# Introduction to CALPHAD

# CALPHAD

- CALculation of PHAse Diagrams (CALPHAD)
- Employs classical thermodynamics
- Many applications: Phase equilibrium, thermochemistry, chemical equilibrium, kinetics, mcirostructure simulation, etc.
- Appropriately renames as Computational Thermodynamics

- Began as a means to calculate phase diagrams
- Why do we need phase diagrams?
  - Road map for materials design
  - Guideline for materials processing
  - Helps to understand performance related issues ...
- Engineering Materials – multi-component
  - Phase diagrams: difficult to obtain by experiments alone
  - Too many to be determined.
- If we consider 10 elements (n=10), then

$$N = \frac{n!}{m!(n-m)!}$$

n=10 m=2 then require 45 binaries,

n=10 m=3 then require 120 ternaries,

n=10 m=4 then require 210 quaternaries are required.

- CALPHAD: a reliable shortcut to generate m-c phase diagrams

# Chronology

- Meijiering (1957): Calculated Cr-Cu-Ni phase diagram
- Kaufman (1969) proposed the acronmy CALPHAD
- Kaufman & Bernstein (1970): Computer Calculations of Phase diagrams
- Hillert & Staffanson (1971): Sublattice formalism
- CALPHAD Annual Conference: 1973
- Eriksson (1975): SOLGASMIX program
- Pelton (1976): F*A*C*T project started
- Lukas (1977): Lukas program
- CALPHAD Journal: 1977
- Agren, Hillert & Sundman (1981): Compound Energy Formalism
- First version of Thermo-Calc: 1981

- First version of ChemSage: 1987
- Dinsdale (1991) SGTE data for pure elements
- Saunders & Miodownik (1998): CALPHAD: A comprehensive guide
- First version of FactSage (2001)
- Lukas, Fries & Sundman (2007): Computational Thermodynamics: The Calphad method

# CALPHAD Vs. Ab initio Methods

**Calphad method**

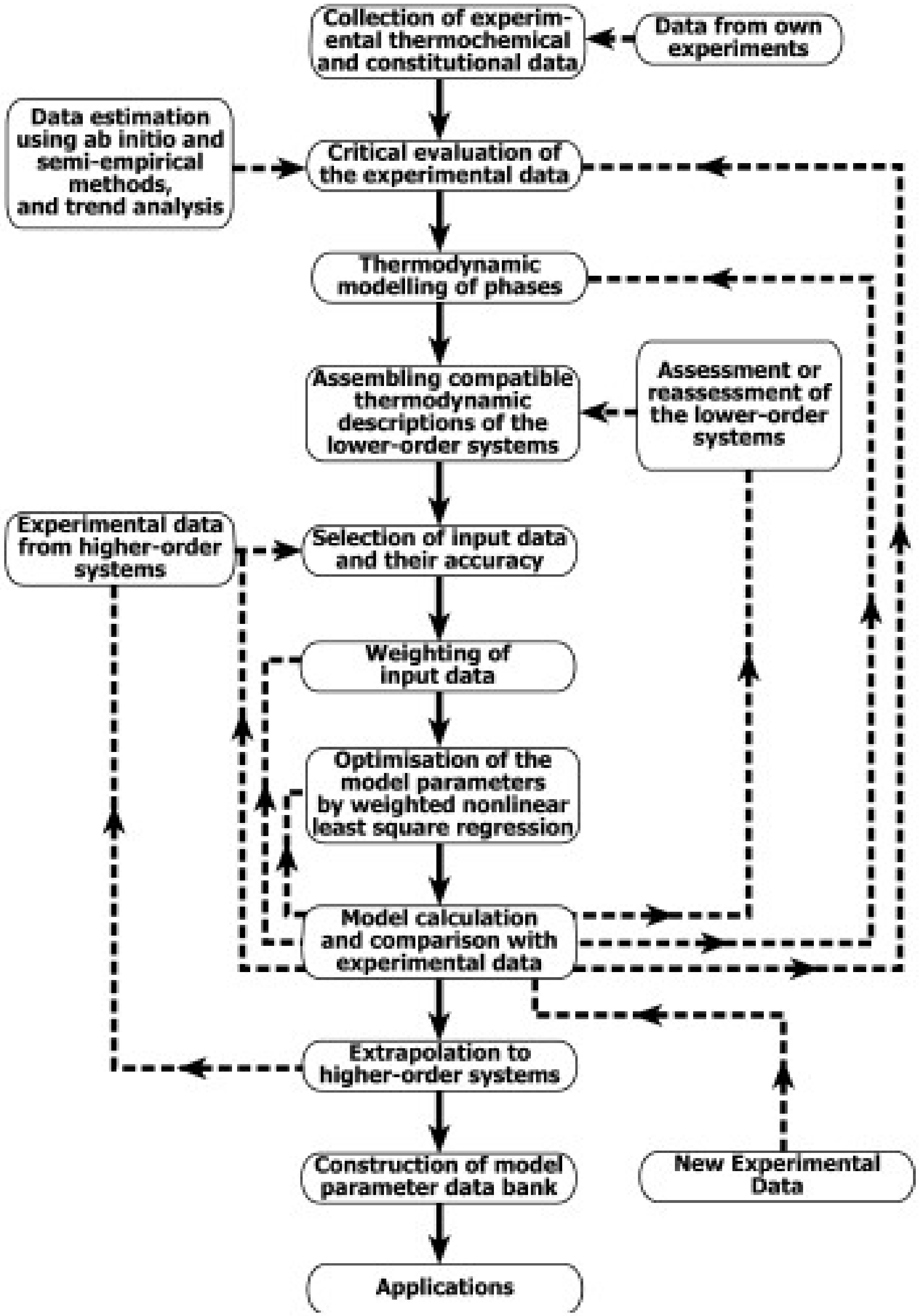
- Classical thermodynamics based
- Phenomenological Gibbs energy models
- Has many adjustable model parameters
- Computationally simple
- Can handle multicomponent-multiphase systems
- Quantitative results, not predictive

**Ab initio methods**

- Quantum thermodynamics
- Few/No adjustable parameters
- Can handle only solid phases
- Computationally tedious, even for binaries
- Multicomponent systems are difficult/impossible
- Results are often qualitative, but predictive

Current trend: CALPHAD assisted by ab initio methods

# CALPHAD: Flow chart



# CALPHAD Method

- Gibbs energy model parameters are estimated through a computer assisted modelling procedure (Thermodynamic optimization, Themodynamic assessment)
- Uses experimental thermochemical and constitutional data as input
- Extrapolative (unlike ab initio methods)

  Unary →Binary→Ternary→Quaternary→Multi-Component
- Experimental data beyond ternary are generally not necessary
- High quality experimental data in lower-order systems are a key to reliable multicomponent thermodynamic descriptions.

# Computer Programs

- Free
  - Lukas program
  - SOLGASMIX
  - Themo-Calc for academic use
- Commercial
  - Thermo-Calc, FactSage, MTDATA, Pandat, CatCalc
- Application programs
  - DICTRA: Diffusion controlled transformation
  - MICRESS: Microstructure simulation using phase field
  - TC-Prisma, MatCalc: Precipitation simulation

# $1^{st}$ law of thermodynamics

It is the application of the conservation of energy principle to heat and thermodynamic process.

Definition: "The internal energy of an isolated system is constant."

$$\Delta U = Q - W$$

"The change in internal energy of a system is equal to the heat (Q) added to the system minus the work done by the system (W)"

$$\Delta U = Q - W$$

# $1^{st}$ law of thermodynamics

$$\Delta U = Q - W$$

Note: Thermodynamic sign conventions for heat and work:

| Process | Convention |
|---|---|
| Heat added to the system | $Q>0$ |
| Heat removed from the system | $Q<0$ |
| Work done by the system | $W<0$ |
| Work done on the system | $W>0$ |

- For closed system, the change is energy is equal to the energy that passes through its boundary as heat or work.
- For isolated system, $Q = W$ $\Delta U = 0$

## Expansion Work of an Ideal Gas

The gas confined in a cylinder with frictionless piston. Sudden expansion of the gas, undergoes at constant temperature. The work done is

$$w = -\int_{V_1}^{V_2} P dV$$

$$\boxed{w = -P(V_2 - V_1)}$$

# Enthalpy

"Total heat content of the system is called as enthalpy."

$$H=E+PV$$

"The total heat content of a system at constant pressure is equivalent to the internal energy E plus the PV energy"

$$H=E+PV$$

*Enthalpy is a state function*
*Enthalpy is an extensive property*
*Molar enthalpy is a specific intensive property*

If Δ *H be the difference of enthalpy of a system in the final state (H2) and that in the initial state* (*H1*),

$$\Delta H = H2 - H1$$

*Where H1= E1 + P1V1 and H2= E2 + P2V2*

Substituting the values of *H2 and H1 in the above equation,*

$$\Delta H = (E2 + P2V2) - (E1 + P1V1)$$

$$= (E2 - E1) + (P2V2 - P1V1)$$

$$= \Delta E + + (P2V2 - P1V1)$$

If *P is constant while the gas is expanding, we can write*

$$\Delta H = \Delta E + P\Delta V$$

$$\Delta H = \Delta E + w \ (w = \text{work})$$

According to the First Law, $\Delta E = q - w$

where *q = heat transferred*

$$\Delta H = q$$

$$\Delta H = q_p$$

where subscript *p means constant pressure.*

Thus Δ*H can be measured by measuring the heat of a process occurring at constant pressure.*

If *ΔH be the difference of enthalpy of a system in the final state (H2) and that in the initial state* (*H1),*

$$\Delta H = H2 - H1$$

*ΔH = +ve then H2 > H1 and the process is endothermic.*

*ΔH = -ve then H1 > H2 and the process is exothermic.*

*Unit: Joule or calorie*

Relation Between *ΔH and ΔE:*

*If n1 moles of gases before reaction, and n2 moles of gases after it. Assuming* ideal gas behaviour at isothermal condition, then e

$$PV_2 = n_2RT$$

$$P\,V_1 = n_1RT$$

$$\therefore P\,(V_2 - V_1) = (n_2 - n_1)\,RT$$

$$\text{or } P\Delta V = \Delta nRT$$

Then, $\Delta H = \Delta E + \Delta nRT$

**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,

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

Heat and heat capacity are path function.

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 at constant volume.

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

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 at constant pressure.

# Relation between $C_P$ and $C_V$

w.k.t. ,

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

By definition, *H=E+PV*

*H=E+nRT*

Differentiate the above equation w.r.t. to T,

$$\frac{dH}{dT} = \frac{dE}{dT} + nR$$

The above equation can be written as,

$$\boxed{C_P = C_V + nR}$$

NOTE: $C_P$ is always greater than $C_V$.

