Phase Rule

- Phase rule is an important and versatile tool for study of heterogeneous equilibria
- It relates the conditions that must be specified to describe the state of system at equilibria
- The rule is stated in terms of number of component (C) , number of phases (P) and degree of freedom (F)

$$F + P = C + 2$$

Phase (P)

- A part of system which is homogenous throughout and separated from other part by definite boundary
- phase is physically distinct and mechanically separable part of system

A system made up of gaseous mixture forms a single phase

In case of liquid depending on their solubility one or more phases can be exist

Decomposition of $CaCO_3$ is example of three phase system

Components (C)

- The minimum number of constituents necessary to define composition of the system
- In case of water system phases that are present are ice, water , water vapor and all can define by single component that is H_2O hence water is one component system

Aqueous NaCl is two component system as in order to define it we need to consider two component H_2O and NaCl

Degree of Freedom (F)

- The smallest number of independent variables such pressure ,temperature and concentration that must be specified in order to completely describe the sta
- In order to describe the system the of the gaseous system only two variables are enough so as define the system as third one gets automatically known from equation
- These could be P and V or T and V or T and P

Examples of degree of Freedom

In the system of a gas PV=RT, if two quantities are fixed the third quantity will have definite value. i.e. the degree of freedom is two. i.e. the system is bi-variant.

A system of water in equilibrium with its vapours, temperature is the only quantity which has to be fixed, hence its degree of freedom is one. i.e. uni-variant. F = 1-2+2 =1

A mixture containing 40% CO_2, 60% N_2 at 25^0C and 760 mm pressure is perfectly defined. It has degree of freedom three. i.e. tri-variant.

One component system

- In water system the following systems exist in equilibrium depending on their pressure and temperature

- A) H_2O (s) $\longleftrightarrow$ H_2O (l)
- B) H_2O (l) $\longleftrightarrow$ H_2O (g)
- C) H_2O (g) $\longleftrightarrow$ H_2O (s)

Curve AOC,BOC and AOB in phase Diagram

- If P=1 , C=1 then applying phase rule
- F= 1 +2 -1 = 2 , (P and T)
- Phase rule predict that both the pressure and temperature has to be specified to define any single Phase (H_2O (s), H_2O (l), H_2O (g))
- The state of single phase (AOB/AOC/BOC)in equilibrium is bivariant (Pressure and Temperature)

Curve OA, OB and OC

- For Curve OA /OB/OC we have P=2 and C=1
- Applying phase rule

- F + P = C + 2

  F = C - P +2

  F =1-2+2

  F =1

Curve OA, OB and OC in Phase diagram

- Curve OA is refer as sublimation curve of ice .it gives the condition under which ice is in equilibrium with vapor

  P=2 C=1 hence F=1 (univariant)
- The curve OB represent the equilibrium between H_2O (l) and H_2O (g) and curve is known as vaporization curve of water .the curve OB is also univariant (F=1)
- The curve OC is univariant and is called as fusion curve of ice which tells us about temperature (or P) at which ice and water can coexist in equilibrium, Here also P=2 C =1 and therefore F=1

