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

Applications of Thermodynamics – I

Partial Properties and Chemical Potential

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Class 4

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

Mixture of ideal gas - Chemical potential of ‘*i*’ th constituent

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

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

Since the *'i' th* constituent behaves ideally, its state in a mixture at partial pressure 1 atm and temperature T is same as the state of the pure substance at 1 atm and temperature T. So

$$\mu_{i(p_i=1\,atm)} = \mu^{*}_{i\,(P=1\,atm)} = \mu_i^0$$

where, $\mu_{i(p_i=1\,atm)} = chemical\ potential\ of\ 'i'\ th\ constituent\ at\ partial\ pressure\ 1\ atm\ in\ the\ mixture$

$\mu^{*}_{i\,(P=1\,atm)} = chemical\ potential\ of\ the\ pure\ 'i'\ th\ constituent\ at\ 1\ atm$

$and\ \mu_i^0 = \text{standard}\ chemical\ potential\ of\ the\ pure\ 'i'\ th\ constituent.$

Therefore equation (g) can be written as

$$\mu_{i(P\,atm)} = \underline{\mu^{*}_{i\,(P=1\,atm)} + RT\ln\frac{P\,atm}{1\,atm}} + RT\ln x_i$$

$$= \underline{\mu^{*}_{i(P\,atm)}} + RT\ln x_i \qquad \text{...........(h)}$$

where, $\mu^{*}_{i\,(P\,atm)} = chemical\ potential\ of\ the\ pure\ 'i'\ th\ constituent\ at\ P\ atm$

$and\ \mu_{i(P\,atm)} = chemical\ potential\ of\ the\ 'i'\ th\ constituent\ in\ the\ mixture\ at\ total\ pressure\ P\ atm$

x_i **being a fraction is <1 , so** $\mu_{i(P\,atm)} < \mu^{*}_{i(P\,atm)}$ **i.e. any gas has the spontaneous tendency to form a mixture by diffusion since it is associated with $\Delta\mu_i$ = - ve**

Therefore chemical potential of '*i*' th constituent having mole fraction x_i and partial pressure p_i in an ideal gas mixture at total pressure P and temperature T can be expressed in different ways,

If the standard state is considered as the state of the constituent in the mixture at a total pressure of 1 atm, then at total pressure P,

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

If the standard state is considered as the state of the constituent in the mixture at a partial pressure of 1 atm, then at partial pressure p_i,

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

If the standard state is considered as the state of the pure constituent at pressure P atm, same as that of the mixture (when mole fraction of the constituent is x_i)

$$\mu_{i(P\,atm)} = \mu^{*}_{i(P\,atm)} + RT\ln x_i$$

Change in Thermodynamic properties during mixing of ideal gases

Let us consider n_1 , n_2 , n_3 …….moles of different ideal gases at temperature T and pressure P. The gases are allowed to mix at the same temperature and pressure. After mixing the mole fractions of the constituent gases become respectively, x_1 , x_2 , x_3….. etc.

The total free energy before mixing is

$$G_{initial} = n_1\mu_1^* + n_2\mu_2^* + n_3\mu_3^* + ...$$

where $\mu_1^*, \mu_2^*, \mu_3^*........$ **respectively represent the chemical potentials of the pure constituents at pressure P and temperature T. If in the mixture the corresponding chemical potentials be** $\mu_1, \mu_2, \mu_3........$ **etc, then**

$$G_{final} = n_1\mu_1 + n_2\mu_2 + n_3\mu_3 + ...$$

$$Therefore, \Delta\mathrm{G}_{\mathrm{mixing}} = G_{final} - G_{initial} = n_1(\mu_1 - \mu_1^*) + n_2(\mu_2 - \mu_2^*) + n_3(\mu_3 - \mu_3^*) + ...$$

$$= n_1 RT\ln x_1 + n_2 RT\ln x_2 + n_3 RT\ln x_3 + ...$$

$$or, (\Delta\mathrm{G}_{\mathrm{mixing}} / mole) = \frac{n_1}{\sum n_i} RT\ln x_1 + \frac{n_2}{\sum n_i} RT\ln x_2 + \frac{n_3}{\sum n_i} RT\ln x_3 + ...$$

$$= x_1 RT\ln x_1 + \mathrm{x}_2 RT\ln x_2 + x_3 RT\ln x_3 + ...$$

$$= \mathrm{RT}\sum_{\mathrm{i}} x_i \ln x_i$$

$$\Delta S_{mixing}/mole = -\frac{\partial\left(\Delta G_{mix}/mole\right)}{\partial T} = -R\sum_i x_i \ln x_i$$

$$\begin{aligned}\Delta H_{mixing}/mole &= (\Delta G_{mixing}/mole) + (T\Delta S_{mixing}/mole)\\ &= \mathrm{RT}\sum_i \mathrm{x_i} \ln x_i - \mathrm{RT}\sum_i \mathrm{x_i} \ln x_i\\ &= 0\end{aligned}$$

$$\Delta V_{mixing}/mole = \frac{\partial}{\partial P}(\Delta G_{mixing}/mole) = 0$$

, Since no pressure term in ΔG_{mixing}

Thermodynamic criteria of ideal solution

(i) $\Delta H_{mixing} = 0$ **, when interaction (intermolecular forces) among same kind of molecules is equal to that among unlike molecules.**

(ii) $\Delta V_{mixing} = 0$ **, when the molecular sizes of all the constituents of the solution are same.**

Next Class

- **Fugacity and fugacity coefficient.**