Correction: $G = H + TS$ is true even if not constant temp and pressure.

We showed last week that:

$$\Delta G = \Delta H - T\Delta S$$ does require constant T, P

Can look up ΔH_f° (or H_f°) and $\bar{S}^\circ$ (or $\bar{G}_f^\circ$) in the Appendix.

We saw that this allows calculation of ΔG_{RXN}

We showed friday, that this allows prediction of the potential spontenaity of the reaction.

Tables are at 25°C and 1 atm.

As before, what about other T and P?

IF (and this is NOT true for protein folding). ΔH and ΔS are independent of temperature

THEN

$$\Delta G_{T_2} = \Delta H_{25°C} - T_2 \Delta S_{25°C}$$

SINCE

$$\Delta G_{25°C} = \Delta H_{25°C} - (298K)\Delta S_{25°C}$$

SUBTRACTING

$$\Delta G_{T_2} - \Delta G_{25°C} = 0 + (298 - T_2)\Delta S_{25°C}$$

This means that:

If $\Delta S < 0$, then ΔG increases (less spont) with T↑ → reaction leads to more order ⇒ Increased T disfavors the reaction

If $\Delta S > 0$, then ΔG decreases (more spont) with T↑ → reaction leads to more disorder ⇒ Increased T favors the reaction

---

We can manipulate the previous equations to solve for this in terms of ΔH and T_2

$$\frac{\Delta G_{T_2}}{T_2} = \frac{\Delta H_{25}}{T_2} - \Delta S_{25}$$

$$\frac{\Delta G_{25}}{298K} = \frac{\Delta H_{25}}{298K} - \Delta S_{25}$$

Subtract →

$$\frac{\Delta G_{T_2}}{T_2} - \frac{\Delta G_{25}}{298} = \frac{\Delta H_{25}}{T_2} - \frac{\Delta H_{25}}{29} - \cancel{\Delta S_{25}} + \cancel{\Delta S_{25}}$$

$$\frac{\Delta G_{T_2}}{T_2} = \frac{\Delta G_{25}}{298} + \Delta H_{25}\left[\frac{1}{T_2} - \frac{1}{298K}\right]$$

If ΔH and/or ΔS depends on temperature over 298K → T_2 then

$$\frac{\Delta G_{T_2}}{T_2} = \frac{\Delta G_{298}}{298K} - \int_{T_1}^{T_2} \frac{\Delta H(T)}{T^2}\, dT$$

(will not show how we got this).

easy to derive back

Pressure Dependence of G

$$G(P_2) - G(P_1) = \int_{P_1}^{P_2} V\,dP$$

IF constant volume

THEN $G(P_2) - G(P_1) = V(P_2 - P_1)$

IF constant volume and an ideal gas

THEN $G(P_2) - G(P_1) = \int_{P_1}^{P_2} \frac{nRT}{P}\,dP = nRT \ln P_2/P_1$

We have to apply this to each product and to each reactant (not blindly to the final reactions).

IF all products and reactants are NOT gases,
THEN $\Delta V = V_{PRODUCTS} - V_{REACTANTS}$

IF one or more of products and reactants IS a gas, then the gas volume dominates all other volumes

$\Delta G_{P_2} - \Delta G_{P_1} = \Delta V (P_2 - P_1)$

THEN

$$\Delta G_{P_2} - \Delta G_{P_1} = \Delta n RT \ln P_2/P_1$$

Phase Changes

If a phase change takes place at it's equilibrium temperature and pressure

THEN $\Delta G = 0$ (equilibrium!)

To calculate at other T's, etc. do as previously.

WATER — IT DEFINES US!!

$$NaCl(s) \longrightarrow Na^+(g) + Cl^-(g)$$

$$\Delta H^\circ_{298} = +785 \text{ kJ/mol}^{-1}$$

Must put in lots of heat.
Makes sense: strong ionic attraction

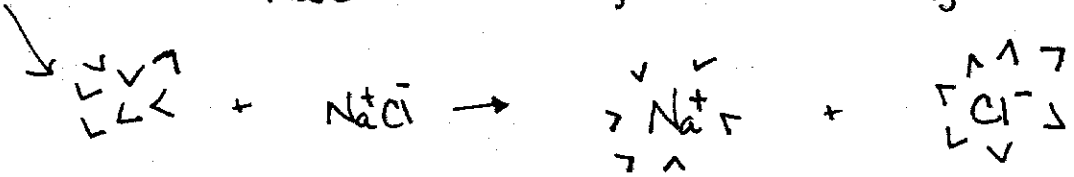
$$NaCl(s) + \infty H_2O(l) \longrightarrow Na^+(aq) + Cl^-(aq)$$

$$\Delta H^\circ_{298} = +4 \text{ kJ/mole}$$

20-Fold decrease! WHY? ⇒ water solvation

Why include?