# ΔE expression in terms of heat capacity

For one mole of ideal gas,

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

The above equation can be written as,

$$dE = C_V dT$$

$$dE = C_V\left(T_2 - T_1\right)$$

For n moles,

$$\boxed{dE = nC_V\left(T_2 - T_1\right)}$$

# ΔH expression in terms of heat capacity

For one mole of ideal gas,

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

The above equation can be written as,

$$dH = C_P dT$$

$$dH = C_P \left(T_2 - T_1\right)$$

For  n moles,

$$\boxed{dH = nC_P \left(T_2 - T_1\right)}$$

Heat capacity (C) is expressed by an empirical formula (polynomial equation form),

$$\boxed{C = a + bT + cT^{-1} + dT^{-2}}$$

a, b, c and d are co-relation constant

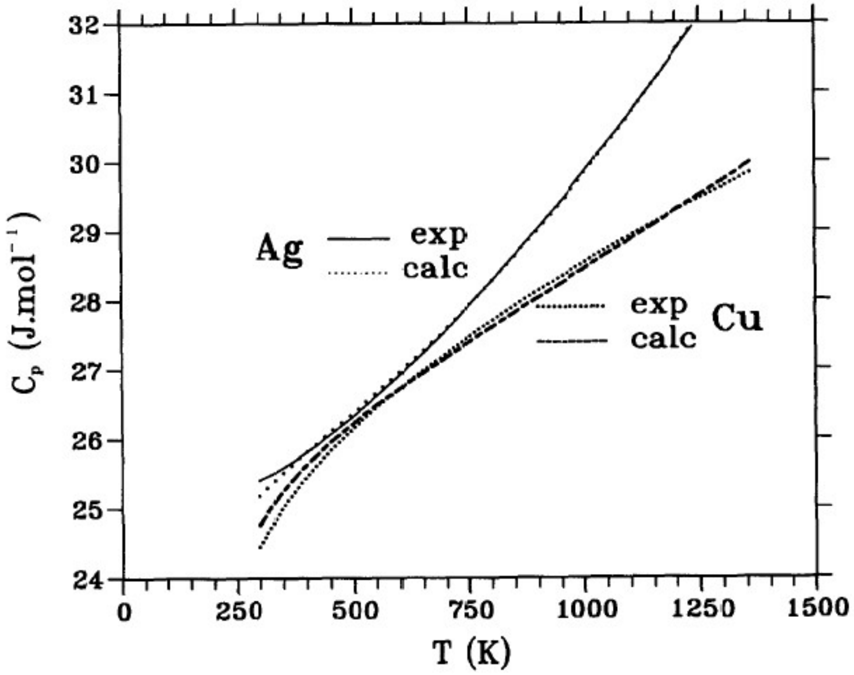


Fig.1 : Calculated and experimental Cp for fcc Ag and Cu

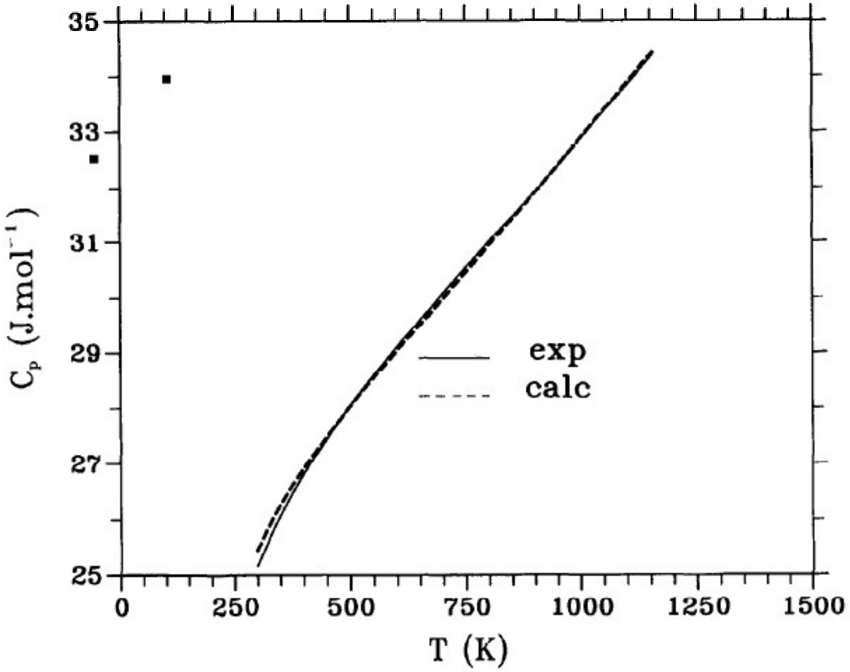


Fig.2 : Calculated and experimental Cp for hcp Ti

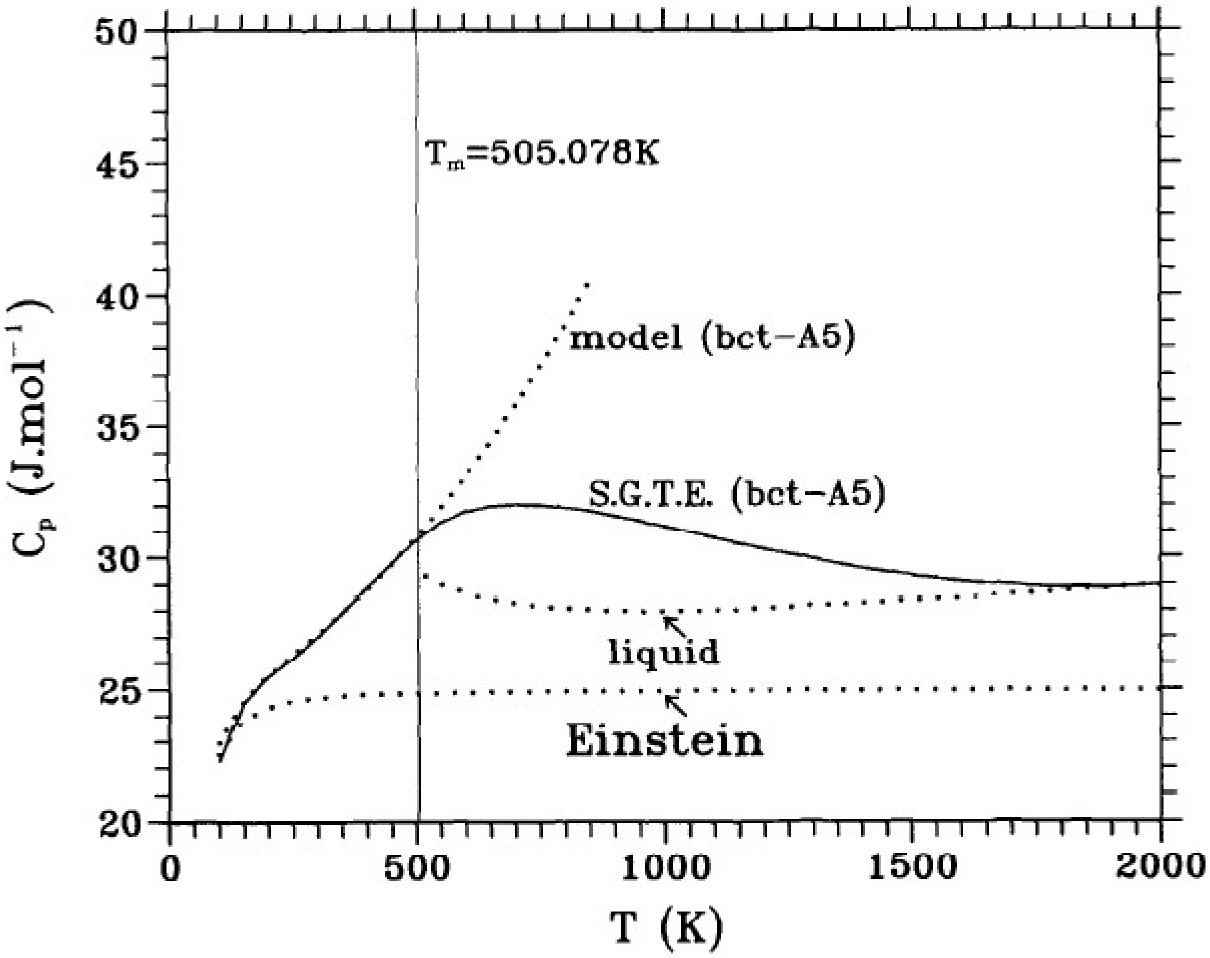


Fig. 3: Calculated and experimental $C_p$ for bct−A5 and liquid Sn.

The change in enthalpy, entropy and Gibbs energy is expressed as,

$$\boxed{\Delta H_T = \int_{298.15}^{T} \Delta C_p dT}$$

$$\boxed{\Delta S_T = \int_{298.15}^{T} \frac{\Delta C_p}{T} dT}$$

$$\boxed{\Delta G_T = \Delta H - T\Delta S}$$

# Gibbs Energy as a Function of Temperature

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

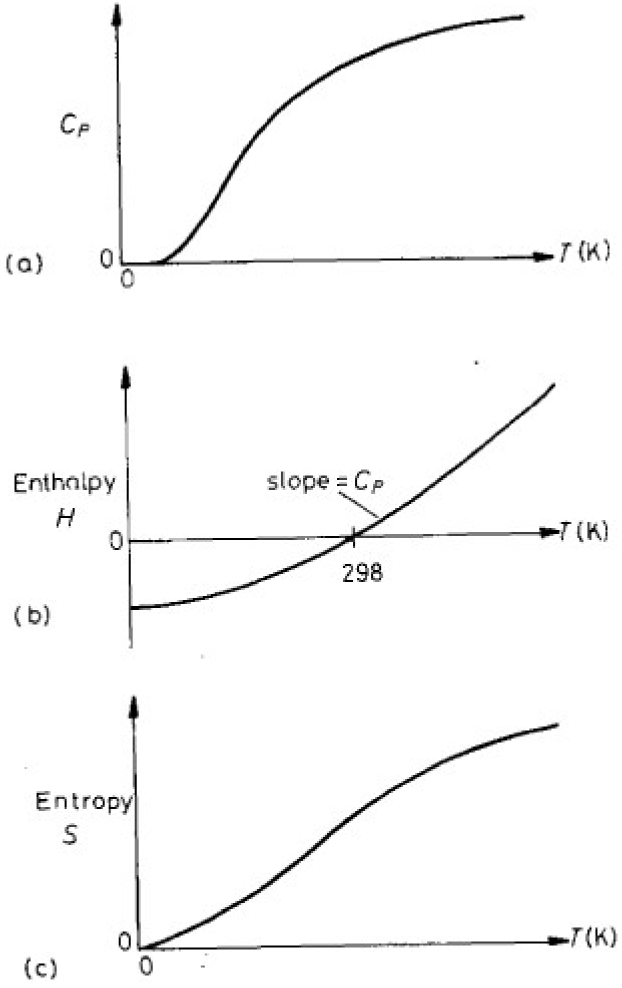
$$\boxed{\left(\frac{dH}{dT}\right)_P = C_P}$$

