PHASE Equilibrium:

The Phase Rule.

The phase rule was discovered by J.W. Gibbs in 1876 is a generalisation dealing with the behaviour of heterogenous systems in Equilibrium.

$$F = C - P + 2. \text{ (Phase Rule)}$$

F = Number of Independent variables. (Degrees of freedom).

C = Number of components.

P = Number of stable phases. (for a given System)

Before discussing phase Rule there needs a clear ~~concept~~ of understanding the terms used in phase Rule i.e. Phase, component and Degrees of Freedom.

PHASE: A phase is defined as any homogenous part of the system that is chemically & physically bounded by a distinct interface with other phases & physically ~~~~ separated from other ~~phase~~ phases.

Examples of different types of phases.

(1) pure substances: A substance that has a fixed chemical composition through one is a pure substance. water, Air, N_2, O_2, Fe, Cu, .

Water: Ice, liquid water, water vapour (They are pure substance but different physical properties & three separate phases.

(2) Mixture of Gases: All gases are miscible with each other in all proportions & physically mechanically can not be separated. Hence Mixture of gases always constitute a single phase.

Air: CO_2, N_2, O_2, ... 1 phase only.

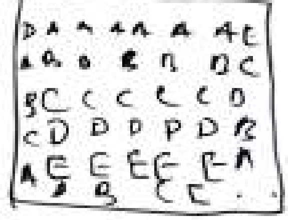
In general gases constitute a single phase.

Dont ignore

Specific case to understand

Let us imagine a cylinder comprises a Mixture of gases ABCDE

No of Phases = 1.



Suppose A is a easily liquifying gas its Vanderwall forces of attraction is very very high i.e.

Now if pressure inside the container is increased it ~~at~~ & the pressure exerted on A is greater then critical pressure then in that case droplets of A will start forming i.e. A gets liquified.

So along with the gas mixture liquid drops will be seen ~~around the container~~ at the wall of container.

ON THAT CASE No of phase = 2

1 (Mixture of gases) & the other is liquid.

(3) Liquids:

(1) True homogenous solutions always constitute a single phase.

e.g ~~(aggregate, (as) thick~~ True homogenous solⁿ. (salt solⁿ, Sugar. solⁿ .. . .)

(2) Solⁿ can be of 3 types.

(1) True solⁿ (2) Collidal solⁿ (3) Suspension.

True solⁿ always phase = 1.
Collidal solⁿ are heterogenous in nature phase > 1
Suspension > 1.

(3) Miscible liquids: (Like dissolves like)

Completely miscible liquids always 1 phase they form homogenous solⁿ.

e.g Ethanol + water, CCl_4. diethyl ether, . . .

Immiscible liquids: **No of Layers = No of Phases**

CCl_4, water — 2 phase. oil - water = 2 phase

(4) Aqueous solution: The aqueous solution of a solid solution is uniform through out. is therefore Considered a single phase system.

~~As above~~ However Saturated solution in contact with excess of solute is ~~a~~ not homogenous & hence no of phases > 1.

*
Let us take 2 Beaker containing 250ml water each & Add a salt NaCl Let the solubility 5gm/Lit.

In beaker 1 if let us add 1 gm of NaCl gradually with stirring.

It will form and unsaturated soln (True & homogenous Hence No of phase = 1.

In beaker no 1 let us add 3 gm of salt gradually with stirring beyond 1.25 gm the rest of the salt will get deposited at the bottom.

No of phase = 2 (1 soln & 1 solid).

You ~~can extrapolate it~~.

Hence beyond saturation no of phase > 1, & depending on no of solute present - (If mixture of salts taken)

⑤ Mixture solids:

Solids always constitute a single phase.

If we take mixture of solids they will form Heterogenous mixture Hence No of Phases = No of solid.

Cu + Zn + Mn + Fe = 4 phase.

ALLOYS always constitute a single phase
Alloys are homogenous solid soln.

⑥ Decomposition of $CaCO_3$

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

Two solids + one gas = 3 phase

Each solid constitute a single phase

$CaCO_3(s)$, $CaO(s)$, $CO_2(g)$ = 3
1 1 1

$Fe(s) + H_2O(g) \rightleftharpoons FeO(s) + H_2(g)$

Two solids & Two gases.

