

# ***SOLIDIFICATION OF PURE METAL***

PRESENTED BY :– SAURABH MALPOTRA

# INTRODUCTION

- Pure metals in its solid state have low strength and good ductility.
- It can be formed into any shape.
- In case of pure material the distance between atoms is of the order of 0.1nm.
- It can diffract X-rays having wavelength of similar order.

# COOLING CURVE

- The best way to monitor the process of solidification is to measure its temperature by a thermocouple. Figure 1 gives a plot of temperature (T) as a function of time (t). It shows that temperature keeps dropping continuously till it reaches a temperature when cooling stops till the liquid gets transformed totally into solid. Thereafter temperature keeps dropping again.
- **Fig 1:** Shows cooling curve of pure metal as it cools from liquid state. Gibb's phase rule gives a simple relationship between numbers of phases (P), number of component (C), and degree of freedom (F) for a given system. This is stated as  $P+F = C+2$ . Note that  $C = 1$  since it is a pure metal &  $P = 1$  since there is only one phase above  $T_m$  (melting point). Therefore  $F = 2$ . It means this state can have 2 controllable variables. These are temperature and pressure.

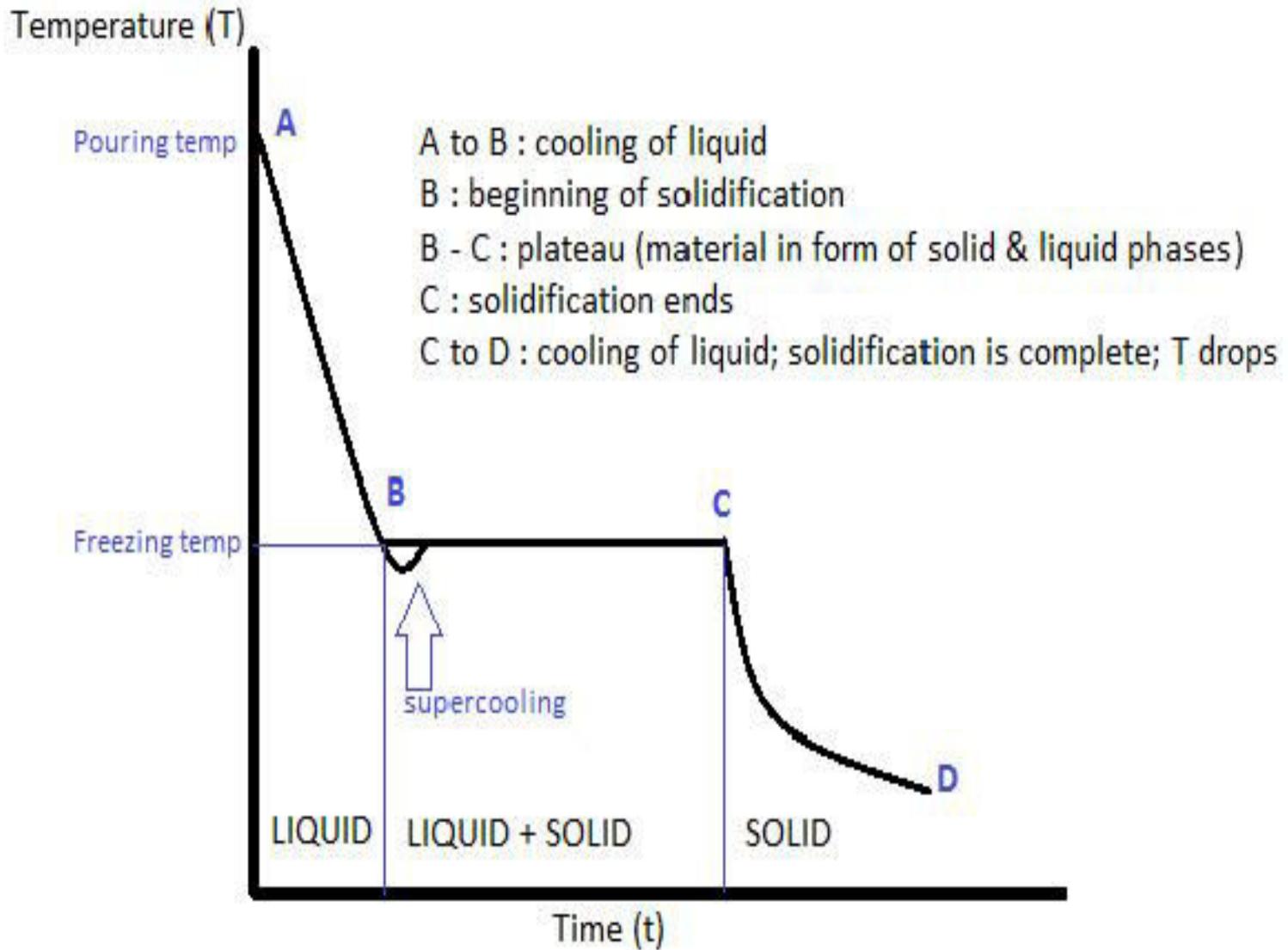


Diagram showing cooling curve of a pure metal

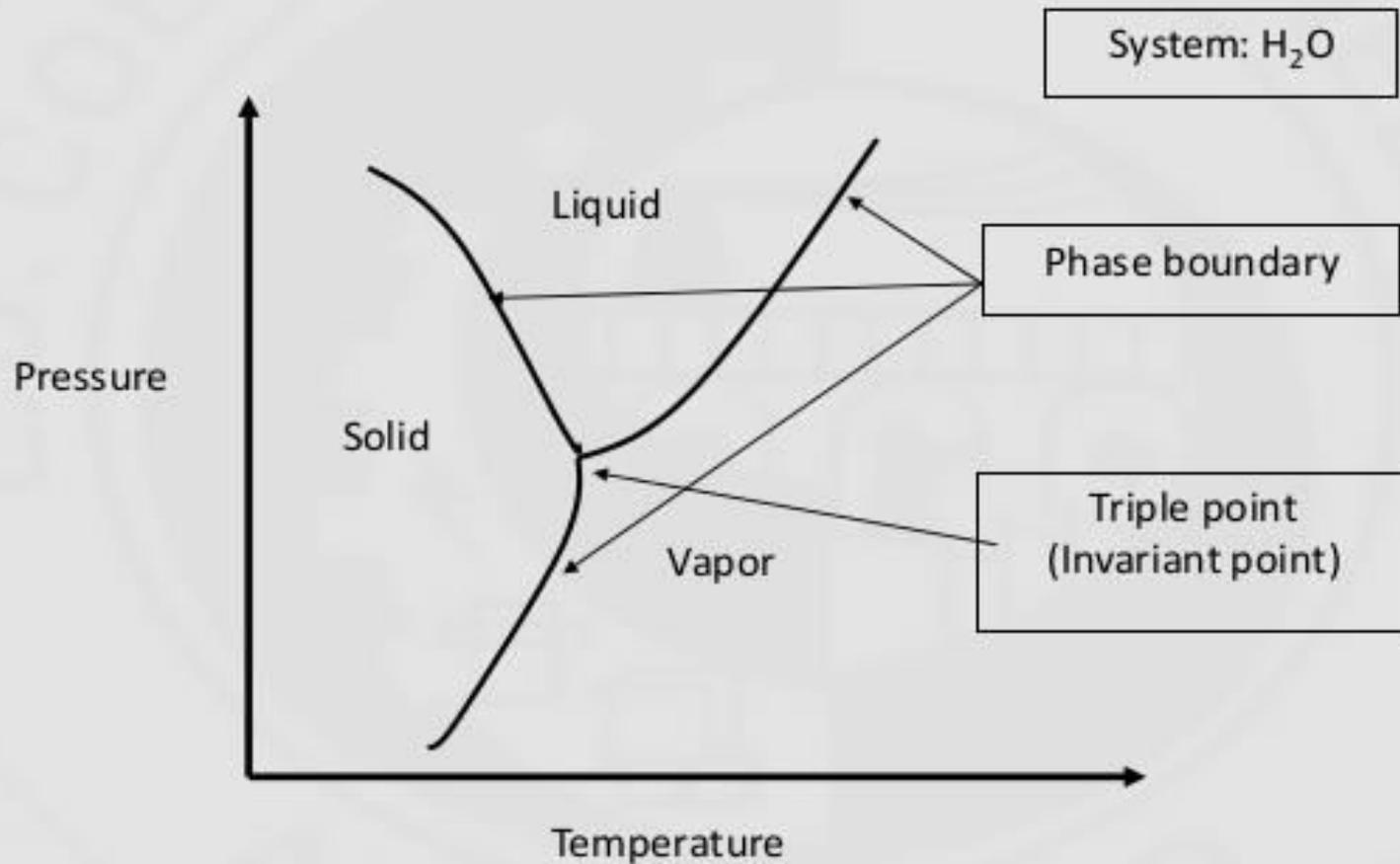
# **GIBB'S PHASE RULE ( $P+F = C+2$ )**

- The degree of freedom that determines the number of control parameters (like temperature, volume, pressure, composition) for any closed system follows Gibbs phase rule as stated in the caption of fig1. Above the melting point this is equal to 2. Clearly these variables here are the temperature and pressure.
- The cooling curve given above has been obtained at atmospheric pressure which is of course fixed. Therefore what the phase rule tells us is that the **liquid state is stable over a range of temperature.**
- Let us apply this to the state where both liquid and solid can co-exist. Here  $P = 2$  and  $C = 1$ . From phase rule  $F = 1$ . This state can have only one variable which in this case is pressure.
- This means in the case of a pure metal liquid & solid can coexist only at a definite temperature which happens to be its melting point.

# PHASE DIAGRAM OF PURE METAL

- Phase diagram of a pure metal or a substance is a graphical representation of the domain in which a given state is stable. For example it gives the range of temperature and pressure over which it exists as solid (S), liquid (L) or gas (G). Figure 2 gives a typical phase diagram of a pure metal.
- **Fig 2:** A schematic phase diagram of a pure metal indicating the pressure temperature domain where it can exist as solid, liquid or gas. The line indicates boundary between two phases. On any point on the line two phases are equally stable. There is a point where three lines meet. This is a critical point (triple point) where three phases can coexist. Apply phase rule. This gives  $F=0$  meaning that it has no degree of freedom. Three phases can coexist only at a fixed temperature & pressure. For water the triple point is at 0.006 atmosphere  $0.01^{\circ}\text{C}$ .

# A simple phase diagram



# GIBB'S FREE ENERGY (G)

- Gibb's free energy (G) is a measure of the stability of a phase at a given temperature and pressure.
- The lower the free energy higher is its stability.
- At a given temperature (T) this is defined in terms of molar enthalpy (H) and molar entropy (S) of a particular phase as follows:-

