Phase Relationships

Raoult’s Law for ideal solutions \( (\gamma_A = 1) \)

\[ P_A = \gamma_A P_A^* \]

\[ \text{vapor pressure of } A \text{ (EtOH) (or H}_2\text{O)} \]

\[ \gamma_A = \frac{\text{mole fraction of } A \text{ in solvent (EtOH) or H}_2\text{O}}{\text{mole EtOH or mole H}_2\text{O}} \]

\[ \text{Henry’s Law} \quad \text{what about things like gases, etc.} \]

\[ P_B = k_A X_A \]

\[ \text{vapor pressure of solute } B \]

\[ k_A \quad \text{Henry's Law constant for solute } B \text{ in solvent } A \]

\[ X_A \quad \text{mole fraction of } A \text{ in solvent } A \]

\[ \text{Depends on temperature and on the particular solvent} \]

Implications: Vapor pressure lowering can be used to measure solute concentrations

\[ \text{Prote}n \Rightarrow X_p = 10^{-8} \quad X_{H_2O} = 1 - 10^{-8} \quad \text{vapor pressure lowering} \]
At equilibrium:

\[ \text{O}_2 (aq) = \text{O}_2 (g) \]
\[ \text{H}_2\text{O} (aq) = \text{H}_2\text{O} (g) \]
\[ \text{A}_2 (aq) = \text{A}_2 (g) \] etc.

We saw before that this lead to Raoult's Law

\[ X_2 = \frac{\text{P}_2}{\text{P}} = 4.7 \times 10^{-6} \] (dissolved)

**Equilibrium Dialysis**

<table>
<thead>
<tr>
<th>INSIDE</th>
<th>OUTSIDE</th>
</tr>
</thead>
<tbody>
<tr>
<td>M A A A</td>
<td>M A A A</td>
</tr>
<tr>
<td>M A A A</td>
<td>M A A A</td>
</tr>
</tbody>
</table>

Membrane Permeable to ligand A but not to macromolecule M

M = macromolecule is NOT at equilibrium between the left and right sides. (Similarly, MA is NOT)

A = ligand will equilibrate

but also have \[ M + A \rightleftharpoons MA \]

\[ K = \frac{[MA]}{[M][A]} \]

\[ M_A^\text{in} = M_A^\text{out} \]
\[ A_A^\text{in} = A_A^\text{out} \]
\[ C_A^\text{in} = C_A^\text{out} \]

\[ C_M = C_M + C_{MA} = [M] + [MA] \]

\[ C_A^\text{TOTAL} = [A]^\text{IN} + [MA]^\text{IN} \]

\[ C_A^\text{INSIDE} = C_A^\text{OUTSIDE} \]
Measurable Quantities

\[ C_M = [\text{MA}] + [M] \]

You know this because you set it up that way.

\[ C_{A,\text{outside}} = [A]_{\text{out}} \]

\[ C_{A,\text{inside}} = [A] + [\text{MA}] \]

\[ C_A = [\text{MA}] = \frac{C_A}{C_A - C_{A,\text{inside}}} = \frac{C_A - C_{A,\text{outside}}}{C_{A,\text{outside}}} \]

Then

\[ R = \frac{[\text{MA}]}{[\text{MA} + [M]]} = \frac{C_A - C_A}{C_A - C_{A,\text{outside}}} \]

ugly, but doable

\[ K = \frac{C_A - C_A}{(1 - \omega)C_A} = \frac{C_A}{(1 - \omega)A} \]

\[ \frac{C_A}{[A]} = \frac{K(1 - \omega)}{1 - \omega} = K - \omega K \]

More Commonly

\[ R = \frac{[\text{MA}]}{[\text{MA} + [M]]} = \frac{C_A - C_A}{C_A - C_{A,\text{outside}}} \]

Then

\[ K = \frac{C_A - C_{A,\text{outside}}}{(1 - \omega)C_A} = \frac{C_A}{(1 - \omega)A} \]

\[ \frac{C_A}{[A]} = \frac{K(1 - \omega)}{1 - \omega} = K - \omega K \]
That all assumed \( M + A \rightarrow MA \) \( \beta \) goes from 0 to 1

What if more than 1 \( A \) can bind to \( M \)?
(MULTIPLE BINDING SITES)

IF \( N \) sites, then \( \beta \) goes 0 to \( N \)

Replacing \( \frac{[A]}{[M]} \)

\[
\frac{[A]}{[M]} = K - \frac{K}{N} \frac{2}{K}
\]

\[
\frac{2}{[A]} = KN - K
\]

SCATCHARD EQUATION
SCATCHARD PLOT

Valuable, particularly when you don't know how many sites there are.

If NOT a straight line, then the model is too simple (usually need cooperativity etc.)

Reminder

\( \beta \) = average \# A's bound per macromolecule
\( N \) = Number of binding sites per macromolecule

\( \frac{\beta}{N} \) goes from 0 \( \rightarrow \) 1 (always)