(i) Mixture of gases constitute a single phase

$H_2O(g) + H_2(g)$ = Mixture of gas = 1 phase we can not mechanically separate gaseous mixture.

Two solid Fe(s), FeO(s) + Gas

No of phase = 3.

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

No of phase = 2.

1 solid + 1 mixture of gas.

Sulphur exists in different allotropic form. If we take a mixture $S_R + S_M + S_L + S_V$

No of phase = 4.

If we take a solid mixture of sulphur Rhombic and Monoclinic No of phase = 2.

Imp Hydrated salts constitute diff phase

If we take a mixture of = $CuSO_4 \cdot 10H_2O$ (1), $CuSO_4 \cdot 5H_2O$ (1), $CuSO_4 \cdot H_2O$ (1) & $CuSO_4$ (1)

No of phases = 4.

Components: The number of components of a system at equilibrium is defined as the minimum number of independent of chemical constituents in terms of which the composition of each & every phase can be expressed by virtue of a chemical equation.

*Constituents: or. The substance that can be separated out.

~~I have got multiphase~~

(1) Ice ⇌ Water ⇌ Vapour.

The number of constituents taking part in equilibrium is only one i.e. H_2O [H_2 & O_2 are not considered because water exists as H_2O] ~~the ...~~ H_2O exists in a state of real equilibrium. H_2O exists in a definite proportion 2:1 (H:O) as they combined in a definite proportion to form water & therefore there amounts can not be varied independently.

Imp ONE OF THE WAY TO CALCULATE THE NO OF COMPONENT IN A GIVEN HETEROGENOUS EQULIBRIUM

COMPONENT = NO OF CONSTITUENTS − NO OF RELATION.

IN this case. H_2O(s), H_2O(l), H_2O(v) = 3.

No of reln S ⇌ L L ⇌ V = 2

3 − 2 = 1, (ONE COMPONENT SYSTEM)

Phase = 3, Component = 1.

(2) Mixture of gases: No of Component = No of gases mixed, Air = N_2, O_2, CO_2, Ar,

Mean = Phase = 1

Component = 4

(3) S_R ⇌ S_M ⇌ S_L ⇌ S_V. (Sulphur System)

Component = 1, Phase = 4.

(4) Decomposition of $CaCO_3$

$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$ (3 phase, 2 component)

No of constituent = 3, No of rxn = 1

3 - 1 = 2 component.

(5) $NH_4Cl(s) \rightleftharpoons NH_3(g) + HCl(g)$ (small pressure)

under vacuum pressure of NH_3 & HCl same.

phase = 2, component.

3 constituent - 2 rxn = 1.

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

Arbitrary. 3 - 1 = 2.

(6) $PCl_5(s) \rightleftharpoons PCl_3(s) + Cl_2(g)$.

Constituent 3, rxn = 1 , 2

2 component, 3 phase

(7) Aq (NaCl) → No of phase = 1. (No of constituents = 2, H_2O, NaCl, Rxn = 0

Component = 2. (NaCl & H_2O)

(8) $CuSO_4 5H_2O$, Two component sys.

$CuSO_4 5H_2O \rightleftharpoons CuSO_4 + 5H_2O$. (No of constituent = 3, No of Rxn = 1

3 - 1 = 2.

(A) In calculating No of components involving ions electroneutrality also taken into consideration. After derivation of phase Rule we will take examples & calculate No of components.

(F). Degrees of freedom or variability or Variance of a System:

F = The number of Variable factors such as T, P & C of the component which must be ascertained (or arbitrarily fixed in order that the condition of the system may be perfectly defined

When F = 0, The system is Non-variant or Invariant or Zero-variant.

F = 1, univariant or Monovariant.

F = 2 The system is bivariant.

(1) At triple point of water T, P, both fixed System is self defined zero variant.

(2) water L ⇌ V. At Equilibrium T & P are fixed if we know temp, pressure is automatically known Hence f = 1 Monovariant.

(3) Glass of water (L) or Ice, or water vapour. Both P & T have to be specified f = 2.

