APPLIED CHEMISTRY

Phase Rule

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LEARNING OUTCOMES

By the end of this session participants should be able to

Understand and evaluate ..

✓ The terms phase, components, degrees of freedom and their correlation to phase rule.

✓ Calculation of number of phases, components and degrees of freedom.

✓ Definition of Phase rule and its implications.

Outline : Lecture 1

❑ **Phase Rule: Introduction**

❑ **Description of Terms**
- **Phase**
- **Components**
- **Degrees of freedom**

❑ **Phase Rule: Definition**

Phase Rule : Introduction

States of the matter

- **Solid**
- **Liquid**
- **Gas**

Example.
Water can exist in three states [solid, liquid and gas (vapour)]depending upon the external conditions : Each state corresponds to a phase

Homogeneous and Heterogeneous system

A homogeneous system consists of only **one phase** i.e corresponds to **uniform composition** throughout while in heterogeneous system, **two or more phases** can be present forming **non uniform composition.**

Example of homogeneous system – Air, saline solution

Example of heterogeneous system – sand, oil and water

The main difference between phase of matter and state of matter can be given as: phase of matter explains uniform chemical and physical properties of matter whereas state of matter explains the form of matter at a given temperature and a pressure

Phase Rule : Introduction

- The Phase rule is an important generalisation put forth by Willard Gibbs (1874) on the basis of which behaviour of heterogeneous systems can be explained in the state of equilibrium.

$$H_2O \, (s) \rightleftharpoons H_2O \, (l)$$

$$F = C - P + 2$$

F = Degrees of freedom

C = Number of Components

P = Number of phases

What is a phase?

Definition: A phase is a **homogeneous**, **physically distinct** and **mechanically separable** portion of a system which is separated from other parts of the system via a definite boundary or simply phase is a state of matter which is uniform throughout both with respect to chemical composition and physical state. It is represented by '**P**' in phase rule expression.

Phase Rule

Examples :

For liquid in liquid

- Two completely **miscible** liquids form a homogeneous solution constituting a single phase like a solution of **alcohol** and **water**

  (Polar + Polar = One phase i.e P = 1) and **(Non polar + Non polar = One phase, like CCl_4 + C_2H_5 O C_2H_5 i.e. P = 1)**

- If **mixture of miscible liquids is kept in a closed vessel**, above the liquid mixture, there will be some vapours of liquids hence constituting two phases.

- A mixture of two **immiscible liquids** lead to heterogeneous solution which on standing form separate layers, thus constituting two phases like **oil** and **water** mixture or CCl_4 and **water** **(Polar + Non polar = Two phases, i.e P = 2)**

For gas in liquid

- Gas **soluble** in liquid like NH_3 + H_2O and HCl + H_2O form a homogeneous solution constituting single phase i.e **P = 1**.

- Gas **insoluble** in liquid like SO_2 + H_2O form a heterogeneous solution hence **P = 2**

For gas in gas

- All gases mix freely yielding homogeneous mixtures hence any mixture of gases (O_2, N_2, H_2) form one phase only i.e **P = 1**

Phase Rule

Examples

For solid in liquid

- Complete dissolution : unsaturated aqueous solution of NaCl /sugar forms a homogeneous solution constituting single phase i.e

  P =1

- Insoluble solid or saturated aqueous solution of soluble solid like NaCl / sugar form heterogeneous solution hence **P = 2**
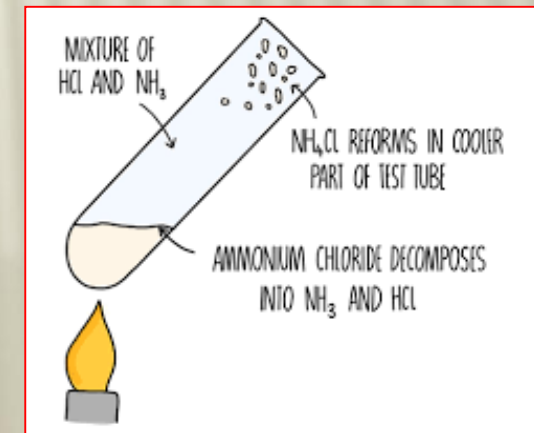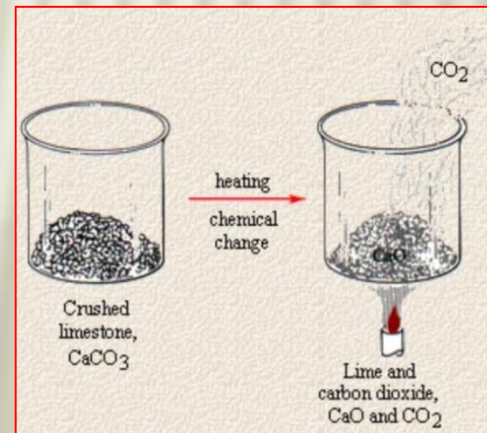
For solid in solid

