

Phase

Equilibria

Phase

→ Any homogeneous & physically distinct part of a system which is separated from other parts of the system by definite boundaries

$P = \text{no. of phases}$

i) Gaseous State

→ Gases diffuse into each other

→ Form homogeneous soln

→ $P=1$

→ Gases are completely miscible in each other

ii) Liquid State

→ $P=1$ for miscible liq. (ex: $\text{H}_2\text{O}, \text{CH}_3\text{CH}_2\text{OH}$)

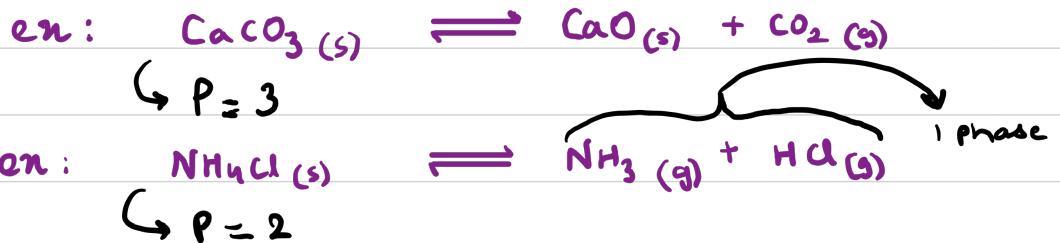
→ $P=1$ for salt solutions (unless saturated)

→ $P = \text{no. of layers of immiscible liq.}$

iii) Solid State

→ $P=1$ for isomorphous alloys only

→ Each Solid, allotrope/polymorph contributes to 1 phase



Component (c)

→ Smallest no. of independent chemical constituents by which each & every phase can be expressed.

→ C can also be 0 & -ve

i) C=1 / Single Component System

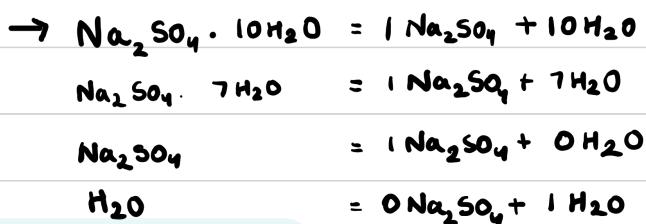
→ Water $\Rightarrow P = 1, C = 1$
either ice, water, vapour

→ At M.P., $\text{ice}(s) \rightleftharpoons \text{water}(l)$
 $P = 2, C = 1$

→ At B.P., $\text{water}(l) \rightleftharpoons \text{vapour}(g)$
 $P = 2, C = 1$

→ At triple point $\text{ice} \rightleftharpoons \text{water} \rightleftharpoons \text{vapour}$
 $P = 3, C = 1$

ii) C=2 / Two Component System



Only 2 components are enough to explain all of the phases



$C = 2$, Can be expressed in 2 comp.



$\downarrow C = 1$

If you add more HCl, NH_4Cl won't account for extra HCl, and then $C = 2$

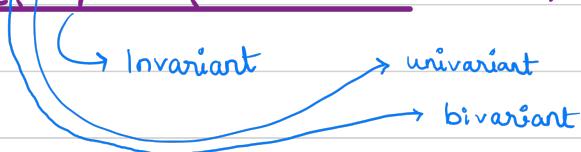
• Degrees Of Freedom / Variance

The min. no of independant variables such as Temp, Pres & Comp. that can be altered w/o disturbing equilibrium

ex: liq water: $F = 2, P = 1, C = 1$ ($T \& P$ can be varied)

solid ice \rightleftharpoons liq. water: $F = 1, P = 2, C = 1$ (T or P can be varied)

solid ice \rightleftharpoons liq. water \rightleftharpoons water vapour: $F = 0, P = 3, C = 1$ (T & P are fixed)



Gibb's Phase Rule

→ In an equilibrium, heterogeneous ^{system} undisturbed by external forces, F is related to C & P by this equation,
 $F = C - P + 2$

Derivation

→ A system at equilibrium should satisfy :

i) Thermal eq \Rightarrow Temp = const.

ii) Mechanical eq \Rightarrow Work done = const. $\Rightarrow P = \text{const.}$ ($W = P\Delta V$)

iii) Chemical/Material eq \Rightarrow Composition = const.

