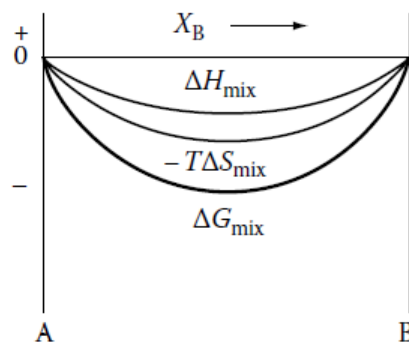
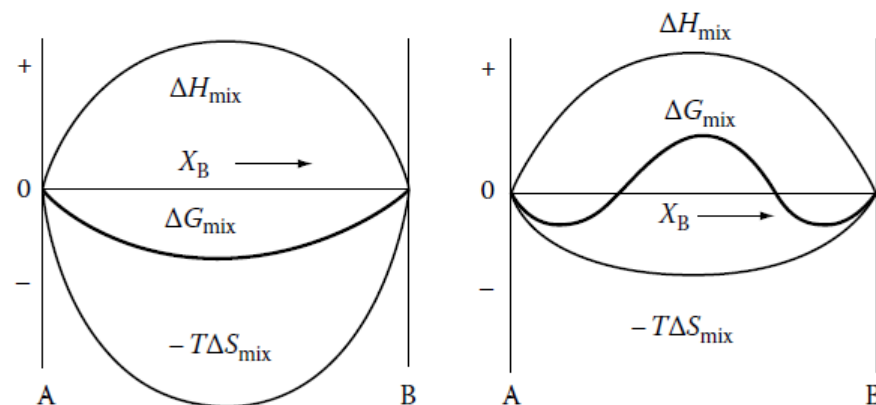


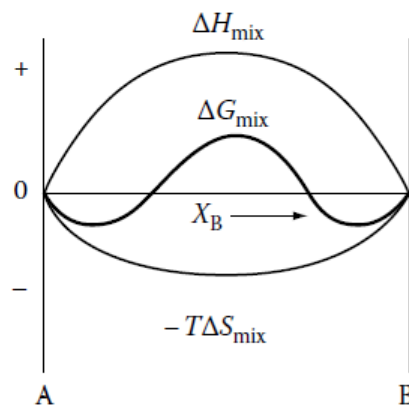
(a) $\Omega < 0$, high T



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



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



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

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

The effect of ΔH_{mix} and T on ΔG_{mix} .

This is shown in Fig. 1.15 for different values of Ω and temperature. For exothermic solutions $\Delta H_{\text{mix}} < 0$ and mixing results in a free energy decrease at all temperatures (Fig. 1.15a and b). When $\Delta H_{\text{mix}} > 0$, however, the situation is more complicated. At high temperatures $T\Delta S_{\text{mix}}$ is greater than ΔH_{mix} for all compositions and the free energy curve has a positive curvature at all points (Fig. 1.15c). At low temperatures, on the other hand, $T\Delta S_{\text{mix}}$ is smaller and ΔG_{mix} develops a negative curvature in the middle (Fig. 1.15d).

Concept of the chemical potential and the activity of elements

Gibb's free energy, G is function of temperature, T , pressure, P and amount of elements, n_A , n_B

$$G = G(T, P, n_A, n_B, \dots)$$

At particular temperature and pressure, partial derivative gives

$$\begin{aligned} dG &= \frac{\partial G}{\partial n_A} dn_A + \frac{\partial G}{\partial n_B} dn_B \\ &= \mu_A dn_A + \mu_B dn_B \end{aligned}$$

$\frac{\partial G}{\partial n_A} = \mu_A$ is the chemical potential of element A. It measures the change in free energy because of very minute change of element A.

$\frac{\partial G}{\partial n_B} = \mu_B$ is the chemical potential of element B. It measures the change in free energy because of very minute change of element B.

➤ It should be noted here that the change should be so minute that there should not be any change in concentration because the chemical potential is a concentration dependent parameter.

- Let us consider an alloy of total x moles where it has x_A mole of A and x_B mole of B.
- Note that x is much higher than 1 mole.
- Now suppose we add small amounts of A and B in the system, keeping the ratio of $x_A:x_B$ the same, so that there is no change in overall composition.
- So if we add four atoms of A, then we need to add six atoms of B to keep the overall composition fixed. Following this manner, we can keep on adding A and B and will reach to the situation when X_A mole of A and X_B mole of B are added and total added amount is $X_A + X_B = 1$.
- Since previously we have considered that the total free energy of 1 mole of alloy after mixing is G , then we can write

$$G = \mu_A X_A + \mu_B X_B \quad \text{will be proven a little bit later}$$

- Previously, we derived

$$G = X_A G_A + X_B G_B + \Omega X_A X_B + RT [X_A \ln X_A + X_B \ln X_B]$$

Further, we can write $X_A X_B = X_A^2 X_B + X_A X_B^2$ HW or Q : Prove

$$G = X_A (G_A + \Omega X_B^2 + RT \ln X_A) + X_B (G_B + \Omega X_A^2 + RT \ln X_B)$$

Further, comparing the expressions for free energy, we can write

$$\mu_A = G_A + \Omega X_B^2 + RT \ln X_A$$

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

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

In terms of activity

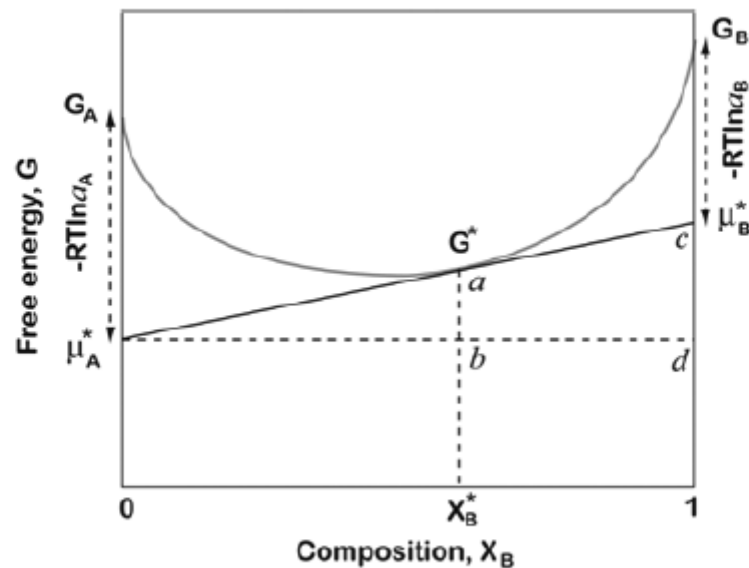
$$\mu_A = G_A + RT \ln a_A$$

$$\mu_B = G_B + RT \ln a_B$$

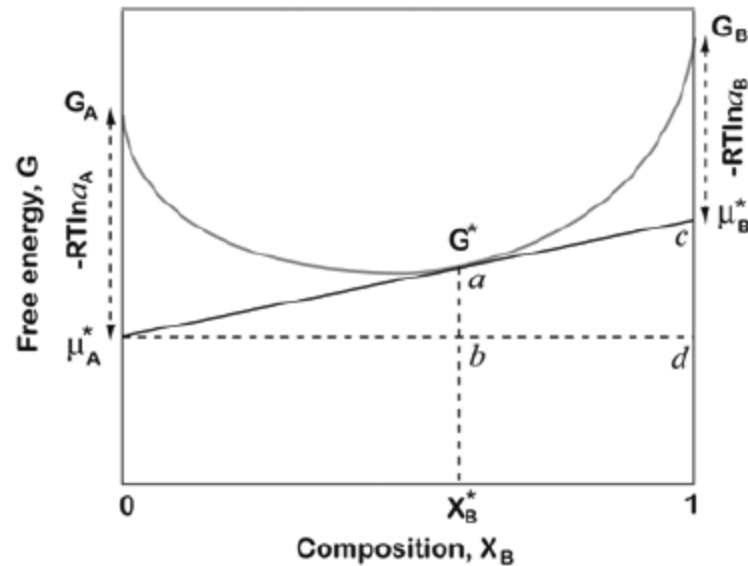
So the relations between the chemical potential and activity are

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

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



- Activities and chemical potentials are determined from a free energy curve after taking a slope, as explained in the figure.
- If we are interested to determine the activities or chemical potentials in a binary system A-B, let say at X_B^* , we need to take a slope on the free energy curve at the free energy, G^* and extend it to pure element, A ($X_B=0$) and pure element B ($X_B=1$).
- The point at which it hits $N_B = 0$, the value corresponds to the chemical potential of element A (μ_A^*).
- From previous slide, we can write $-RT \ln a_A = G_A - \mu_A^*$
- So, once the chemical potential is known, the activity of the element can be calculated using the above equation, as explained in the graph.



