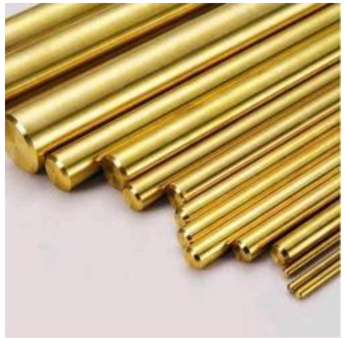
Alloying for Corrosion Protection

- Alloy is a homogeneous substance formed by mixing two or more elements, at least one of them being a metal
- Types: Alloys are of three types.
  - Formed by two or more metals; eg. Cu-Zn (Brass)
  - Formed between a metal & a non-metal; eg. WC
  - Formed between mercury & another metal; eg. Zinc amalgam



Characteristics of alloys:

⇒ Hardness and tensile strength of the alloy is higher

- Tensile strength of Fe 10 fold increases by alloying with 1% Carbon

⇒ Melting points of alloys is generally lower

- Solder melts at 183°C; while Pb melts at 327°C and Sn melts at 232°C

⇒ Alloys are less conductive than pure metals

- Small quantity of impurities in copper will reduce its conductivity

⇒ Colour of alloy gets modified

- Red coloured copper & Silver white Zinc provide Yellowish brown brass

⇒ Chemical Properties are modified

- Dissolution of alloy in HCl is lower compared to its constituent metals

⇒ Corrosion resistances: Generally alloys are more resistant to corrosion than pure metals.

- Stainless steel (alloy of Fe, C, Ni & Cr) is not corroded by atmospheric conditions though pure Fe corrodes heavily in moist environment.

Alloying for Corrosion Protection

❑ Significance of Alloying

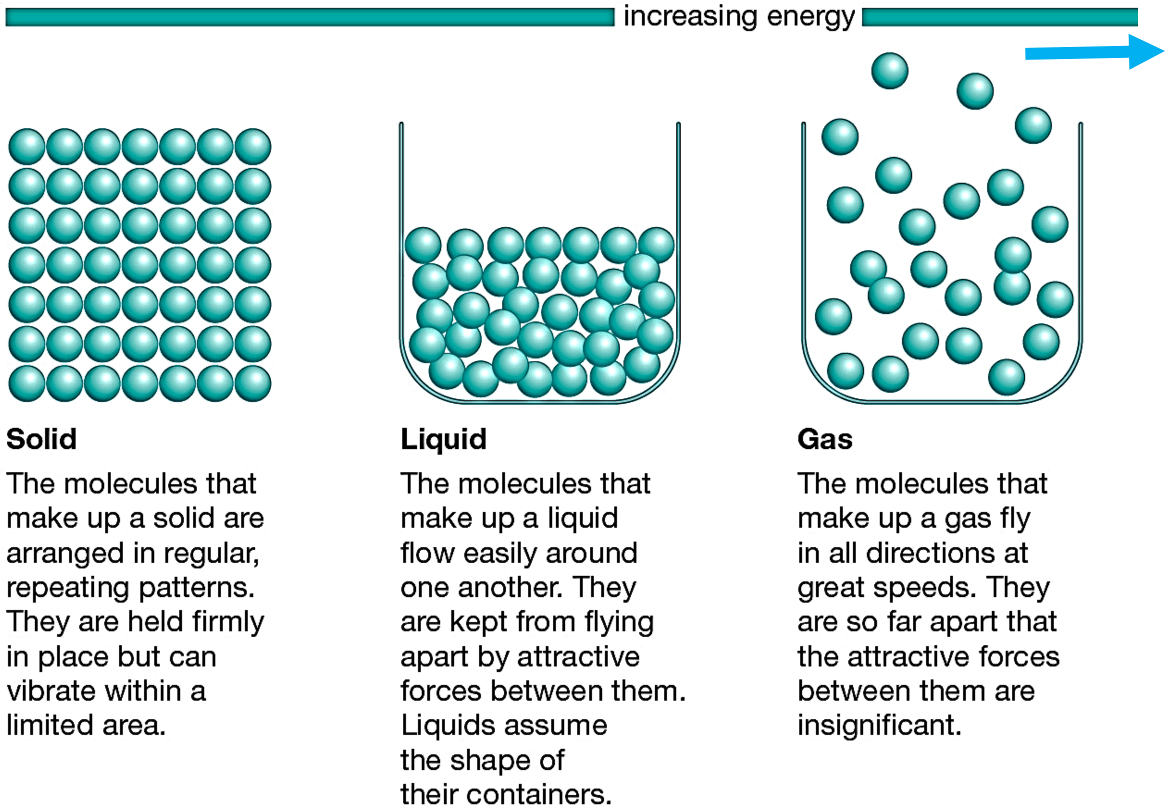
- The alloy coatings bring quality, reliability and durability for process vessel linings and pipe linings along with the surface protection of components and equipment against extreme conditions such as high temperature, higher abrasion or high acidity surroundings.
- Alloying Increases mechanical strength, reduce chemical reactivity, change electrical conductivity, increase corrosion protection

❑ Examples

- ✓ Lead-Tin alloys – for soldering purpose
- ✓ Nickel alloys – for resistance to extreme corrosion & high temperature requirements.
- ✓ Copper-nickel alloys – for anti-fouling resistance.
- ✓ Iron-nickel alloys – for low thermal expansion

