Phase Rule

- Rule given by J. willard Gibbs.
- Iss rule ki help se hum predict kr skte hai effect of temp., pressure and conc. for a heterogenous system.
- let ek aisa equilm jispe external effect nhi padta kisi bhi property ka jaise electrical forces, gravity, magnetic forces etc!- but that equilm is influenced by temp., pressure, and concentration. tab iss tarah ke jo bhi equilm honge woh phase rule follow krenge.

i.e. $$F + P = C + 2$$

where, F = no of Degree of freedom
P = no of phase
C = no of component

* Phase (P) :-

- phase may be define as physically distinct, mechanically seperable by such parts of system.

eg:- Ice (s) $\rightleftharpoons$ water (L) $\rightleftharpoons$ vapour (G)

isme 3 phases jo physically distinct hai, aur mechanically seperable bhi

- Solids :- Solid jitni baar alg hai seperate phase banate hai. eg. salt & sand → dono solid hai aur physically distinct hai to 2 phase count hoga.
- liquid :- liquids mein depend krega means agar dono liquid miscible hai toh woh 1 phase form krenge aur if both liq. are immesible then they form 2 phase.
  eg water & alcohol → mix krenge to 1 phase banyenge
- Gases :- gases hamesha 1 phase banati hai because atmosphere mein bohot saare gases ke molecules hote hai they are homogeneous unhe alag se identify nhi kr skte, ∴ gases always forms 1 phase. (↳ means they are not physically distinct)
- Solution :- Solution separate phase banayenge. eg. agar sugar ko water mein dissolve kre toh jab tk sol^n unsaturated hai tab tk sugar dissolve hogi aur humko 1 phase milega jaise hi sol^n saturated hua then sugar dissolve hona band kr degi aur sugar and sol^n alag dikenge aur humko fir 2 phase milega.

eg: find phases in reac^n $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$

Ans) 3 phases → solid, solid, gas.

(Solid hamesh seperate phase banata hai ∴ 2 baar liya)

* Component (c) :-

- kisi bhi system mein jitni bhi phase present hai unke chemical composition ko ~~repre~~ represent krne wali smallest no' is called component.

eg. Ice $\rightleftharpoons$ water $\rightleftharpoons$ vapour

Isme ice, water & vapour ko H_2O se represent kr skte hai Sq 3 phase ko represent krne k liye 1 chemical composition chahiye hai i.e H_2O therefore it is 1 component system.

* Degree of freedom :-

- no' of intensive variable i.e temp., pressure & conc. jinko hum independently change kr ske, hamare equillm mein jo bhi phase hai usko bina disturb kiye, iss no' ko kehte hai degree of freedom.

If $f = 0$, the system is non varient

$f = 1$, then system is Univarient

$f = 2$, then system is bivarient

* Advantages of phase rule :-

1) Phase rule helps in classifying various equillm in terms of no' of phase, no' of components & no' of degree of freedom.
2) We can predict the behaviour of any system with changes in the variable such as temp., pressure & conc.
3) Applicable to both physical & chemical equilibria.
4) The different system, which are having same value of degree of freedom, they would behave similarly.
5) It have extensive use in study of heterogenous system, this rule is useful in metallurgy and provide useful info. about complex formation.

* Disadvantages of phase rule :-

1. Not easy to identify no' of phases, no' of component and no' of degree of freedom.
2. This rule apply only on simple equillm state and does not tells us about the no' of other possible equilibria present in system.
3. phase rule deals with macroscopic study and it does not tell anything about molecular structure.
4. phase rule does not give any info. regarding time taken for the system to attain equillm.

Q:- calculate no' of phases in given equill^{m} :-

1. $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$
   3 phases - solid, solid, gas → solid hamesha seperate phase banata hai
2. $PCl_5(s) \rightleftharpoons PCl_3(l) + Cl_2(g)$
   3 phases - 1 (solid), 1 (liq.), 1 (gas) → gas hamesh single phase banata hai
3. $2CaSO_4(s) \rightleftharpoons 2CaO(s) + 2SO_2(g) + O_2(g)$
   3 phases - solid, solid, gas.

