We saw previously that for the (passive) transport of ions across a bilayer, we could write

\[ \Delta G_{\text{transport Na}^+ \text{ out}} = RT \ln \frac{[\text{Na}^+ \text{ out}]}{[\text{Na}^+ \text{ in}]} + ZFV \]

But if the process is unfavorable (i.e., conc of Na\(^+\) is greater outside than inside), then the reaction is not spontaneous.

Q: How do we make it spontaneous?

A: Couple it to a reaction which is more favored (spontaneous) than this is unfavorable, so that the NET process is favored (spontaneous).

\[ \Delta G_{\text{total Xport}} = 3 \Delta G_{\text{Na}^+ \text{ out}} \quad \text{eg.} \]
\[ + 2 \Delta G_{\text{K}^+ \text{ in}} \]
\[ = +42.8 \text{ kJ/mole} \]

(Not favored)

BUT \[ \text{ATP} + \text{H}_2\text{O} \rightarrow \text{ADP} + \text{phosphate} \quad \Delta G = -31 \text{ kJ/mole} \]

\[ \Delta G = -43 \text{ to } -49 \text{ kJ/mole} \]
Surfaces, Membranes

including any interface between two surfaces

A Surface is 2-Dimensional (unlike a solution, which is 3D)

Conc is $\frac{\text{mol}}{\text{cm}^2}$ instead of $\frac{\text{mol}}{\text{cm}^3}$

\[
\left\{
\begin{array}{l}
\text{Surf pressure is } \frac{\text{F}}{\text{length}} \text{ instead of } \frac{\text{F}}{\text{area}} \Rightarrow (\frac{\text{J}}{\text{m}^2} \text{ instead of } \frac{\text{J}}{\text{m}^3}) \\
\text{Surface free energy is } \frac{\text{J}}{\text{m}^2} \text{ instead of } \frac{\text{J}}{\text{m}^3}
\end{array}
\right.
\]

Increased surface tension is equivalent to increasing the energetic price to create a surface.

so liquids with very high surface tension form drops readily (a sphere has the lowest surface volume) despite the fact that gravity disfavors drops.

E.g.
- Mercury $487 \text{ mN m}^{-1}$ little balls everywhere
- Water $72 \text{ mN m}^{-1}$
- Acetone $24 \text{ mN m}^{-1}$ ever seen acetone bead up? — No.

Ethanol too
Molecular Interpretation

Some solutes in a liquid will raise the surface tension. Others will lower it. What's happening?

1) Solutes which raise the surface tension will distribute away from the surface (so as to not raise the overall free energy)

2) Solutes which lower the surface tension will concentrate at the surface (so as to lower the overall free energy)

Examples of (2) → surfactants, detergents.

What happens?

Pure water

\[
\begin{array}{c}
\text{water} \\
\text{molecules at interface are unsatisfied.}
\end{array}
\]

\[\text{Cost to form a surface}\]

\[\text{Water} + \text{Detergent} \rightarrow \begin{array}{c}
\text{air} \\
\text{water} \\
\end{array}
\]

Nonpolar tails want to get away from the water (why?)

So they line up at interface

Not so bad... i.e., lowers energy of the surface
Vapor Pressure and Surface Tension

Net transfer of water from small drops to big. WHY? How?

Surface tension \[ \rightarrow \] Vapor Pressure

\[ \text{liquid} \leftrightarrow \text{gas} \]

\[ (\frac{dG}{dN})_{P,T} \]

Used to have: \[ \Delta G = -S \Delta T + V \Delta P + \mu_{H_2O} \Delta n_{H_2O} \]

Now: \[ \Delta G = -S \Delta T + V \Delta P + \sigma \Delta A + \mu_{H_2O} \Delta n_{H_2O} \]

Surface tension \[ \rightarrow \] \[ (\Delta G)_{P,T} \]

Note: This line is **not** an activity coefficient!

