SEM –III (Hons)
CEMACOR05T: PHYSICAL CHEMISTRY-II

Applications of Thermodynamics – I

Partial Properties and Chemical Potential

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Class 3

- **Gibbs - Duhem Equation**

- **Pure ideal gas-its Chemical potential and other thermodynamic functions and their changes during a change of Thermodynamic parameters of mixing.**

Gibbs - Duhem Equation

Variation of Chemical Potential with Composition

We know for any reversible process within open systems or closed systems with composition change,

$$dG = -SdT + VdP + \sum \mu_i \, dn_i \qquad \text{.......................(a)}$$

On integrating equation (a) keeping T &P constant, we have

$$G = \sum n_i \mu_i \qquad \text{.......................(b)}$$

On differentiation equation (b) gives,

$$dG = \sum n_i d\mu_i + \sum \mu_i dn_i \qquad \text{.......................(c)}$$

Substituting equation (c) in equation (a), we have

$$\sum n_i d\mu_i = -SdT + VdP$$

$$= 0$$ **, at constant temperature and pressure** ....(d)

This relation is known as Gibbs- Duhem equation. It shows that if composition varies, the chemical potentials do not change independently but in a related way.

For example, for a system of two constituents equation (c) becomes

$$n_1 d\mu_1 + n_2 d\mu_2 = 0$$

Rearranging, we have $$d\mu_2 = -\left(\frac{n_1}{n_2}\right) d\mu_1$$

i.e. if a given variation in composition produces a change $d\mu_1$ in the chemical potential of the first component, the corresponding change in the chemical potential $d\mu_2$ of the second component is given by the above equation. This represents variation of chemical potential with composition when temperature and pressure are constant.

Similar relations can be derived for any of the partial quantities and in general we can write

$$\sum n_i d\overline{Y}_i = 0$$

Where $\overline{Y}_i$ is any partial molar quantity, e.g. Gibbs- Duhem equation involving partial molar volume is given by

$$\sum n_i d\overline{V}_i = 0$$

Pure ideal gas-its Chemical potential

Let us consider an ideal gas at pressure P and temperature T. So for *n* mole of the gas

$$V = n\frac{RT}{P}$$

$$\therefore \left(\frac{\partial V}{\partial n}\right)_{P,T} = \frac{RT}{P}$$

Again we know, $$\therefore \left(\frac{\partial \mu_i}{\partial P}\right)_{T.n_j} = \left\{\frac{\partial}{\partial n_i}(V)\right\}_{T,P,n_j} = \overline{V}_i$$

$$or, \left(\frac{\partial \mu}{\partial P}\right)_T = \left\{\frac{\partial}{\partial n}(V)\right\}_{T,P} = \overline{V} = \frac{RT}{P}$$ **, for a pure ideal gas**

So at constant temperature, $$d\mu = RT\frac{dP}{P} = RTd\ln P$$

Integrating the expression from pressure *1 atm* to *P atm;*

$$\int_{\mu_{(P=1atm)}}^{\mu_{(P\,atm)}} d\mu = RT\int_{1\,atm}^{P\,atm} d\ln P$$

or, $$\mu_{(P\,atm)} = \mu_{(P=1\,atm)} + RT\ln\frac{P\,atm}{1\,atm}$$

Here the value of μ at *P =1 atm* is regarded as the standard state to know the chemical potential of the ideal gas at any other pressure *P* at constant temperature.

Mixture of ideal gas - Chemical potential of '*i*' th constituent

Let us consider a mixture of ideal gas at total pressure *P* and temperature *T*. So for total volume *V*

$$V = (n_1 + n_2 + n_3 + \ldots)\frac{RT}{P}$$

$$\therefore \left(\frac{\partial V}{\partial n_i}\right)_{P,T,n_j} = \frac{RT}{P}$$

Again , $$\left(\frac{\partial \mu_i}{\partial P}\right)_{T.n_j} = \left\{\frac{\partial}{\partial n_i}(V)\right\}_{T,P,n_j} = \overline{V}_i = \frac{RT}{P}$$

So at constant temperature, $$d\mu_{i,T} = RT\frac{dP}{P} = RTd\ln P \quad \ldots\ldots\ldots\ldots\ldots\ldots\text{(e)}$$

Integrating the expression from total pressure *1 atm* to *P atm;*

$$\int_{\mu_{i(P=1atm)}}^{\mu_{i(P\,atm)}} d\mu_i = RT\int_{1\,atm}^{P\,atm} d\ln P$$

or, $$\mu_{i(P\,atm)} = \mu_{i(P=1\,atm)} + RT\ln\frac{P\,atm}{1\,atm}$$

Here $\mu_{i\ (P=1\ atm)}$ represents the chemical potential of the '*i*' th constituent in the mixture of given composition when total pressure of the mixture is 1 atm. This state is regarded as the standard state to know the chemical potential of the '*i*' th constituent at any other total pressure *P* at constant temperature.

If p_i be the partial pressure of the *'i' th* constituent in the gas mixture at total pressure *P*, then $p_i = x_i P$, where x_i =mole fraction of the *'i' th* constituent.

$$\therefore \ln p_i = \ln x_i + \ln P$$

Since for a given composition, x_i remains constant,

$$d \ln p_i = d \ln P$$

So from equation (e) we have,

$$d\mu_{i,T} = RTd \ln p_i$$

$$\int_{\mu_{i(p_i=1atm)}}^{\mu_{i(p_i\,atm)}} d\mu_i = RT \int_{1\,atm}^{p_i\,atm} d \ln p_i$$

$$\mu_{i(p_i\,atm)} = \mu_{i(p_i=1\,atm)} + RT \ln \frac{p_i\,atm}{1\,atm} \qquad \text{..........(f)}$$

In this expression chemical potential of the *'i' th* constituent is expressed in terms of its partial pressure instead of the total pressure of the mixture. However, at constant temperature and composition, $\mu_{i(P\,atm)} = \mu_{i(p_i\,atm)}$

Substituting, $p_i = x_i P$ in the equation (f) we have

$$\mu_{i(P\,atm)} = \mu_{i(p_i\,atm)} = \underline{\mu_{i(p_i=1\,atm)} + RT \ln \frac{P\,atm}{1\,atm}} + RT \ln x_i$$

Next Class

- Continuation of ideal gas mixture---Chemical potential and other thermodynamic functions and their changes during a change of Thermodynamic parameters of mixing.