➤ It can be proved that, by taking slope and then extending to $X_B=0$ and $X_B=1$, we can find the chemical potentials. We can write

$$G^* = \mu_A^* + ab$$

➤ Further, we can write

$$\frac{ab}{X_B^*} = \frac{cd}{1}$$

$$ab = X_B^* cd = X_B^* (\mu_B^* - \mu_A^*)$$

➤ That becomes

$$G^* = \mu_A^* X_A^* + \mu_B^* X_B^*$$

Concept of chemical potential and activity

Further, we can write

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

$$a_A = X_A \exp\left[\frac{\Omega}{RT}(1 - X_A)^2\right] = \gamma_A X_A$$

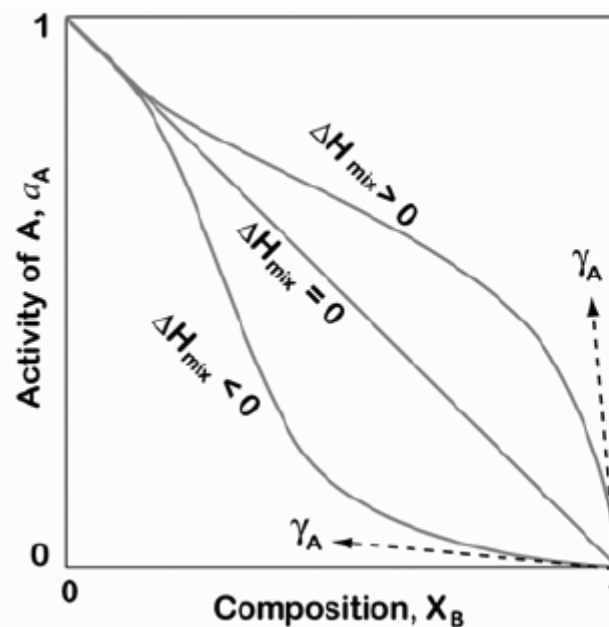
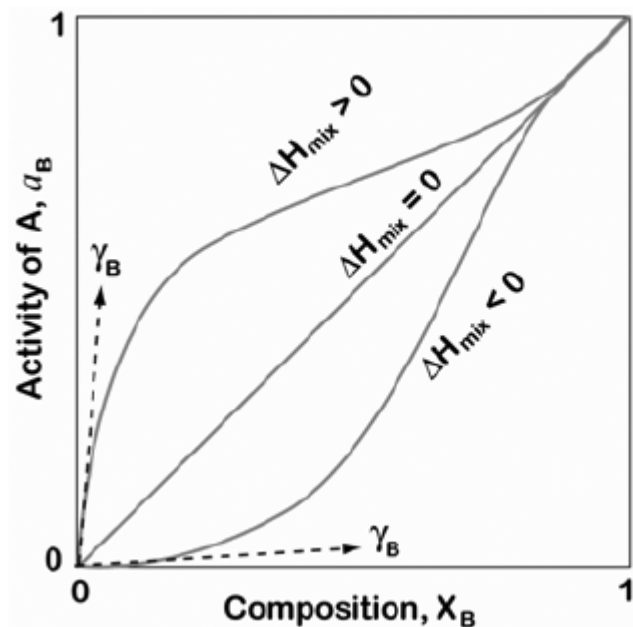
$$\gamma_A = \exp\left[\frac{\Omega}{RT}(1 - X_A)^2\right]$$

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

$$a_B = X_B \exp\left[\frac{\Omega}{RT}(1 - X_B)^2\right] = \gamma_B X_B$$

$$\gamma_B = \exp\left[\frac{\Omega}{RT}(1 - X_B)^2\right]$$

- γ_i are the activity coefficient of element i.
- In an ideal solution, $\Omega=0$ and $a_i = X_i$.
- In a non ideal solution, activity coefficient indicates the deviation from the ideal line.



$$\gamma_A = \exp\left[\frac{\Omega}{RT}(1 - X_A)^2\right]$$

$$\gamma_B = \exp\left[\frac{\Omega}{RT}(1 - X_B)^2\right]$$

In the case of positive enthalpy of mixing, activity deviates positively and in the case of negative enthalpy of mixing activity deviates negatively from the ideal mixing line.

$$X_A \rightarrow 0, \gamma_A \rightarrow \exp(\Omega/RT)$$

$$X_B \rightarrow 0, \gamma_B \rightarrow \exp(\Omega/RT)$$

$$X_A \rightarrow 1, \gamma_A \rightarrow 1$$

$$X_B \rightarrow 1, \gamma_B \rightarrow 1$$

Henry's law: activity of elements is more or less the constant in a very dilute solution.

Rault's law: activity is equal to the mole fraction near the mole fraction of 1

Equilibrium conditions between different phases

As explained previously, while discussing the phase diagrams, we have shown that at certain conditions two phases, such as solid and liquid or two solid phases α and β can stay together.

This can be explained with respect to chemical potential of elements. For the sake of explanation let us consider that there are two phases α and β which are staying together.

If we remove dn_B of element B from the β phase and add them to α phase, then the change in free energy of the α and β phases will be

$$dG^\alpha = \mu_B^\alpha dn_B$$

$$dG^\beta = -\mu_B^\beta dn_B$$

So the total free energy change of the system will be

$$dG = \mu_B^\alpha dn_B - \mu_B^\beta dn_B = (\mu_B^\alpha - \mu_B^\beta) dn_B$$

However, we know that in equilibrium condition $dG = 0$. That means the chemical potential of element B in both the phases should be the same.

That further means that even if a small amount of material is transferred from the β to the α phase, there will be no difference in equilibrium as long as the chemical potential of elements are the same in both the phases.

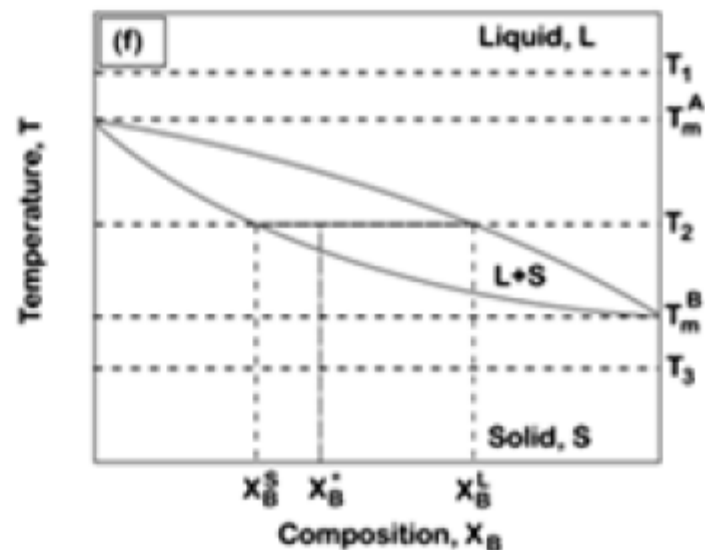
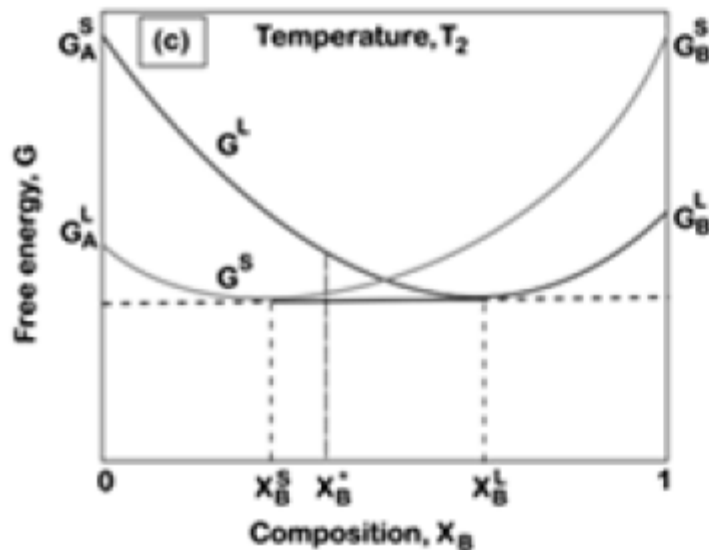
➤ Previously, we have shown that the system will not be in equilibrium that is it will go through irreversible transformation if $dG < 0$. That means

$$(\mu_B^\alpha - \mu_B^\beta) dn_B < 0$$

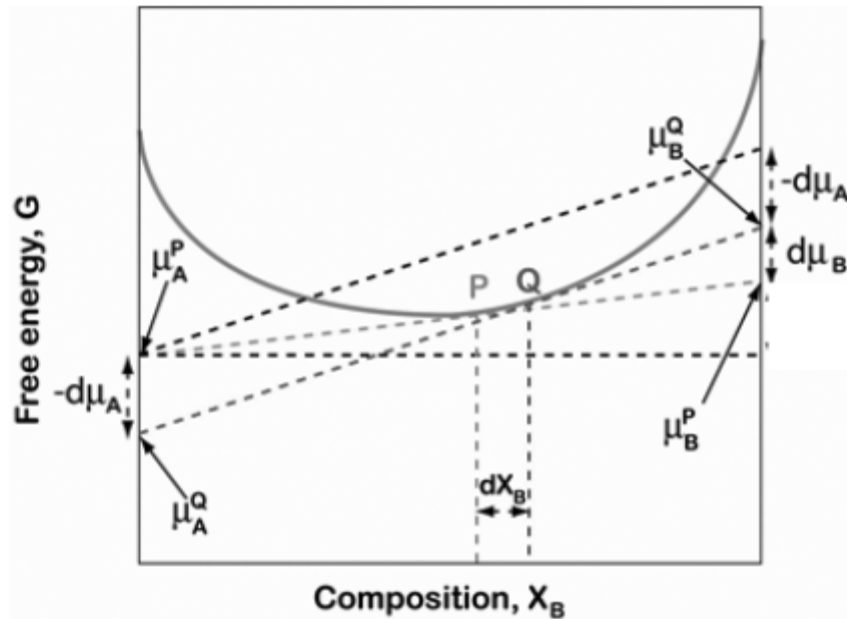
➤ This indicates that the chemical potential of B in the α phase is less than the chemical potential of the same element in the β phase.

