Chemical Potential of Real Gases and Fugacity

The difference betⁿ real gas and ideal gas is molecular interactions ∴ For a real gas $V_m \neq \frac{RT}{P}$ and therefore $d\mu \neq RT d\ln P$. Hence a new variable which has dimensions and different general properties of pressure is introduced in the chemical pot. equation. This new variable is called fugacity derived from latin fugere ie to "flee" or "escaping tendency". It is denoted by f. this is a corrected pressure which applies to real gases. All the effects arising due interactions (molecular) are contained in "f".

The chemical potential of a pure real gas is

$\mu = \mu^0 + RT\ln(f/atm)$ where μ^0 is standard chemical potential at unit fugacity

At very low Pressure $\lim_{P \to 0} \left(\frac{f}{P}\right) = 1$.

The ratio $\left(\frac{f}{P}\right) = \gamma$ is called fugacity coefficient. For an ideal gas $f = P$ and $\gamma = 1$. But for real gases $\left(\frac{f}{P}\right) \neq 1$ ie. fugacity is not the actual Pressure.

eg $f_{25°C,\,1000\,atm\,(N_2\,gas)} = 1839\,atm$ $f_{25°C,\,1000\,atm,\,ideal\,gas} = 498\,atm$

For real gas $\mu = \mu^0 + RT\ln\left(\frac{\gamma P}{atm}\right) = \mu^0 + RT\ln\frac{P}{atm} + RT\ln\gamma$

For ideal gas $\mu = \mu^0 + RT\ln\left(\frac{P}{atm}\right)$ ie $RT\ln\gamma$ is above eqⁿ accounts for non idality

It there is no interaction in gas (idalgas) $RT\ln\gamma = 0$. since RT cannot be equal to zero therefore [$\ln\gamma = 0$ or $\gamma = 1$.] for a gas ~~when~~ having no interactions This for ideal gas

for real gas ~~$f \neq 0$~~ $\gamma \neq 1$

Calculation of fugacity of a Gas

$d\mu = V_m dP$ for a real & ideal gas

Let there is a change in state of the system from intial P' to a final Pressure P. For real gas f' be the fugacity of the real gas at Pressure P' and f the " " " " at Pressure P.

$$\int_{\mu'}^{\mu} d\mu_{(ideal)} = \int_{P'}^{P} V_{m(ideal)} dP$$

$$\mu_{(ideal)} - \mu'_{(ideal)} = \int_{P'}^{P} V_{m(ideal)} dP \quad — ①$$

$$\mu_{(real)} - \mu'_{(real)} = \int_{P'}^{P} V_{m(real)} \times dP \quad — ②$$

substitue the value of 'μ' for idal and realgas

$\therefore$ eq ① becomes

$$\mu_{ideal} - \mu'_{(idal)} = RT \ln\left(\frac{P}{P'}\right) = \int_{P'}^{P} V_{m(ideal)} dP \quad — ③$$

eq ② become

$$\mu_{real} - \mu'_{(real)} = RT \ln\left(\frac{f}{atm}\right) - RT \ln\left(\frac{f'}{atm}\right) = \int_{P'}^{P} V_{m(real)} dP$$

$$\mu_{real} - \mu'_{(real)} = RT \ln\left(\frac{f}{f'}\right) = \int_{P'}^{P} V_{m(real)} dP \quad — ④$$

subtract eq. (4) from eq ③

$$RT \ln\left(\frac{f}{f'}\right) - RT \ln\left(\frac{P}{P'}\right) = \int_{P'}^{P} [V_{m(real)} - V_{m(ideal)}] dP$$

$$RT \ln\left(\frac{f}{P}\right) - RT \ln\left(\frac{f'}{P'}\right) = \quad " \quad — ⑤$$

