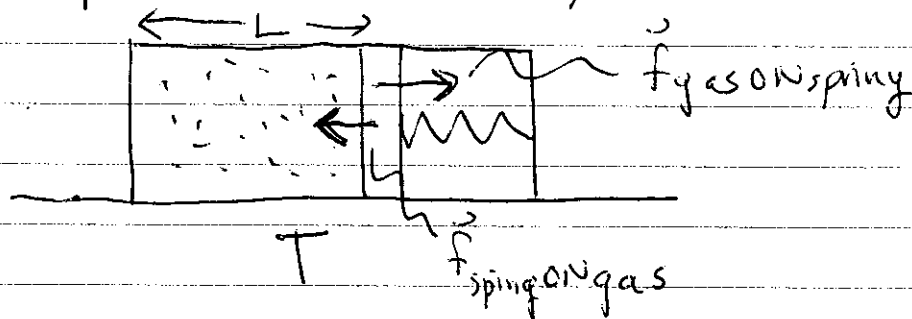


# Topic 8 Entropic Forces

Phy 347

①

gas pushes back on piston



• Newton's 3rd Law:  $\vec{f}_{\text{spring on gas}} = -\vec{f}_{\text{gas on spring}}$

• We found:  $f_{\text{gas on spring}} = -\frac{dF}{dL}$

• or generally:  $f = -\frac{dF}{dx}$  ; entropic force

where  $F = E(x) - TS(x)$

pressure:  $p = \frac{f}{A}$  or  $p = -\frac{dF}{dV}$  Volume

For ideal gas:  $F = \underbrace{N \frac{3}{2} k_B T}_E - T \underbrace{[N k_B (\ln(E^{3/2}) + \ln V)]}_S$

so

$$p = -\frac{dF}{dV} = T N k_B \left(\frac{1}{V}\right) = \frac{N k_B T}{V}$$

as expected

# Osmotic flow:

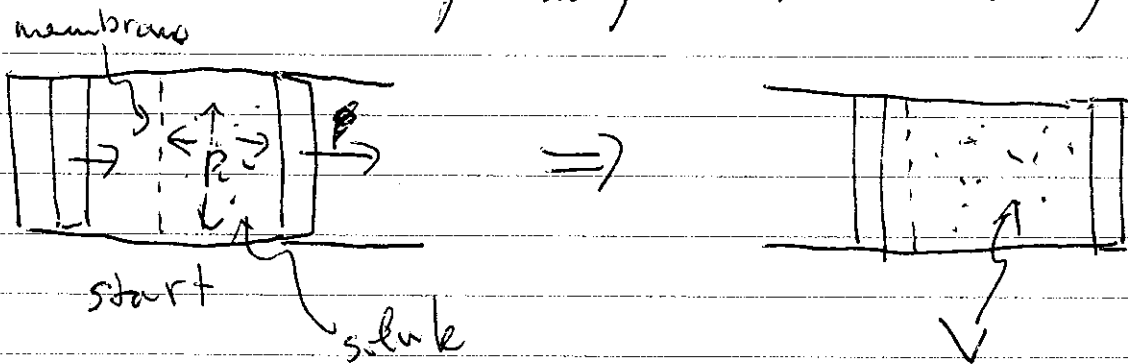
- Recall, that when there are different concentrations there is a flow

$$j = -D \frac{dC}{dx} \leftarrow \text{concentration gradient}$$

- If there are barriers, this can lead to pressure
- Biology: there are always concentration differences between the outside and inside of cells  
→ causes pressure on cell

Q: How does a cell withstand this pressure.

expt: you can lyse cells by putting them in a big enough concentration gradient.



