

Fugacity and Activity

Concept of Fugacity:-

The great American chemist, G.N. Lewis introduced the concept of fugacity for representing the actual behaviour of real gases which is distinctly different from the behaviour of ideal gases.

We know $\left(\frac{\partial G}{\partial P}\right)_T = V$

This equation is applicable to all gases whether ideal or non-ideal.

If one mole of a gas is under consideration, then V refers to molar volume. For an ideal gas, the above equation may be written as

for n moles as $(dG)_T = nRT \frac{dP}{P} = nRT d(\ln P)$
 --- ①

Integration eqⁿ ①

$$G = G^* + nRT \ln P \text{ --- ②}$$

where, G^* the integration constant, is the free energy of n moles of the ideal gas at tempⁿ T , when the pressure P unity.

Integration of eqⁿ ① between pressure P_1 and P_2 , at const T ,

$$\Delta G = \int_{P_1}^{P_2} nR \frac{dP}{P} = nRT \ln \frac{P_2}{P_1}$$

The corresponding equation for 1 mole of the gas,

$$\Delta G = RT \ln \frac{P_2}{P_1}$$

In order to make these simple equation applicable to real gases, Lewis introduced a new function f , called fugacity function. It takes the place of P in eqⁿ ①, real gases

may be expressed as

$$(dG)_T = nRT d(\ln f) \quad - (3)$$

Equⁿ (2) may be represented as

$$G = G^* + nRT \ln f \quad - (4)$$

where G^* is the free energy of n moles of a real gas when its fugacity happens to be 1.

Thus, fugacity is a sort of 'fictitious pressure' which is used in order to retain for real gases simple forms of equation which are applicable to ideal gases only.

Equⁿ (4) evidently gives free energy of a real gases at temperature T and pressure P at which its fugacity can be taken as f .

Equⁿ (3), on integration between fugacities f_1 and f_2 at constant temperature T , yields.

$$\Delta G = nRT \ln \left(\frac{f_2}{f_1} \right) \quad - (5)$$

The corresponding equation for 1 mole gas

$$\Delta M = RT \ln \left(\frac{f_2}{f_1} \right) \quad - (6)$$

5 and 6 are applicable to real gases.

Fugacity at low pressure:

The ratio f/P , where P is the actual pressure, approaches to unity when P approaches zero, since in that case a real gas approximates to ideal behaviour. The fugacity function defined as,

$$\lim_{P \rightarrow 0} \frac{f}{P} = 1.$$

Evidently at low pressure, fugacity is equal to pressure. The two terms differ ~~main~~ materially only at high pressure.

The fugacity coefficient:-

$\frac{f}{P} = \phi$ ϕ is known as the fugacity coefficient.

$$\lim_{P \rightarrow 0} \frac{f}{P} = \lim_{P \rightarrow 0} \phi = 1.$$

The fugacity is expressed in the same unit of pressure and thus the fugacity coefficient is a pure number.

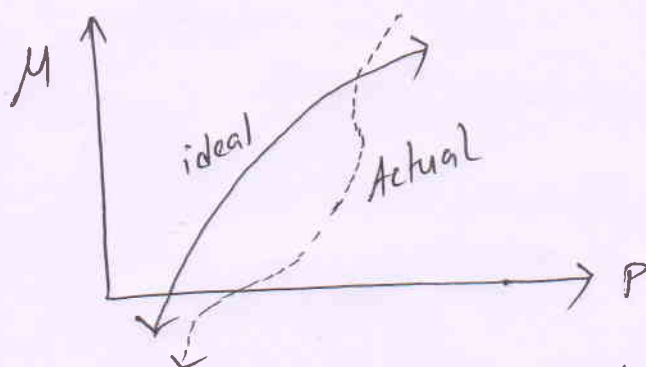


Fig. The actual behavior of the chemical potential versus the real pressure of a gas is shown.