➤ So to reach to the equilibrium system will transfer B from the β phase to the α phase.

➤ Now we understand, why both solid and liquid phases can stay together in certain composition range. It can be understood from the common tangent between X_B^S and X_B^L chemical potential of any of the elements are the same in both the phases.



Gibb's Duhem relation and the driving force for diffusion



➤ It can be seen that when we move from alloy P to Q that is to a B-rich alloy, the chemical potential of B increases and the chemical potential of A decreases.

➤ At any point P or Q, we can write

$$-\frac{d\mu_A}{X_B} = \frac{d\mu_B}{X_A}$$

So we can write

$$X_A d\mu_A + X_B d\mu_B = 0 \quad \text{This is called Gibb's-Duhem relation}$$

Another useful relation can be derived from this:

$$-X_A \frac{d\mu_A}{dX_B} = X_B \frac{d\mu_B}{dX_B} \quad \text{By dividing } dX_B$$

Further, from

$$\mu_B = G_B + RT \ln a_B = G_B + RT \ln \gamma_B X_B$$

$$\frac{d\mu_B}{dX_B} = \frac{RT}{X_B} \frac{d \ln a_B}{d \ln X_B}$$

$$\mu_A = G_A + RT \ln a_A = G_A + RT \ln \gamma_A X_A$$

$$\frac{d\mu_A}{dX_B} = -\frac{RT}{X_A} \frac{d \ln a_A}{d \ln X_A} \quad \text{since } X_A + X_B = 1$$

$$\frac{d \ln a_A}{d \ln X_A} = \frac{d \ln a_B}{d \ln X_B}$$

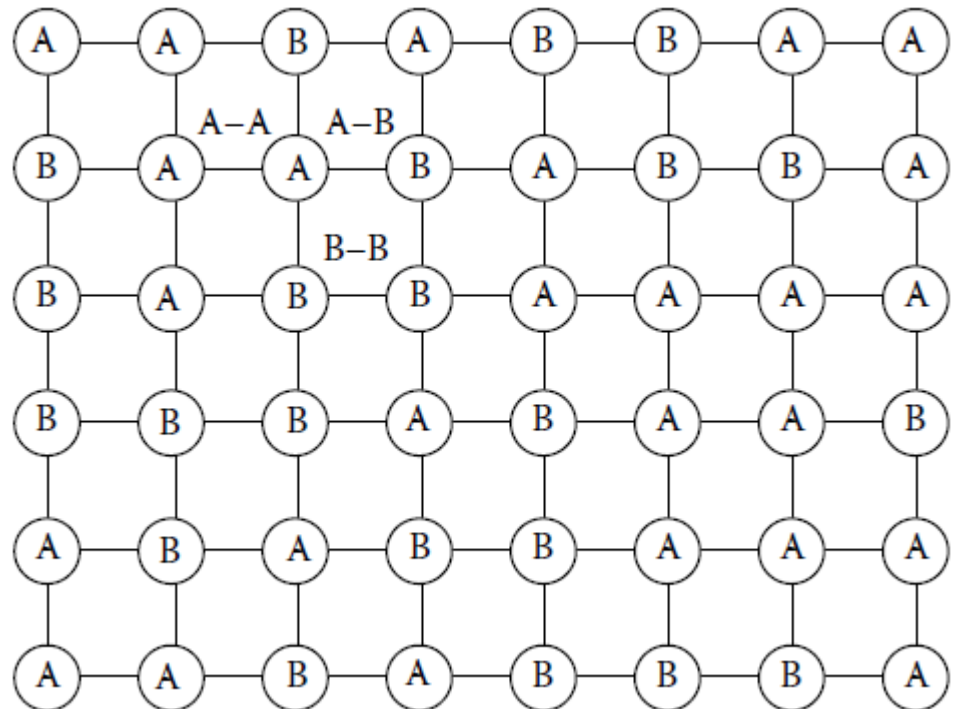
This is very useful equation in diffusion studies.

Regular Solutions

In solid solution model it has been assumed that $\Delta H_{\text{mix}} = 0$; but in practice mixing is endothermic or exothermic. Therefore the model for ideal solution must be extended such that it includes ΔH_{mix} term by using the quasi-chemical approach.

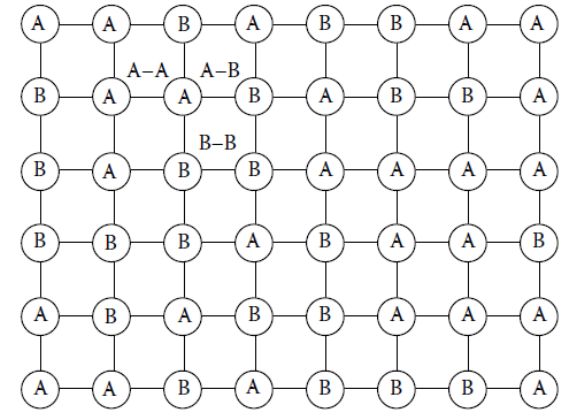
In quasi-chemical model ΔH_{mix} is only due to the bond energies btw adjacent atoms.

1. A—A bonds each with an energy ϵ_{AA} ,
2. B—B bonds each with an energy ϵ_{BB} ,
3. A—B bonds each with an energy ϵ_{AB} .



Regular Solutions

1. A—A bonds each with an energy ϵ_{AA} ,
2. B—B bonds each with an energy ϵ_{BB} ,
3. A—B bonds each with an energy ϵ_{AB} .



$$\Delta H_{\text{mix}} = P_{AB} \Delta \epsilon \longrightarrow E = P_{AA} \epsilon_{AA} + P_{BB} \epsilon_{BB} + P_{AB} \epsilon_{AB}$$

$$\Delta \epsilon = \epsilon_{AB} - \frac{1}{2}(\epsilon_{AA} + \epsilon_{BB})$$

$\Delta \epsilon$ is the difference btw A-B bond energy and the average of A-A and B-B bond energies

If $\Delta \epsilon = 0$ and $\Delta H_{\text{mix}} = 0$ and the solution is ideal, atoms arrange randomly, and the entropy of mixing, $\Delta S_{\text{mix}} = -R[X_A \ln X_A + X_B \ln X_B]$. In such solutions;

$$P_{AB} = N_a z X_A X_B \text{ bonds mol}^{-1} ; \text{ where } N \text{ is Avogadro's Number, and } z \text{ is the number of bonds/atom}$$

If $\Delta \epsilon < 0$ the atoms in the solution prefer to be surrounded by atoms of the opposite type, Which result in increase in P_{AB}

Regular Solutions

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➤ If $\Delta\epsilon<0$ the atoms in the solution prefer to be surrounded by atoms of the opposite type, Which result in increase in P_{AB}

➤ If $\Delta\epsilon>0$ P_{AB} will tend to be less than in random solution.

• However, $\Delta\epsilon$ is not too different than 0; therefore $P_{AB} = N_a z X_A X_B \text{ bonds mol}^{-1}$ is a good approx. in which case $\Delta H_{\text{mix}} = \Omega X_A X_B$ where $\Omega = N_a z \Delta\epsilon$

Real Solutions

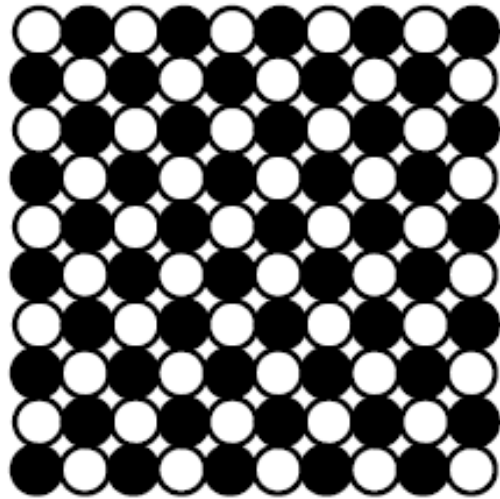
As already indicated, in alloys where the enthalpy of mixing is not zero ($\Delta\varepsilon$ & $\Omega \neq 0$) the assumption that a random arrangement of atoms is the equilibrium, or most stable arrangement is not true, and the calculated value for ΔG_{mix} will not give the minimum free energy.