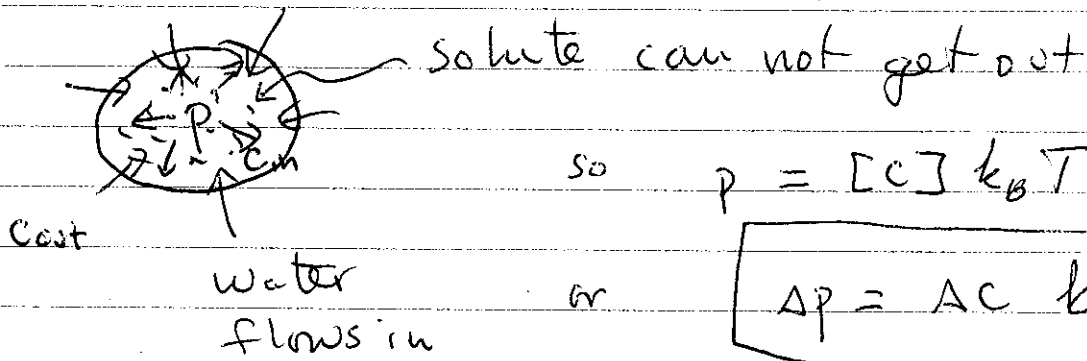
- Osmotic flow will push piston to right, so that solute becomes more dilute.
- Dilute solution is just like an ideal gas!

pressure due to solute,

$$p = \frac{N_{solute} k_B T}{V} \equiv \text{osmotic pressure}$$

$$[c] = N/V$$

example:



so  $p = [c] k_B T$

or  $\Delta p = \Delta c k_B T$

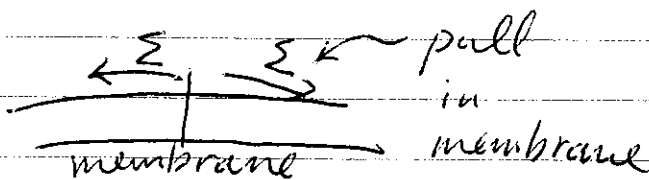
$$\Delta c = [c_{in}] - [c_{out}]$$

- cell contains  $[c] = 1.2 \times 10^{-4} M$  of protein
- osmotic pressure due to protein

$$p = \frac{(1.2 \times 10^{-4}) (6.02 \times 10^{23}) (1.38 \times 10^{-23}) (293)}{(1 \times 10^{-3})} = 300 \text{ Pa}$$

• Is 300 Pa significant for cell?

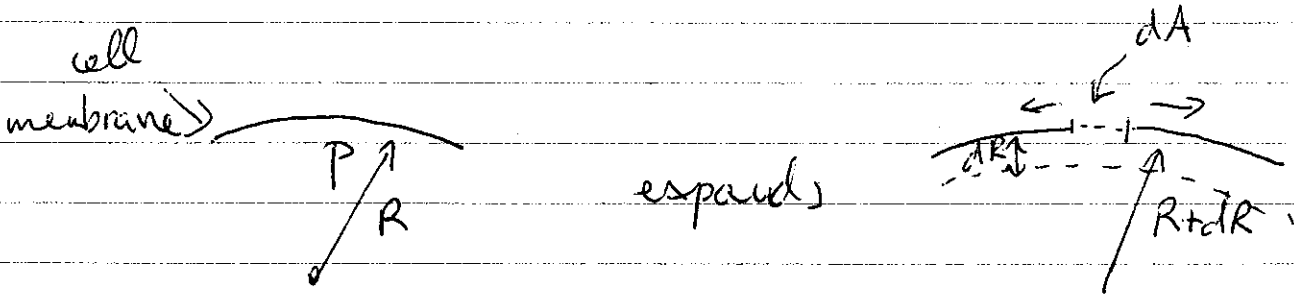
### Surface Tension



$$\Sigma = \frac{f}{L}$$

$\Sigma = \text{surface tension} = \frac{\text{force}}{\text{length}}$

- Surface tension: how hard is it to pull the membrane apart?
- Osmotic pressure pushes out on membrane causing the cell to expand.



