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

Applications of Thermodynamics – I

Partial Properties and Chemical Potential

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Class 5

- **Fugacity and fugacity coefficient.**

- **Chemical potential of pure solid and pure liquids, Ideal solution –Definition**

Chemical potential of a pure ideal gas is represented by

$$\mu = \mu^0 + RT \ln \frac{P\,atm}{1\,atm}$$

where μ^0 represents standard chemical potential of the gas at temperature T.

Spontaneous change at constant temperature is associated with $d\mu < 0$. Similarly μ decreases with pressure decrease. Therefore gas spontaneously flows from higher chemical potential to lower chemical potential i.e. escaping tendency or fleetness of an ideal gas is determined by the pressure of it.

Again we know,

$$\left(\frac{\partial \mu}{\partial P}\right)_T = \overline{V}$$

$$\text{or, } d\mu_T = \overline{V} dP$$

$$Therefore,\ \mu - \mu_0 = \int_1^P \overline{V} dP$$

For real gas we have to express $\overline{V}$ in terms of P which depends upon the nature of the gas. Therefore to eliminate the dependence and to retain the same form of μ as in ideal gas Lewis expressed μ for real gas as

$$\mu = \mu^0 + RT\ln\frac{f\ atm}{1\,atm}$$

where actual pressure of the real gas, P *is* replaced by f, called fugacity. f has the same dimension as pressure and it expresses the effective pressure which takes care of the effects of all the forces responsible for deviation from ideal behaviour. In case of ideal gas $f = P$ but for real gas $f \neq P$. Hence for both real and ideal gas in general,

$$\mu = \mu^0 + RT\ln\frac{f\ atm}{1\,atm}$$

and $f = \phi P$, where ϕ is called fugacity coefficient.

So for real gas, we have,

$$\mu_{real} = \mu^0 + RT\ln\frac{P\ \text{atm}}{1\,\text{atm}} + RT\ln\phi$$

$$= \mu_{ideal} + RT\ln\phi$$

If whole of the deviations from ideal gas behaviour are to be ascribed to ϕ, μ^0 must have the characteristics of an ideal gas. Thus standard state of a real gas is some hypothetical state in which the gas behaves ideally at *f* =1 atm.

- **When the deviation from ideal behaviour is due to attractive force, effective pressure *f* becomes less than the actual pressure *P*, i.e., $\phi < 1$.**

Hence, $\mu_{real} < \mu_{ideal}$ i.e. in presence of attractive force molecules become more stable and has low affinity to escape.

- **When deviation is due to intermolecular repulsion $f > P$ or, $\phi > 1$.**

Under this condition $\mu_{real} > \mu_{ideal}$.

- ***When P tends to zero, any real gas behaves ideally and f tends to P so that ϕ tends to 1.***

Relation between fugacity and pressure

Let us consider the transformation of state of an ideal gas from very low pressure *P'* to moderately high pressure *P* and the state of a real gas from the corresponding fugacity *f'* to *f* at temperature T. Also let at actual pressure *P'* and P, the fugacity of the real gas be *f'* and *f* respectively.

$$\int_{P'}^{P} d\mu_{real} - \int_{P'}^{P} d\mu_{ideal} = \int_{P'}^{P} \overline{V_{real}}\, dP - \int_{P'}^{P} \overline{V_{ideal}}\, dP$$

$$or,\ RT\ln\frac{f}{f'} - RT\ln\frac{P}{P'} = \int_{P'}^{P} Z\overline{V_{ideal}}\, dP - \int_{P'}^{P} \overline{V_{ideal}}\, dP \qquad \text{since, } Z = \frac{\overline{V}_{real}}{\overline{V}_{ideal}}$$

$$or,\ RT\ln\frac{f\times P'}{f'\times P} = \int_{P'}^{P} (Z-1)\frac{RT}{P}\, dP$$

Since all gases approach ideality in the limit of zero pressure, we can write $\lim_{P'\to 0}\frac{f'}{P'} = 1$

$$or,\ RT\ln\frac{f}{P} = RT\int_{0}^{P}\frac{(Z-1)}{P}dP$$

$$or,\ \ln\frac{f}{P} = \int_{0}^{P}\frac{(Z-1)}{P}dP$$

$$\boxed{\ln\frac{f}{P}=\int_0^P\frac{(Z-1)}{P}dP}$$

- **Value of *f* depends upon the value of *Z*.**

In case of van der Waals gas at lower pressure where attractive molecular forces predominates, we can write

$$\left(P+\frac{a}{\overline{V}^2}\right)\left(\overline{V}\right)=RT$$

$$or,\ Z=\frac{P\overline{V}}{RT}=1-\frac{a}{\overline{V}RT}$$

$$i.e.\qquad Z<1$$

Hence, *f* less than *P* when attractive molecular forces predominate.
At high pressure, where excluded volume plays the dominating role, van der Waals equation takes the form

$$P\left(\overline{V}-b\right)=RT$$

$$or, Z=\frac{P\overline{V}}{RT}=1+b\frac{P}{RT}$$

$$i.e.\qquad \mathrm{Z}>1$$

Hence, *f* greater than *P* when repulsive intermolecular forces predominate.