- Each solid constitutes a separate phase so in a mixture of solids (heterogeneous system), **number of phases = no of solids.**

- Mixture of solids that form solid solutions i.e alloys constitute a single phase i.e **P = 1** like Cu and Zn to form Brass.

  - Decomposition of $CaCO_3$:

    $$CaCO_3(s) \rightleftharpoons CaO\ (s) + CO_2\ (g) \qquad \textbf{P = 3}$$

  - Decomposition of NH_4Cl:

$$NH_4Cl(s) \rightleftharpoons NH_3\ (g) + HCl\ (g) \qquad \textbf{P = 2}$$

CO2
heating
chemical change
Crushed limestone, CaCO3
Lime and carbon dioxide, CaO and CO2

MIXTURE OF HCL AND NH3
NH4CL REFORMS IN COOLER PART OF TEST TUBE
AMMONIUM CHLORIDE DECOMPOSES INTO NH3 AND HCL

Phase Rule

What are components ?

Definition : For a system at equilibrium, the number of components is the smallest number of independently variable constituents, in terms of which composition of each phase present can be expressed directly or in the form of a chemical equation. The components of a system do not represent the number of constituents or chemical individuals present in the system. It is represented by '**C**' in the phase rule expression.

> Examples: Systems involving physical equilibria

❑ **Water system has three phases**: Ice (s) ⇌ Water (l) ⇌ Water vapor (g)

Each of these phases is a different physical form of the same chemical compound i.e H_2O, so the composition of all three phases can be expressed in terms of one component i.e H_2O, therefore it is a **one component**, **three phase** system.

❑ **Sulphur system has four phases** : Rhombic, monoclinic, liquid and vapour $S_{(r)}$ ⇌ $S_{(m)}$ ⇌ $S_{(l)}$ ⇌ $S_{(v)}$

The composition of each phase can be expressed in terms of **sulphur** alone i.e one component sulphur is sufficient to express the composition of all the four phases of the equilibrium.

❑ **Aqueous salt solution or sugar solution** form a homogeneous mixture (**P=1**) but to express the concentration of the solution the amount of both **salt /sugar** and **water** is required, hence it is a **two** component system.

Phase Rule

To evaluate the number of components (C)

Reacting systems

$C = N - E$

N = Number of constituents (every substance that can be separated from the system)

E = Number of independent equations relating the concentrations of N species

Conditions:

1. Each independent chemical equilibrium involving the constituents counts as one equation.

2. A solution being electrically neutral also counts as one equation if ions are considered as constituents.

Alternatively:

Components are number of chemical constituents of the system minus the number of equations relating to those constituents in an equilibrium state

Phase Rule

Examples

Thermal decomposition of $CaCO_3$

The system consists of three phases: i. Solid $CaCO_3$ ii. Solid CaO iii. Gaseous CO_2

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

The composition of all the three phases i.e solid $CaCO_3$, solid CaO and gaseous CO_2 can be expressed in terms of minimum two constituents as demonstrated:

Case-1: CaO and CO_2 as constituents

Phase	Components
$CaCO_3$	$CaO + CO_2$
CaO	$CaO + 0CO_2$
CO_2	$0CaO + CO_2$

Case-2: $CaCO_3$ and CO_2 as constituents

Phase	Components
$CaCO_3$	$CaCO_3 + 0CO_2$
CaO	$CaCO_3 - CO_2$
CO_2	$CaCO_3 - CaO$

