PHASE TRANSFORMATION AND HEAT TREATMENT OF MATERIALS

MODULE I

METALLURGICAL AND MATERIAL'S ENGINEERING
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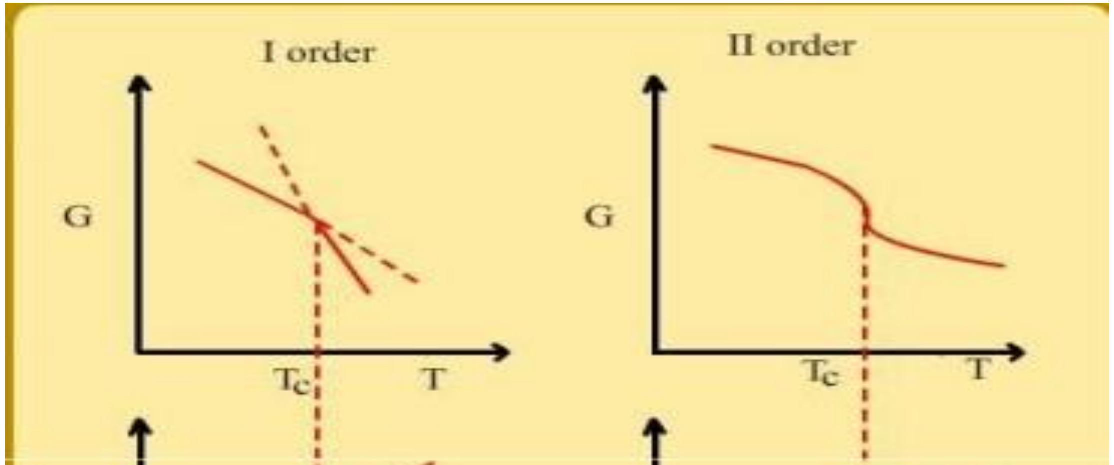
DISCLAIMER

INTRODUCTION

Phase is defined as the physically homogeneous state of matter, where the phase has the same chemical composition and has its own distinct physical and mechanical properties. Many alloys have different phases at the same time.

Phase diagram is a graphical representation of the physical states of a substance’s under different conditions of temperature and pressure. The most common phase diagram is the water system where the axis of the graph represents pressure and temperature as shown below



This figure represents the thermodynamics classification of order of derivative with respect to temperature, the 1st order is represented by the discontinuity in the slope

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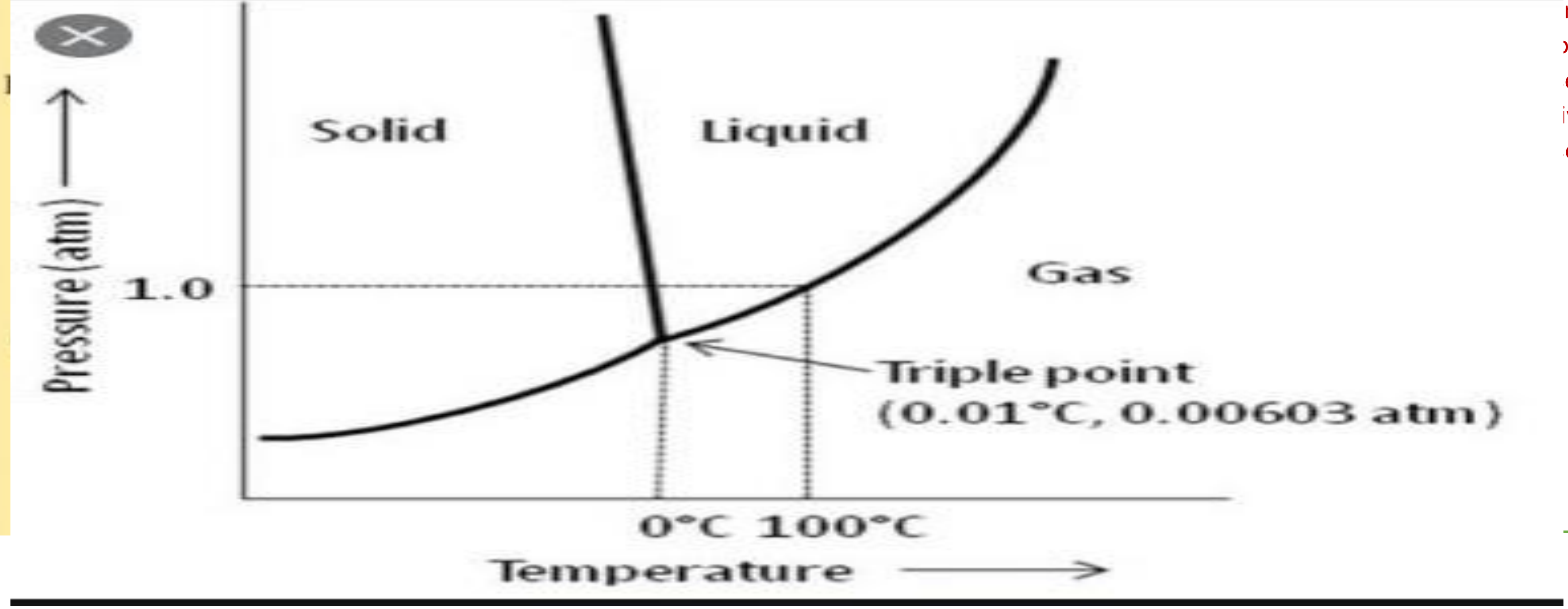


Phase transformation occur when there is a change in composition and structure. The transformation can be caused by a change in temperature or it reacts with other materials. Most of the characteristics of transformation involves change in gibbs free energy and temperature or composition. We know that whenever a phase changes there is a decrease in free energy of the system so according to changes in thermodynamic parameter with respect to change in other parameters the orders of transformation are classified. Whereas the phase transformation is classified as according to thermodynamics, kinetics and mechanism

ZEROTH LAW OF THERMODYNAMICS:

IT TELLS THE EQUILIBRIUM OF THE SYSTEM. IF OBJECT A IS EQUILIBRIUM WITH OBJECT B AND OBJECT B IS EQUILIBRIUN WITH OBJECT C THEN BOTH A AND C WILL REMAIN IN EQILIBRIUM