- calculate phase & component

$NH_4Cl(s) \rightleftharpoons NH_3(g) + HCl(g)$

phases - 2, (Solid, Gas)
Component - 1 (NH_4Cl) → NH_3 aur HCl ka proportion same hi hota hai as NH_4Cl so yeh equill^{m} hai toh it is one component system.

If NH_3 or HCl present in excess - 2 component.

→ aisa system jiska component 1 ho

* Application of phase rule :-

- one component system - water system

we know that $\boxed{F + P = C + 2}$

* F = no' of degree of freedom
  P = No' of phase
  C = no' of component

eg:- water system i.e. Ice (s) $\rightleftharpoons$ water (L) $\rightleftharpoons$ Vapour (g)
In teeno system ko represent krne ke liye ek component i.e H_2O req. hai ∴ it is ~~one~~ one component system.

phase diagrams:-

- equill^{m} mein jo bhi phases present hai unke behaviour ka complete description is called phase diagram.

eg: for one component system → one compont system hai toh yeh '1' ho jayega.

$F + P = C + 2$

$F + P = 1 + 2$

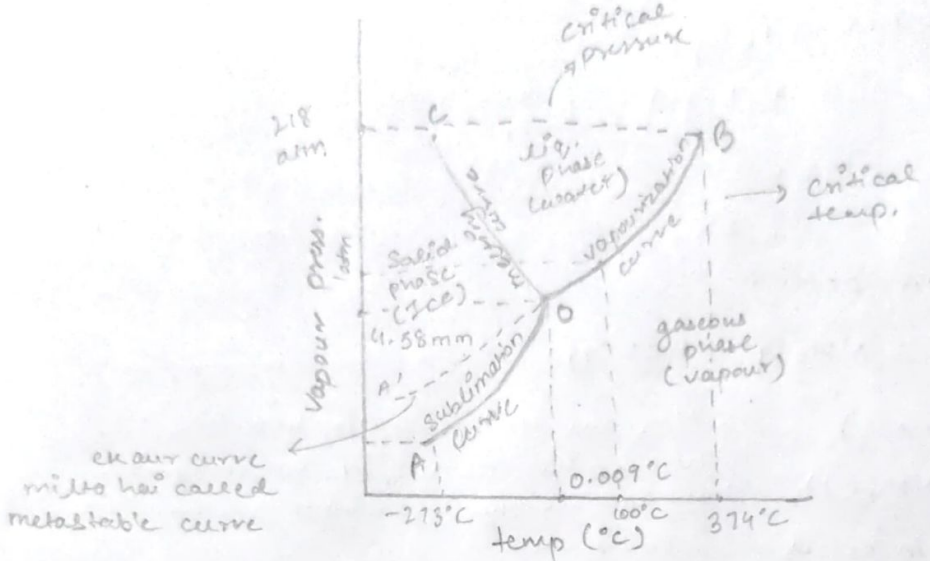
$\boxed{F = 3 - P}$ → that will depend on system ki hamare system mein kitne phase hai usse hamari degree of freedom calculate hogi. yani calculate krenge from phase digram of water

If P = 1, then F = 2 → called Bivarient → matlb humhe uss system ko completely describe krne ke liye 2 variables chahiye

P = 2, then F = 1 → called univarient → ek variable chahiye woh temp., pressure ya concentration kuch bhi ho skta hai

P = 3, then F = 0 → called non varient → variables must be specified and fixed

* phase digram of water system :-



- phase rule apply krenge hamm area pr.

So, • Area

AOC - 1 phase i.e Solid phase hai
AOB - 1 phase i.e gas. phase hai
BOC - 1 phase i.e liq. phase hai

Now, w.k.t for one component system.

$f = 3 - p$

$f = 2 - 1 \rightarrow f = 2$ → Yeh f AOC, AOB aur BOC ke liye 2 hi ayega.

that mean hamm area bivariant hai

mean hamm area mein jo bhi phase present hai usko maintain krne ke liye 2 variable req. honge i.e temp. as well as pressure.