$\alpha = V_{m(idal)} - V_{m(Real)}$

eq (5) becomes

$$RT \ln\left(\frac{f}{P}\right) - RT \ln\left(\frac{f'}{P'}\right) = \int_{P'}^{P} (-\alpha) dP = \int_{0}^{P} \alpha dP - \int_{0}^{P'} \alpha dP$$

$$\therefore RT\ln\left(\frac{f}{P}\right) - RT\ln\left(\frac{f'}{P'}\right) = -\int_0^P \alpha\, dP + \int_0^{P'} \alpha\, dP \quad ⑥$$

If P' is very low then gas behaves ideally then $V_{m(ideal)} \simeq V_{m(real)}$ & $\lim_{P' \to 0}\left(\frac{f'}{P'}\right) = 1$

$\therefore$ 2nd term on L.H.S. & R.H.S of eq ⑥ becomes zero

$$RT\ln\left(\frac{f}{P}\right) = -\int_0^P \alpha\, dP$$

$$\ln\left(\frac{f}{P}\right) = \frac{-1}{RT}\int_0^P \alpha\, dP$$

Taking antilog on both sides

$$\frac{f}{P} = \exp\left(-\frac{1}{RT}\int_0^P \alpha\, dP\right)$$

$$f = P\exp\left(-\frac{1}{RT}\int_0^P \alpha\, dP\right)$$

$$= P\exp\left[\frac{1}{RT}\int_0^P (V_{m(Real)} - V_{m(ideal)}\right] dP \quad ⑦$$

$\because \alpha = V_{m(ideal)} - V_{m(Real)}$

'f' can be calculated at a given P if real / ideal volume of gas at given P & T is known. There are various ways to calculate 'f' if we know to evaluate the integrals.

a) If α is considered to constt & independent of Pressure 'P' eq (7) becomes of Pressure 'P', eq (7) becomes

$$\int_0^P \alpha\, dP = \alpha P$$ eq (7) becomes

$$f = P\exp\left(-\frac{\alpha P}{RT}\right) = P\left[1-\frac{\alpha P}{RT}+\frac{1}{2!}\left(\frac{\alpha P}{RT}\right)^2+\cdots\right]$$

Neglecting higher powers of $\frac{\alpha P}{RT}$.

$$f = P\left[1-\frac{\alpha P}{RT}\right] = \frac{P}{RT}\left[RT-\alpha P\right] \quad — ⑧$$

$RT = PV_{m(ideal)}$, $\alpha = V_{m(ideal)} - V_{m(Real)}$

$$RT-\alpha P = PV_{m(ideal)} - PV_{m(ideal)} + PV_{m(real)}$$

∴ eq ⑧ becomes $f = P\left[\frac{PV_{m(Real)}}{RT}\right] = \frac{PV_{m(Real)}}{PV_{m(ideal)}}$

$$\frac{f}{P} = \frac{(PV_m)_{Real}}{(PV_m)_{ideal}}$$

If molar volumes of ideal & real gases are equal but Pressures are not equal then

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

$$f \times P_{ideal} = P^2$$

$$P = \sqrt{f \cdot P_{ideal}}$$

The true pressure is the geometric mean of the fugacity & ideal Pressure

Fugacity can be calculated from observed P & ideal Pressure

(b) Fugacity from compressibility factor $Z = \left(\frac{PV_m}{RT}\right)$

For ideal gas $Z = 1$, $\rightarrow V_{m(ideal)} = \frac{RT}{P}$

For real gas $V_m = Z\frac{RT}{P}$

eq (7) becomes

$$f = P\left[\exp\frac{1}{RT}\int_0^P\left(\frac{ZRT}{P} - \frac{RT}{P}\right)\right]dP$$

$$f = P\int_0^P \exp\left(\frac{Z-1}{P}\right)dP \quad — ⑨$$

Z values for different gases are available in the charts & hence integral can be calculated & thus f.

(c) From equation of state for gases. From vander waal gas, or virial eq.