According to phase eq, chemical potential (μ) will be constant for each component across the phase

Now, F can be found by this expression,

$$\text{Total no. of independent intensive variables} = \frac{\text{Total no. of intensive variables}}{\boxed{1}} - \frac{\text{Total no. of eq. connecting the variables}}{\boxed{2}}$$

(3)

For ①, we know, sum of mole fractions of all components

is equal to 1, for all phases

c-1 variables are independent

en :

n_1	n_2	n_3
0.1	0.4	0.5
0.2	0.6	0.2

Fixed



So, For P phases, $P(c-1)$ independently variable mole fractions,

$$\begin{aligned} n_1^\alpha + n_2^\alpha + n_3^\alpha + \dots + n_c^\alpha &= 1 \Rightarrow c-1 \\ n_1^\beta + n_2^\beta + n_3^\beta + \dots + n_c^\beta &= 1 \Rightarrow c-1 \\ &\vdots \\ n_1^P + n_2^P + n_3^P + \dots + n_c^P &= 1 \Rightarrow c-1 \end{aligned} \quad \left. \right\} P(c-1)$$

- In addition, T & P are 2 intensive variables of the system

$$\Rightarrow \text{Total no. of independent variables} = P(c-1) + 2 \quad \boxed{1}$$

For ②,

Let μ_i^P be chem. potential of i^{th} comp. in P^{th} phase

so, 1st comp. must have same chem pot. in every phase.

$$\Rightarrow \mu_1^\alpha = \mu_1^\beta = \mu_1^\gamma = \dots = \mu_1^P \Rightarrow P-1$$

$$\mu_2^\alpha = \mu_2^\beta = \mu_2^\gamma = \dots = \mu_2^P \Rightarrow P-1$$

⋮

$$\mu_c^\alpha = \mu_c^\beta = \mu_c^\gamma = \dots = \mu_c^P \Rightarrow P-1$$

$c(P-1)$

For 'c' no. of components, total no. of eq related to chemical potential = $c(P-1)$

②

Now, Total no. of eq connecting the variables = $c(P-1)$

Put ① & ② in ③,

$$F = (CP - P + 2) - (cP - c)$$

$$F = C - P + 2$$

→ Gibbs Phase Rule eqⁿ

Phase Diagram

→ The diagram that represents conditions under which a substance exists in different phases in a system

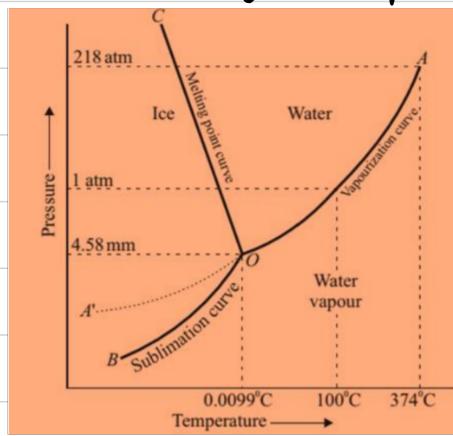
ex: For a 1 component System, $F = 3 - P$

Single Phase : $F = 2 \Rightarrow$ Area in a diagram

2 phases : $F = 1 \Rightarrow$ line in a diagram

3 phases : $F = 0 \Rightarrow$ point in a diagram

→ Phase Diagram of Water



1) Fusion Curve OC

→ ice \rightleftharpoons water ; $F = 1$; monovariant system

→ Slope = -ve \Rightarrow ice melts as Volume + (v) Density \uparrow

$$\rightarrow \frac{dp}{dT} = \frac{\Delta H_{\text{fusion}}}{T \Delta V} = -ve \quad \begin{matrix} \text{+ve, endothermic} \\ \text{Clausius - Clapeyron} \\ \text{Equation} \end{matrix}$$

2) Sublimation Curve OB

→ ice \rightleftharpoons water vapour ; $F = 1$; Monovariant System

$$\rightarrow +ve \text{ Slope} \Rightarrow \frac{dp}{dT} = \frac{\Delta H}{T \Delta V} = +ve \quad \begin{matrix} \text{+ve, endothermic} \\ \text{+ve} \end{matrix}$$

