

Module 3

Iron – Carbon System

Equilibrium Diagrams

Definition & Basic Concepts

Component: substances whose presence is necessary & sufficient to make a system (elements / compounds present in mixture)

Phase: physically & chemically homogeneous portion of a system separated by interface, i.e. pure material, solid, liquid, gas

System: whole complex of phases of one or several components at different pressures, composition & temperatures, e.g. Fe-C system

Homogeneous System: contains a single phase, e.g. liquid solution

Heterogeneous System: contains two or more phases , e.g. co-existence of liquid and its crystals is a two phase system

Phase Boundary: interface between different phases across, which the physical and / or chemical properties changes abruptly, e.g. sugar-water, water-ice, FCC iron-BCC iron

Solid-Solution: consists of atoms at least two different types; the solute atoms occupy either substitutional or interstitial position in the solvent lattice and the crystal structure of solvent is maintained

Solubility Limit: maximum concentration of solute atoms that may dissolve in the solvent to form a solid solution

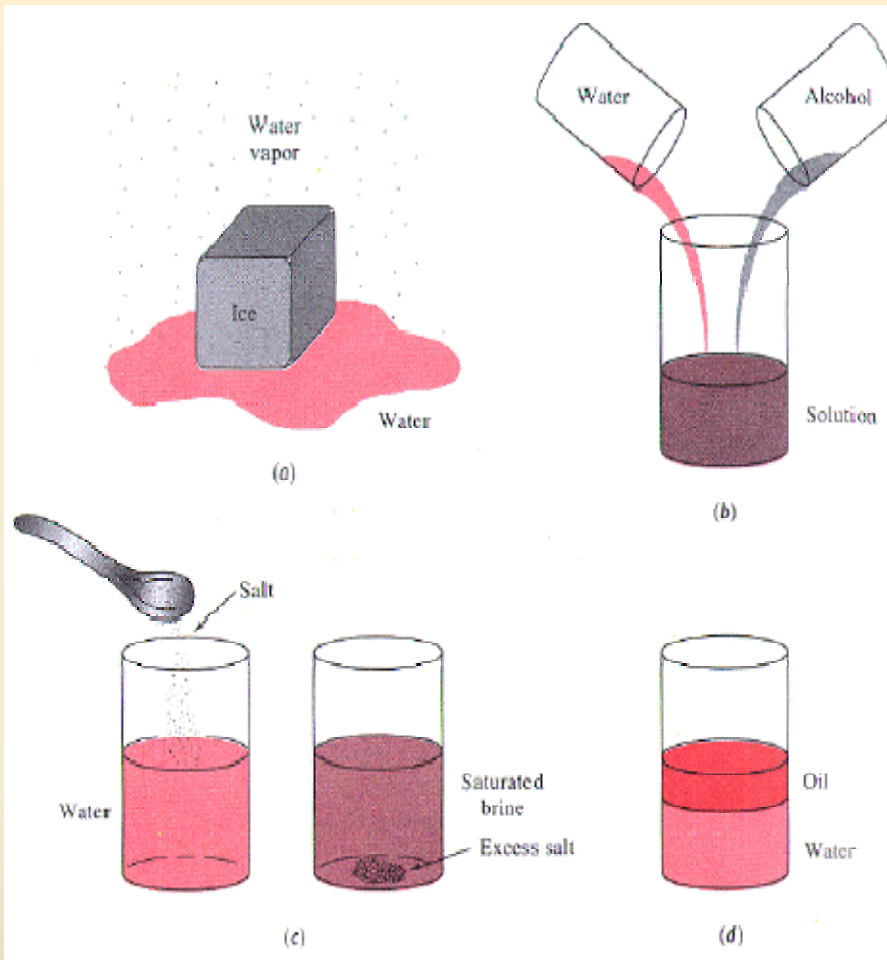


Illustration of Phases & Solubility

(a). Three forms of water – gas, liquid & solid – are each a phase

(b). Water & alcohol have unlimited solubility

(c). Salt & water have limited solubility

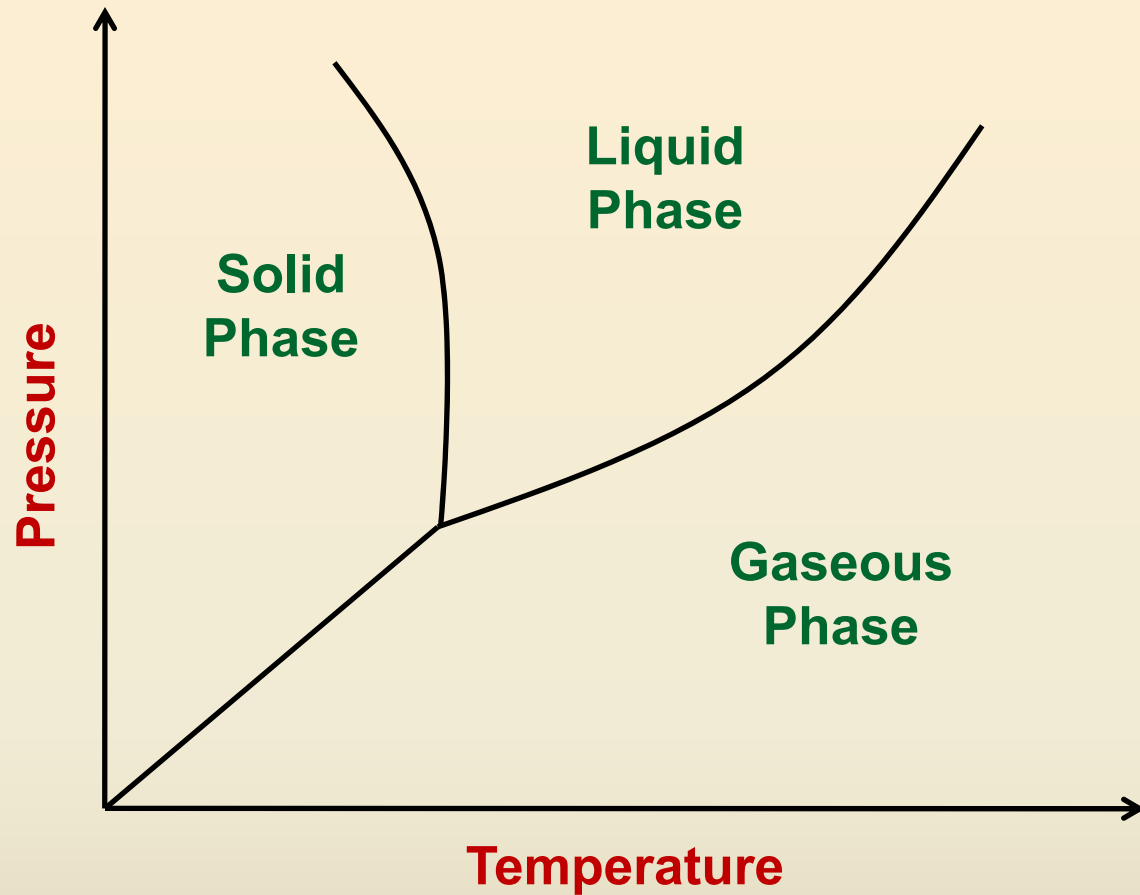
(d). Oil & water have virtually no solubility

Equilibrium: system is at equilibrium, if its free energy is at minimum under some specified combination of temperature, pressure, and composition, e.g. characteristics of the system do not change with time and system is therefore stable

Phase Equilibrium: refers to an equilibrium state to a system containing two or more phases, in which the characteristics of phases do not change with time