❑ Basic concepts of Eutectic composition

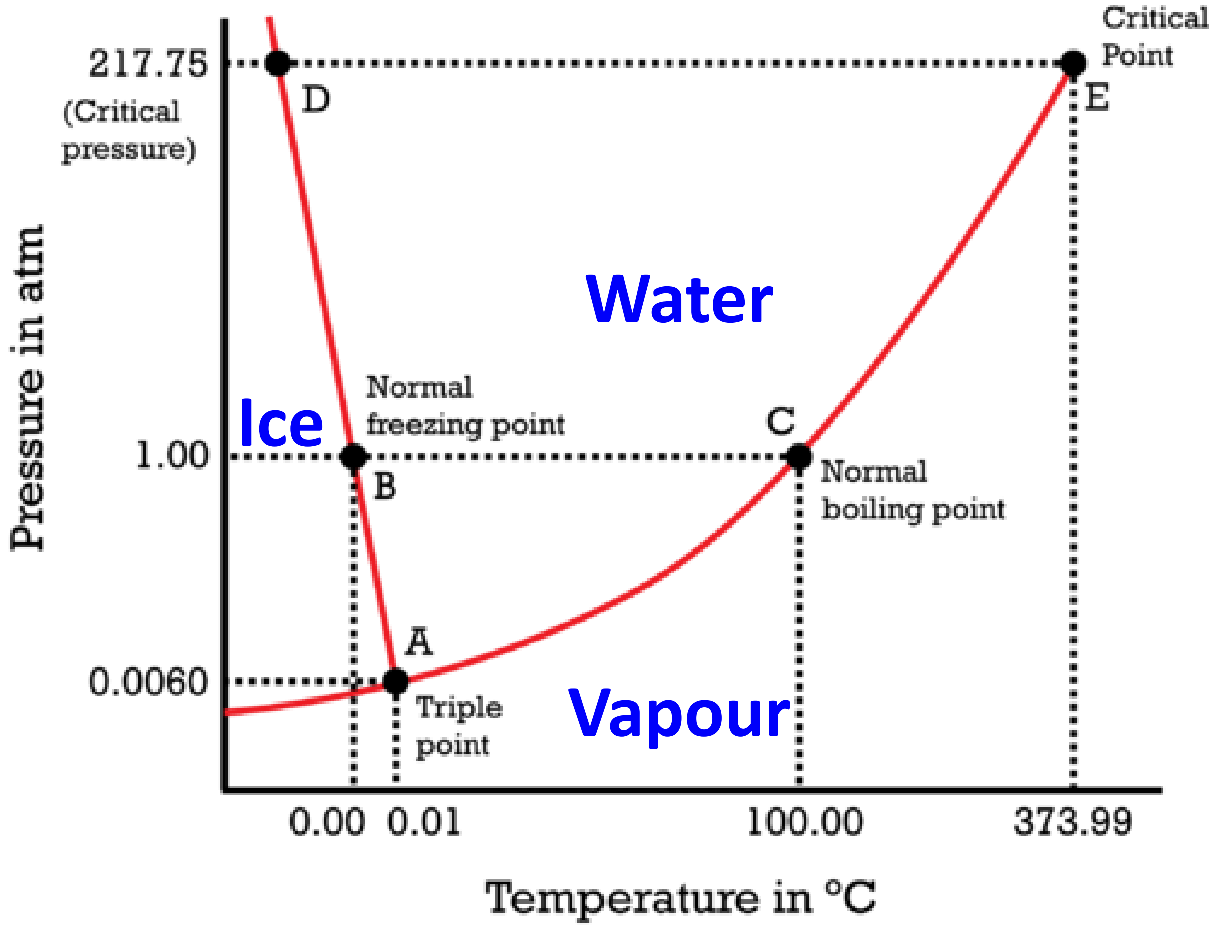
- Phase



- When a phase in one form is altered to another form, a phase change is said to have occurred. Phase change generally occurs by addition/removal of thermal energy
- A heterogeneous system is defined as a system consisting of a number of phases in equilibrium

