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Assignment - 2 (Derivation)

$$dG = VdP \qquad \left(V = \frac{RT}{P}\right)$$

$$\int_{P_1}^{P_2} dG = \frac{RT}{P} dP = RT\, d\ln P \quad -(i)$$

for non ideal: $\int_{P_1}^{P_2} dG = RT \ln f$ where f is fugacity

for a real gas: $\alpha = V^{real} - V^{id}$

$$= V^{real} - \frac{RT}{P}$$

$$V = \left(\alpha + \frac{RT}{P}\right) \quad — (ii)$$

Therefore: $RT\, d\ln f = \left(\alpha + \frac{RT}{P}\right) dP$

$$\Rightarrow d\ln f = \frac{\alpha}{RT} dP + d\ln P$$

$$\Rightarrow \int_{P_0}^{P} d\ln f = \int_{P_0}^{P} d\ln P + \frac{1}{RT}\int_{P_0}^{P} \alpha\, dP$$

$$\Rightarrow \ln f_P - \ln f_{P_0} = \ln P - \ln P_0 + \frac{1}{RT}\int_{P_0}^{P} \alpha\, dP$$

here $\ln f_{P_0} = \ln P_0$ therefore eqn simplifies to:

$$\ln f_P = \ln p + \frac{1}{RT}\int_{P_0}^{P} \alpha\, dP$$

$$\ln f/p = \ln \gamma_i = \frac{1}{RT}\int_{P_0}^{P} \left(V - \frac{RT}{P}\right) dP \quad \text{for pure gas}$$

for a mixture:

$$\ln \gamma_i = \frac{1}{RT}\int_{P_0}^{P} \left(\bar{V}_i - \frac{RT}{P}\right) dP$$

$$\Rightarrow \ln \gamma_i = \frac{1}{RT} \int_V^\infty \left[\left(\frac{\partial P}{\partial n_i} \right)_{j,T} - \frac{RT}{V} \right] dV$$

→ Fraunsity Equation

Taking volume of fluid mixture as $V_t = n_t V$ where n_t is the total no of moles and V is molar volume.

$$\Rightarrow \ln \gamma_i = \frac{1}{RT} \int_{V_t}^\infty \left[\left(\frac{\partial P}{\partial n_i} \right)_{T, V_t, n_i} - \frac{RT}{V_t} \right] dV_t - \ln \left(\frac{P V_t}{RT} \right)$$

Using the MRK Eqn:

$$\Rightarrow P = \frac{RT}{V-b} - \frac{q}{T^{1/2} V(V+b)}$$

for $(H_2O - CO_2)$ mix

$$q_{mix} = \sum_{i=1}^{n} \sum_{j=1}^{n} x_i x_j q_{ij}$$

$$= x_{H_2O}^2 q_{H_2O} + 2 x_{H_2O} x_{CO_2} q_{H_2O-CO_2} + x_{CO_2}^2 q_{CO_2}$$

$$b_{mix} = \sum_{i=1}^{n} x_i b_i$$

$$= x_{H_2O} b_{H_2O} + x_{CO_2} b_{CO_2}$$

Hence,

$$\ln \gamma_i = \ln \left(\frac{V}{V-b} \right) + \frac{b_i}{V - b_{mix}} - \frac{2 \sum_{j=1}^{m} x_j q_{ij}}{RT^{3/2} b_{mix}} \ln \left(\frac{V + b_{mix}}{V} \right)$$

$$+ \frac{q_{mix} b_i}{RT^{3/2} b_{mix}} \times \left[\ln \left(\frac{V + b_{mix}}{V} \right) - \frac{b_{mix}}{V + b_{mix}} \right] - \ln \left(\frac{PV}{RT} \right)$$