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

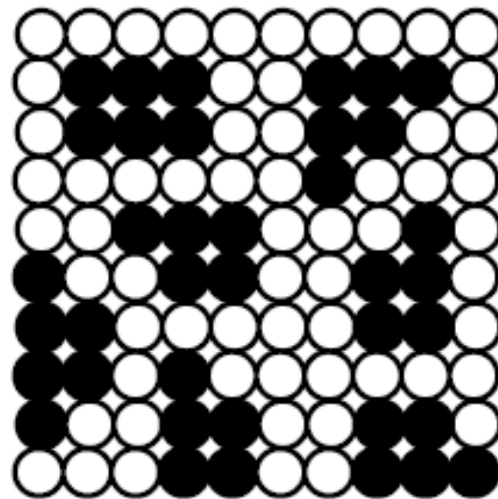
$$\Omega = N_0 Z \Delta\varepsilon \quad \Delta\varepsilon = \varepsilon_{AB} - \frac{1}{2}(\varepsilon_{AA} + \varepsilon_{BB})$$

The actual arrangement of atoms will be a compromise that gives the lowest internal energy consistent with sufficient entropy, or randomness, to achieve the minimum free energy.

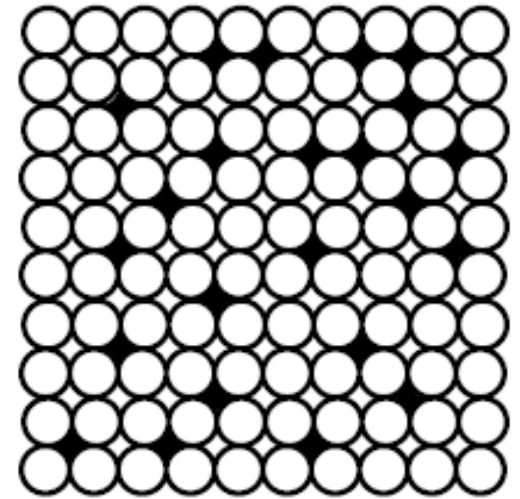
In systems with $\varepsilon < 0$ the internal energy of the system is reduced by increasing the number of A—B bonds, i.e. by ordering the atoms as shown in Fig. If $\varepsilon > 0$ the internal energy can be reduced by increasing the number of A—A and B—B bonds, i.e. by the clustering of the atoms into A-rich and B-rich groups



(a)



(b)



(c)

Schematic representation of solid solutions: (a) ordered substitutional, (b) clustering, (c) random interstitial.

In systems where there is a size difference between the atoms the quasi-chemical model will underestimate the change in internal energy on mixing since no account is taken of the elastic strain fields which introduce a strain energy term into ΔH_{mix} . When the size difference is large this effect can dominate over the chemical term.

When the size difference between the atoms is very large then *interstitial solid solutions* are energetically most favourable,

In systems where there is strong chemical bonding between the atoms there is a tendency for the formation of intermetallic phases. These are distinct from solutions based on the pure components since they have a different crystal structure and may also be highly ordered. Intermediate phases and ordered phases are discussed further in the next two sections.

Ordered Phases

Assume atoms in a substitutional solid are completely randomly arranged. In such solutions P_{AB} the number of A-B bonds is given ;

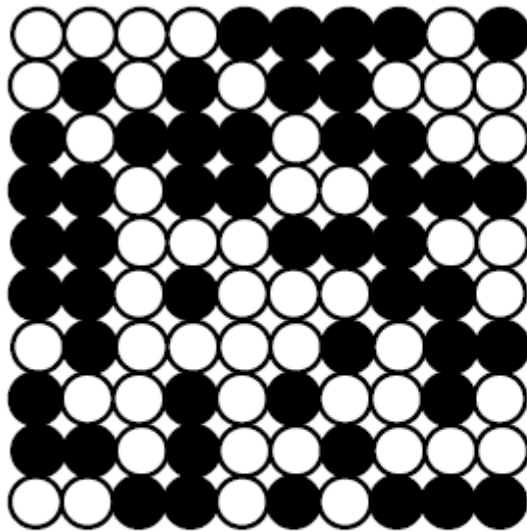
$$P_{AB} = N_a z X_A X_B \text{ bonds mol}^{-1}$$

If $\Omega < 0$ and the number of A-B bonds are greater than this, the solution is said to contain Short Range Order (SRO). The degree of SRO is quantified such as

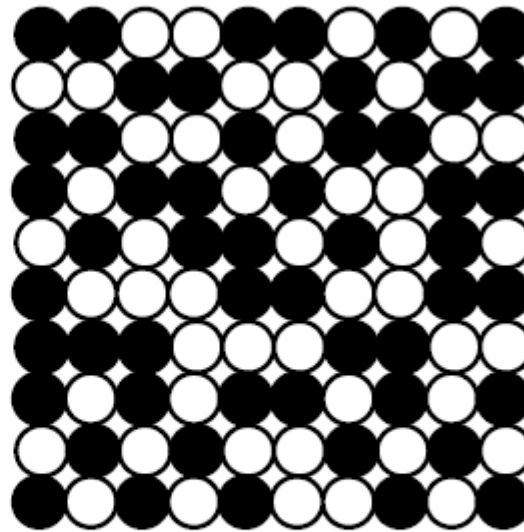
$$S = \frac{P_{AB} - P_{AB}(\text{random})}{P_{AB}(\text{max}) - P_{AB}(\text{random})}$$

; where $P_{AB}(\text{max})$ and $P_{AB}(\text{random})$ refers to maximum possible #of bonds and the #of bonds for a random solution, respectively.

Ordered Phases



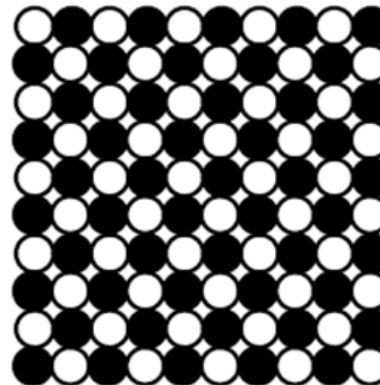
(a)



(b)

(a) Random A-B solution with a total of 100 atoms and $X_A = X_B = 0.5$, $P_{AB} \sim 100$, $S = 0$. (b) Same alloy with short-range order $P_{AB} = 132$, $P_{AB}(\text{max}) \sim 200$, $S = (132 - 100)/(200 - 100) = 0.32$.

In $P_{AB}(\text{max})$ case \longrightarrow long-range order

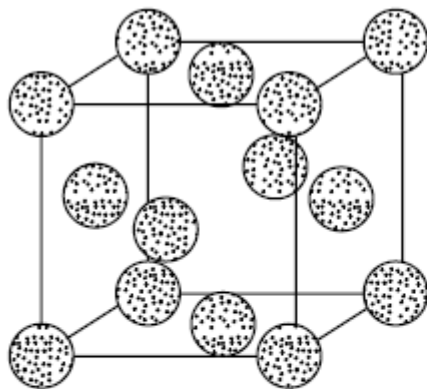


Example

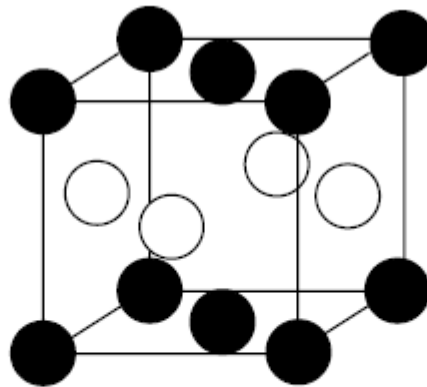
Cu-Au alloy, both FCC and totally soluble in each other.

At high T, Cu or Au atoms can occupy any lattice site randomly.

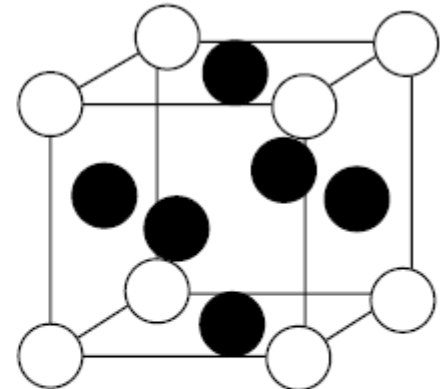
At low T, (and with $X_{\text{Cu}}=0,5$) they form an ordered structure in which Au and Cu are arranged in alternate layers (CuAu superlattice). Cu_3Au is another superlattice.



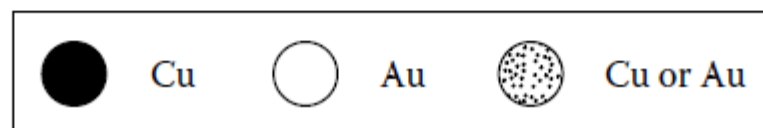
(a)



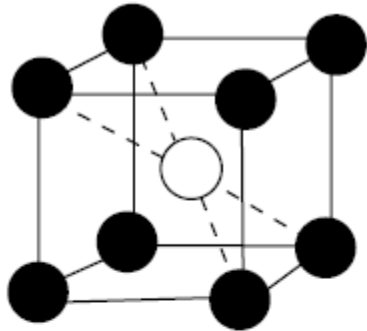
(b)



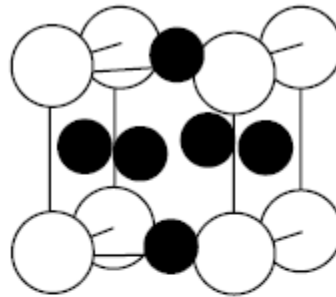
(c)



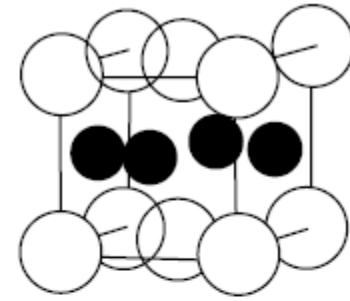
The most common ordered lattices in some other systems are illustrated.



