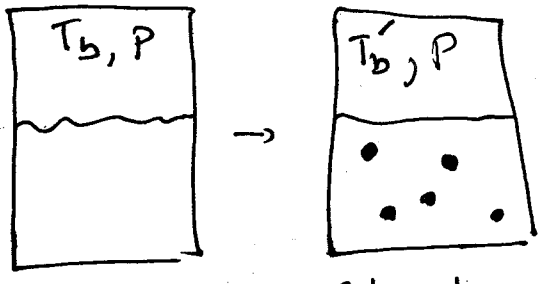
Boiling-Point Elevation



Assume non-volatile solute (only in liquid phase)

$x + x_\bullet = 1$

$\mu^G(T_b, P, \text{pure solvent}) =$

$= \mu^L(T_b, P, \text{pure solvent})$

$\mu^G(T_b', P, \text{pure solvent}) = \mu^L(T_b', P, x) \Rightarrow$

$$\underbrace{\mu^G(T_b', P, \text{pure}) - \mu^L(T_b', P, \text{pure})}_{\Delta\mu} = k_B T_b' \ln x$$

$$\left.\frac{\partial \mu}{\partial T}\right)_P = -s \quad \text{(no good)} \qquad \left.\frac{\partial(\mu/T)}{\partial T}\right)_P = -\frac{s}{T} - \frac{\mu}{T^2} = -\frac{Ts+\mu}{T^2}$$

$$\Rightarrow \frac{\partial(\mu/T)}{\partial T} = -\frac{h}{T^2} \qquad \frac{\partial(\Delta\mu/T)}{\partial T} = -\frac{\Delta h_{vap}}{T^2}$$ ← assume constant

$\Delta\mu = 0$ @ $T_b \Rightarrow \dfrac{\Delta\mu(T_b')}{T_b'} - \dfrac{\Delta\mu(T_b)}{T_b} = \Delta h_{vap}\left(\dfrac{1}{T_b'} - \dfrac{1}{T_b}\right)$

$$\therefore k_B T_b' \ln x = \Delta h_{vap}\left(1 - \frac{T_b'}{T_b}\right) \Rightarrow T_b' = T_b \frac{1}{1 + \frac{k_B T_b}{\Delta h_{vap}} \ln x}$$

$T_b' > T_b$ since $\ln x < 0$

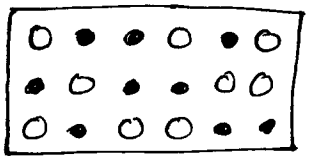
At the limit $x \to 1$: $\ln x \simeq -x_\bullet$, $\dfrac{1}{1 - \frac{k_B T_b}{\Delta h_{vap}} \cdot x_\bullet} \simeq 1 + \dfrac{k_B T_b x_\bullet}{\Delta h_{vap}}$

$$\Rightarrow T_b' \simeq T_b\left(1 + \frac{k_B T_b x_\bullet}{\Delta h_{vap}}\right)$$

A very similar derivation applies for freezing point depression of a solution at equilibrium with a pure crystal (solvent).
In this case the freezing point of the solution is always smaller than the pure solvent's (why?)

Osmotic pressure, boiling-point elevation and freezing point depression only depend on $x_\bullet$, not its chemical character; they are known as "colligative" properties.

Mixing w/ interactions



Similar model to that of ideal solutions, except now there are interactions w_{oo} $w_{o\bullet}$ $w_{\bullet\bullet}$

Mean-field approximation: each particle has the same (average) environment. $N = N_\bullet + N_o$

Coordination (# of nearest neighbors) = z

There are $\frac{zN_o}{N}$ particles of type "o" around each position

$\frac{zN_\bullet}{N}$ " " " "$\bullet$" "

$$E = \frac{1}{2}\left[N_o w_{oo}\frac{zN_o}{N} + N_o w_{\bullet o}\frac{zN_\bullet}{N} + N_\bullet w_{\bullet o}\frac{zN_o}{N} + N_\bullet w_{\bullet\bullet}\frac{zN_\bullet}{N}\right]$$

↑ to avoid double-counting

$$= zN\left[\frac{w_{oo}}{2}x_o^2 + w_{\bullet o}x_o x_\bullet + \frac{w_{\bullet\bullet}}{2}x_\bullet^2\right]$$

$$\Delta E_{mix} = E - \underbrace{N_0 \frac{z w_{00}}{2} - N_\bullet \frac{z w_{\bullet\bullet}}{2}}_{\text{pure components}} = E - Nz\left[\frac{w_{00}}{2} x_0 + \frac{w_{\bullet\bullet}}{2} x_\bullet\right]$$