Basic Concepts of Eutectic Composition

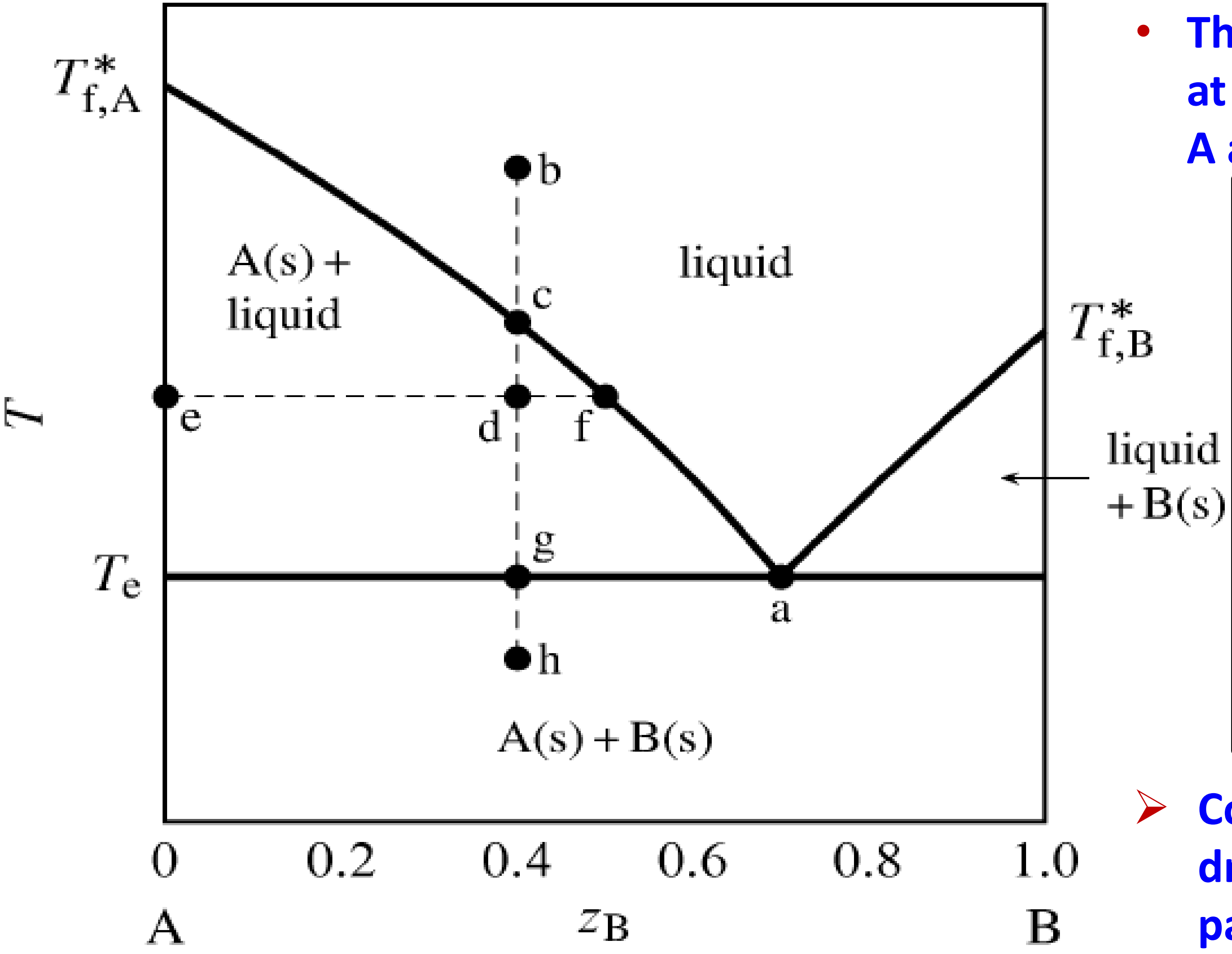
- A phase diagram is a type of chart used to show conditions (pressure, temperature, volume) at which thermodynamically distinct phases (such as solid, liquid or gaseous states) occur and coexist at equilibrium



- Generally the phases at equilibrium are studied under the conditions considering following variables
  - Temperature & Pressure or Temperature & Composition
- Phase diagram is one of the most succinct ways of presenting the physical changes of state that a substance can undergo.
  - For two component systems
    - Temperature, pressure and composition are required to define the system
    - This leads to 3-dimensional figures which cannot be explained on a paper. Hence one of the three variable to be kept constant.
    - The composition variable z_B is the mole fraction of component B in the system as a whole.
    - The measurement is carried out in an open vessel to keep the system under constant atmospheric pressure

Basic Concepts of Eutectic Composition

- $T_{f,A}^*$ = freezing point of A
- $T_{f,B}^*$ = freezing point of B



- The curve $T_{f,A}^*$ = FP of B to which A is being added
- The curve $T_{f,B}^*$ = FP of A to which B is being added
- These two curves represent condition of temperature at which the liquid mixture is in equilibrium with solid A and solid B

Point 'a' = meeting point of the curves $T_{f,A}^*$ & $T_{f,B}^*$. At this point three phases, solid A, solid B and the liquid mixture, are in equilibrium.

The point 'a' correspond to a temperature below which any liquid mixture of A and B will freeze as a whole. This is known as the Eutectic Point.

The composition at this point is the eutectic composition, and the temperature here (denoted T_e) is the eutectic temperature

- Composition of any point, say d, can be obtained by drawing a horizontal line passing through the particular point to find where it cuts the curves $T_{f,A}^*$ & $T_{f,B}^*$

