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1. Learning Outcomes

In this module,

☐ You shall learn about the information regarding the Systems, Homogeneous system and heterogeneous system.

☐ You shall learn about the Gibb's Phase rule.

☐ You shall learn about the various terms involved in Gibb's Phase rule .

☐ Examples

2. Introduction:

Homogeneous and Hetrogeneous system

SYSTEM- It is a part of universe which is under observation. In this part the change in temperature, pressure or concentration can be carried out to study the effect of such changes on equilibrium.

HOMOGENEOUS SYSTEM- The system in which all the reactants and products are present in one phase is called Homogeneous System.

➢Eg. $CH_3COOCH_3(l) + H_2O(l) = CH_3COOH\ (l) + CH_3OH\ (l)$

HETROGENEOUS SYSTEM- The system in which the reactants and products are present in more than one phase is called as Heterogeneous System.

$$CaCO_3\ (S) = CaO\ (S) + CO_2\ (G)$$

It is possible to study the different homogeneous reaction by the application of law of mass action. However the heterogeneous reaction, It is difficult to apply the law of mass action because so many limitations involving.

Thus the effect of changes of temperature, pressure, or concentration on heterogeneous system in equilibrium can be well study by the application of phase rule. This relationship governing all heterogeneous equilibria was 1st discovered in 1875 by an America physicist Willard Gibbs.

3.Gibbs phase rule

hence rule is known as Gibbs phase rule mathematically, It can be stated as,

$$F = C-P+2$$

Where 'F' is the no. of degrees of freedom 'C' is the number of components and 'P' is the number of phases of the system. The terms 'phase' 'components' and degree of freedom involved in the statement of the phase rule have specific significance.

4.Terms involved in Gibbs Phase rule

PHASE [P]-

A phase may be defined as "It is homogeneous, physically distinct, mechanically separable part of the system."To be physically distinct phase would have a definite boundary. The term mechanically separable means each term can be separated from the every other phase by simple process like filtration, Decantation or using separating funnel.

A system may consist of one phase or more than one phases.

i) A system containing only liquid water is one phase(P=1).ii) A system containing liquid water and water vapour (a gas) is a two phase system(P=2) iii) A system containing liquid water, water vapour and solid ice is three phase system(P=3)

A system containing of one phase only is called as homogeneous system. A system containing of two or more phases is called as heterogeneous system.

Ordinarily three states of matter gas, liquid and solid are known as phases.

Examples: To understand the meaning of the term phase,

I) PURE SUBSTANCES:

A pure substance (Solid ,Liquid or Gas) made of one chemical species only, is considered as one phase. Thus oxygen (O_2),benzene(C_6H_6)& ice(H_2O) are all one phase systems. It must be remembered that a phase may or may not be continuous. Thus whether ice is present in one block or many pieces, It is considered one phase.

2)MIXTURES OF GASES:

All gases mix freely to form homogeneous mixtures. Therefore any mixture of gases ,say O_2 and N_2 is a one phase system.

3)MISCIBLE LIQUIDS:

Two completely miscible liquids yield a uniform solution. Thus a solution of ethanol and water is a one phase system.

4)NON-MISCIBLE:

A mixture of two non-miscible liquids on standing forms two separate layers. Hence mixture of water and carbon tetrachloride constitutes two phase system.

5)AQUEOUS SOLUTIONS:

An aqueous solution of solid substance like sodium chloride (or sugar) is uniform through out therefore it is a one phase system. However a saturated solution of sodium chloride in contact with excess solid sodium chloride is two phase system.

6)MIXTURE OF SOLID :

A mixture of two or more chemical substance contains many phases

(1) Mixture of $CaCO_3$& CaO - TWO PHASES

(2) Decomposition of $CaCO_3$ - THREE PHASES

$$\mathbf{CaCO_3\ (S)} \quad \mathbf{CaO\ (S)} + \mathbf{CO_2}\ (G)$$

(3) NaCl crystal are along with copper sulphate crystals----- TWO PHASES

COMPONENTS [C]:

The symbol 'C' in the phase rule equation stands for the number of components of a system in equilibrium. The term component may be defined as "The number of components chemically independent species by means of which the composition of every phase can be expressed either directly or by chemical equation."

Zero or negative quantities of components are allowed.

Examples:

(1). The water system and sulphur system.

The simplest example of water system, where

ICE= WATER= WATER VAPOUR .

Here all the three phases can be expressed in terms of one chemical individual **H_2O**. hence water system has one component. Similarly in sulphur system all four phases that is Rhombic sulphur, Monoclinic sulphur, Vapour sulphur & Liquid sulphur are expressed by means of single chemical individual "S". Hence it is one component system.

(2) Mixture of Gases :

A mixture of gases say O_2& N_2.

PHASE	COMPONENTS
Gaseous mixture	$xO_2 + yN_2$

Hence mixture of oxygen & nitrogen has two components

(3) Sodium chloride solution :

A solution sodium chloride in water is a one phase system. Its composition is expressed in terms of two chemical individuals.