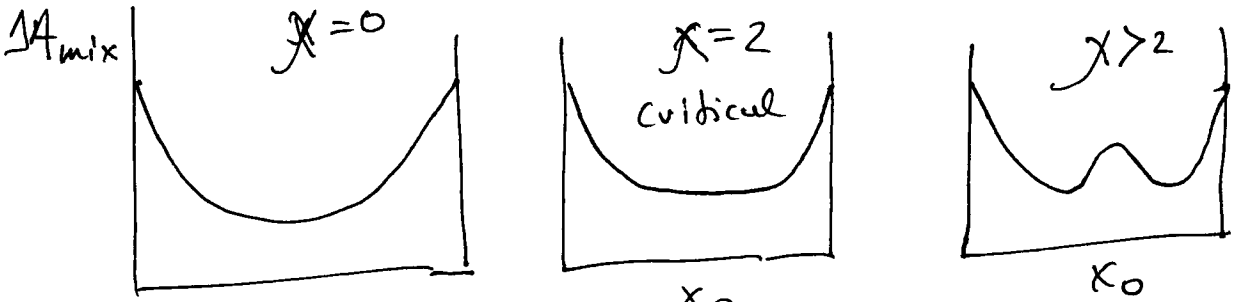
$$\Rightarrow \Delta E_{mix} = zN\left[\frac{w_{00}}{2} x_0^2 - \frac{w_{00}}{2} x_0 + w_{0\bullet} x_0 x_\bullet + \frac{w_{\bullet\bullet}}{2} x_\bullet^2 - \frac{w_{\bullet\bullet}}{2} x_\bullet\right]$$

$$= zN\left[-\frac{w_{00}}{2} x_0 x_\bullet + w_{0\bullet} x_0 x_\bullet - \frac{w_{\bullet\bullet}}{2} x_0 x_\bullet\right] \Rightarrow$$

$$\Rightarrow \Delta E_{mix} = N x_0 x_\bullet k_B T \chi_{0\bullet} \quad \text{where } \chi_{0\bullet} = \frac{z}{k_B T}\left[w_{0\bullet} - \frac{w_{00} + w_{\bullet\bullet}}{2}\right]$$

If $\chi_{0\bullet} = 0 \longrightarrow$ athermal mixture (ideal)

$$\Delta A_{mix} = \Delta E_{mix} - T\Delta S_{mix} = NkT\left[x_0 \ln x_0 + x_\bullet \ln x_\bullet + x_0 x_\bullet \chi_{0\bullet}\right]$$



Gibbs-Duhem relationship

$$dE = TdS - PdV + \sum_{i=1}^{C} \mu_i dN_i = dy^{(0)}$$

$$y^{(C+2)} = y^{(0)} - \Sigma \xi_i x_i \Rightarrow y^{(C+2)} = E - TS + PV - \sum \mu_i N_i = 0$$

(from Euler integration of E)

$$\therefore dy^{(C+2)} = 0 = -SdT + VdP - \sum_{i=1}^{C} N_i d\mu_i$$

At const. T and P $\boxed{\sum_{i=1}^{c} N_i d\mu_i = 0}$ Gibbs-Duhem

This provides a way to link chemical potentials - e.g. for a binary system, $N_1 d\mu_1 + N_2 d\mu_2 = 0 \Rightarrow$

$\frac{d\mu_1}{d\mu_2} = -\frac{N_2}{N_1}$ (consistency relations between μ_i's)

Partial Molar Quantities

$\bar{B}_i = \left(\frac{\partial B}{\partial N_i}\right)_{T,P,N_{j\neq i}}$ where B can be <u>any</u> of $E, S, A, H, G, V, \cdots$ (<u>extensive</u>)

e.g. $\bar{G}_i = \left(\frac{\partial G}{\partial N_i}\right)_{T,P,N_{j\neq i}} = \mu_i$

$\bar{V}_i = \left(\frac{\partial V}{\partial N_i}\right)_{T,P,N_{j\neq i}}$

mixture properties, depend on T, P, composition

Key property: $dB = \left(\frac{\partial B}{\partial T}\right) dT + \left(\frac{\partial B}{\partial P}\right) dP + \sum_{i=1}^{c} \bar{B}_i dN_i$

Since B is extensive → Euler integrate to get

$\boxed{B = \sum_{i=1}^{c} \bar{B}_i N_i}$

All relationships for thermodynamic potentials and derivatives also apply to partial molar quantities - e.g.

$A = E - TS \Rightarrow \bar{A}_i = \bar{E}_i - T\bar{S}_i$