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Module 8: Phase Rule

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Module outline:
Introduction
Phase Rule
Application to one component system
(water and sulphur)

8.1. INTRODUCTION

The Phase rule was proposed by J.W. Gibbs in 1874. According to the phase rule, "for any heterogeneous system in equilibrium the sum of number of phases and degrees of freedom is greater than the number of components by two."

Mathematically,

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

Where, P – Number of phases
F – Degrees of freedom
C – Number of component

8.2. PHASES

The physically distinct, homogenous and mechanically separable part of heterogeneous system in equilibrium is called a 'Phase'. For example, water at freezing temperature exists in three forms in equilibrium as follows

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

It is three phase system.

System can be classified into two categories based on the number of phases.

8.2.1. Homogeneous System

A system containing one phase only ($P = 1$) is called homogeneous system. Examples

1. Any gaseous mixture- air
2. Two miscible liquids- water + alcohol
3. An aqueous solution- sugar solution
4. Homogeneous solid solution- Mohr's salt
5. Any pure substance- O_2, benzene, ice

8.2.2. Heterogeneous System

A system containing more than one phases ($P > 1$) is called heterogeneous system. Examples

1. Two immiscible liquids- H_2O + oil ($P = 2$)
2. Saturated sugar solution ($P = 2$)
3. Mixture of solids- $MgCO_3 + MgO$ ($P = 2$). Here $MgCO_3$ (s) and MgO (s) but different physical and chemical properties and makes separate phase.
4. Freezing water mixture ($P = 3$)
5. $H_2O\,(s) \rightleftharpoons H_2O\,(l) \rightleftharpoons H_2O\,(g)$
6. $CaCO_3\,(s) \rightleftharpoons CaO\,(s) + CO_2\,(g)$ ($P = 3$)

8.3. COMPONENT

The number of components of a system in equilibrium is defined as the minimum number of independently variable constituents, which are required to express the composition of each phase. For example,

i. In the water system

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

It is one component system because the constituent of each phase can be expressed in term of water only.

ii. The sulphur system consists of four phases, rhombic, monoclinic, liquid and vapour, the chemical components of all phases is **S**. Hence it is one component system.

iii. In the dissociation of NH_4Cl in a closed vessel,

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

The proportions of NH_3 and HCl are equivalent and hence, the composition of both phases (solid and gaseous) can be expressed in terms of **NH_4Cl** alone. Hence, the number of component is one. However, if **NH_3 or HCl is in excess**, the system becomes a **two** component system.

i. A system of saturated solution of NaCl consists of solid salts, salt solution and water vapour. The chemical composition of all the three phases can be expressed in terms of NaCl and H_2O. Hence, it is a two component system.

ii. In the thermal decomposition of $CaCO_3$

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

The composition of any phase can be expressed in terms of at least any two of the independent variable constituents, $CaCO_3$, CaO and CO_2. Suppose $CaCO_3$ and CaO are chosen as the two components, then the composition of different phases is represented as follows:

$CaCO_3$ solid phase	$CaCO_3 = CaCO_3 + 0Ca$
CaO solid phase	$CaO = 0CaCO_3 + CaO$
CO_2 gaseous phase	$CO_2 = CaCO_3 - CaO$

Thus it is a two component system.

i. In the dissociation reaction,

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

The composition of each phase can be represented by the simplest components, $CuSO_4$ and H_2O. Hence, it is a two component system.

Number of components of a system *may alternatively be defined as the number of chemical constituents of the system minus the number of equations relating to those constituents in equilibrium state.* For example:
Dissociation of $KClO_3$ in a closed vessel: Following equilibrium exists:

$$2\ KClO_3(s) \rightleftharpoons 2\ KCl(s) + 3\ O_2(g)$$

∴ N0. of constituents = 3

Now $$Keq = \frac{[KCl]^2[O2]^3}{[KClO_3]^2} = [O2]^3$$

[Active mass of solid is taken constant]
No. of equations relating the concentration of constituents = 1.
Hence, number of components = 3 – 1 = 2 *i.e.,* it is a *two component* system.