(4) NaCl (s) ⇌ NaCl(aq) ⇌ water vapour (g)

We have to state either temp/pressure, Saturation solubity is fixed. F = 1

(5) For gaseous mixture, = Both temp & pressure has to be specified.

$PV = nRT$.

Phase Rule ⇒ $\boxed{F + P = C + 2}$ Gibb's phase Rule.

Advantages of Phase Rule:

(1) Phase rule is applicable to both chemical as well as physical equilibrium.

(2) Applicable to system in bulk (Macroscopic System) Hence no of information required regarding molecular micro structure.

(3) The behaviour of the given system can be predicted under different conditions.

(4) The equilibrium states can be classified in terms of phases components and degrees of freedom.

(5) With same degree of freedom different system behaves in a similar fashion.

(6) With the knowledge of phase Rule under a given set of conditions The predictions. of
(i) Existence of Equilibrium among various substances.
(ii) Inter convergence of substance
(iii) Disappearance of some of the substance.

Limitations.
(1) Applicable only to system in Equilibrium.
(2) Equilibrium is controlled by P, V, C only.
(3) Under similar condition of temperature & pressure all phases must be present.
(4) Only number of phases is considered not the amount of substance.

Derivation of Phase Rule:

Gibb's phase rule $F + P = C + 2$ is a general rule applicable to all Heterogenous system wheather a system (Physical Heterogenous eqm & Chemical Heterogenous Equilibrium) system reactive & non reactive.

Derivation of Phase rule for NON REACTIVE SYSTEM:

Let us consider a heterogenous system comprising of p phases in equilibrium with each other.

Let us consider all p phases comprise of C no of components.

In order to describe the system. We must describe the variables & number of relationships

THE VALUE OF VARIABLES THAT MUST BE SPECIFIED IN ORDER TO DEFINE A GIVEN SYSTEM COMPLETELY.

VARIBALES	NUMBER
1. Temperature of the system (For a given system at eqm there can be only one temperature)	1
(2) PRESSURE OF THE SYSTEM	1
(3) Concentrations of each and every phases. As each phases contains C concentrations terms. So all the P phases contains 'C' concentrations terms each. (Total Conc^n	PC

In order to define the given system the number of variables need to be specified. $= PC + 2$

Values of these variables can be obtained through solving the equations which are applicable when the system is at equilibrium.

In this ~~type~~ heterogenous equilibrium two types of ~~Equilibrium~~ Equations available.

TYPES & NUMBER OF EQUATIONS AVAILABLE.

Equations	Numbers
(1) Sum of mol mol fraction in any phase = 1. (Each phase contains of C components)	P.
$x_{1(1)} + x_{2(1)} + \cdots + x_{C(1)} = 1$ $x_{1(2)} + x_{(2)(2)} + \cdots + x_{C(2)} = 1$ $\vdots$ $x_{1(P)} + x_{2(P)} + \cdots + x_{C(P)} = 1$	P
No of equations = No of phases. (Total number of phases = P & hence no of equations = P.	
(2) Thermodynamic conditions of Phase Equilibria. The species will distribute itself in such a manner that the value of Gibb's free energy at equilibrium is minimum. The condition for this the chemical potential μ of any component will have the same value in all P phases	C (P − 1)
$\mu_{1(1)} = \mu_{1(2)} = \cdots = \mu_{1(P)}$ $\mu_{2(1)} = \mu_{2(2)} = \cdots = \mu_{2(P)}$ $\vdots$ $\mu_{C(1)} = \mu_{C(2)} = \cdots = \mu_{C(P)}$	
For each component (P−1) eqn for C components	Total NO eqns available = P + C(P−1)

From our basic knowledge of mathematics we know the number of variables that can be obtained from from a set of equations = Number of equations

To find x & y we need two eqn to get the value of x & y
e.g. $4x + 3y = 11$ 2 − 1
$7y + 4x = 18$ $= 4y = 7$, $y = 7/4$ & x can

If no of eqn = No of variables then all the variables can be solved.

