PHASE RULE

Gibb's Phase rule

- Phase is useful in study of heterogenous equilibria.
- It is possible to predict qualitatively, the effect of change in temperature, pressure & concentration on a heterogenous equilibrium.
- The equilibrium may involve a physical or a chemical change.

Statement

The sum of number of degrees of freedom (F) and number of phases (P) is greater than number of components (C) by two, for a heterogenous system.

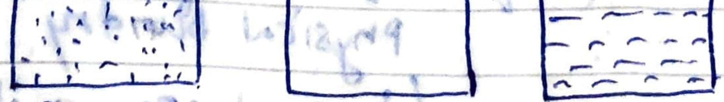
$F = C - P + 2$ OR $F + P = C + 2$

where F = Degrees of freedom, 2 = two ~~addition~~ variables operating on the system (temp, pressure)
C = Number of components
P = Number of phases

- Phase (P)

A phase is physically distinct, chemically homogenous and mechanically separable part of a heterogenous system at equilibrium. (separated by a definite boundry).

1) Pure substance - Either solid or liquid or gas



Pure O_2 Pure Ice Pure benzene

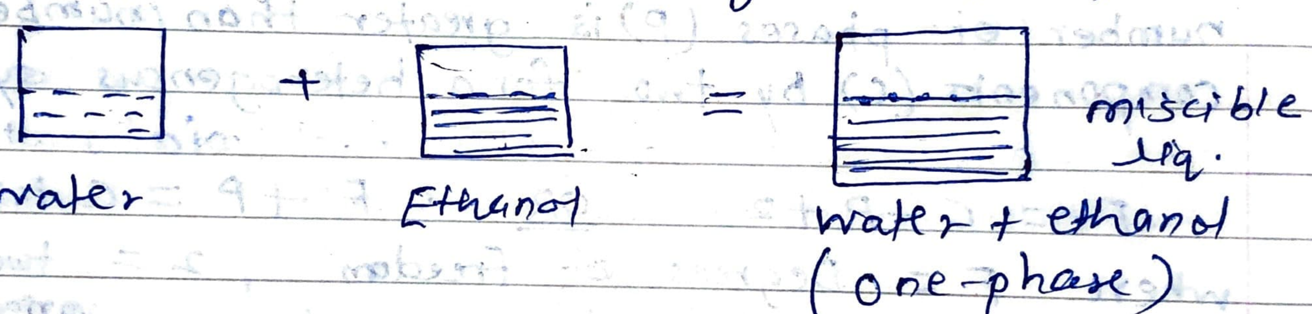
} One phase systems

- Consider water at freezing point (at 0°C)
At 0°C, the system will have all three phases present i.e. solid (ice), liquid and water vapour in equilibrium.

$$\text{Ice}_{(s)} \rightleftharpoons \text{Liquid water}_{(l)} \rightleftharpoons \text{Water vapour}_{(g)}$$

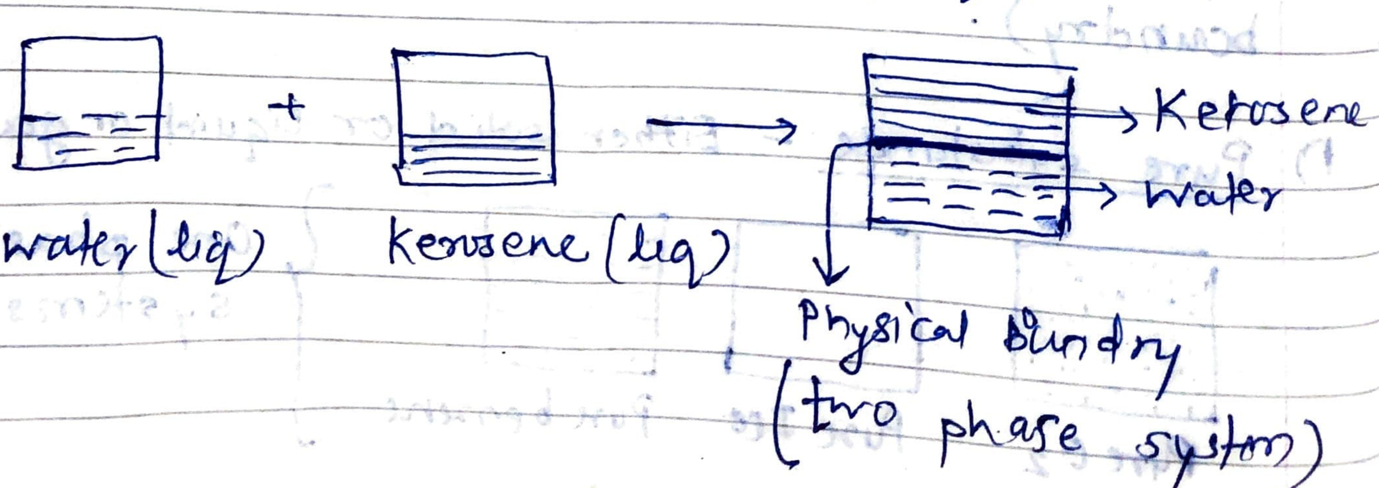
∴ this is 3-phase system.

