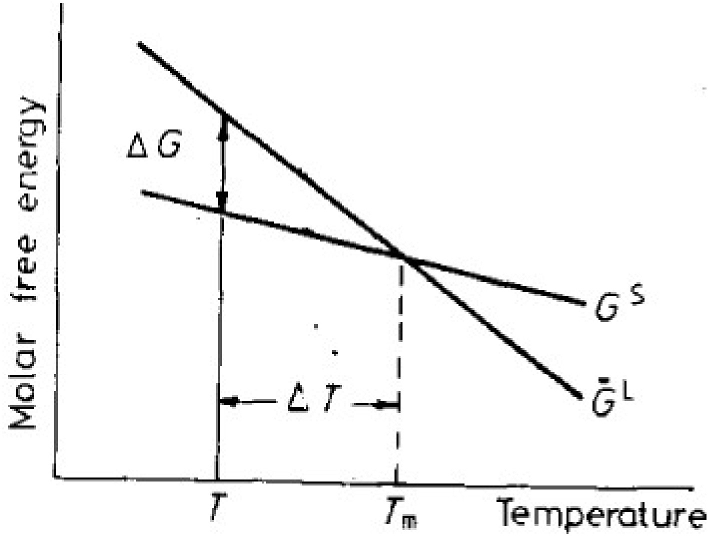
$$\Delta G = \Delta H - T\Delta S$$

At Tm, ΔG=0

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

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

Entropy of fusion



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

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

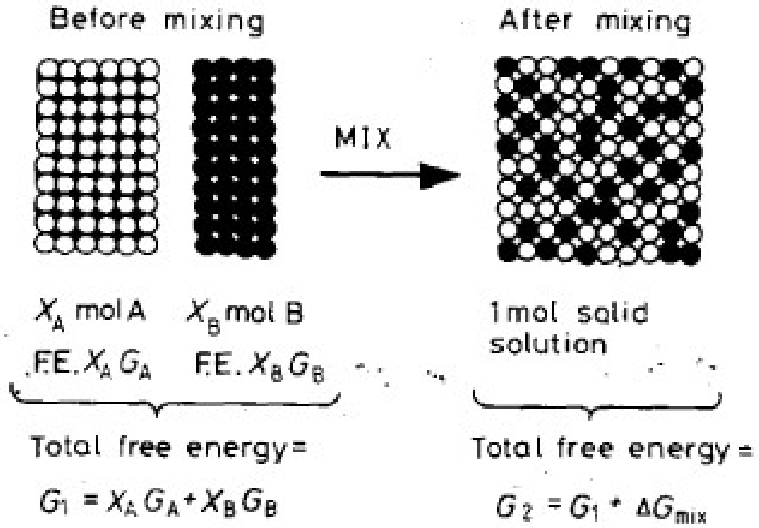
Binary systems : Ideal solutions

- Let us assume that A and B have the same crystal structure and can be mixed in any proportions to make solid solutions.
- Two species in the mixture: consider mole fractions X_A and X_B

$$\boxed{X_A + X_B = 1}$$

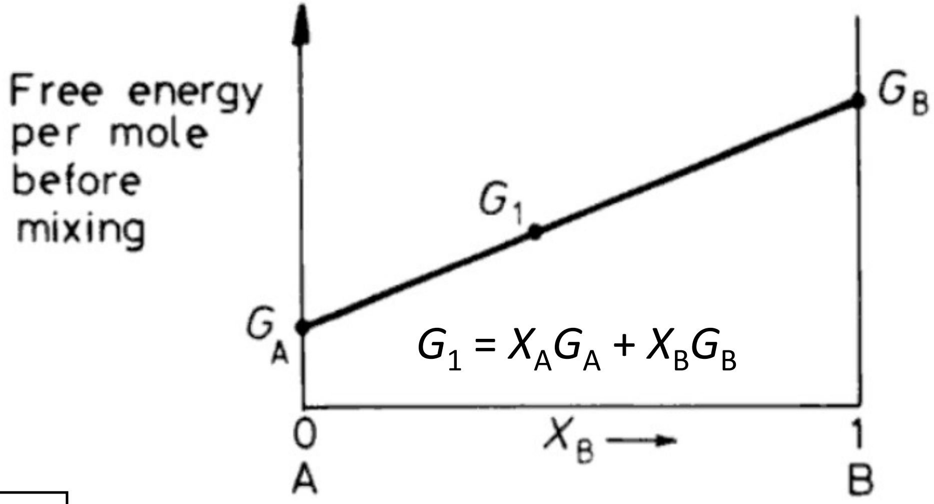
For mixing,

- Bring together X_A mol of pure A and X_B mol of pure B
- Allow the A and B atoms to mix together



contributions to G from mixing two components together:

1. G_1 – weighted molar average of the two components
2. Free Energy of mixing



$$\boxed{\Delta G_{MIX} = \Delta H_{mix} - T\,\Delta S_{MIX}}$$

ΔH_{mix} is the heat absorbed or evolved during mixing or *heat of solution*

ΔS_{MIX} is the entropy difference between the mixed and unmixed states

Simplest case : Ideal solution : $\Delta H_{\mathrm{MIX}} = 0$

Some assumptions :

1. Free energy change is only due to entropy
2. Species A and B have the same crystal structure (no volume change)
3. A and B mix to form substitutional solid solution

$\boxed{S = k_{\mathrm{B}} \ln(\Omega)}$ S is the configurational entropy

$$\boxed{\Omega = \frac{(N_A + N_B)!}{N_A!\,N_B!}}$$

Ω - total number of microstates of system or total number of distinguishable ways of arranging the atoms

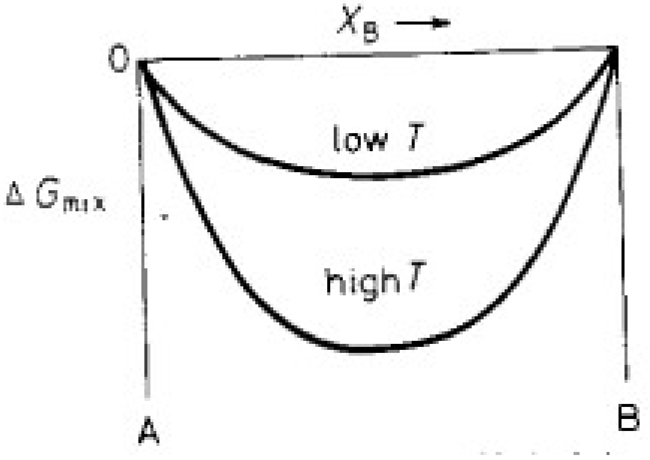
Using Stirling's approximation and $N_a k_{\mathrm{B}} = R$

$$\boxed{\Delta S_{\mathrm{MIX}} = -R(X_{\mathrm{A}} \ln X_{\mathrm{A}} + X_{\mathrm{B}} \ln X_{\mathrm{B}})}$$

$$\boxed{\Delta G_{\mathrm{MIX}} = RT(X_{\mathrm{A}} \ln X_{\mathrm{A}} + X_{\mathrm{B}} \ln X_{\mathrm{B}})}$$

Mixing components lowers the free energy!

$$\boxed{\Delta G_{MIX} = RT(X_A \ln X_A + X_B \ln X_B)}$$

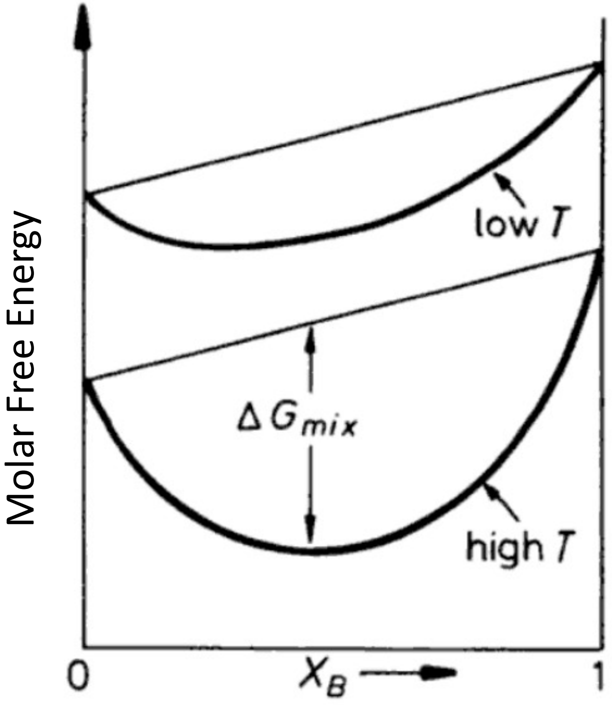


Mixing components lowers the free energy!

$$G_2 = G_1 + \Delta G_{mix}$$

Total Gibbs energy of the systems is

$$\boxed{G_2 = X_A G_A + X_B G_B + RT(X_A \ln X_A + X_B \ln X_B)}$$



Chemical potential

When small quantity dn_A mole added to A, then the change in Gibbs energy become,

$$dG' = \mu_A dn_A \quad (T,\ P,\ n_B \text{ constant})$$

The proportionality constant μ_A is called as partial molar Gibbs energy or chemical potential.

$$\mu_A = \left(\frac{\partial G'}{\partial n_A}\right)_{T,P,n_B}$$

Then two component contribution at constant T and P,

$$dG' = \mu_A dn_A + \mu_B dn_B$$

The above equation can be written as,

$$G = \mu_A X_A + \mu_B X_B \quad \text{J mol}^{-1}$$

The change in Gibbs energy with respect T, P and mole, can written as,

$$dG' = -SdT + VdP + \mu_A dn_A + \mu_B dn_B$$

$$G = \mu_A X_A + \mu_B X_B \quad \mathrm{J\ mol^{-1}}$$

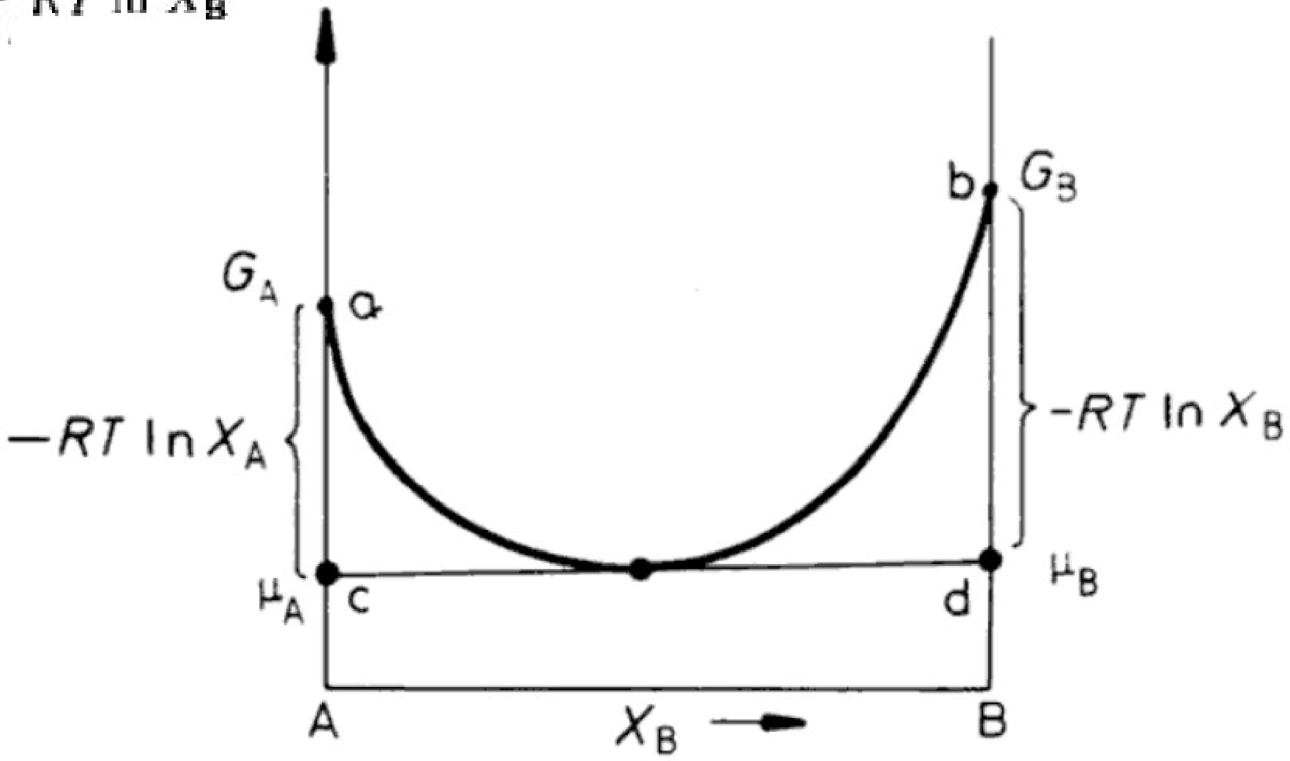
Total Gibbs energy of ideal solution is,

$$\boxed{G_2 = X_A G_A + X_B G_B + RT(X_A \ln X_A + X_B \ln X_B)}$$

Simplified equations for an ideal liquid:

$$\mu_A = G_A + RT \ln X_A$$
$$\mu_B = G_B + RT \ln X_B$$

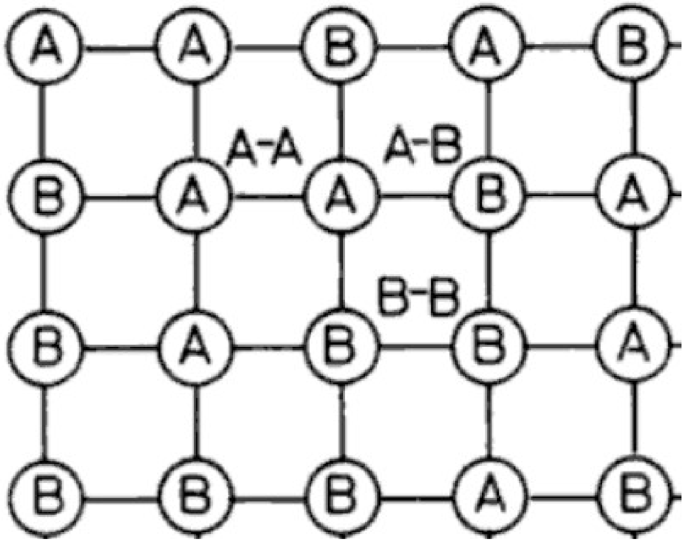
The relationship between the free energy curve and chemical potentials for ideal solution