- Pressure does work  $p \cdot dV$  against surface tension which costs energy  $\Sigma dA$

• Balancing these gives:

$$\Sigma = \frac{R p}{2}$$

- For cell with  $R = 10 \mu\text{m}$  &  $p = 300 \text{ Pa}$

$$\rightarrow \Sigma = 1.5 \times 10^{-3} \text{ N m}^{-1} = 1.5 \text{ pN/nm}$$

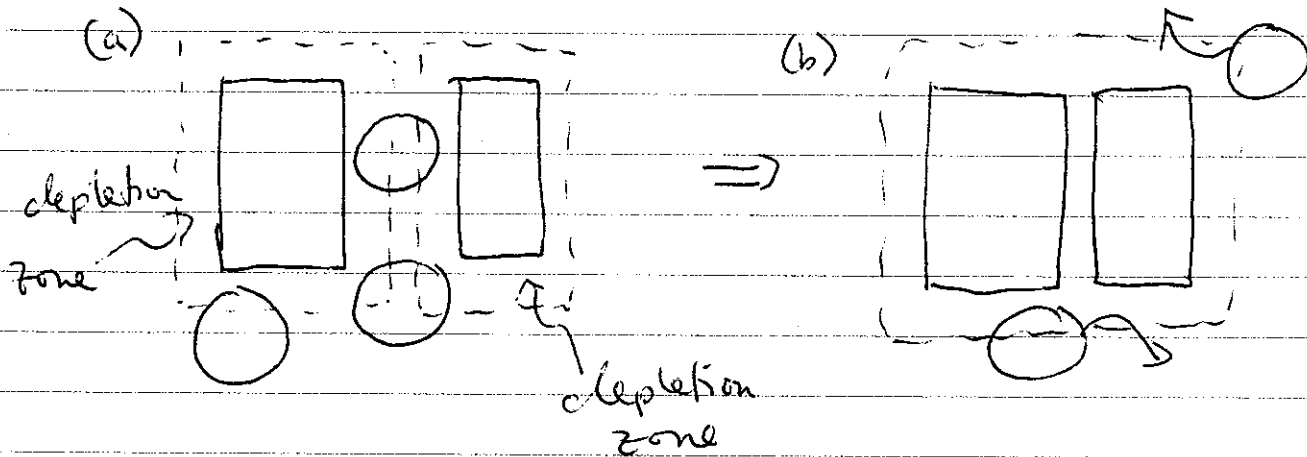
- Tension to rupture most cells  $\sim 3 \text{ pN/nm}$

$\Rightarrow$  osmotic pressure is significant to the stability of cells

- For  $[\text{Na}]$  in cells,  $[\text{c}] = 1 \text{ M} \rightarrow p \sim \text{kPa}$   
if  $\text{cost} = 0 \Rightarrow$  lyse in pure water

