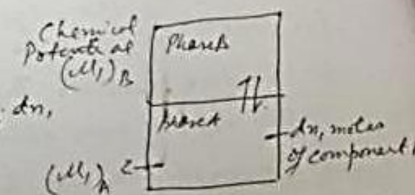
Study Material $\quad$ 21/8/2020

Criterion of phase equilibrium $\quad$ Page -1

Suppose a two component system exists in two phases A and B in equilibrium with each other at constant temperature and pressure. Let a small quantity dn_1 moles of component-1 is transferred from phase A to phase B. If $(\mu_1)_A$ and $(\mu_1)_B$ are the chemical potentials of phases A and B then



The change in free energy of phase A $= -(\mu_1)_A \cdot dn_1$

-ve sign indicates the decrease in free energy

and change in free of phase B $= (\mu_1)_B\, dn_1$

The net change in free energy dG

$$dG = -(\mu_1)_A dn_1 + (\mu_1)_B \cdot dn_1 \quad -①$$

As system is in equilibrium, the change in free energy for any small change in composition is equal to zero.

$$\text{i.e.} \quad dG = -(\mu_1)_A \cdot dn_1 + (\mu_1)_B \cdot dn_1 = 0$$

$$(\mu_1)_A \cdot dn_1 = (\mu_1)_B \cdot dn_1 \quad -②$$

$$(\mu_1)_A = (\mu_1)_B \,. \quad -③$$

In general if a system consists of a no. of phase A, B, C, D. then

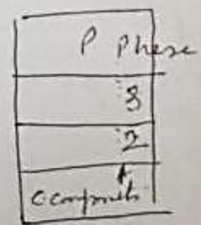
$$(\mu_1)_A = (\mu_1)_B = (\mu_1)_C = (\mu_1)_D \quad -④$$

It is concluded therefore that when a heterogeneous system is in equilibrium at constant temperature and pressure, the chemical potential of any given component has the same value in

Deduction of phase Rule.

Let us consider a heterogeneous system in equilibrium consisting of a number, C component distributed in P different phases. In a single phase the no. of independent concentration is C-1 because the composition of the remaining component can be obtained by taking the difference. For P phases this becomes P(C-1). Besides these concentration variables, the temperature and pressure of the system which are the same for all the phases are also variables.

It therefore follows That
Total no. of variables = $P(C-1)+2$



For thermodynamic point of view when a system is in equilibrium the chemical potential of a component must be the same in all the phases.

For component 1

$$\mu_{11} = \mu_{12} = \mu_{13} = \cdots \mu_{1P}$$

For component 2.

$$\mu_{21} = \mu_{22} = \mu_{23} = \cdots \mu_{2P}$$

For component 3

$$\mu_{31} = \mu_{32} = \mu_{23} = \cdots \mu_{3P}$$

For component c

$$\mu_{c1} = \mu_{c2} = \mu_{c3} = \cdots \mu_{cP}$$

the total no. of independent equations are C(P

According to mathematical definition of degr
of freedom. If there are m equation for
Solution of a problem and the no. of variab
whose value are to be determined are n,
then the no. of degree of freedom is m-n

20.8.20 Pages

Hence, the number of unknown variables

i.e. degree of freedom, F is.

$$F = P(C-1) + 2 - C(P-1)$$

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

$$\boxed{F = C - P + 2}$$ Gibbs phase rule.