2) <u>Miscible liquids</u> : If two completely miscible liquids obtain uniform soln, then it forms one-phase system (homogenous system)



3) <u>Mixture of gases</u> - When two gases are mixed form a homogenous mixture, they are one-phase systems.

4) <u>Immiscible liquids</u> : Kerosene & water are immiscible liquids.



5) The mixture of two solids

(i) Mix. of two allotropic forms of sulphur i.e. monoclinic & rhombic sulphur.
The chemical properties of these two forms are same but they are different physically.
∴ mix. constitutes two-phase system.

(ii) Two allotropic forms of carbon.
Diamond + Graphite = mixture
Differ in physical properties ∴ the mixture is 2-phase system.

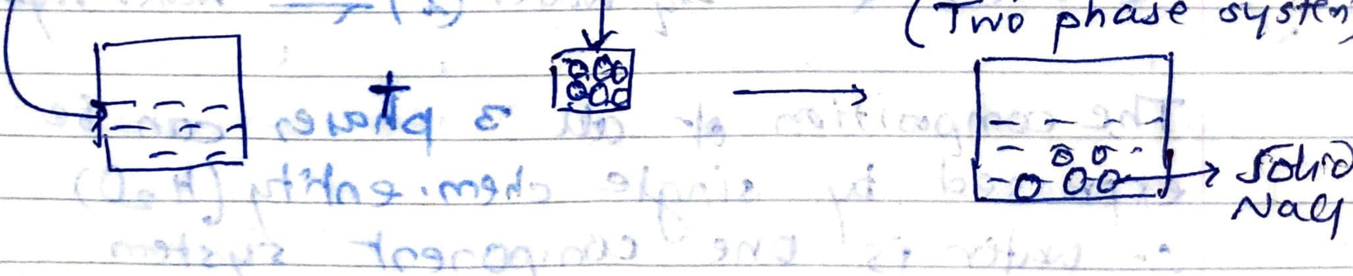
(iii) Decomposition of $CaCO_3$: Heat $CaCO_3$ in closed container

$$CaCO_{3(s)} \rightleftharpoons CaO(s) + CO_2(g)$$

Two solids are physically & chemically different ∴ this is 3-phase system.

(iv) Aqueous solutions :

Saturated NaCl soln + NaCl ⟶ Super saturated NaCl soln.
(Two phase system)



Component (C)

- A component is defined as the minium no. of independent chemical species necessary to define the composition of all the phases present in the system either directly or in the form of a chemical equateion.

- Rules for calculating no. of components in the system.

(i) On LHS, write chem. formula representing the phase composition

(ii) On RHS, write rest of chem. constituents existing independently in the system as represented by chem. formulae

(iii) The quantities of constituents of RHS can be made minus or zero in order to get composition of phas on LHS.

