

Mixtures of Ideal Gases

N_1, N_2, \dots, N_n moles of each component

$$PV = (N_1 + N_2 + \dots + N_n)RT = NRT$$

$$\bar{V}_i^{IG} = \left(\frac{\partial V}{\partial N_i} \right)_{T, P, N_{j \neq i}} = \frac{\partial}{\partial N_i} \left[\frac{NRT}{P} \right] = \frac{RT}{P}$$

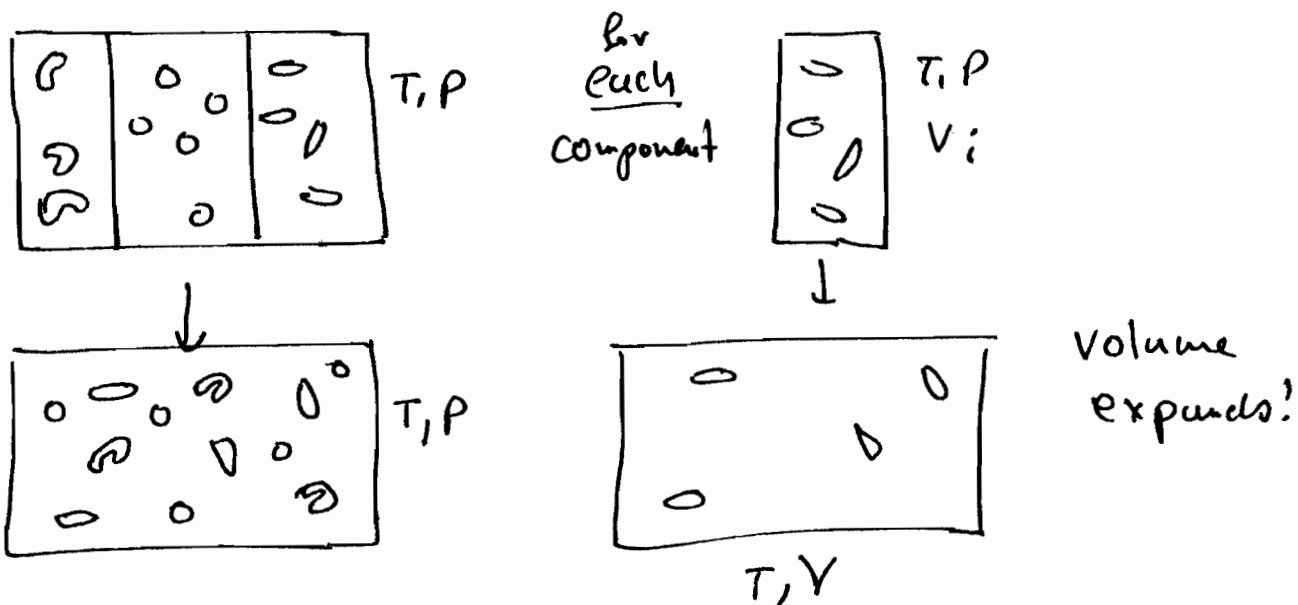
molar volume of pure component at same T, P

$$\underline{V}_i^{IG} = RT/P = \bar{V}_i^{IG} \Rightarrow \Delta V_{mix}^{IG} = 0$$

Since molecules are isolated, $\Delta U_{mix}^{IG} = 0$

$$\Delta H_{mix}^{IG} = \Delta U_{mix}^{IG} + P \Delta V_{mix}^{IG} = 0$$

But... ΔS_{mix}^{IG} is not zero!



The entropy of each component is now greater in the expanded volume (more microstates)

$$\underline{\Delta S}_i = R \ln \frac{V}{V_i} = R \ln \frac{N}{N_i} = -R \ln x_i$$

$$\Delta S_{mix}^{IG} = \sum_{i=1}^n N_i \Delta \underline{S}_i = -R \sum_{i=1}^n N_i \ln x_i$$

$$\Rightarrow \Delta \underline{S}_{mix}^{IG} = -R \sum_{i=1}^n x_i \ln x_i$$

$$\Delta G_{mix}^{IG} = \Delta H_{mix}^{IG} - T \Delta S_{mix}^{IG} = RT \sum_{i=1}^n x_i \ln x_i \quad (1)$$

