

# Phase Diagram of 1 Component System. ①

Phase diagram or simple explanation is a diagram of different phases.

We define a system in terms of its variance or degree of freedom. A phase diagram depicts these parameters i.e. Temperature, Pressure & Composition in terms of a diagram i.e. graphical representation.

Hence for 1 component system

The degree of freedom  $F$  is given by

$$F = C - P + 2 \quad \text{General Gibbs phase rule}$$
$$= 1 - P + 2 = 3 - P.$$

$\therefore$  for a 1 component system

$$F = 3 - P$$

→ General rule according to Gibbs phase rule.

(1) If one component system has only one phase only e.g. water in either solid (ice) or liquid (water) or gas (vapour) phase.  $S$  or  $L$  or  $V$ .

Value of  $F = 3 - 1 = 2$ . Therefore two variables have to be specified to define the system completely. Temperature & pressure. (since composition is 100%)

(2) If one component system has two phases.  $S$  or  $L$  or  $V$ ,  $F = 3 - 2 = 1$

Any one of the variable  $T$  or  $P$  is sufficient to define the system completely. If temperature is specified pressure is automatically known or vice versa.  $\Rightarrow$  System is in equilibrium between the two phases  $S \rightleftharpoons L$ ,  $L \rightleftharpoons V$  or  $S \rightleftharpoons V$

in that case degree of freedom is 1 in case of a 1 component system.

(iii) If one component system has three phases

$$F = 3 - P = 3 - 3 = 0$$

and system is invariant i.e. three phases in equilibrium at a definite value of temperature and pressure.

Thus the maximum number of phases at equilibrium is for one component system is <sup>THREE</sup> and maximum degrees of freedom is two.

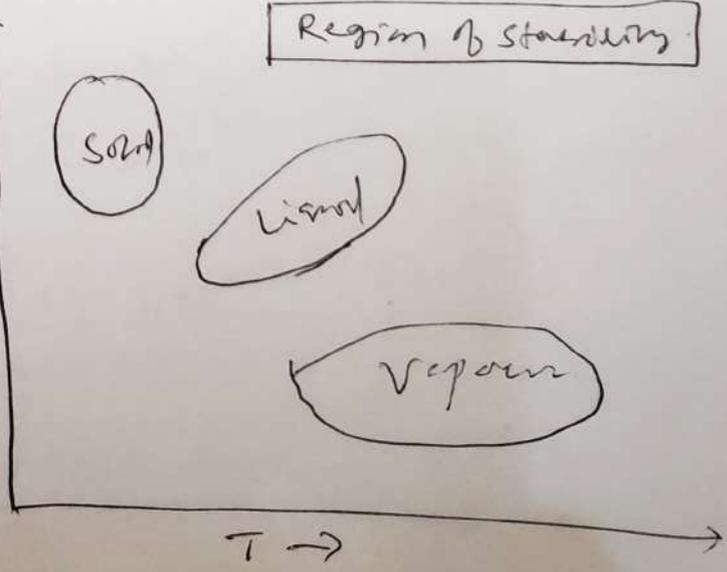
Hence the phase diagram of one component system can be drawn in two dimension using temperature and pressure as variable in Cartesian - coordinate system. RECTANGULAR AXES representing Temperature & pressure as variables. Since composition is 100% in one component system.

The phase diagram of a 1 component system will include the following aspects.

Representation of a single phase:

① A single phase will be represented over a region (Area) since the given phase can exist under different conditions of temperature & pressure. [Both temperature & pressure can be varied independently over a range of values with out affecting the existence of a single phase.]

Solid phase - Stable at low temp & high pressure. P  
Liquid - In between solid & gas.  
Gaseous phase - High temperature & low pressure.