Case-3: $CaCO_3$ and CaO as constituents

Phase	Components
$CaCO_3$	$CaCO_3 + 0CaO$
CaO	$CaO + 0CaCO_3$
CO_2	$CaCO3 - CaO$

Therefore, it forms a two component system

Examples

Dissociation of NH_4Cl

$$NH_4Cl(s) \rightleftharpoons NH_4Cl(g) \rightleftharpoons NH_3(g) + HCl(g)$$
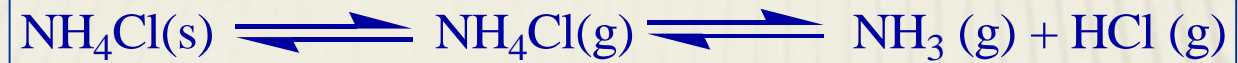
• **In a closed vessel, implying $p_{NH3} = p_{HCl}$, a case when gaseous mixture is formed by sublimation of NH_4Cl (s)**

The system consists of two phases i.e solid ammonium chloride and homogeneous mixture of NH_3 and HCl gases. **Also, an equimolar mixture of NH_3 and HCl in vapour phase may be regarded as NH_4Cl in the vapour state i.e the constituents of the mixture are present in the same proportion in which they are combined in solid NH_4Cl.** Therefore, the composition of each phase can be represented by NH_4Cl alone forming one component system.

• **In an open vessel, implying $p_{NH3} \neq p_{HCl}$ or NH_3 / HCl is introduced in the system in excess.**

In this case the system becomes two component system, as the partial pressures of gases NH_3 and HCl gases are no longer same and the composition of vapour phase can no longer be expressed in terms of NH_4Cl alone.

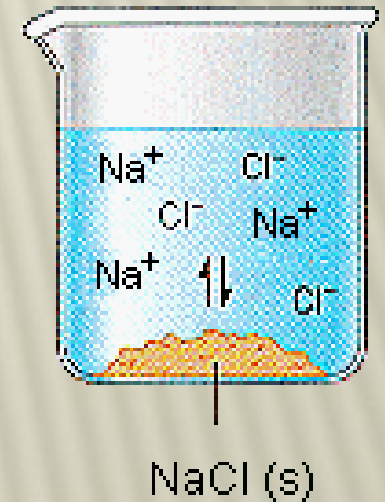| Phase	Components
NH_4Cl (s)	NH_4Cl
NH_3 (g) + HCl (g), equimolar mixture	NH_4Cl (g)
NH_3 (g) + HCl (g), excess NH_3	NH_4Cl (g) + NH_3 (g)
NH_3 (g) + HCl (g), excess HCl	NH_4Cl (g) + HCl (g)

Phase Rule

Examples

NaCl – H$_2$O system

•Unsaturated aqueous solution of NaCl: **One phase two component system.** The composition of the solution (xNaCl.yH$_2$O) can be expressed in terms of NaCl and H$_2$O.

•Saturated solution of NaCl: **Two phase two component system.** It has two phases aqueous solution of NaCl and solid NaCl. Also, the composition of both can be expressed in terms of NaCl and H$_2$O. Hence a two component system.

Phase	Components
Aqueous solution of NaCl	xNaCl + yH$_2$O
Solid NaCl	NaCl + 0H$_2$O

Na$^+$ Cl$^-$
Cl$^-$ Na$^+$
Na$^+$
Cl$^-$

NaCl (s)

Q1. Calculate number of phases and components for the following systems:
i.   Mixture of N$_2$ and H$_2$ contained in a vessel
ii. For equilibrium C (s) $\rightleftharpoons$ CO (g) $\rightleftharpoons$ CO$_2$ (g) $\rightleftharpoons$ O$_2$ (g)

Sol: i. **P =1** (homogeneous mixture) **, C = 2** because concentration of both nitrogen gas and hydrogen gas has to be specified to define the system completely.

ii. **P = 2**[C(s) and homogeneous mixture of gases (CO +CO$_2$ +O$_2$), **C = 2** (carbon and oxygen).

Examples

Q2. Explain why KCl-NaCl-H$_2$O system is regarded as three component system while KCl-NaBr-H$_2$O as four component system?