Binary systems : Regular solutions

$\Delta H_{MIX} \neq 0$ i.e. internal energy of the system must be considered

In a binary, 3 types of bonds: A-A, B-B, A-B of energies ε_{AA}, ε_{BB}, ε_{AB}



The internal energy of the solution E depend on the number of bonds of each type P_{AA}, P_{BB} and P_{AB}, such that,

$$E = P_{AA}\varepsilon_{AA} + P_{BB}\varepsilon_{BB} + P_{AB}\varepsilon_{AB}$$

Then,

$$\Delta H_{mix} = P_{AB}\varepsilon$$

$$\varepsilon = \varepsilon_{AB} - \frac{1}{2}(\varepsilon_{AA} + \varepsilon_{BB})$$

If $\varepsilon = 0$, $\Delta H_{mix} = 0$ the solution becomes ideal solution.

For completely random solution,

$$P_{AB} = N_a z X_A X_B \quad \text{bonds mol}^{-1}$$

where N_a is Avogadro’s number and Z is the number bonds per atom

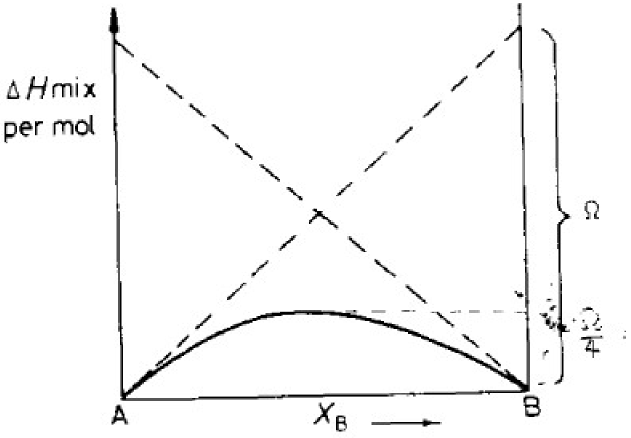
$\boxed{\Delta H_{MIX} = \Omega X_A X_B}$ Where $\Omega = N_a z \varepsilon$,

If $\Omega < 0 \Rightarrow$ A-B bonding preferred

If $\Omega > 0 \Rightarrow$ AA, BB bonding preferred

$$\boxed{\Delta G_{MIX} = \Delta H_{MIX} + RT(X_A \ln X_A + X_B \ln X_B)}$$

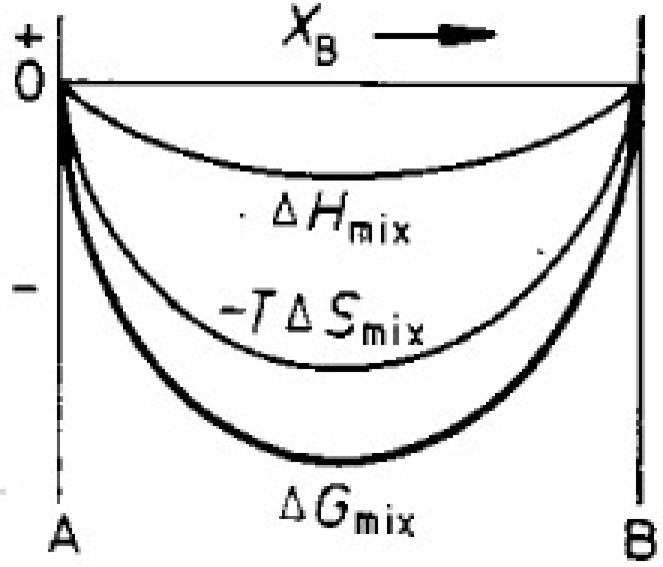
$$\varepsilon = \varepsilon_{AB} - \tfrac{1}{2}(\varepsilon_{AA} + \varepsilon_{BB})$$



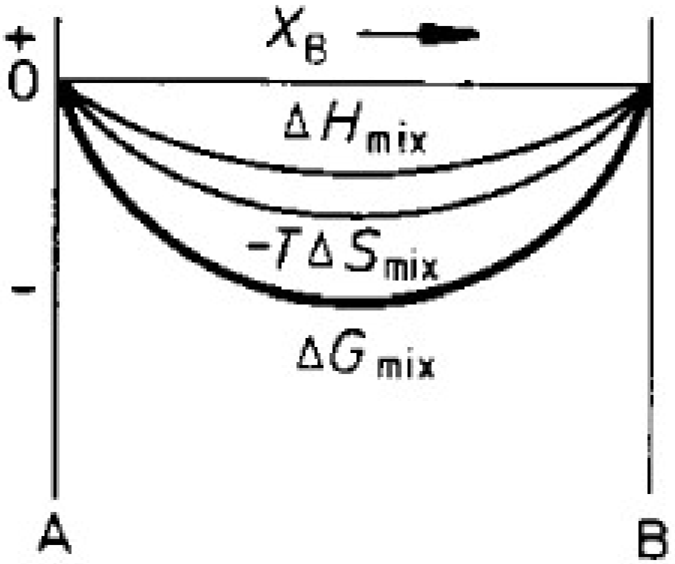
$$\Delta G_{mix} = \underbrace{\Omega X_A X_B}_{\Delta H_{mix}} + \underbrace{RT(X_A \ln X_A + X_B \ln X_B)}_{-T\Delta S_{mix}}$$

Effect of ΔH_{mix} and T on ΔG_{mix}

$\Omega < 0$, then $\Delta H_{mix} < 0$ → exothermic reactions

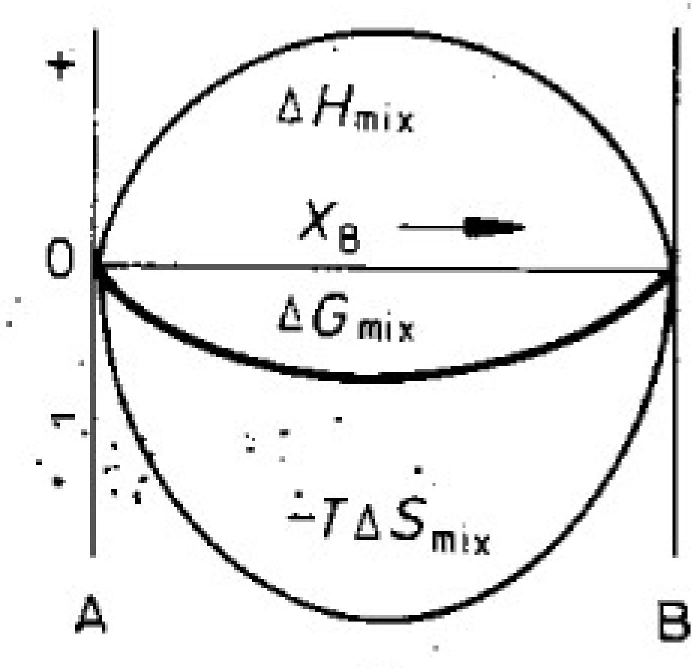


(a) $\Omega < 0$, high T

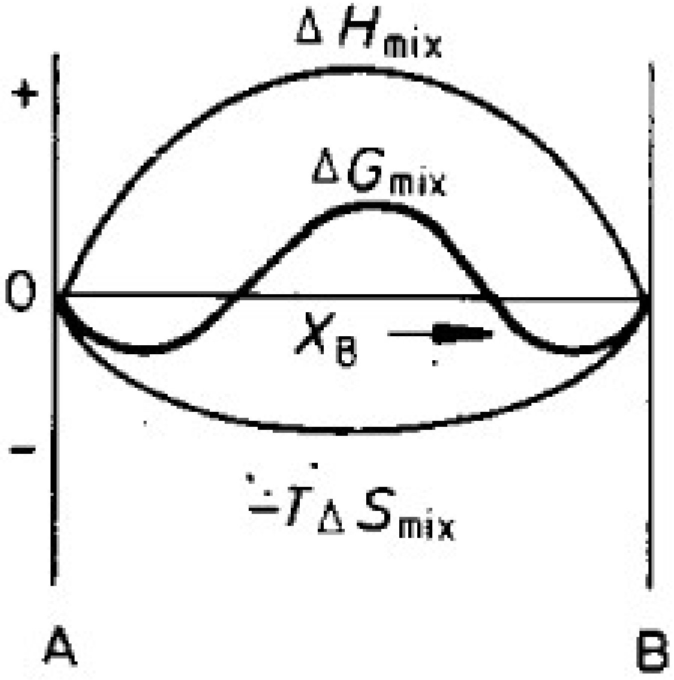


(b) $\Omega < 0$, low T

$\Omega > 0$, then $\Delta H_{mix} > 0$ → exdothermic reactions

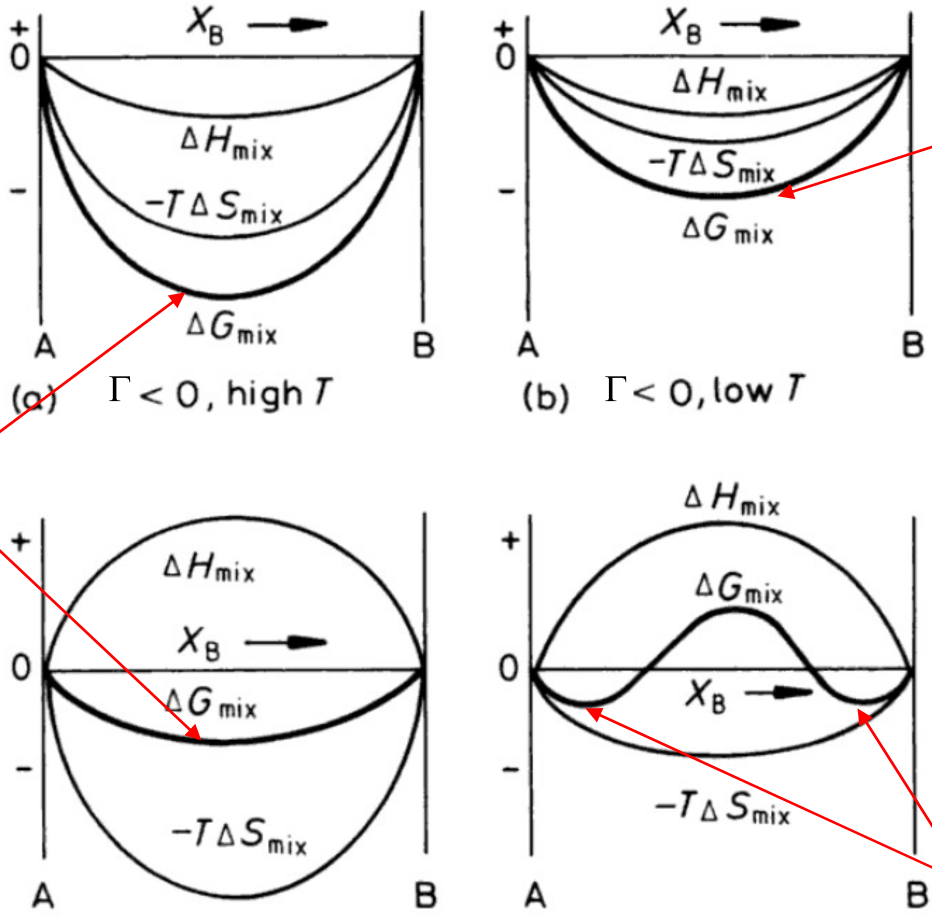


(c) $\Omega > 0$, high T



(d), $\Omega > 0$ low T

Free energy curves for various conditions:



(a) $\Gamma < 0$, high T

(b) $\Gamma < 0$, low T

(c) $\Gamma > 0$, high T

(d) $\Gamma > 0$ low T

Mixing if A and B atoms bond

Mixing always occurs at high Temp. despite bonding

A and B atoms repel Phase separation in to 2 phases.