Example

1) The water system

$$\text{Ice (S)} \rightleftharpoons \text{Liq. water (l)} \rightleftharpoons \text{Water vapour (g)}$$

The composition of all 3 phases can be expressed by single chem. entity (H_2O)
∴ water is one component system

Phase	Component	
(Solid) Ice	$= H_2O$	One
(Liquid) Water	$= H_2O$	
(Vapour) Water	$= H_2O$	

2) Sodium chloride system

(i) $NaCl_{(s)}$ + $water_{(l)}$ $\longrightarrow$ saturated NaCl soln. (l)

Phase — NaCl

Component — $NaCl = xNaCl + yH_2O$

} 1 phase, 2 component

(ii) NaCl soln(l) (saturated) + NaCl (s) $\longrightarrow$ NaCl soln (Supersaturated)

Phase		Components
(liq.) NaCl soln	=	$x\,NaCl + y\,H_2O$
(solid) NaCl	=	NaCl

} 2 phase, 2 components

3) Mixture of gases : O_2 & N_2

(g) O_2 + N_2(g) $\longrightarrow$ mixture

Phase		Components
(gas) O_2	=	O_2
(gas) N_2	=	N_2

} phase – 1, components = 2

4) Decomposition of $CaCO_3$: when $CaCO_3$ is heated in closed container.

$$CaCO_3 (s) \rightleftharpoons CaO(s) + CO_2 (g)$$

Phases: $CaCO_3$, CaO, CO_2 } 3

Components: Composition of all 3 phases can be expressed with the help of two components only as →

(i) Consider that the composition of all phases is to be expressed in terms of CaO & CO_2

Phase		Components
Solid $CaCO_3$	=	$CaO + CO_2$
Solid CaO	=	$CaO + 0\ CO_2$
Gas CO_2	=	$CO_2 + 0\ CaO$

(ii) Consider that the composition is to be expressed in terms of $CaCO_3$ & CO_2

Phase		Components
Solid $CaCO_3$	=	$CaCO_3 + 0\ CO_2$
Solid CaO	=	$CaCO_3 - CO_2$
Gas CO_2	=	$0\ CaCO_3 + CO_2$

(iii) Consider that the composition of all three phases is to be expressed in terms of $CaCO_3$ & ~~CO_2~~ CaO

Phase		Components
Solid $CaCO_3$	=	$CaCO_3 + 0\ CaO$
Solid CaO	=	$CaO + 0\ CaCO_3$
Gas CO_2	=	$CaCO_3 - CaO$

- To define the composition of all three phases, we need at least two phases.
  ∴ it is 3-phase, 2-component system.

- Component of system means 'total no. of chemical entities required to describe all the phases in system.

Degrees of freedom

It can be defined as 'the total number of factors that can be varied without altering the total no. of phases in the system at equilibrium'.

Example

(i) Ice - water - vapour system, F=0

Ice $\rightleftharpoons$ Water $\rightleftharpoons$ Vapours

by phase rule

No. of Phases = 3, No. of components = 01

$F = C - P + 2$

$= 1 - 3 + 2 = 0$

∴ System is zero varient system

For water → freezing temp. is fixed value
→ vapour pressure is fixed value

System has two variables temp. & pressure and both these are already fixed.
∴ No need to specify variable ∴ No degree of freedom.

(ii) Water - Water vapour system, F=1

Water $\rightleftharpoons$ Water vapour, C=1, P=2

$F = C - P + 2$

$F = 1 - 2 + 2 = 1$

∴ system has one degree of freedom & it is monovarient system.

At definite temp, vapour pressure has only one fixed value & vice versa. Thus if one variable is specified, other automatically gets fixed.
∴ water-water vapours has one degree of freedom (F=1)

(iii) Sat. NaCl soln. in eq^m with solid NaCl & water vapour

~~R = 1~~, ~~component = 2~~

$\cancel{F = C - P + 2}$

$\cancel{2 - 1 + 2}$

$$NaCl_{(s)} \rightleftharpoons NaCl\ (soln) \rightleftharpoons \text{water vapour}$$

$P = 3$, $C = 2$

$$F = C - P + 2$$
$$= 2 - 3 + 2 = 1$$

(iv) Pure gas,

$P = 1$, $C = 1$

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

(v) Mixture of gases: O_2 & N_2

$P = 1$, $C = 2$

$$F = C - P + 2$$
$$= 2 - 1 + 2 = 3$$

* The degrees of freedom related to concentratn of components are fixed

Phase Diagram

Phase diagram is a plot showing the conditions of either pressure and temperature or temperature and concentration or pressure & concentration under which two or more physical states (phases) can exist together in a state of dynamic eqm.

