- → Partial molar property is a **thermodynamic quantity** which describes the variation of an **extensive property** of a solution or mixture with changes in the molar composition of the mixture at constant temperature and pressure.
- → The concept of partial molar property was introduced by **G.N.Lewis** scientist.

Learning Objective

- → Know types of properties like an extensive and intensive.
- → Know different thermodynamic partial molar property such as Gibbs free energy, entropy etc. & variation with variable as temperature, pressure and composition.
- → Know Chemical potential & its importance.
- → Know effect of Chemical potential variable as temperature, pressure and composition.
- → Know Gibbs-Duhem equation.
- → Be able to use Chemical potential derive and confirm various law such as Raoult law, Henry law and Nernst Distribution law.

Introduction

Extensive Property: If the property depends on the amount of matter present, it is an extensive property. For eg. mass, volume, heat capacity etc.

Intensive property: If the property of a sample of matter does not depend on the amount of matter present, it is an intensive property. For eg. **density**, **temperature, molar heat capacity**.

Open system: A system exchange both **energy** and **matter** between system and surrounding.

Closed system: A system exchange **only energy** but **not matter** between system and surrounding.

Partial molar properties

- → Some thermodynamic properties like entropy, enthalpy, internal energy, etc., are known as extensive properties because their values change by varying mass of the system.

- → In many thermodynamic equations, the change of state was due to variation of temperature and pressure only.

- → Accordingly, it was assumed that in the case of a closed system there is no change in mass of the system, while in the case of an open system containing two or more components, the number of moles of various components can also be changed.

→ In such case the extensive property (X) must be function of number of moles of various components of the system, in addition to temperature and pressure of the system.

- **Expression of Partial molar quantity**

→ Suppose the temperature of the system be T and pressure be P and n_1, n_2 n_3 , ... n_J be the corresponding number of moles of the components 1, 2, 3, ….., j. Thus accordingly the property X must be the function of temperature, pressure and the number of moles of the various components of the system, i.e.,

$$X = f\,(T\ P\ n_1\ n_2\ n_3 \ldots\ n_j)$$

→ The symbol Xi , where X is an extensive property of a homogeneous mixture and the subscript i identifies a constituent species of the mixture, denotes the partial molar quantity of species i defined by

$$X_i \overset{\text{def}}{=} \left(\frac{\partial X}{\partial n_i}\right)_{T,p,n_{j\neq i}}$$

→ This is the rate at which property X changes with the amount of species i added to the mixture as the temperature, the pressure, and the amounts of all other species are kept constant. A partial molar quantity is an intensive state function. Its value depends on the temperature, pressure, and composition of the mixture.

→ Partial molar Gibbs energy: $(\frac{\partial G}{\partial ni})_{T,\ P,\ n1\ n2\ldots ni} = \bar{G}_i$

Physical Significance of Partial molar properties

→ The quantity **Xi** represents the actual value of X per mole of the **i**th component of the system. This value may be same or different from the actual molar value X*in the pure state.

→ These two values i.e. **partial molar value** and **actual molar value** are same in the case of ideal systems.

→ While in the case of **non-ideal systems**, these two values are different because of the interactions between the constituents, i.e., actual molar value get modified to partial molar value.

→ This partial molar value may not be same throughout the whole solution since the extent of interactions vary according to the amount of the constituents in the system.

→ Hence the partial molar value is dependent on the **composition** of the system.

→ Therefore, the partial molar quantities are meant for the individual components of the system, but their values are not only dependent on the nature of the particular component in consideration but also on the **nature** and **amounts** of the other components of the system.

Short Quesittion/blank	**Answers**
1. Who introduce partial molar property?	G.N.Lewis
2. Give any two example of intensive property?	Density and Temperature
3. Give any two example of an extensive property?	Mass and Volume
4. Partial molar property as__________	intensive property

Chemical potential

→ The partial molar free energy (Gi), is the most important partial molar quantity in the physical chemistry. It is known as Chemical Potential .

→ It is represented as μ_i

→ The equation of chemical potential as given below,

$$\left(\frac{\partial G}{\partial ni}\right)_{T,\, P,\, n1\ n2\ldots ni} = \bar{G}_i = \mu_i$$

→ Thus, chemical potential is the change in the free energy of the system which results on the addition of one mole of that particular substance to a very large system such that the overall composition of the system does not change, while keeping the temperature and pressure constant.

→ **<u>Temperature</u>** and **<u>Pressure</u>** main factor affect on Chemical potential.

Physical Significance of Chemical potential

→ Chemical potential is an **intensive properties**.

→ Chemical potential and Gibbs free energy are related to their relevant properties in same manner. i.e. G=H-TS and

→ The sum of 'product of number of mole of each constitute (n_i) and their respective chemical potential' represent the total value of Gibbs free energy of the system.

i.e. $\mathbf{G = \Sigma \mu_i n_i}$

Gibbs-Duhem equation

→ Gibbs-Duhem equation, thermodynamic relationship expressing changes in the chemical potential of a substance (or mixture of substances in a multicomponent system) in terms of changes in the temperature T and pressure P of the system.

→ Gibbs-Duhem equation can be written as $n_1 d\mu_1 + n_2 d\mu_2 + \ldots\ldots + n_i d\mu_i$

→ For binary mixture can be written as $n_1 d\mu_1 + n_2 d\mu_2$

→ General form of Gibbs-Duhem equation as $\mathbf{\Sigma n_i d\mu_i}$.

Application of Chemical potential

- Derivation of **Nernst distribution law** with the help of Chemical potential.

Nernst distribution law at equilibrium, the ratio of the concentrations of a third component(solute) in two immiscible liquid phases is a constant(K_D).

i.e. $K_D = \frac{CA}{CB}$

- Derivation of **Henry's law** with the help of Chemical potential.

Henry's law is a gas law that states that the amount of dissolved gas in a liquid is proportional to its partial pressure above the liquid.

i.e. $p = K_H . X$

- <u>Derivation of **Raoult's law** with the help of Chemical potential.</u>

Raoults law "the relative lowering of vapour pressure of vapour pressure is equal to the mole fraction of the solute".

i.e. $\frac{P0-p}{p0} = X_2$

Short Quesittion/blank	**Answers**
1. Chemical potential denoted as____	μ_i
2.Chemical potential as ___________ property	intensive
3. Write general form of Gibbs-Duhem equation.	Σnidμi
4. Give the name of law derive from chemical potential.	Raoult law,Henry law and Nernst distribution law.

Learning Outcome

- In thermodynamic system any extensive properties describe it intensive properties kept constant system variable such as temperature, pressure and mole composition.
- An intensity properties chemical potential related to Gibbs free energy, its useful thermodynamic properties.
- With help of chemical potential another law in chemistry like Raoult, Henry and Nernst distribution proved.
- With help of chemical potential derive important Gibbs-Duhem equation.