Eutectic System

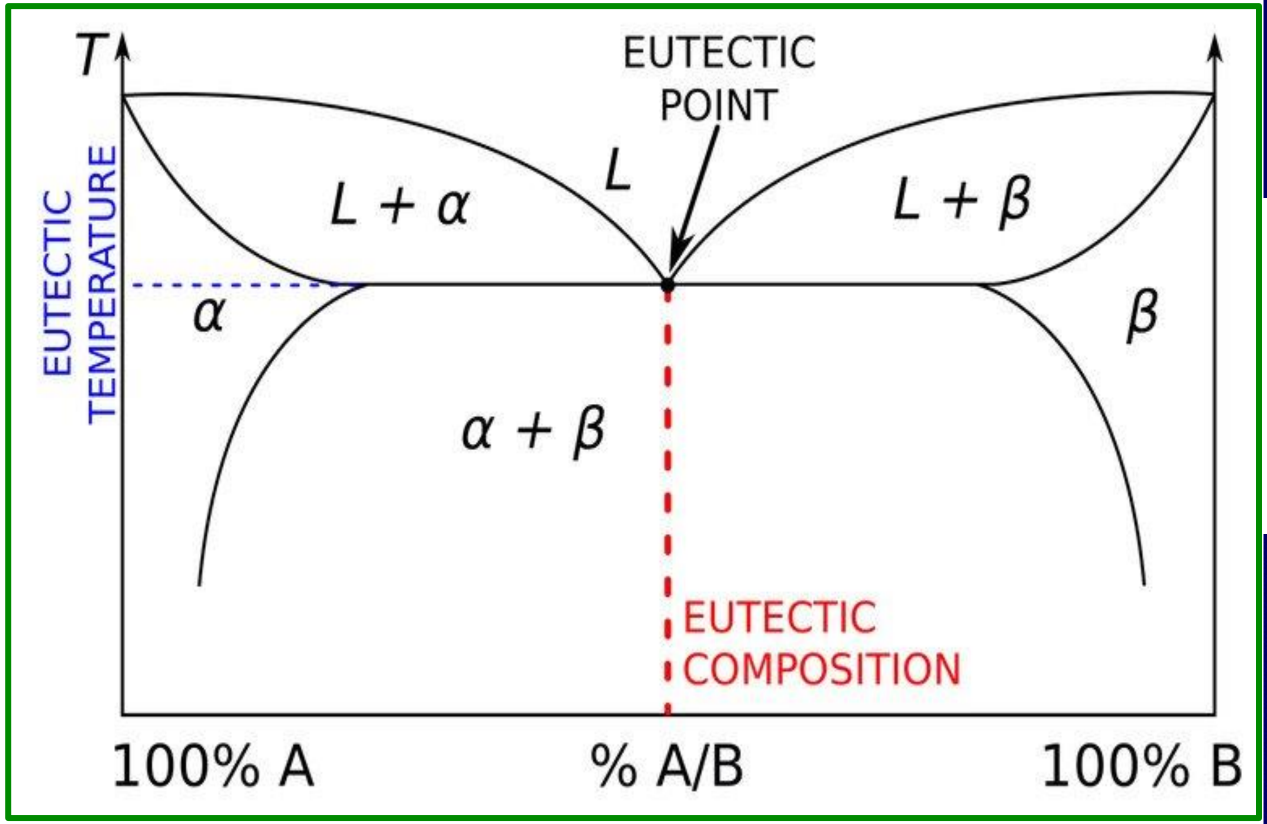
- _The line connecting the composition of the solid and liquid phases in equilibrium is called the tie line
- Eutectic system is a homogeneous, solid mixture of two or more substances that form a super-lattice; the mixture either melts or solidifies at a lower temperature than the melting point of any of the individual substances.
- Eutectic point: Minimum freezing point attainable corresponding to the eutectic mixture is called eutectic point.
- A eutectic system contains two solid phases at low temperature. These phases may have different crystal structures, or the same crystal structure with different lattice parameters.

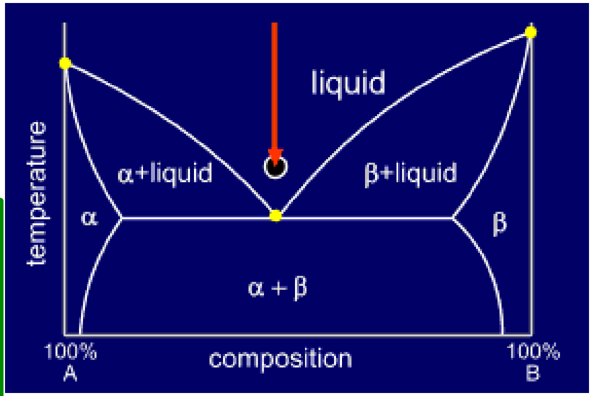
- **Examples:**

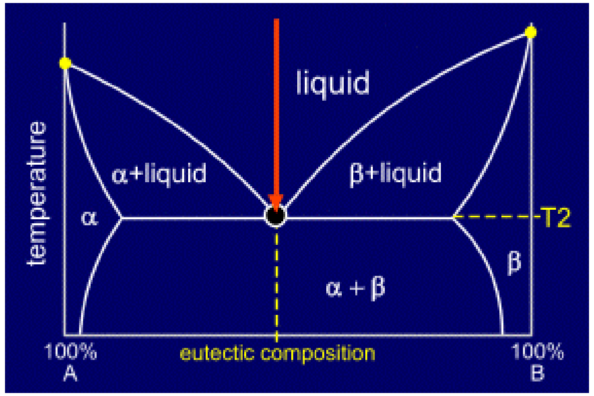
These mixtures typically have useful properties that are not possessed by any single constituent substance.

- Sodium chloride and water form a eutectoid (23.3% salt by mass with a eutectic point at -21.2 °C. The system is used to make ice cream and to melt ice and snow.
- Eutectic alloys are used for many purposes:
  - ✓ Pb (FCC) and Sn (tetragonal) - solder systems
  - ✓ Fe (BCC) and C (graphite - hexagonal) - cast irons
  - ✓ Al (FCC) and Si (diamond cubic) - cast aluminum alloys
  - ✓ Cu(FCC) and Ag(FCC) – high temperature solder
- Eutectoid glassy metals exhibit extreme corrosion resistance and strength.
- Inkjet printer ink is a eutectic mixture
- Galinstan is a liquid metal alloy (composed of gallium, indium, and tin) used as a low-toxicity replacement for mercury