### Representation of Two phases in Equilibrium:

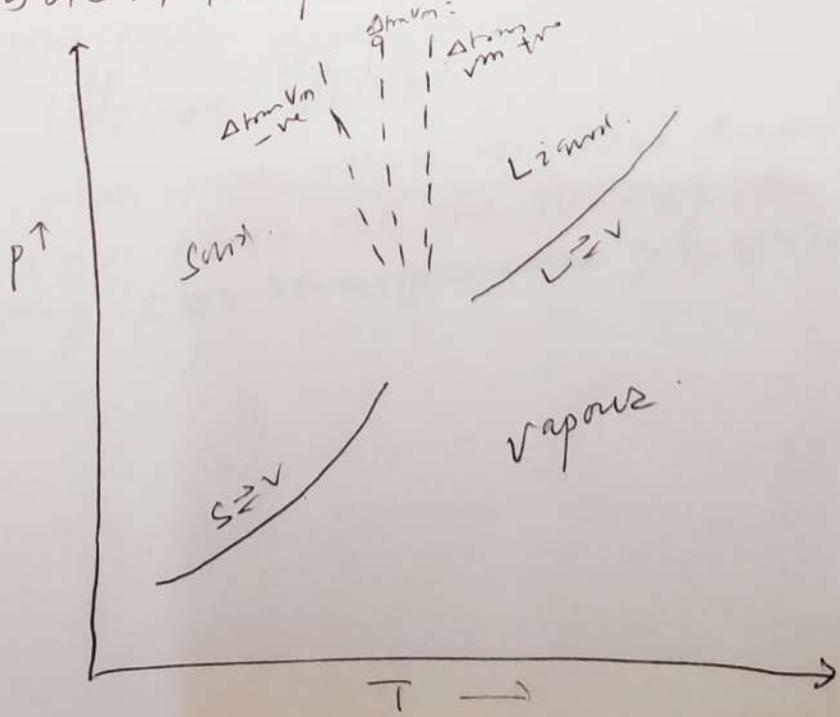
(I) Two phases in equilibrium will be represented on a line since in two phases ~~equilibrium~~ <sup>eqm</sup> equilibrium there is need to state only one variable either temperature or pressure  $A \xrightleftharpoons[P]{T} B$  (since at eqm P & T is fixed if we state temperature pressure is automatically fixed or vice versa).

So if temperature is stated the corresponding equilibrium value of pressure can be determined from the line and vice versa.

The number of lines in a Phase diagram will be the number of equilibria (TWO PHASE EQUILIBRIA) which the system can possess.

The slope  $\frac{dp}{dT}$  of these lines follows the CLAPEYRON equation i.e.  $\frac{dp}{dT} = \frac{\Delta_{trans} H_m}{T \Delta_{trans} V_m}$

$\Delta_{trans} H_m$  &  $\Delta_{trans} V_m$  are the respective changes in the molar enthalpy and molar volume during the transformation of one phase to the other at the equilibrium temperature T.



In general the  $\frac{dp}{dT}$  (slope) is much steeper than in case of  $S \rightleftharpoons L$  than  $S \rightleftharpoons V$  &  $L \rightleftharpoons V$  as  $\Delta_{trans} V_m$  for  $S \rightleftharpoons L$  is very small. Since  $\Delta_{trans} H_m$  (fusion) is always +ve  
 So slope  $\frac{dp}{dT}$  is +ve in fusion as melting point curve depends when  $\Delta_{trans} V_m$  +ve or -ve or zero.

If Solid is denser than liquid  $\Delta_{trans} V_m$  +ve  
 Liquid is denser than solid  $\Delta_{trans} V_m$  -ve  
 If Density of solid = Density of liquid.  $\Delta_{trans} V_m = \text{zero}$   
 Slope is 0.

Representation of Three phases in Equilibrium:

Three phases in equilibrium is represented by a point since both the variables (Temp & pressure) for such type of equilibrium have definite value. The three line comprising  $S \rightleftharpoons L$ ,  $L \rightleftharpoons V$  &  $S \rightleftharpoons V$  meet one another at this point. This point is known as triple point of the system.