Phase diagram of water system

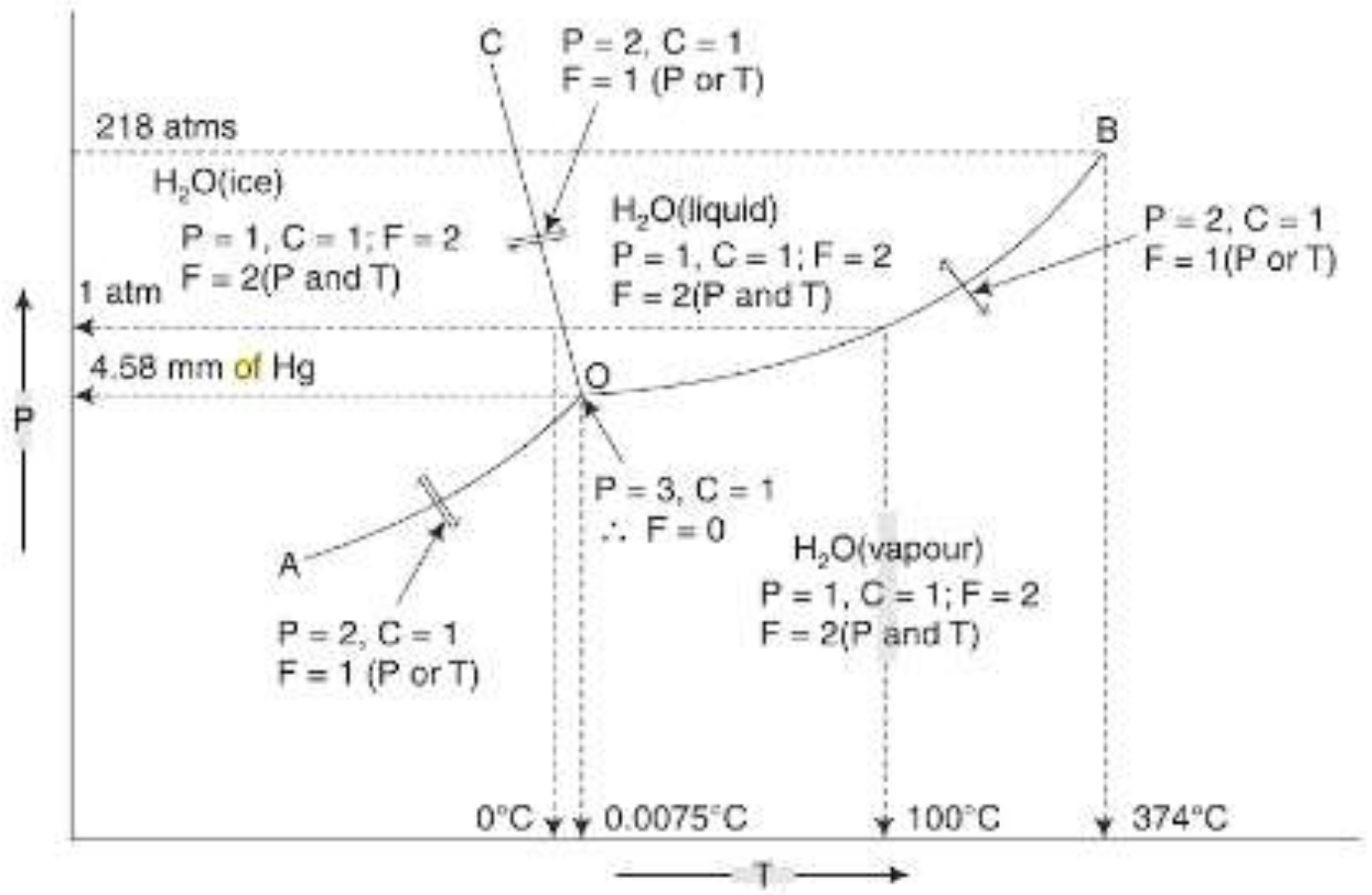

Diagram : Engineering chemistry O G Palanna

Advantages of phase rule

- applicable to both physical and chemical equilibrium
- requires no information regarding molecular/micro structure since it is applicable to macroscopic system
- predicts the behavior of a system under different sets of variables
- shows that different systems with same degree of freedom behave similarly
- does not take into account the nature and quantity of component

Limitations of Phase Rule

- fails for slow equilibrium attaining systems.
- applicable for single equilibrium system but gives no information regarding other possible equilibriums in the system.
- Much care is required in deciding the number of phases existing in equilibrium state since it requires no. of phases rather than their amounts.
- All phases must be present simultaneously under given sets of conditions like temperature and pressure.
- does not give information if solid-liquid phases are present in finely divided state, otherwise deviations occur.