Equilibrium Diagram / Phase Diagram / Constitutional Diagram

- Defines the regions of stability of phases that can occur in an alloy system under different conditions of temperature & composition (at constant pressure)
- Temperature & pressure are two external factors determining the state of system, but in case of metals, the effect of pressure is neglected (there is only one external factor)
- Coordinates of the diagram are temperature (ordinate, y-axis) and composition (abscissa, x-axis)
- Only in case of single component phase diagram, variables temperature & pressure are used as shown in the figure



Single Component Phase Diagram

Phase Diagram enables following:

- **Average composition of components in the alloy at any temperature**
- **Phase transformation to be followed during heating or cooling of the alloy under equilibrium conditions, i.e. when all processes in given system are reversible**
- **Phase content of the alloy at any temperature & average composition by Lever Rule**
- **Composition of the components in different phases at any temperature & average composition by Lever Rule**

Phase Rule

- Establishes the relationship between the No. of Degrees of Freedom, the No. of Components and the No. of phases present in the alloy system
- All changes taking place in the alloy system in accordance with the external conditions conform to this rule
- Mathematically,

$$F = (C + n - P) = (C + 1 - P)$$

F: No. of Degrees of Freedom

C: No. of Components

n: No. of external factors (temp. & press.) = 1

P: No. of Phases in equilibrium

Degrees of Freedom

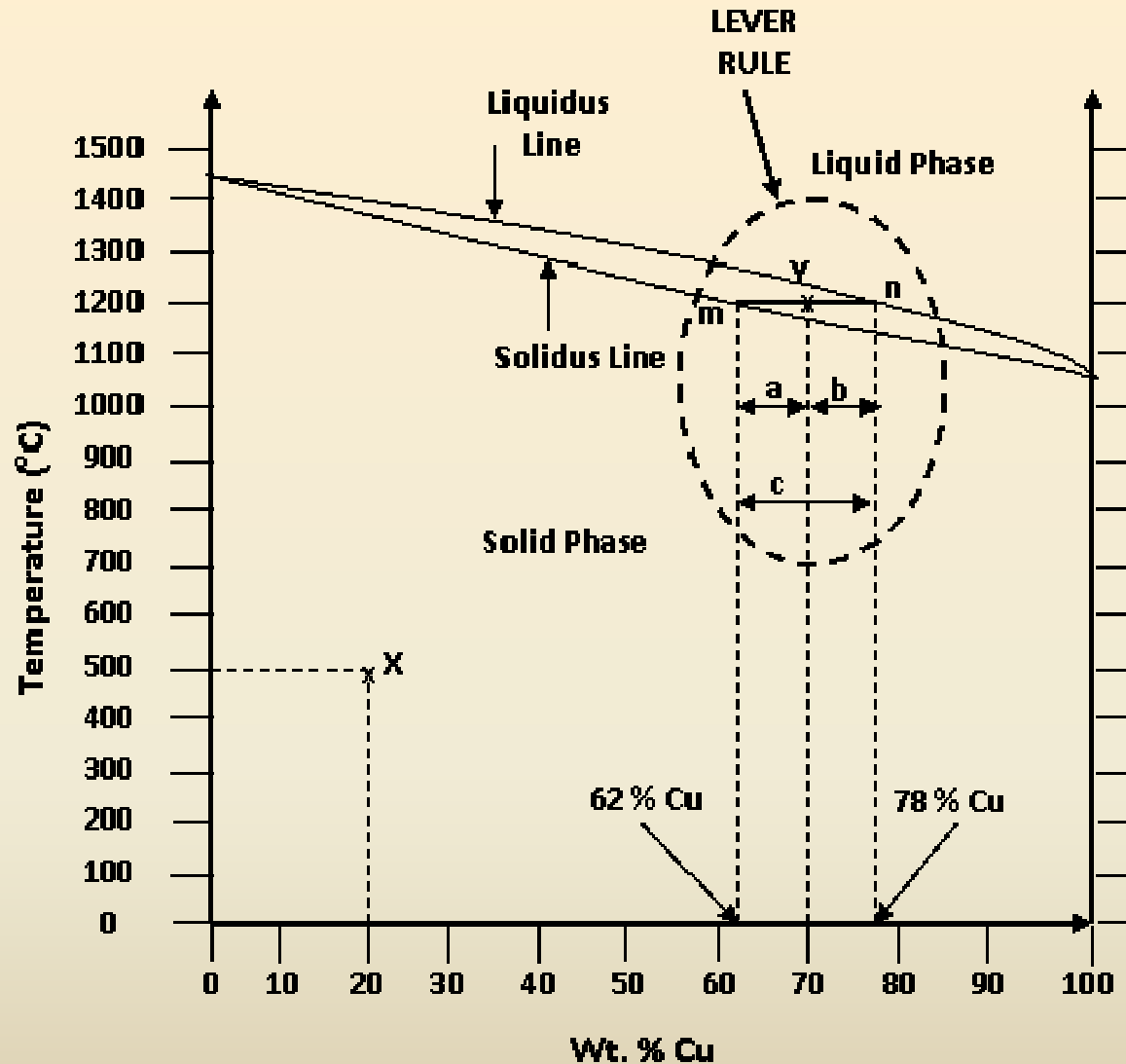
No. of independent external or internal factors (temperature, pressure & composition), which may be altered without causing the formation of a new phase or disappearance of an existing phase in the system

Pure metal at solidification temp.	One component, two phase system ($C = 1$ & $P = 2$)	$F = 0$ Non-Variant System
Alloy of two metals at the start of solidification	Two component, two phase system ($C = 2$ & $P = 2$)	$F = 1$ Mono-Variant System
$F = 2$ is a Divariant system, where system may be at equilibrium at different temperatures and composition		

Isomorphous Alloy System

- Complete solid solubility for all compositions and having same homogeneous crystal structure for all ratios of the components, i.e. Components are completely soluble in the liquid & solid states
- **Example:** Copper – Nickel alloy
- **Essential Conditions:**
 - Components should have same type of crystal
 - Sizes of atoms should be very similar (size difference should not exceed more than 8 %)

Alloys forming homogeneous solid solution like isomorphous alloy system are widely used as engineering materials



