Lecture 2: Molecular Forces, Water & Hydrogen Bonds

Key Terms:

- Enthalpic Interactions:
  - Electrostatics
  - van der Waals
  - Hydrogen bonds
- Polar bonds
- Electronegativity
- Polar solvents
- Water structure
- Hydrogen bond (donor & acceptor)
- Driving force for dissolving ions
- Hydrophilic (polar) compounds.
- Hydrophobic (nonpolar) compounds and entropy of water.
- Amphipathic/amphiphilic compounds.

Key Concepts:

- Importance of weak interactions in biological systems
- Identification and properties of hydrogen bonds
- Contribution of enthalpy and entropy to molecular behavior

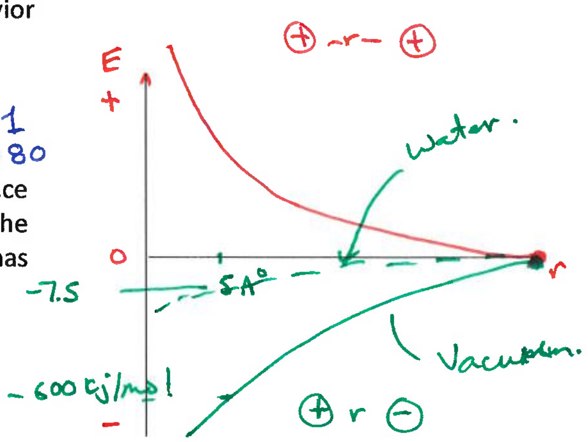
2A. Molecular interactions

i) Electrostatics: The force between two charged particles is:

$$E \propto \frac{q_1 q_2}{Dr}$$

q_1 q_2 Vac $D=1$ H_2O $D=80$

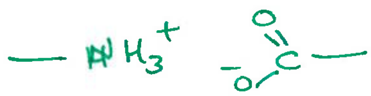
The force depends on the charges of the particles (q_1, q_2), distance (r) between the two charges, and the dielectric constant (D) of the media. The dielectric constant depends on the solvent. Water has a high dielectric constant.



How strong are electrostatic interactions?

Na^+ Cl^- = ~-600 kJ/mol *in vacuum* (r = 5Å)

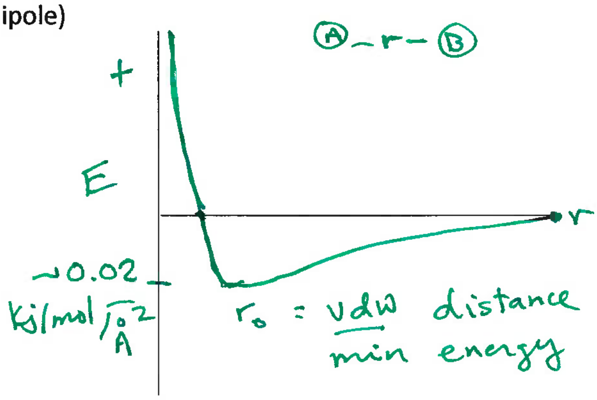
Given that the dielectric constant of water is 80, what is the energy of interaction in water (D=1 in vacuum).

