

Ideal (liquid or solid) Mixtures

Fugacities f_i describe chemical potentials - most useful for gases or fluids described by E.O.S.
 $f_i \rightarrow z_i P$ as $P \rightarrow 0$ (ideal gas)

Need a measure of chemical potentials that does not rely on ideal gases - esp. for proteins, electrolytes, metals etc

Ideal Mixture: $\Delta U_{mix}^{IM} = \Delta V_{mix}^{IM} = 0$

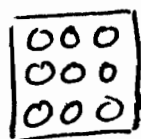
- e.g. - mixing similar non-polar liquids
- mixing similar-sized atoms in solids

→ Ideal Gas mixtures special case of ideal mixtures

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

Since $\Delta U_{mix}^{IM} = \Delta V_{mix}^{IM} = \Delta H_{mix}^{IM} \Rightarrow \left\{ \begin{array}{l} \bar{u}_i^{IM} = \underline{u}_i \\ \bar{v}_i^{IM} = \underline{v}_i \\ \bar{h}_i^{IM} = \underline{h}_i \end{array} \right\}$

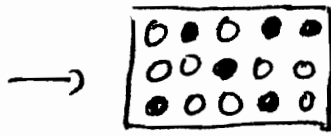
But ΔS_{mix}^{IM} is not zero



N_A, T, P



N_B, T, P



$N_A + N_B$

T, P

$$Q_{mix} = \binom{N_A + N_B}{N_A}$$

$$= \frac{(N_A + N_B)!}{N_A! N_B!}$$

$$\frac{\Delta S_{mix}^{IM}}{k_B} = \ln Q_{mix} = (N_A + N_B) \ln(N_A + N_B) - N_A \ln N_A - N_B \ln N_B$$

$$\Rightarrow \frac{\Delta S_{mix}^{IM}}{k_B} = -N_A \ln \frac{N_A}{N_A+N_B} - N_B \ln \frac{N_B}{N_A+N_B} \Rightarrow$$

$$\Delta S_{mix}^{IM} = -R [N_A \ln x_A + N_B \ln x_B] \quad \text{Convert } N_A, N_B \text{ from molecules to moles}$$

$$\Rightarrow \Delta S_{mix}^{IM} = -R [x_A \ln x_A + x_B \ln x_B]$$

$$\Delta G_{mix} = \Delta H_{mix} - T \Delta S_{mix} \Rightarrow \Delta G_{mix}^{IM} = RT \sum_{i=1}^n N_i \ln x_i$$

Pressure dependence: $\left. \frac{\partial \mu_i^{IM}}{\partial P} \right)_{T, \{N_j\}} = \bar{V}_i = \underline{V}_i \quad \left. \vphantom{\frac{\partial \mu_i^{IM}}{\partial P}} \right\} \text{from pure comp.}$

Temp. dependence of μ_i : $\frac{\partial \mu_i^{IM}/T}{\partial T} = -\frac{\bar{H}_i}{T^2} = -\frac{H_i}{T^2}$

Since $\underline{V}_i \neq \frac{RT}{P}$ for liquids, the simple fugacity expression $f_i^{IG} = x_i P$ is not valid.

Fugacity is not as useful for liquids.

The composition dependence of μ_i^{IM} , however, is the same as that for ideal gas mixtures:

$$\begin{aligned} \left. \frac{\partial \Delta G_{mix}^{IM}}{\partial N_i} \right)_{T, P, N_{j \neq i}} &= \mu_i^{IM} - \mu_i(T, P, \text{pure } i) = \\ &= \frac{\partial}{\partial N_i} \left[RT \sum_{i=1}^n N_i \ln \frac{N_i}{N} \right] = RT \ln x_i \end{aligned}$$

$$\Rightarrow \mu_i^{IM}(T, P, \{x_j\}) = \underbrace{\mu_i(T, P, \text{pure } i)}_{\text{in liq. or solid phase}} + RT \ln x_i$$

By now, you have seen this enough times to anticipate the next step. Since $\mu_i \rightarrow -\infty$ as $x_i \rightarrow 0$, we define a transformed μ_i

$$RT \ln \left(\frac{a_i}{a_i^0} \right) \equiv \mu_i(T, P, \{x\}) - \mu_i(T, P, \underbrace{\text{pure } i}_{\text{liq. or solid}})$$

a_i is the activity of a component in a mixture

We usually (but not always) set $a_i^0 = 1$ at $x_i = 1$

Unlike ϕ , we don't bother with units for a — it is dimensionless. If $a_i^0 = 1$,

$$RT \ln a_i = \mu_i(T, P, \{x\}) - \mu_i(T, P, \underbrace{\text{pure } i}_{\text{liq. or solid}})$$

For ideal mixtures, $a_i^{\text{IM}} = x_i$

Activity is a measure of chemical potentials, not concentration!

Activity coefficient $\gamma_i \equiv \frac{a_i}{x_i}$ $\gamma_i = 1$ for I.M.

$$RT \ln a_i = \mu_i(T, P, \{x\}) - \mu_i(T, P, \text{pure } i) =$$

$$= [RT \ln \gamma_i - \mu_i^{\text{IG}}(T, P^0, \text{pure } i)] - [RT \ln \gamma_i(\text{pure}) - \mu_i^{\text{IG}}(T, P^0, \text{pure } i)]$$

$$\Rightarrow a_i = \gamma_i x_i = \frac{\gamma_i(T, P, \{x\})}{\gamma_i(T, P, \text{pure } i)}$$

Excess Functions

$$B^{EX}(\tau, P, \{N\}) = B(\tau, P, \{N\}) - B^{IM}(\tau, P, \{N\})$$

(Difference between real and ideal mixture)

$$\underline{B}^{EX}(\tau, P, \{x\}) = \underline{B}(\tau, P, \{x\}) - \underline{B}^{IM}(\tau, P, \{x\})$$

$$\bar{B}_i^{EX} = \bar{B}_i - \bar{B}_i^{IM} \quad \Delta B_{tot}^{EX} = (B - B^{IM}) - \sum N_i \bar{B}_i + \sum N_i \bar{B}_i^{IM} = B^{EX}$$

For ideal mixtures, $\Delta u_{mix}^{IM} = \Delta H_{mix}^{IM} = \Delta V_{mix}^{IM} = 0$

$$\bar{u}_i^{IM} = \underline{u}_i \quad \bar{H}_i^{IM} = \underline{H}_i \quad \bar{v}_i^{IM} = \underline{v}_i$$

→ Table 8.1 summarizes mixture property relationships

Particularly important excess property:

$$\bar{G}_i^{EX} = \mu_i(\tau, P, \{x\}) - \mu_i^{IM}(\tau, P, \{x\}) =$$

$$= RT \ln a_i + \mu_i(\tau, P, pure i) - RT \ln x_i - \mu_i(\tau, P, pure i)$$

$$= RT \ln a_i / x_i = RT \ln \gamma_i \Rightarrow \boxed{\bar{G}_i^{EX} = RT \ln \gamma_i}$$

Activity coefficients are measures of the excess Gibbs partial molar property.

γ_i 's follow same relationships as G :

$$RT \left(\frac{\partial \ln \gamma_i}{\partial P} \right)_{\tau, \{x\}} = \bar{v}_i^{EX} \quad \frac{\partial \ln \gamma_i}{\partial T} = - \frac{\bar{H}_i^{EX}}{RT^2}, \text{ Gibbs-Duhem etc}$$