- 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,

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



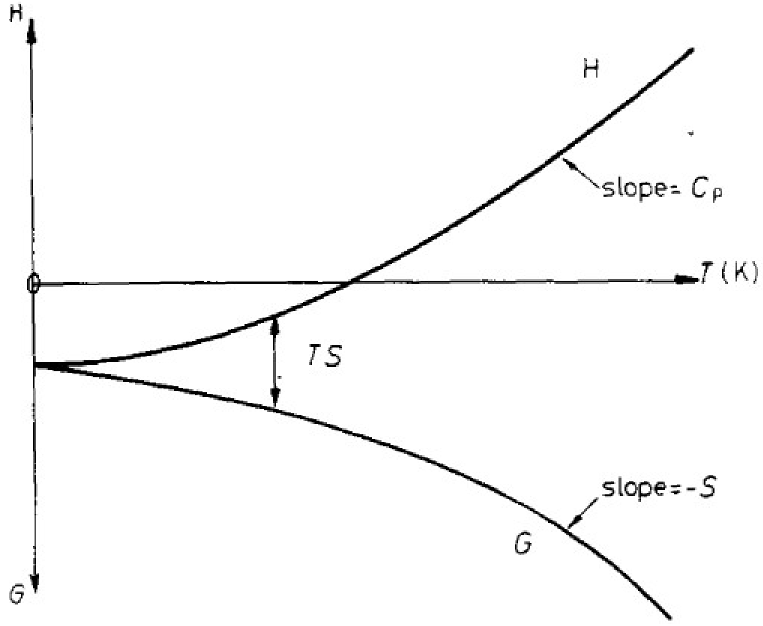
When temperature and pressure vary the changes in G can be obtained by,

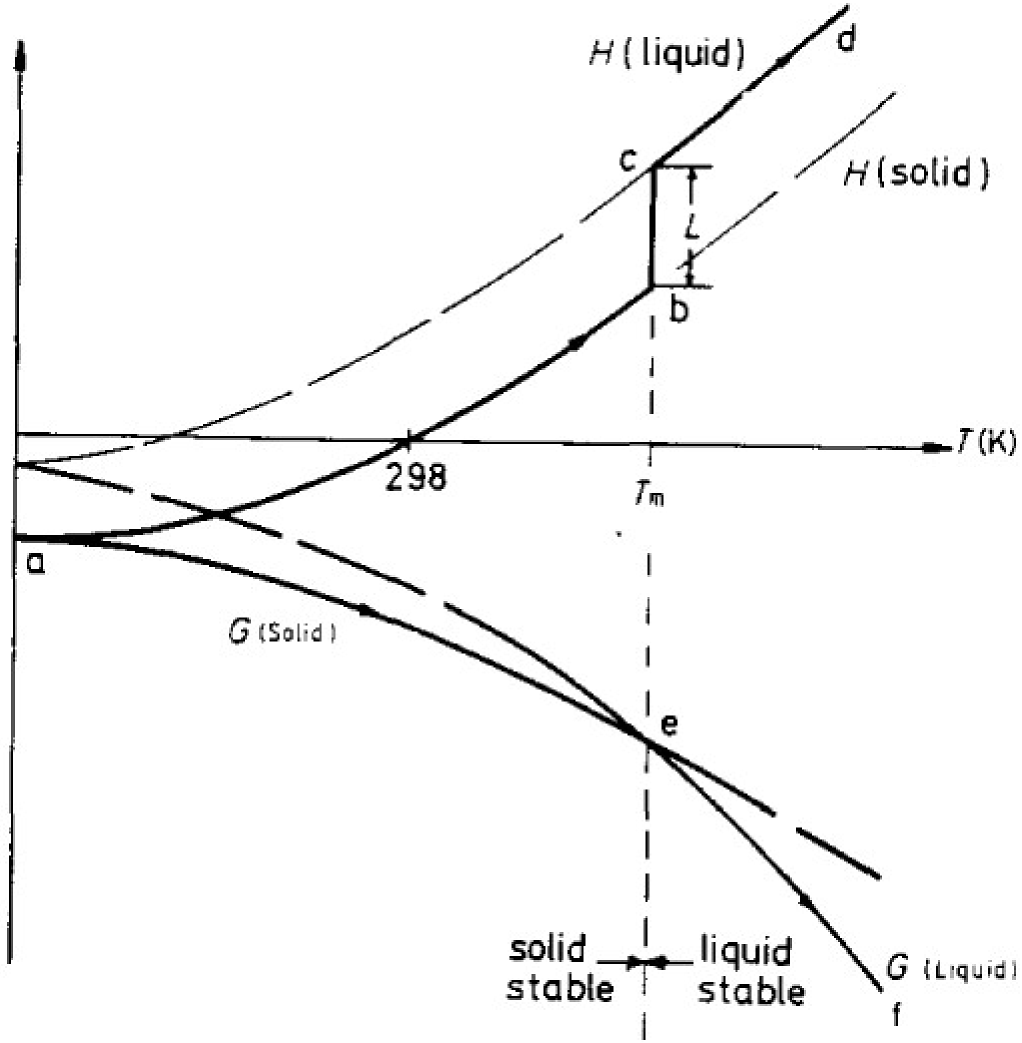
$$dG = -SdT + VdP$$

At constant P, dP=0

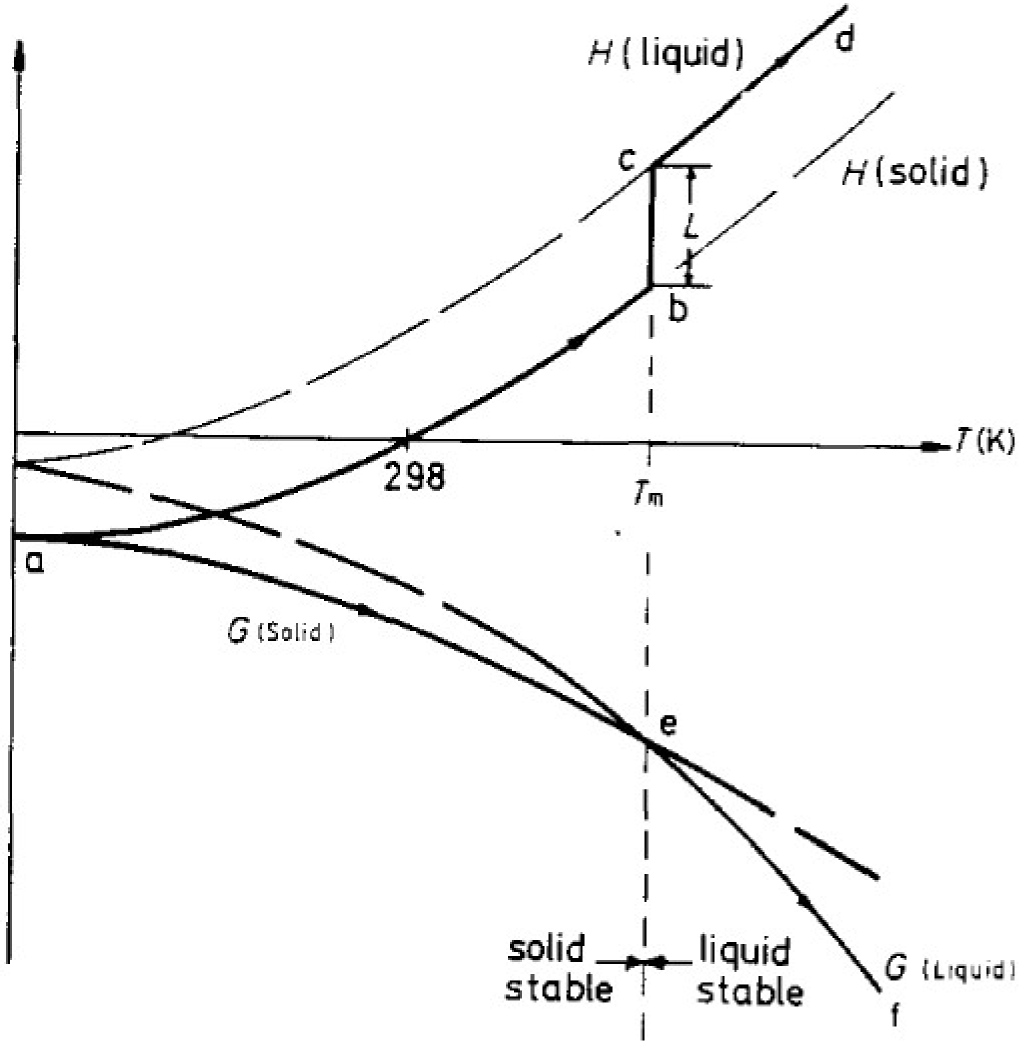
$$\left(\frac{\partial G}{\partial T}\right)_P = -S$$

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)

# 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 $X_B$

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

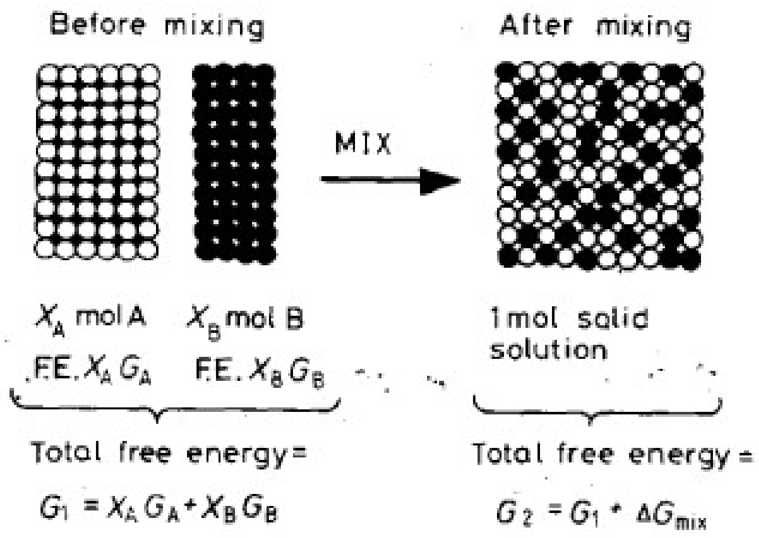
For mixing,

- Bring together $X_A$ mol of pure A and $X_B$ mol of pure B

$$\boxed{G_1 = X_A G_A + X_B G_B}$$

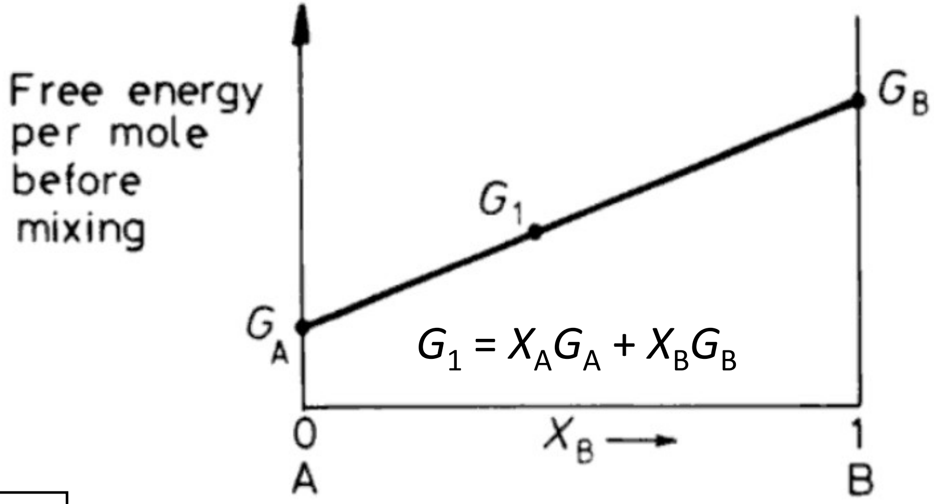
- Allow the A and B atoms to mix together