In general we have

$\Delta_{sub} H_m = \Delta_{fus} H_m + \Delta_{vap} H_m$   
 $S_{ub} = \text{Sublimation}$        $f_{us} = \text{fusion}$        $v_{ap} = \text{Vaporization.}$   
 $\Delta_{sub} H_m = \Delta_{fus} H_m + \Delta_{vap} H_m$

$\Delta_{sub} H_m > \Delta_{vap} H_m$

Clapeyron eqn.

$\left(\frac{dp}{dT}\right)_{S \rightleftharpoons V} = \left(\frac{dp}{dT}\right)_{L \rightleftharpoons V}$

Thus at triple point where the three lines representing  $S \rightleftharpoons V$ ,  $L \rightleftharpoons V$  &  $S \rightleftharpoons L$  meet one another, the slope of the line representing  $(S \rightleftharpoons V)$  transformation  $>$   $(L \rightleftharpoons V)$  transformation.

# Construction of PHASE DIAGRAM OF ONE COMPONENT SYSTEMS:

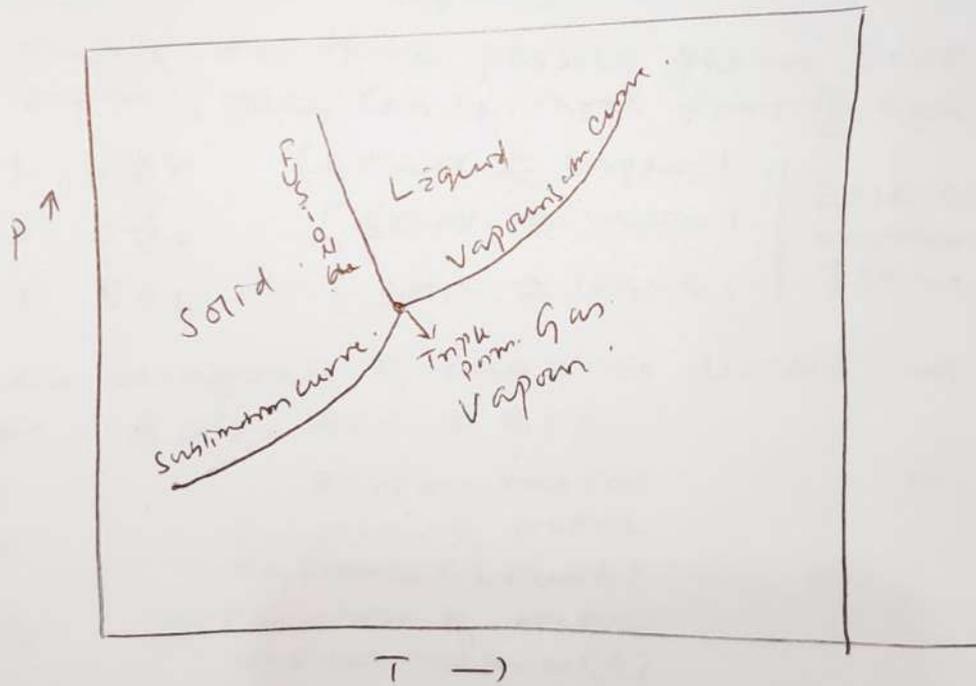
Phase diagram is a graphical representation of the physical states of a substance under the different conditions of temperature and pressure. Conventionally in a phase diagram X-axis Temperature & Y-axis pressure.

~~As the line of the curve~~

As we cross the Lines/curves on the phase diagram, a phase change occurs.

At a point on line it is possible for two to (three) phases co-exist at equilibrium. In other regions of the plot only one phase exists at equilibrium.

A phase diagram is a common way to represent the various phases of a substance and the condition under which each phase exists.