For nonideal gas $\mu = \mu^0 + RT\ln\left(\frac{f}{atm}\right)$

At const T, $d\mu = RT\,d\ln\left(\frac{f}{atm}\right)$ $\qquad \because d\mu = V_m\,dP$

$\therefore V_m\,dP = RT\,d\ln\left(\frac{f}{atm}\right)$ for real gas

$$V_{m(ideal)}\,dP = RT\,d\ln\left(\frac{P}{atm}\right)$$

$$\therefore \left[V_{m(real)} - V_{m(ideal)}\right]dP = RT\,d\ln\left(\frac{f}{P}\right) \quad — ⑩$$

Let us consider vander waal gas eq, considering $a = 0$

$$\left(P + \frac{a\cancel{V}}{V_m^2}\right)(V_m - b) = RT.$$

$$P(V_m - b) = RT$$

$\left(V_m = \frac{RT}{P} + b\right)$ where b is excluded volume

Sub. this value in eq 10)

$$\left(\frac{RT}{P} + b - \frac{RT}{P}\right) dP = RT\, d\ln\frac{f}{P}$$

$$\int_0^P b\, dP = \int_{\left(\frac{f}{P}\right)=1}^{\left(\frac{f}{P}\right)=\frac{f}{P}} RT\, d\ln\frac{f}{P}$$

$$\because \lim_{P\to 0} \frac{f}{P} = 1$$

$$bP = RT\ln\left(\frac{f}{P}\right)$$

$$\ln\frac{f}{P} = \frac{b\cdot P}{RT}$$

$$\left(\frac{f}{P}\right) = \exp\left(\frac{bP}{RT}\right) \text{ — ⑪}$$

d) when intermolecular forces are not absent ie $a \neq 0$

$$\left(P + \frac{a}{V_m^2}\right)(V_m - b) = RT$$

$$P = \frac{RT}{V_m - b} - \frac{a}{V_m^2}$$ Multiply both sides by V_m

$$PV_m = \frac{RTV_m}{V_m - b} - \frac{a}{V_m}$$

$$= RT\left(1 - \frac{b}{V_m}\right)^{-1} - \frac{a}{V_m}$$

$$= RT\left[1 + \frac{b}{V_m} + \frac{1}{2}\left(\frac{b}{V_m}\right)^2 + \cdots\right] - \frac{a}{V_m}$$

= higher Powers Neglected

$$PV_m = RT\left[1 + \left(b - \frac{a}{RT}\right)\frac{1}{V_m}\right]$$

$$V_m = \frac{RT}{P}\left[1 + \left(b - \frac{a}{RT}\right)\frac{1}{V_m}\right]$$

$$= \frac{RT}{P} + \left(b - \frac{a}{RT}\right)\frac{RT}{PV_m}$$

$$V_m = \frac{RT}{P} + (bRT - a)\frac{1}{PV_m}$$

$PV_m \approx RT$

$$= \frac{RT}{P} + (bRT - a)\frac{1}{RT}$$

$$V_m = \frac{RT}{P} + \left(b - \frac{a}{RT}\right)$$

eq (7)

$$V_{m(real)} - V_{m(ideal)} = \frac{RT}{P} + \left(b - \frac{a}{RT}\right) - \frac{RT}{P}$$

$$= \left(b - \frac{a}{RT}\right)$$

Sub in eq (7)

$$\int_0^P \left(b - \frac{a}{RT}\right) dP = \int^{\frac{f}{P}} RT\, d\ln\left(\frac{f}{P}\right)$$

$$\left(\frac{f}{P}\right) = 1$$

$$\left(b - \frac{a}{RT}\right)P = RT\,\cancel{d}\ln\left(\frac{f}{P}\right) \quad —— \quad ⑫$$

If 'a' & 'b' are known then f can be evaluated at a given P & T.

If b = 0. then eq (12) reduces to

$$\left(-\frac{a}{RT}\right) P = RT \, d \ln \frac{f}{P}$$

$$d \ln\left(\frac{f}{P}\right) = \frac{-aP}{(RT)^2}$$

$$\frac{f}{P} = \exp\left[-\frac{aP}{(RT)^2}\right]$$

$$f = P \exp\left(-\frac{aP}{(RT)^2}\right]$$

when a = 0. eq (12) reduces to

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

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

$$f = P \exp\left(\frac{bP}{RT}\right)$$