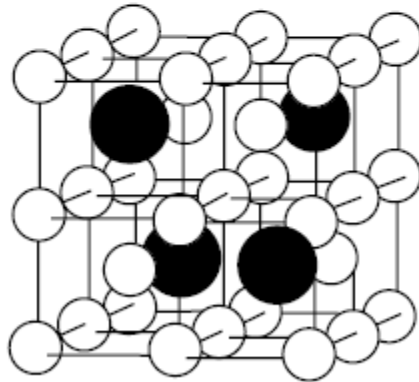
(a) ● Cu ○ Zn



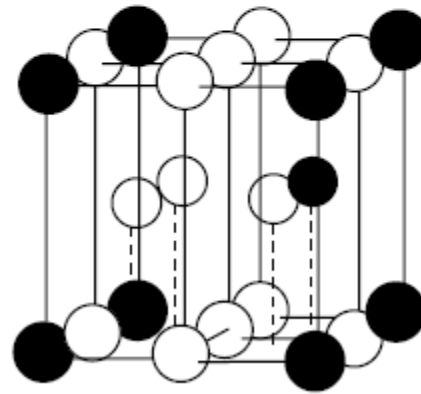
(b) ● Cu ○ Au



(c) ● Cu ○ Au



(d) ● Al ○ Fe



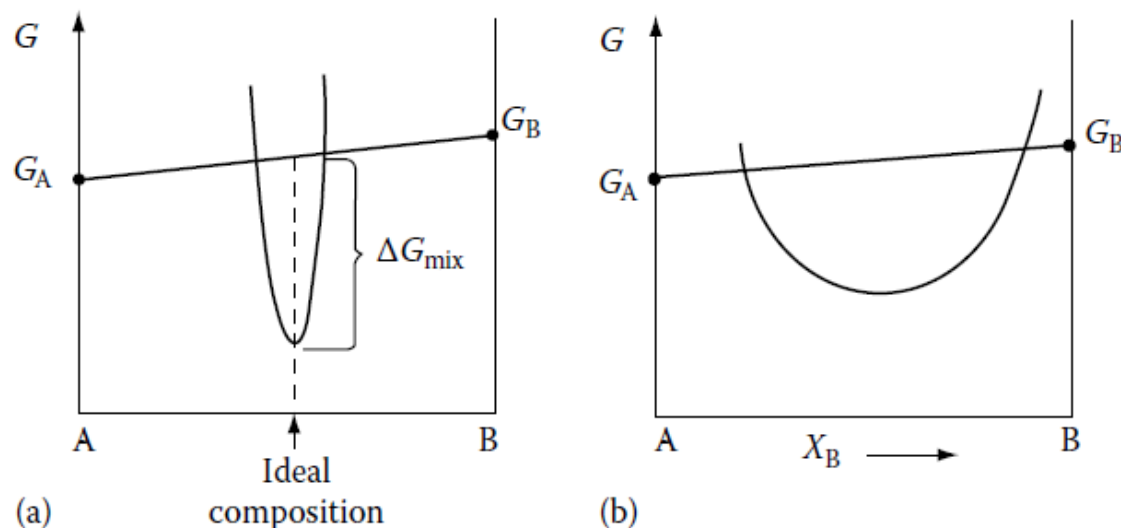
(e) ● Cd ○ Mg

Critical T for loss of LRO increases with increasing Ω , or ΔH_{mix} . In many systems LRO is stable up to melting T

Intermediate Phases

Often the configuration of atoms that has the minimum free energy after mixing does not have the same crystal structure as either of the pure components. In such cases the new structure is known as an *intermediate phase*.

Intermediate phases are often based on an ideal atom ratio that results in a minimum Gibbs free energy. For compositions that deviate from the ideal, the free energy is higher giving a characteristic 'U' shape to the G curve, as



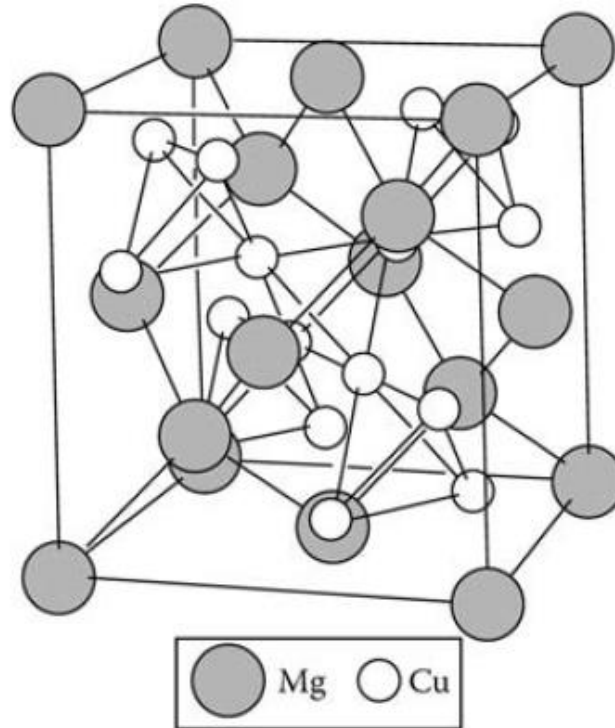
Free energy curves for intermediate phases: (a) for an intermetallic compound with a very narrow stability range, (b) for an intermediate phase with a wide stability range.

Intermediate Phases

The structure of intermediate phase is determined by 3 main factors;

- Atomic size
- Valency
- Electronegativity

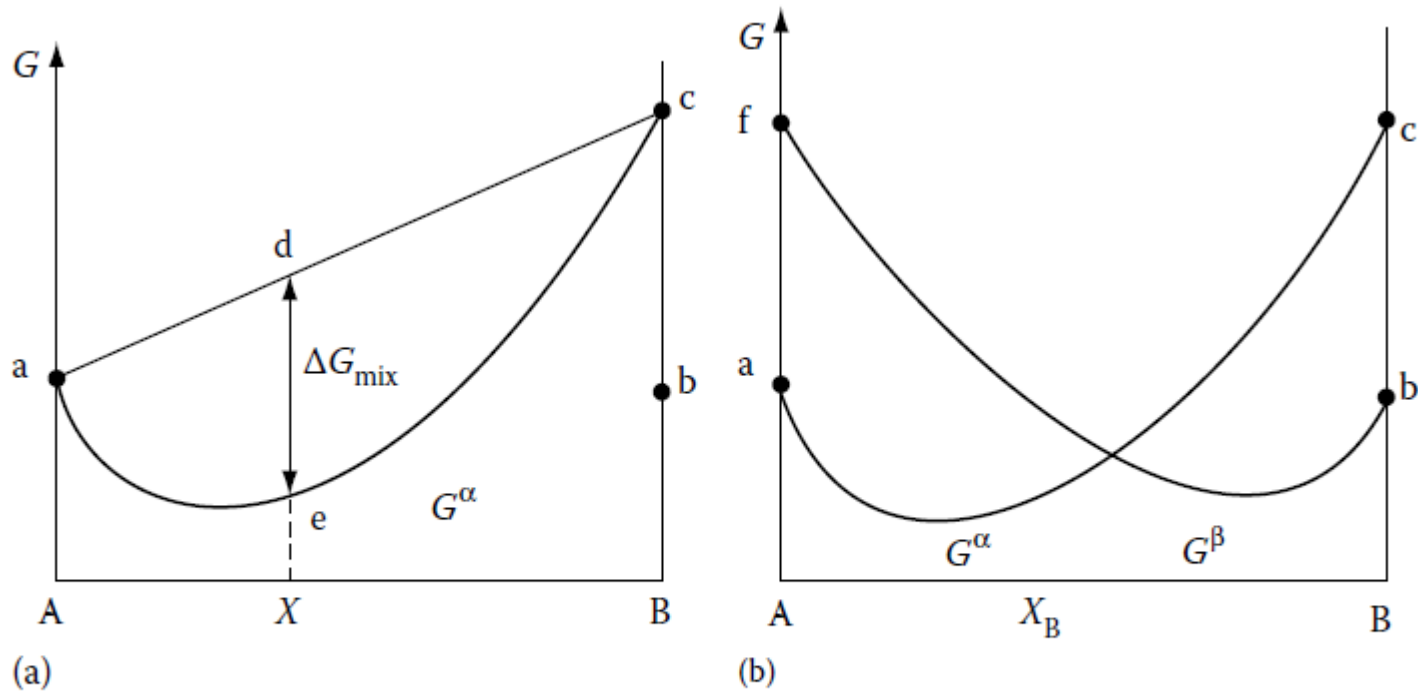
When the atoms differ in size about 1.1 – 1.6 it is possible to fill space most efficiently



The structure of MgCu_2 (A Laves phase). (From J.H. Wernick, chapter 5 in *Physical Metallurgy*, 2nd edn., R.W. Cahn (Ed.) North Holland, 1974.)