## Depletion Force:

Idea - big objects will find each other in a mixture of small objects

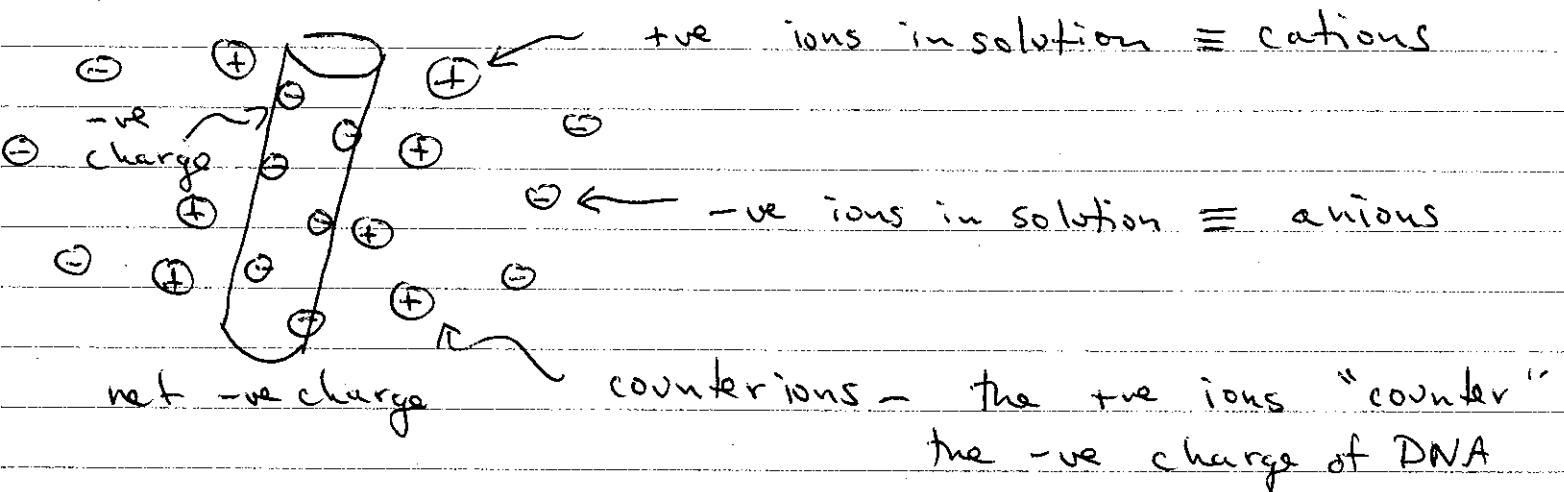


- in (a), solute between the 2 large objects is confined & has low entropy. getting out of this region would increase its entropy and so  $F$  would go down by  $-T\Delta S$
- Thus purely by increasing the entropy of the solute, big objects will attract each other
- This depletion force can be significant in cells and can help large proteins "find" each other
- Note: this is an extremely short range force unlike the electric force which is long range
- Thus increasing the "disorder" of the solvent can lead to the spontaneous assembly of large objects

## Charged Objects:

- so far we've ignored the charge of the solvent and the solute
- But, most biological molecules have charge, so how does that change things?

### DNA:



- How do the counterions distribute themselves around the charged macromolecule?

diffuse away  $\rightarrow$  greater  $S \Rightarrow \Delta F_s = -T\Delta S \downarrow$

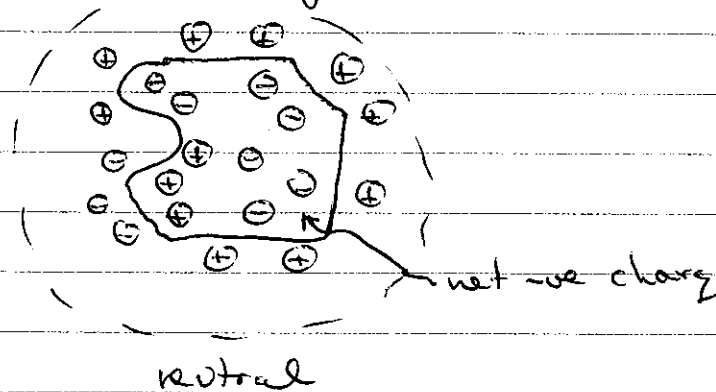
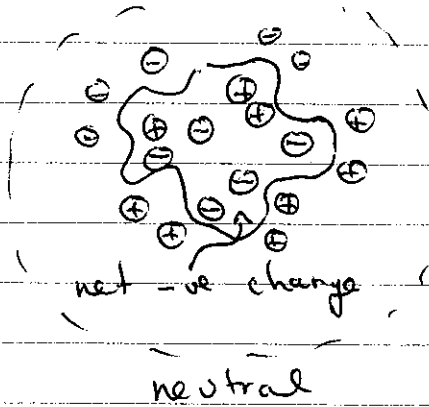
$\downarrow$   
lose electrostatic energy  
so  $E \downarrow \Rightarrow \Delta F_E = E \uparrow$