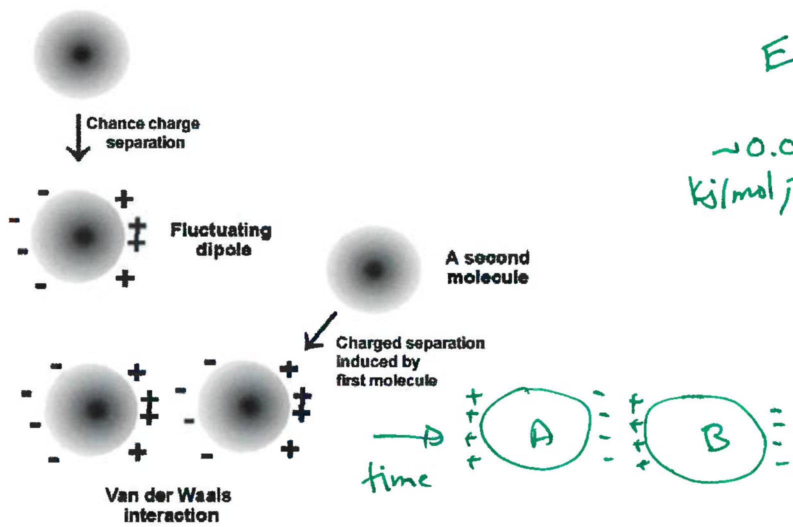


E drops to ~-7.5 kj/mol

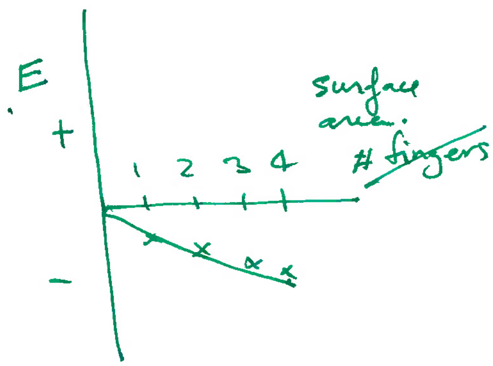
Very weak. → allows reversibility

ii) van der Waals (induced dipole-induced dipole < induced dipole-dipole < dipole-dipole) – an electrostatic interaction that does **not** involve **formal charges**. Partial charges may be temporary (induced dipole) or permanent (dipole). van der Waals interactions between molecules with permanent dipoles are generally stronger.





Although weak, the effects of van der Waals are easily observed→



Boiling points of hydrocarbons:

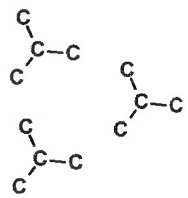
isobutane: 261 K

butane: 272 K

Same number of carbons, why the difference in boiling points?

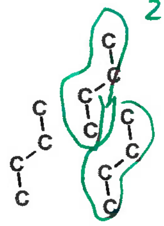
How strong are van der Waals forces?

261



low surface area low vdW

272



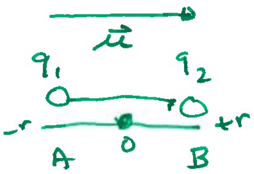
high surface Area high vdW

Reflection: *What is an advantage of weak interactions?*

2B. Polar bonds & Molecules

Polar Bond: A bond is polar if there is a *significant* difference in the electronegativities of the participating atoms, giving an *appreciable* dipole moment. (The electronegativities increase across the periodic table).

1 H 2.1							2 He
3 Li 1.0	4 Be 1.5	5 B 2.0	6 C 2.5	7 N 3.0	8 O 3.5	9 F 4.0	10 Ne



Bond	|Δ e|	
δ_0 C—C δ_0 (2.5, 2.5)	0.0	Non-polar
δ^- C—H δ^+ (2.5, 2.1)	0.4	
δ^+ C—N δ^- (2.5, 3.0)	0.5	
C—O (2.5, 3.5)	1.0	Polar.
δ^- O—H δ^+ (3.5, 2.1)	1.4	

The **dipole moment, μ,** is defined by the following equation: $\boxed{\mu = \sum_{\text{All atoms}} qr}$.

The dipole moment is proportional to the difference in the electronegativities of the two atoms: $|\mu| = \Delta E$

Reflection: *How do we know which bonds are polar?* $\rightarrow |\Delta e| > 0.4$

Polar molecule: A molecule is considered polar if it is has a *permanent dipole moment* associated with it. *Is CO_2 a polar molecule? Why or why not?*

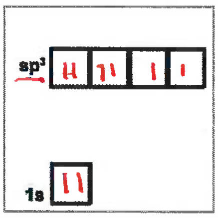
$\overleftarrow{\mu_1}$ $\overrightarrow{\mu_2}$

O=C=O

$\mu_{TOT} = \vec{\mu}_1 + \vec{\mu}_2$

$= 0$

2C. Structure of Water

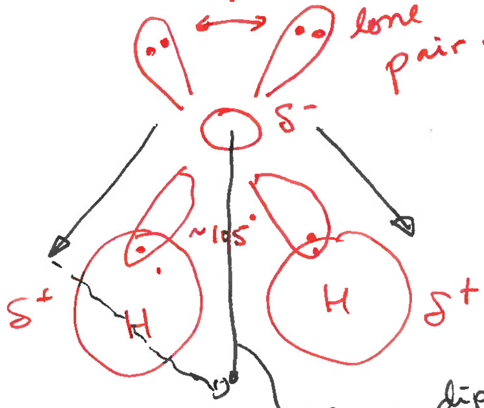


i. Oxygen has 8 electrons. The molecular orbitals in water are complex, however we can understand most of the properties of water by assuming that oxygen forms sp^3 hybrid orbitals.

ii. The orbitals in oxygen are populated such that two orbitals are filled and two contain one electron each.

iii. The filled orbitals cannot form bonds and are often called *lone pairs.*

iv. The half-filled orbitals participate in the formation of a *sigma* bond between oxygen and hydrogen.