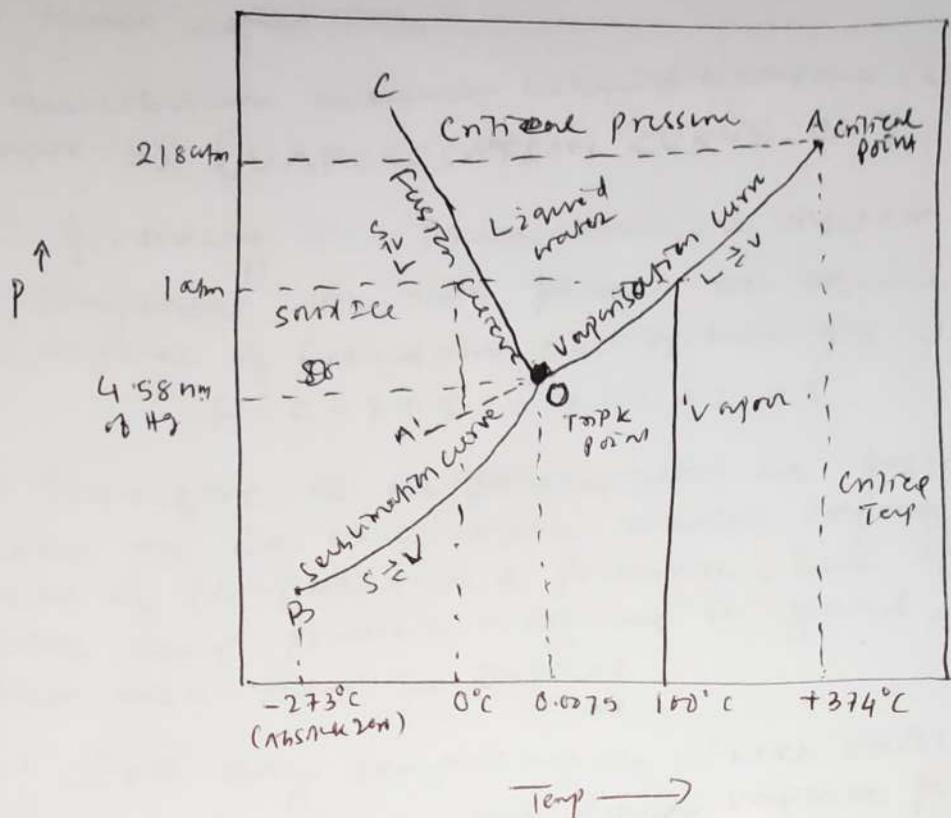
At any point in the ~~separated areas~~ Areas separated by curves P & T allow only one phase (S/L/G) to exist.

At any point on the curves the temp & pressure allows two phases to exist in equilibrium. (S ⇌ L, S ⇌ V, L ⇌ V)

At the line melting temp for various pressures can be found. Junction of 3 points is called triple point.

\* PHASE DIAGRAM ARE SPECIFIC FOR EACH SUBSTANCE & MIXTURE

# PHASE DIAGRAM OF WATER:



Water exists in three possible phases Solid (Ice), Liquid (water) and vapour, there can be three forms of equilibrium.

1.  $L \rightleftharpoons V$  (Liquid  $\rightleftharpoons$  Vapour)
  2.  $S \rightleftharpoons V$  (Solid  $\rightleftharpoons$  Vapour)
  3.  $S \rightleftharpoons L$  (Solid  $\rightleftharpoons$  Liquid)
- Each equilibrium involves two phases.

The phase diagram of water is divided into three areas AOB, AOC & BOC

Areas	Representation	No of phase
AOC	Condition of water existence (Liquid)	1
AOB	Condition of water vapour existence (g)	1
BOC	Condition of Ice existence (solid)	1

IN all areas  $C = 1, P = 1$ .

$$F = C - P + 2 = 1 - 1 + 2 = 2 \text{ Hence the System}$$

is bivariant.

Due to three forms of equilibrium the phase diagram has three lines.