Equilibrium in Heterogeneous Systems

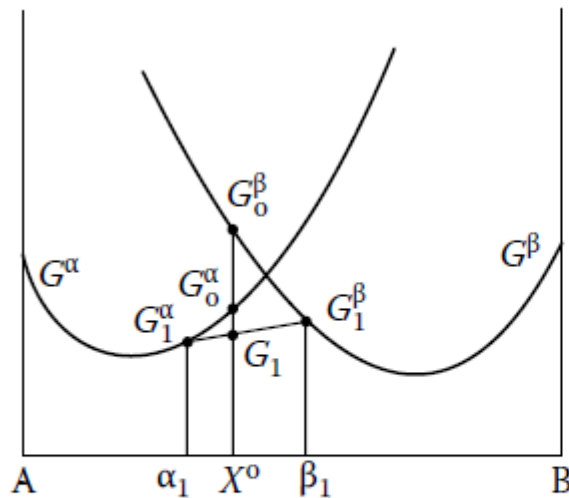
Usually A and B don't have the same crystal structure. Therefore 2 separate free energy curves must be drawn.



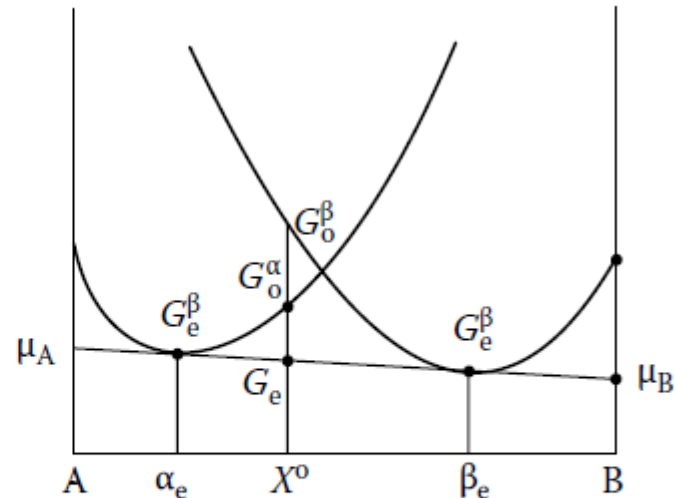
(a) The molar free energy curve for the α phase, (b) Molar free energy curves for α and β phases.

Equilibrium in Heterogeneous Systems

Suppose an alloy consists of 2 phases; α and β and their molar free energies are G^α and G^β , respectively.



(a)



(b)

(a) Alloy X^0 has a free energy G_1 as a mixture of $\alpha_1 + \beta_1$. (b) At equilibrium, alloy X^0 has a minimum free energy G_e when it is a mixture of $\alpha_e + \beta_e$.

Equilibrium in Heterogeneous Systems

Equilibrium btw 2 phases requires the common tangents to each G curve. Thus, each component have to have same chemical potential in the 2 phases.

$$\mu_A^\alpha = \mu_A^\beta, \quad \mu_B^\beta = \mu_B^\alpha$$

remember

$$\mu_A = G_A + RT \ln a_A$$

$$\mu_B = G_B + RT \ln a_B$$



$$a_A^\beta = a_A^\alpha, \quad a_B^\beta = a_B^\alpha$$

Thermodynamics and phase diagrams

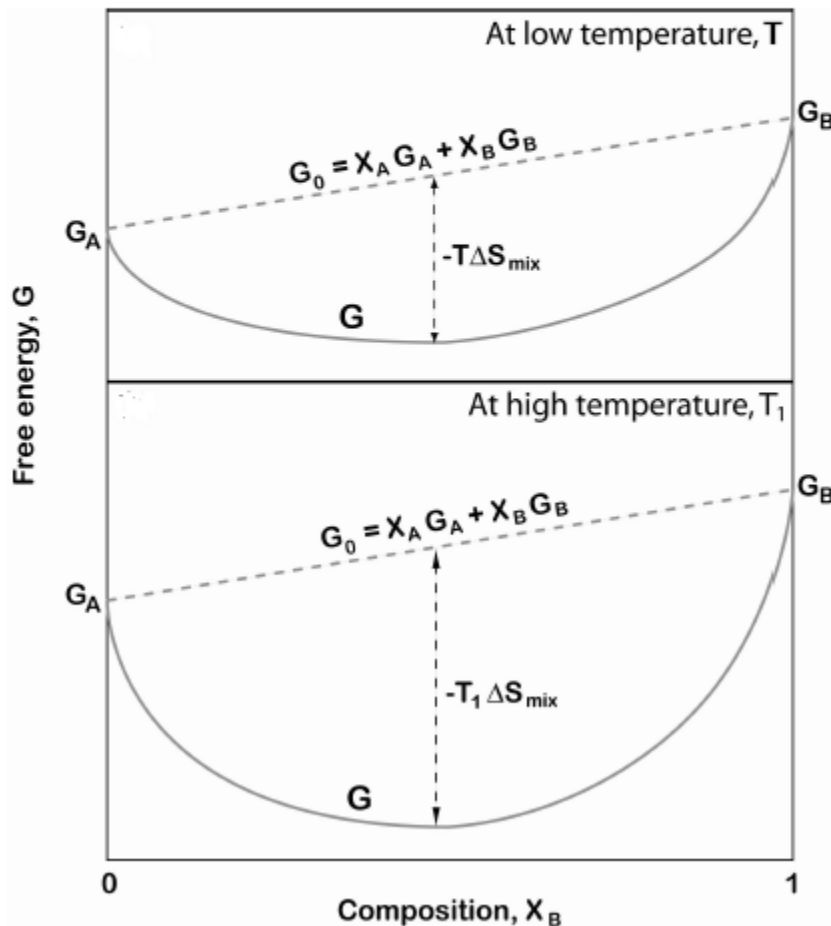
We need to consider three situations for different kinds of enthalpy of mixing

Situation 1: Enthalpy of mixing is zero

$$G = G_0 + \Delta G_{mix}$$

$$= G_0 - T\Delta S_{mix}$$

$$= X_A G_A + X_B G_B + RT[X_A \ln X_A + X_B \ln X_B]$$



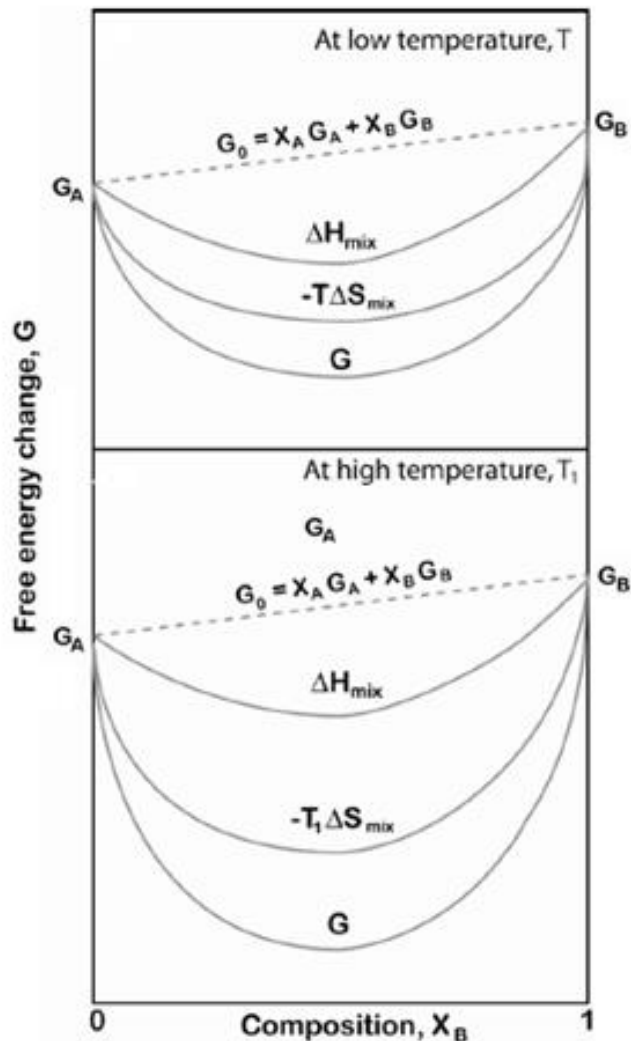
➤ With the increase in temperature, $-T\Delta S_{mix}$ will become even more negative.

➤ The values of G_A and G_B also will decrease.

➤ Following the slope G_0 might change since G_A and G_B will change differently with temperature.