The Gibbs energy of the alloy in regular solution can be written as

$$G = X_A G_A + X_B G_B + \Omega X_A X_B + RT(X_A \ln X_A + X_B \ln X_B)$$

Using the relationship, $X_A X_B = X_A^2 X_B + X_B^2 X_A$

The regular solutions represented as,

$$\mu_A = G_A + \Omega(1 - X_A)^2 + RT \ln X_A$$

and

$$\mu_B = G_B + \Omega(1 - X_B)^2 + RT \ln X_B$$

.

Activity: Escaping tendency of an atom to leave the solution.

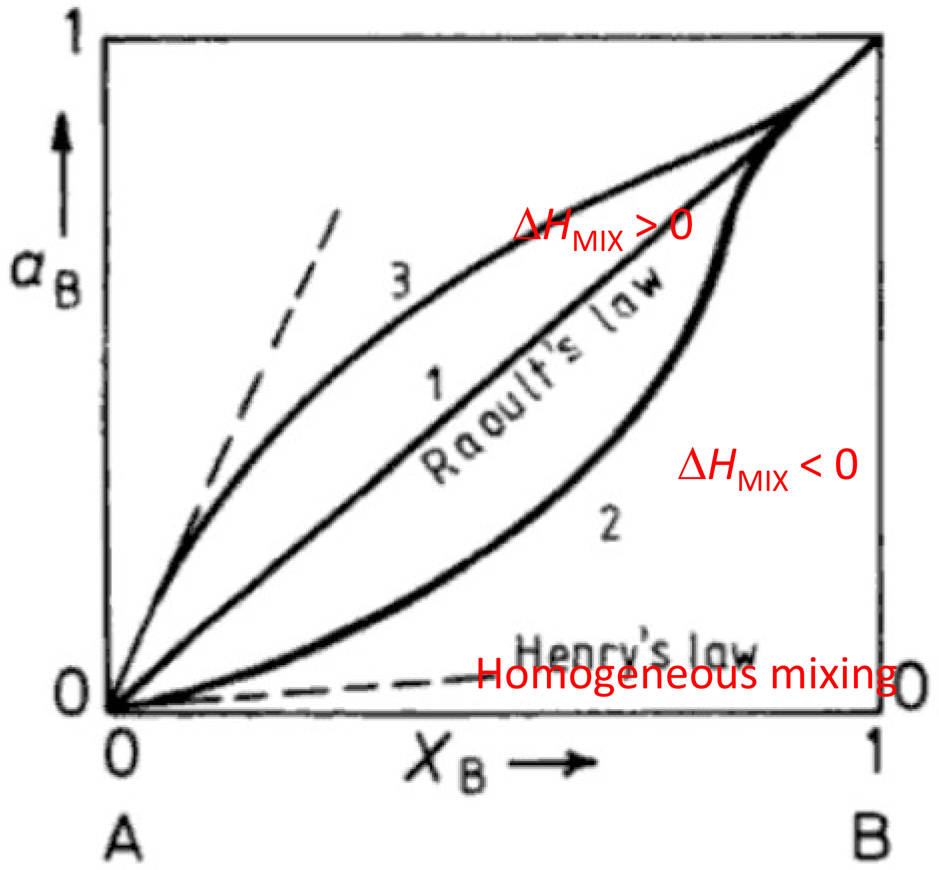
$$a_A \alpha X_A$$

$$a_A = \gamma_A X_A$$

γ_A is activity coefficient
For Ideal solution, $\gamma_A = 1$ therefore (line 1)

$$\gamma_A = \frac{a_A}{X_A} = 1$$ Raoult's law

$$a_A = X_A$$



If $\Delta H_{mix} > 0$ or $\Delta H_{mix} < 0$, then it deviates take path 3 and 1 respectively .

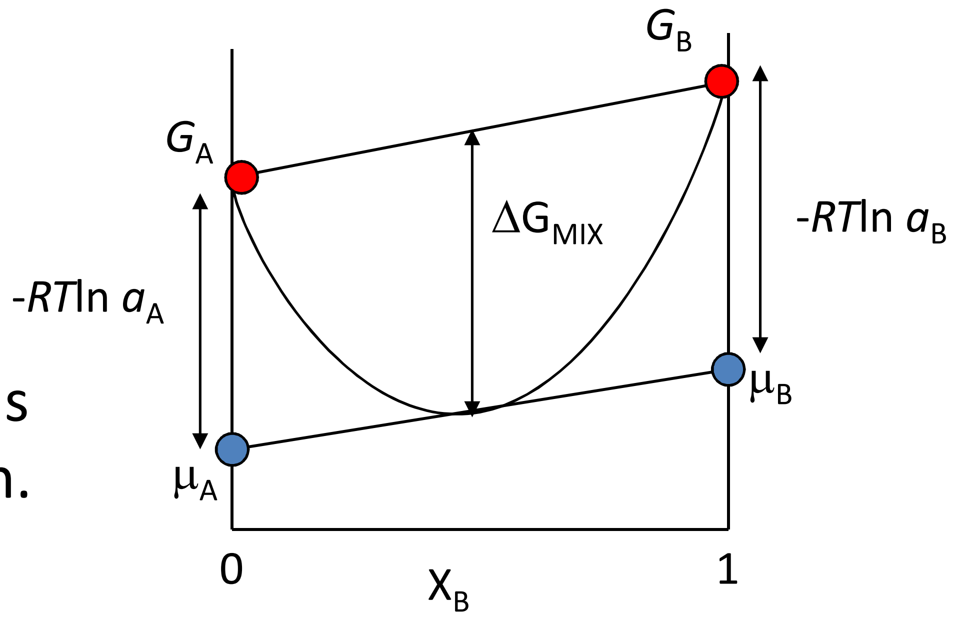
For dilute solution, $\gamma_A = \frac{a_A}{X_A}$ = Constant Henry's law

Activity is simply related to chemical potential by:

$$\boxed{\mu_A = G_A + RT \ln a_A}$$

$$\boxed{\mu_B = G_B + RT \ln a_B}$$

Low activity means that the atoms are reluctant to leave the solution.



$$\ln\left(\frac{a_A}{X_A}\right) = \frac{\Omega}{RT}(1 - X_A)^2 \qquad \ln\left(\frac{a_B}{X_B}\right) = \frac{\Omega}{RT}(1 - X_B)^2$$

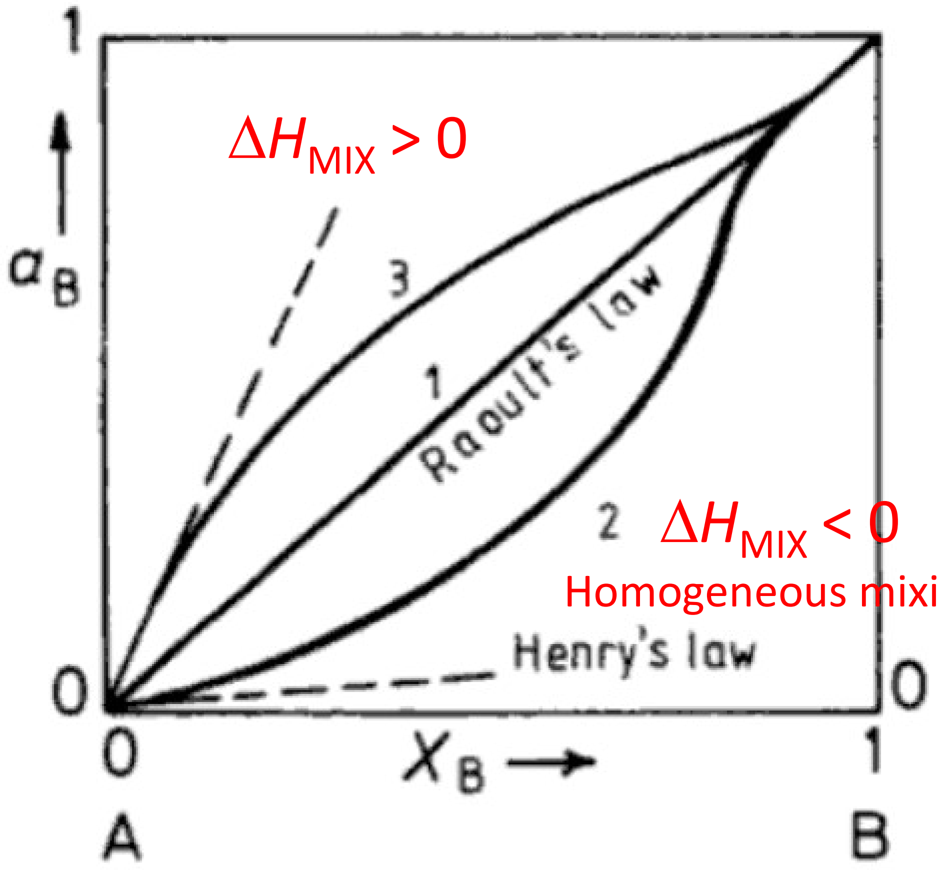
i.e. For homogeneous mixing, $\Omega<0 \Rightarrow a_A<X_A$ and $a_B<X_B$

So the activity is the tendency of a component to leave solution

For low concentrations of B (X_B<<1)

$$\boxed{\gamma_B = \frac{a_B}{X_B} \approx \text{const.}}$$ Henry's Law (or everything dissolves)