- thus there is a balance between gaining entropy and losing interaction energy

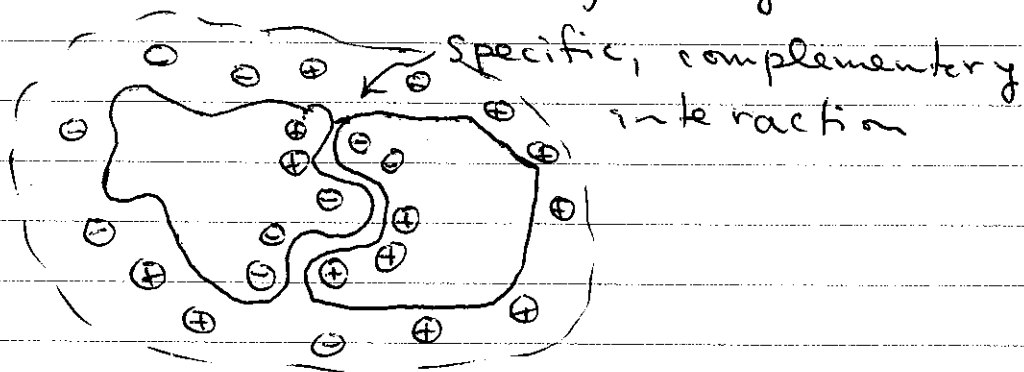
The result is that the counterions form a cloud around the macromolecule, so that from a distance it appears to have no charge  $\equiv$  screening

$\Rightarrow$  In solution, charged objects are screened and therefore the electrostatic (Coulomb) interaction's range is reduced from long to short.

Biology: this screening leads to specificity! Since macromolecules (ie. proteins) only interact @ short distances, they will see the detailed charge pattern of each other, and only interact with those which are complementary.

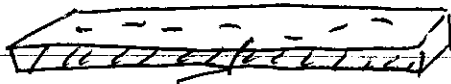
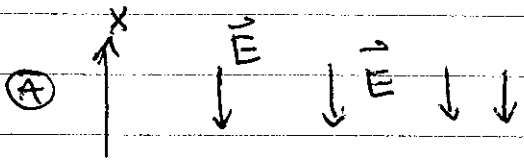


(if there was no screening, they would repel)



# Some first year physics:

How do the counterions screen?

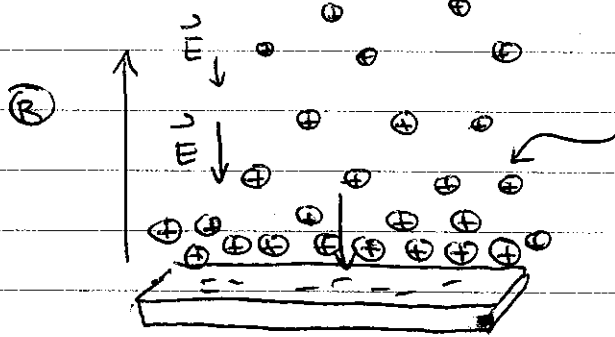


surface charge  $\sigma_q \sim [e/m^2]$

$$\vec{E} = -\frac{\sigma_q}{\epsilon} \hat{x}$$

(from Gauss's Law)

(B) counterions



• counterions screen the surface, ~~is~~ described by charge density  $\rho(x)$

• these +ve charges reduce the electric field in (A)

Find:

$$\frac{d\vec{E}}{dx} = -\frac{\rho(x)}{\epsilon}$$

(1)

strong screening

for water,  $\epsilon = 80\epsilon_0$

What is  $\rho(x)$ ?