Q. For a van der Waals gas, express the fugacity as a function of V , T , R and the van der Waals constant.

Solⁿ $\Rightarrow$ For one mole of gas $RT d \ln f = V dP$ — (1)

Integrating

$$RT \int d \ln f = \int V dP \quad \text{--- (2)}$$

Integration by parts

$$\int V dP = PV - \int P dV \quad \text{--- (3)}$$

for one mole gas $P = \frac{RT}{V-b} - \frac{a}{V^2}$ — (4)



From eqnⁿ (2), (3), and 4

$$RT \ln f = PV - \int \left[\frac{RT}{v-b} - \frac{a}{v^2} \right] dv$$
$$= RT - RT \ln(v-b) - \frac{a}{v} + C \quad \text{--- (5)}$$

To evaluate C , we recall that $f \rightarrow P$ as $P \rightarrow 0$. Also $P \rightarrow 0$ at constant T , $v \rightarrow \infty$, so that $(v-b) \rightarrow v$, $\frac{1}{v} \rightarrow 0$.

$$\text{Hence, } RT \ln P = RT - RT \ln v + C$$
$$= RT - RT \ln \left(\frac{RT}{P} \right) + C$$
$$= RT - RT \ln RT + RT \ln P + C$$

$$C = RT \ln RT - RT \quad \text{--- (6)}$$

Substituting for C in eqnⁿ (5) we get

$$RT \ln f = PV - RT \ln(v-b) - \frac{a}{v} + RT \ln RT - RT$$

Rearranging the van der Waals eqnⁿ after expansion neglecting the term $\frac{ab}{v^2}$ and later the term $\frac{a}{v^2}$ as

$$PV - RT = \frac{RTb}{v-b} - \frac{a}{v}$$

$$\text{Hence } \ln f = \frac{b}{(v-b)} + \ln \frac{RT}{v-b} - \frac{2a}{RTv}$$

which is required expression for fugacity.

Fugacity of a Gas in Gaseous Mixture

For one mole of any gaseous component i of a gaseous mixture

$$d\mu_i = RT d(\ln f_i)$$

$$\mu_i = \mu_i^* + RT \ln f_i$$

μ_i^* is the chemical potential of the gaseous component i and its unit fugacity.

Physical Significance of fugacity:-

In order to understand the physical significance of the term fugacity, consider a system consisting of liquid water in contact with its vapour. Water molecules in the liquid phase will have a tendency to escape into the vapour phase by evaporation while those in the vapour phase will have a tendency to escape into the liquid phase by condensation. At equilibrium, the two escaping tendencies will be equal. It is now accepted that each substance in a given state has a tendency to escape from that state. This escaping tendency was termed by Lewis as fugacity.

Activity

Defⁿ:- The variation of chemical potential with pressure of an ideal gas is given by

$$\mu_i = \mu_i^0 + RT \ln \left(\frac{P_i}{P^0} \right)$$

where μ_i^0 is the standard chemical potential of the i th gas at the standard state pressure (P^0) of 1 bar. To have the same type of dependence of any substance i.e. gas, liquid solid, G.N. Lewis modified this equation as,

$$\mu_i = \mu_i^0 + RT \ln a_i$$

where a_i , a dimensionless quantity is known as activity of the i th substance.

The activity of a substance existing in different conditions may be defined as follows -

1) For a substance in the gas phase:-

$$\text{For ideal gas } a_i = \frac{P_i}{P^0}$$

$$\text{real gas } a_i = \frac{f_i}{f^0} \quad f = \text{fugacity}$$



2.) For Components in ideal liquid solution

Since each component of liquid solution is in equilibrium with its vapour, we have

$$\mu_i(l) = \mu_i(g)$$

$$\mu_i(l) = \mu_i(l) + RT \ln a_i$$

$$\mu_i(g) = \mu_i(g) + RT \ln \left(\frac{P_i}{P^0} \right)$$

$$\mu_i^0(l) + RT \ln a_i = \mu_i^0(g) + RT \ln \left(\frac{P_i}{P^0} \right)$$

For pure liquid $a_i = 1$, $P_i = P_i^*$

$$\mu_i^0(l) = \mu_i^0(g) + RT \ln \left(\frac{P_i^*}{P^0} \right)$$

Substituting this in previous expression, we get

$$\mu_i^0(g) + RT \ln \left(\frac{P_i^*}{P^0} \right) + RT \ln a_i = \mu_i^0(g) + RT \ln \left(\frac{P_i}{P^0} \right)$$

$$\text{or } RT \ln a_i = RT \ln \left(\frac{P_i}{P_i^*} \right)$$

$$a_i = \frac{P_i}{P_i^*}$$

Since the liquid solution behaves ideally

$P_i = x_i P_i^*$ according to Raoult's law

$$a_i = x_i$$

3.) For components in non-ideal liquid solution

The components of a non-ideal solution exhibit deviations from Raoult's-law.

