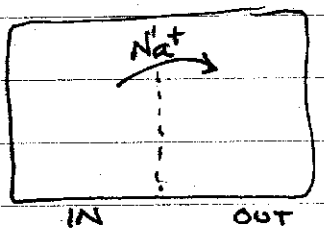
We saw previously that for the (passive) transport of ions across a bilayer, we could write

$$\Delta G \text{ (transport } Na^+ \text{ out)} = RT \ln \frac{a_{Na^+(out)}}{a_{Na^+(IN)}} + ZFV$$

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



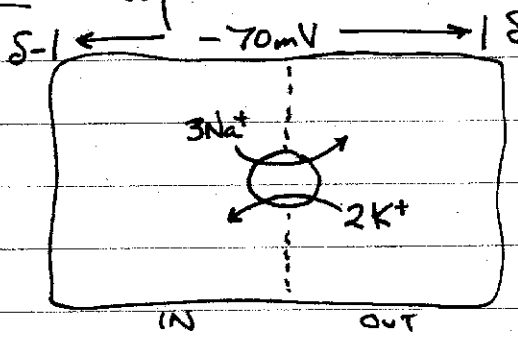
Q: How do we make it spontaneous?

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

$\Delta G \text{ (Total Xport)} = 3\Delta G(Na^+ \text{ out}) + 2\Delta G(K^+ \text{ in})$ eg.

$= +42.8$ kJ/mole

(NOT FAVORED)



BUT $ATP + H_2O \rightarrow ADP + \text{phosphate}$ $\Delta G^\circ = -31$ kJ/mole

$\Delta G = -43$ to -49 kJ

$$\Delta G^\circ + RT \ln Q$$

Surfaces, Membranes

↳ including any interface between two surfaces

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

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

Surface Tension

- Surf pressure is $\frac{F}{length}$ instead of $\frac{F}{area}$ $\Rightarrow$ ($\frac{J}{m^2}$ instead $\frac{J}{m^3}$)
- Surface free energy is $\frac{J}{m^2}$ instead of $\frac{J}{m^3}$

T, P

surface area

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

∴ liquids with very high surface tension form drops readily (a sphere has the lowest $\frac{surface}{volume}$) despite the fact that gravity disfavors drops.

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

Ethanol too

Molecular Interpretation

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

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 → air / water

water molecules at interface are unsatisfied.

∴ Cost to form a surface

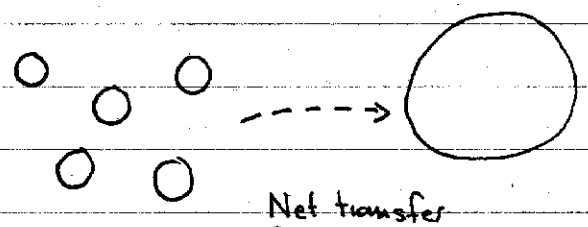
Water + Detergent → air / detergent / water

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

So they line up at interface

Not so bad.... ie. lowers energy of the surface

Vapor Pressure and Surface Tension



Net transfer of water from small drops to big

WHY? How?

→ Surface tension

→ Vapor Pressure

liquid ⇌ gas

$\left(\frac{\partial G}{\partial n}\right)_{P,T}$ ← Remember

Used to have: $\partial G = -S\,\partial T + V\partial P + \mu_{H_2O}\,\partial n_{H_2O}$

Now: $\partial G = -S\,\partial T + V\partial P + \gamma\partial A + \mu_{H_2O}\,\partial n_{H_2O}$

surface tension $\Rightarrow \left(\frac{\partial G}{\partial A}\right)_{P,T}$

Note γ here is NOT activity coefficient!

So we ultimately have to worry about

TOTAL CHEMICAL POTENTIAL

↓

Surface tension
electrical potential
chemical potential
(centrifugal) gravitational potential → either earth's or centrifuge-equivalent

Colligative Properties

- Depend on the collection of molecules
- Depend on the number of solute molecules,
  Ideally → 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 → determine molecular weight.

Classic examples: Freezing point depression, Boiling point elevation } auto anti-freeze

Boiling Point Elevation

$$A\ (\text{pure liquid}) \rightarrow A\ (g) \qquad K = \frac{a_A\ (\text{gas})}{a_A\ (\text{pure liquid})}$$

From what we learned before:

$$a_A\ (\text{gas}) = P_A\ (\text{atm})$$
$$a_A\ (\text{pure liquid}) = 1 \quad (\text{standard state})$$

$$\therefore \quad K = \frac{P_A}{1} = P_A \quad (\text{partial pressure}) \leftarrow \text{vapor pressure}$$

$$\ln \frac{K_2}{K_1} = \ln \frac{P_2}{P_1} = -\frac{\Delta H_{VAP}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \qquad \Delta H_{VAP} = \bar{H}_{gas} - \bar{H}_{liq}$$

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

Shows how this depends on T (assuming ~constant ΔH)

What must the pressure be in order to "boil" water at 37° C?

$\Delta\bar{H}_{VAP}^{H_2O} \approx 42{,}000$ J/mol

Q: ASSUMPTION?
A: ΔH_{VAP} independent of temperature

$P_1 = 1$ atm $\qquad P_2 = x$

$T_1 = 100°C = 373K \qquad T_2 = 37°C = 310K$

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

$$x = (e^{-2.75})(1\text{ atm}) = 0.064\text{ atm}$$

NOT ALL THAT LOW!

Melting Point Temperature

$X_s \rightarrow X_\ell$

(1) At equilib $\bar{G}_s = \bar{G}_\ell$

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

So let's raise T_1 by dT but also raise P by dP accordingly to maintain equilib

(2) $\therefore \quad \bar{G}_s + d\bar{G}_s = \bar{G}_\ell + d\bar{G}_\ell$

(2)-(1) leads to $d\bar{G}_s = d\bar{G}_\ell$

Remembering $d\bar{G} = -\bar{S}\,dT + \bar{V}\,dP$

then $-\bar{S}_s\,dT + \bar{V}_s\,dP = -\bar{S}_\ell\,dT + \bar{V}_\ell\,dP$

$$-\bar{S}_s \frac{\partial T}{\partial P} + \bar{V}_s = -\bar{S}_\ell \frac{\partial T}{\partial P} + \bar{V}_\ell$$

$$\frac{\partial T}{\partial P}(\bar{S}_s - \bar{S}_\ell) = \bar{V}_s - \bar{V}_\ell$$

$$\frac{\partial T}{\partial P} = \frac{\bar{V}_s - \bar{V}_\ell}{\bar{S}_s - \bar{S}_\ell} = \frac{\Delta \bar{V}_{fusion}}{\Delta S_{fusion}}$$

Since this is reversible at it's melting/fusion point,

$$\Delta S_{fusion} = \frac{\Delta H_{fusion}}{T}$$

$\therefore$ $$\frac{\partial T}{\partial P} = \frac{T\,\Delta V_{fusion}}{\Delta H_{fusion}}$$

General for phase transitions