$$G = H - T S \dots\dots\dots 1$$

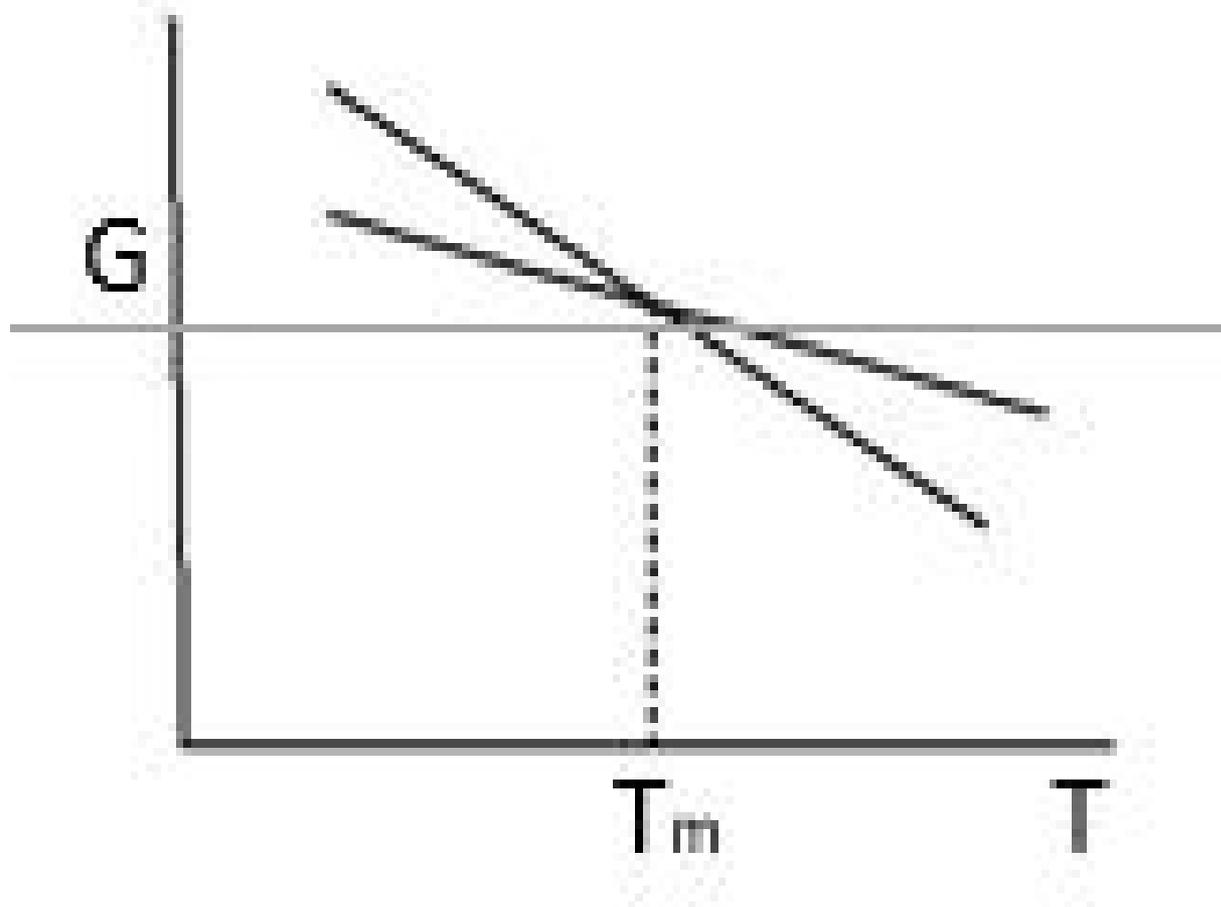
- This can be written in differential form in terms of pressure (P) & temperature (T), the two common variables for most transformation processes, as:-

$$dG = V dP - S dT \dots\dots\dots 2$$

- The equation 2 is valid both for solid and liquid. Let us write these explicitly for the two using subscript S (for solid) & L (for liquid).
- Figure 3 gives a schematic plot showing how free energy varies with temperature for the two phases at 1 atmosphere pressure. The point where the two lines intersect denotes the melting point at 1 atm.

$$dG_L = V_L dP - S_L dT - \text{ for liquid} \dots\dots\dots 3$$

$$dG_S = V_S dP - S_S dT - \text{ for solid} \dots\dots\dots 4$$



**Fig 3:** A sketch showing how G varies as a function of T for solid (S) and liquid phase (L). The two intersect at melting point  $T_m$ . Below this temperature solid is stable whereas above  $T_m$  liquid is stable. At any temperature the difference between the two is the driving force for the transformation.

At the melting point the free energy of solid and liquid should be the same. Equating equation 3 & 4 and subsequent rearrangement of the terms one gets the following expression:-

$$\frac{dP}{dT} = \frac{S_L - S_S}{V_L - V_S} = \frac{T_m}{T_m} \left( \frac{\Delta S_{L-S}}{\Delta V_{L-S}} \right) = \frac{\Delta H_{L-S}}{T_m \Delta V_{L-S}}$$

Apply this to ice making. When water becomes ice there is an increase in volume and it is accompanied by release of heat.

Therefore  $V_{L-S}$  is positive; whereas  $H_{L-S}$  is negative.