Isomorphous Alloy System, e.g. Cu-Ni alloy system

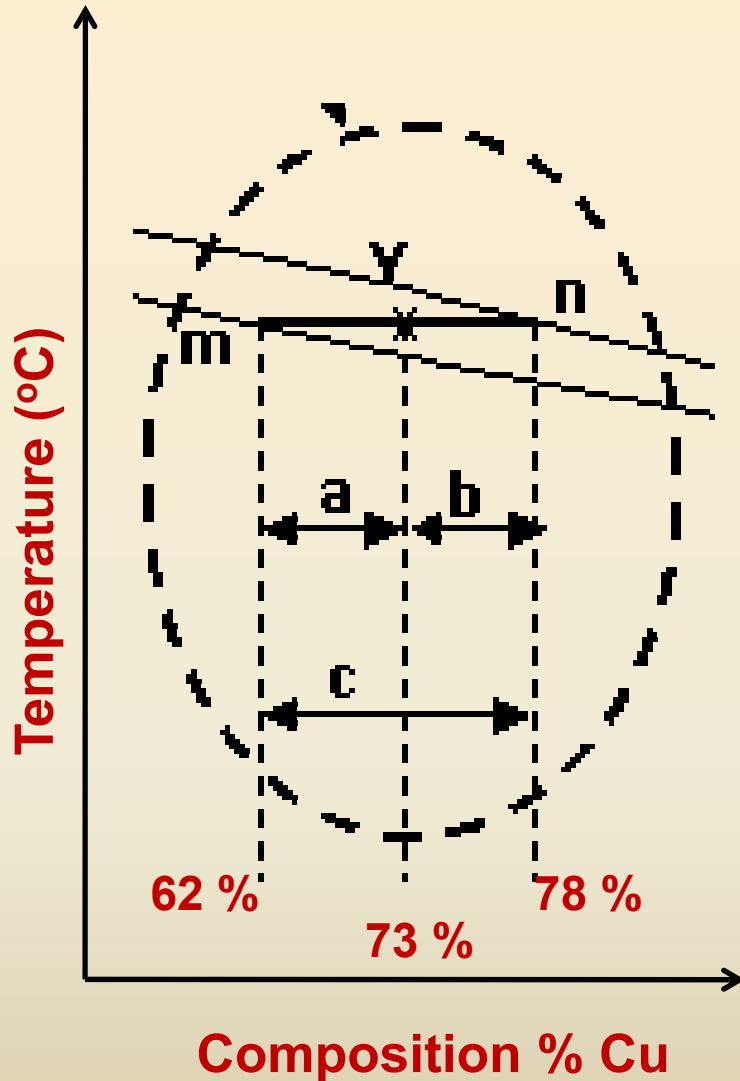
Lever Rule

- Important relationship applied to any two-phase region of a two-component (Binary) phase diagram, which aids in following:
 - Determination of the composition of two phases
 - Determination of the relative amount of the two phases
- **Tie Line** is constructed across the two-phase region at a particular temperature of alloy under consideration and average alloy composition is located on it
- Fraction of one phase is computed by taking the length of tie line from average alloy composition to phase boundary for other phase and dividing it by the total tie line length

- **Fraction of other phase is determined in the same manner**
- **Each phase is multiplied by 100, If phase percentages are desired**
- **If composition axis is scaled in wt. %, the phase fractions computed are mass (or weight) of a specific phase divided by the total alloy mass (or weight)**
- **Mass of each phase is computed from the product of each fraction and total alloy mass**

How to construct a Tie Line

- 1. Tie line is constructed across the two-phase region at temperature of alloy**
- 2. Intersections of tie line and phase boundaries on either side are noted**
- 3. Perpendiculars are dropped from these intersections to horizontal composition axis from which composition of each of respective phases is noted**



- Consider an alloy corresponding to point 'Y' (temp. – 1200 °C & average composition of 73 % Cu) having both solid & liquid phases
- According to Tie Line, the solid phase in the alloy sample has 62 % Cu and the liquid phase in the alloy sample has 78 % Cu
- Assume the alloy sample to be of 100 gms, then wt. of Cu and Ni in the sample are 73 gms and 27 gms respectively

- Assume wt. of solid phase in alloy sample to be 'w'
- Therefore, wt. of Cu in the solid and liquid phases will be '0.68 w' and '0.78 (100-w)' respectively
- Also, the total wt. of Cu in the alloy = Sum of the wts. of Cu in solid and liquid phases

or $73 = 0.62 w + 0.78 (100-w)$

or $78 - 73 = (0.78 - 0.62) w$

or $w/100 = [(0.78 - 0.73) / (0.78 - 0.62)]$

Hence, **wt. % solid** = **(b / c)**

& **wt. % liquid** = **(a / c)**

Eutectic Alloy System

➤ *Types:*

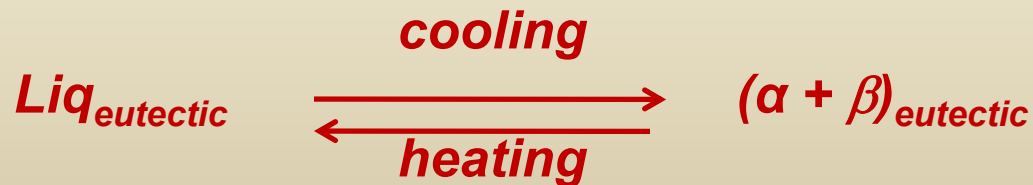
(Type I): Components are completely soluble in the liquid state but are insoluble in each other in the solid state

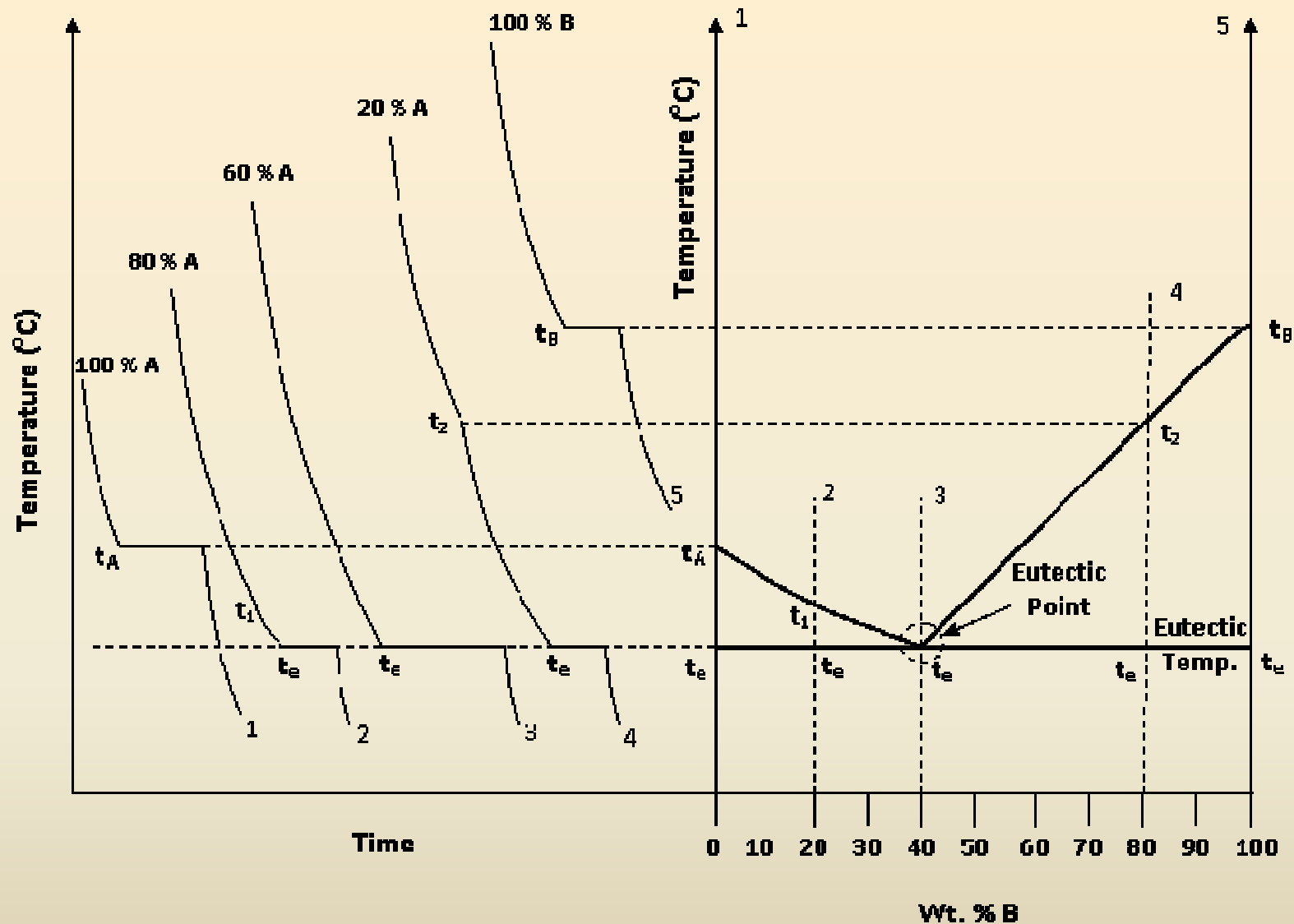
(Type II): Components are completely soluble in the liquid state but partially soluble in solid state