Situation 2: Enthalpy of mixing is negative

$$G = \underbrace{X_A G_A + X_B G_B}_{G_0} + \underbrace{\Omega X_A X_B}_{\text{Negative } \Delta H_{\text{mix}}} + \underbrace{RT[X_A \ln X_A + X_B \ln X_B]}_{-T\Delta S_{\text{mix}}}$$



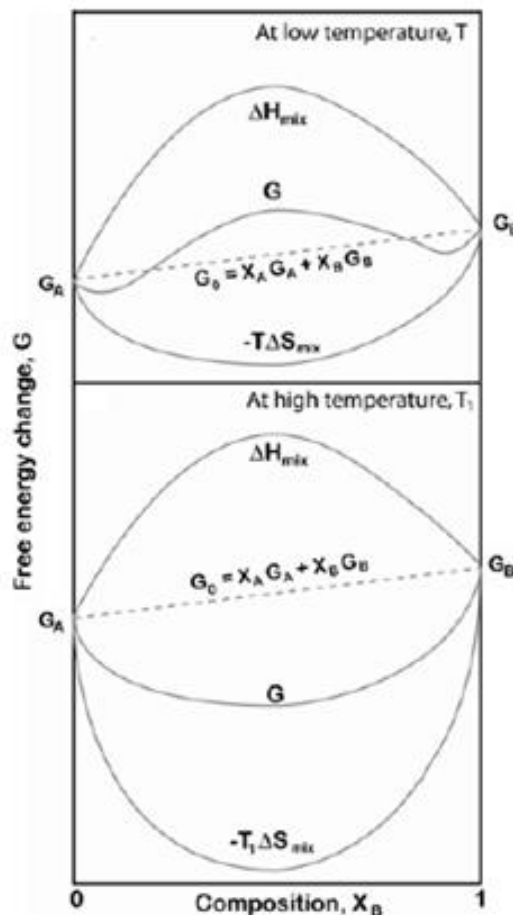
➤ Here both ΔH_{mix} and $-T\Delta S_{\text{mix}}$ are negative.

➤ With increasing temperature G will become even more negative.

➤ Note that here also G_0 may change the slope because of change of G_A and G_B differently with temperature.

Situation 3: Enthalpy of mixing is positive

$$G = \underbrace{X_A G_A + X_B G_B}_{G_0} + \underbrace{\Omega X_A X_B}_{\text{Positive } \Delta H_{\text{mix}}} + \underbrace{RT[X_A \ln X_A + X_B \ln X_B]}_{-T\Delta S_{\text{mix}}}$$

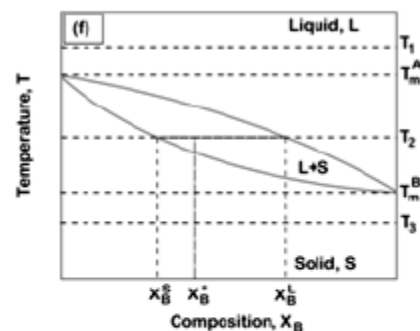
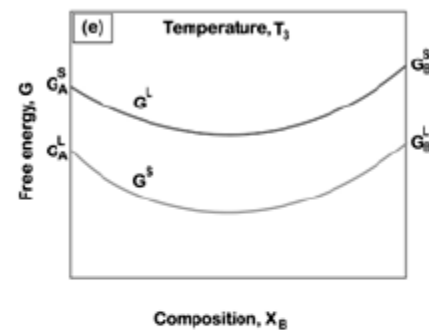
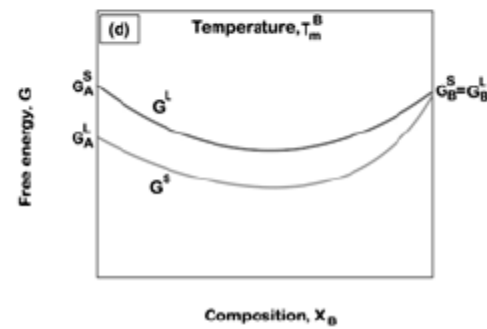
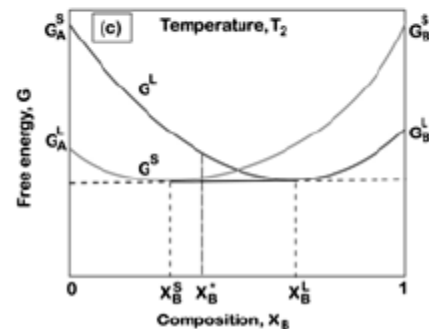
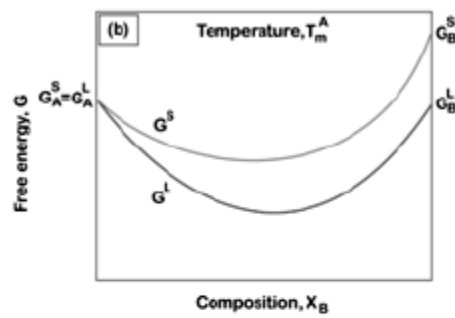
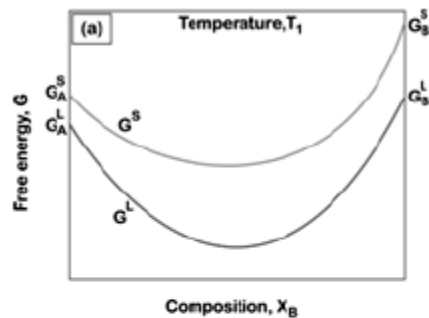


➤ ΔH_{mix} is positive but $-T\Delta S_{\text{mix}}$ is negative. At lower temperature, in a certain mole fraction range the absolute value of ΔH_{mix} could be higher than $T\Delta S_{\text{mix}}$ so that G goes above the G_0 line.

➤ However, close to G_A and G_B , G will always be lower than G_0 , since ΔH_{mix} has a finite slope, whereas ΔS_{mix} has infinite slope. The composition range, where G is higher than G_0 will depend on the temperature i.e. $-T\Delta S_{\text{mix}}$.

➤ Because of this shape of the G , we see miscibility gap in certain phase diagrams.

➤ At higher temperature, when the absolute value of $T\Delta S_{\text{mix}}$ will be higher than ΔH_{mix} at all compositions, G will be always lower than G_0 .



➤ With decreasing temperature, free energy for the solid, G^S and liquid phase G^L will change differently with different rates of change of G_A and G_B .

➤ At higher temperature, $G^L < G^S$ (Fig. a), so that the liquid phase is stable. At lower temperature $G^S < G^L$ (Fig. e) so that the solid phase is stable.

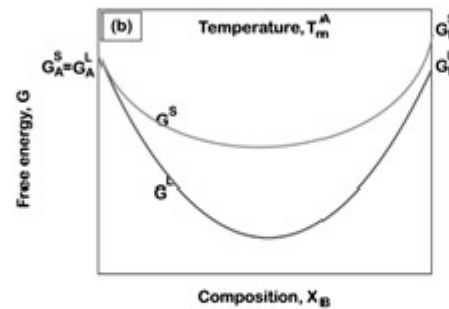
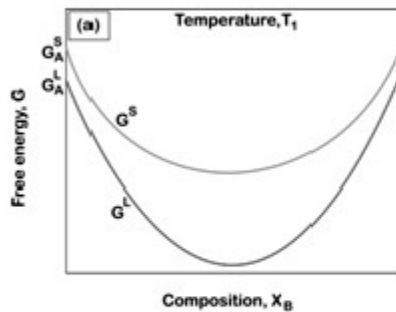
➤ In between, G^S and G^L intersects to find the situation as explained in Fig. c.

➤ Common tangent drawn gives the composition range where both solid and liquid phases can be found together.

➤ That means, if the average composition is X_B^* as shown in the phase diagram, it will have the solid phase with composition of X_B^S and the liquid phase with composition of X_B^L . Phase fractions can be found with the help of Lever rule.

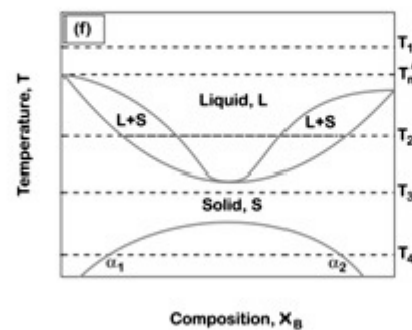
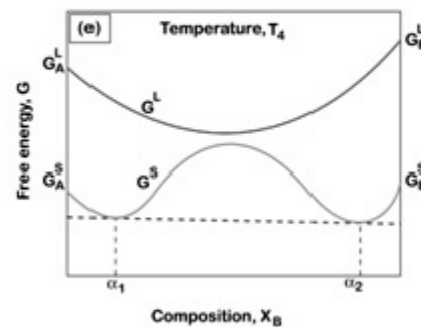
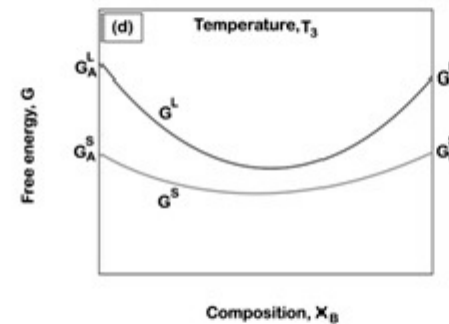
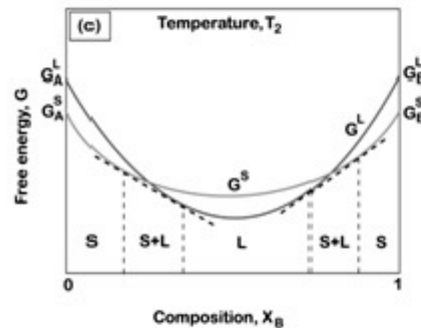
➤ Both the liquid and solid phases can stay together because overall free energy will be less than the free energy when considered separately.