For non-ideality, the activity is defined

$$\text{as } a_i = x_i \gamma_i$$

where, γ_i known as activity coefficient is the measure of deviation from Raoult's law

$$\gamma_i \rightarrow 1 \text{ as } x_i \rightarrow 1.$$

The components exhibiting positive deviations from Raoult's law, γ_i is greater than unity and those exhibiting negative deviations, γ_i is less than unity.

$$a_i = \frac{P_i}{P_i^*}$$

$$x_i \gamma_i = \frac{P_i}{P_i^*}$$

$$\gamma_i = \frac{P_i}{x_i P_i^*}$$

4. > For electrolyte in solution

The chemical potential of a completely dissociated electrolyte is given by

$$\mu(M_x X_y) = x \mu(M^{y+}) + y \mu(X^{x-})$$

$$\text{As } \mu = \mu^0 + RT \ln a$$

$$\begin{aligned} \mu(M_x X_y) &= x (\mu^0(M^{y+}) + RT \ln a_{M^{y+}}) + y [\mu^0(X^{x-}) + RT \ln a_{X^{x-}}] \\ &= x \mu^0(M^{y+}) + y \mu^0(X^{x-}) + RT \ln \left\{ (a_{M^{y+}})^x (a_{X^{x-}})^y \right\} \end{aligned}$$

$$= \mu^0(M_x X_y) + RT \ln a_{M_x X_y}$$

$$a_{M_x X_y} = (a_{M^{y+}})^x (a_{X^{x-}})^y$$

Simply, it can be written as

$$a = (a_+)^x (a_-)^y$$

Activity in terms of molality

For electrolytic solutions molality is used to express its concentration. The expressions relating activities of ions the corresponding molalities are

$$a_+ = \left(\frac{m_+}{m^0} \right) \gamma_+ \text{ and } a_- = \left(\frac{m_-}{m^0} \right) \gamma_-$$

where m^0 is the standard state molality and is equal to 1 mole/kg.

Taken m_0 to be 1, we can write.

$$a_+ = m_+ \nu_+ \quad a_- = m_- \nu_-$$

Expressions of Mean Activity:

The activity of an ion in terms of mean activity of the electrolyte. The expression is

$$(a_{\pm})^{\nu} = (a_+)^x (a_-)^y$$

where $\nu = x+y$ is the total number of ions produced due to the dissociation of 1 molecule of electrolyte.

$$M_{x^y} \quad a = (a_{\pm})^{\nu}$$

$$\begin{aligned} a_+ &= m_+ \nu_+ & a_- &= m_- \nu_- \\ (a_{\pm})^{\nu} &= (m_+ \nu_+)^x (m_- \nu_-)^y \\ &= (m_+^x m_-^y) (\nu_+^x \nu_-^y) \\ &= m_{\pm}^{\nu} \nu_{\pm}^{\nu} = (m_{\pm} \nu_{\pm})^{\nu} \end{aligned}$$

$$a_{\pm} = m_{\pm} \nu_{\pm}$$

Mean molality $m_{\pm}$ of the electrolyte M_{x^y} in terms of its molality can be written as

$$\begin{aligned} m_{\pm}^{x+y} &= m_+^x m_-^y = (xm)^x (ym)^y = x^x y^y m^{x+y} \\ m_{\pm} &= (x^x y^y)^{\frac{1}{x+y}} \cdot m \end{aligned}$$

Thus,

$$a_{MX} = (a_{\pm})^2 = m_{\pm}^2 \nu_{\pm}^2 = (m_+ m_-) \nu_{\pm}^2 = m^2 \nu_{\pm}^2$$

$$a_{MX_2} = (a_{\pm})^3 = m_{\pm}^3 \nu_{\pm}^3 = (m_+ m_-^2) \nu_{\pm}^3 = m (2m)^2 \cdot \nu_{\pm}^3 = 4m^3 \nu_{\pm}^3$$

$$a_{MX_3} = a_{\pm}^4 = m_{\pm}^4 \nu_{\pm}^4 = (m) (3m)^3 \cdot \nu_{\pm}^4 = 27m^4 \nu_{\pm}^4$$

$$\text{e.g. } a_{MX_2} = a_{CdCl_2} = 4m^3 (\nu_{\pm})^3 \quad \text{e.g. } a_{MX} = a_{NaCl} = m^2 \nu_{\pm}^2$$