➤ **Example:** Tin-Zinc alloy, Cadmium-Bismuth alloy

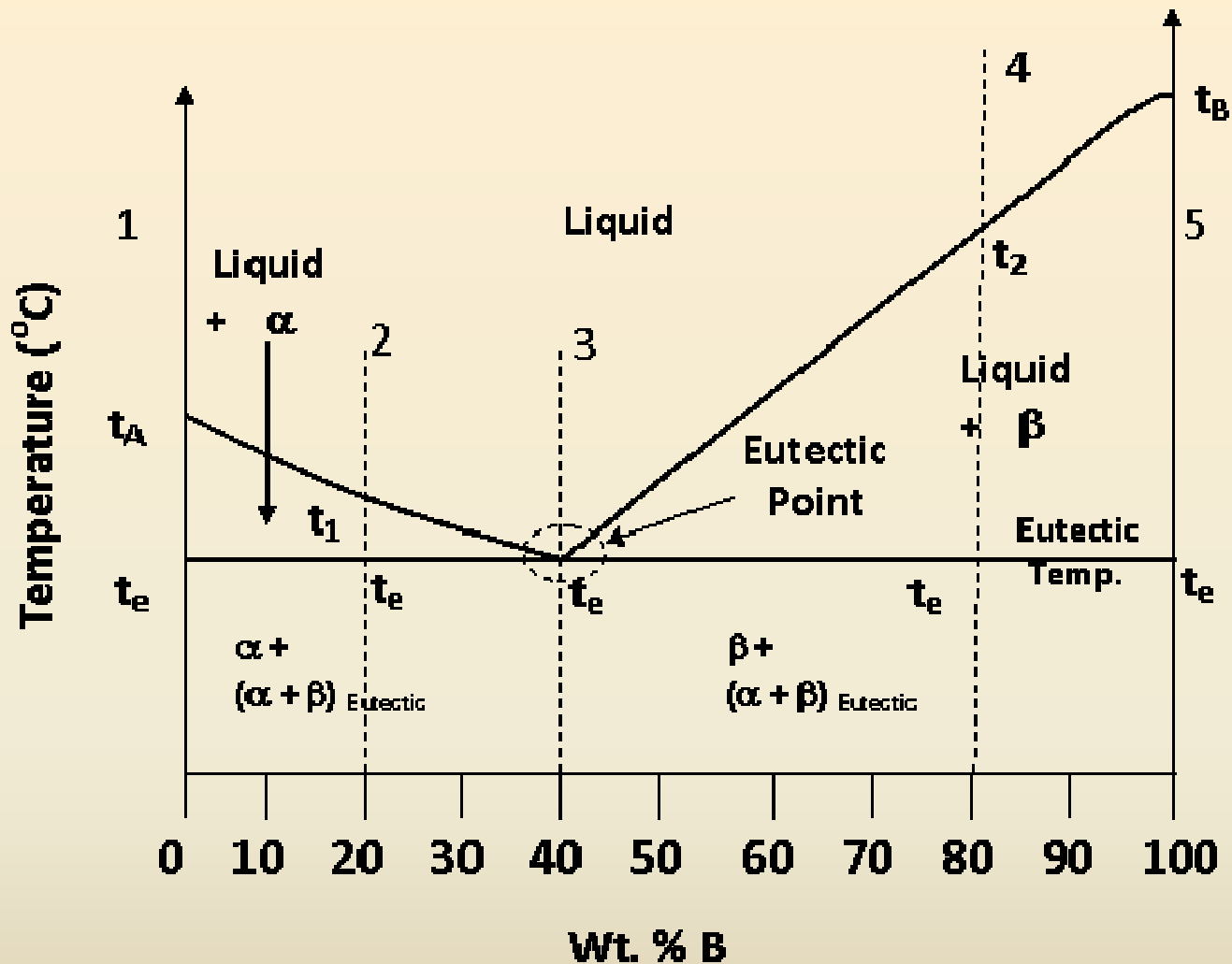
➤ **Main Characteristics: (Eutectic Point)**

- Eutectic composition & temperature
- Eutectic reaction

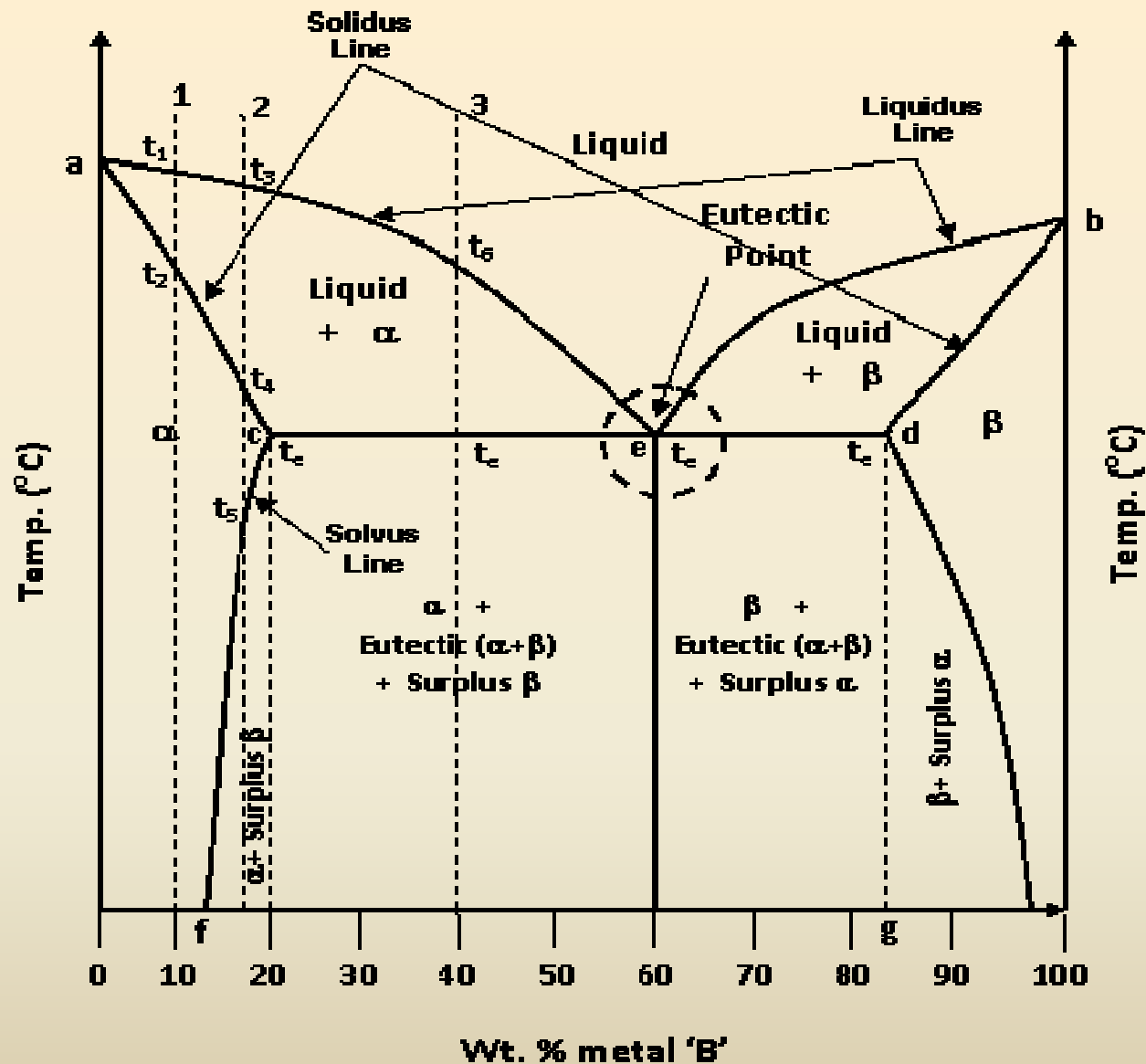




Construction of Eutectic Alloy System (Type – I)