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



contributions to $G$ from mixing two components together:

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



$G_1 = X_A G_A + X_B G_B$

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

$\Delta H_{mix}$ is the heat absorbed or evolved during mixing or *heat of solution*

$\Delta S_{MIX}$ 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

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

$\Omega$ - total number of microstates of system or total number of distinguishable ways of arranging the atoms

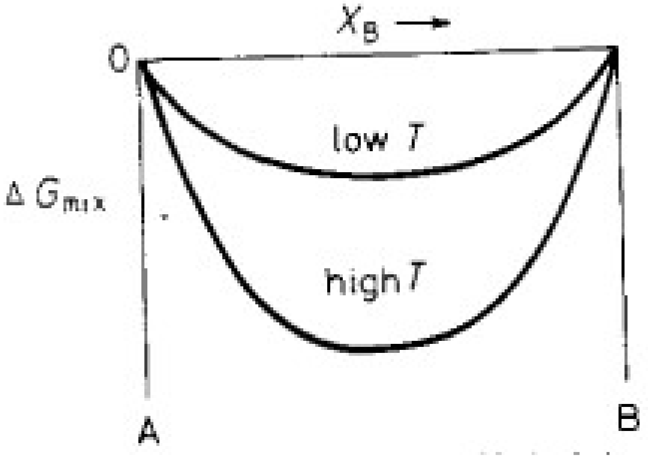
Using Stirling's approximation and $N_a k_\mathrm{B} = R$

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

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

<u>Mixing components lowers the free energy!</u>

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

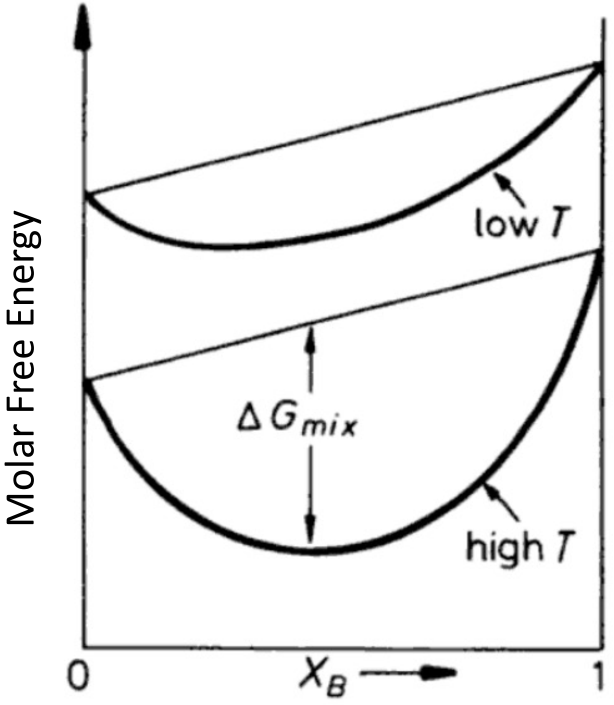


Mixing components lowers the free energy!

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

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,

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

The proportionality constant $\mu_A$ 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,

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

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

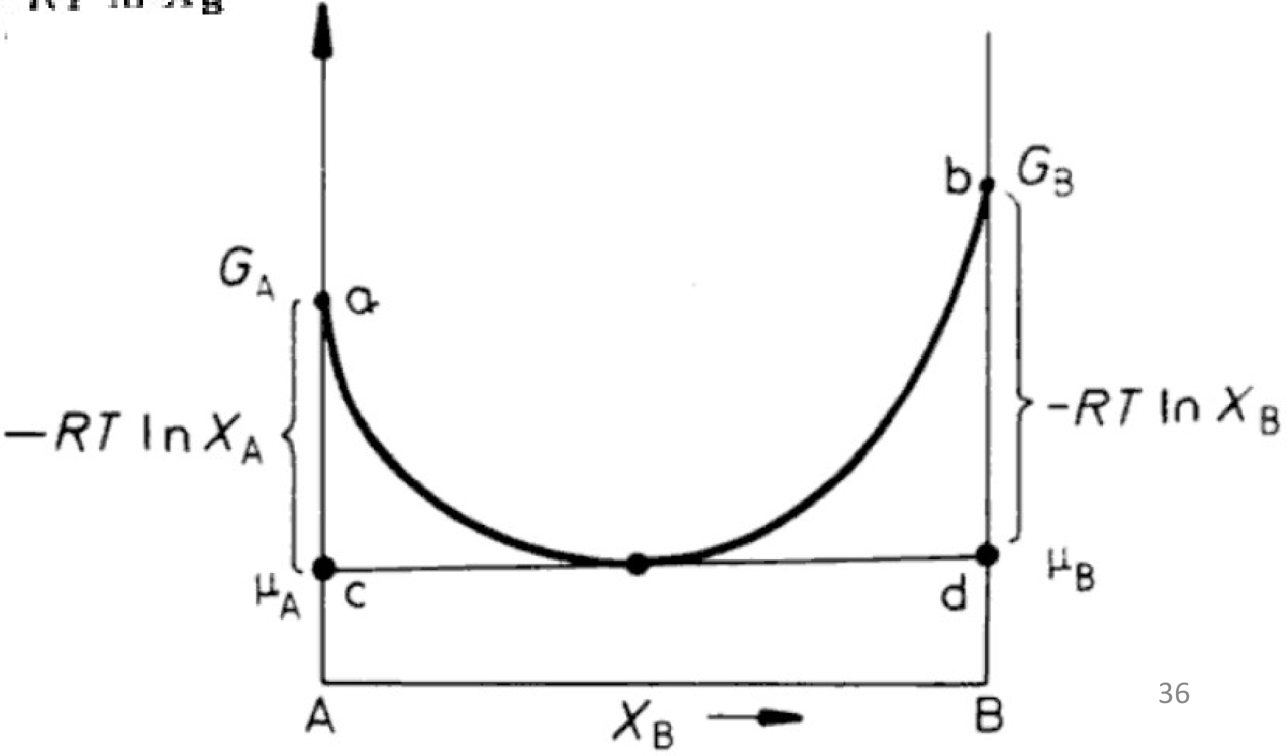
Total Gibbs energy of ideal solution is,

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

Simplified equations for an ideal liquid:

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

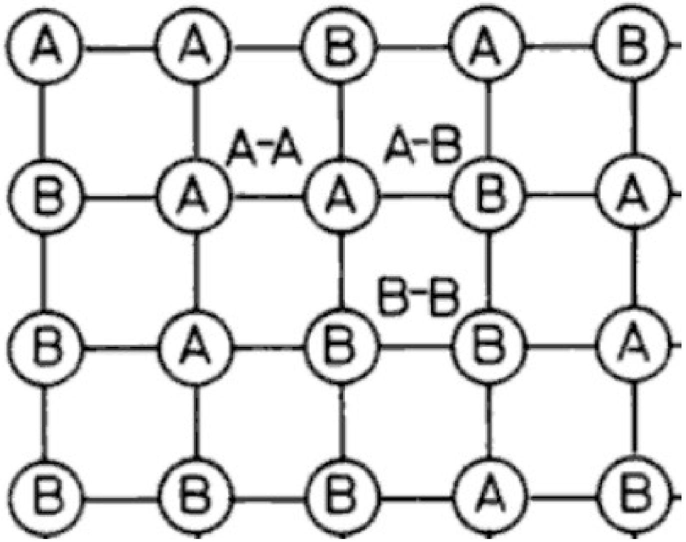
The relationship between the free energy curve and chemical potentials for ideal solution



# 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 $\varepsilon_{AA}$, $\varepsilon_{BB}$, $\varepsilon_{AB}$



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,

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

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

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 $\Omega = N_a z \varepsilon$,

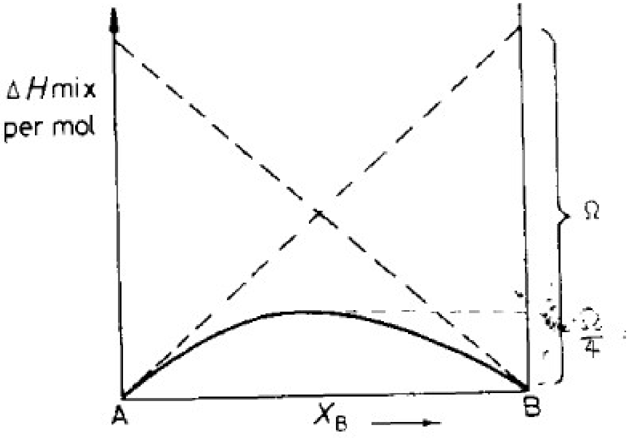
If $\Omega < 0 \Rightarrow$ A-B bonding preferred

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

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

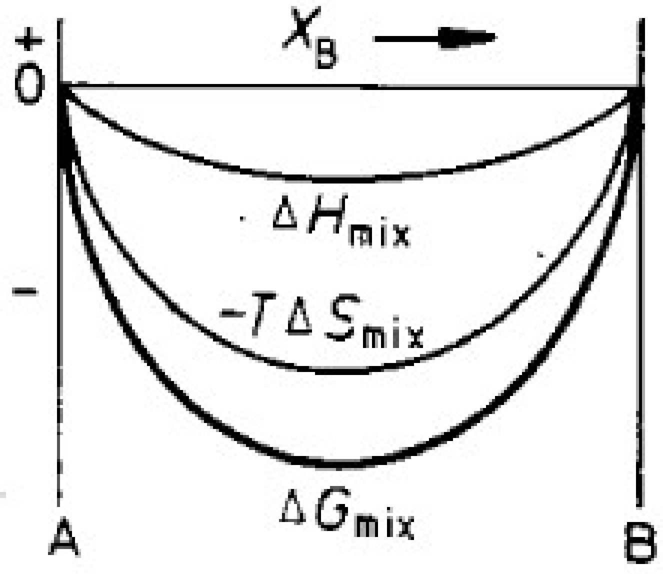
$$\Delta G_{mix} = \underbrace{\Omega X_A X_B}_{\Delta H_{mix}} + \underbrace{RT(X_A \ln X_A + X_B \ln X_B)}_{-T\Delta S_{mix}}$$

