OUTLINE OF CHAPTER 11

SOLUTE PARTITION

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

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

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,

\[ N_1 = N_1^I + N_1^II \quad \text{and} \quad \bar{f}_1(T, P, \chi) = x_1 y_1(T, P, \chi) f_1^I(T, P) \]

Then

\[ x_1^I y_1^I(T, P, \chi^I) = x_1^II y_1^II(T, P, \chi^II) \]

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!)

\[ f_{\text{solvent}}^I = f_{\text{solvent}}^{II} \]

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

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:

\[ \frac{dS}{dt} = \frac{\dot{Q}}{T} + \dot{S}_{\text{gen}} \]

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

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

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

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

Now using
\[ dN^{II}_i = -dN^I_i \Rightarrow \]
\[ \left( \frac{\partial G^*}{\partial N^I_i} \right)_{T,P,N_{j\neq i}} = \overline{G}^I_j(T,P^I,\chi^I) + \sum N^I_j \left( \frac{\partial \overline{G}^I_j(T,P^I,\chi^I)}{\partial N^I_i} \right)_{T,P,N_{j\neq i}} \]
\[ - \left[ \overline{G}^{II}_i(T,P^{II},\chi^{II}) + \sum N^{II}_j \left( \frac{\partial \overline{G}^{II}_j(T,P^{II},\chi^{II})}{\partial N^I_i} \right)_{T,P,N_{j\neq i}} \right] \]

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

\[
\left( \frac{\partial G^*}{\partial N_i} \right)_{T,P,N_m} = 0 = \bar{G}_i^I(T, P_i^I, \chi^I) - \bar{G}_i^II(T, P_i^II, \chi^II)
\]

\[
\Rightarrow \bar{G}_i^I(T, P_i^I, \chi^I) = \bar{G}_i^II(T, P_i^II, \chi^II)
\]

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

\[
\bar{f}_i^I(T, P_i^I, \chi^I) = \bar{f}_i^II(T, P_i^II, \chi^II)
\]

**Then**

\[
f_{solvent}^I = \bar{f}_{solvent}^{II}
\]

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

**But**

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

**liquid assumed incompressible**

\[
\int_{P^I}^{P^{II}} V_{solvent}^{L} dP = \frac{V_{solvent}^{L}(P^{II} - P^{I})}{RT}
\]

**Then**

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

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

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

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

Then

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

\[ = RT C_{\text{solute}}/m_{\text{solute}} \]

A very useful formula