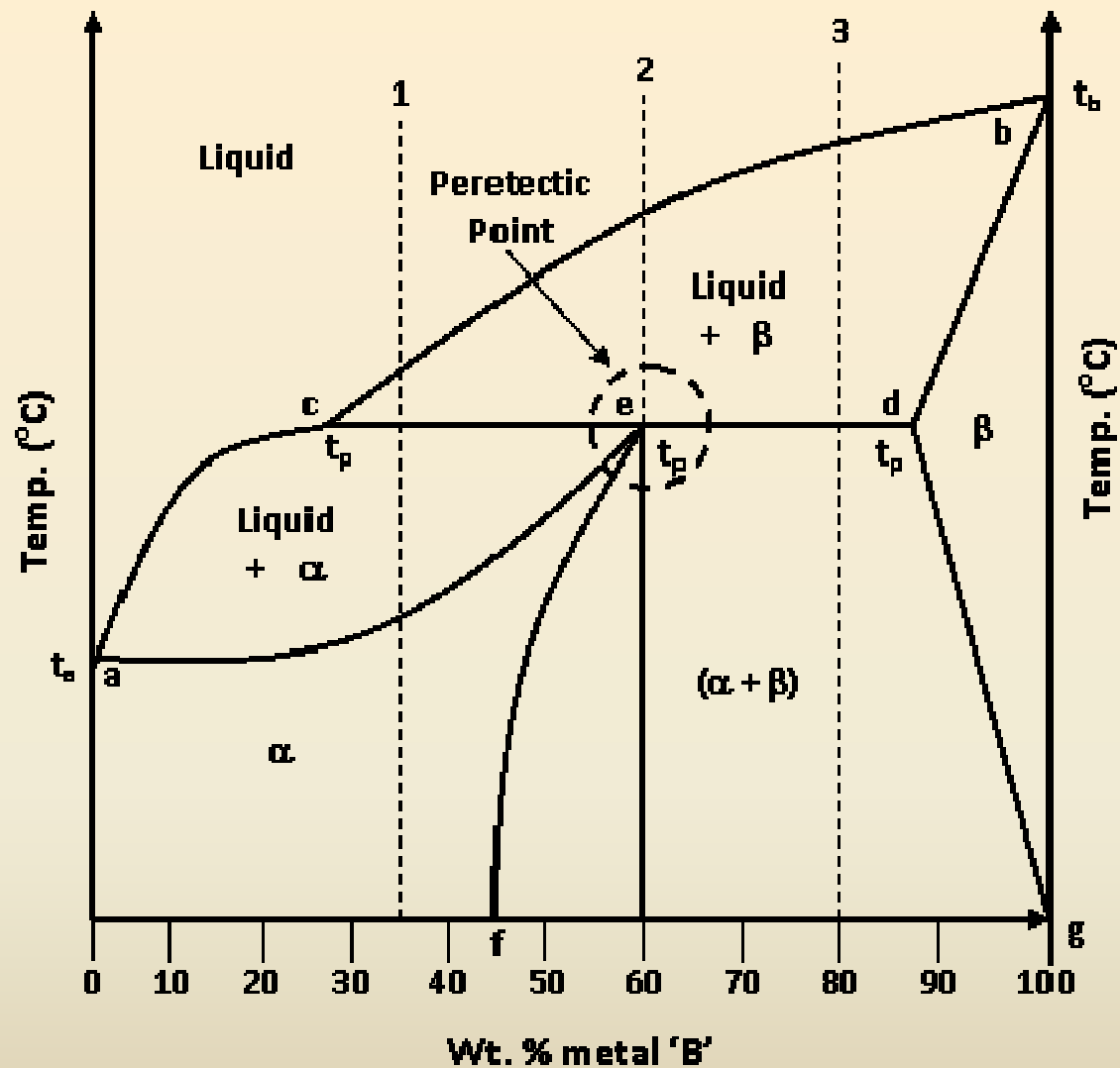
Eutectic Alloy System (Type – I)



Eutectic Alloy System (Type – II)

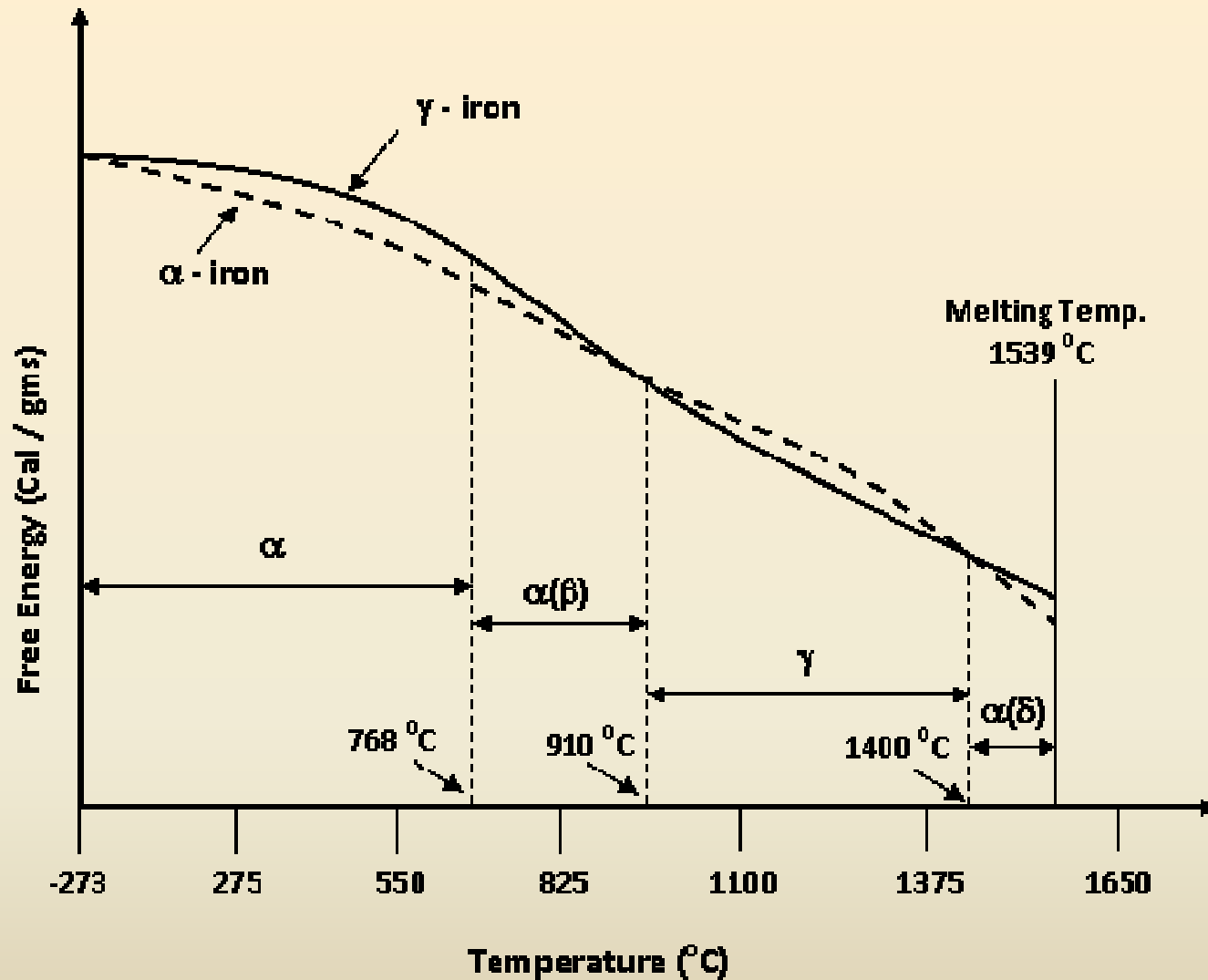
Peritectic Alloy System

- Components have complete mutual solubility in liquid state and limited solubility in solid state
- it differs from the eutectic alloy system (Type-II), as the crystals of β -solid solution precipitated at the beginning of solidification reacts with liquid alloy of definite composition to form new crystals of α -solid solution
- **Example:** Fe-C alloy
- **Main Characteristics:** Reaction occurs at constant temperature