PHASE	COMPONENTS
Aqueous solution of NaCl	$xNaCl + yH_2O$

Therefore an aqueous solution of NaCl or any other solute is a two component system.

4)Saturated solution of sodium chloride in contact with excess of solid sodium chloride has two phases, namely aqueous solution & sodium chloride. The composition of both phases can expressed in terms of two chemical individuals NaCl & H_2O

PHASE	COMPONENTS
i) Aqueous solution of NaCl	$xNaCl + yH_2O$
ii) Solid sodium chloride	$NaCl + 0.H_2O$

hence saturated solution of NaCl or any other solute in contact with solid solute,isa two component system.

5)Decomposition of Calcium Carbonate:

When calcium carbonate is heating in aclosed vessel, the following equilibrium system results

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

It has three phases two solids & one gaseous. The composition of all phases can be expressed in terms of any two of the three chemical substances in equilibrium .

Let us select **CaO** **&** **CO_2** as the components ,then we can write.

	PHASE		**COMPONENTS**
i.	**CaO**	=	**CaO + O.CO_2**
ii	**CO_2**	=	**CO_2 + O.CaO**
iii	**$CaCO_3$**	=	**CaO + CO_2**

Again selecting **$CaCO_3$ & CaO** as components,We have,

	PHASE		**COMPONENTS**
i.	**$CaCO_3$**	=	**O.CaO + $CaCO_3$**
ii	**CaO**	=	**CaO + O.$CaCO_3$**
iii	**CO_2**	=	**$CaCO_3$ - CaO**

Again selecting**$CaCO_3$ & CO_2**as components, We have,

	PHASE		**COMPONENTS**
i.	**$CaCO_3$**	=	**$CaCO_3$ + O.CO_2**
ii.	**CO_2**	=	**CO_2 + O.$CaCO_3$**
iii.	**CaO**	=	**$CaCO_3$ - CO_2**

Thus decomposition of calcium carbonate is two component system.

VARIABLES:

Certain factors such as temperature, pressure & concentration are the important conditions of an equilibrium. We can change or adjust these conditions according to our new view. These factors are called variables.

Degree of Freedom or Variance:[F]:

The degree of freedom of a (substance) system is a number of variable that can be varied independently without changing the number of phases present at equilibrium. The term degree of freedom represented by " F " in the phase rule equation. A system with F=0 is known as INVARIANT system or having no degree of freedom. A system with F=1 is known as MONOVARIANT system or having one degree of freedom. A system with F=2 is known as BIVARIANT system or having two degree of freedom.

Let us consider some examples:

1.For pure gases: F=2.

$$F=C-P+2 \qquad = 1 - 1 + 2 = 2.$$

For a given sample of any pure gas PV=RT, If the value of pressure (P) and temperature (T) be specified, volume (V) can have only one definite value or that the volume is fixed automatically. Hence the system containing pure gas two degrees of freedom (F=2).

2.For a mixture of two gases: F=3.

$$F=C-P+2 \qquad = 2 - 1 + 2 = 3.$$

A system containing a mixture of two or more gases is completely defined when its composition, temperature & pressure are specified, If pressure & temperature only are specified the third variable i.e composition could be varied. Hence it is necessary to specify three variables to defined the system completely. Hence mixture of gases has three degree of freedom. (F=3)

3. For Water = Water vapour: (F=1)

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

For the system Water =Water vapour , out of two variables (temperature & pressure)we can very only one variable. At a definite temperature the vapour pressure of water can have only one fixed value. Thus if one variable (temperature& pressure) is specified, the other is fixed automatically. Hence the system Water = W.V. has one degree of freedom.(F=1)

.Examples:

1.Calculate no. of phases, F, C for a mixture of five different gases enclosed in a cylinder.
Here P=1 and C=5
Therefore, F = C – P + 2 =5-1+2 =6

2.Calculate the degree of freedom for water system in which ice=w=w.v.
C=1,P=3 F=? F=C-P+2 F=1-3+2 =0 hence no degree of freedom.

3.Calculate F for the system water =water vapour.
C=1,P=2 F=? F=C-P+2 =1-2+2 =1 hence monovariant system.

4.For a saturated solution of NaCl in equilibrium with solid NaCl & water vapour.
NaCl (S)NaCl solution(L) W.V.(G)
P=3, C=2. F=C-P+2 = 2-3+2=1 hence system has one degree of free

5.Summary

1.Two types of systems i) Homogeneous system and Hetrogeneous system
2. Gibbs Phase rule F = C - P + 2
3.Terms involved in Gibbs phase rule:
PHASE (P),
COMPONENTS(C),
VARIANCE OR DEGREE OF FREEDOM (F)
EXAMPLES

VIDEO

1. https://youtu.be/0xhUGYDKpGw

2.https://www.youtube.com/hashtag/degreesoffreedomphaserule

3. https://youtu.be/OPeePZIXm10

4.Assignment
Google form(quiz)
https://docs.google.com/forms/d/e/1FAIpQLSdKtXokVTRuMibE53rN9g-FDdMz2NYdTrg10oYast87kdrb8g/viewform?usp=sf_link

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