Boltzmann: each +ve charge has potential energy  $\phi = eV(x)$

so

$$\frac{\rho(x)}{\rho(0)} = e^{-eV(x)/kT} \quad (2) \text{ from Boltzmann}$$

(9)

Now recall,  $E = \frac{dV(x)}{dx}$  (from 1st year physics)

Putting ① & ② together

$$\frac{d^2V}{dx^2} = - \frac{f_0}{E} e^{-eV(x)/kT}$$

Define:  $\bar{V}(x) = \frac{eV(x)}{kT}$

and

$$\boxed{l_B = \frac{e^2}{4\pi\epsilon_0 kT}} \equiv \text{Debye length}$$

$\equiv$  distance we can push two like charge particles together with  $k_B T$  of energy

so

$$\boxed{\frac{d^2\bar{V}}{dx^2} = -4\pi l_B f_0 e^{-\bar{V}}}$$

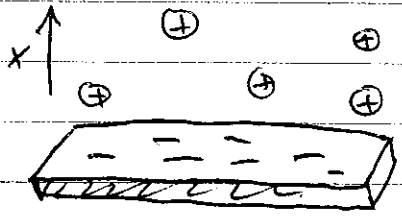
$\equiv$  Poisson-Boltzmann equation

- tells us how the counterions will distribute themselves around a charged object.

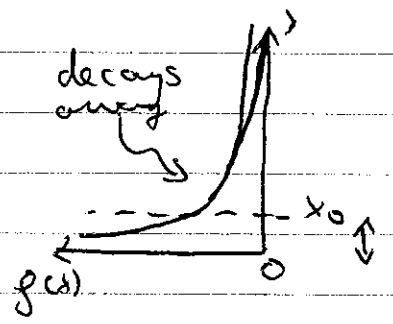
- Hard to solve, I won't ask you to solve it.

Find  $\bar{V}(x) \rightarrow f(x) = f_0 e^{-\bar{V}(x)}$

For charged surface



$$f(x) = \frac{f_0}{(1 + \frac{x}{x_0})^2}$$



• So counterions form a layer with characteristic thickness,  $x_0$

$$x_0 = \frac{e}{2\pi l_B \sigma_q}$$

• Will see some #'s later in assignments.

WATER:

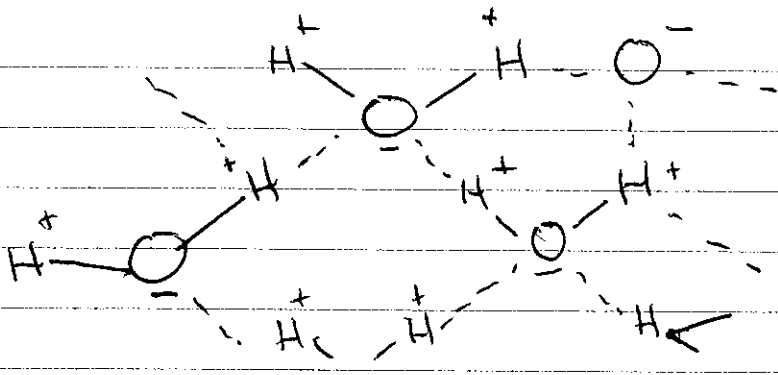
- why do oil & vinegar separate?

hypothesis: ① oil loses free energy due to some attractive interaction that brings the fat drops together

OR

② oil comes together because it allows the entropy of the water to increase a la depletion force.

Some unmixing is due to ①, but for water it is mostly ②.



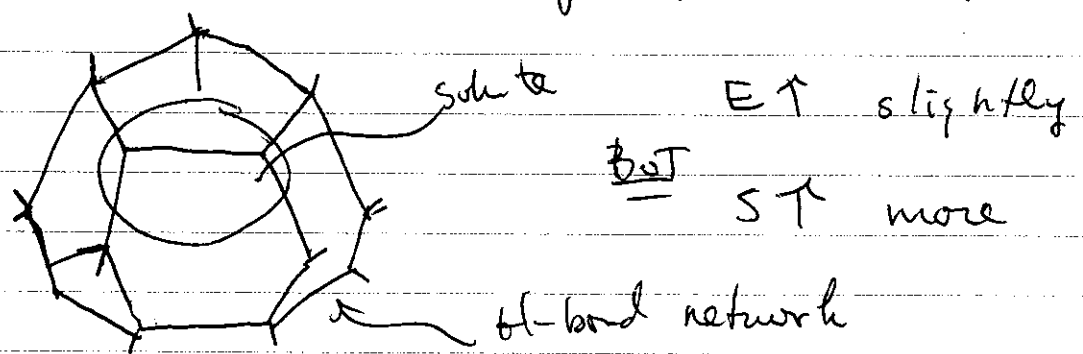
• H<sub>2</sub>O forms a lattice (tetrad) of ~~hydrogen~~ hydrogen bonds between molecules. = ice