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

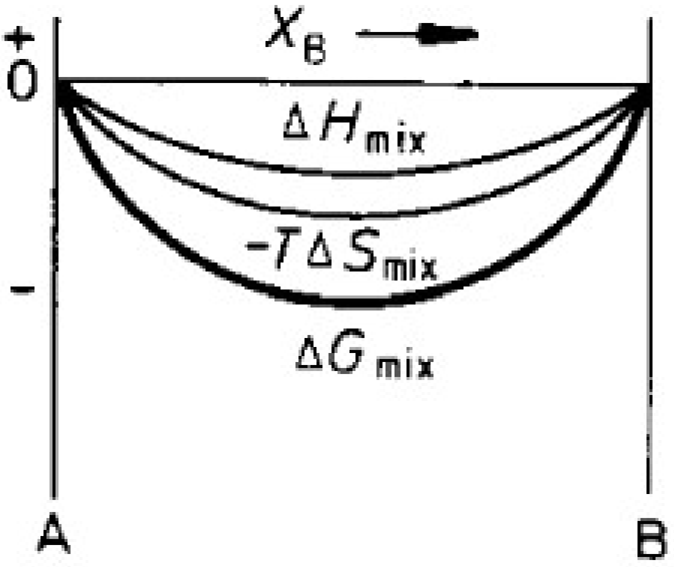


# Effect of $\Delta H_{mix}$ and T on $\Delta G_{mix}$

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

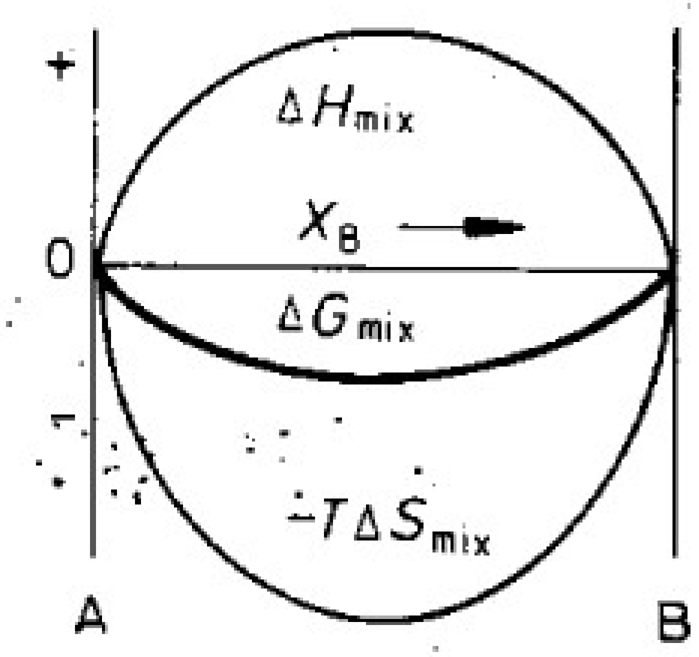


(a) $\Omega < 0$, high $T$

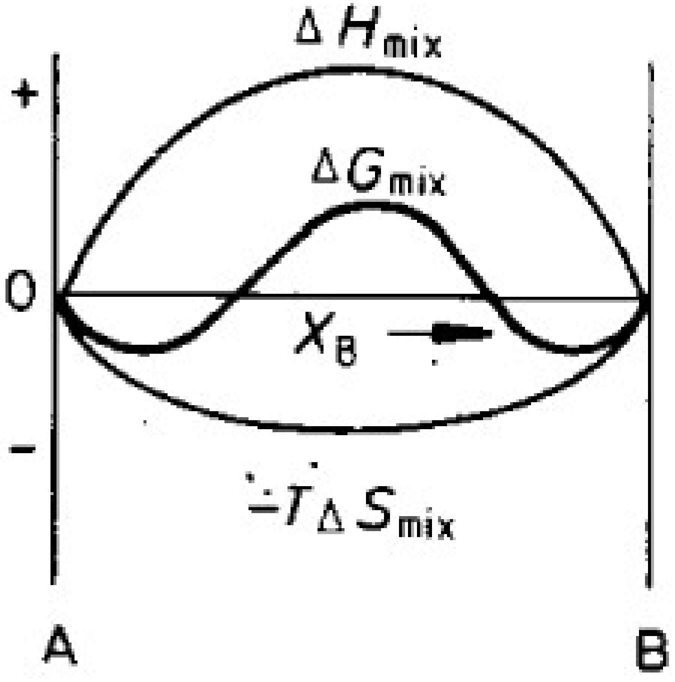


(b) $\Omega < 0$, low $T$

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

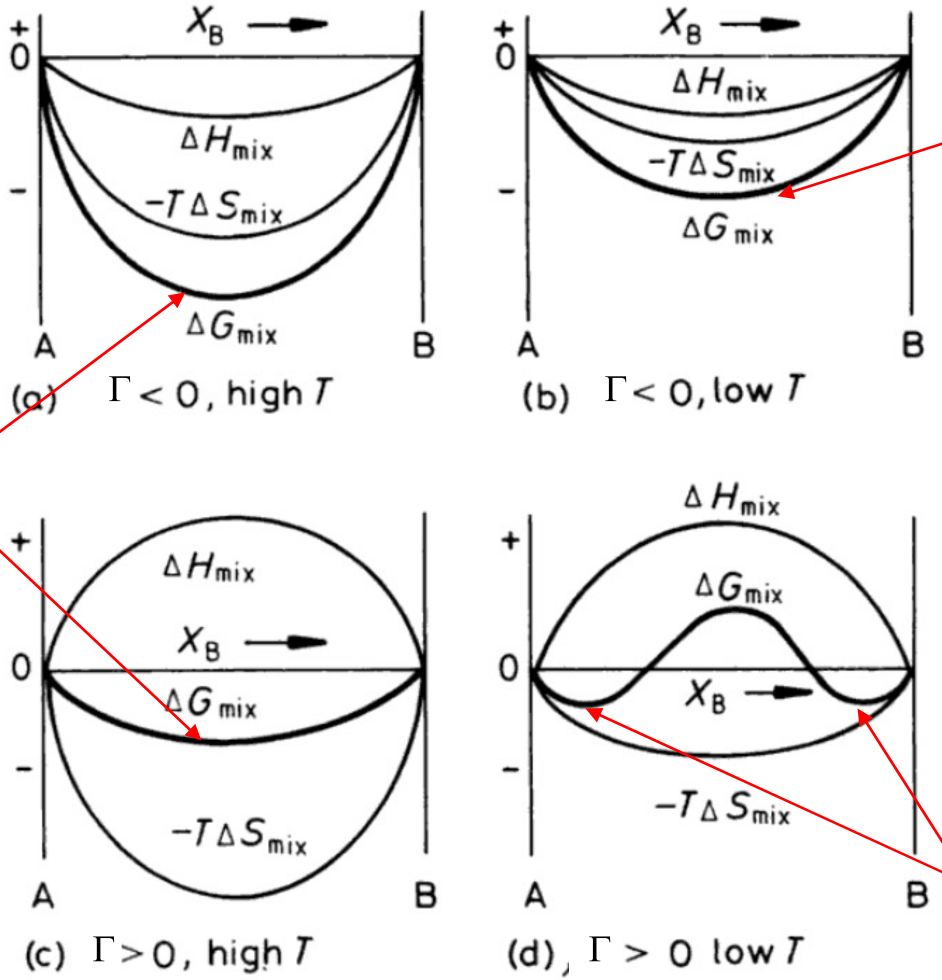


(c) $\Omega > 0$, high $T$



(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.

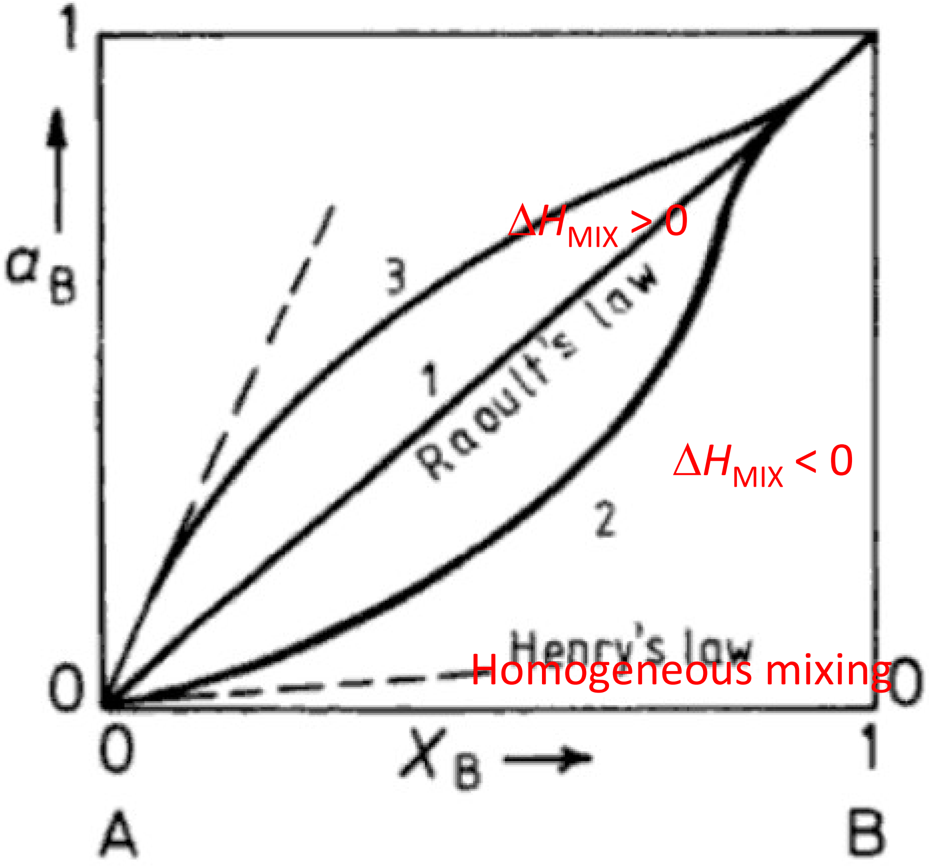
$$a_A \alpha X_A$$

$$a_A = \gamma_A X_A$$

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

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

$$a_A = X_A$$



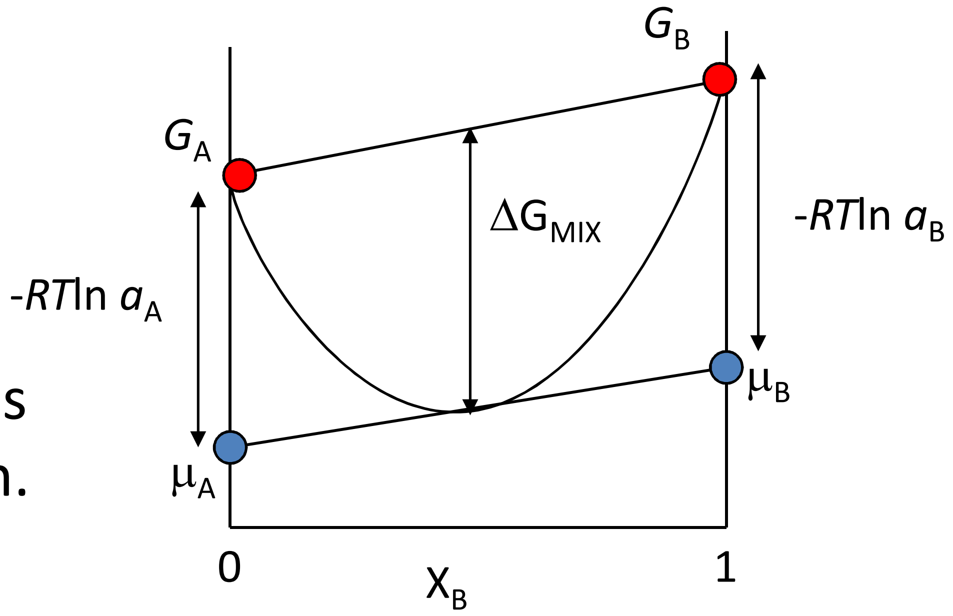
If $\Delta H_{mix} > 0$ or $\Delta H_{mix} < 0$, then it deviates take path 3 and 1 respectively .