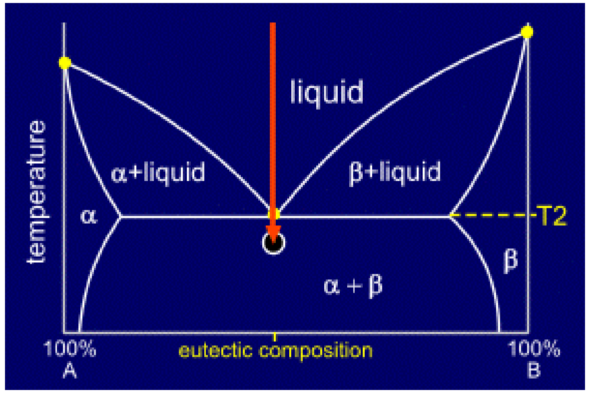
Eutectic System

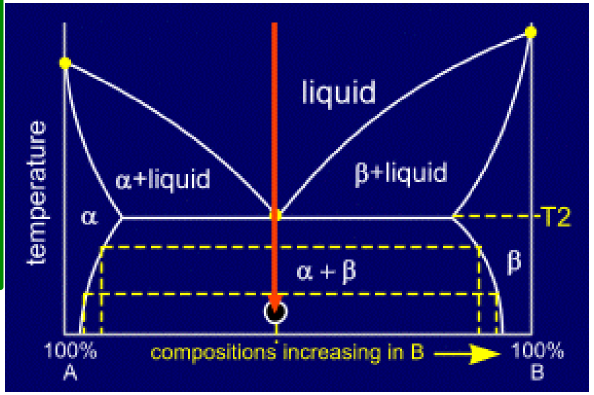




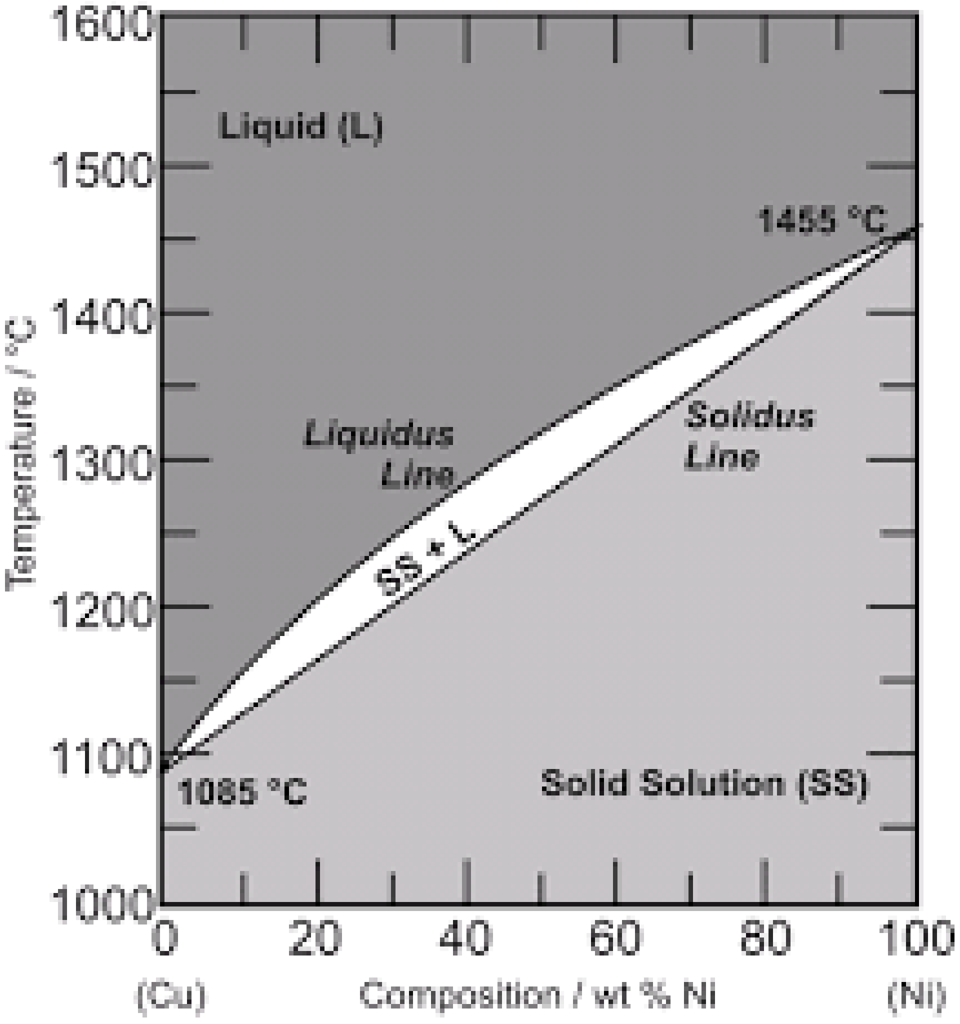


- ➢ **Solidification starts @ nucleation sites**
- ➢ **Nucleation sites grow**
- ➢ **Entire alloy becomes solid**