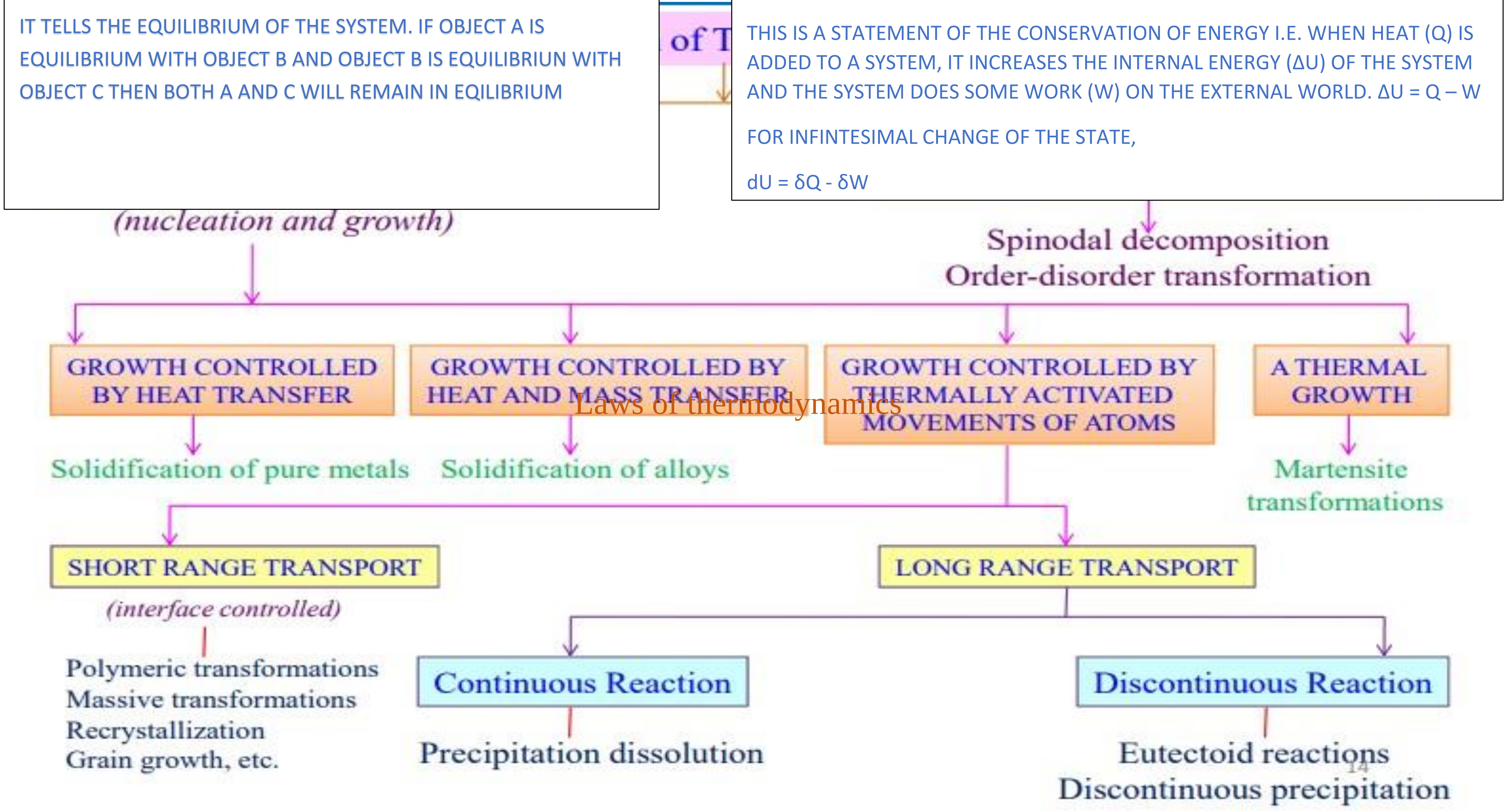
1^{ST} LAW OF THERMODYNAMICS:

THIS IS A STATEMENT OF THE CONSERVATION OF ENERGY I.E. WHEN HEAT (Q) IS ADDED TO A SYSTEM, IT INCREASES THE INTERNAL ENERGY (ΔU) OF THE SYSTEM AND THE SYSTEM DOES SOME WORK (W) ON THE EXTERNAL WORLD. $\Delta U = Q - W$

FOR INFINTESIMAL CHANGE OF THE STATE,

$dU = \delta Q - \delta W$

Laws of thermodynamics



(nucleation and growth)

Spinodal decomposition
Order-disorder transformation

GROWTH CONTROLLED BY HEAT TRANSFER

Solidification of pure metals

GROWTH CONTROLLED BY HEAT AND MASS TRANSFER

Solidification of alloys

GROWTH CONTROLLED BY THERMALLY ACTIVATED MOVEMENTS OF ATOMS

A THERMAL GROWTH

Martensite transformations

SHORT RANGE TRANSPORT

(interface controlled)

Polymeric transformations
Massive transformations
Recrystallization
Grain growth, etc.

LONG RANGE TRANSPORT

Continuous Reaction

Precipitation dissolution

Discontinuous Reaction

Eutectoid reactions
Discontinuous precipitation

INTENSIVE PROPERTY: The property which are independent of the size of the system are known as intensive property

Ex: P, T, molar volume etc

EXTENSIVE PROPERTY: The property which are dependent on the size of the system are known as extensive property

Ex: Gibbs free energy, volume, enthalpy, entropy

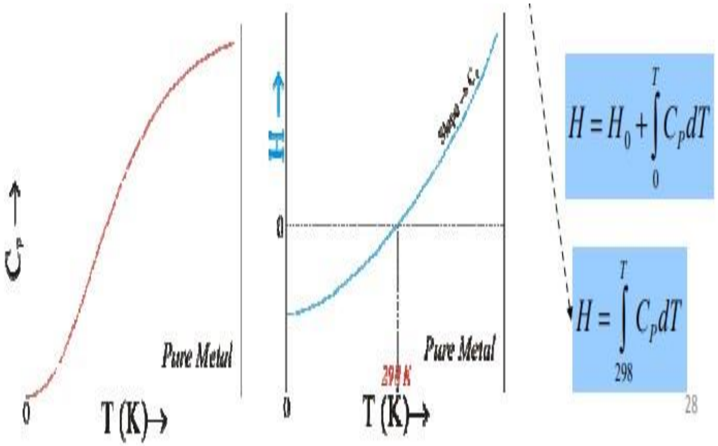
Enthalpy

H = INTERNAL ENERGY + PV

MEASURES THE HEAT CONTENT OF THE SYSTEM

FOR CONDENSED PHASE H ~ E

SLOPE OF H AND T GIVES Cp



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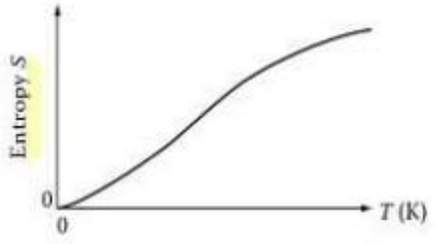
THIRD LAWS OF THERMODYNAMICS:

The entropy of a perfect crystal is zero when the temperature of the crystal is equal to absolute zero (0 K).