$$Na^+Cl^- \rightarrow Na^+(g) + Cl^-(g) \quad \text{VERY UNFAVORABLE}$$



$$NaCl\,(s) \longrightarrow Na^{+}\,(aq) + Cl^{-}\,(aq)$$

Use data in Table A.5 (p. 749)

NaCl(s) - about strength of a covalent bond!

$$\Delta H_{298} = [-240.12 - 167.16] - [-411.15] = -3.87\ kJ\ mol^{-1}$$

$$\Delta S_{298} = [59.0 + 56.5] - [72.13] = +43.4\ kJ\ K^{-1}\ mol^{-1}$$

Entropy increases a bit...
Predict that rxn should go more to right at higher temp (salt more soluble)
We know this.

Book discusses covalent bonds (~400 kJ/mol)
versus hydrogen bonds (~15-20 kJ/mol)

But net H-bond strength is less.

"This weak bond becomes even weaker in aqueous solution"

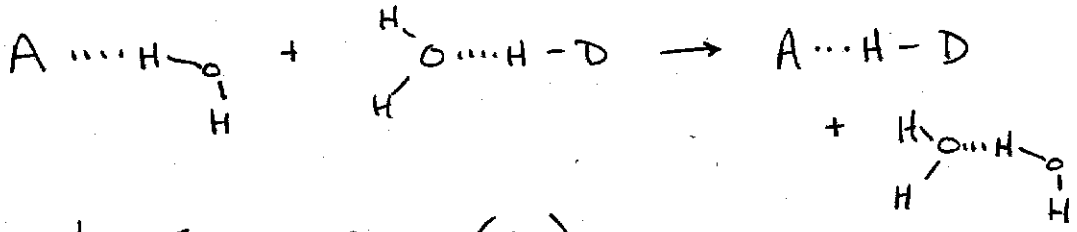
I'm not sure that's a proper way to phrase it.

Everything is relative
or rather it's the NET or bottom line that matters.

In other words,

$$A + H\text{-}D \rightarrow A\cdots H\text{-}D$$

should <u>really</u> be written



AND IT'S THE OVERALL (NET) energy that is important.

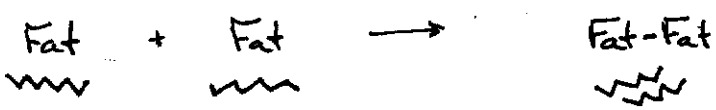
Typically, the net for the ~~[illegible]~~ above, for most protein/DNA donors/acceptors

is about ~~[illegible]~~ -5 kJ/mol ≈ 0

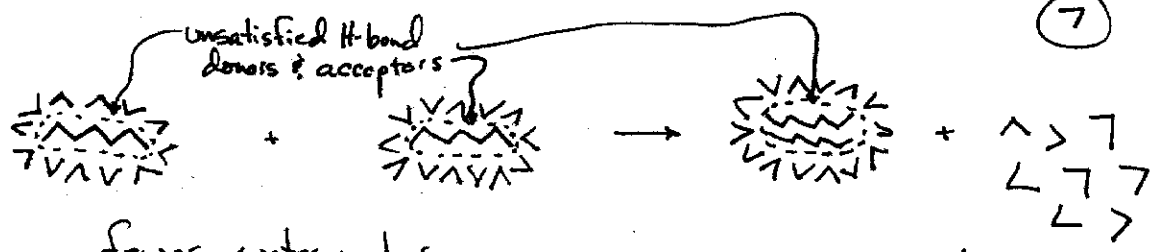
$(\sim -(1 \text{ to } 2 \text{ kcal/mol}))$

<u>NOT MUCH</u>. Some argue it's even less than that...

<u>Hydrophobic "interactions"</u>



favorable → <u>Why?</u>



fewer water-water interactions?

Many ordered waters.

More water-water interactions?

More disordered waters.

At the "oil"-water interface, there are "unsatisfied" H-bond donors and acceptors.

So nature minimizes the interface!
Oil "wants" to aggregate, not because "it" really wants to, but because the water wants it to

(Really → lower energy of whole system).

Examples Table 3.2 p. 105

Simple, model α-helix → coil ΔH° = 4.5 kJ/mole/amide (≈1 H-bond)
ΔS° = ?

Double-helix to ss (RNA): $\Delta H^\circ \approx 40$ kJ/mol/base pair
(DNA): ≈ 35 kJ/mol/base pair

More H-bond equivs than we might have thought. Why?