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)

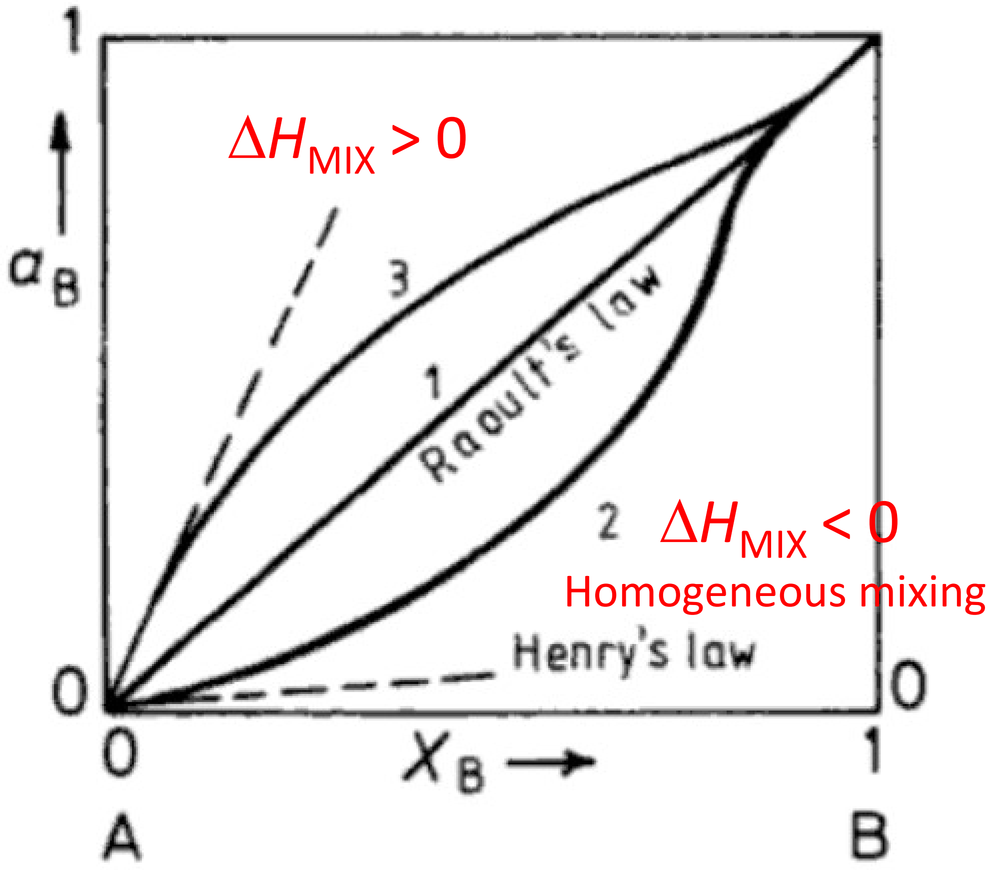
$$\boxed{\gamma_B = \frac{a_B}{X_B} \approx \text{const.}}$$

Henry's Law (or everything dissolves)

And…

$$\boxed{\gamma_A = \frac{a_A}{X_A} \approx 1}$$

Raoult's Law



# Gibbs energy diagram of Isothermal Solid Solution

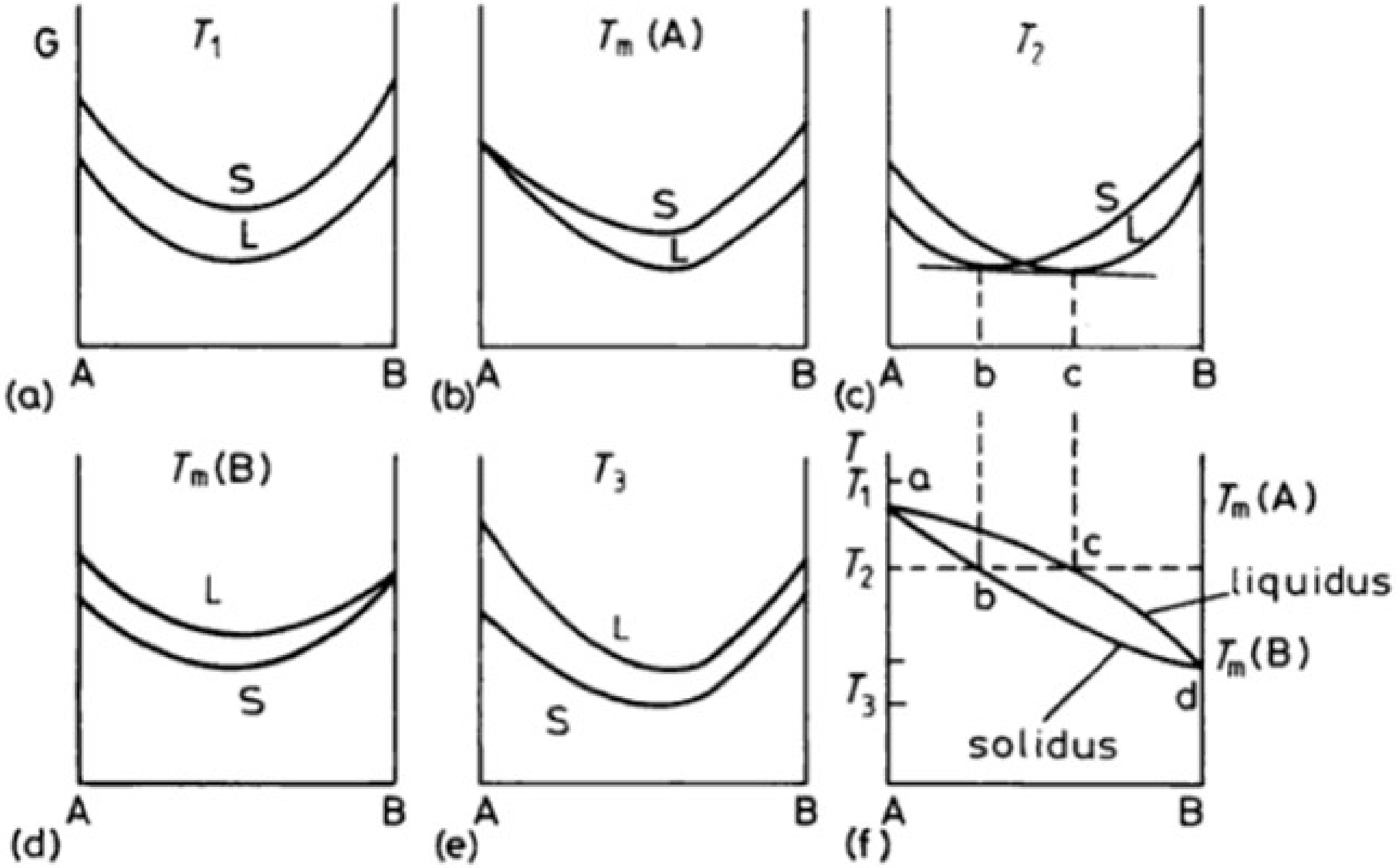
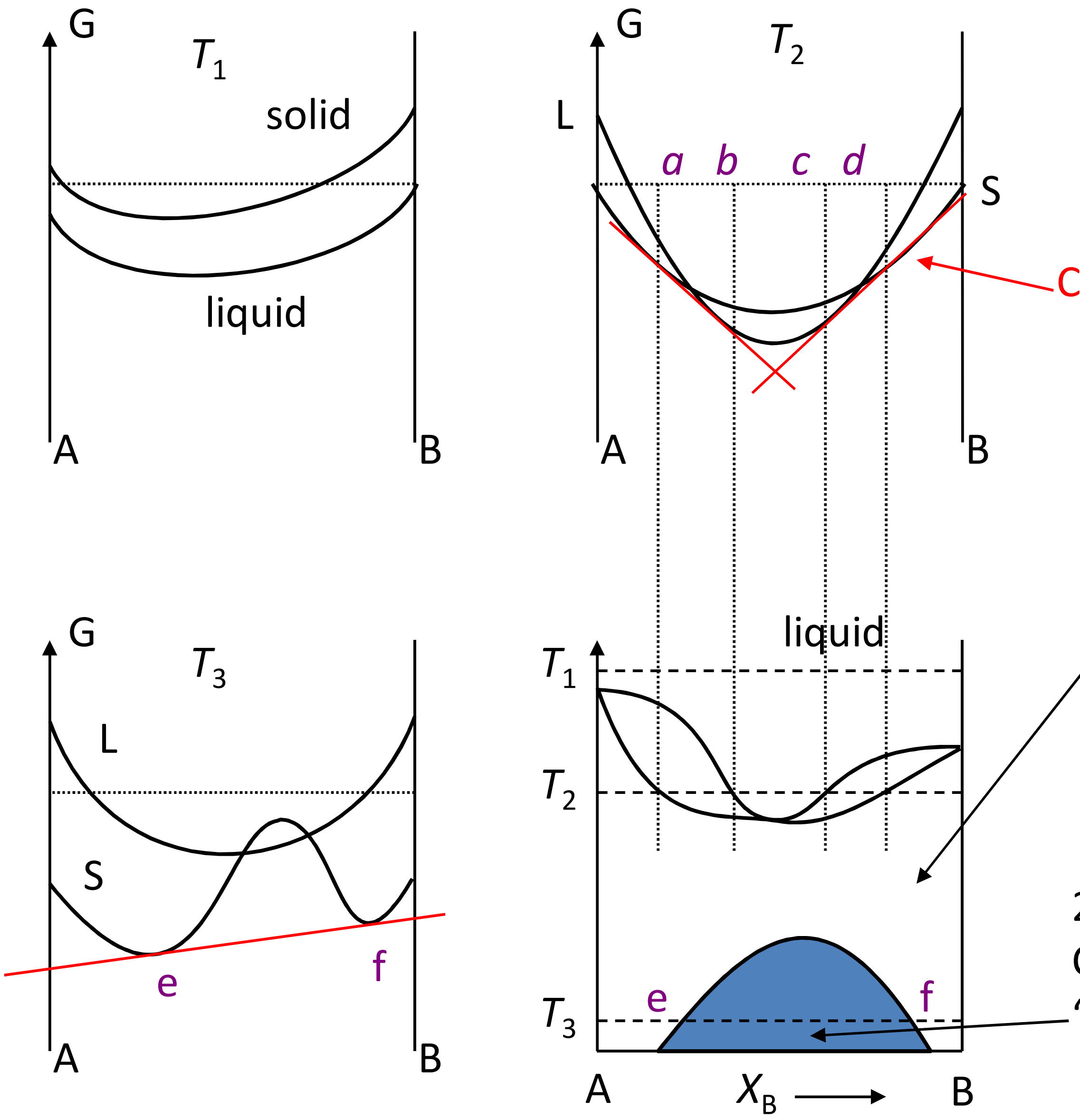


Fig. 1.29 The derivation of a simple phase diagram from the free energy curves for the liquid (L) and solid (S).