ENTROPY

IT MEASURES THE ENTROPY OF THE SYSTEM

ENTROPY ALWAYS TAKES PLACE WHENEVER A REACTION’S OCCURS

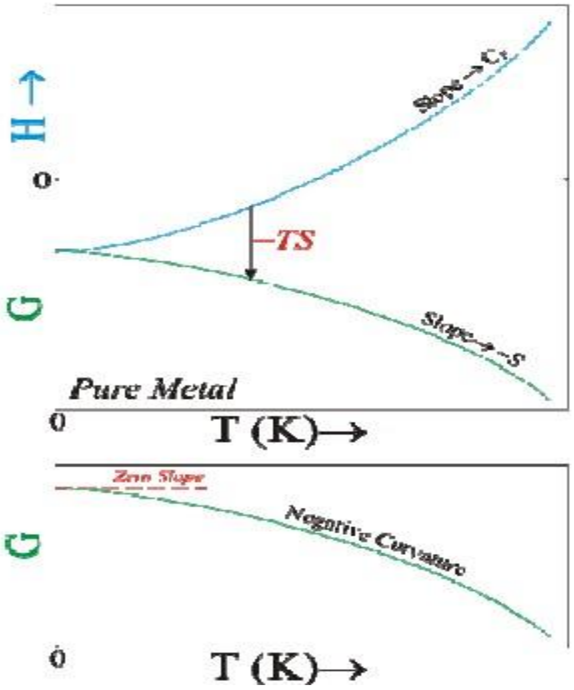
TWO TYPES: THERMAL AND CONFIGURATIONAL ENTROPY

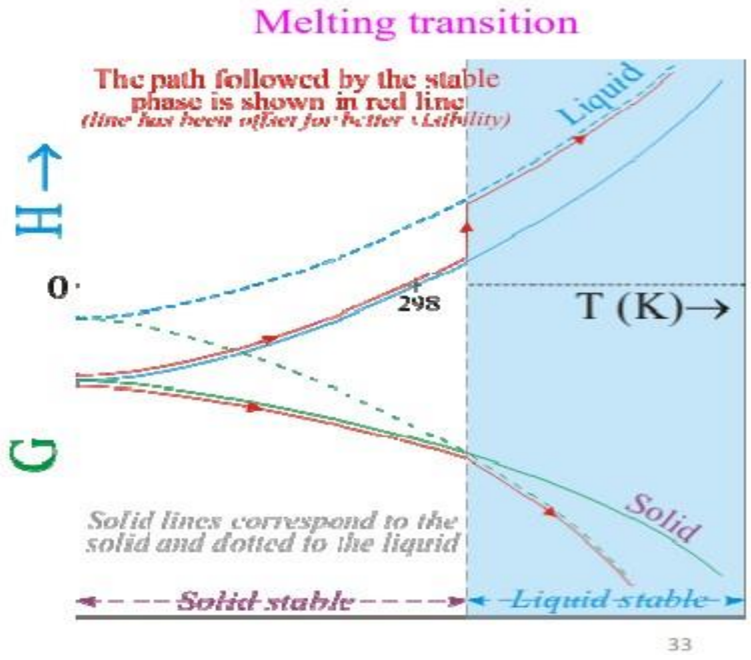
GIBB'S FREE ENERGY

- G is defined by G = H – TS , where T = temperature, H = enthalpy and S = entropy
- G always decreases when a reaction is followed
- ΔG = -ve(spontaneous), ΔG = +ve(non-spontaneous)
- For a reaction to take place spontaneously the system has to reduce its Gibbs Free Energy (at constant P & T). For a system to go from 'state' 1 → 2 the change in G would be:

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

Even during endothermic reaction, the G value decreases because at high temperature the entropy increases thus decreases the G value





CHANGE IN FREE ENERGY DUE TO MIXING OF TWO ELEMENT

CHANGE IN ENTROPY DUE TO MIXING

$\Delta S = k\ln\omega$ where ω = no of ways an atom is placed in a lattice point

Where $\omega = \frac{(nA+nB)!}{nA!nB!}$ where nA and nB are numbers of atoms A and B

Following Sterling's approximation $\ln N! = N\ln N - N$ and putting the value

$nA = X_AN_o$

$nB = X_BN_o$ in the above expression we get

$\Delta S = -kN(X_A\ln X_A + X_B\ln X_B)$

$\Delta S = -R(X_A\ln X_A + X_B\ln X_B)$

ENTHALPHY OF MIXING

After mixing the system can have different bonding likes A-A, B-B and A-B bond, depending upon the energy of the bond the sign of ΔH is decided

So we can expressed $\Delta H = ZN_0X_AX_B\Delta\varepsilon$, where $\Delta\varepsilon = \varepsilon_{AB} - \frac{\varepsilon AA+\varepsilon BB}{2}$

So, finally the $\Delta H = \Omega X_AX_B$

For the following condition, ΔH value will be

$\Delta H = 0$(for unlike and like bonds equal or ideal condition)

$\Delta H < 0$(unlike bond favourable)

$\Delta H > 0$(like bond favourable)

So depending upon the ΔH value the tendency for ordering is decided and the graph for G is plotted and the curve is different for for different condition.

FREE ENERGY OF MIXING

SITUATION: ENTHALPY OF MIXING IS ZERO

$G = = X_AG_A + X_BG_B + RT(X_A\ln X_A + X_B\ln X_B)$

G will decrease with increase in temperature

THIS IS THE CASE FOE IDEAL SOLUTION ALSO

SITUATION: ENTHAPY OF MIXING IS NEGATIVE

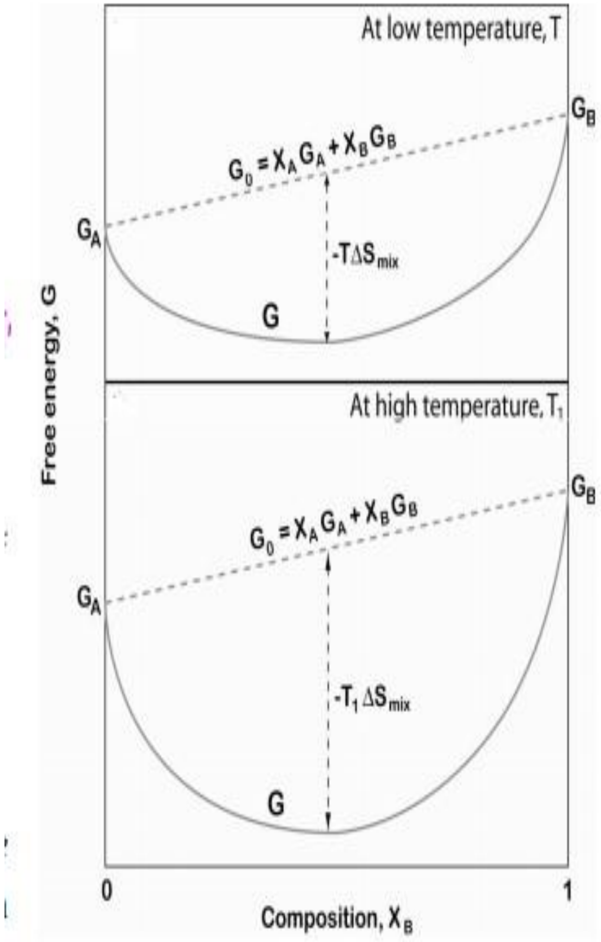
$G = X_AG_A + X_BG_B + \Omega X_AX_B + RT\ (X_A \ln X_A + X_B \ln X_B)$