1. Equilibrium between liquid & vapour ( $L \rightleftharpoons V$ ) vaporisation curve.  $\Rightarrow$  [VAPORISATION CURVE OA]

(i) According to phase rule, a system comprising of one component in two phases in equilibrium has one degree of freedom i.e. system is UNIVARIANT.

$$F = C - P + 2 = 1 - 2 + 2 = 1.$$

(ii) Therefore it is possible will be possible for liquid water to co-exist with water vapour at different values of temperature & pressure, but if one the variable factor temp, pressure or volume is fixed, the state of the system will then be defined.

(iii) For any temperature, there exist only one vapour pressure. Similarly for each vapour pressure only one vapour pressure can be maintained.

(iv) If the points indicating, the values of pressure corresponding different temperatures are joined then curve OA is obtained called vaporisation curve represents variation of pressure with temperature.

(v) Along this curve liquid (water)  $\rightleftharpoons$  water (vapour) in equilibrium with each other. 2 Phases one component.  
 $f = C - P + 2 = 1 - 2 + 2 = 1.$

Hence the SYSTEM ALONG THE CURVE OA IS UNIVARIANT.

(vi) The slope of the curve OA at any point is given by Clapeyron eqn.

$$\left(\frac{dp}{dT}\right)_{L \rightleftharpoons V} = \frac{\Delta H_{\text{vap}}}{T(V_g - V_l)}$$

(~~Enthalpy~~ Enthalpy of vaporisation ( $\Delta H$  of the transition process))  
( $H_v - H_l$ ) (Enthalpy of vapour -  $E_n$ )  
- Molar enthalpy of vaporisation of vapour  
- Molar enthalpy of liquid.

$V_g$  &  $V_L$  are molar volume of vapour & liquid respectively &  $T$  is equilibrium temperature i.e. vaporisation temp.

The curve has an upper limit at critical temperature & critical pressure.

(vii) With increase in temperature pressure the density of vapour must increase.  $\rho_v \propto P$   
Also with increase in temperature the density of liquid must decrease.  $\rho_L \propto 1/T$

As  $L \rightleftharpoons V$  the density of vapour increasing with pressure & density of liquid decreasing with temperature.

A stage will come when  $\rho_L = \rho_v$ , the system ceases to be will be homogenous. The temp at which this occurs is called critical temperature. & corresponding pressure at critical temperature & will be critical pressure.

The curve will end abruptly at this point.

(viii) As liquification above this point is not possible irrespective of pressure applied.

Critical pressure - 218 atm  
critical temperature - 374°C.

(viii) Above critical temperature it is impossible to condense a gas into liquid just by increasing pressure. The particles have too much energy for the intermolecular attraction to hold them together as a liquid.

A critical point is the end point of a phase equilibrium curve.

e.g.  $L \rightleftharpoons V$  (liquid vapour critical point, the end point of  $P$  vs  $T$  curve that designates conditions under which a liquid vapour co-exist. At critical point - phase boundary vanishes.

② Sublimation curve of Ice (OB) solid  $\rightleftharpoons$  vapour  
(Ice  $\rightleftharpoons$  ~~water (liquid)~~) (Ice  $\rightleftharpoons$  vapour)

(i) The condition of equilibrium between Ice & ~~water~~ vapour will be represented by a line or curve showing depicting the variation of Temperature with pressure.  $S \rightleftharpoons V$  representing condition of equilibrium between Solid & its vapour represented by OB called Sublimation curve.

(ii) Temperature represented by any point in this curve, the solid ice sublimes into vapour. Lower end B extends to absolute zero. Along this curve BO ice is in equilibrium with its vapour. Solid & vapour are in equilibrium with each other.

$\therefore F + P = C + 2$  or  $F = C - P + 2$  or  $F = 1 - 2 + 2 = 1$   
System is UNIVARIANT ~~ON THE LINE~~ along the curve.