8.4. DEGREES OF FREEDOM

The minimum number of variable factors such as Temperature (T), Pressure (P) and Concentration (C/V) that can be independently changed without altering the state of system in equilibrium is called degree of freedom. In other words, the minimum number of variable factors, such as Pressure, Temperature and Concentration, which should be fixed in order to define the system completely, is called Degrees of Freedom (F). Degree of system may be 0, 1, 2……

For Examples:

i. In case of water system,

$$\text{Ice (s)} \rightleftharpoons \text{Water (l)} \rightleftharpoons \text{Vapour (g)}$$

If all the three phases are present in equilibrium, then no conditions need to be specified, as the three phases can be in equilibrium only at particular temperature and pressure. The system is therefore, zero variant or non-variant or invariant or has no degree of freedom. If condition (e.g., temperature or pressure) is altered, three phases will not remain in equilibrium and one of the phases disappears.

ii. For the system consisting of water in contact with its vapour,

$$\text{Water (l)} \rightleftharpoons \text{Water vapour (g)}$$

We must state either the temperature or pressure to define it completely. Hence, degree of freedom is one or *system is univariant*.

iii. For a system consisting of water vapour phase only, we must state the values of both the temperature and pressure in order to describe the system completely. Hence, *the system is bivariant* or has two degree of freedom.

iv. For the system consisting of,

$$\text{NaCl (s)} \rightleftharpoons \text{NaCl-water (aq)} \rightleftharpoons \text{Water vapour (g)}$$

we must state either the temperature or pressure, because the saturation solubility is fixed at a particular temperature or pressure. Hence, *the system is univariant*.

8.5. SIGNIFICANCE OF TRIPLE POINT

Triple point is a characteristic property of pure substances. It is the condition of temperature and pressure at which the three phases exist in equilibrium. It marks the lowest temperature at which liquid can exist. At triple point, P=3, C=1 and therefore, F=1-3+2=0 (Zero).

8.6. PHASE DIAGRAM OF WATER SYSTEM

Under normal conditions the system water is a three phase and one component system. The three phases are liquid, ice and vapour. All these are represented by one chemical entity (H_2O), hence it is one component system.

On the basis of experimental data obtained for water system a plot of relationships between various phases namely solid ice, liquid water and water vapour under different conditions of temperature and pressure are shown in Fig. 8.1.