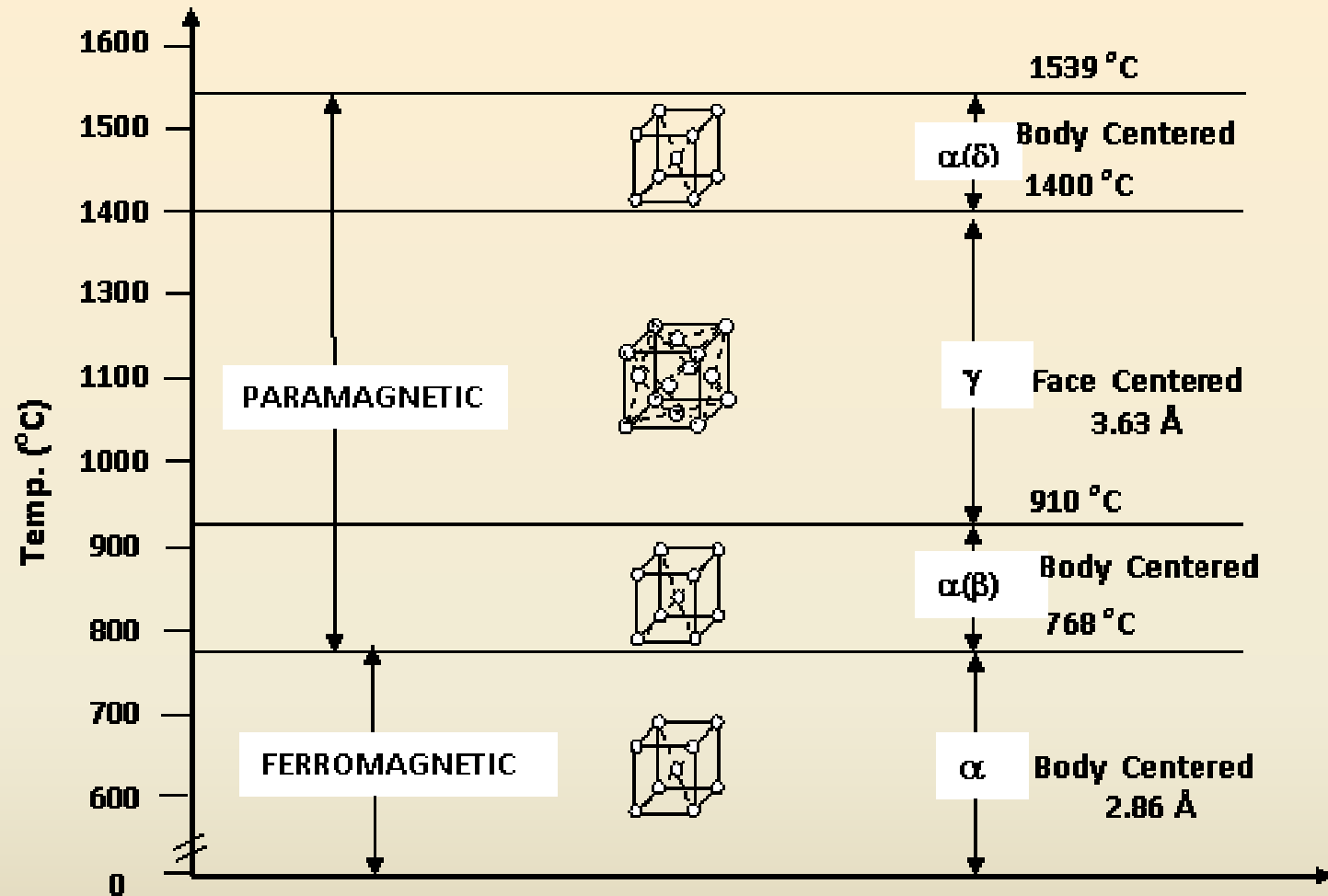


Peritectic Alloy System

Fe – C Equilibrium Diagram

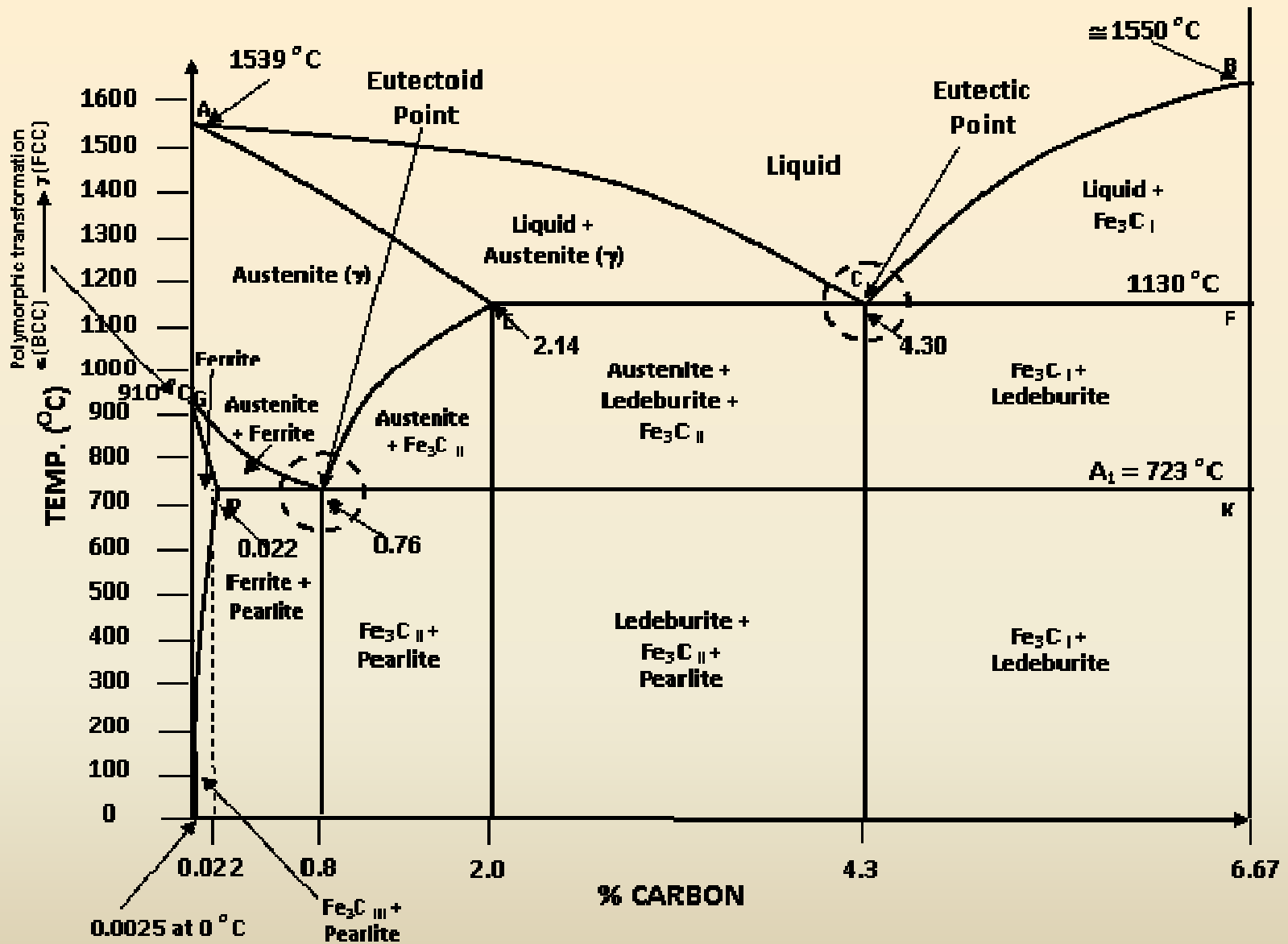


Free Energy Curve of Iron



Allotropic Forms of Iron

- Two allotropic forms of Fe: α -iron (BCC, 2.86 Å) & γ -iron (FCC, 3.63 Å)
- α -iron exists up to temp. 910 °C and between 1400 °C to 1539 °C (910 °C and 1400 °C are the intersection points of two curves)
- From 768 °C to 910 °C, α -iron is referred as α (β)-iron and is paramagnetic (magnetically weak) in behavior, i.e. from 768 °C onwards iron changes its behavior from ferromagnetic (magnetically strong) to paramagnetic
- From 1400 °C to 1539 °C, α -iron is referred as $\alpha(\delta)$ -iron, i.e. from 1400 °C onwards iron changes its allotropic form from FCC to BCC structure
- Between 910 °C to 1400 °C, iron exists as γ -iron with FCC structure



Simplified Fe-C Equilibrium Diagram

- Critical points along line GS are designated as A_3 , i.e. A_{c3} is for heating & A_{r3} is for cooling
- Critical points along line SE are designated as A_{cm} (to distinguish secondary / pro-eutectoid cementite, i.e. Fe_3C_{II})
- Critical points along line PSK are designated as A_1 , i.e. A_{c1} is for heating & A_{r1} is for cooling

Nomenclature:

A: Arrest

C: Chauffage (heating)

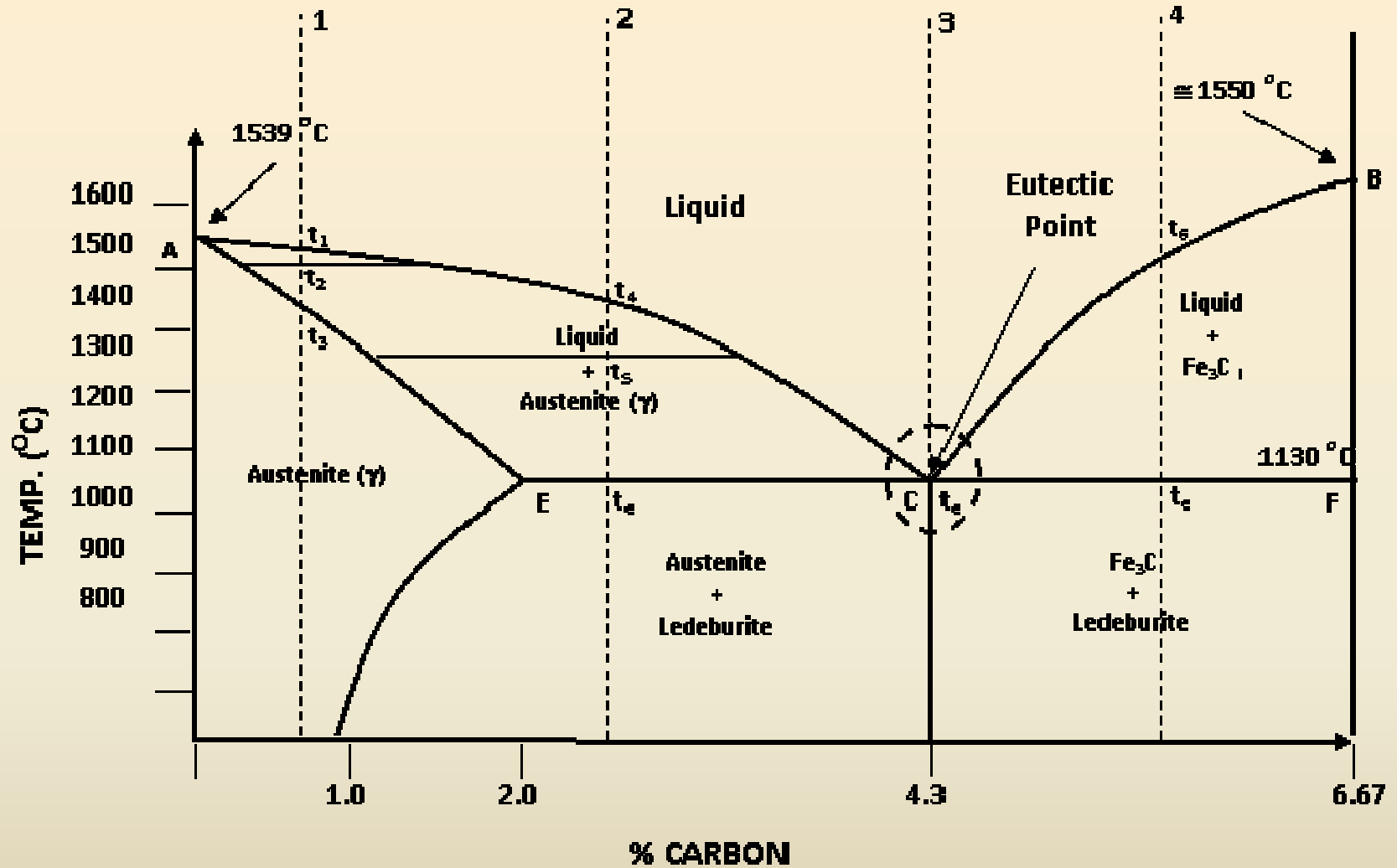
R: Refroidissement (cooling)

- Fe-C alloys having carbon percent up to 2.0 % are Steels
- Fe-C alloys having carbon percent more than 2.0 % & less than 6.67 % are Cast Irons (CI)
- Solid solution of carbon in α -iron: Ferrite
- Solid solution of carbon in γ -iron: Austenite