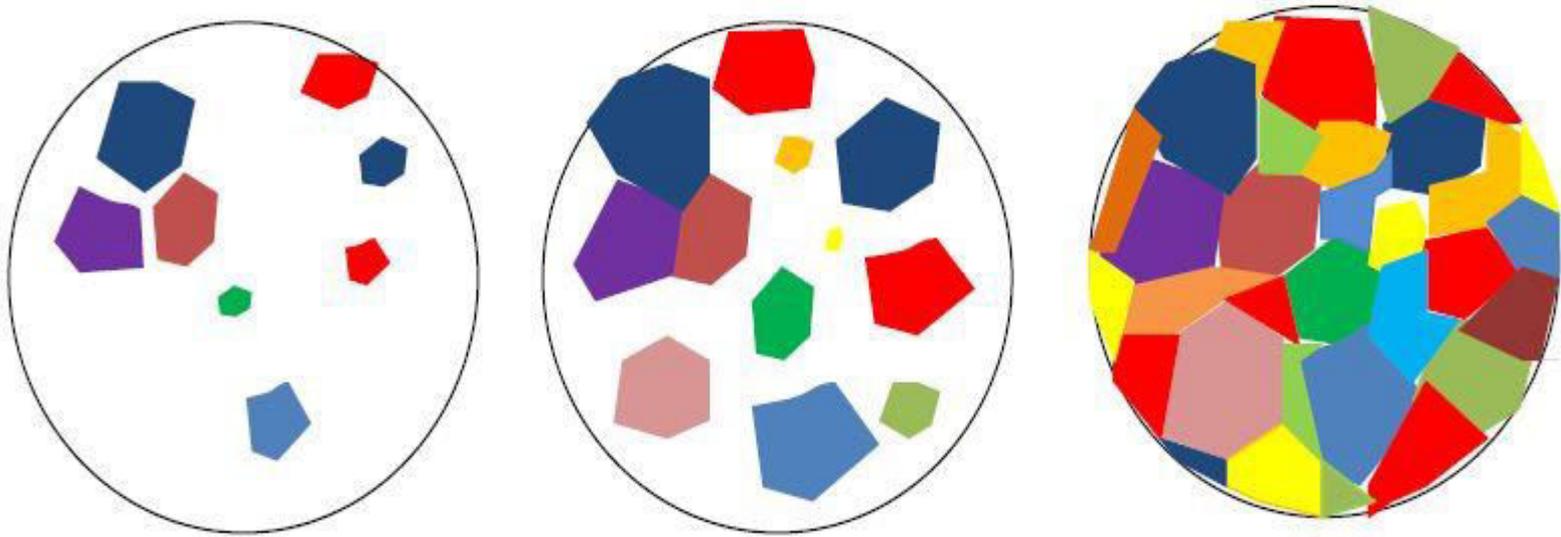
Consequently (dP/dT) or the slope of the line denoting L-S equilibrium should be negative signifying that at higher pressure ice forms at lower temperature.

# MECHANISM OF CRYSTALLIZATION

- **Concept of nucleation and growth :-**
  - ✓ Solidification takes place by nucleation and growth.
  - ✓ Atoms in a solid or in a liquid are never stationary.
  - ✓ Assume that in a pool of molten metal there is a virtual boundary that separates a potential stable nucleus (embryo) from the surrounding liquid. Such virtual nuclei infinitesimally small in size may be assumed to be present in the liquid that is about to solidify. Atoms keep trying to cross the barrier.
  - ✓ Let  $\nu_0$  be the number of attempts per unit time made by an atom to cross the boundary. The number of successful attempt is given by the Boltzmann statistics. This is represented mathematically as follows:

$$\nu = \nu_0 \exp \left( -\frac{E}{kT} \right)$$

- ✓ Note that  $k$  is Boltzmann constant and  $E$  is the energy needed by atom to overcome the barrier to cross the boundary.
- ✓ In this case this corresponds to  $\Delta fT \max$ . ( where  $\Delta f$  is the size of the atom)
- ✓ However this represents the total energy needed by all the atoms in a unit volume ( $n$ ).
- ✓ Therefore the energy needed by a single  $E = \Delta fT \max / n$ .
- ✓ This shows that with increasing  $E$  the probability of formation of stable nuclei should decrease.
- ✓ Once stable nuclei form they would continue to grow. Initially the growth occurs at same rate in all direction until the growth is hindered due to impingement.
- ✓ The size of the grains may differ depending on whether it developed from a nucleus formed right in the beginning or towards the end of the process. This is shown pictorially in fig 9.



**Fig 9:** A sketch showing a schematic representation of nucleation and growth of solid nuclei during solidification from the molten liquid state. Colours denote different orientations of grains. (a) Initially there are fewer nuclei. Some of them have grown. (b) Shows that growth ceases along certain directions due to impingement. A few more nuclei have formed. All of these continue to grow. (c) Shows a state when most of the space is filled up indicating that the process is nearly complete. Grains appear to be randomly oriented.