3) Vaporization Curve OA

→ water \rightleftharpoons vapour ; $F = 1$; monovariant system

$$\rightarrow +ve \text{ slope} \Rightarrow \frac{dp}{dT} = \frac{\Delta H}{T \Delta V} = +ve \quad \begin{matrix} \text{+ve, endo} \\ \text{+ve} \end{matrix}$$

4) Triple Point 'O' :

- Equilibrium b/w liq, vapour & ice
- All 3 phases present together
- $F=0$, invariant

0.0098°C &
4.58 mm Hg

5) Critical Point 'A' :

- Interface b/w water & vapour vanishes
- Water doesn't exist as liq. above this point

374°C &
220 atm

6) Metastable Equilibrium (OA') :

- Ice fails to form at triple point & water continues to exist in liquid phase.
- Vapour Pressure of liquid continues along OA'.
- ↳ called Super cooled water & represents metastable equilibrium involving liq & vapour phases.
- Any DISTURBANCE causes system to go back to equilibrium

<https://youtu.be/L44h2T5MK90>

- Usually, measurement of 2 component system is carried out at atmospheric pressure

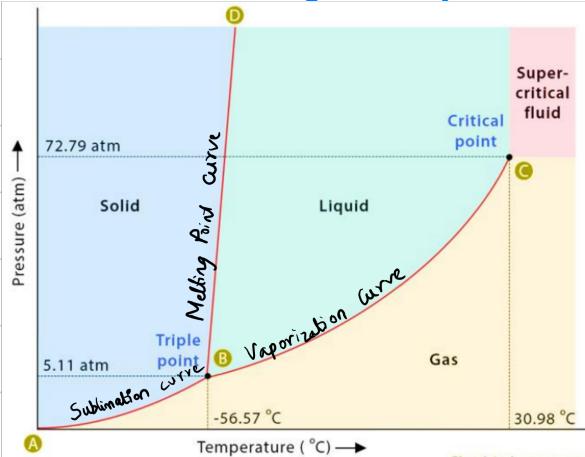
$$F = C - P + 2 - 1$$

$$\Rightarrow$$

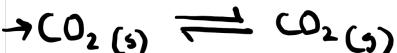
$$F = C - P + 1$$

↳ Condensed Phase Rule

• Phase diagram of CO_2



• **Sublimation (A-B) :**



$\rightarrow F=1$; mono variant

\rightarrow slope = +ve

$$\rightarrow \frac{dP}{dT} = \frac{\Delta H_{\text{sub}}}{T \Delta V} \rightarrow +\text{ve}$$

• **Melting (B-D) :**

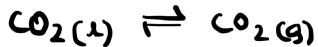


$\rightarrow F=1$; Mono variant

\rightarrow +ve slope

$$\rightarrow \frac{dP}{dT} = \frac{\Delta H_{\text{fus}}}{T \Delta V} \rightarrow +\text{ve}$$

Vaporization (B-C) :



$F=1$; Mono variant

+ve slope

$$\frac{dP}{dT} = \frac{\Delta H_{\text{vap}}}{T \Delta V} \rightarrow +\text{ve}$$

Triple Point (B) :

\rightarrow Represent equilibrium b/w sol, liq & gas

$\rightarrow F=0$; Invariant

\rightarrow lies on -56.57°C &

5.11 atm

Critical Point (C) :

\rightarrow Max Temp & Pressure to which liq & vapor are distinguishable

\rightarrow Gas can't go back to liq at such high temp

\rightarrow Lies at 30.98°C & 72.79 atm

\rightarrow Beyond C, its a supercritical fluid

Supercritical Fluid

- Supercritical CO₂ widely used as solvent for industrial extraction process
- Decaffeinating of coffee
- Dry-cleaning solvent
- Natural refrigerant