- Points 'A' & 'G' corresponds to allotropic transformation , i.e. point 'A' is for formation of austenite (γ -iron) & point 'B' is for formation of ferrite (α -iron)
- Max. solubility of carbon in α -iron is 0.022 % (at 723 °C, i.e. point 'P') and 0.0025 % (at 0 °C)
- Max. solubility of carbon in γ -iron is 2.0 % at 1130 °C (point 'E')

Iron carbide (Fe_3C) / Cementite

- Chemical compound having 6.67 % carbon (constant)
- Orthorhombic lattice with close-packed atoms
- Melting point of 1550 °C & ferromagnetic up to temp. 217 °C
- High hardness , i.e. $\text{BHN} \geq 700$ & low ductility
- Under definite conditions, cementite can be decomposed to form free carbon as graphite
- Allotropic transformation of $\alpha(\delta)$ -iron to γ -iron at high temperatures is neglected & not shown in the simplified Fe-C diagram, as it is of no practical use, i.e. $\alpha(\delta)$ -iron crystal precipitation from liquid is not shown and only direct precipitation of γ -iron crystals from liquid is shown

Primary Solidification



Primary Solidification

Transformation from liquid to solid state for Fe-C alloys

Line 'ACB' is liquidus line , where liquid alloys begin to solidify

Line 'AECF' is solidus line, where complete solidification of liquid alloy takes place

Austenite precipitates along line 'AC' & its composition vary along line 'AC', whereas composition of liquid vary along line 'AE' (proportion of phases may be obtained by Lever Rule)

Cementite precipitates along line 'BC' having constant composition of 6.67 % carbon, where as composition of liquid vary along line 'BC' (proportion of phases can be obtained by Lever Rule)