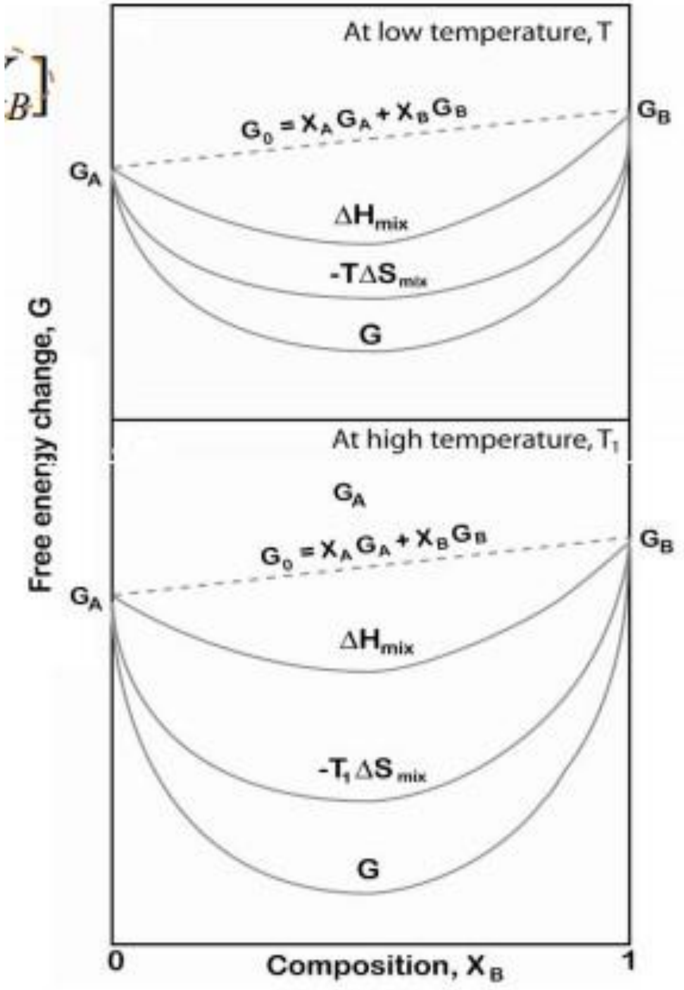
G will decrease more with increase in temperature because of negative enthalpy

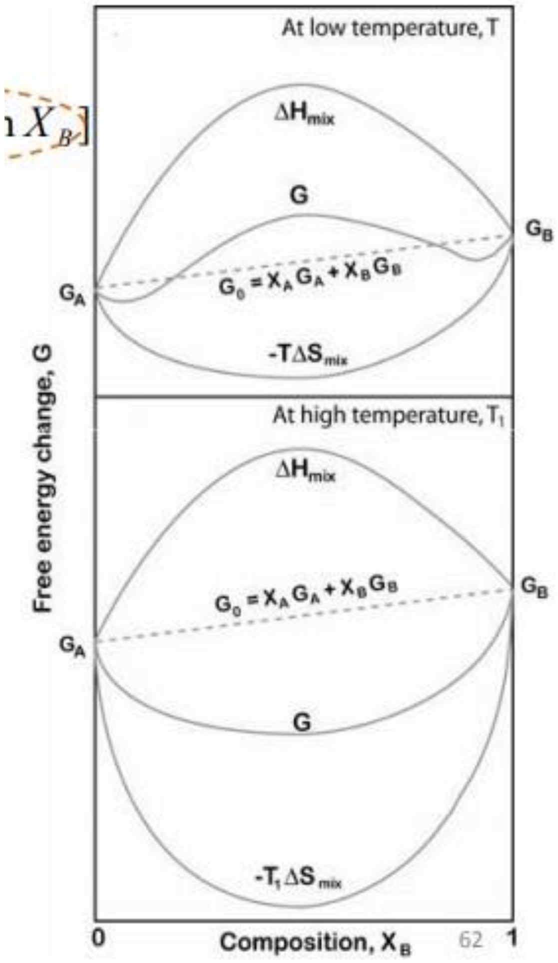
SITUATION: ENTHALPY OF MIXING IS POSITIVE

$G = X_AG_A + X_BG_B + \Omega X_AX_B + RT\ (X_A \ln X_A + X_B \ln X_B)$

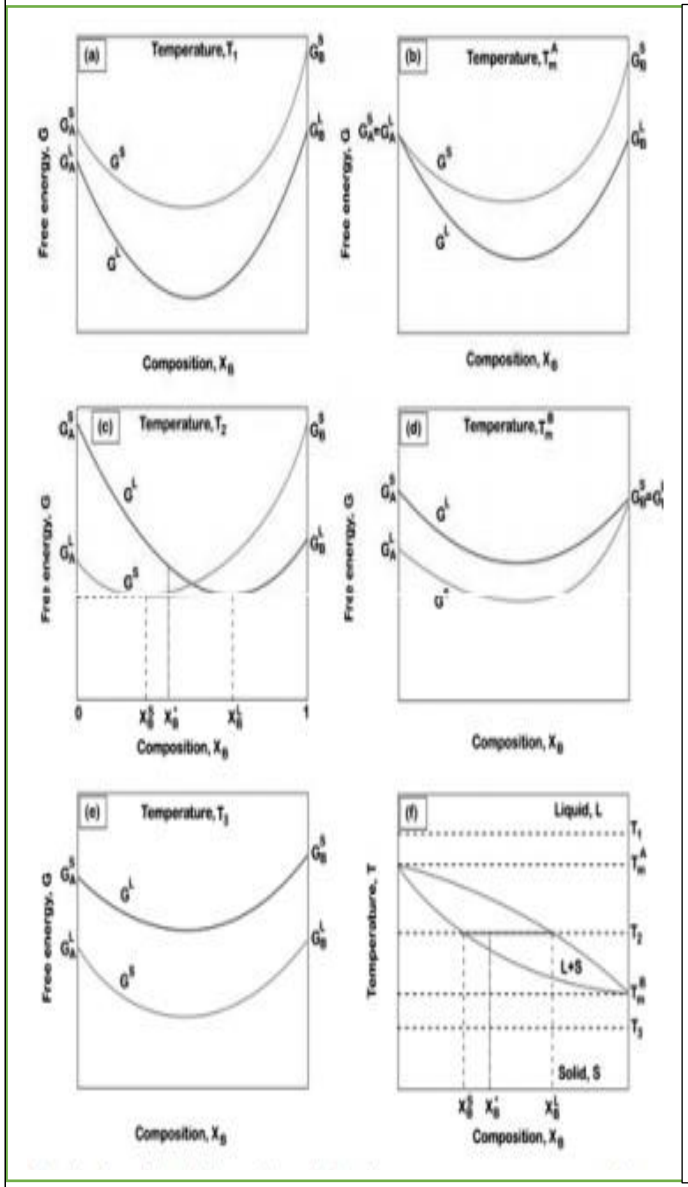
G will increase at lower temperature whereas G will decrease at higher temperature