• Curve :- total 3 curve hai

Sublimation curve

Curve OA - 2 (S, G) → uss curve pe 2 phase hai i.e Ice & gas

OC - 2 (S, L)

OB - 2 (L, G)

w.k.t $f = 3 - p$ → 2 phase hai on every curve

$= 3 - 2 \rightarrow f = 1$ →

means every curve is univariant means hamare system ko describe krne ke liye ek variable either press. or temp req. hai

• point 'O' :- Yaha pe teeno curve aake mil rhe hai means teeno equilm mein hai. this pt. also called triple point. Yeh pt. hume 0.0098°C aur 4.50 mm pressure pe milta hai

3 phase in equilm → 3 (S, L, G)

So, $f = 3 - p \rightarrow 3 \rightarrow \boxed{f = 0}$ → nonvariant hai matlb agar hum kisi bhi ek variant ko const. krte hai to equilm mein se ek phase disappear hojayegi

- metastable curve :- yaha pr solid liq. aur ~~water~~ vapour equill^m mein hote hai
  i.e solid liq. ⇌ vapour

agar hum water ke freezing pt. i.e. 0°C se niche uss paani ko cool krte rhe toh woh ice mein convert nhi hota isko hum super cooled water bolte hai.

- metastable curve is also known as vapour pressure curve of super cooled water.
- Degree of freedom $F = 3 - P$ (2 phase hai i.e liq. & water)
  $= 3 - 2$
  $F = 1$

- **Tabular form :-**

Curve / area / point	~~no of phases~~	no of phases	phases in equilibrium	Degree of freedom	System
Areas	AOC	1	Solid	$F = 3 - P$ $= 3 - 1$ $= 2$	Bivariant
	BOC	1	liq.		
	AOB	1	gaseous		
Curves	OA	2 (Sublimation)	solid ⇌ vapour	$F = 3 - P$ $= 3 - 2$ $= 1$	Univariant
	OB	2 (melting)	liq ⇌ solid		
	OC	2 (Vapourisation)	vapour ⇌ liq.		
Triple point	O	3	~~100~~ S ⇌ l ⇌ G	$F = 3 - 3$ $= 0$	Invariant
metastable curve	OA'	2	S ⇌ G	$F = 3 - 2$ $= 1$	Univariant

* Determine no of phases and components in saturated and unsaturated salt / sugar sol^n :-

1. unsaturated salt / sugar sol^n :-

→ since yeh unsaturated sol^n hai toh isme 1 phase present hoga.

Salt sol^n :- $NaCl(s) + H_2O(l) \longrightarrow NaCl.H_2O$ (sol^n)

phase → 1 (sol^n)

Compent → 2 component system (NaCl & H_2O)

similarly for sugar sol^n
Bss NaCl ki jagah sabme $C_6H_{12}O_6$ aa jayega.

2. Saturated Salt / sugar soln :-

a) Saturated soln at room temp. :- → Since yeh saturated soln hai toh yaha pr 2 phase show hoga.

$NaCl_{(s)} + H_2O(l) \longrightarrow NaCl \cdot H_2O$ (saturated soln)

phase - 2 phases (soln, solid)

component - 2 component ($NaCl, H_2O$)

→ Sugar ke case mein NaCl ki jagah $C_6H_{12}O_{11}$ likh dete

b) Saturated soln at boiling point :-

$NaCl(s) + H_2O(l) \longrightarrow NaCl \cdot H_2O$ (soln)

→ water jab boil hoga toh obviously vapour ni lega.

phases - 3 phases (solid, solution, vapour)

component - 2 component ($NaCl, H_2O$)

* One component system - Sulphur System

- Iske 4 phases system mein present hote hai

1. Rhombic sulphur (solid) (S_R)
2. Monoclinic sulphur (solid) (S_M)
3. liq. sulphur (S_L)
4. Vapour sulphur (S_V)

→ Aise system jisme 2 or more solid state exist krti hai in equilm then it is called Polymorphic system

→ Inn chaaro phase ko represent krne ke liye ek chemical 'S' ki zarurat hai ∴ it is one component system.

