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

Applications of Thermodynamics – I

Partial Properties and Chemical Potential

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Class 2

- **Variation of thermodynamic functions for systems with variable composition; Equations of states for these systems.**

- **Expression of Chemical Potential in terms of other thermodynamic state functions.**

- **Variation of Chemical potential (μ) with temperature and pressure.**

For a homogeneous open system or closed system (consisting of '*k*' different substances) with variable composition, internal energy (*U*) becomes a function of *S*, *V* and number of moles of all the constituents present, i.e.

$$U = f(S, V, n_1, n_2, n_3, \ldots\ldots n_k)$$

where '*n*' denotes the number of moles of the substance indicated by the suffix. The total differential of *U* will be

$$dU = \left(\frac{\partial U}{\partial S}\right)_{V, n_1, n_2 \ldots n_k} dS + \left(\frac{\partial U}{\partial V}\right)_{S, n_1, n_2 \ldots n_k} dV + \left(\frac{\partial U}{\partial n_1}\right)_{S, V, n_2 \ldots n_k} dn_1 + \ldots\ldots\ldots + \left(\frac{\partial U}{\partial n_k}\right)_{S, V, n_1 \ldots n_{k-1}} dn_k$$

$$= \left(\frac{\partial U}{\partial S}\right)_{V, n_i} dS + \left(\frac{\partial U}{\partial V}\right)_{S, n_i} dV + \sum \left(\frac{\partial U}{\partial n_i}\right)_{S, V, n_j} dn_i \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(3)$$

where the subscript n_i means that the number of moles of all the constituents in the system are held constant and the subscript n_j means that all the mole number are held constant except for the one involved in the derivative.

For any reversible process if $dn_i = 0$, i.e. when the system is closed with fixed composition the equation (3) will be reduced to

$$\boxed{dU = TdS - PdV}$$

Therefore in general for any reversible process within open systems or closed systems with composition change, we can write

$$dU = TdS - PdV + \sum\left(\frac{\partial U}{\partial n_i}\right)_{S,V,n_j} dn_i \qquad \text{........................(4)}$$

By definition, $G = H - TS$

Or, $$dG = dU + PdV + VdP - TdS - SdT$$

Or, $$dU = dG - PdV - VdP + TdS + SdT$$

Or, $$dU = \cancel{-SdT} \cancel{+VdP} + \sum\left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_j} dn_i - PdV \cancel{-VdP} + TdS \cancel{+SdT} \qquad \text{[Using equation (2)]}$$

Or, $$dU = TdS - PdV + \sum\left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_j} dn_i \qquad \text{........................(5)}$$

Comparing equation (4) & (5) we get, $$\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_j} = \left(\frac{\partial U}{\partial n_i}\right)_{S,V,n_j}$$

By following the same argument that led to the equation (5) we can obtain the following expressions for enthalpy (*H*) and Helmholtz free energy (*A*)

$$dH = TdS + VdP + \sum \mu_i dn_i \quad \text{......................(6)}$$

$$dA = -SdT - PdV + \sum \mu_i dn_i \quad \text{......................(7)}$$

Therefore chemical potential may then be defined in the following four different ways

$$\boxed{\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_j} = \left(\frac{\partial U}{\partial n_i}\right)_{S,V,n_j} = \left(\frac{\partial H}{\partial n_i}\right)_{S,P,n_j} = \left(\frac{\partial A}{\partial n_i}\right)_{T,V,n_j}}$$

It is apparent from equation (5) that $-\sum \mu_i dn_i$ represents the work (other than PV work) done by a closed system due only to its change of composition in a reversible process.

But chemical potential is often represented in terms of *G* because in that case the condition of constancy of Pressure (P) and Temperature (T) can be achieved easily.

Definition of Partial Molar Quantities

In general *partial molar quantity of a thermodynamic function (say Y)[w.r.t. constituent 'i'] is the change in Y when 1 mole of a constituent 'i' is added to a system of infinite mass at constant temperature and pressure so that the composition of the system practically does not change.*

Alternatively, it is the change in Y per mole of constituent 'i' at constant temperature and pressure when an infinitesimal quantity of this constituent is added to the system so that its composition practically does not change.

So far we became familiar with one such partial molar quantity

Chemical Potential, $$\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_j}$$

***** Other expressions of chemical potential are not partial molar quantities, as the constant natural independent variables are different from P & T.**

Mathematical form of partial molar quantities of some thermodynamic functions

Partial molar internal energy:

$$\overline{U_i} = \left(\frac{\partial U}{\partial n_i}\right)_{T,P,n_j}$$

Partial molar enthalpy:

$$\overline{H_i} = \left(\frac{\partial H}{\partial n_i}\right)_{T,P,n_j}$$

Partial molar work function:

$$\overline{A_i} = \left(\frac{\partial A}{\partial n_i}\right)_{T,P,n_j}$$

Partial molar entropy:

$$\overline{S_i} = \left(\frac{\partial S}{\partial n_i}\right)_{T,P,n_j}$$

Partial molar volume:

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

Variation of Chemical Potential with Temperature

We know,

$$\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_j}$$

$$\therefore \left(\frac{\partial \mu_i}{\partial T}\right)_{P.n_j} = \left\{\frac{\partial}{\partial T}\left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_j}\right\}_{P,n_j}$$

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

(Order of differentiation does not matter as *G* is a state function)

$$= \left\{\frac{\partial}{\partial n_i}(-S)\right\}_{T,P,n_j} = -\overline{S}_i$$

Variation of Chemical Potential with Pressure

We know,

$$\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_j}$$

$$\therefore \left(\frac{\partial \mu_i}{\partial P}\right)_{T.n_j} = \left\{\frac{\partial}{\partial P}\left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_j}\right\}_{T,n_j}$$

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

(Order of differentiation does not matter as *G* is a state function)

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

Next Class

- **Gibbs - Duhem Equation**

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