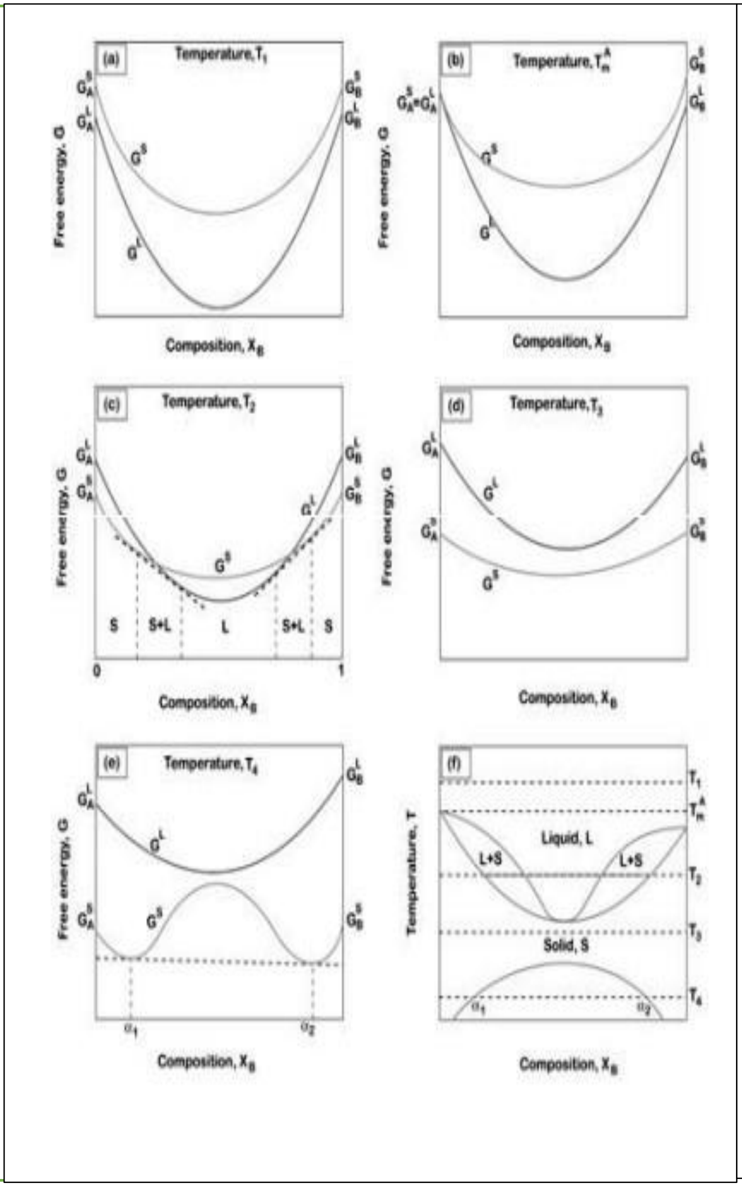

At low temperature, T
G_B
$G_0 = X_A G_A + X_B G_B$
G_A
$-T\Delta S_{mix}$
G
At high temperature, T_1
G_B
$G_0 = X_A G_A + X_B G_B$
G_A
$-T_1\Delta S_{mix}$
G
Free energy, G
0
1
Composition, X_B

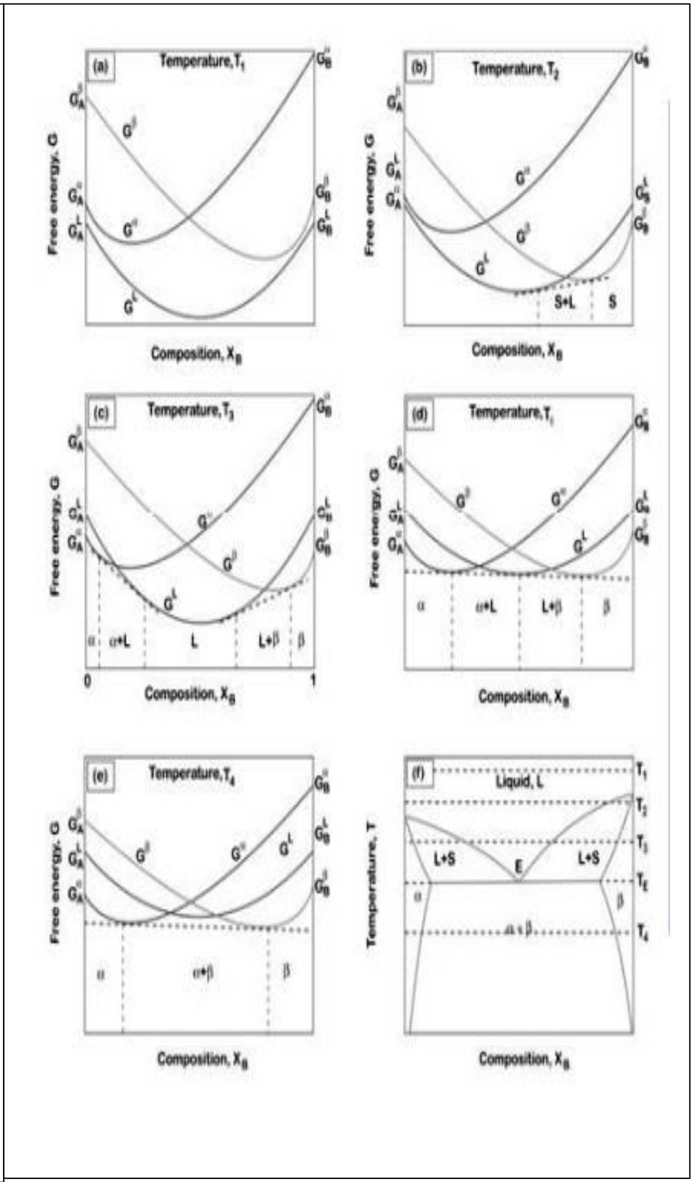

At low temperature, T
G_B
$G_0 = X_A G_A + X_B G_B$
G_A
ΔH_{mix}
$-T\Delta S_{mix}$
G
At high temperature, T_1
G_A
$G_0 = X_A G_A + X_B G_B$
G_B
G_A
ΔH_{mix}
$-T_1\Delta S_{mix}$
G
Free energy change, G
0
1
Composition, X_B


At low temperature, T
ΔH_{mix}
G
G_B
$G_0 = X_A G_A + X_B G_B$
G_A
$-T\Delta S_{mix}$
At high temperature, T_1
ΔH_{mix}
$G_0 = X_A G_A + X_B G_B$
G_B
G_A
G
$-T_1\Delta S_{mix}$
Free energy change, G
0
1
Composition, X_B
62

