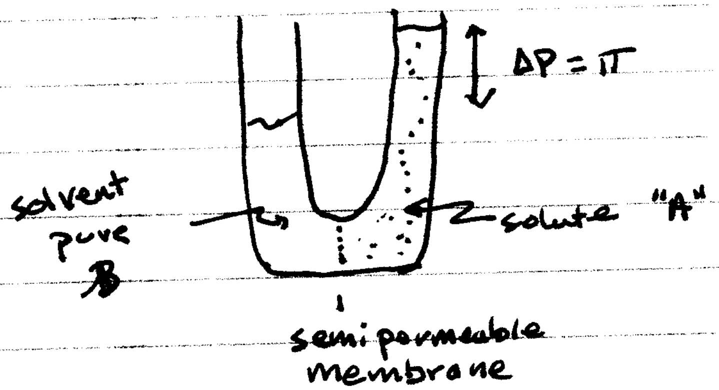
Lecture #23

11/7/05

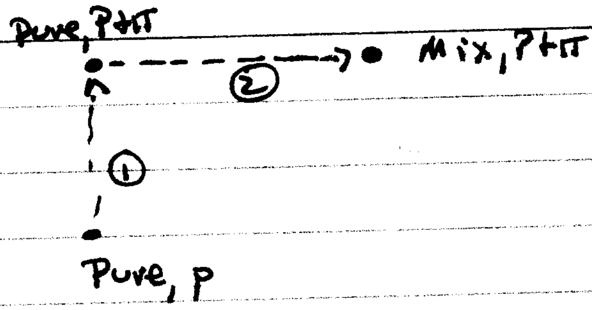
Collegative properties cont'd : Osmotic pressure



Goal: Get $\Pi(x_A)$

Phase equilibria

$$\mu_{B,pure}(P) = \mu_{B,mix}(P+\Pi, x_A)$$



① $P \to P+\Pi$ $\quad \mu_{B,pure}(P+\Pi) = \mu_{B,pure}(P) + \int_P^{P+\Pi} \frac{\partial \mu_B}{\partial P} dP$

Get $\frac{\partial \mu_B}{\partial P}$ from Maxwell Relation:

$$dG = -SdT + VdP + \mu dN$$

$$\text{const } T \Rightarrow \left.\frac{\partial V}{\partial N}\right)_{T,P} = \left.\frac{\partial \mu}{\partial P}\right)_{T,N}$$

↓ molar volume

$v_B \cong$ constant

$$\mu_{B,pure}(P+\Pi) = \mu_{B,pure}(P) + v_B \Pi$$

② Add Solute

$$\underline{\mu_{B,mix}(P+\Pi, x_B)} = \underline{\mu_{B,pur}(P)} + v_B\Pi + RT\ln\gamma_B x_B$$

must be equal at eq^m

thus

$$-v_B\Pi = RT\ln\gamma_B x_B$$

For dilute solution

$x_A << 1$

$x_B \to 1$ thus $\gamma_B \to 1$

$\ln(1-x_A) \approx -x_A$

$$\Pi = \frac{RT\,x_A}{v_B}$$

Usually prefer to use in terms of c_A $\frac{\text{moles}}{L}$

for $x_A << 1$, $x_A \approx N_A/N_B$ and $V = N_B v_B$

$$\Pi = \frac{RT\left(\frac{N_A}{N_B}\right)}{V/N_B} = c_A RT$$

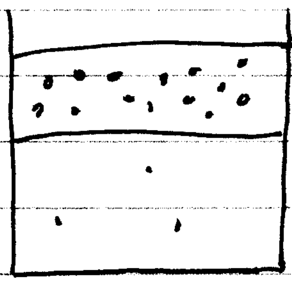
$$\boxed{\Pi = c_A RT}$$

Solute in Phase Partitioning

What if you add a lipophilic dye to the oil/water (salad dressing) mix we discussed before

Now a 3-component system

call dye "s" = solute



oil = B, x_{SB}

water = A, x_{SA}

at eq^m $\mu_s(A) = \mu_s(B)$

$$\frac{z\omega_{ss}}{2} + kT\left[\ln x_{SA} + \chi_{SA}(1-x_{SA})^2\right] = \frac{z\omega_{ss}}{2} + kT\left[\ln x_{SB} + \chi_{SB}(1-x_B)^2\right]$$

rearrange

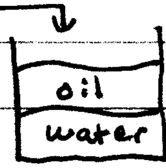
$$\ln\frac{x_{SB}}{x_{SA}} = \chi_{SA}(1-x_{SA})^2 - \chi_{SB}(1-x_{SB})^2$$

$$\equiv \ln K_A^B \quad \leftarrow \text{partition coefficient}$$

Usually, you measure K_A^B

Think about this expt:

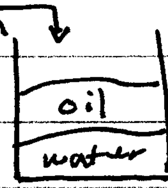
tiny bit of dye →



$x_{SB} = 0.001$

$x_{SA} = 10^{-5}$

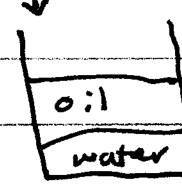
2× "tiny" →



$x_{SB} = 0.002$

$x_{SA} = 2\times10^{-5}$

10,000× (saturation) →



$x_{SB} = .02$

$x_{SA} = 2\times10^{-4}$

$K_A^B = \frac{x_{SB}}{x_{SA}} = 100$ $\qquad K_A^B = \frac{.002}{2\times10^{-5}} = 100$ $\qquad K_A^B = \frac{.02}{2\times10^{-4}} = 100$