➤ Further clarifications will be given once the concept of chemical potential of elements is introduced.

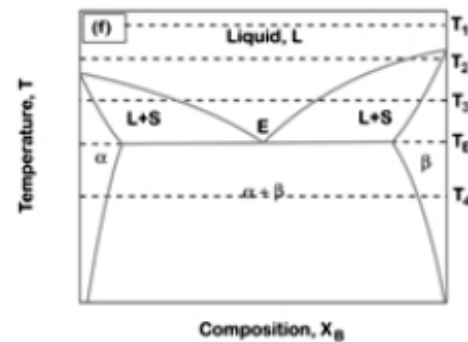
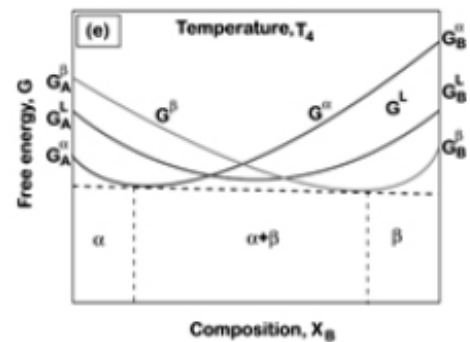
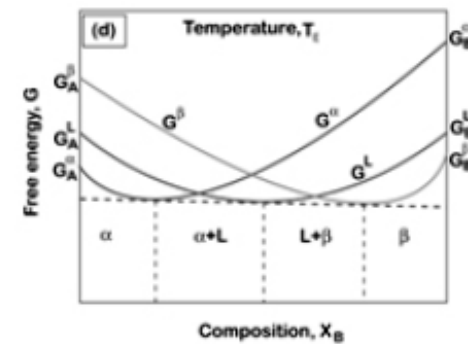
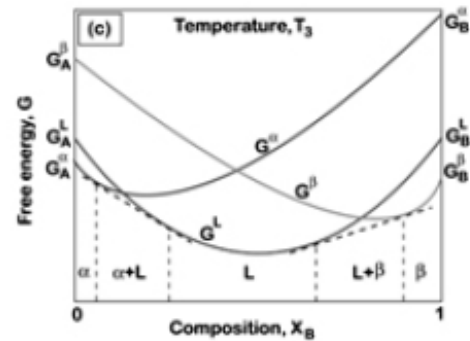
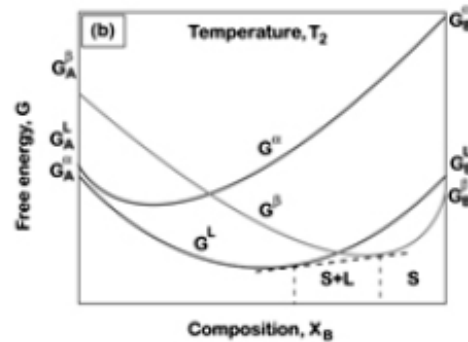
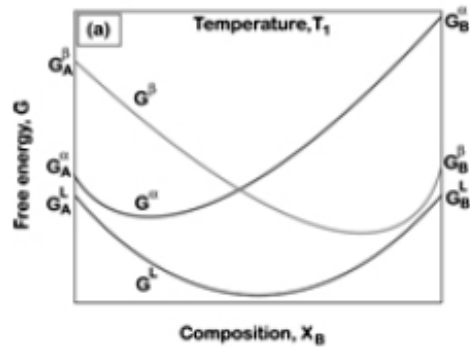


➤ This kind of phase diagram is found when the system has positive enthalpy of mixing, especially for the solid phase.

➤ Because of the shape of the G^S at low temperature as shown in Fig. e, it is possible to draw a common tangent, which indicates that the solid phase with the average composition between α_1 and α_2 , will have a phase separation. This corresponds to the miscibility gap in the phase diagram.



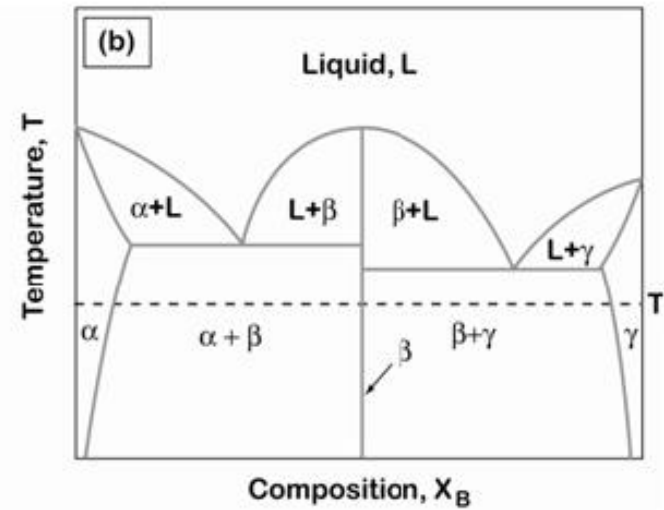
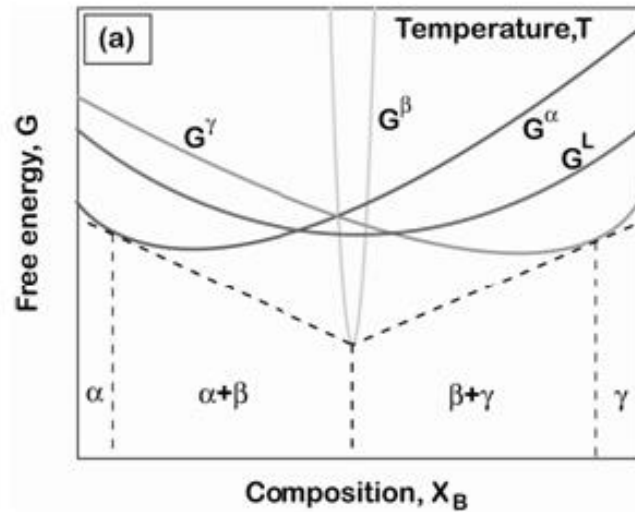
➤ It may also come to the situation, as it is shown in Fig. c, G^L and G^S intersects twice. In that case these will be two separate regions where both the solid and liquid phases coexist.



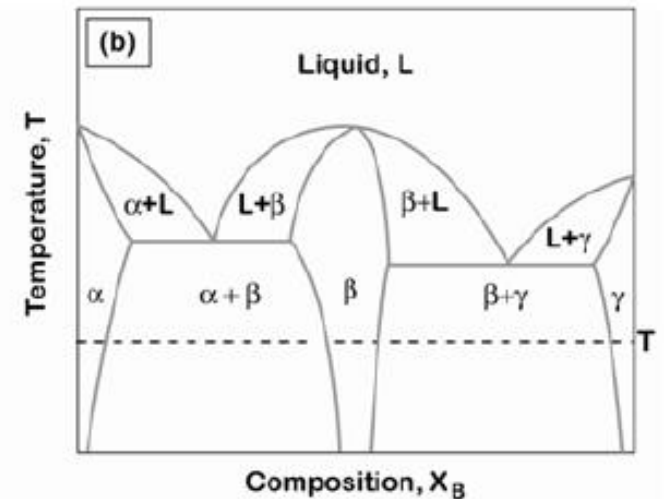
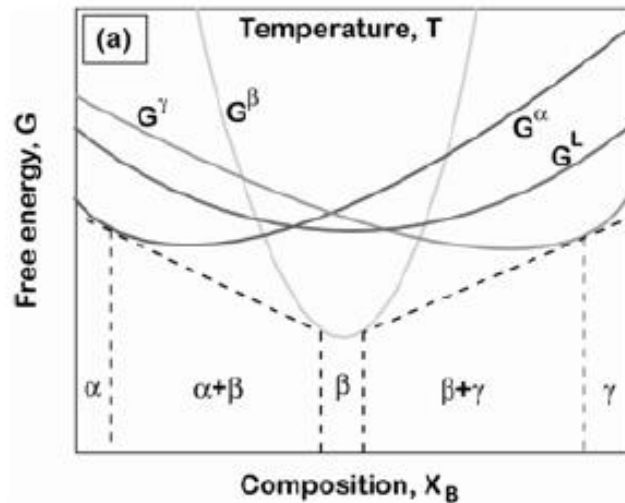
➤ In this system, there are two solid state phases and one liquid phase. So three free energy curves should be considered.

➤ At certain temperature, T_E , one common tangent can be drawn, which will touch all the free energy curves.

➤ This indicates that all the three phases at a particular composition E, as shown in Fig. d and f can coexist. This is called eutectic point.



β phase is an intermetallic compound that is an ordered phase with very narrow homogeneity range.



Sometimes β phase can be found with wider homogeneity range.