FREE ENERGY VS COMPOSITION PHASE DIAGRAM

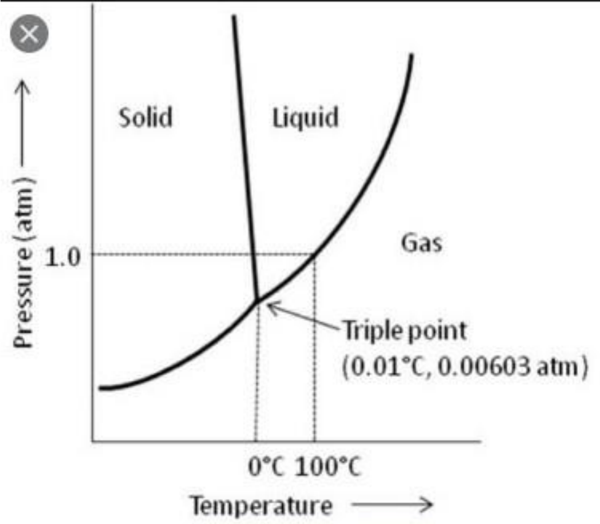






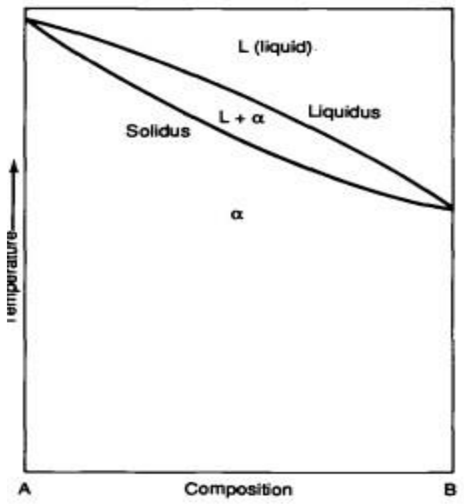
TYPES OF PHASE DIAGRAM

UNARY PHASE DIAGRAM



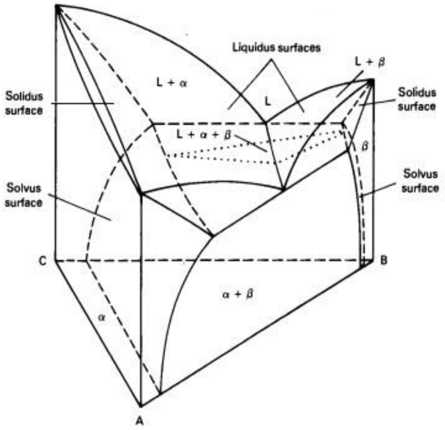
- SINGLE COMPONENT SYSTEM
- AT TRIPLE POINT IN THE PHASE DIAGRAM THE DEGREE OF FREEDOM IS ZERO

BINARY PHASE DIAGRAM



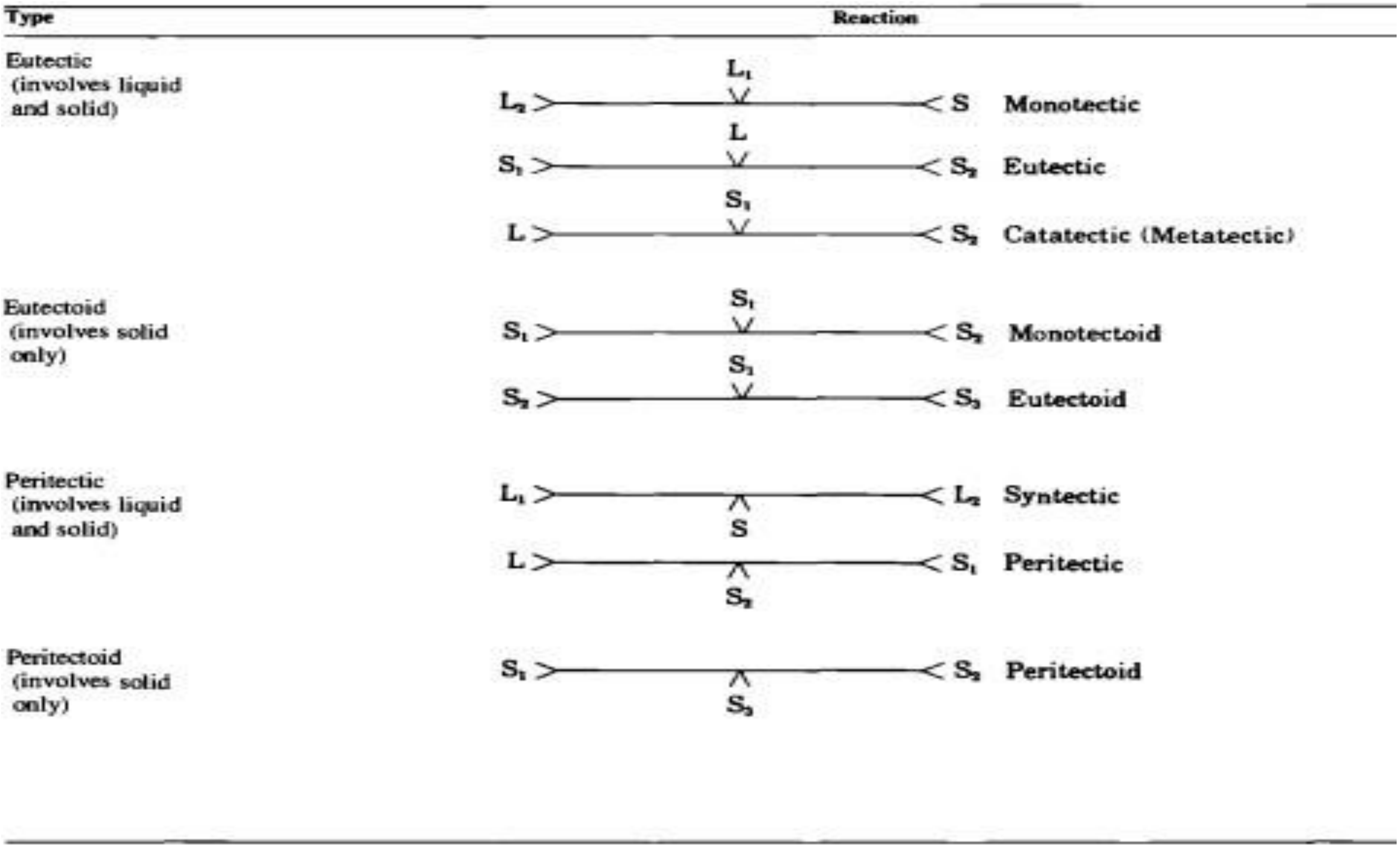
- TWO COMPONENT SYSTEM
- TWO SINGLE PHASE FIELD IS DIVIDED BY TWO PHASE FIELD
- ALL BINARY PHASE ARE DRAWN WITH P=1(CONDENSED PHASE)

TERNARY PHASE DIAGRAM



- THREE COMPONENT SYSTEM
- PROJECTION OF ISOTHERMAL SECTION ON TWO DIMENSIONS EQUILATERIAL TRAINGLE ARE USED TO FIND OUT THE COMPOSITION

INVARIANT REACTION IN A PHASE DIAGRAM

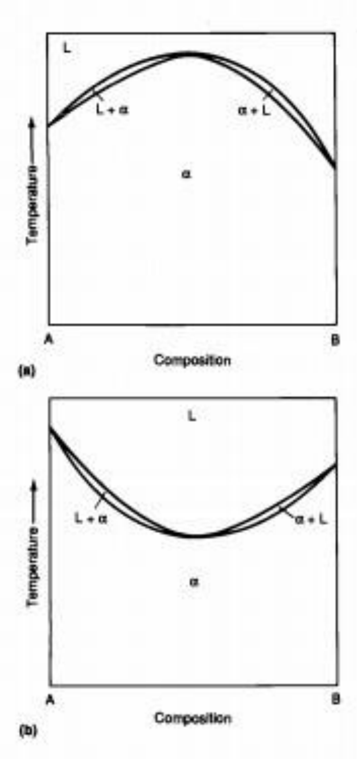


Type	Reaction	
Eutectic (involves liquid and solid)	$L_2 > \overset{L_1}{\vee} < S$	**Monotectic**
	$S_1 > \overset{L}{\vee} < S_2$	**Eutectic**
	$L > \overset{S_1}{\vee} < S_2$	**Catatectic (Metatectic)**
Eutectoid (involves solid only)	$S_1 > \overset{S_1}{\vee} < S_2$	**Monotectoid**
	$S_2 > \overset{S_1}{\vee} < S_3$	**Eutectoid**
Peritectic (involves liquid and solid)	$L_1 > \underset{S}{\wedge} < L_2$	**Syntectic**
	$L > \underset{S_2}{\wedge} < S_1$	**Peritectic**
Peritectoid (involves solid only)	$S_1 > \underset{S_3}{\wedge} < S_2$	**Peritectoid**