Point 'C' is Eutectic Point with Eutectic Temp. (t_e) 1130 °C & Eutectic Composition of 4.3 % carbon, where both austenite and cementite (eutectic mixture is called Ledeburite) precipitates out simultaneously

All Fe-C alloys having carbon % more than 2.0 (i.e. cast iron) will completely solidify at 1130 °C (along line ECF) to form eutectic solid solution, i.e. ledeburite

Fe-C alloy at line 'ECF' having any carbon % will have liquid phase with composition same as that of eutectic composition, i.e. along line 'ECF', complete liquid phase will form eutectic ledeburite

Eutectic Transformation / Reaction:

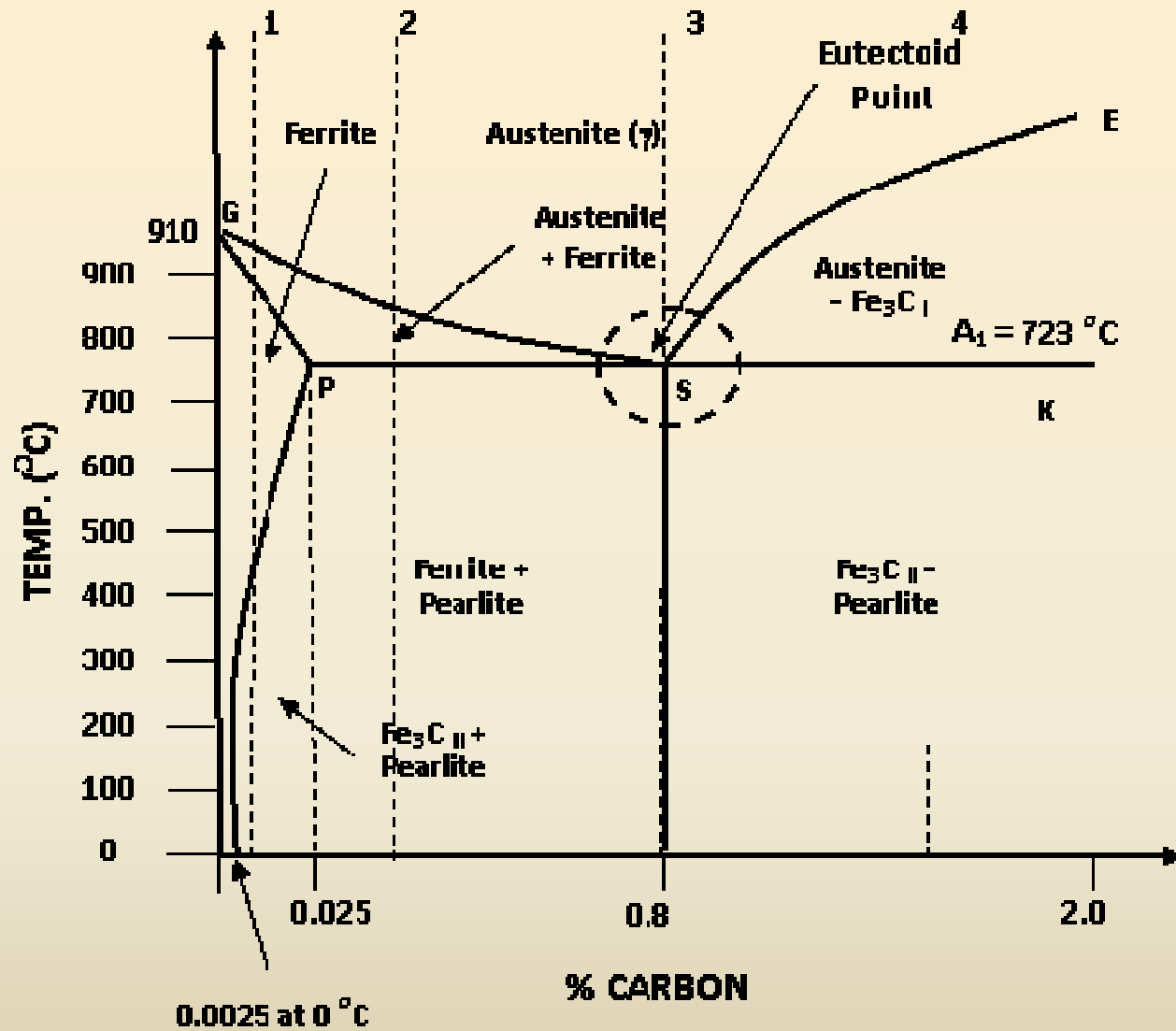
Liquid \rightleftharpoons Ledeburite (Austenite + Cementite)

C = 2 (Fe & C), P = 3 (Liquid, Austenite & Cementite) & F = 0, therefore it is a non-variant system / reaction, where all the three phases have definite carbon composition at constant temperature of 1130 °C, i.e. liquid = 4.3 %, eutectic ledeburite (austenite = 2.0 % & cementite = 6.67 %)

Fe-C alloy with carbon % more than 2.0 & less than 4.3 are known as 'Hypo-Eutectic' cast iron and consists of austenite and eutectic ledeburite

Fe-C alloy with carbon % more than 4.3 are known as 'Hyper-Eutectic' cast iron and consists of eutectic ledeburite and primary cementite

Secondary Solidification



Secondary Solidification

Transformation from solid to solid state for Fe-C alloys

Allotropic transformation of γ -iron to α -iron, as well as decomposition of austenite into ferrite & cementite (cementite precipitates as an excess carbon

Line 'GS' indicates beginning of the decomposition of austenite and precipitation of ferrite

Critical points along line 'GS' are designated as A_{c3} in heating and A_{r3} in cooling

Line 'SE' indicates precipitation of excess carbon as cementite, known as secondary / pre-eutectoid cementite

Temperatures along line 'SE' are designated as A_{cm} points

Transformation from solid to solid state for Fe-C alloys

Allotropic transformation of γ -iron to α -iron, as well as decomposition of austenite into ferrite & cementite (cementite precipitates as an excess carbon

Line 'GS' indicates beginning of the decomposition of austenite and precipitation of ferrite

Critical points along line 'GS' are designated as A_{c3} in heating and A_{r3} in cooling

Line 'SE' indicates precipitation of excess carbon as cementite, known as secondary / pre-eutectoid cementite, which indicates reduction in the solubility of carbon in γ -iron (austenite) with decrease in temperature

Temperatures along line 'SE' are designated as A_{cm} points

Point 'S' corresponds to minimum temp. of 723 °C with 0.8 % carbon at which austenite exists in a state of equilibrium

Point 'S' is also referred as 'Eutectoid' point with Eutectoid Temp. of 723 °C & eutectoid composition of 0.8 % carbon

At this point, austenite decomposes with simultaneous precipitation of ferrite and cementite (secondary cementite), i.e. eutectoid mixture known as Pearlite

Eutectoid Transformation / Reaction:

Austenite \rightleftharpoons Pearlite(ferrite + cementite)

$C = 2$ (Fe & C), $P = 3$ (austenite, ferrite & cementite) & $F = 0$, therefore, it is a non-variant system / reaction

Line 'PSK' indicates complete decomposition of austenite at constant temperature 723 °C, with critical points at which pearlite is formed during cooling designated as A_{r1} and also transformation of pearlite to austenite upon heating as A_{c1}

Pearlite structure consists of thin alternating plates / lamellae of ferrite and cementite and hence, also referred as Lamellar Pearlite

Depending upon heat treatment process, granular pearlite may be formed consisting of rounded globules of cementite in ferrite field

Line 'PQ' represents in the decrease in the solubility of carbon in α -iron with decrease in the temperature and the excess carbon precipitates out as 'Tertiary Cementite'

Fe-C alloys less than 0.8 % carbon and from 0.8 to 2.0 % carbon are called as hypo-eutectoid & hyper-eutectoid steels