And… $$\boxed{\gamma_A = \frac{a_A}{X_A} \approx 1}$$ Raoult's Law



$\Delta H_{MIX} > 0$

$\Delta H_{MIX} < 0$

Homogeneous mixing

Gibbs energy diagram of Isothermal Solid Solution

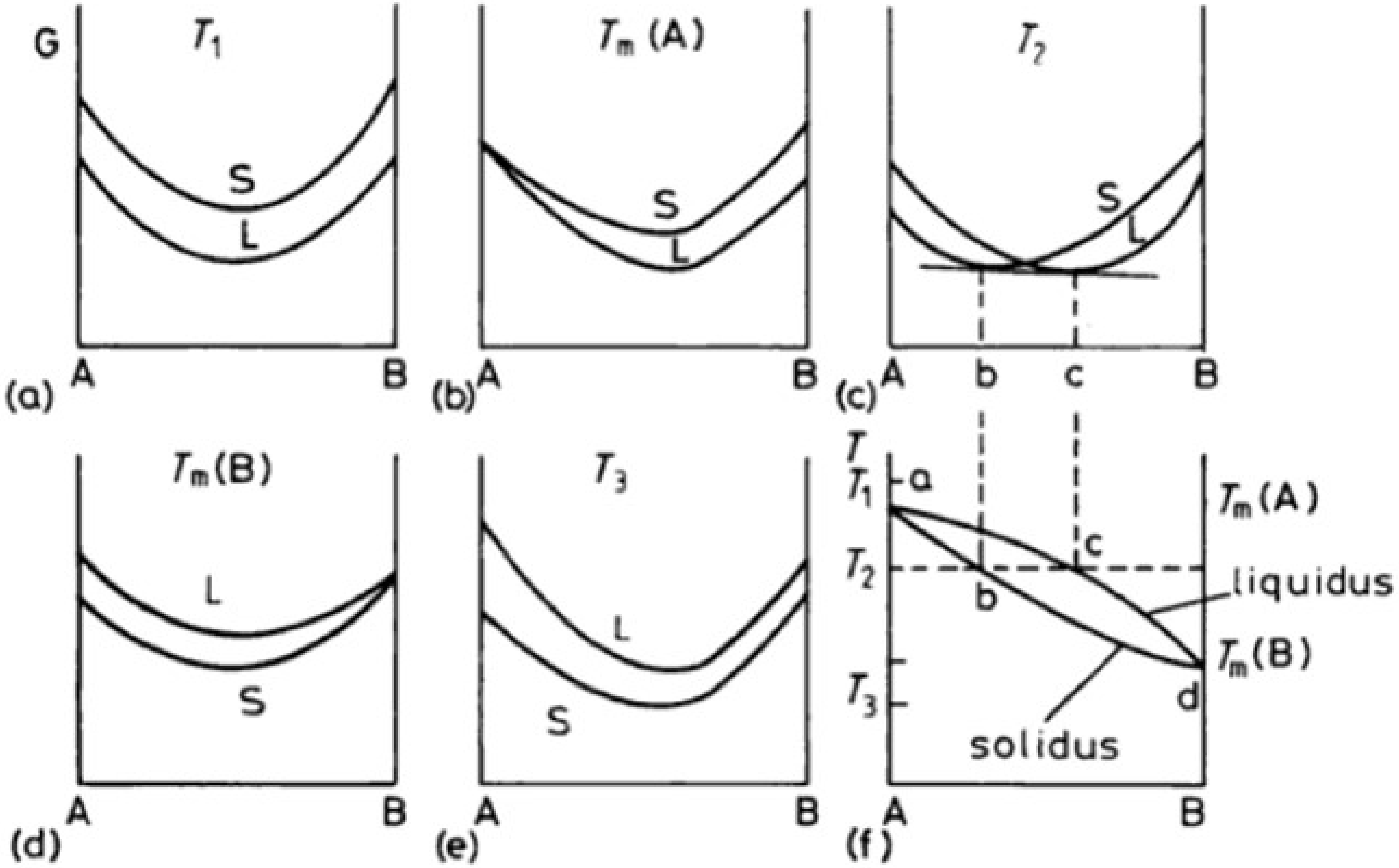
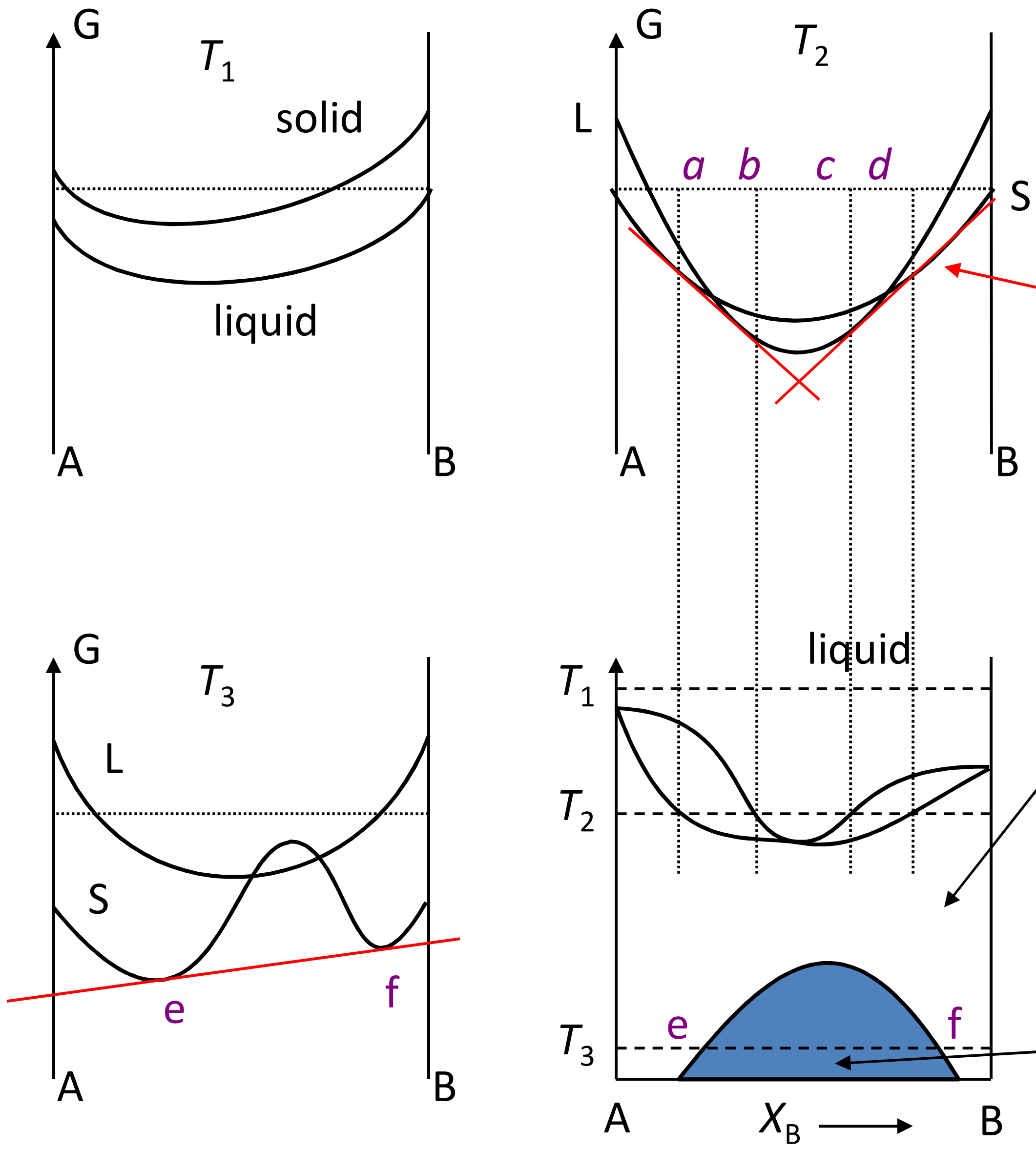


Fig. 1.29 The derivation of a simple phase diagram from the free energy curves for the liquid (L) and solid (S).

5. Binary phase diagrams : The Miscibility gap

$\Delta H_{MIX} > 0$

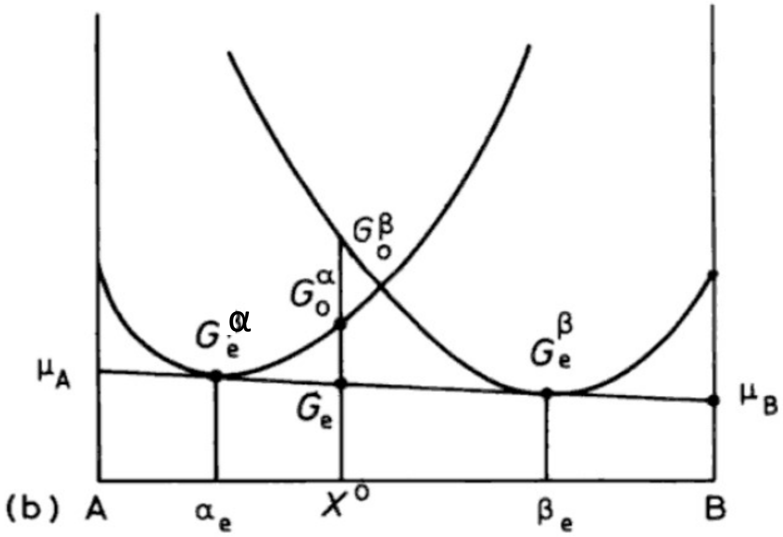


Common tangent

Single phase, mixed solid

2 phase: (A+δB) and (B+δA)
Compositions e and f ;
"The miscibility gap"

Equilibrium in heterogenous systems



Equilibrium in heterogeneous systems

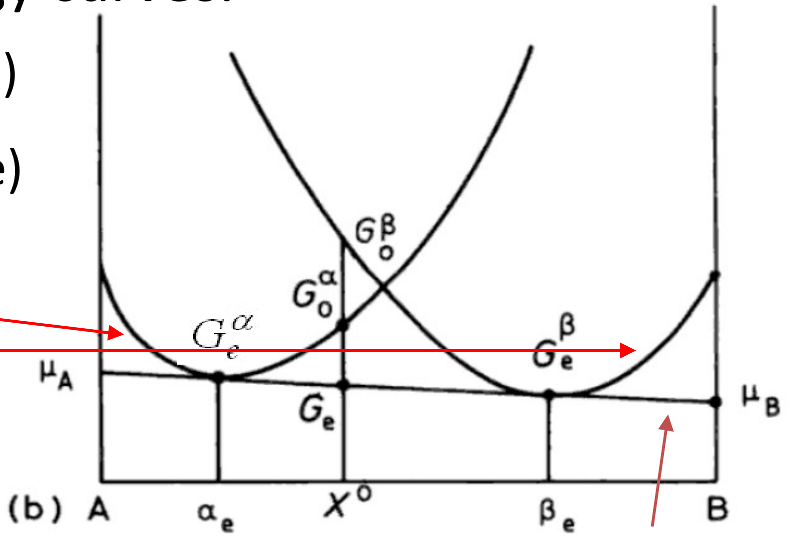
For systems with phase separation (α and β) of two stable structures (e.g. *fcc* and *bcc*), we must draw free energy curves.

G^α is the curve for A and B in *fcc* structure (α phase)

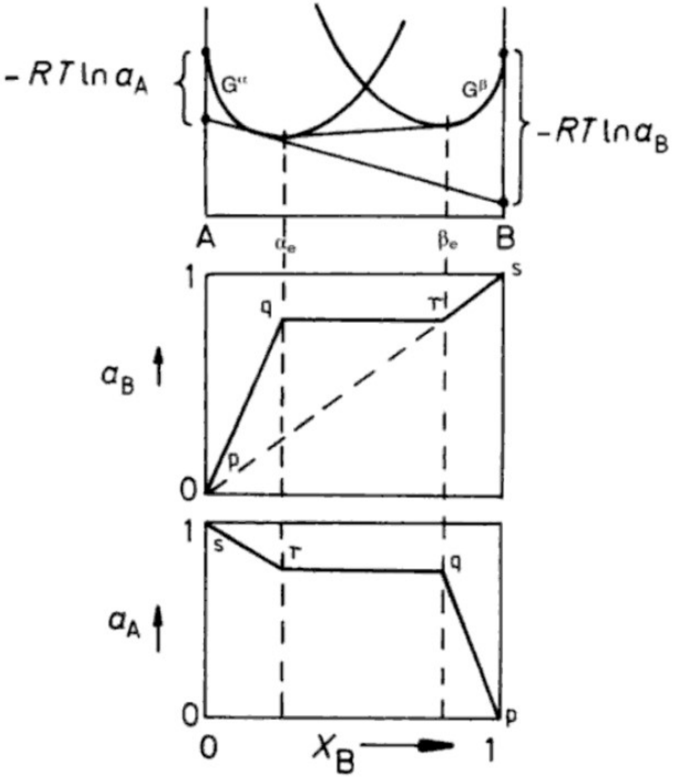
G^β is the curve for A and B in *bcc* structure (β phase)

For: $X^0 < \alpha_e$ → α phase only

$X^0 > \beta_e$ → β phase only



Common tangent



If $\beta_e < X^0 > \alpha_e$ then minimum free energy is G_e

And two phases are present. When two phases exist in equilibrium, the activities of the components must be equal in the two phases:

$$\boxed{a_A^\alpha = a_A^\beta} \qquad \boxed{a_B^\alpha = a_B^\beta}$$

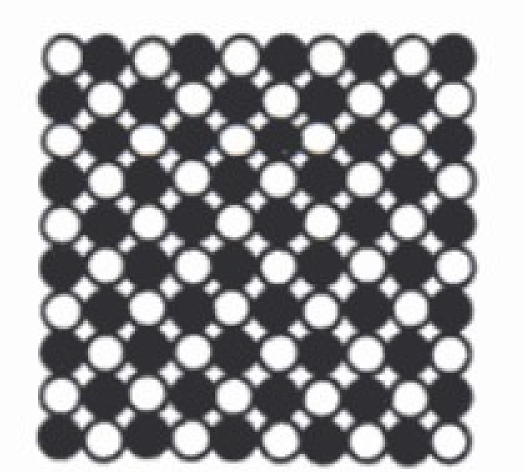
Binary (two component) systems : *Ordered phases*

Previous model gross oversimplification : need to consider size difference between A and B (strain effects) and type/strength of chemical bonding between A and B.

Systems with strong A-B bonds can form *Ordered* and/or *intermediate phases*

Ordered phases occur for (close to) integer ratios.

i.e. 1:1 or 3:1 mixtures.
But entropy of mixing is very small so increasing temperature can disorder the phase. At some critical temperature, long range order will disappear.