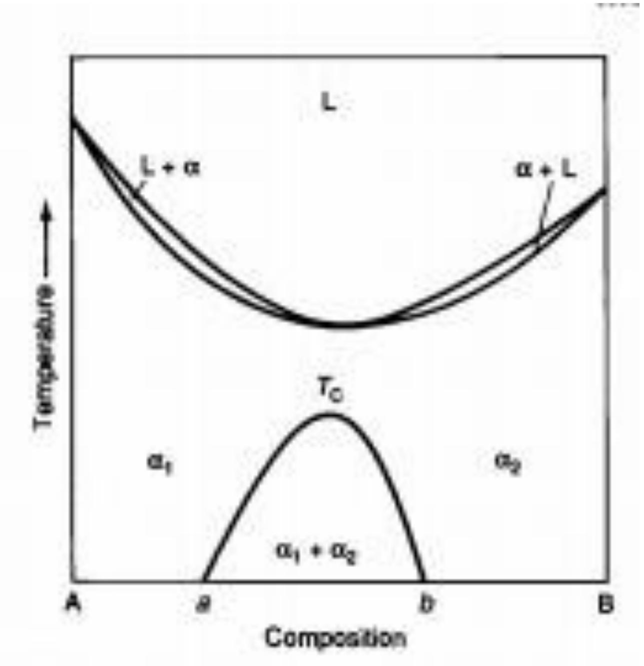
MISCIBILITY GAP IN A PHASE DIAGRAM

In common binary system, two single phase field is separated by a two phase field. The boundary between the liquid field and the two phase field is called the liquidous as shown in above figure and the boundary between two phase and solid phase is called the solidus. The phases in equilibrium across the two phases are called the CONJUGATE PHASES.

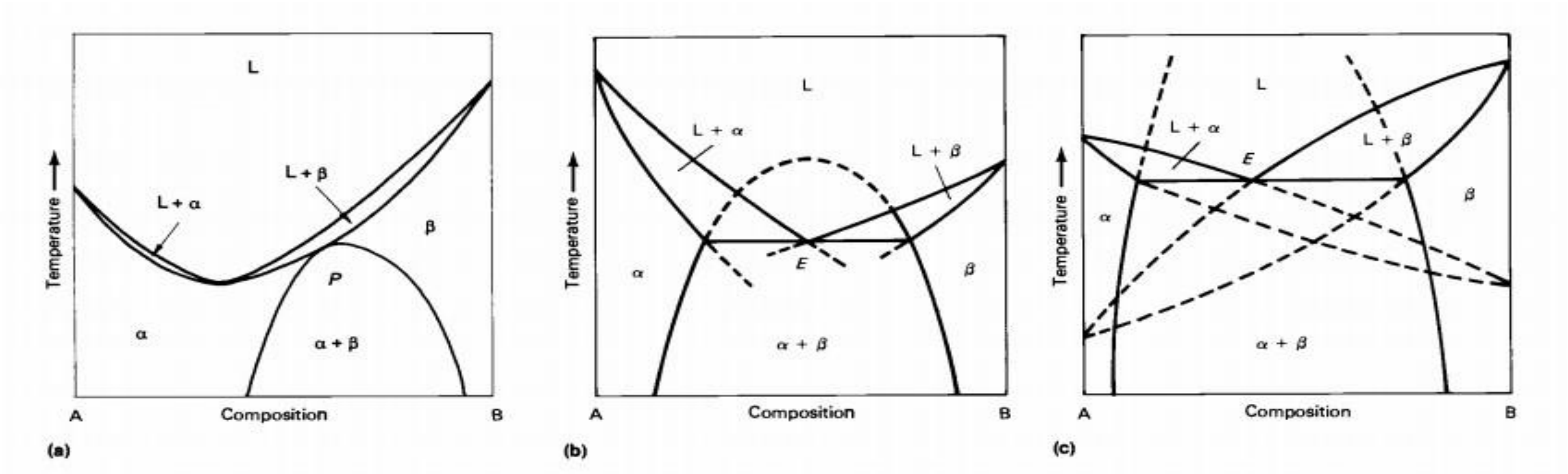
Miscibility arises when the solidus and liquidus meet tangentially at some point, a maximum or minimum is produced in the two portions as shown in figure. Another type of miscibility gap arises where two phases are indistinguishable as shown below. The solid separating from two solid phase field is called solvus line and it indicates the solubility of component A in B and B in A.



Schematic binary phase diagrams with solidstate miscibility where the liquidus shows a maximum (a) and a minimum (b)