Slope of the curve at any point as given by Clapeyron equation

$$\left(\frac{dp}{dT}\right)_{S \rightleftharpoons V} = \frac{\Delta H_{sub}}{T(V_g - V_s)} \quad \text{or} \quad \ln \frac{P_2}{P_1} = \frac{\Delta H_{sub}}{R} \left[ \frac{T_2 - T_1}{T_1 T_2} \right]$$

③ FUSION CURVE (OC)  $\Rightarrow$  (S  $\rightleftharpoons$  L) (Ice  $\rightleftharpoons$  water)

(i) The curve representing (T & P) at which Ice and water are in equilibrium will represent the change in melting point with pressure.

(ii) Known as fusion curve of Ice represented by OC

(iii) With increase in pressure m.p of Ice lower i.e. why curve OC inclined towards pressure axis.

Slope at any point is given by

$$\left(\frac{dp}{dT}\right)_{S \rightleftharpoons L} = \frac{\Delta H_{fus}}{T(V_L - V_S)}$$

(iv) Since  $\rho_{ice} < \rho_{water}$   $V_{ice} > V_{water}$  ( $V_s > V_L$ )

Hence  $\left(\frac{dp}{dT}\right)_{S \rightleftharpoons L}$  is -ve (Negative)

OC is slightly tilted towards Pressure Axis.

(v) Along this curve liquid water and ice are in equilibrium ( $S \rightleftharpoons L$ )

$F = C - P + 2 = 1 - 2 + 2 = 1$  (UNIVARIANT)

\* Imp [The slope of the fusion curve in case of water is negative as a result water can melt at a temperature near its f.p. when subjected to pressure.]

The ease with which ICE SKATERS GLIDE with across a frozen pond can be explained by the fact that the pressure applied by / exerted by their skates melts a small portion of ice that lies beneath the blades.

(4) Triple point ( $S \rightleftharpoons L \rightleftharpoons V$ )

(i) At a temperature  $0.0075^\circ C$  & pressure  $4.58 \text{ mmHg}$  three curves (OA, OB & OC) intersect.

(ii) At this point Ice, water & vapour are in equilibrium with each other.

(iii) Known as triple point represented by O.

At O three phases in equilibrium.

$F = 1 - 3 + 2 = 0$  (INVARIANT)

(iv) At O  $S \rightleftharpoons V$  (OB) is greater than that of  $L \rightleftharpoons V$  (OA) can be shown by Clapeyron eqn

$\left(\frac{dp}{dT}\right)_{S \rightleftharpoons V} = \frac{\Delta H_{sub}}{T(V_g - V_s)}$   $V_g - V_s \rightleftharpoons V_g - V_L$

$\left(\frac{dp}{dT}\right)_{L \rightleftharpoons V} = \frac{\Delta H_{vap}}{T(V_g - V_L)}$

(iv) At the triple point.

$$\Delta \bar{H}_{\text{sub}} = \Delta \bar{H}_{\text{vap}} + \Delta \bar{H}_{\text{fusion}}$$

Since  $\Delta \bar{H}_{\text{sub}} > \Delta \bar{H}_{\text{vap}}$

$$\left(\frac{dp}{dT}\right)_{S \rightleftharpoons V} > \left(\frac{dp}{dT}\right)_{L \rightleftharpoons V}$$

(5) Supercooled water, Metastable state.

(i) Sometimes it is possible to cool water below its freezing point without the separation of ice. The water is then said to be supercooled & can be kept for a long time if solid particles are avoided.

(ii) If curve AO ( $L \rightleftharpoons V$ ) is cooled rapidly ice may fail to form at the triple point & the vapour pressure of liquid continue along OA'

(iii) The  $L \rightleftharpoons V$  along OA' called metastable equilibrium. As soon as a small particle of ice is brought in contact with the supercooled liquid entire liquid solidifies.

(iv) curve OA' lies above OB. Metastable system has a higher V.P than stable one.