Basic Concepts of Eutectic Composition



- Isomorphous phase diagrams

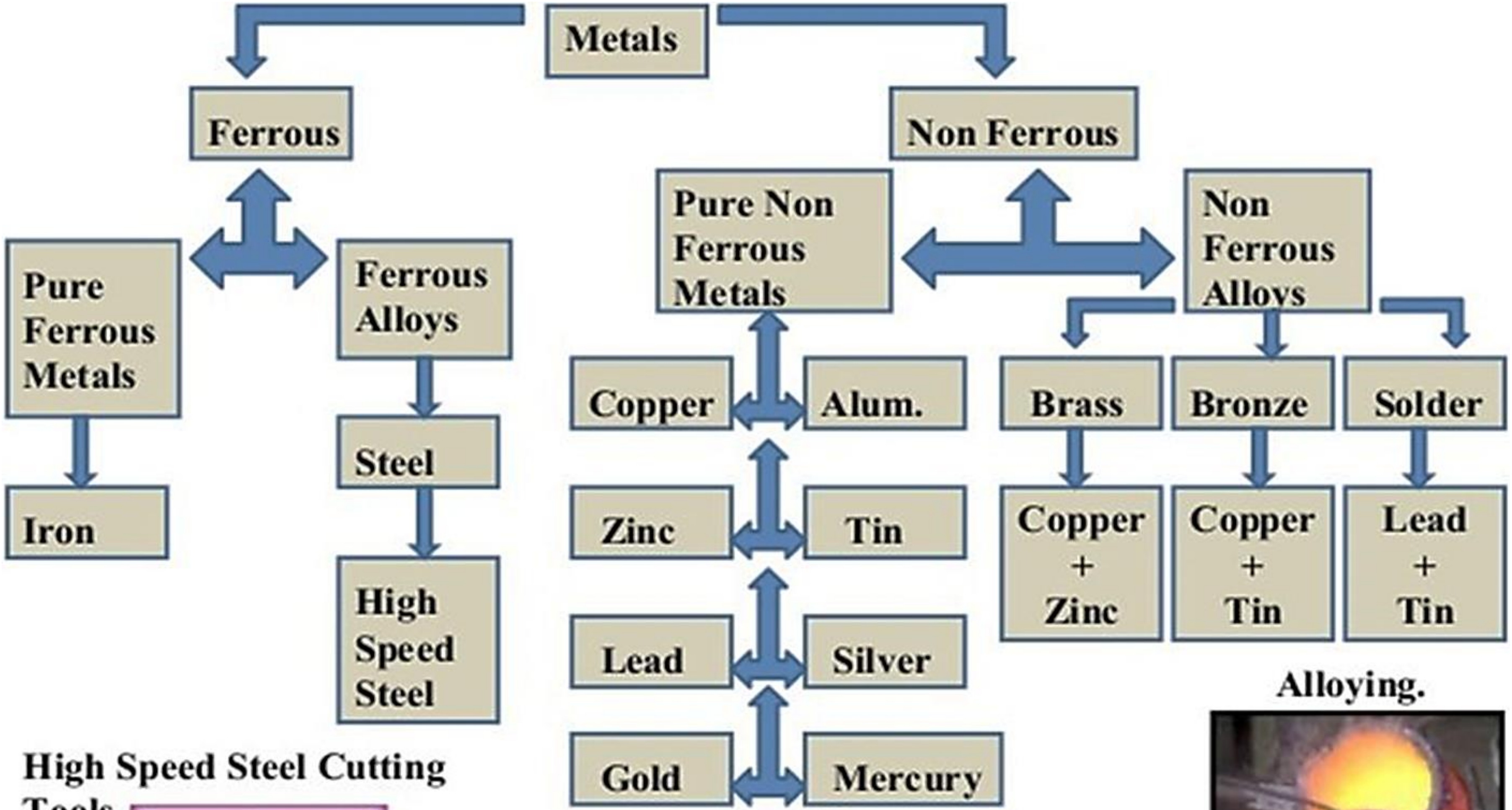
- In crystallography crystals are described as isomorphous if they are closely similar in shape.

  - Cu-Ni Alloys follow Hume-Rothery rules

Hume-Rothery rules for solid solutions

1. The atomic radius of the solute and solvent atoms must differ by no more than 15%.
2. The crystal structures of solute and solvent must be similar.
3. Complete solubility occurs when the solvent and solute have the same valency. (A metal of higher valency is more likely to dissolve in a metal with lower valency).
4. The solute and solvent should have similar electronegativity (If the electronegativity difference is too great, the metals tend to form intermetallic compounds instead of solid solutions).