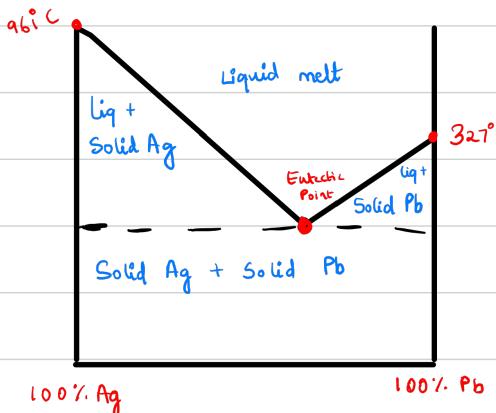
For 2 Component System

- Ordinary phase rule doesn't apply
- One of the 3 variables is kept constant

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

$$F = C - P + 1 \rightarrow \text{Reduced Phase Rule}$$

Pb - Ag System



Eutectic Point :

Pb 97.4% + 2.6% Ag

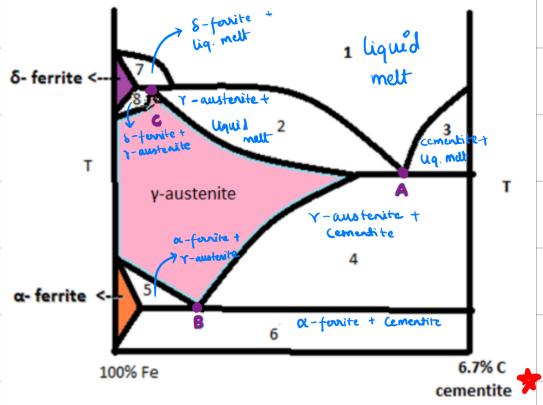
303°C

Pattinson's Process for desilverisation of argentiferous lead

→ The process of heating argentiferous lead containing small quantity of silver & cooling it to get pure lead & liquid richer in silver

- i) Argentiferous Lead is heated above MP of Pure lead
- ii) The melt is allowed to cool
- iii) Temp. reaches Freezing Point of Lead & starts to separate
- iv) As system cools further, more Lead separates & liquid in equilibrium with solid Lead gets richer in Silver
- v) Lead starts to float & continuously removed by ladles
- vi) After further cooling, It solidifies to give mixture with Eutectic composition $(2.67\% \text{ Ag})$ which is subjected to other processes of recovery of Silver

Fe - C System



α -ferrite \Rightarrow 0 - 900°C

γ -austenite \Rightarrow 900°C - 1400°C

δ -ferrite \Rightarrow 1400°C - 1540°C

Above 1540°C, Fe melts

$\rightarrow \alpha$ -Ferrite :

- Solid solⁿ of C in BCC Fe
- Stable form of iron at room temp
- Transforms to FCC γ -austenite at 900°C

$\rightarrow \gamma$ -austenite :

- Solid solⁿ of C in FCC Fe
- Transforms to BCC δ Ferrite at 1400°C

$\rightarrow \delta$ -Ferrite :

- Solid solⁿ of C in BCC Fe
- Same as α -Ferrite
- Stable only at high temp. (above 1400°C)
- Melts at 1540°C

$\rightarrow \underline{\text{Fe}_3\text{C}}$

- Iron Carbide / Cementite
- Intermetallic Compound

A → Eutectic Point

→ Liq. melt of Fe-C transforms into 2 different solid phases γ -austenite & cementite (Fe_3C) on cooling



→ Corresponds to 4.3% C, $1130^\circ C$

→ 3 phases in eq \Rightarrow γ -austenite, Cementite, Liq. melt

→ $F=0$; Invariant

B → Eutectoid Point

→ γ -austenite phase transforms into 2 diff. solid phases



→ Corresponds to 0.8% C, $723^\circ C$

→ 3 phases in eq \Rightarrow (α -ferrite, Cementite, γ -austenite); $F=0$; Invariant

C → Peritectic Point

→ Liq. melt of Fe-C transforms into 2 diff. solid phases



→ Corresponds to 0.16% C, $1498^\circ C$

→ 3 phases in eq \Rightarrow (γ -austenite, δ -ferrite, Liquid melt); $F=0$; Invariant

Ferrous Alloys

Wrought Iron \Rightarrow $<0.008\% C$

$\Rightarrow 0.008 - 2.14\% C$

Steel $\Rightarrow 0.008 - 2.14\% C$

Cast Iron $\Rightarrow 2.14 - 6.7\% C$