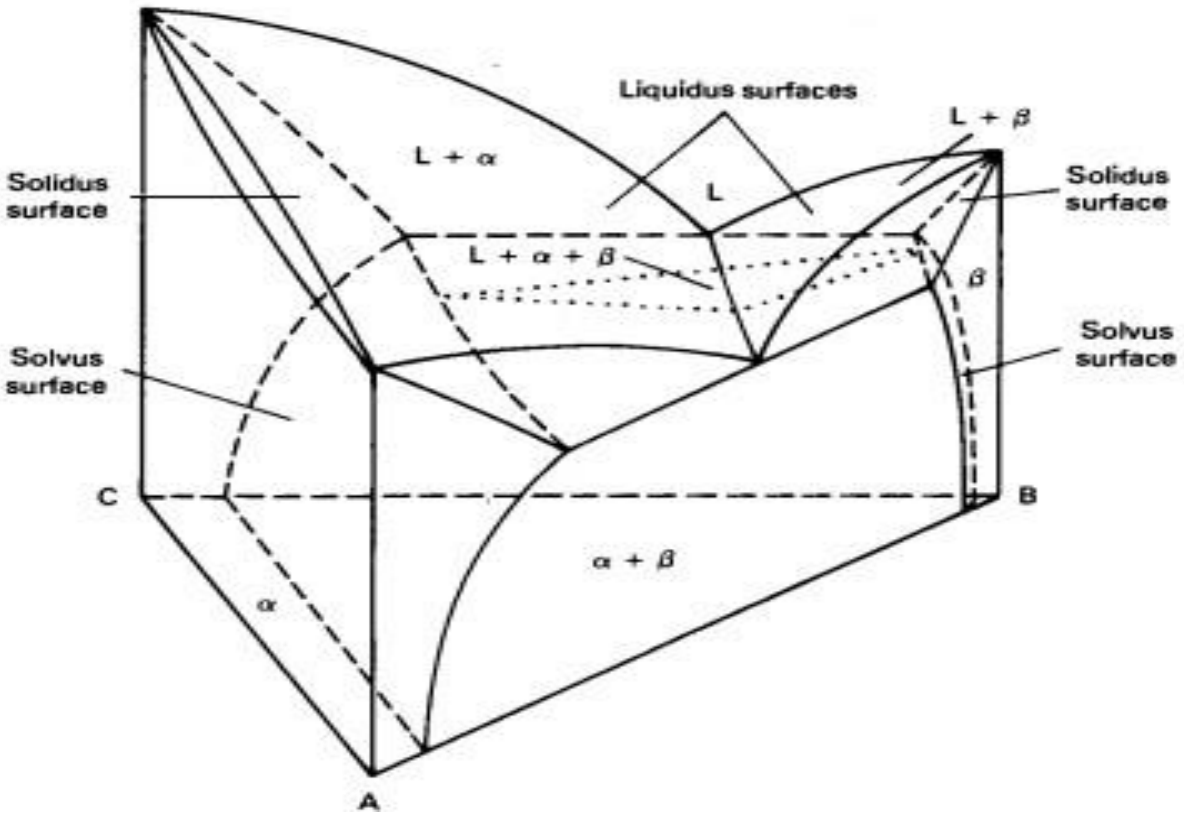


Schematic binary phase diagram with a minimum in the liquidus and a miscibility gap in the solid state



Schematic binary phase diagrams with invariant points. (a) Hypothetical diagram of the type shown in F, except that the miscibility gap in the solid touches the solidus curve at invariant point P; an actual diagram of this type probably does not exist. (b) and (c) Typical eutectic diagrams for components having the same crystal structure (b) and components having different crystal structures (c); the eutectic (invariant) points are labeled E. The dashed lines in (b) and (c) are metastable extensions of the stable-equilibria lines.

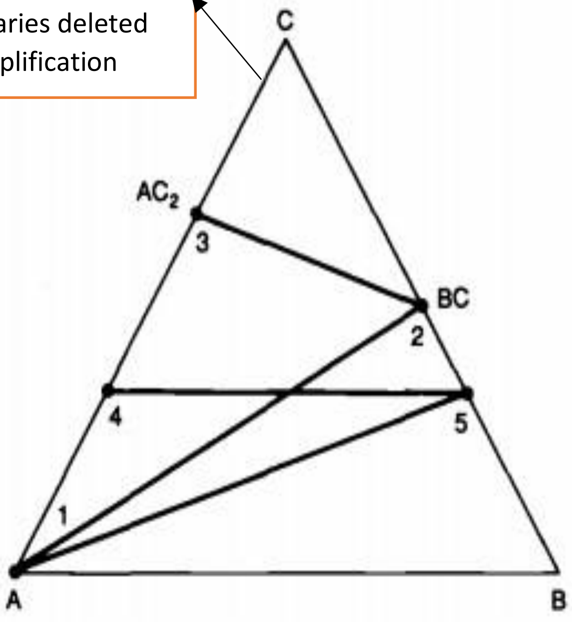
TERNARY PHASE DIAGRAM



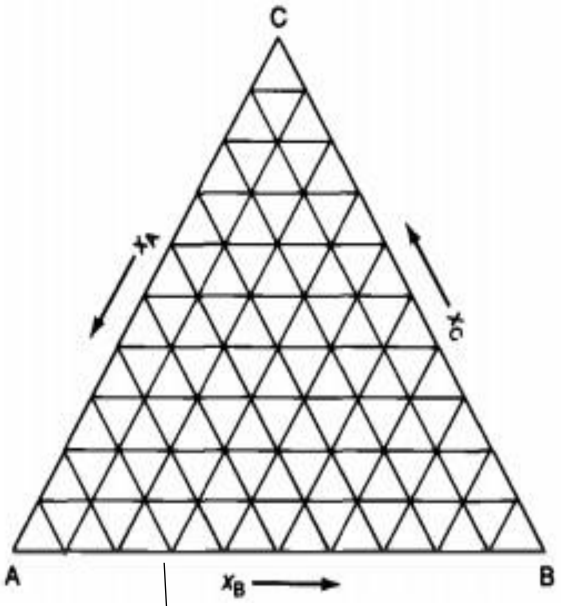
Ternary phase diagram showing three-phase equilibrium

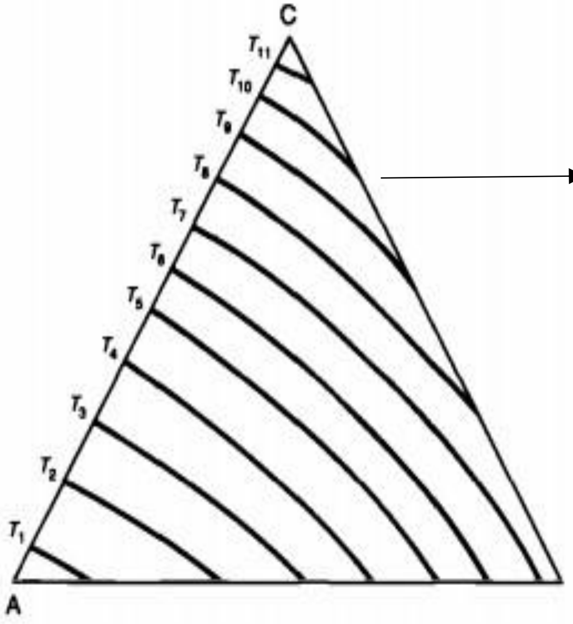
Three component present in the ternary system. In this figure the liquidus line of all three component meet at one point and is called as triple point.

Here, boundaries of single-phase fields (liquidus, solidus, and solvus lines in the binary diagrams) become surfaces; single- and two phase areas become volumes; three-phase lines become volumes; and four-phase points, while not shown in Fig, can exist as an invariant plane. The composition of a binary eutectic liquid, which is a point in a two-component system, becomes a line in a ternary diagram,



Isothermal section of a ternary diagram with phase boundaries deleted for simplification





Liquidus projection of a ternary phase diagram showing isothermal contour lines.

Triangular composition grid for isothermal sections; x is the composition of each constituent in mole fraction or percent

Isothermal Sections. Composition values in the triangular isothermal sections are read from a triangular grid consisting of three sets of lines parallel to the faces and placed at regular composition intervals. Normally, the point of the triangle is placed at the top of the illustration, component A is placed at the bottom left, B at the bottom right, and C at the top. The amount of component A is normally indicated from point C to point A, the amount of component B from point A to point B, and the amount of component C from point B to point C. This scale arrangement is often modified when only a comer area of the diagram is shown.

Projected Views. Liquidus, solidus, and solvus surfaces by their nature are not isothermal. Therefore, equal-temperature (isothermal) contour lines are often added to the projected views of these surfaces to indicate their shape. In addition to (or instead of) contour lines, views often show lines indicating the temperature troughs (also called "valleys" or "grooves") formed at the intersections of two surfaces. Arrowheads are often added to these lines to indicate the direction of decreasing temperature in the trough.

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