- Application of Phase rule to one component system

According to Phase rule

$P + F = C + 2$ or $F = C - P + 2$

For $C = 1$

when $P = 1$

$F = 1 - 1 + 2 \quad \therefore F = 2$ (bivariant system)

when $P = 2$

$F = 1 - 2 + 2 \quad \therefore F = 1$ (Uni / Monovariant sys)

when $P = 3$

$F = 1 - 3 + 2 \quad \therefore F = 0$ (Invariant system)

$\therefore$ for one component system, maximum no. of degrees of freedom i.e. $F = 2$

$\therefore$ such system can be completely represented by a two-dimensional diagram.

$\therefore$ Temp. & pressure are convenient variables (degrees of freedom) to describe eqm conditions of one component system.

- Phase Diagram for one component system

The equilibrium conditions in a one component system may be convenniently represented with the help of phase diagram, taking into consideration temperature & pressure.

These phase diagrams are known as pressure-temperature (p-t) diagrams.

Important parts of phase diagram are

I) Area II) Boundary line/curve III) Point

I) Area : It represents bivariant system. Because to define system completely at any point in the area both temperature & pressure shd be fixed.

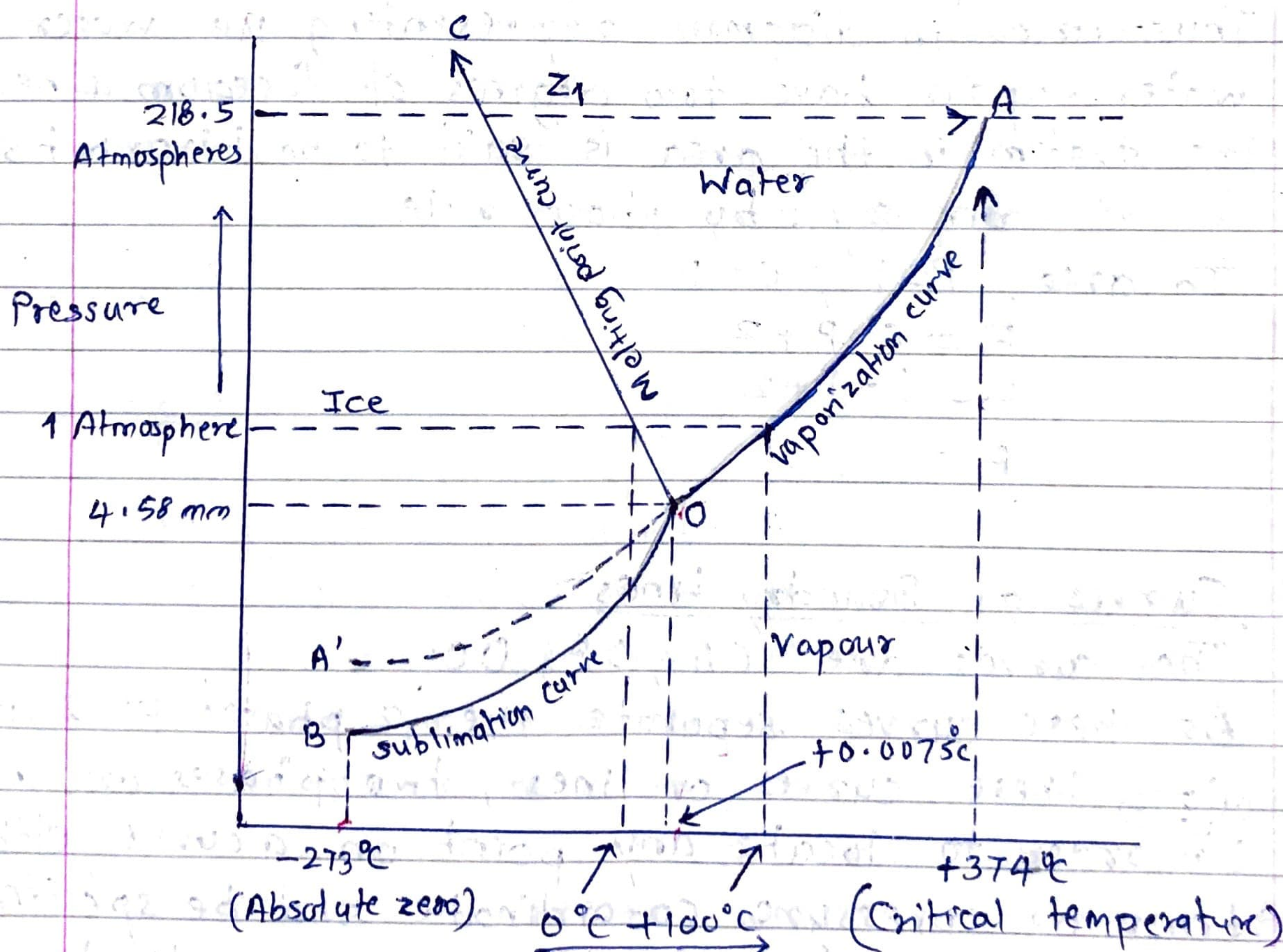
II) Boundary line or curve : Lines or curves represent monovariant system. Because equilibrium condition at any point on the line could be completely defined by either fixing temperature or pressure as the other variable gets fixed automatically.