Metals and Alloys



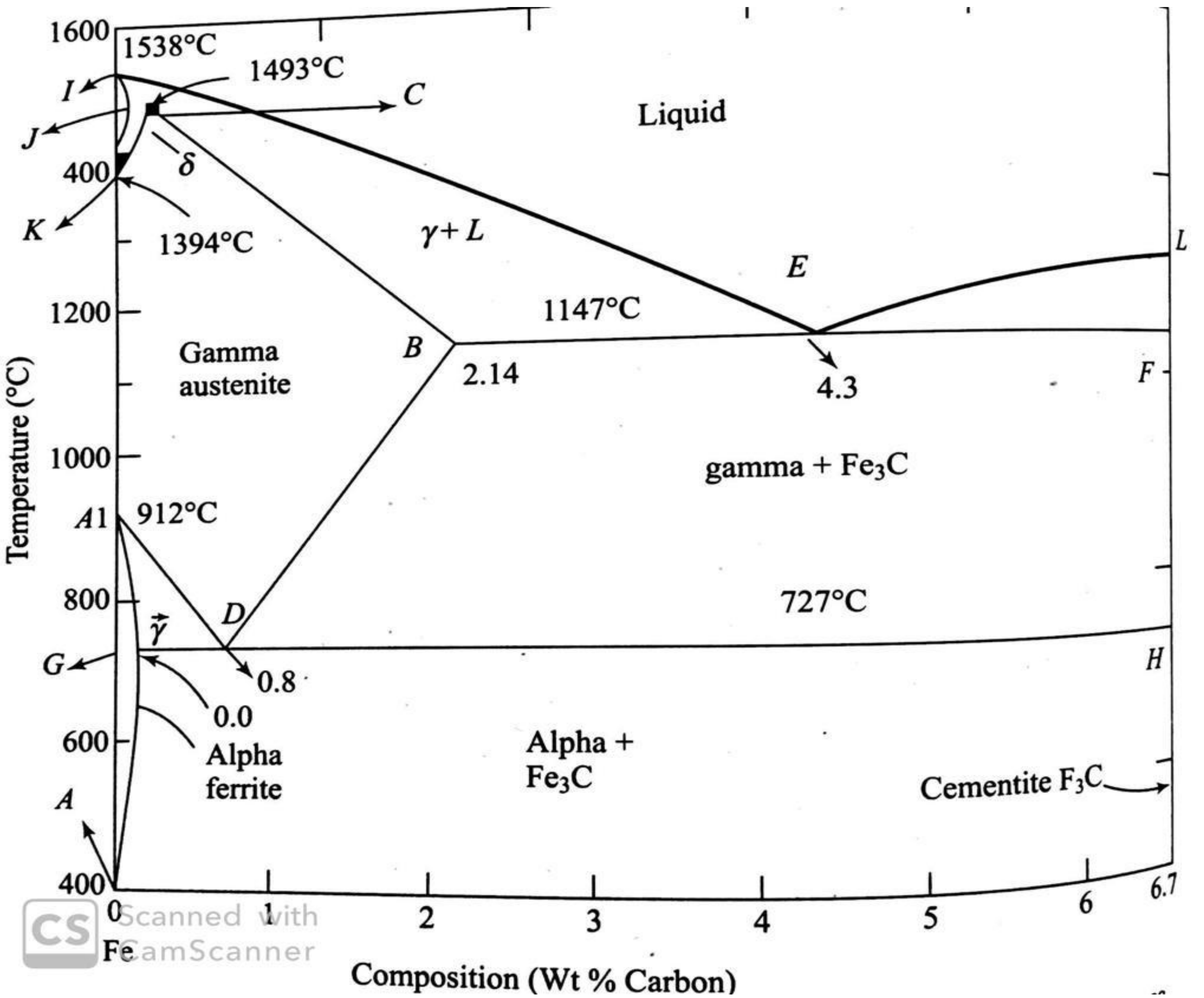
High Speed Steel Cutting Tools

Mercury is the only non ferrous metal that is liquid at room temperature.

Alloying.

- ❑ **Applications of Ferrous alloys**
  - ✓ Ferrous steel is produced as sheet for automobiles, appliances, and containers
  - ✓ As plates for ships, boilers and bridges
  - ✓ Bar products for leaf springs, gears axles, crank shaft and railroad rails
  - ✓ As wire and fasteners such as bolts, rivets and nuts
  - ✓ Ferrous materials comprise 70% to 85% by weight of virtually all structural members and mechanical components.
  - ✓ Carbon steels are least expensive.

Ferrous Alloy



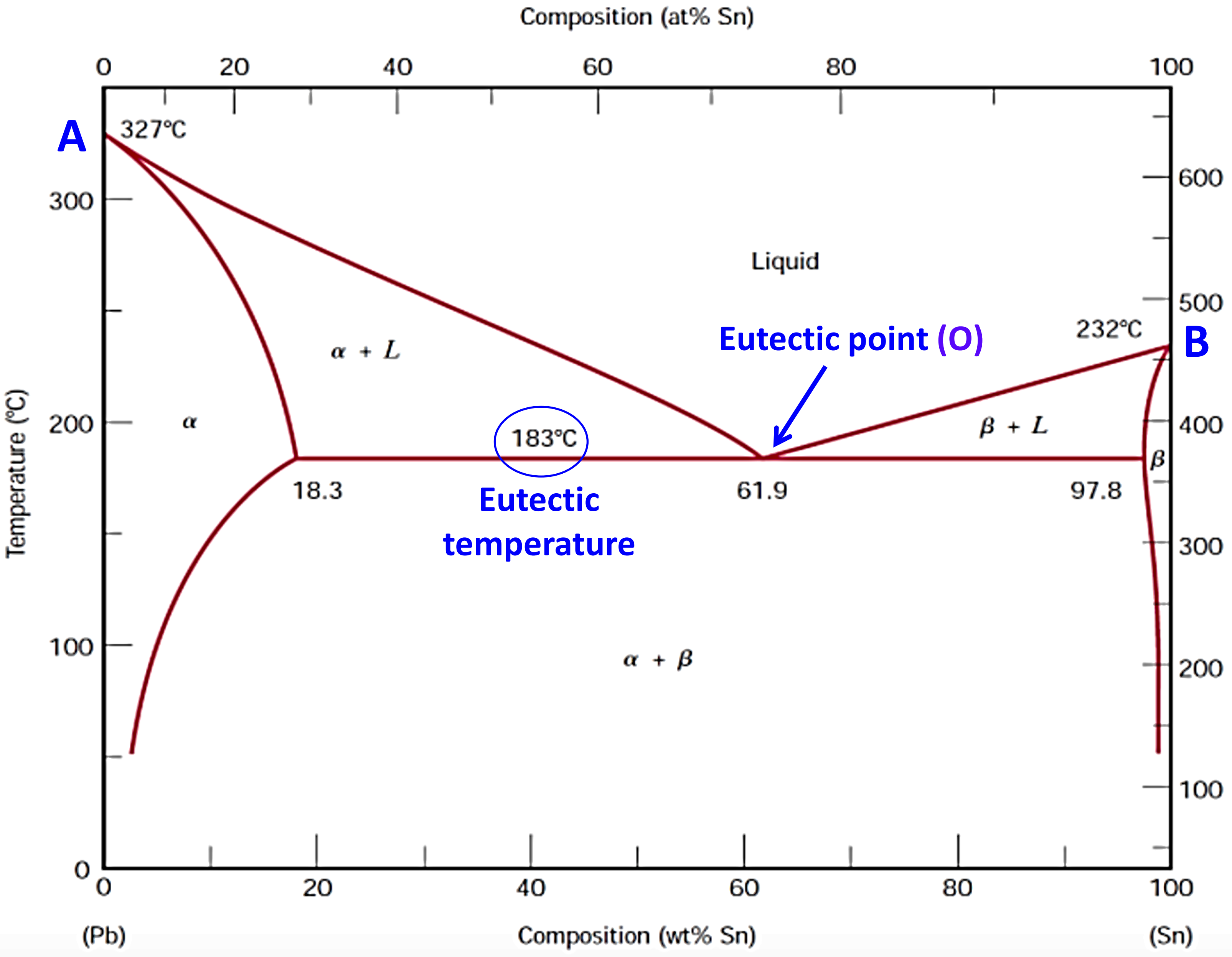
- **The Iron -Iron Carbide (Fe-Fe_3C) Phase Diagram**
  - ⇒ C: an interstitial impurity in Fe
  - ⇒ It forms a solid solution with α, γ, δ phases of iron
  - ⇒ maximum solubility in BCC α-ferriteis 0.022 wt % @ 727 °C.
  - ⇒ Maximum solubility in FCC austenite is 2.14 wt% at 1147 °C
  - ⇒ Mechanical properties: Cementite (Fe_3C) is hard and brittle: strengthens steels
  - ⇒ Mechanical properties also depend on microstructure: how ferrite and cementite are mixed
  - ⇒ Magnetic properties: α-ferrite is magnetic below 768 °C
  - ⇒ Austenite is non-magnetic