# GRAIN ORIENTATION

- The process of nucleation described above is totally random. Grains may nucleate anywhere in the melt. It is also known as homogeneous nucleation.

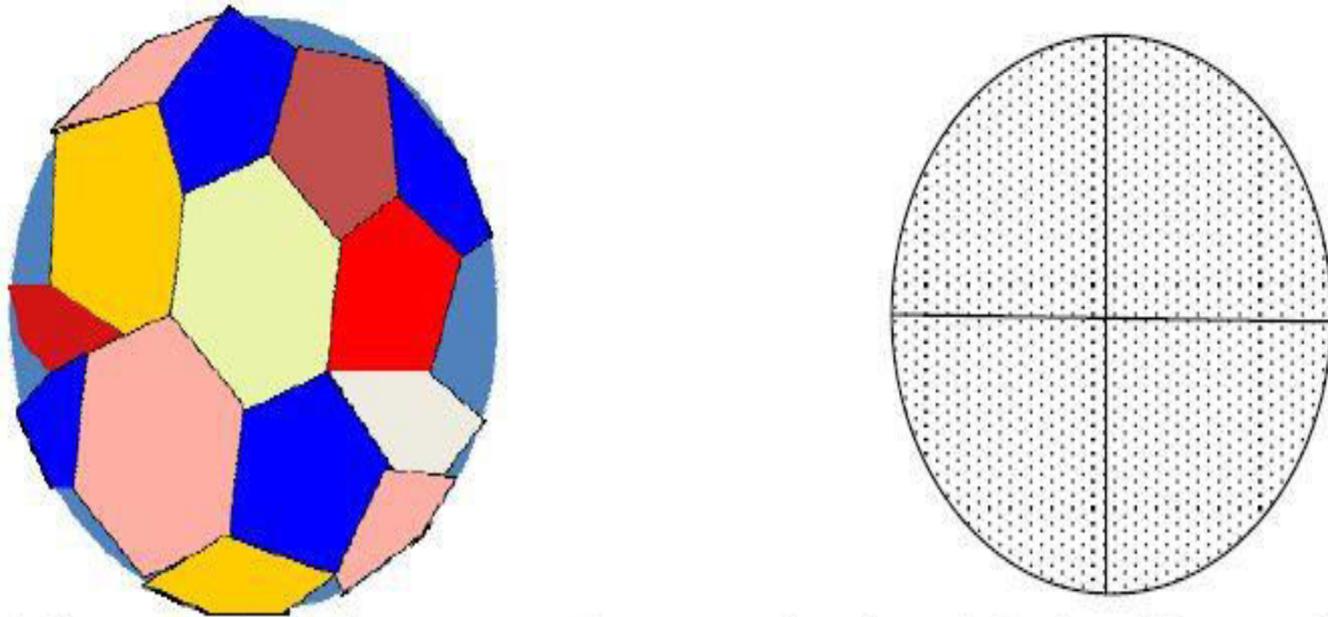
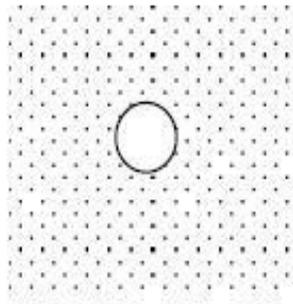


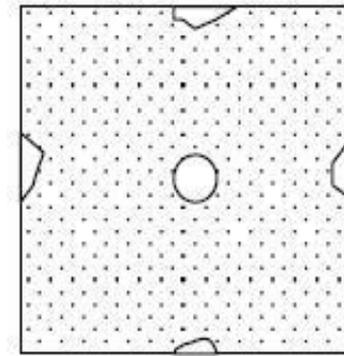
Fig 10: (a) Shows a typical microstructure of pure metal each grain having different orientations. Sometimes grain lustre depends on its orientation. (b) This shows distribution of  $\langle 001 \rangle$  poles of all the grains on a standard projection. This type of diagram is known as pole figure.