$$\left. \frac{\partial \Delta G_{mix}^{IG}}{\partial N_i} \right|_{T, P, N_{j \neq i}} = \frac{\partial}{\partial N_i} \left[G^{IG} - \sum_{i=1}^n N_i \mu_i^{IG}(\text{pure}) \right] =$$

$$= \mu_i^{IG}(T, P, \{x\}) - \mu_i^{IG}(\text{pure } i @ T, P) \quad (2)$$

$$\text{From (1)} \quad \frac{\partial \Delta G_{mix}^{IG}}{\partial N_i} = \frac{\partial RT \sum N_i \ln x_i}{\partial N_i} = RT \frac{\partial}{\partial N_i} \left(\sum N_i \ln N_i - N_i \ln N \right)$$

$$= RT \left(\ln N_i + 1 - \ln N - \frac{N_i}{N} \right) = RT \ln x_i \quad (3)$$

$$\text{Setting (2) = (3)} \Rightarrow \mu_i^{IG}(T, P, \{x\}) = \mu_i^{IG}(T, P, \text{pure } i) + RT \ln x_i$$

$$\text{From } \left. \frac{\partial H}{\partial P} \right|_T = V = \frac{RT}{P} \quad \text{for pure comp, ideal gas}$$

$$\Rightarrow \mu_i^{IG}(T, P, \text{pure } i) = \mu_i^{IG}(T, P^0, \text{pure } i) + RT \ln \frac{P}{P^0}$$

$$\therefore \mu_i^{IG}(T, P, \{x\}) = \mu_i^{IG}(T, P^0, \text{pure } i) + RT \ln \frac{x_i P}{P^0}$$

$$\mu_i^{\text{IG}}(\tau, P, \{x_i\}) \rightarrow -\infty \quad \text{as } x_i \rightarrow 0 \quad \text{or } P \rightarrow 0$$

As previously, we define a transformed μ , the fugacity f_i

$$RT \ln \frac{f_i}{f_i^0} \equiv \mu_i(\tau, P, \{x_i\}) - \mu_i^0(\tau, P^0, \text{pure } i)$$

If we select $f_i^0 = 1 \text{ bar}$ for $P^0 = 1 \text{ bar}$,

$$RT \ln f_i = \mu_i(\tau, P, \{x_i\}) - \mu_i^0(\tau, P^0, \text{pure } i)$$

For ideal gases, $f_i = x_i P$

$x_i P$ is defined as the "partial pressure" P_i of a component

Fugacity coefficient $\phi = \frac{f_i}{P_i} = \frac{f_i}{x_i P}$

Pressure dependence: $\left. \frac{\partial \mu_i}{\partial P} \right|_{\tau, \{N_j\}} = \bar{V}_i \Rightarrow$

$$RT \left. \frac{\partial \ln f_i}{\partial P} \right|_{\tau, \{N_j\}} = \bar{V}_i \Rightarrow RT \ln \frac{f_i(P_2)}{f_i(P_1)} = \int_{P_1}^{P_2} \bar{V}_i dP$$

Difference from ideal-gas fugacity

$$RT \ln \frac{f_i}{x_i P} = RT \ln \phi_i = \int_0^P \left(\bar{V}_i - \frac{RT}{P} \right) dP$$

Fugacities from pressure-explicit EOS are harder to obtain - see Example 8.6

Final result

$$\ln \frac{f_i}{x_i P} = \ln \phi_i = \frac{1}{RT} \int_{\infty}^v \left[\frac{RT}{v} - N \left(\frac{\partial P}{\partial N_i} \right)_{T, v, N_{j \neq i}} \right] dv - \ln z$$

In order to apply this for -say- vdW EOS

$$P = \frac{RT}{v-b} - \frac{a}{v^2} \quad \text{need } a, b \text{ as functions of composition}$$

Usual mixing rules:

$$a = \sum_{i=1}^n \sum_{j=1}^n x_i x_j a_{ij}$$

[quadratic for a]

$$a_{ij} = (1 - k_{ij}) \sqrt{a_i a_j}$$

↑
empirical "interaction parameter"

$$(k_{ii} = 0)$$

[Linear for b]

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