If one variable is not solved (Mono variant)
If two = Bi variant & so on

Variance = No of variables that need to be Specified − No of equations that are available.

$$F = (PC + 2) - \{P + C(P-1)\}$$

$$= PC + 2 - P - PC + C$$

$$\boxed{F + P = C + 2}$$ Phase Rule.

For 1 Component sys

If phase = 1		F = 2
If	" = 2	F = 1
If	" 3	F = 0

$P \frac{1}{\alpha} F$ after C

For 1 Phase $P = 1$

$F + P = C + 2$

$= F + 1 = C + 2$

For 1 Phase 1 Component system

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

$F = 2$ (Bi-variant)

2 Phase 1 Component.

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

or $F = 1$ (Mono variant)

3 phases in eqm

$F + P = C + 2$ $F + 3 = 1 + 2 = 0$

Non variant.

Phase Rule when one of the component is missing from one phase [ONE OF THE COMPONENT IS PRESENT ONLY IN (P-1) phases]

Let us consider a system in heterogenous equilibrium. Let the system comprises of P no of phases containing C number of components in equilibrium at a constant temperature and pressure.

Let component 1 is missing from phase no 1.

VALUES OF VARIBALES TO BE KNOWN TO DEFINE THE SYSTEM

Variables	Number
Temperature	1
pressure	1
Concentration of component in different phase For First phase (C − 1) concn term for (P − 1) phases C concentration term	$(C-1)+C(P-1)$
Total	$CP+1$

Total no of equation
Types of eqns available

Eqns	Nos.
① Condition of mol fraction For phase 1: $x_{2(1)}+x_{3(1)}+\cdots+x_{c(1)}=1$ For Rest of phase: $x_{1(2)}+x_{2(2)}+x_{3(2)}+\cdots+x_{c(2)}=1$ ⋮ $x_{1(P)}+x_{2(P)}+x_{3(P)}\cdots+x_{c(P)}=1$	P
② Condition for thermodynamic eqm For Component − 1 $\mu_1(2)=\mu_1(3)\cdots=\mu_1(P)$ For other comm $\mu_2(1)=\mu_2(2)\cdots=\mu_2(c)$ $\mu_{c(1)}=\mu_{c(2)}\cdots\mu_{c(P)}$	$(P-2)$ $C(P-1)$

To compute the number of components in a system
General formula.

Component 'C' = No of constituents − No of relationship

In case of electrolyte

Component 'C' = No of constituents C' − No of relations r − No of electroneutrality condition Z

example.

(1) A solution containing Na^+, Cl^-, Ag^+, NO_3^-, $AgCl(s)$ and H_2O

implies (aq) NaCl, $NaNO_3$, $AgNO_3$ & Solid AgCl & H_2O,

$5 + Ag^+ + Na^+ + Cl^- + NO_3^- + H^+ + OH^- = 11$

No of constituents = 11. $c' = 11$

No of Relationship.

$NaCl \rightleftharpoons Na^+ + Cl^-$

$NaNO_3 \rightleftharpoons Na^+ + NO_3^-$

$AgNO_3 \rightleftharpoons Ag^+ + NO_3^-$ $r = 5$

$AgCl \rightleftharpoons Ag^+ + Cl^-$

$H_2O \rightleftharpoons H^+ + OH^-$

Electroneutrality

$x_{Ag^+} + x_{Na^+} = x_{Cl^-} + x_{NO_3^-}$ $Z = 2$

$x_{H^+} = x_{OH^-}$

Component C $= c' - r - z$

$= 11 - 5 - 2 = 4$.

It is a four component system.

(2) A solution containing H^+, OH^-, Na^+, Cl^-, Ag^+, NO_3^-, $AgCl(s)$, H_2O.

In this case no of constituent = 15

$NaCl$, $NaNO_3$, $NaOH$, $AgCl$, $AgNO_3$, $AgOH$, HCl, HNO_3, H_2O + H^+ + OH^- + Na^+ + Cl^- + Ag^+ + NO_3^- = 15.