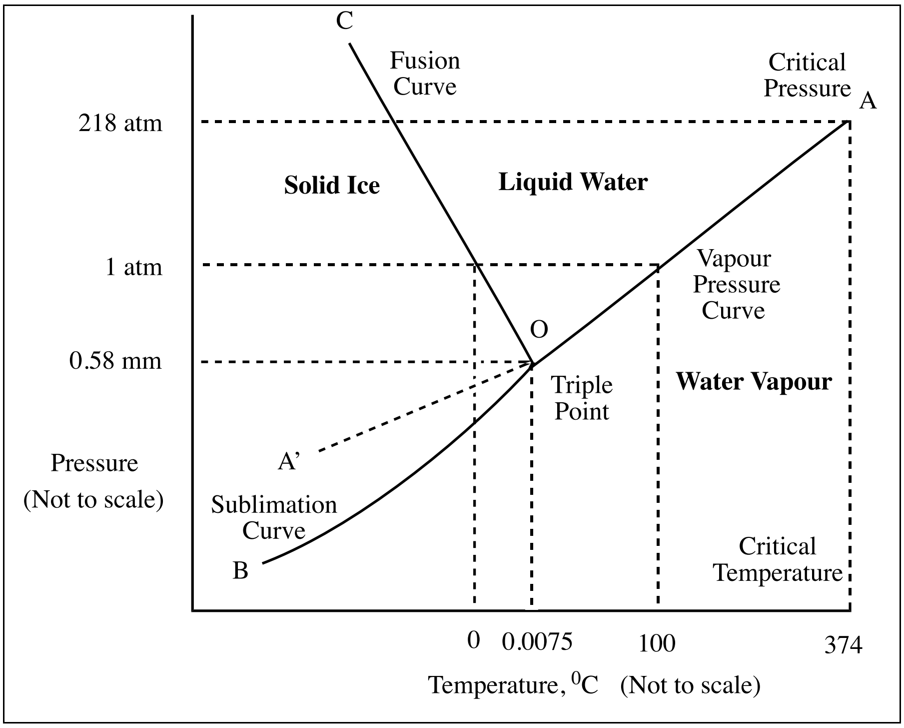

Fig. 8.1. Phase diagram of water system

The phase diagram consist of

1. Areas AOB, BOC and AOC
2. Curves OA, OB, OC & OA'
3. Triple point O

The salient features of phase diagram are given as below

S. No.	Areas /Points/ Curves	Name	Phases in equilibrium	Degree of freedom (Variance)
1	Curve OA	Vapour pressure curve	Liquid $\rightleftharpoons$ vapour	1 (univariant)
2	Curve OB	Sublimation curve	Solid $\rightleftharpoons$ vapour	1 (univariant)
3	Curve OC	Fusion curve	Liquid $\rightleftharpoons$ Solid	1 (univariant)
4	Area AOB	-------	Vapour	2 (bivariant)
5	Area BOC	-------	Solid	2 (bivariant)
6	Area AOC	---------	Liquid	2 (bivariant)
7	Point O	Triple Point	Liquid $\rightleftharpoons$ Solid $\rightleftharpoons$ vapour	0 (non variant)
8	Curve OA'	Metastable curve (Supercooled and unstable state)	Liquid $\rightleftharpoons$ vapour	1 (univariant)

8.7. PHASE DIAGRAM OF SULPHUR SYSTEM

It is one component, four phase system. The four different phases are Rhombic Sulphur (S_R), Monoclinic Sulphur (S_M), Liquid Sulphur (S_L), Vapour Sulphur (S_v). As all the four phases can be represented by only one chemical entity 'Sulphur' (S), it is one component system.
The phase diagram consists of

1. Six stable curves AB, BC, CD, BE, EG & CE
2. Three metastable curves FB, FC & FE
3. Four triple points B, C, E & F
4. Four areas ABCD, DCEG, BCE & ABEG