Example problem:

Show that if equation of state for a gas is

$$P\left(\overline{V} - b\right) = RT$$

where b is a constant, the fugacity of the gas is given by

$$\ln\frac{f}{P} = \frac{bP}{RT}$$

Also show that if $\frac{bP}{RT}$ is small (at low pressure) this equation reduces to

$$\frac{f}{P} = \frac{P}{P_{ideal}}$$

where P_{ideal} is the pressure of the ideal gas with same molar volume as the real gas at pressure P.

Solution: $P(\overline{V} - b) = RT$

$$or, \qquad Z = \frac{P\overline{V}}{RT} = 1 + \frac{Pb}{RT}$$

Again we know

$$\ln\frac{f}{P} = \int_0^P \frac{(Z-1)}{P}\,dP$$

$$or, \qquad \ln\frac{f}{P} = \int_0^P \frac{b}{RT}\,dP = \frac{bP}{RT}$$

$$or, \frac{f}{P} = e^{bP/_{RT}} = 1 + \frac{bP}{RT} \qquad (\text{if } \frac{bP}{RT} << 1)$$

$$= \frac{RT + bP}{RT}$$

$$or, \qquad \frac{f}{P} = \frac{P\overline{V}}{RT} \qquad \text{since } RT + bP = P\overline{V}$$

$$= \frac{P}{P_{ideal}} \qquad \text{where } P_{ideal} = \frac{RT}{\overline{V}}$$

Chemical potential of pure solid and pure liquids, Ideal solution –Definition

For a pure substance chemical potential is expressed as $\mu = \dfrac{G}{n}$

Change in chemical potential for a finite process at constant temperature in case of a pure substance is given by

$$\int_{\mu_1}^{\mu_2} d\mu = \int_{P_1}^{P_2} \overline{V} dP$$

$$or,\ \mu_2 - \mu_1 \approx \overline{V}(P_2 - P_1)$$

for solids and liquids the molar volume does not vary significantly with pressure

For pure ideal gas change in chemical potential for a finite process at constant temperature is given by

$$\mu_2 - \mu_1 = RT \ln \frac{P_2}{P_1}$$

When a pure liquid A remains in equilibrium with its vapour at any given temperature, the condition of equilibrium is

$$\mu^*_{A(l)} = \mu^*_{A(vap)} = \mu^0_{A(vap)} + RT\ln\frac{P^*}{P^0} \qquad \text{..........(i)}$$

where P^* is the vapour pressure of pure liquid and $\mu^0_{A(vap)}$ is the standard chemical potential of pure A at vapour pressure $P^0 = 1$ atm

Let us consider an binary liquid mixture containing liquid A and B and having mole fraction of A as x_A . Let partial vapour pressure of A be p_A when total vapour pressure is P. At equilibrium chemical potential of A in the liquid mixture is given by

$$\mu_{A(l)} = \mu_{A(vap)} = \mu^0_{A(vap)} + RT\ln\frac{p_A}{p^0_A}$$

where $\mu^0_{A(vap)}$ is the standard chemical potential of pure A at $p^0_A = 1\,atm$

$$= \mu^*_{A(l)} + RT\ln\frac{p_A}{p^0_A} - RT\ln\frac{P^*}{P^0}$$

, substituting the value of $\mu^0_{A(vap)}$ from eqn. (i)

$$= \mu^*_{A(l)} + RT\ln\frac{p_A}{P^*}$$

when $p^o_A = P^0 = 1\,atm$

If $x_A = 1$, i.e. only pure liquid A is present, then $p_A = P^*$ and $\frac{p_A}{P^*} = 1$. Similarly when $x_A = 0$, $p_A = 0$ and $\frac{p_A}{P^*} = 0$.

If the solution behaves in the same manner in the entire composition range the solution is called ideal solution.

Therefore for an ideal solution at any composition $x_A = \frac{p_A}{P^*}$.

For an ideal solution at any composition $x_A = \dfrac{p_A}{P^*}$.

The partial vapour pressure of a component of a liquid solution is equal to the vapour pressure of that pure component multiplied by its mole fraction in the solution. This is called Rault's law.

Therefore chemical potential of a component A in an ideal solution can be expressed as

$$\boxed{\mu_{A(l)} = \mu^*_{A(l)} + RT \ln x_A}$$