No of relationship = 9

$$NaCl \rightleftharpoons Na^+ + Cl^-$$
$$NaNO_3 \rightleftharpoons Na^+ + NO_3^-$$
$$NaOH \rightleftharpoons Na^+ + OH^-$$
$$AgCl \rightleftharpoons Ag^+ + Cl^-$$
$$AgNO_3 \rightleftharpoons Ag^+ + NO_3^-$$
$$AgOH \rightleftharpoons Ag^+ + OH^-$$
$$HCl \rightleftharpoons H^+ + Cl^-$$
$$HNO_3 \rightleftharpoons H^+ + NO_3^-$$
$$H_2O \rightleftharpoons H^+ + OH^-$$

Electroneutrality = 1

$$x_{Na^+} + x_{Ag^+} + x_{H^+} + x_{Cl^-} = x_{Cl^-} + x_{OH^-} + x_{NO_3^-}$$

$$C = C' - r^0 - z = 15 - 9 - 1 = 5$$

$$C = 5$$

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(3) A solution containing

$H_2O, Na^+, Cl^-, K^+, NO_3^-, NH_4^+,$ [redacted] $, H^+, OH^-$

$NaCl \rightleftharpoons Na^+ + Cl^-$

$NaNO_3 \rightleftharpoons Na^+ + NO_3^-$

$NaOH \rightleftharpoons Na^+ + OH^-$

$KCl \rightleftharpoons K^+ + Cl^-$

$KNO_3 \rightleftharpoons K^+ + NO_3^-$

$KOH \rightleftharpoons K^+ + OH^-$ $\qquad r = 12$

$NH_4Cl \rightleftharpoons NH_4^+ + Cl^-$

$NH_4NO_3 \rightleftharpoons NH_4 + NO_3^-$

$NH_4OH \rightleftharpoons NH_4^+ OH^-$

$H_2O \rightleftharpoons H^+ + OH^-$

$HCl \rightleftharpoons H^+ + Cl^-$

$HNO_3 \rightleftharpoons H^+ + NO_3^-$

$$x_{NH_4^+} + x_{K^+} + x_{Na^+} + x_{H^+} = x_{OH^-} + x_{NO_3^-} + x_{Cl^-}$$

$$z = 1$$

$$C = C' - r - z = 19 - 12 - 1 = 6$$

$$\boxed{C = 6}$$

(9)

An (aq) solution containing H_3PO_4, $H_2PO_4^-$, HPO_4^{2-}, PO_4^{-3} at 1 atm pressure $Na^+ + H^+$.

$+ H_2O + NaH_2PO_4 + OH^-$

$H_3PO_4 \rightleftharpoons 3H^+ + PO_4^{-3}$

$NaH_2PO_4 \rightleftharpoons Na^+ + H_2PO_4^-$

$H_2PO_4^- \rightleftharpoons H^+ + HPO_4^{-2}$

$HPO_4^{-2} \rightleftharpoons H^+ + PO_4^{-3}$

$H_2O \rightleftharpoons H^+ + OH^-$

$c' = 9$.

$r = 5$

$x_{Na^+} = x_{PO_4^{-3}} + x_{HPO_4^{2-}} + x_{H_2PO_4^-}$

$x_{H^+} = 2x_{PO_4^{3-}} + x_{HPO_4^{2-}} + x_{OH^-}$

$z = 2$.

$c = c' - r - z = 9 - 5 - 2 = 2$.

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Calculation of No of components of some simple system.

(i) $Na_2SO_4 \cdot xH_2O$.

(a) Neglecting all dissociation.
No of chemical constituents 2 i.e. Na_2SO_4 & H_2O
No of rxn = 0, Restricted condn = 0
$C' = C - r - z = 2 - 0 - 0 = 0$

Complete dissociation of the salt
Na^+, SO_4^{-2}, H_2O.
restriction:
$x_{Na^+} = 2x_{SO_4^-}$
$C' = C - r - z = 3 - 0 - 1 = 2$.

Partial dissociation of the salt.
$Na_2SO_4 \rightleftharpoons 2Na^+ + SO_4^{-2}$ — chemical constituent = 4: Na_2SO_4, Na^+, SO_4^{-2} & H_2O.
Restricted condn. $x_{Na^+} = 2x_{SO_4^{-2}}$
$4 - 1 - 1 = 2$.