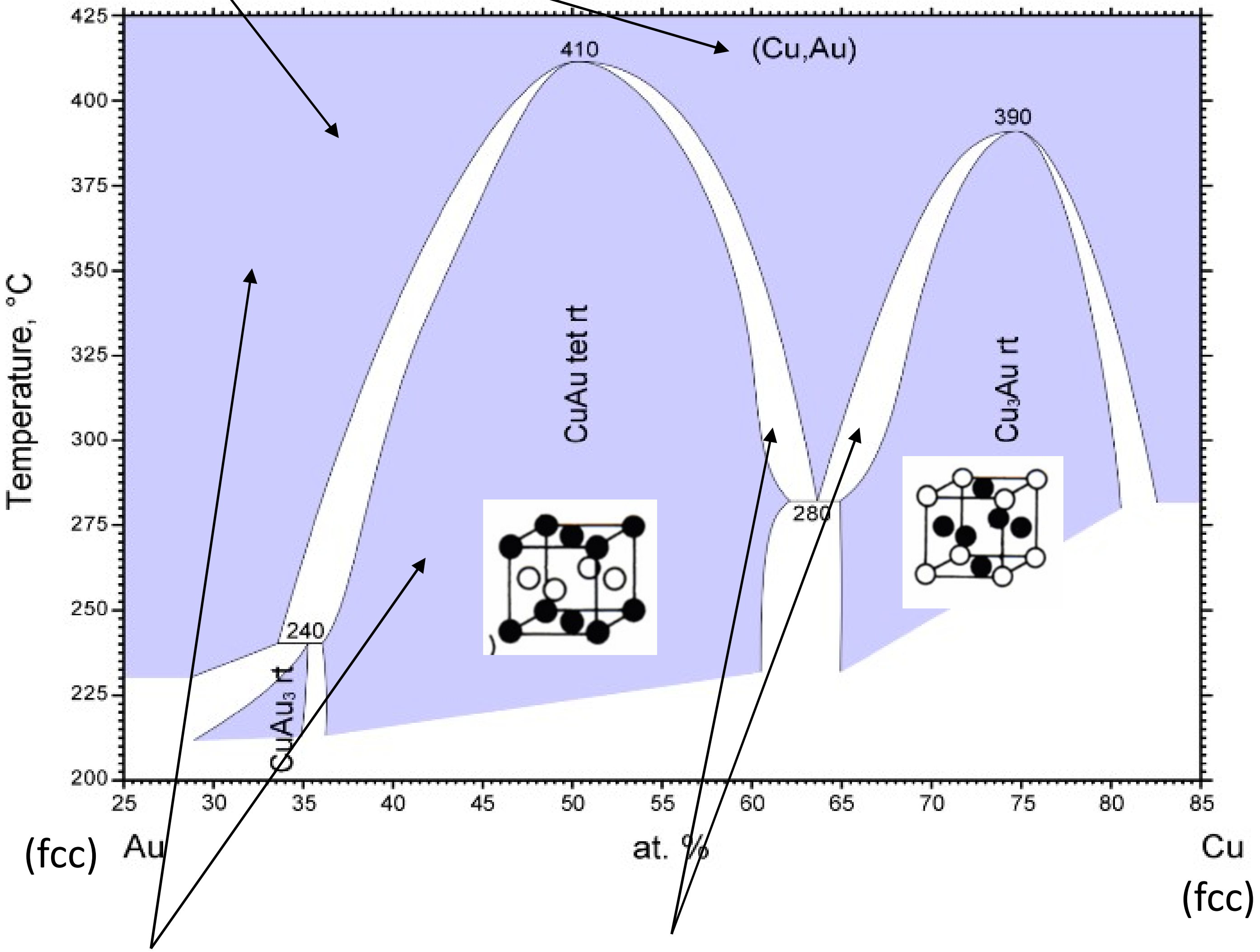


Ordered substitutional

Ordered structures can also tolerate deviations from stoichiometry. This gives the broad regions on the phase diagram

The Copper-Gold system

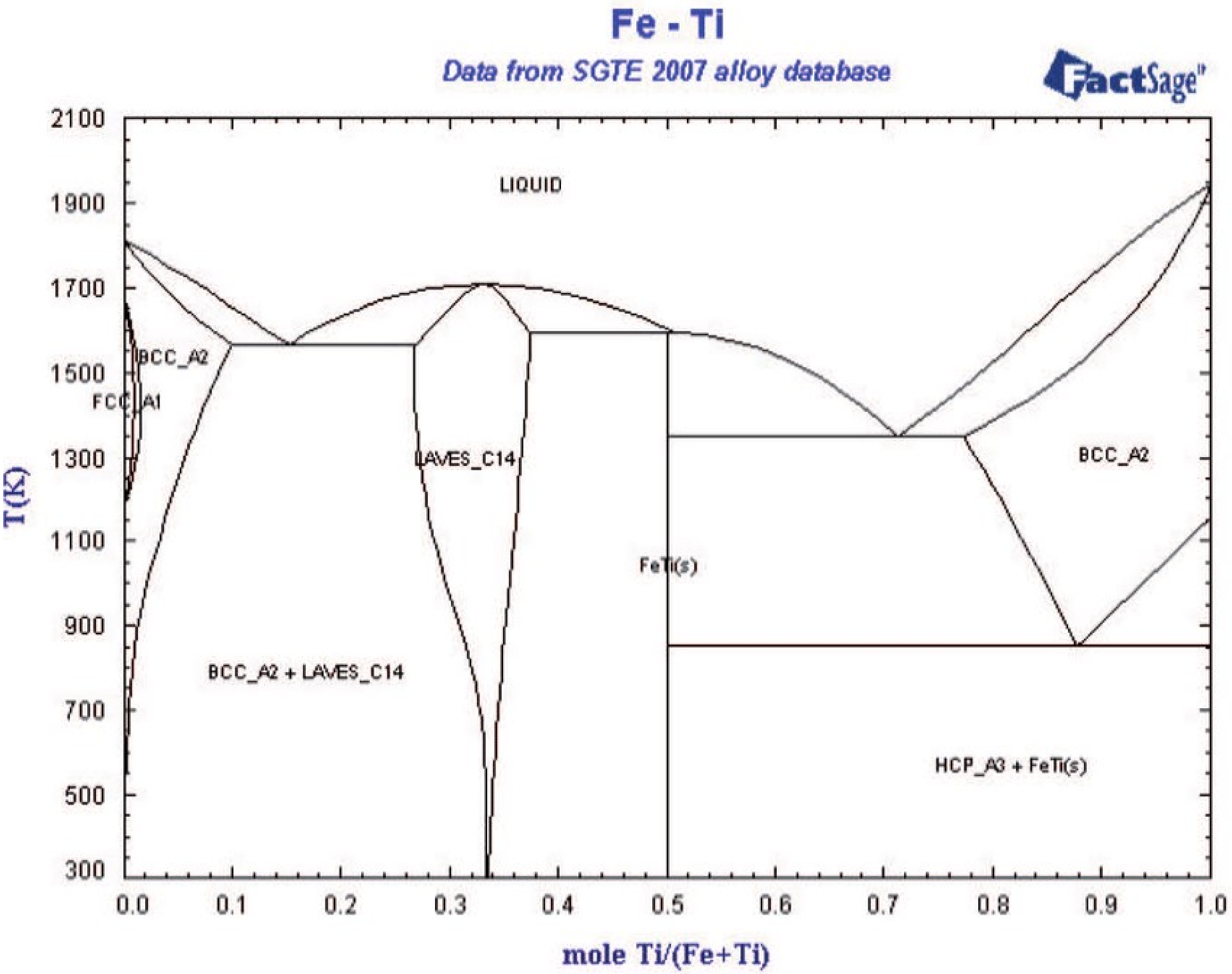
Random mixture



Single phases

Mixed phases

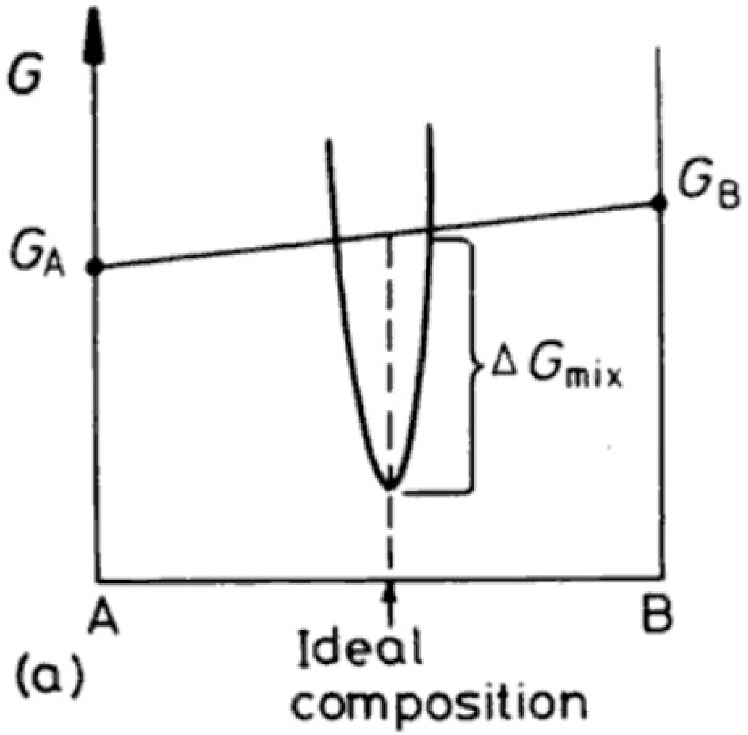
N.B. Always read the legend!!! (blue is not always 'singe phase')


Fe - Ti
Data from SGTE 2007 alloy database
FactSage
LIQUID
BCC_A2
FCC_A1
LAVES_C14
BCC_A2
FeTi(s)
BCC_A2 + LAVES_C14
HCP_A3 + FeTi(s)
T(K)
2100
1900
1700
1500
1300
1100
900
700
500
300
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
mole Ti/(Fe+Ti)

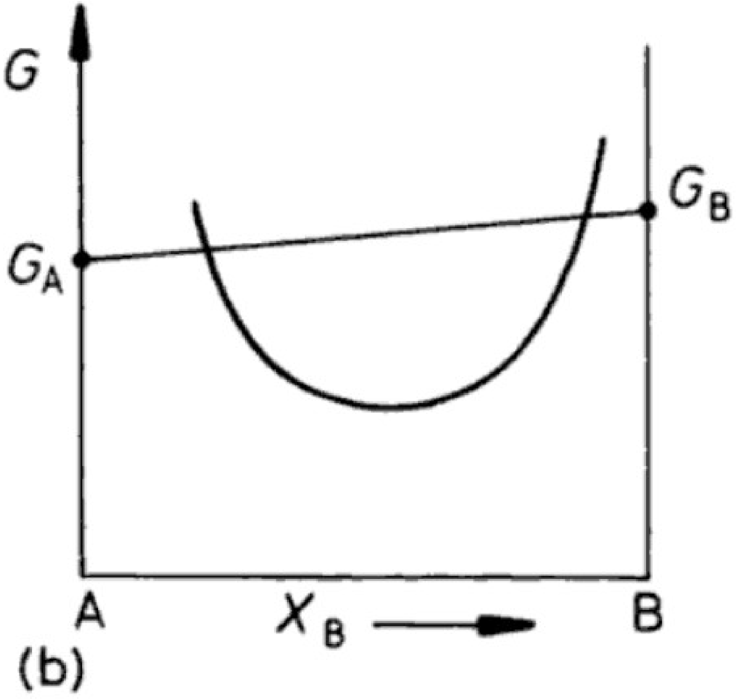
An *intermediate* phase is a mixture that has different structure to that of either component

Range of stability depends on structure and type of bonding (Ionic, metallic, covalent…)

Intermetallic phases are intermediate phase of integer stoichiometry (e.g. Ni_3Al) and congruent melting point



Narrow stability range



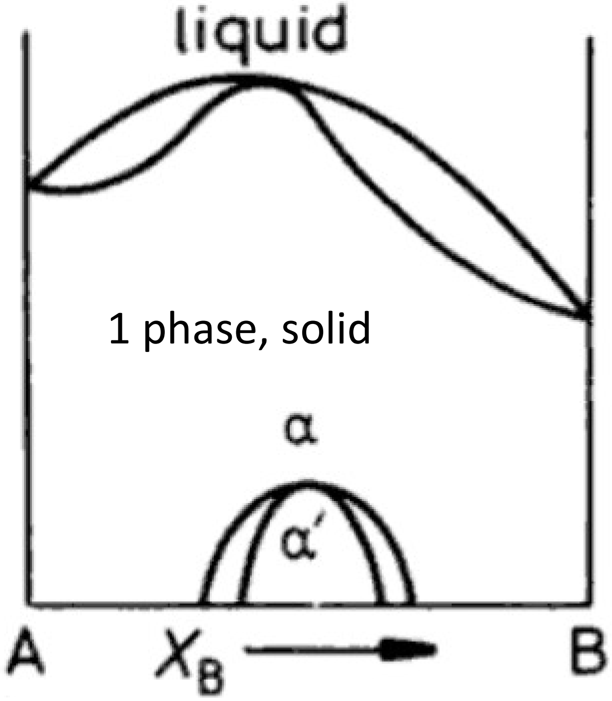
broad stability range

Binary phase diagrams : Ordered phases

$\Delta H_{MIX} < 0$

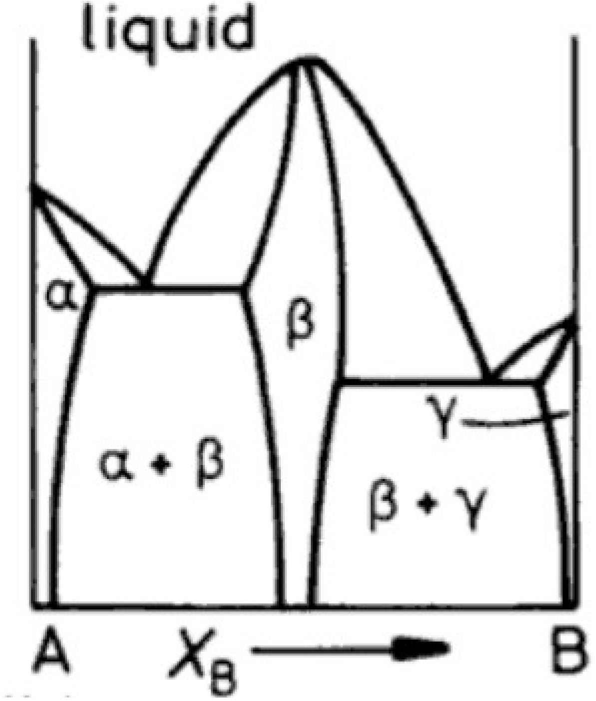
Peak in liquidus line : attraction between atoms

