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

Applications of Thermodynamics – I

Partial Properties and Chemical Potential

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Class 1

So far we were dealing with closed systems (having fixed mass) with no composition change. For such systems you are already familiar with these fundamental equations..

$$\boxed{\begin{aligned} dU &= TdS - PdV \\ dH &= TdS + VdP \\ dA &= -SdT - PdV \\ dG &= -SdT + VdP \end{aligned}}$$

?

Are these expressions valid for homogeneous as well as heterogeneous closed systems having overall composition fixed ?

How does this change…………

if we allow the composition of a closed system to change? Like in a chemical reaction or a biochemical process?

or

for open systems where mass can flow in or out (consequently composition changes)?

Let us consider the effect on Gibbs free energy (*G*) when dealing with open systems or closed systems with composition change. For this purpose we are to treat G as extensive property depending not only on the intensive variables temperature (T) and pressure (P) but also on the number of moles of the constituents of the system. Then for a homogeneous system consisting of '*k*' different substances we can write in general

$$G = f(P, T, n_1, n_2, n_3, \ldots\ldots n_k)$$

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

$$dG = \left(\frac{\partial G}{\partial T}\right)_{P,n_1,n_2\ldots n_k} dT + \left(\frac{\partial G}{\partial P}\right)_{T,n_1,n_2\ldots n_k} dP + \left(\frac{\partial G}{\partial n_1}\right)_{P,T,n_2\ldots n_k} dn_1 + \ldots\ldots\ldots + \left(\frac{\partial G}{\partial n_k}\right)_{P,T,n_1\ldots n_{k-1}} dn_k$$

$$= \left(\frac{\partial G}{\partial T}\right)_{P,n_i} dT + \left(\frac{\partial G}{\partial P}\right)_{T,n_i} dP + \sum \left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_j} dn_i \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(1)$$

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 (1) will be reduced to

$$dG = -SdT + VdP$$

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

$$dG = -SdT + VdP + \sum \left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_j} dn_i \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots(2)$$

In this equation, the partial derivative $\left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_j}$ is known as partial molar free energy of constituent *'i'* and is called chemical potential of constituent *'i'*. This term 'Chemical Potential' was introduced by Gibbs to facilitate the discussion of open systems or closed systems with composition change and is denoted by

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

Therefore chemical potential of a constituent *'i'* in a phase is the change in free energy (G) of the phase per mole of that constituent, added in infinitesimal amount at constant temperature and pressure so that composition of the system practically does not change.

***Alternatively chemical potential of a constituent *'i'* in a phase is defined as the change in free energy (G) of the phase per mole of that constituent added to the infinite mass of the phase at constant temperature and pressure so that composition of the system practically does not change.

Note:

- Chemical potential, unlike Gibbs free energy (which is an extensive property), is an intensive quantity and for a particular constituent in a particular phase it depends only on the intensive properties pressure, temperature and composition of the phase concern.

- Chemical potential of each substance or constituent in any phase of a system at equilibrium must have the same value everywhere within the phase.

- Chemical potential of each substance or constituent have always the same value in all the phases of an equilibrated system.

- The relation (2) holds only in case of reversible process, but relation (1) holds for any process (reversible or irreversible).

Next Class

- **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.**