Dissociation of water also.
$Na_2SO_4 \rightleftharpoons 2Na^+ + SO_4^{-2}$ | 2
$H_2O \rightleftharpoons H^+ + OH^-$
$x_{Na^+} = 2x_{SO_4^{-2}}$, $x_{H^+} = x_{OH^-}$

Na_2SO_4, H_2O, H^+, OH^-, Na^+, SO_4^{-2} = 6
$6 - 2 - 2 = 2$

Sodium Dihydrogen phosphate - water system.
$NaH_2PO_4 \cdot xH_2O$

(1) Neglecting all dissociation (2)
$C' = C - r - z = 2 - 0 - 0 = 2$

(2) Single dissociation of salt.
$NaH_2PO_4 \rightleftharpoons Na^+ + H_2PO_4^-$ | 2
$4 - 1 - 1 = 2$.
$x_{Na^+} = x_{H_2PO_4^{-2}}$

R = 2 [?]
NaH_2PO_4, Na^+, $H_2PO_4^-$, H_2O = 4
eqn −1 −2 = 1
r = 1

Multiple dissociation:

$$NaH_2PO_4 \rightleftharpoons Na^+ + H_2PO_4^-$$

$$H_2PO_4^- \rightleftharpoons H^+ + HPO_4^{-2}$$

$$HPO_4^{-2} \rightleftharpoons H^+ + PO_4^{-3}$$

Constituents. NaH_2PO_4, Na^+, $H_2PO_4^-$, HPO_4^{-2}, PO_4^{-3} & H_2O
= 7

Chemical Rexⁿ = 3

Restricted condition.

$$x_{Na^+} = x_{PO_4^{-3}} + x_{HPO_4^{-2}} + x_{H_2PO_4^-}$$

$$x_{H^+} = 2x_{PO_4^{-3}} + x_{HPO_4^{-2}}$$

$$C' = C - r - z = 7 - 3 - 2 = 2.$$

Dissociation of water also

Constituent = 8.

Rexⁿ = 4 addition

$$H_2O \rightleftharpoons H^+ + OH^-$$

$$x_{Na^+} = x_{PO_4^{-3}} + x_{HPO_4^{-2}} + x_{H_2PO_4^-}$$

$$x_{H^+} = 2x_{PO_4^{-3}} + x_{HPO_4^{-2}} + x_{OH^-}$$

$$= 8 - 4 - 2 = 2$$

$AlCl_3 \cdot xH_2O$ ✓

In this $AlCl_3$ combines with water according to the equation.

$$AlCl_3 + 3H_2O \rightleftharpoons Al(OH)_3 + 3HCl.$$

Some of the $Al(OH)_3$ is precipitated out.

Dissociation of various species

$$AlCl_3 \rightleftharpoons Al^{3+} + 3Cl^- \qquad Al(OH)_3 \rightleftharpoons Al^{+3} + 3OH^-$$

$$H_2O \rightleftharpoons H^+ + OH^- \qquad HCl \rightleftharpoons H^+ + Cl^-$$

Total no of constituent = 8.

$AlCl_3$, H_2O, $Al(OH)_3$, HCl, Al^{+3}, Cl^-, H^+, OH^-

No of chemical reacn = 4

Restriction.

$$3x_{Al^{+3}} + x_{H^+} = x_{OH^-} + x_{Cl^-}$$

$$8 - 1 - 4 = 3$$

If we assume complete dissociation of $AlCl_3$ & HCl.

$$c = 6, \; r = 2, \; z = 1.$$

$$c' = c - z - r = 6 - 1 - 2 = 3.$$

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Show that $NH_4Cl(s)$, $NH_3(g) - HCl(g)$ system in which $p_{NH_3} = p_{HCl}$ is a 1 component system otherwise 2.

Number of reacn $r = 1$

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

No of constituent = 3, $NH_4Cl(s)$, $NH_3(g)$, $HCl(g)$

Number of restriction condition

$$p_{NH_3} = p_{HCl}$$

$$c' = c - r - z = 3 - 1 - 1 = 1$$

If $p_{NH_3} \neq p_{HCl}$ $\quad z = 0$,

$$c'' = 3 - 1 - 0 = 2.$$