III) Point : Point in diagram, where the three lines meet, usually 3 phases are in contact with each other, represent an invarient system. Because it is completely defined by itself.

- ## The Water System

For water system, component = H_2O (only one)
3 phases = ice, water, water vapour

The actual no. of phases existing in the equilibrium at a particular instance depends upon the condition of temperature & pressure. At different conditions of temperature & pressure, phase diagram for water system is as follows:



Water System

The phase diagram consists of

I) Areas : 3 areas i.e. AOB, AOC & BOC.

These areas represent conditions of temp. & pressure under which only one ~~set~~ of the 3 phases i.e. Ice water, water vapour exist & is stable.

Area AOB : water vapour exist

AOC : Water

BOC : Ice

In order to define the system completely at any point in the area, it is essential to specify both temp. and pressure co-ordinates to locate the point. Thus area in diagram, representing ice, water & water vapour have two degrees of freedom & hence, the system in the area is said to be bivariant system

∴ We can say, by phase rule

In area, $P = 1$, $C = 1$

$F = C - P + 2$

$F = 1 - 1 + 2$

$F = 2$

II) Curves or Boundary Lines

The curves are OA, OB, OC.

As these curves separate the 2 phases or 2 areas along these curves or lines, two phases are in eq^m.

In order to locate any point on a curve either temp. or pressure co-ordinate shd be specified because for fixed value of one co-ordinate the second is automatically fixed. Thus, any point on boundry lines has one degree of freedom or system is uni or monovariant along the boundry line.

This also follows phase rule as $P=2$, $C=1$

$\therefore F = C - P + 2$

$F = 1 - 2 + 2$

$F = 1$

i) Curve OA : It divides liquid region from the vapour region. Thus along curve OA, water & water vapour co-exist. ∴ This curve is called as vaporization curve.

ii) Curve OB: Along OB, ice & water vapour co-exist and are at eqm. Curve OB is called as sublimation curve.

iii) Curve OC : It divides solid ice region from the liquid water region. Along OC, ice & water co-exist. Curve OC is called as melting point or fusion curve or freezing point curve.

III) Point

The curves OA, OB & OC meet in point 'O'. This point 'O' is called the triple point. At this point, ice, water & water-vapour can co-exist and are at equilibrium. Only one set of condition is possible for 3 phases to exist. The triple point 'O' corresponds to a temperature 0.0075°C & a pressure 4.5 mm. At this point, system has zero degree of freedom which can be justified as

At point 'O', $P = 3$ & $C = 1$

$F = C - P + 2$

$F = 1 - 3 + 2$

$F = 0$

∴ System at triple point in non-variant / invariant.

Water System

Number of components = 1

Sr. No.	Name of the system as represented in the phase diagram	Phases in eq^m	Degrees of freedom $F = C - P + 2$
I]	Area a) BOC b) AOC c) BOA	One Ice Water Water vapour	$F = 1 - 1 + 2$ $\therefore F = 2$ Bivariant system
II]	Curves a) OA (Vaporization) b) OB (Sublimation) c) OC (Fusion or melting point)	Two Water & water vap. Ice & water vapour Ice & water	$F = 1 - 2 + 2$ $\therefore F = 1$ Mono or univariant system
III]	Point O (Triple point)	Three Ice, water, water vapour	$F = 1 - 3 + 2$ $\therefore F = 0$ (zero) Invariant system