# 5. Binary phase diagrams : The Miscibility gap

$\Delta H_{MIX} > 0$

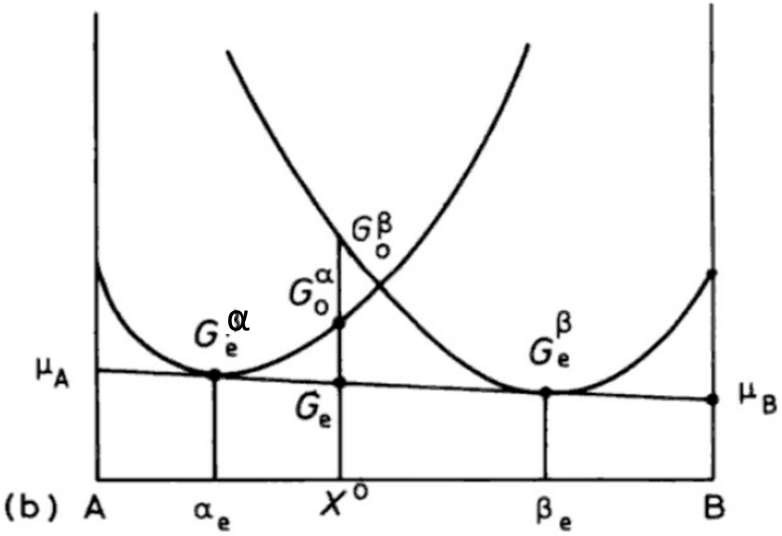


Common tangent

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

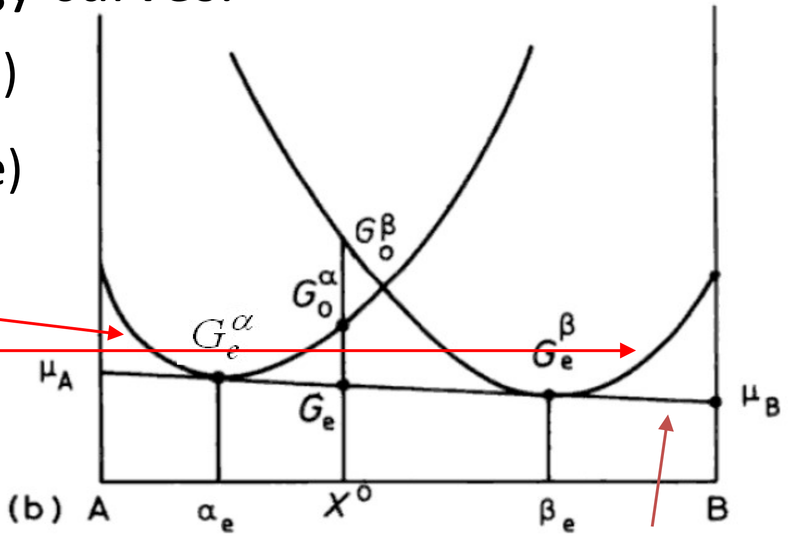
For systems with phase separation ($\alpha$ and $\beta$) of two stable structures (e.g. *fcc* and *bcc*), we must draw free energy curves.

$G^{\alpha}$ is the curve for A and B in *fcc* structure ($\alpha$ phase)

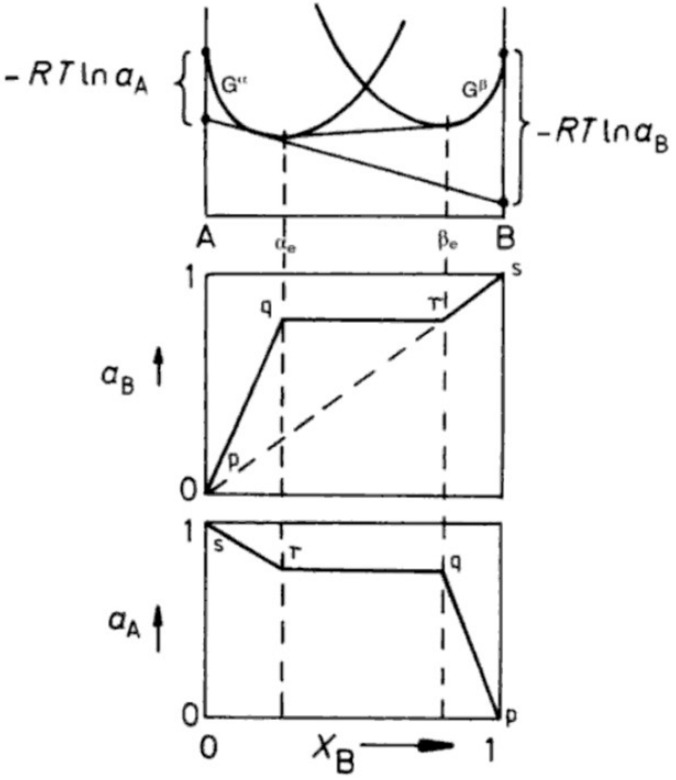
$G^{\beta}$ is the curve for A and B in *bcc* structure ($\beta$ phase)

For: $X^0 < \alpha_e$ → $\alpha$ phase only

$X^0 > \beta_e$ → $\beta$ 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:

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

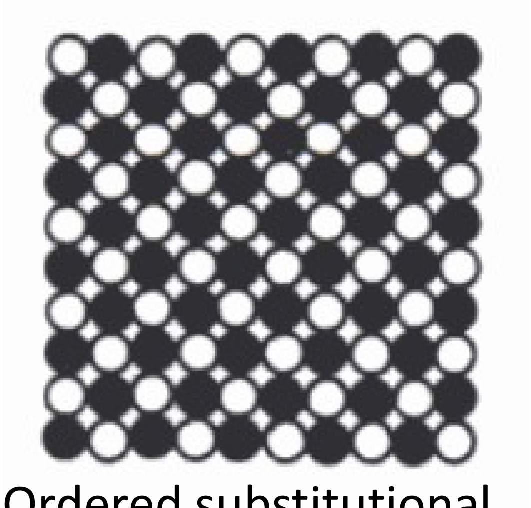
# Binary (two component) systems : *Ordered phases*

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.