Sol: For **KCl-NaCl-H$_2$O system, N = 3,** while there is no independent equation that correlates the concentration of the constituents (no equilibrium), hence E = 0.

So, to apply C = N- E, the following conditions exist
N = 3
E = 0
Hence C = 3-0 = 3 i.e. **three component system**.

While, for **KCl-NaBr-H$_2$O** system, N = 5 (KCl, NaBr, H$_2$O, KBr, NaCl) and number of independent equation is 1 i.e E =1 as shown below:

$$KCl + NaBr \rightleftharpoons KBr + NaCl$$ Hence, C = N- E = 5-1 = 4 i.e **four component system**.

Q3. Calculate number of phases and components in the following system:

$$CuSO_4.5H_2O \ (s) \rightleftharpoons CuSO_4.3H_2O \ (s) + 2H_2O \ (g)$$

Sol: P = 3 (two solid phases and one gaseous) while C = 2, because the composition of each phase can be expressed with the help of two components **CuSO$_4$** and **H$_2$O**.

Phase Rule

Definition: The degree of freedom of a system is defined as the minimum number of independent variables such as temperature, pressure and concentration (or composition) which must be specified in order to define the system completely. It is represented by "**F**" in the phase rule expression (**F = C – P + 2**).

> **F = 0** (**Invariant system**)
>
> **F = 1** (**Univariant / monovariant system**)
>
> **F = 2** (**Bivariant system**)
>
> **F = 3** (**Trivariant system**)

Examples:

UNIVARIANT / MONOVARIANT SYSTEM $H_2O \ (l) \rightleftharpoons H_2O \ (g)$

The system will have only **one degree of freedom** because at a given temperature, the equilibrium vapor pressure of water can have only one fixed value. Thus, if temperature is specified, pressure becomes known automatically and vice-versa.

Phase Rule

Examples:

BIVARIANT SYSTEM

For a pure gas, PV = RT, if P and T are specified there can be only one definite value of **V** i.e the volume gets automatically fixed. Hence for the gaseous system, two factors must be stated in order to define the system completely so **bivariant** system

TRIVARIANT SYSTEM

A mixture of two or more gases is completely defined only when P, T and composition are specified. If P and T are specified the third variable i.e composition may be varied. Since it is necessary to specify three variables to define the system completely hence three degrees or **trivariant**

NON-VARIANT SYSTEM

$$H_2O \text{ (s)} \rightleftharpoons H_2O \text{ (l)} \rightleftharpoons H_2O \text{ (g)}$$

This system will have **no degree of freedom**. The reason is that these three phases can coexist only at one particular temperature (freezing point of water) under one particular pressure. Since both the variables are already fixed, system automatically gets defined and there is no need to specify any variable hence **non variant system**.

Examples

Q. Calculate the degrees of freedom for the following systems:

i. A solution of a solid in a liquid in equilibrium with solvent vapor.

Sol : $F = C - P + 2$

Components = 2 (solid + liquid) ; phases = 2 (solution of solid in liquid + vapour)

Hence $F = 2 - 2 + 2 = 2$ (Bivariant system)

ii. Thermal decomposition of $MgCO_3$: $MgCO_3 \text{ (s)} \rightleftharpoons MgO \text{ (s)} + CO_2 \text{ (g)}$

Sol: $F = C - P + 2$

Components = 2 ($MgO + CO_2$), Phases = 3 (two solids and gas)

Hence $F = 2 - 3 + 2 = 1$ (Univariant system)

iii. If $NH_4Cl(s)$ is allowed to dissociate in a vessel already containing some $NH_3(g)$, what is the value of the degree of freedom.

$F = C - P + 2$

Components = 2 ($NH_4Cl + NH_3$); Phases = 2 [$NH_4Cl(s)$ + {$NH_4Cl(g)$ & $NH_3(g)$ }]

Hence, $F = 2 - 2 + 2 = 2$

Phase Rule

Advantages of Phase rule

- It is applicable both to physical and chemical equilibria.
- It requires no information regarding molecular / micro-structure, since it is applicable to macroscopic system.
- It is a convenient method of classifying equilibrium states in terms of phases, components and degrees of freedom.
- It helps in deciding whether under a given set of condition:

a. various substances would exist together in equilibrium or

b. some of the substances present would be interconverted or

c. some of the substances present would be eliminated .