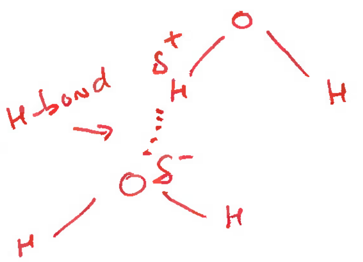


Reflection: *Is water a polar solvent?* Yes.

large dipole moment ∴ water polar solvent. → high dielectric — effective screening of

The interaction between the oxygen on one molecule and the hydrogen on another is an example of a **hydrogen bond.**

Total Energy 90% electrostatic
10% electron sharing

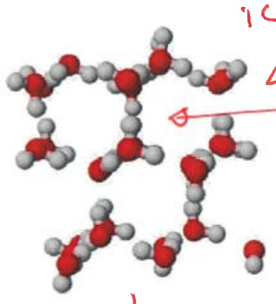


Biochemical Significance of Hydrogen Bonds in Water:

i). In ice, the hydrogen bonds cause the formation of cavities in the ice, lowering the density of the solid.

ii) In liquid water, the hydrogen bonds persist, and are transient, generating small short-lived (ns lifetime) clusters of "ice" in liquid water.

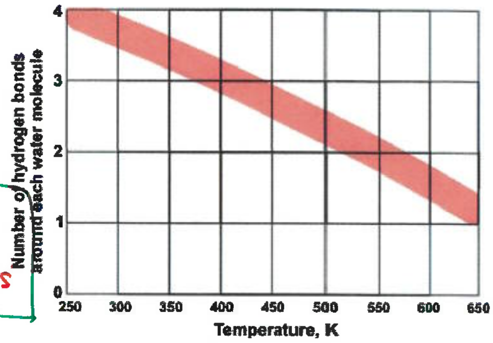
iii) Hydrogen bonds are present over a wide temperature range 3-3.5 bonds/water at room temperature. Note that water molecules in vapor (i.e. steam) can form hydrogen bonds. This allows water to absorb heat without a large increase in temperature, giving water a high heat capacity.



ice
4 H bonds / molecule
empty space

liq H_2O
2 - 3 H bonds

H_2O vap



2D. General Description of Hydrogen Bonds

i) Formation of H-bonds is primarily an electrostatic attraction between:

- Electropositive hydrogen, attached to an electronegative atom is the hydrogen bond **donor** (*i.e.* NH).
- Electronegative hydrogen bond **acceptor** (*e.g.* the lone pairs of oxygen in the case of water, or C=O group of an amide).

*Note that the proton is **NOT** transferred to the acceptor, it remains covalently bonded to the donor. The Hydrogen bond is the interaction between the donor and acceptor.*

δ^- δ^+ δ^-
N—H ...... O=C
donor acceptor

δ^- δ^+ δ^-
Y—H X

donor
N—H

Acceptor
N

- The energy released when H-bonds form depends on the distance and angle of the bond.
  You should know the ideal distance and angle. This will be explored in the next recitation.

2E. Solvation – It is all about reaching the lowest energy.

ΔH° : Enthalpy – A change in the electronic configuration of the system that either releases heat ($\Delta H^\circ < 0$) or absorbs heat ($\Delta H^\circ > 0$). **Release of heat is favorable.**

ΔS°: Entropy – A change in the number of configurations of the system (disorder). Either increasing the disorder ($\Delta S^\circ > 0$) or decreasing the disorder ($\Delta S^\circ < 0$). **Increase in entropy is favorable. Ordering systems is unfavorable, it takes energy.**

"I blame entropy."

Balance of net changes in enthalpy and entropy determine the equilibrium position of the reaction.

$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$

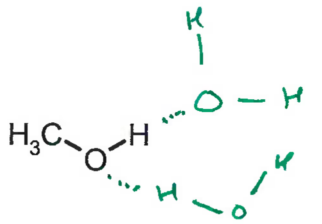
What is the sign of ΔG° if a compound is very soluble in water? Positive or negative?

$A \rightleftharpoons B$

ΔG° defines eq position.