• At higher temperatures, entropy wants to increase the disorder → liquid. But, in liquid H<sub>2</sub>O still makes many H-bonds.

scale: covalent ~ 50-350 k<sub>B</sub>T    H-bond ~ 9 k<sub>B</sub>T  
 VdW ~ 0.5-1.6 k<sub>B</sub>T

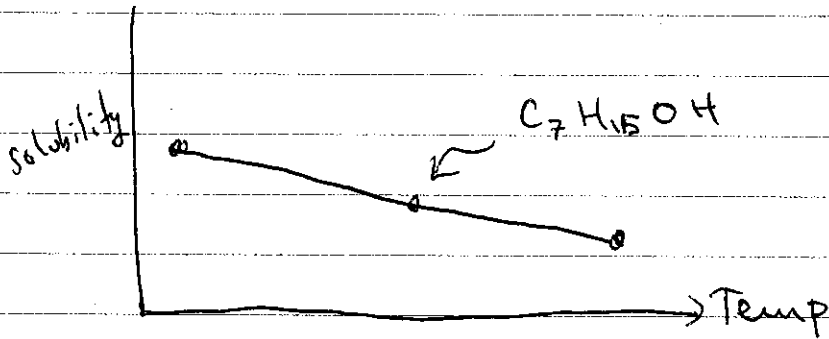
Solubility:

- Some substances (polar) mix well with water meaning that they don't alter the H-bond network
- Non-polar (no charge) do not fit well with H-bond network → hard to mix (like hydrocarbon)
- Water forms "clathrate" cage around solute

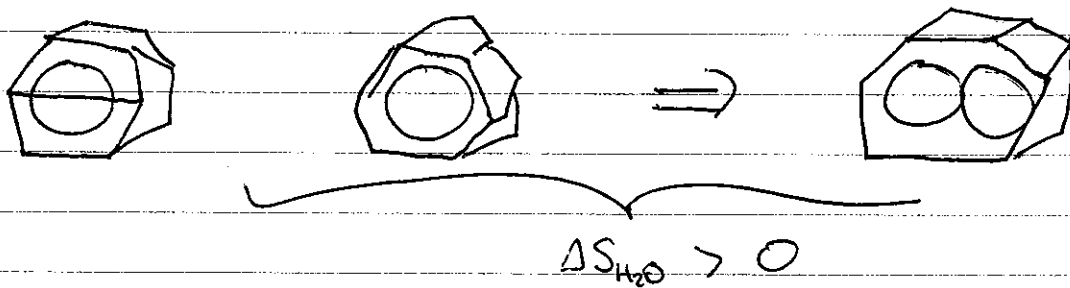


So mixing non-polar substance ~~increases~~ ~~the~~ ~~entropy~~ ~~of~~ ~~water~~ decreases the entropy of water.

- Thus solubility tends to decrease with temperature  
 $\Delta S_{\text{solute}} \uparrow$  but  $\Delta S_{\text{H}_2\text{O}} \downarrow$  and  $|\Delta S_{\text{H}_2\text{O}}| > |\Delta S_{\text{solute}}|$



Hydrophobic interaction:



- Water gains entropy when ~~two~~ non polar objects come to gether so  $\Delta F = -T\Delta S$  which should increase as  $T \uparrow$

- Expt: can favoure macromolecule assembly @ higher temperatures

e.g. microtubules assemble better @ higher temperature.