- It does not take into cognizance of either the nature or quantities of component present in the system.

Limitations of Phase rule

- The phase rule is applicable to heterogeneous systems in equilibrium, so, it is therefore of no use for such systems which are slow in attaining the equilibrium state
- It is applicable to a single equilibrium state, so it never gives information about the other possible equilibrium in the system.
- All the phases in the system must be present under the same temperature, pressure and gravitational force
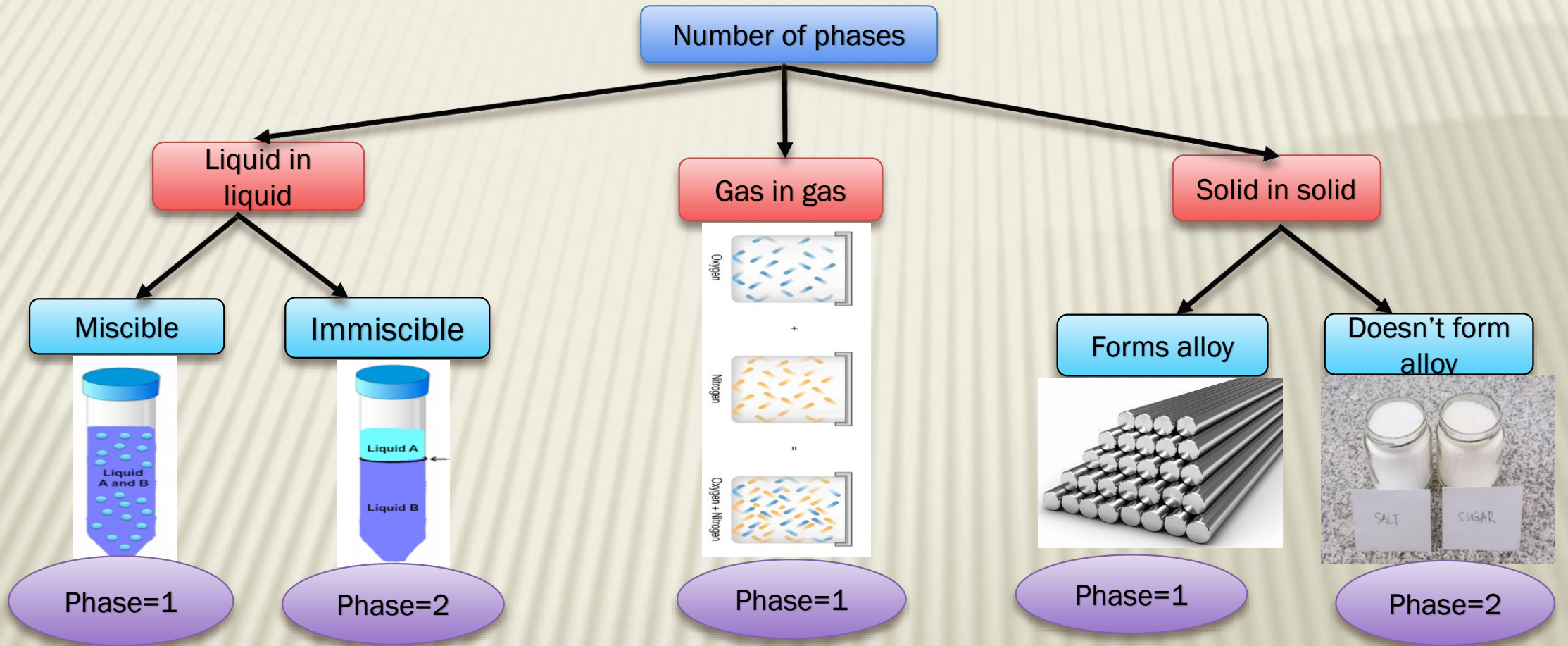
Phase Rule

Examples

In Na_2SO_4 system, calculate number of components for the following cases:
Case I : Na^+ (aq), SO_4 (aq), H_2O (l)

