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

We showed last week that:

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

(f°)

Can look up $$\Delta H_f$$ and $$\Delta S^0$$ (or $$\Delta G^0_f$$) in the Appendix.

We saw that this allows calculation of $$\Delta G_{\text{rxn}}$$.

We showed Friday, that this allows prediction of the potential spontaneity 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), $$\Delta H$$ and $$\Delta S$$ are independent of temperature.

THEN

$$\Delta G_T = \Delta H_{25} - T \Delta S_{25}$$

SINCE

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

Subtracting

$$\Delta G_T - \Delta G_{25} = 0 + (298 - T) \Delta S_{25}$$
This means that:

If $\Delta S < 0$, then $\Delta G$ increases (less spontanous) with $T \uparrow$
If $\Delta S > 0$, then $\Delta G$ decreases (more spontanous) with $T \uparrow$

We can manipulate the previous equations to solve for this in terms of $\Delta H_{298}$ and $T_2$

\[
\frac{\Delta G_{T_2}}{T_2} = \frac{\Delta H_{298}}{T_2} - \Delta S_{298}
\]

\[
\frac{\Delta G_{298}}{298K} = \frac{\Delta H_{298}}{298K} - \Delta S_{298}
\]

Subtract

\[
\frac{\Delta G_{T_2}}{T_2} - \frac{\Delta G_{298}}{298} = \frac{\Delta H_{298}}{T_2} - \frac{\Delta H_{298}}{298} - \Delta S_{298} + \Delta S_{298}
\]

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

If $\Delta H$ and/or $\Delta S$ depends on temperature over $298K \rightarrow T_2$ then

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

(Will not show how we got this).
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** \[ G(p_2) - G(p_1) = \int_{p_1}^{p_2} \frac{nRT}{P} dP = nRT \ln \frac{p_2}{p_1} \]

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** \[ \Delta V = V_{products} - V_{reactants} \]

\[ \Delta G_{p_2} - \Delta G_{p_1} = Delta \frac{RT \ln \frac{p_2}{p_1}}{P} \]

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

**THEN** \[ \Delta G_{p_2} - \Delta G_{p_1} = \Delta n RT \ln \frac{p_2}{p_1} \]
Phase Changes

If a phase change takes place at its equilibrium temperature and pressure

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

To calculate at other Ts, etc. do as previously.

---

WATER — IT DEFINES US!!

\[ \text{NaCl (s)} \rightarrow \text{Na}^+ (g) + \text{Cl}^- (g) \]

\[ \Delta H_{298}^\circ = +785 \text{ kJ/mol}^{-1} \]

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

\[ \text{NaCl (s)} + \infty \text{H}_2\text{O}(l) \rightarrow \text{Na}^+ (\text{aq}) + \text{Cl}^- (\text{aq}) \]

\[ \Delta H_{298}^\circ = +4 \text{ kJ/mole} \]

20-fold decrease! WHY? water solvation.

\[ \text{Na}^+ \text{Cl}^- \rightarrow \text{Na}^+ (g) + \text{Cl}^- (g) \]

VERY UNFAVORABLE
\[ \text{NaCl (s)} \rightarrow \text{Na}^+ (aq) + \text{Cl}^- (aq) \]

Use data in Table A.5 (p. 749) for NaCl(s) - about strength of a covalent bond!

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

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

Entropy increases a bit...

Predict that NaCl 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 not 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,

\[ A + H-D \rightarrow A \cdots H-D \]

should really be written

\[ A \cdots H-O_i + H^+O\cdots H-D \rightarrow A \cdots H-D + H_2O \]

AND it's THE OVERALL (NET) energy that is important.

Typically, the net for the above, for most protein/DNA donors/acceptors is about \(-5 \text{ kJ/mol} \approx 0\)

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

NOT MUCH. Some argue it's even less than that...

---

Hydrophobic "interactions"

\[ \text{Fat} + \text{Fat} \rightarrow \text{Fat-Fat} \]

favorable \(\rightarrow\) Why?
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).

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Examples Table 3.2 p.105

- α-helix → coil
  \[ \Delta H^\circ = 45 \text{kJ/molamide} \]
  \[ \Delta S^\circ = ? \]

- Double-helix to ss (RNA): \[ \Delta H^\circ \approx 40 \text{kJ/mol base pair} \]
  (DNA): \[ \Delta H^\circ \approx 35 \text{kJ/mol base pair} \]

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