$X_{solid} \rightleftharpoons X_{Aq}$ $\Delta G^\circ < 0$ for fav reaction

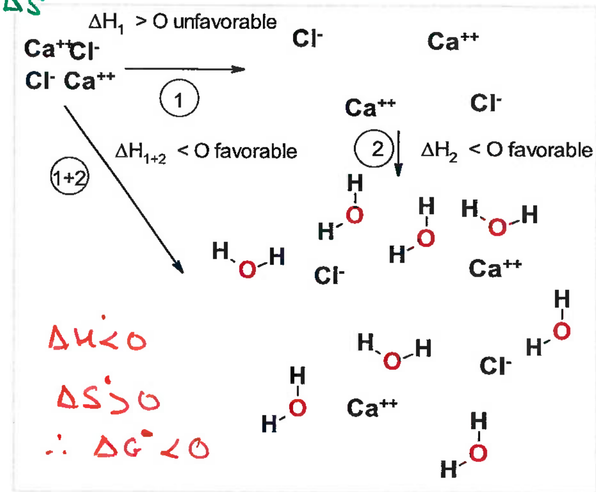
i) Hydrophilic (water-loving, polar) compounds (*e.g.* methanol):



- $\Delta H<0$ – usually favorable
- $\Delta S>0$ – always favorable (entropy of mixing, see separate handout)

large neg $\Delta G^\circ = \underset{\text{neg}}{\Delta H^\circ} - T\overset{\text{pos}}{\Delta S^\circ}$

ii) Solvation of ions ($\Delta H<0$ & $\Delta H>0$)

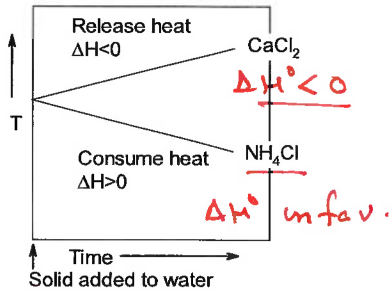


- Energy is required to break the ionic bonds in the crystal. $\Delta H^\circ >> 0$. Heat was added to system, very unfavorable.
- A large dipole moment on water means that the solvent molecules can interact favorably with charged solute molecules. This is energetically very favorable. $\Delta H^\circ<0$, releases heat.
- Overall ΔH° can be positive (unfavorable) or negative (favorable), depending on the balance of these two terms. It depends on the salt. For $CaCl_2$ heat is released, i.e. the interactions with water release more heat than was consumed to break the ionic bonds.

Hypothetical reaction for forming a solution of Ca+Cl, the atoms are first separated in vacuum (1) and then the ions are dissolved in water (2). The net change in enthalpy is negative, heat is released when $CaCl_2$ is dissolved in water.

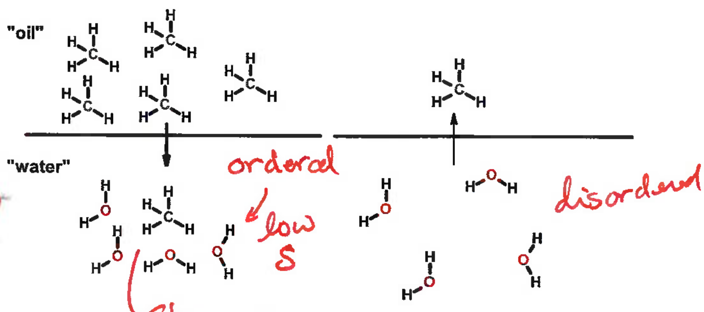
Question: *When ammonium ~~sulfate~~ chloride (NH_4Cl) dissolves in water the solution becomes cold, indicating that the reaction consumes heat, and therefore should be unfavorable from an enthalpic point of view. Why is ammonium sulfate still very soluble in water?*

large ΔS° increase drives the solubility

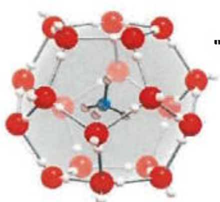


iii) Hydrophobic (water-hating, nonpolar) compounds (*e.g.* methane).

$\Delta H<0$ – favorable (stronger vdw with water than non-polar solvent)



If heat is released when methane goes into water (favorable from an enthalpic point of view), why is its solubility low?