i.e. A and B attract



Weak attraction

Ordered phase α

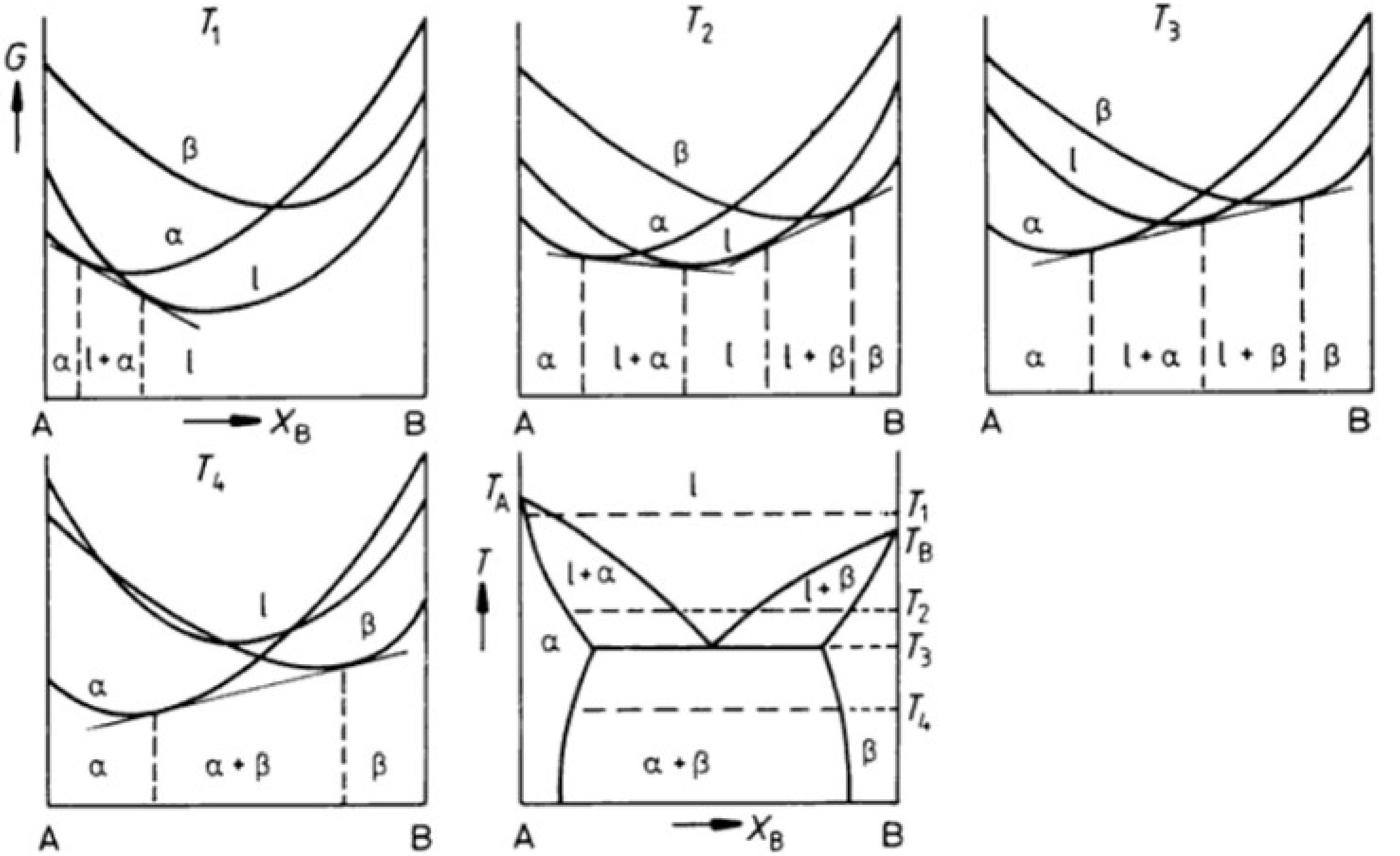


Strong attraction

Ordered β phase extends to liquid phase

Binary phase diagrams : Simple Eutectic systems

$\Delta H_{MIX} \neq 0$; A and B have different crystal structures



The Kinetic of Phase Transformation

G_1 and G_2 are initial and final state of energy, Then deriving force for transformation is,

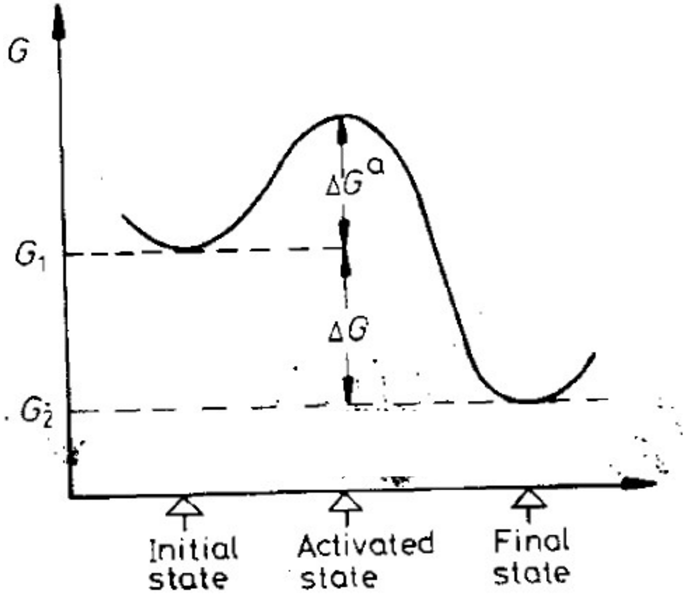
$$\Delta G = G_2 - G_1$$

According to kinetic theory, the probability of reaching the activated energy is,

$$\text{rate} \propto \exp\left(-\frac{\Delta G^a}{kT}\right)$$

ΔG^a is the activation energy, K is Boltzmann constant (R/Na), T is temperature .

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



Converting atomic to molar quantities, the equation can be written as,

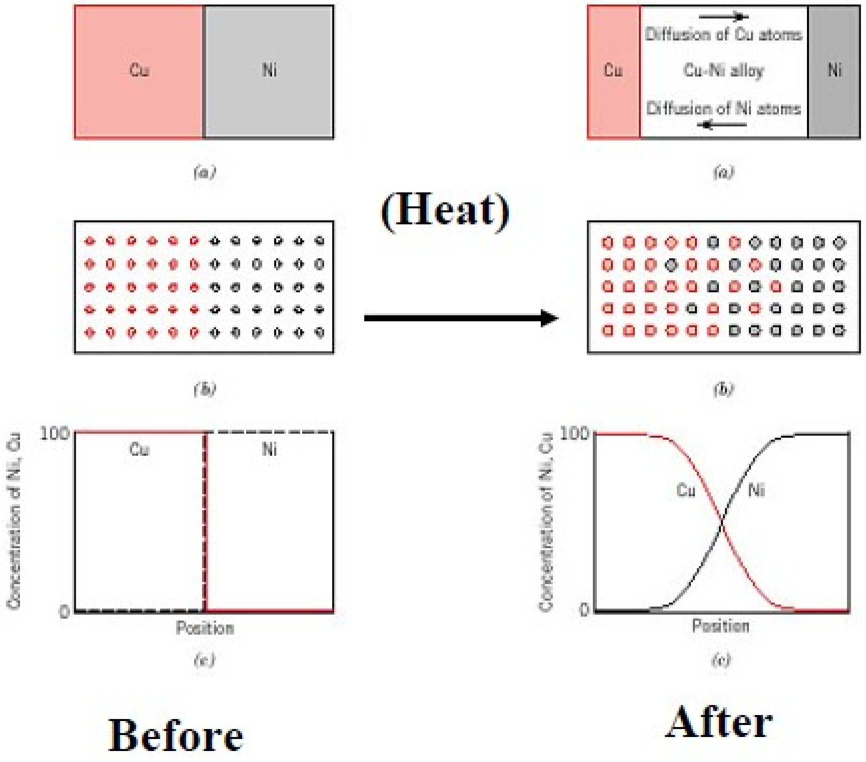
$$\text{rate} \propto \exp\left(-\frac{\Delta H^a}{RT}\right)$$

Diffusion

- **Review of Diffusion:**
  - Atomics Mechanisms of Diffusion
    - Interstitial diffusion
    - Substitutional Diffusion
      - Self-Diffusion
      - Vacancy Diffusion
      - Diffusion in Substitutional Alloys

Diffusion

- Diffusion is material transport by atomic motion
- Interdiffusion (or impurity diffusion) occurs in response to a concentration gradient
- Types of diffusion
  - Interstitial diffusion
  - Substitutional diffusion

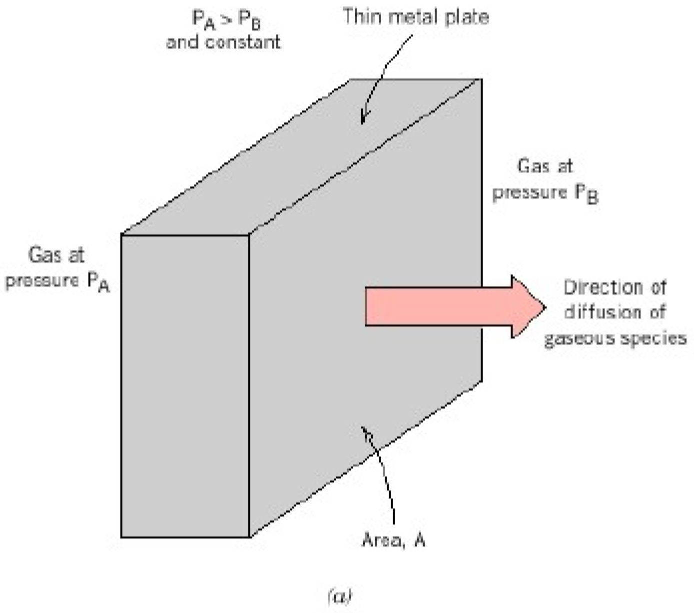


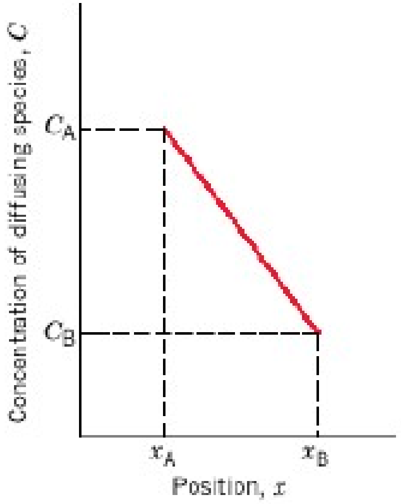
Kinetics - Terminology

- The flux is defined as number of atoms diffusing through unit area per unit time (atoms/m^2-second)
- The flux is also defined as mass of atoms diffusing through unit area per unit time (kg/m^2-second)

$$\mathbf{J = M / At \cong (1/A)\,(dM/dt)}\ (\mathrm{Kg\ m^{-2}\ s^{-1}})$$

- Steady state diffusion: The diffusion does not change with time.
- Concentration profile: Concentration of atoms/molecules of interest as function of position in the sample
- Concentration gradient: dC/dx (Kg/m^{-4}): the slope at a particular point on concentration profile





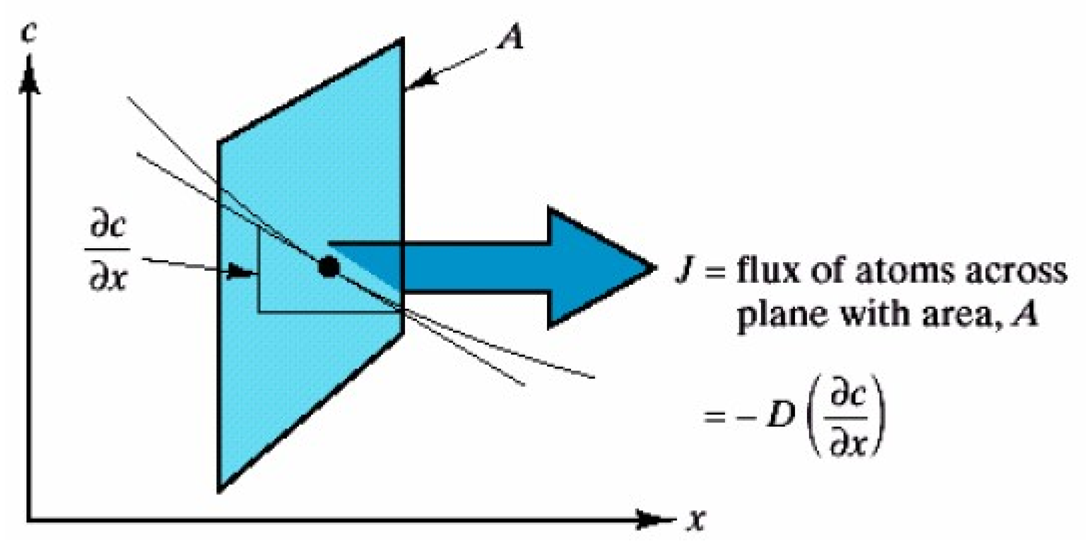
$$\frac{dC}{dx} \cong \frac{\Delta C}{\Delta x} = \frac{C_A - C_B}{x_A - x_B}$$

Fick's first law: The diffusion flux along direction x is proportional to the concentration gradient.

$$J = -D\frac{dC}{dx}$$

Where D is the diffusion coefficient.