Homogeneous versus heterogeneous nucleation

# HOMOGENOUS VS HETROGENOUS NEUCLEATION



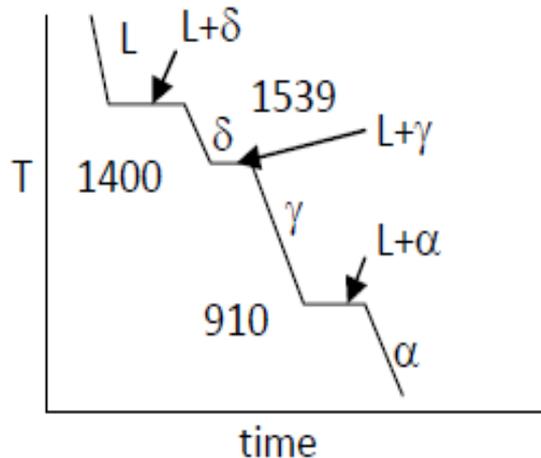
**Fig 11 a)** A sketch showing homogeneous nucleation of a solid spherical ball in a molten pool of metal in a hypothetical mould without any boundary.



**Fig 11 b)** Sketch showing a case where apart from an embryo at the centre there are several nuclei each formed on the interface between the mould wall and the liquid metal.

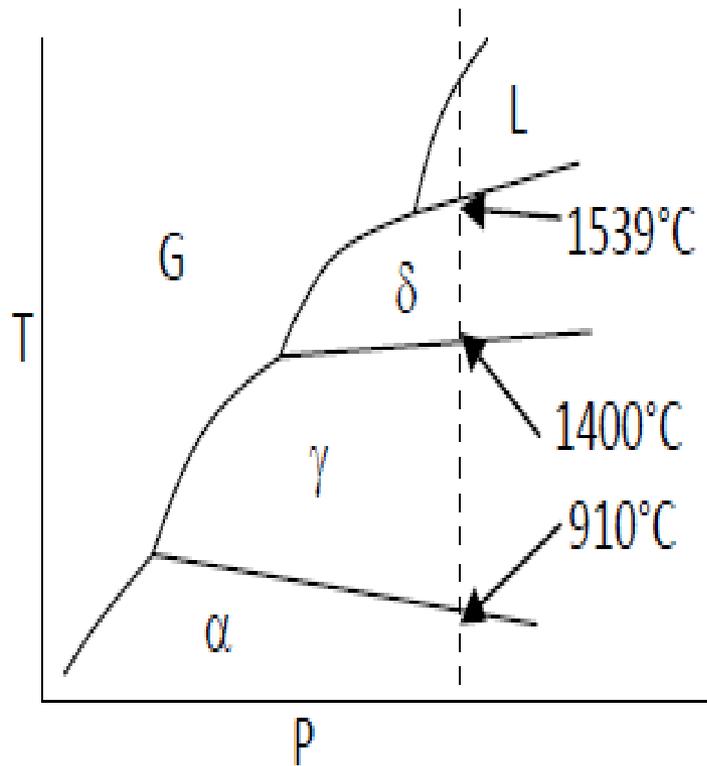
# PHASE DIAGRAM OF PURE IRON

- Iron can exist in more than one crystalline form.
- Melting point of pure iron is 1539°C.
- If it is cooled from its molten state it first solidifies in the form a bcc phase. This form of iron is known as **ferrite**.
- As the temperature goes down at 1400°C it transforms from  $\delta$  phase to fcc phase. This is commonly known as **iron** or **austenite**.
- Later at 910°C it again transforms into bcc crystal known as **ferrite**.
- Each of these transformations is associated with a change in volume and enthalpy.



**Fig 4:** Cooling curve for pure iron showing three steps representing following transformations:

L =  $\delta$  at 1539°C  
 $\delta$  =  $\gamma$  at 1400°C  
 $\gamma$  =  $\alpha$  at 910°C