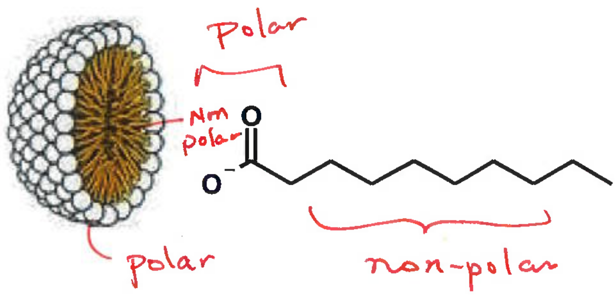


$\underset{\text{pos}}{\Delta G^\circ} = \underset{\text{neg.}}{\Delta H^\circ} - \underset{\text{neg.}}{T\Delta S^\circ}$

$NP_{pure} \rightarrow NP_{Aq}$

http://chem.ps.uci.edu/~kcjanda/Group/Research_hydrates.html

iv) Amphipathic (or amphiphilic) compounds are both polar (usually charged) and have a substantial nonpolar section (*e.g.* fatty acids). These can form micelles if the nonpolar part is sufficiently large. Micelles are aggregates of amphipathic molecules that sequester the nonpolar part on the inside, much like the inside of an orange.



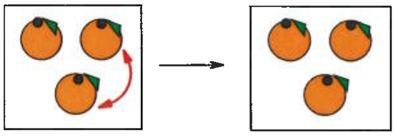
Entropy of Mixing:

One thermodynamic effect that favors high solubility of solutes in water (or any other solvent) is the increase in entropy when two pure compounds are mixed. The entropy of a system (S) can be calculated using the relationship derived by Boltzmann, which relates the number of conformations of a system (W) to the entropy of the system:

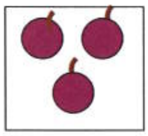
$$S = R \ln W$$

- Crystals have an entropy of zero because all of the atoms are fixed in position and there is only one way to arrange the atoms.
- Solutions of pure substances have low entropy because all of the molecules are identical. Since there can be a slight variation in the positon of the molecules, as well as their orientation, the entropy is not quite zero. If we make the assumption that all molecules in solution are in the same orientation and their positon is fixed to defined points in space, then the entropy of the liquid is also zero because all of the particles are interchangeable with each other.

*When two pure substances are mixed, there is an increase in entropy because we now have a mixture of two different molecules and there are many ways to arrange the molecules because the molecules are different. This is referred to as the **entropy of mixing**.*

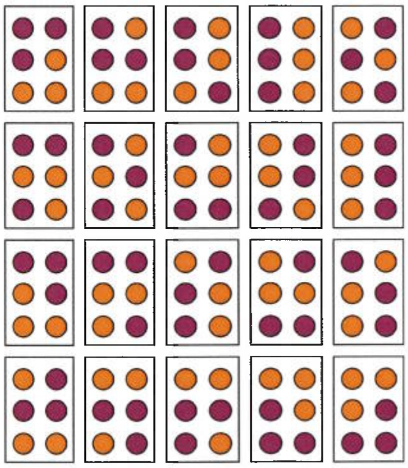


In the following simple example, let's look at the entropy of a bowl of fruit. If we have three oranges in the bowl, all of the oranges are identical and there is only one distinguishable way to organize the oranges, so the entropy of pure oranges is zero. If we interchange the position of two identical oranges, the system still looks the same.



Similarly, if we have three plums in a bowl the entropy of the plums is zero as well.

Now if we mix the oranges and plums, there are many different ***distinguishable*** ways to organize the oranges and plums. In this example, there are exactly 20 different ways to organize the six pieces of fruit, as shown below. Thus the entropy of the mixture is: $S_{MIX}=R\ln 20 = 24$ J/mol-K. This is also equal to the overall entropy changes, since the entropy of the reactants (unmixed fruit) was zero: $\Delta S = S_{Products}-S_{Reactants} = (24-0) = 24$ J/mol-K.



We can calculate the number of possible configuration of the mixed fruit using combinatorial theory:

The number of ways of arranging n things is n!, which is 6x5x4x3x2x1 in this case.

However, the three oranges and three plums are identical, so this reduces the number of possible arrangements by $(3!)^2$, since there are 3x2x1 ways of arranging three objects. The total number of ways of arranging the three oranges and three plums is: $6!/(3!\,3!) = 20$.

Entropy and the Hydrophobic Effect:

Non-polar compound are not very water soluble. The low solubility is due to the entropy changes of the water. If we add a non-polar liquid (e.g. butane), the entropy of the dissolved butane is positive and favorable because it is no longer in pure butane. However, the water interacts with the dissolved butane by forming a cage of organized hydrogen bonded water around the butane, as illustrated on the right. This causes a large decrease in the entropy of the water, much more than the entropy of mixing, so the overall entropy change is negative, or unfavorable.