OUTLINE OF CHAPTER 11

SOLUTE PARTITION

Starting Point (looks familiar??? where is this coming from?)

\[ \tilde{f}_1^I(T, P, \tilde{x}^I) = \tilde{f}_1^II(T, P, \tilde{x}^II) \]

We define as partition coefficient of a solute between two liquid phases as

\[ K = \frac{\text{Concentration of solute in phase I}}{\text{Concentration of solute in phase II}} \]

Now,

\[ N_1 = N_1^I + N_1^II \]

and

\[ \tilde{f}_1(T, P, \tilde{x}) = x_1y_1(T, P, \tilde{x})f_1^I(T, P) \]

Then

\[ x_1^Iy_1^I(T, P, \tilde{x}^I) = x_1^IIy_1^II(T, P, \tilde{x}^II) \]

\[ \frac{x_1^I}{x_1^II} = K_x = \frac{y_1^II(T, P, \tilde{x}^II)}{y_1^I(T, P, \tilde{x}^I)} \]

Thus given info on activity coefficients $K$ is known…
**OSMOTIC PRESSURE**

Two cells (at different pressures) separated by a membrane that only allows solvent to pass. One cell has pure solvent, the other has solvent + solute

*We start with (Oh surprise!)*

\[ f^{1}_{\text{solvent}} = f^{II}_{\text{solvent}} \]

*Why we do not write the same for the solute? The system is not at the same pressure, so why do we write the condition anyway? Here is why*

![Diagram](image)

System:

- Energy balance:
  \[ \frac{dU}{dt} = \dot{Q} + \dot{W}_S - P^I \frac{dV^I}{dt} - P^II \frac{dV^{II}}{dt} \]

- Entropy balance:
  \[ \frac{dS}{dt} = \frac{\dot{Q}}{T} + S_{gen} \]

Constraints: \( \dot{W}_S = 0 \), system is isothermal, \( P^I \) and \( P^{II} \) are constant thus

\[ \dot{Q} = T \frac{dS}{dt} - TS_{gen} = \frac{d}{dt}(TS) - TS_{gen} \]

*Then*
\[
\frac{dU}{dt} = \frac{d}{dt}(TS) - T\dot{S}_{\text{gen}} - P^I dV^I - P^{II} dV^{II} = \frac{d}{dt}(TS) - T\dot{S}_{\text{gen}} - \frac{d}{dt}(P^I V^I) - \frac{d}{dt}(P^{II} V^{II}) \\
\Rightarrow \frac{d}{dt}(U - TS + P^I V^I + P^{II} V^{II}) = \frac{dG^*}{dt} = -T\dot{S}_{\text{gen}}
\]

where \(G^* = U - TS + P^I V^I + P^{II} V^{II}\)

Then
\[
\frac{dG^*}{dt} = -T\dot{S}_{\text{gen}} \leq 0 \Rightarrow G^* = \text{minimum at equilibrium}
\]

But
\[
G^* = U - TS + P^I V^I + P^{II} V^{II} = (U^I + U^{II}) - T(S^I + S^{II}) - P^I V^I - P^{II} V^{II} = G^I(T, P^I, N^I) + G^{II}(T, P^{II}, N^{II})
\]

OR
\[
G^* = \sum N^I_j \overline{G}^I_j(T, P^I, x^I) + \sum N^{II}_j \overline{G}^{II}_j(T, P^{II}, x^{II})
\]

Now using
\[
dN^{II}_i = -dN^I_i \Rightarrow
\[
\left(\frac{\partial G^*}{\partial N^I_i}\right)_{T, P, N, \text{other}} = \overline{G}^I_i(T, P^I, x^I) + \sum N^I_j \left(\frac{\partial \overline{G}^I_j(T, P^I, x^I)}{\partial N^I_i}\right)_{T, P, N, \text{other}}
\]

minus sign arises from \(dN^{II}_i = -dN^I_i\)
Now both summation terms vanish upon application of the Gibbs-Duhem equation to each phase. Thus we have, at equilibrium, that

\[
\left( \frac{\partial G^*}{\partial N_i^j} \right)_{T,P,N_{jm}} = 0 = \overline{G}_i^j(T, P^i, \chi^i) - \overline{G}_i^\Pi(T, P^\Pi, \chi^\Pi)
\]

\[
\Rightarrow \overline{G}_i^j(T, P^i, \chi^i) = \overline{G}_i^\Pi(T, P^\Pi, \chi^\Pi)
\]

for each permeable \( i \) species, or equivalently

\[
\overline{f}_i^j(T, P^i, \chi^i) = \overline{f}_i^\Pi(T, P^\Pi, \chi^\Pi)
\]

Then

\[
f_{\text{solvent}}^I = \overline{f}_{\text{solvent}}^\Pi
\]

\[
\Rightarrow f_{\text{solvent}}(T, P^I) = x_{\text{solvent}}^\Pi \gamma_{\text{solvent}}^\Pi f_{\text{solvent}}(T, P^\Pi)
\]

But

\[
f_{\text{solvent}}(T, P^\Pi) = f_{\text{solvent}}(T, P^I) \exp \left[ \frac{V_{\text{solvent}}^L (P^\Pi - P^I)}{RT} \right]
\]

liquid assumed incompressible (\( \int_{P^I}^{P^\Pi} \frac{V_{\text{solvent}}^L}{P_{\text{solvent}}} dP \approx \frac{V_{\text{solvent}}^L (P^\Pi - P^I)}{RT} \))

Then

\[
1 = x_{\text{solvent}}^\Pi \gamma_{\text{solvent}}^\Pi \exp \left[ \frac{V_{\text{solvent}}^L (P^\Pi - P^I)}{RT} \right]
\]

\[
\Pi = P^\Pi - P^I = -\frac{RT}{V_{\text{solvent}}^L} \ln(x_{\text{solvent}}^\Pi \gamma_{\text{solvent}}^\Pi)
\]
\[ \Pi = P^{\Pi} - P^1, \text{ called the osmotic pressure}, \]

For small concentrations we have:

\[ \Pi = -\frac{RT}{V_{\text{solvent}}} \ln(x_{\text{solvent}}) \approx \frac{RT}{V_{\text{solvent}}} (1 - x_{\text{solvent}}) \]

But

\[ x_{\text{solvent}} + x_{\text{solute}} = 1 \]

Also

\[ x_{\text{solute}} = \frac{\text{Moles solute}}{\text{Moles solute} + \text{Moles solvent}} \approx \frac{\text{Moles solute}}{\text{Moles solvent}} = \frac{C_{\text{solute}}/m_{\text{solute}}}{C_{\text{solvent}}/m_{\text{solvent}}} \]

\[ \frac{C_{\text{solvent}}}{m_{\text{solvent}}} = \frac{1}{V_{\text{solvent}}} \]

Then

\[ \Pi = \frac{RT}{V_{\text{solvent}}} x_{\text{solute}} \approx \frac{RT C_{\text{solute}}/m_{\text{solute}}}{V_{\text{solvent}} C_{\text{solvent}}/m_{\text{solvent}}} \]

\[ = R T C_{\text{solute}}/m_{\text{solute}} \]

A very useful formula