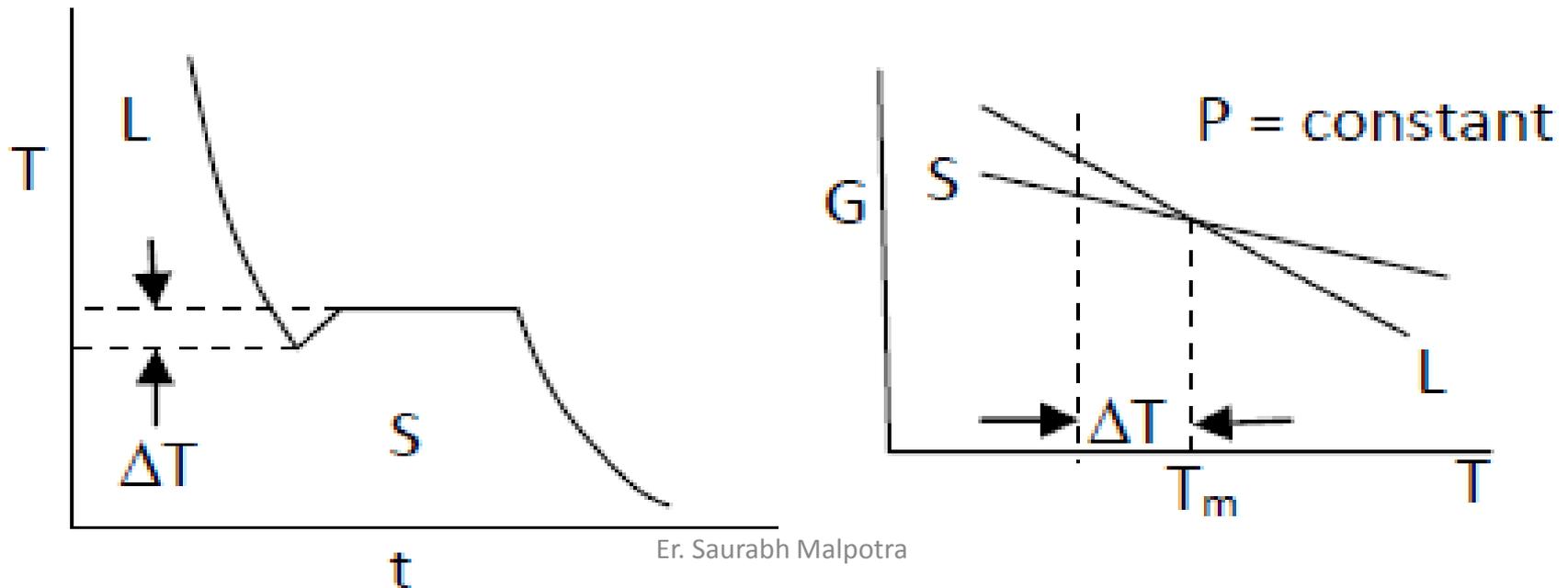


**Fig 5:** A sketch showing the phase diagram of pure iron. This gives the stability of  $\alpha$ ,  $\gamma$ ,  $\delta$ , L & G phases in various temperature pressure domains.

- The phase diagram of pure iron is shown in fig 5. This shows the effect of pressure on the temperatures at which transformation of iron from one crystalline form to another takes place.

# REAL COOLING CURVE: SUPER (UNDER) COOLING

- The cooling curve of a pure metal as shown in fig 1 is indeed an idealization of the solidification process. In reality the transformation from liquid to solid state begins only after it has cooled below its melting point.
- Figure 6 shows a sketch of real cooling curve.
- **Fig 6: A sketch showing real cooling curve.** Along with this G versus T plot of the solid and liquid phases have been shown. At a temperature lower than its melting point  $G_S < G_L$  signifying S is more stable than L.



- When a solid forms in a pool of liquid a new surface is created (see fig 7). This has a finite energy. It is seen from fig 6 that  $G_S < G_L$  when solidification begins. This difference in free energy acts as the driving force for solidification.
- Once this is large enough for a stable nucleus of solid to form then process of solidification begins. Until then unstable nuclei may appear and disappear again and again. Soon after a stable nucleus forms it keeps growing. Thus the process of solidification can be visualized as one of nucleation and growth.
- Fig 7: A sketch showing a spherical nucleus of solid of radius  $r$  formed in a pool of liquid. This has a volume  $\frac{4\pi}{3}r^3$  and surface area  $4\pi r^2$ . The creation of a new surface needs energy. Note that  $G_S < G_L$ ,  $\Delta G_{L-S} < 0$ . This can help do so. Assuming that surface energy / unit area is  $\sigma$  and free energy change /unit volume is  $\Delta f_v$  it is possible to derive an expression for the total change in energy for solidification.