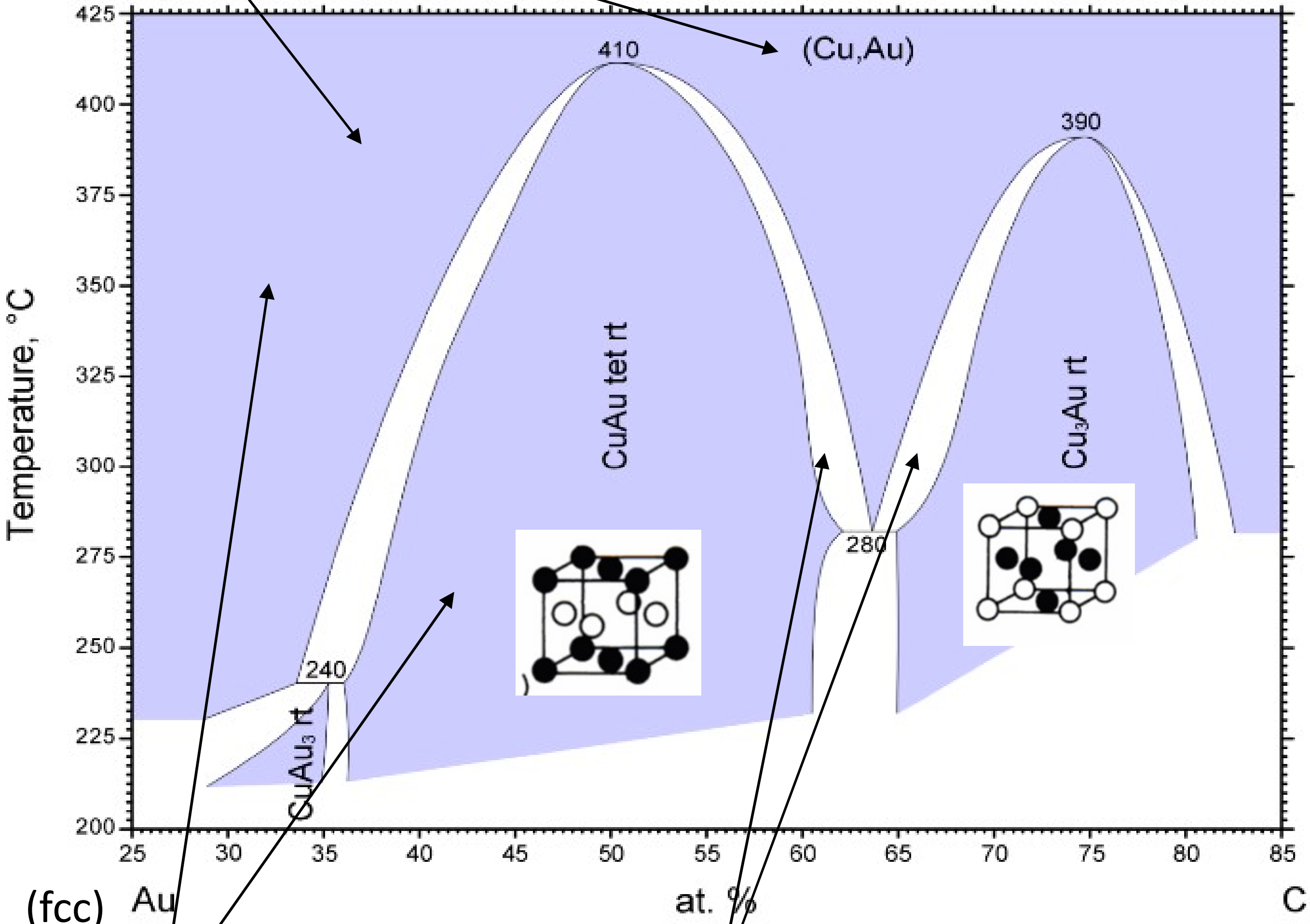


Ordered substitutional

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

# The Copper-Gold system

Random mixture



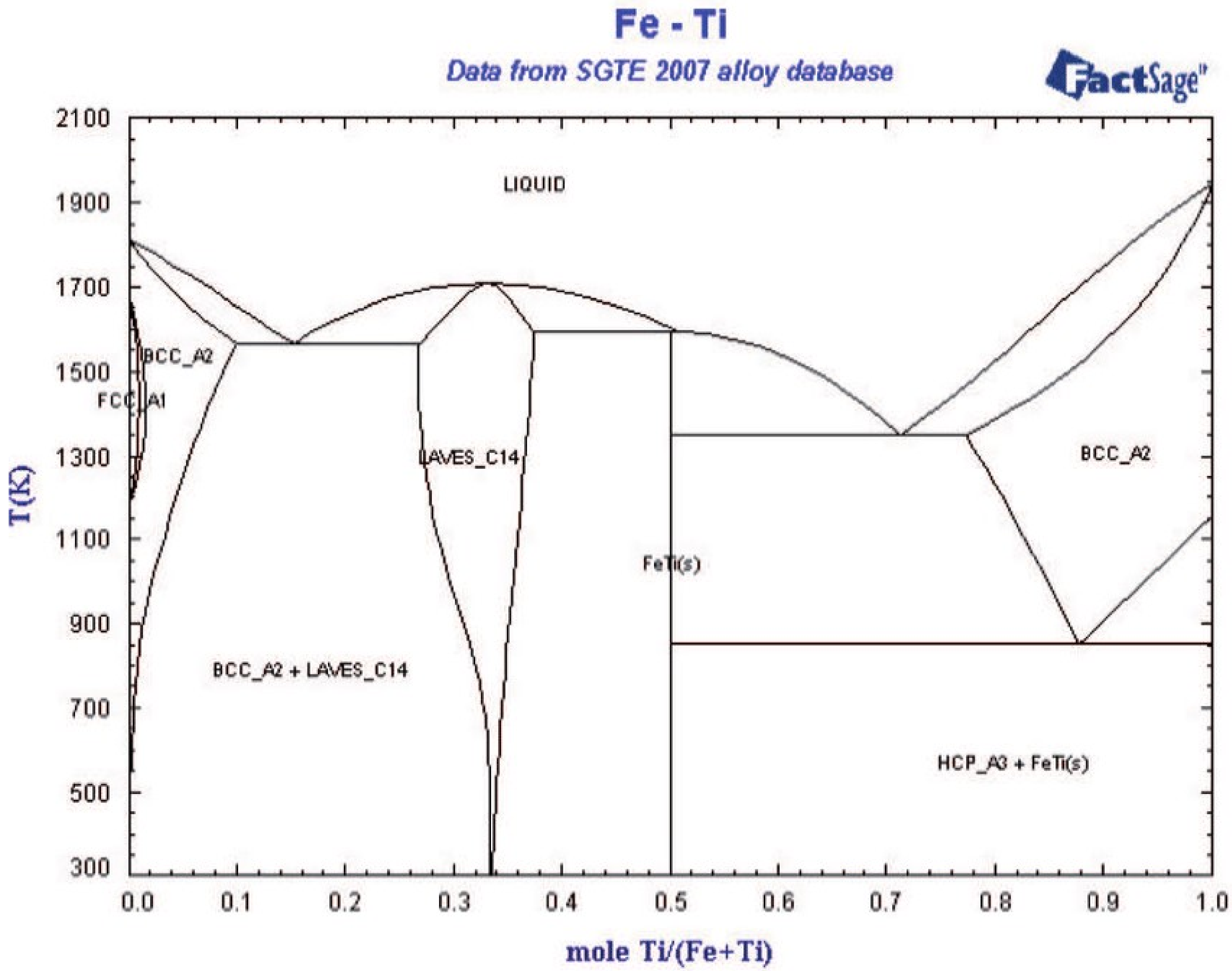
(fcc)

(fcc)

Single phases

Mixed phases

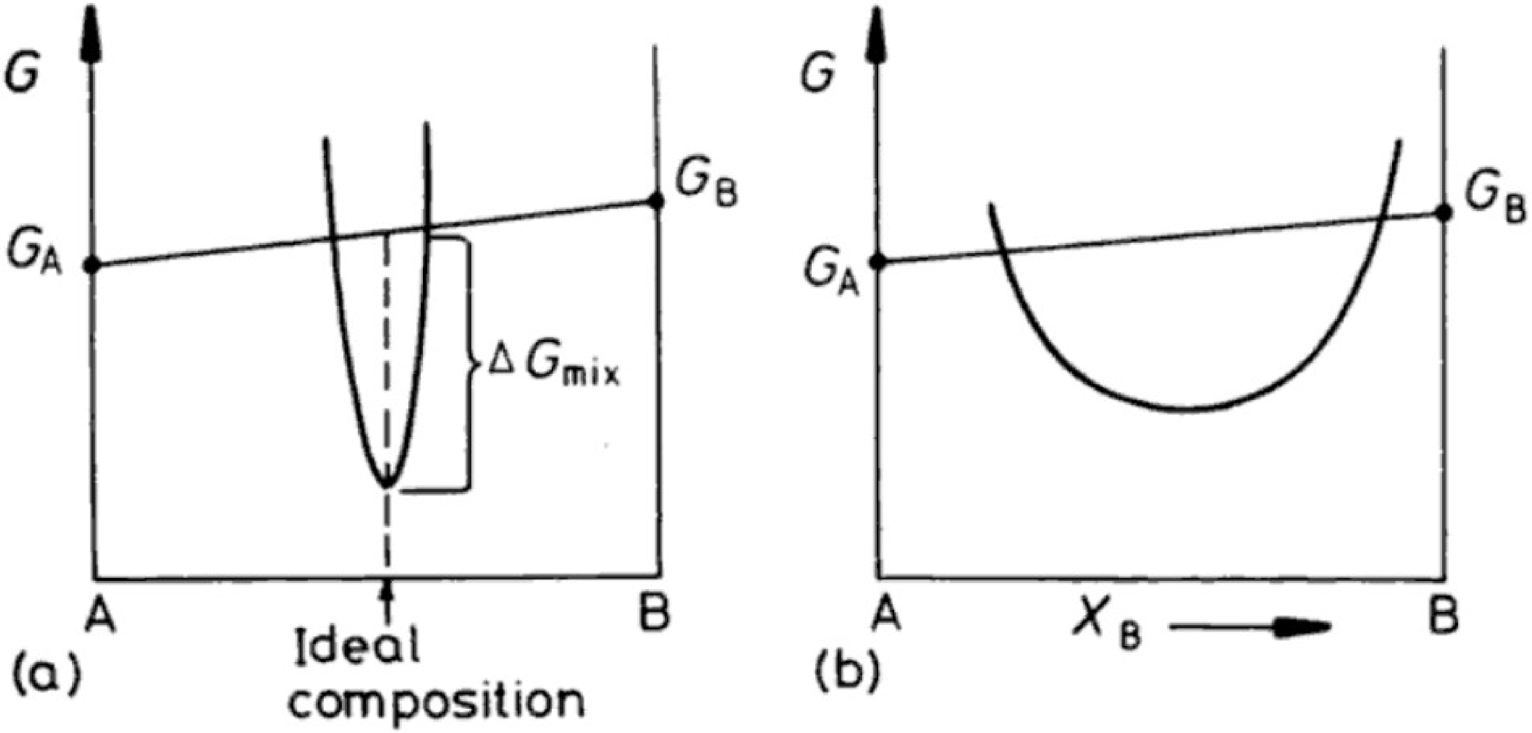
N.B. Always read the legend!!! (blue is not always ‘singe  phase’)


Fe - Ti
Data from SGTE 2007 alloy database
FactSage
2100
1900
1700
1500
1300
1100
900
700
500
300
T(K)
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)
LIQUID
BCC_A2
FCC_A1
LAVES_C14
FeTi(s)
BCC_A2
BCC_A2 + LAVES_C14
HCP_A3 + FeTi(s)

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

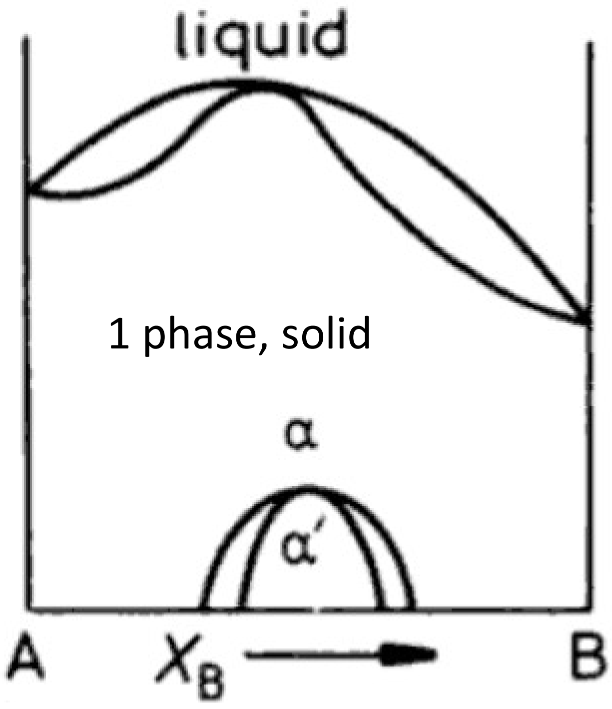
broad stability range

# Binary phase diagrams : Ordered phases

$\Delta H_{MIX} < 0$

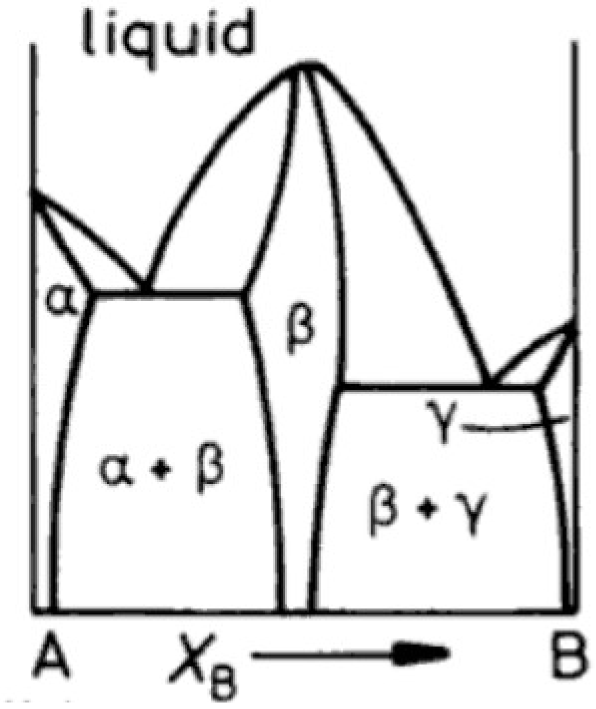
Peak in liquidus line : attraction between atoms

*i.e. A and B attract*



Weak attraction

Ordered phase $\alpha$



Strong attraction

Ordered $\beta$ phase extends to liquid phase

# Binary phase diagrams : Simple Eutectic systems

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