Non-ferrous Alloys

Some applications of non-ferrous alloys

- **Copper Alloys:**
  - One of the largest usea of Cu is probably in coins.
  - Euro coins are made of Cu-Ni, Cu-Zn-Ni or Cu-Al-Zn-Sn alloys.
  - Brasses and Bronzes are most commonly used alloys of Cu.
  - Brass is an alloy with Zn.
  - Bronzes contain tin, aluminum, silicon or beryllium.
  - More than 400 copper-base alloys are recognized.
- **Magnesium Alloys:**
  - Aerospace industry,
  - High speed machinery
  - Transportation and materials handling equipments
- **Nickel Alloys:**
  - Corrosion resistant parts: Valves, pumps, vanes Heat exchangers, shafts, impellers
  - Heat treatment equipments, Gas turbines, Chemical reactor, etc

VIT
Vellore Institute of Technology
(Deemed to be University under section 3 of UGC Act, 1956)



Lead-Tin Phase Diagram

- The curves AO & BO meet at the point O is called eutectic point. Here, solid Sn, Solid Pb and solution of Sn & Pb are in equilibrium. The point O (183 °C) represents a fixed composition of 61.9 % Sn and 38.1 % Ag, and is called eutectic composition.
- Area above AOB: Ag and Pb exist as solution
- Although lead-tin alloys are too weak for use as structural materials, they are widely used as solders for everything from joining copper plumbing to soldering electrical circuits. However, there is an international effort to develop lead-free solders because of the health concerns associated with lead.

Sample questions:

1. What will happen to an iron rod if it is dipped in a beaker containing aqueous solution of following pH (i) pH= 2 , (ii) pH= 7 (iii) pH= 9? Justify your answer with reference to the anodic and cathodic reactions.
2. What are the differences between chemical corrosion and electrochemical corrosion?
3. What is the law of oxide film growth during corrosion? Provide example(s).
4. Explain the effect of following factors on the rate of corrosion: (i) Nature of corrosion products, (ii) Anodic and cathodic areas.
5. A pure metal rod that is half-immersed vertically in water, starts corroding at the bottom. Give reason with the chemistry involved in it.
6. In what aspects physical vapor deposition technique is different from chemical vapor deposition technique?
7. Why zinc materials are combined with steel ship hulls? Justify your answer with the chemistry involved in it.
8. What are the advantages of using sputtering method over other physical vapor deposition (PVD) methods in very-large-scale integration (VLSI) fabrication?
9. Why does corrosion occur in steel pipe connected to copper plumbing?
10. Why corrosion is a natural process? Explain this from thermodynamic point of view.
11. Why does a part of nail inside the wood undergoes corrosion easily?
12. What are the secondary factors affecting the corrosion rate? Discuss any three of them.
13. What is Pilling–Bedworth ratio? What it is used for?

14. Why does a steel pipe in a large copper tank corrode causing rapid destruction?
15. Which is better between galvanization and tinning? Explain your answer.
16. What are the advantages and disadvantages of chemical vapour deposition technique of metallic coating?
17. How electroless plating process is different from electroplating process?
18. Write down the advantages and disadvantages of sputtering method of metallic coating.
19. Outline the difference in the use of anodic and cathodic coatings for corrosion prevention.
20. Describe pros and cons of physical vapour deposition technique of metallic coating.