w.k.t $f + p = c + 2$

4 phase ho skti hai

$f = 3 - p$

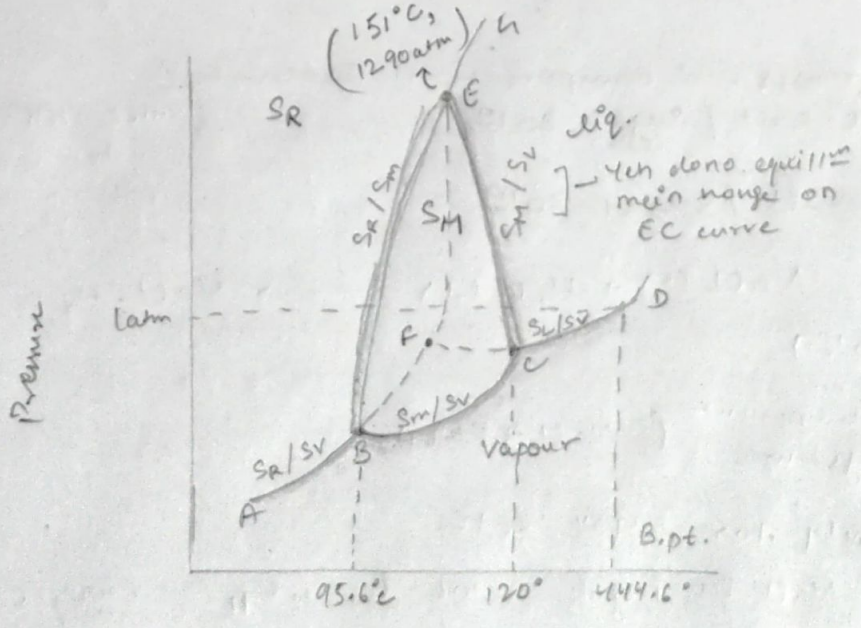
If $p = 1$, then $f = 2$ → Bivarient

$p = 2$, then $f = 1$ → univarient

$p = 3$, then $f = 0$ → Invarient

If $p = 4$, then $f = -1$ → Not possible

→ Kisi bhi system ke liye f -ve nhi ho skta ∴ not possible ∴ kabhi bhi sulphur system ke case mein chaaro phase equilm mein exist nhi kr skti only 3 phases can co exist at a time in sulphur system.



- Applying phase rule on every area.

So, area ABG (Rhombic Sulphur)
BECB (monoclinic sulphur)
GECD (liq. sulphur)
ABCD (vapour phase)

} harr area mein ek phase present hai

W.kt $F + P = C + 2$

$F = 3 - P$

$= 3 - 1 = 2$ → means every area is bivarient and 2 variable i.e temp & pressure required to locate any point

- Curve :- total 6 curves

Curve AB - Vapour pressure curve of S_R , $S_R \rightleftharpoons S_V$
BC - " " " of S_M , $S_M \rightleftharpoons S_V$
CD - " " " of S_L , $S_L \rightleftharpoons S_V$
BE - Transition curve of S_R to S_M , $S_R \rightleftharpoons S_M$
CE - fusion curve of S_M , $S_M \rightleftharpoons S_L$
EG - fusion curve of S_R , $S_R \rightleftharpoons S_L$

} Sabme 2 phases equilm mein exist kri hai so, $P = 2$

Yeh humne effect of press. on transition temp. ke baare mein bataya hai jab S_R convert hota hai S_M mein

- transition curve :- Curve BE mein S_R aur S_M 2 phase (Solid) equilm mein hai aur yeh transition curve hai of S_R to S_M. also curve BE slopes away from pressure axis matlb transition temp. can be raise in increase in pressure.

- fusion curve :- curve CE mein (when) monoclinic aur liq. sulphur exist krti hai. It represent effect of pressure on melting point of S.M. melting point increases with increase in pressure. yaha pe yeh curve point E se khtm hota hai jiska matlb monoclinic sulphur iss point se aage exist nhi krti hai.

W.kt $F = 3 - P$

$\boxed{F = 1}$ (univarient) → means system ko describe krne ke liye ek variable req. hai

- points :-

point B → (95.6°C, 0.006 mm) → S_R, S_M, S_V
C → (120°C, 0.04 mm) → S_M, S_L, S_V
E → (151°C, 1290 atm) → S_R, S_M, S_L

} Yeh teeno equilm pr milegi on that pts.