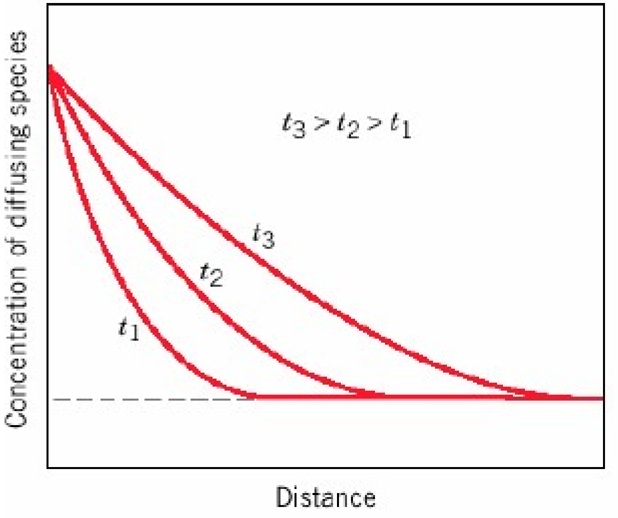
The concentration gradient is called as the driving force in diffusion. The minus sign in the equation means that diffusion is down the concentration gradient



- Nonsteady –state Diffusion: The concentration profile and the concentration gradient are changes with time. The change in concentration profile is described by Fick's second law.

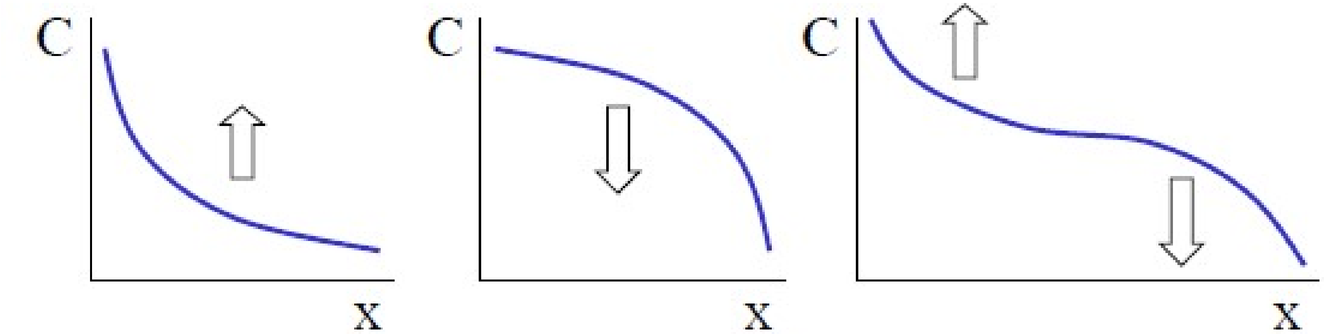
$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x}\left(D \frac{\partial C}{\partial x} \right) = D \frac{\partial^2 C}{\partial x^2}$$

- Concentration profile is function of time, C(x,t)



- Fick's second law relates the rate of change of composition with time to the curvature of the concentration profile.

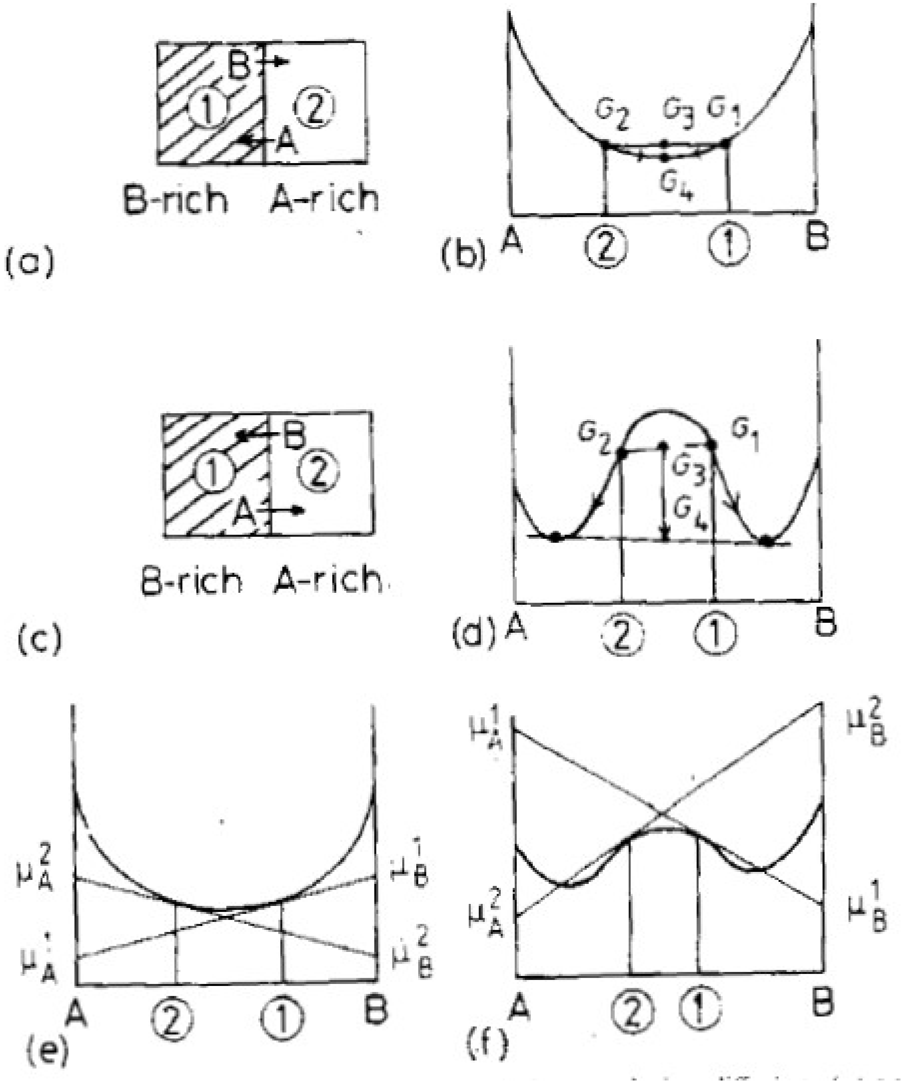
$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2}$$



- Concentration increases with time in those parts of the system where concentration profile has a positive curvature. And decreases where curvature is negative.

Diffusion

- Down the concentration gradient
- Up the concentration gradient

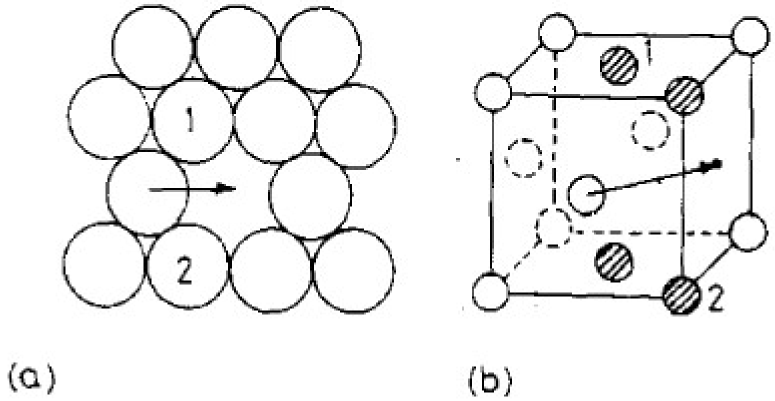


Atomic Mechanism of Diffusion

- Two types of mechanism involved in atoms diffusion
  - Substitutional atoms diffusion by vacancy mechanism
  - Interstitial atoms diffusion by forcing larger atoms.

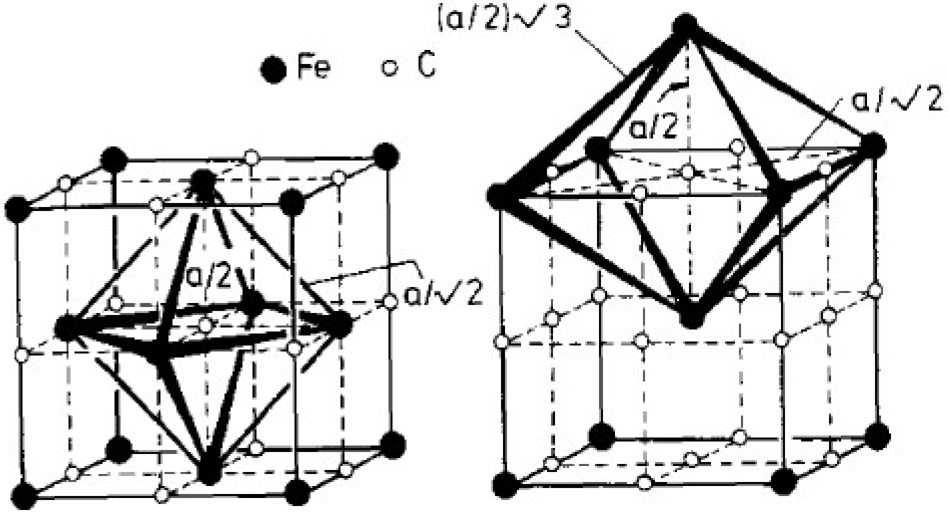
Substitutional Atom Diffusion

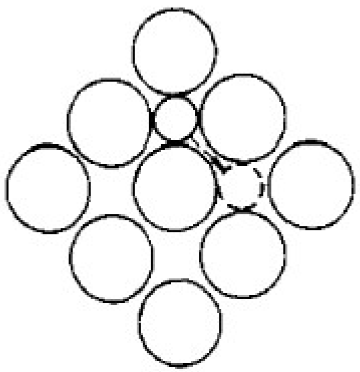
- At reasonable temperature, every atoms posses energy 3kT (Debye frequency) to vibrate from its position.
- Movement of a substitutional atom is limited by its neighbours and availability of vacancy next to it.
- Probability of jumping and concentration of vacancies are depends on temperature



Interstitial Atom Diffusion

- Always interstitial atom is surrounded by vacant sites
- Interstitial atoms jump to another site if thermal energy permits to overcome the strain energy barrier.





Interstitial Diffusion

Consider a dilute interstitial solid solution, where parent atoms are arranged in simple cubic lattice and solute B atoms fit in interstitial site.

If the plane 1 and 2 contains n_1 and n_2 B atoms, Γ_B number of interstitial atom jumps per second any of six vacant position. Then the flux,

$$J_B^1 = \frac{1}{6}\Gamma_B n_1$$

$$J_B^2 = \frac{1}{6}\Gamma_B n_2$$

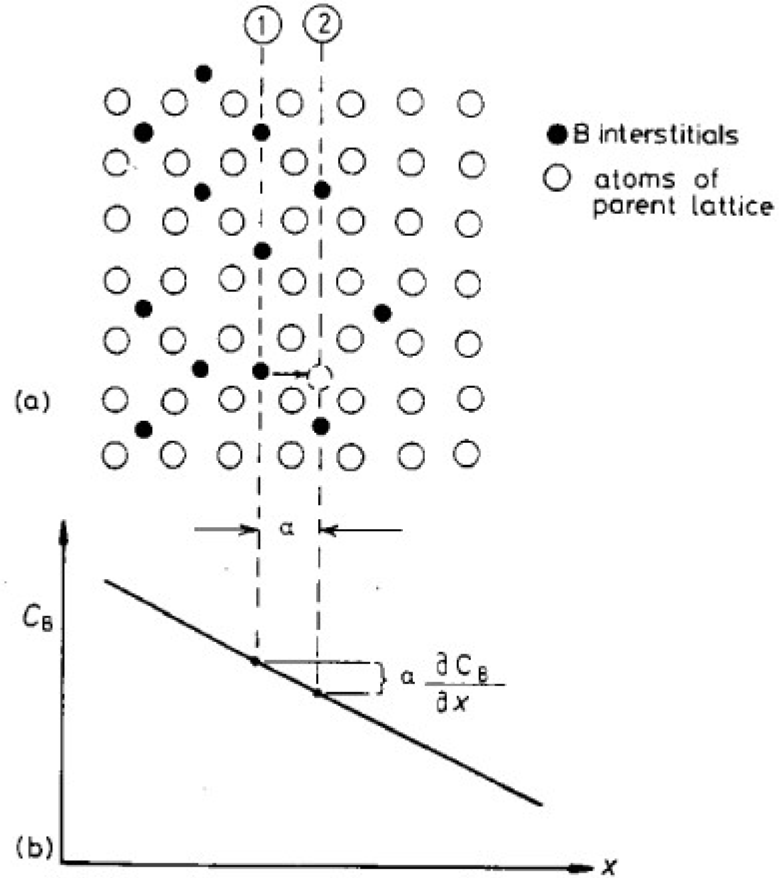


Fig. 2.5 Interstitial diffusion by random jumps in a concentration gradient.