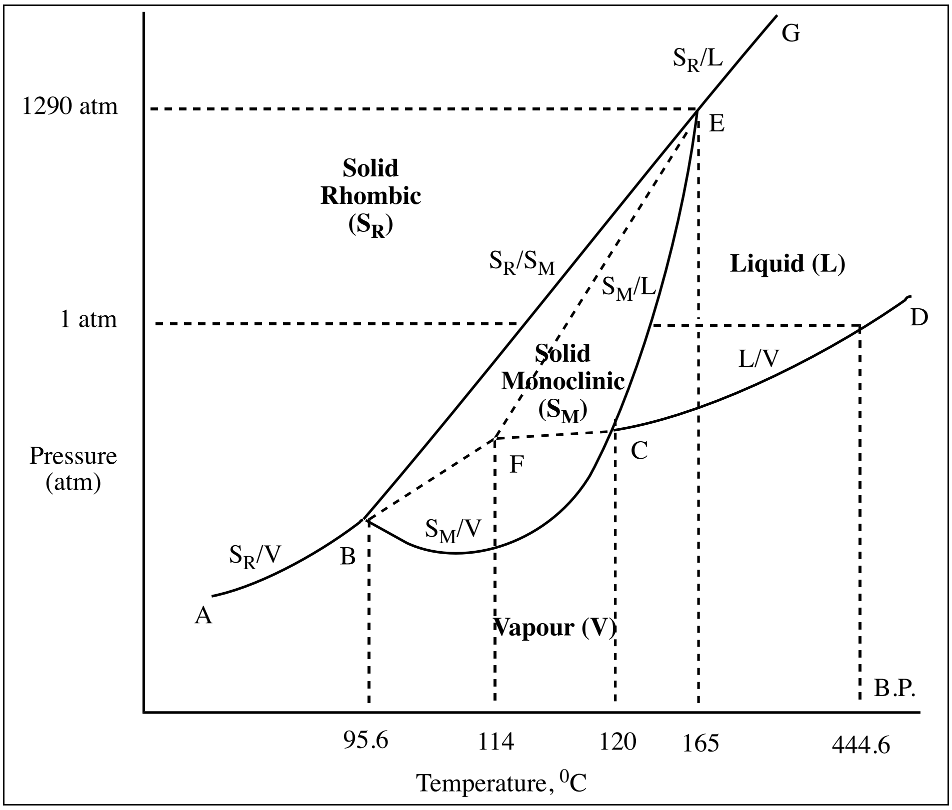

Fig. 8.1. Phase diagram of sulphur system

Summary for salient features of sulphur system is given as follows

S. No.	Areas/ Points/ Curves	Name	Phases in equilibrium	Degree of freedom (Variance)
1	Curve AB	Sublimation curve of S_R	$S_R \rightleftharpoons S_V$	1 (univariant)
2	Curve BC	Sublimation Curve of S_M	$S_M \rightleftharpoons S_V$	1 (univariant)
3	Curve CD	Vapour pressure curve of S_L	$S_L \rightleftharpoons S_V$	1 (univariant)
4	Curve BE	Transition curve	$S_R \rightleftharpoons S_M$	1 (univariant)
5	Curve CE	Fusion curve of S_M	$S_M \rightleftharpoons S_L$	1 (univariant)
6	Curve EG	Fusion curve of S_R	$S_R \rightleftharpoons S_L$	1 (univariant)
7	Point B	First triple point	$S_R \rightleftharpoons S_M \rightleftharpoons S_V$	0 (non variant)
8	Point C	Second triple point	$S_L \rightleftharpoons S_M \rightleftharpoons S_V$	0 (non variant)
9	Point E	Third triple point	$S_R \rightleftharpoons S_M \rightleftharpoons S_L$	0 (non variant)
10	Point F	Metastable triple point	$S_R \rightleftharpoons S_M \rightleftharpoons S_V$	0 (non variant)
11	Region ABCD	---------	S_V	2 (bivariant)
12	Region DCEG	--------	S_L	2 (bivariant)

13	Region BCE	---------	S_M	2 (bivariant)
14	Region ABEG	---------	S_R	2 (bivariant)
15	Curve FB	Meta vaporization curve of S_R	$S_R \rightleftharpoons S_V$	1 (univariant)
16	Curve FC	Meta vaporization curve of S_L	$S_L \rightleftharpoons S_V$	1 (univariant)
17	Curve FE	Meta fusion curve of S_R	$S_R \rightleftharpoons S_V$	1 (univariant)

Note: The degree of freedom cannot have a minus value, therefore out of four possible phases, only three are present at a time. It is not possible for a single component system to have four phases together at equilibrium.

8.8. ADVANTAGES OF PHASE RULE

1. Phase rule is applicable to both physical and chemical equilibrium.
2. It is applicable to macroscopic systems and hence no information is required to regarding molecular/ micro structure.
3. It is a convenient method to classifying equilibrium states in terms of phases, components and degree of freedom.
4. The behaviour of system can be predicted under different conditions.
5. According to phase rule, different systems behave similarly if they have same degree of freedom.
6. It predicts under given conditions whether a number of substances taken together would remain in equilibrium as such or would involve inter-conversion or elimination of some of them.

8.9. LIMITATIONS OF PHASE RULE

1. Phase rule is applicable only for those systems which are in equilibrium. It is not of much of use for those systems which attain the equilibrium state very slowly.
2. Only three degree of freedom viz. temperature, pressure and composition are allowed to influence the equilibrium systems.
3. Under the same conditions of temperature and pressure, all the phases of the system must be present.
4. It considers only the number of phases, rather than their amounts.

Examples 8.1. Explain why KCl – NaCl – H_2O should be regarded as a three component system whereas KCl – NaBr – H_2O should be regarded as four component system?

Solution:
Number of components of a system (C) = Number of chemical constituents of the system (N) - Number of equations relating to those constituents in equilibrium state (E)
For KCl – NaCl – H_2O system
N = 3 (KCl, NaCl, H_2O)
E = 0 (there is no number of equations relating to those constituents in equilibrium state)
C = 3 – 0 = 3
For KCl – NaBr – H_2O system
N = 5 (KCl, NaBr, NaCl, KBr, H_2O)
E = 1 ($KCl + NaBr \rightleftharpoons KBr + NaCl$)
C = N – E = 5 – 1 = 4

Examples 8.2. Is it possible to have a quadruple point on a phase diagram for a one component system?

Solution: From the phase rule, F = C – P + 2
For a quadruple point, P = 4
F = 1 – 4 + 2 = -1
That is, F has negative value, which is ridiculous. Thus the answer is **no**.

Examples 8.3. Write the number of component, phases and degrees of freedom of the following reaction.

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

Solution: Number of components, C = N – E = 1 – 0 = 1
P = 1
F = C – P + 2 = 1 – 1 + 2 = 2

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EXERCISE

1. What is Gibb's phase rule? Define the term; phase, component and degree of freedom. Draw the phase diagram of sulphur system and also give the significance of triple point.
2. With the help of phase rule diagram, show how it is possible to have super cooled water?
3. Define and explain the terms involved in phase rule. Draw a neat labelled diagram of water system and explain the areas, curves and points in this system.
4. Is it possible to have a quadruple point in a phase diagram for one component system? Determine the number of degree of freedom in each of the following systems:

i. Liquid water and water vapour in equilibrium.

ii. Liquid water and water vapour in equilibrium at 1 atmosphere pressure.

5. Define the terms: phases, component and degree of freedom, write the number of component, phases and degrees of freedom of the following reaction

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$