W.k.t $F = 3 - P$

$= 3 - 3 = 0$ → Invarient, means agar temp. aur pressure mein chota sa bhi disturbance krte hai to ek phase disappear ho jayega

- metastable curve :-

(i) Dashed curve BF - Vapour pressure curve of metastable S_R ; $S_R \rightleftharpoons S_V$

(ii) Dashed curve CF - Vapour pressure curve of ~~metastable~~ supercooled liq. S. ; $S_L \rightleftharpoons S_V$

(iii) Dashed curve FE - fusion curve of metastable S_R ; $(S_R \rightleftharpoons S_L)$

with it $f = 3 - P = 3 - 2$

$\boxed{f = 1}$ → univariant

- metastable triple point 'f'

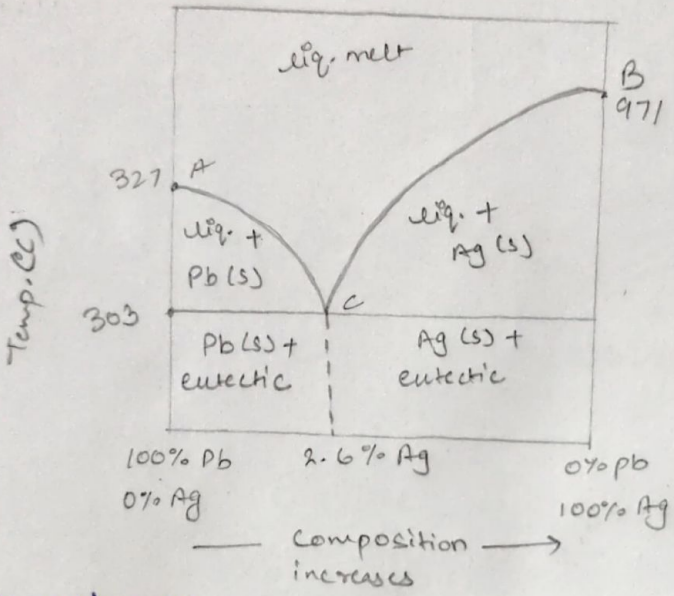
$\boxed{S_R \rightleftharpoons S_L \rightleftharpoons S_V}$

- Tabular form :-

curve / Area / point		no. of phases	phase in equilm	Degree of freedom	System
Area	ABG	S_R	1	$f = 3-P$ $= 3-1$ $= 2$	Bivariant
	BECB	S_M	1		
	GECD	S_L	1		
	ABCD	S_V	1		
curve	AB	$S_R \rightleftharpoons S_V$	2	$f = 3-P$ $= 3-2$ $= 1$	Univariant
	BC	$S_M \rightleftharpoons S_V$	2		
	CD	$S_L \rightleftharpoons S_V$	2		
	BE	$S_R \rightleftharpoons S_M$	2		
	CE	$S_M \rightleftharpoons S_L$	2		
	EG	$S_R \rightleftharpoons S_L$	2		
metastable curve	BF	$S_R \rightleftharpoons S_V$	2	$f = 3-P$ $= 3-2$ $= 1$	Univariant
	CF	$S_L \rightleftharpoons S_V$	2		
	FE	$S_R \rightleftharpoons S_V$	2		
Triple point	B	$S_R \rightleftharpoons S_M \rightleftharpoons S_V$	3	$f = 3-P$ $= 3-3$ $= 0$	invariant
	C	S_M, S_L, S_V	3		
	E	S_R, S_M, S_L	3		
metastable triple pt. ←	F	S_R, S_L, S_V	3		

* 2 component system - Pb & Ag

- 2 solids hai isme i.e Pb, Ag
- Agar dono i.e Pb aur Ag ko melt kre toh dono mix ho jaate hai ache se i.e they are miscible.
- But solid phase mein yeh dono immiscible hote hai. mtlb total 3 phases banenge → solid + solid + melt
- melting point of Pb, Ag is different.
- Aisa system jism yeh above saari properties hoti hai usko eutectic system kehte hai.



- at const. pressure

AC - freezing pt. curve of Pb → 2 phase → so, F = 3 - P = 1 (univariant)

BC - freezing " " " Ag → 2 phase → so, F = 1 (monovariant)

pt. C - Eutectic point → yaha pe teeno phase co-exist krte hai → 3 phases, so, F = 0 (invariant)