Γ_B - Jump frequency per second

If $n_1 > n_2$, then

$$J_B = J_B^1 - J_B^2 = \frac{1}{6}\Gamma_B (n_1 - n_2)$$

Relating number of atoms in terms of concentration, the above equation written as

$$J_B = -\frac{1}{6}\Gamma_B \alpha^2 \frac{\partial C_B}{\partial x}$$

$$D_B = \frac{1}{6}\Gamma_B \alpha^2$$

Diffusion coefficient

$$J_B = -D_B \frac{\partial C_B}{\partial x}$$

Fick’s law of diffusion

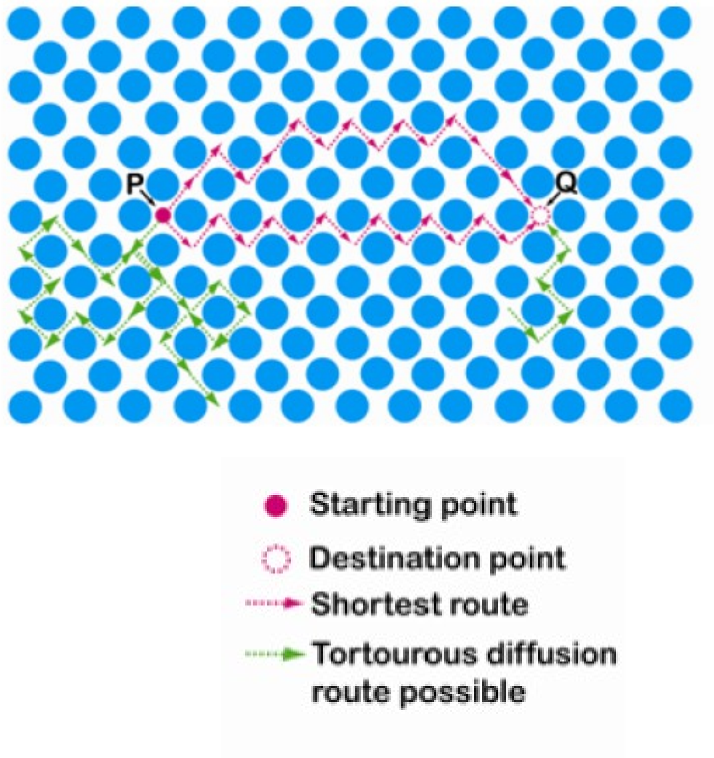
Random Walk

- Random motion of the atoms is random walk.
- The direction of new jump is independent of previous jump in random walk.
- In time t, the average distance moved from the original position is

$$r = \alpha\sqrt{\Gamma t}$$

Substituting the value of Γ,

$$r = 2.4\sqrt{Dt}$$



Effect of Temperature – Thermal Activation

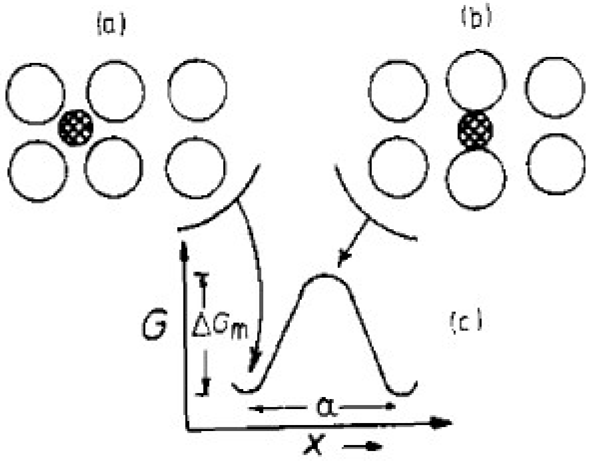
- To jump the atom from one position to another position, it need energy which is called as activation energy ΔG_m (m for migration)
- When an atom surrounded by *z* sites and vibrating with mean frequency ν in 3D space, then jump frequency is

$$\Gamma_B = z\nu \exp\left(\frac{-\Delta G_m}{RT}\right)$$

w.k.t., $\Delta G_m = \Delta H_m - T\Delta S_m$

Therefore,

$$D_B = \left[\frac{1}{6}\alpha^2 z\nu \exp\frac{\Delta S_m}{R}\right]\exp\frac{-\Delta H_m}{RT}$$



$$D_B = \left[\frac{1}{6}\alpha^2 z\nu \exp\frac{\Delta S_m}{R}\right]\exp\frac{-\Delta H_m}{RT}$$

The equation is simplified as Arrhenius-type,

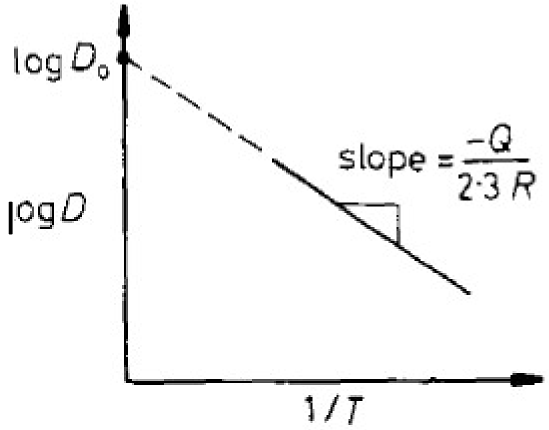
$$D_B = D_{B0}\exp\left(\frac{-Q_{ID}}{RT}\right)$$

Where,

$$D_B = \frac{1}{6}\alpha^2 z\nu \exp\frac{\Delta S_m}{R} \qquad Q_{ID} = \Delta H_m$$

The above equation can be expressed as

$$\log D = \log D_o - \frac{Q_{ID}}{2.3R}\left(\frac{1}{T}\right)$$



Substitutional Diffusion

- Self Diffusion
- Vacancy Diffusion
- Diffusion in Subtitutional Alloys

Self Diffusion

- When diffusion occurs without any presence of driving force, it is called self diffusion.
- Atoms vibrate at their positions and because of some violent jumps, it can cross the activation barrier to make the jump successful.
- Indicates that when a pure metal is kept at elevated temperature jump of atoms is always happening.
- In low melting point metals, like In or Sn, even at room temperature, atoms exchange their position.

The frequency of successful jump of atoms per second is,

$$\Gamma_B = z\nu X_\nu \exp\left(\frac{-\Delta G_m}{RT}\right)$$

Where X_ν is the probability of adjacent site is vacant.

If the vacancies are in thermodynamic equilibrium, then

$$X_\nu = X_\nu^e$$

$$X_\nu^e = \exp\left(\frac{-\Delta G_\nu}{RT}\right)$$

Therefore,

$$D_A = \left[\frac{1}{6}\alpha^2 z\nu\right]\exp\frac{-(\Delta G_m + \Delta G_\nu)}{RT}$$

$$D_A = \left[\frac{1}{6}\alpha^2 z\nu\exp\frac{(\Delta S_m + \Delta S_\nu)}{RT}\right]\exp\frac{-(\Delta H_m + \Delta H_\nu)}{RT}$$

$$D_A = \left[\frac{1}{6}\alpha^2 z \nu \exp\frac{\left(\Delta S_m + \Delta S_\nu\right)}{RT}\right]\exp\frac{-\left(\Delta H_m + \Delta H_\nu\right)}{RT}$$

$$D_A = D_o \exp\frac{-Q_{SD}}{RT}$$

Therefore

$$D_O = \frac{1}{6}\alpha^2 z \nu \exp\frac{\left(\Delta S_m + \Delta S_\nu\right)}{RT}$$

and

$$Q_{SD} = \Delta H_m + \Delta H_\nu$$

Vacancy Diffusion

The jumping of atoms into vacant sites can equal to jumping of vacancies onto atom sites.

If excess vacancies are introduced into the lattice, diffusion vacancies depends on jump frequency.

The vacancy diffusion can be considered as,

$$D_v = \frac{1}{6}\Gamma_B \alpha^2 \qquad D_v = \left[\frac{1}{6}\alpha^2 z \nu \exp\frac{\Delta S_m}{R}\right]\exp\frac{-\Delta H_m}{RT}$$

Comparing self diffusion equation,

$$D_v = D_A / X_v^e$$

Diffusion in Substitutional Alloys

- The rate at which solvent (A) and solute (B) atoms move into vacant site is not equal.
- Solvent and solute atom has own intrinsic diffusion coefficient D_A and D_B.
- Then D_A and D_B can be defined as,

$$J_A = -D_A \frac{\partial C_A}{\partial x}$$

$$J_B = -D_B \frac{\partial C_B}{\partial x}$$

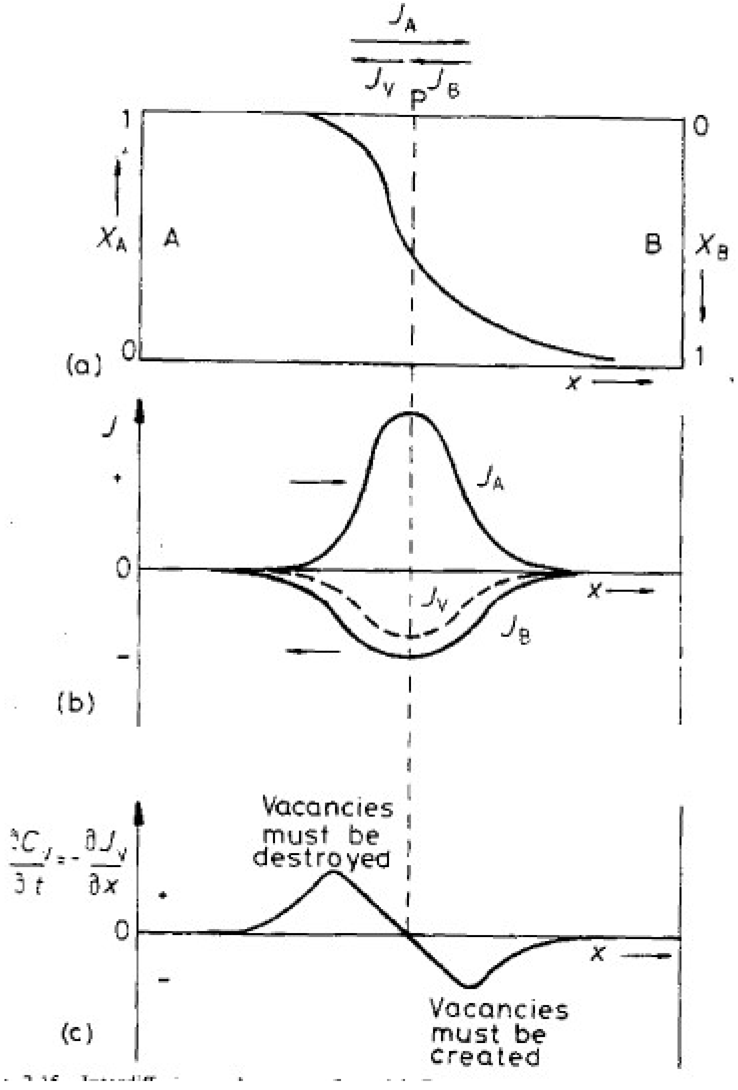
- Consider A and B atoms in a diffusion couple at high temperature. Then the concentration profile can be plotted as

Assume, total number of atoms per unit volume is a constant Co independent of composition, then

$$C_0 = C_A + C_0$$

and

$$\frac{\partial C_A}{\partial x} = \frac{\partial C_B}{\partial x}$$



The concentration gradients driving the diffusion of A and B atoms are equal but opposite direction. Then the fluxes of A and B relative to the lattice.

$$J_A = -D_A \frac{\partial C_A}{\partial x} \qquad J_B = D_B \frac{\partial C_B}{\partial x}$$

Consider $D_A > D_B$ i.e. $J_A > J_B$.

The variation of flux J_v,

$$J_v = -(D_A - D_B)\frac{\partial C_A}{\partial x}$$

Inter-diffusion coefficient $\overline{D}$,

$$\overline{D} = X_A D_A + X_B D_B$$

Then Fick's law,

$$\frac{dC}{dt} = \frac{\partial}{\partial x}\left(\overline{D}\,\frac{dC_A}{dx}\right)$$