The components indicate complete dissociation of the salt in water according to equation below:

$$Na_2SO_4 \longrightarrow 2Na^+ + SO_4^{2-}$$

Hence, the following conditions apply to apply equation C = N – E,

✓N = 3 i.e number of constituents

✓No equilibrium correlates constituents with each other

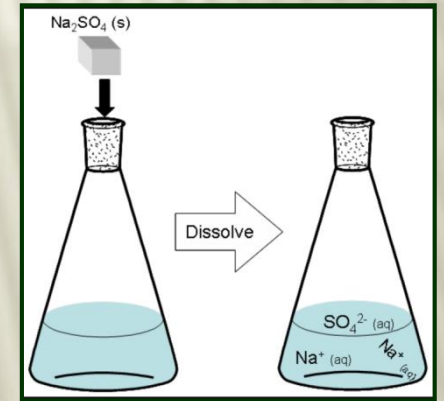✓Electroneutrality i.e total postive charge = total negative charge, hence E =1

Therefore, C = 3 – 0 – 1 = 2, i.e **two component system.**

Case II : Na_2SO_4 (s), Na^+ (aq), SO_4 (aq), H_2O (l)

$$Na_2SO_4 \rightleftharpoons 2Na^+ + SO_4^{2-}$$

The components indicate the presence of equilibrium

So, N = 4 and E = 1, also the electroneutrality condition holds as ions are involved, hence C = 4 – 1 – 1 = 2 i.e **two**
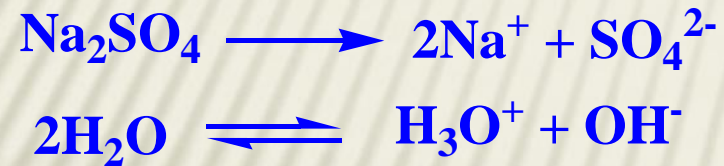
component system.
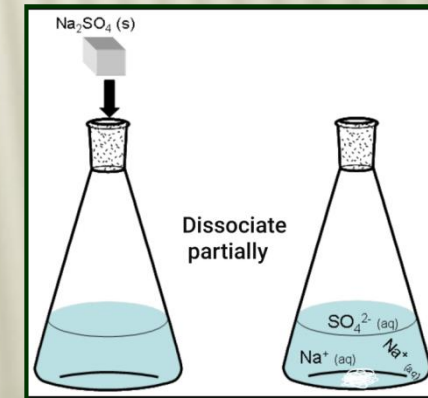
Phase Rule

Examples

Case III :Na$^+$ (aq), SO$_4$ (aq), H$_2$O (l), H$_3$O$^+$ (aq), OH$^-$ (aq)

The components indicate complete dissociation of the salt while H$_2$O (l) along with its ions indicates its partial dissociation, hence the following equations can be deduced:

$$Na_2SO_4 \longrightarrow 2Na^+ + SO_4^{2-}$$

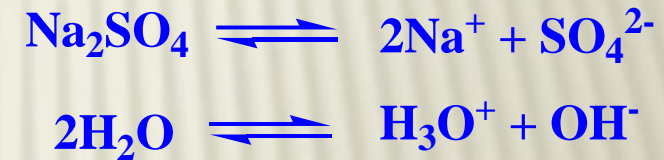$$2H_2O \rightleftharpoons H_3O^+ + OH^-$$

Hence, for equation C = N – E

✓N = 5 and E = 1

✓The condition of electroneutrality as ions are involved

✓[H$^+$] = [OH$^-$] as source is dissociation of water exclusively

✓Therefore C = 5-1-1-1 = 2 i.e **two component system**

Case IV :Na$_2$SO$_4$(s), Na$^+$(aq), SO$_4^{2-}$(aq), H$_2$O (l), H$_3$O$^+$(aq), OH$^-$ (aq)

The components indicate partial dissociation of both salt and water, hence the following equations can be deduced:

$$Na_2SO_4 \rightleftharpoons 2Na^+ + SO_4^{2-}$$

$$2H_2O \rightleftharpoons H_3O^+ + OH^-$$

Hence, for equation C = N – E

✓N = 6 and E = 2

✓The condition of electroneutrality as ions are involved

✓[H$^+$] = [OH$^-$] as source is dissociation of water exclusively

✓Therefore C = 6 – 2 – 1 - 1 = 2 i.e **two component system**