So we ultimately have to worry about **total chemical potential**

\[ \text{Surface tension, electrical potential, chemical potential} \rightarrow \text{either earth's or centrifuge-equivalent potential} \]
Colligative Properties

- Depend on the collection of molecules
- Depend on the number of solute molecules, NOT on the identity/kind of molecules

In some bioanalytical techniques, colligative properties are used to count the # of moles of a known mass of the compound \( \Rightarrow \) determine molecular weight.

Classic examples:
- Freezing point depression \( \Leftrightarrow \) antifreeze
- Boiling point elevation

A (pure liquid) \( \rightarrow \) A (g) \[ K = \frac{A_A \text{ (gas)}}{A_A \text{ (pure liquid)}} \]

From what we learned before:

\[ A_A \text{ (gas)} = P_a \text{ (atm)} \]
\[ A_A \text{ (pure liquid)} = 1 \quad \text{(standard state)} \]

\[ \therefore \quad K = \frac{P_a}{1} = P_a \quad \text{(partial pressure)} \quad \text{vapor pressure} \]

\[ \ln \frac{K}{K_i} = \ln \frac{P}{P_i} = -\frac{\Delta H_{vap}}{RT} \left( \frac{1}{2} - \frac{1}{T} \right) \quad \Delta H_{vap} = H_{gas} - H_{lq} \]

Boiling occurs when the vapor pressure of the liquid equals that of the surrounding atmosphere.

Shows how this depends on \( T \) (assuming \( \Delta H \) constant).
What must the pressure be in order to "boil" water at 37°C?

\[ \Delta H_{vap} = 42,000 \text{ J/mol} \]

Q: ASSUMPTION?
A: \( \Delta H_{vap} \) independent of temperature

\[ P_1 = 1 \text{ atm} \quad P_2 = \chi \]

\[ T_1 = 100^\circ \text{C} = 373K \quad T_2 = 37^\circ \text{C} = 310K \]

\[ \ln \left( \frac{\chi \text{ atm}}{1 \text{ atm}} \right) = \frac{-42,000 \text{ J/mol}}{8.313 \text{ J K}^{-1} \text{ mol}^{-1}} \left( \frac{1}{310K} - \frac{1}{373K} \right) = 2.75 \]

\[ \chi = (e^{-2.75} \chi \text{ atm}) = 0.064 \text{ atm} \quad \text{NOT ALL THAT LOW!} \]

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**Melting Point Temperature**

\( X_S \rightarrow X_L \)

(i) At equilib \[ \Delta G_S = \Delta G_L \]

Intuition: Increasing \( T \) will favor \( X_L \)
Increasing \( P \) will favor solid (except for water!)

So let's raise \( T \) but also raise \( P \) accordingly to maintain equilib

(ii) \[ \Delta G_S + \Delta G_S = \Delta G_L + \Delta G_L \]

(ii)-(i) leads to \[ \Delta G_S = \Delta G_L \]
Remembering \( d\tilde{G} = -\tilde{S}_s \, dt + \bar{V}_s \, dp \)

there \( -\tilde{S}_s \, dt + \bar{V}_s \, dp = -\tilde{S}_l \, dt + \bar{V}_l \, dp \)

\[-\tilde{S}_s \, \frac{dt}{dp} + \bar{V}_s = -\tilde{S}_l \, \frac{dt}{dp} + \bar{V}_l\]

\[\frac{dt}{dp}(\tilde{S}_s - \tilde{S}_l) = \bar{V}_s - \bar{V}_l\]

\[\frac{dt}{dp} = \frac{\bar{V}_s - \bar{V}_l}{\tilde{S}_s - \tilde{S}_l} = \frac{\Delta V_{\text{fusion}}}{\Delta S_{\text{fusion}}}\]

Since this is reversible at its melting/fusion point,

\[\Delta S_{\text{fusion}} = \frac{\Delta H_{\text{fusion}}}{T}\]

\[\therefore \frac{dt}{dp} = \frac{T}{\Delta H_{\text{fusion}}} \quad \text{General for phase transitions}\]