Previously, in Chapter 2, we saw that for simple heating or cooling (no phase change, or reaction).

$$\Delta H = nC_p(T_2 - T_1) = C_p(T_2 - T_1)$$

(what is difference between $\bar{C}_p$ and $C_p$?)

But at constant $V$,

$$\Delta E = C_v(T_2 - T_1)$$

What about $\Delta S$ for heating/cooling?

We know that at:

$$\Delta S = \int_{T_1}^{T_2} \frac{dq_{rev}}{T}$$

but $dq = C \, dT$

so

$$\Delta S = \int_{T_1}^{T_2} \frac{C \, dT}{T}$$

At constant $P$, $C = C_p = constant$

IF $C_p$ is independent of temperature then

$$\Delta S = C_p \int_{T_1}^{T_2} \frac{dT}{T} = C_p \ln \frac{T_2}{T_1}$$

Similarly, at constant $V$, and $C_v$ independent of $T$

$$\Delta S = C_v \int_{T_1}^{T_2} \frac{dT}{T} = C_v \ln \frac{T_2}{T_1}$$
The above is well and good for simple heating with no phase transitions or other chemical changes...

Therefore, 

\[ \Delta S = \left( \frac{C_p A}{C_p A} \right) T_A + \Delta S_A + C_p A T_A \]

Similarly for \( \Delta S \) at some new temperature \( T_B \):

\[ \Delta S = \left( \frac{C_p B}{C_p B} \right) T_B + \Delta S_B + C_p B T_B \]

Before, if we wanted \( \Delta H \) at some new temperature we could use:

\[ \Delta H = \Delta H_f^0 (T_f - T_i) + \Delta H_t + C_p (T_f - T_i) \]

For constant p (p. 47 Chapter 2)
\[ \Delta S \] for phase transitions

\[ \Delta S = \frac{q_{\text{rev}}}{T} \]

If the reaction phase transition occurs at the temperature \( T_m \) at which the transition is reversible (e.g. melting ice at 0\(^\circ\)C or condensing steam at 100\(^\circ\)C), then the process is reversible, and therefore the measured heat \( (\dot{q}_m) \) is \( q_{\text{rev}} \)

and \[ \Delta S = \frac{\dot{q}_m}{T_m} \]

We have seen in the homework how this is useful.

So we know how to figure \( \Delta S \) for temp changes and for (isothermal) phase changes.

Often we need both

\[ \text{ice (-20^\circ C)} \rightarrow \text{ice (0^\circ C)} \rightarrow \text{water liq (0\^\circ C)} \rightarrow \text{water liq (100\^\circ C)} \rightarrow \text{etc.} \]

Pressure dependence \[ S_p^2 - S_p^1 = -nR \ln \frac{P_2}{P_1} \] (gases)
Gibbs Free Energy

Most reactions that life scientists care about occur at constant \( T \) and \( P \)

\[ (P = 1 \text{ atm}) \quad (T = 298 \text{K or } 310 \text{K}) \]

Gibbs Free Energy tells us this \( G = H - TS \)

or \( \Delta G = \Delta H - T \Delta S \) (why not \( \Delta (TS) \)?)

Molar Gibbs Free Energy: \( \overline{G} = \overline{H} - T \overline{S} \) (per mole)

(to a 1st approx)

In principle, the chemical potential is given by

\[ \mu = \overline{G} \]

\( \Delta \mu < 0 \Rightarrow \text{Reaction or process CAN occur spontaneously} \)

\( \Delta \mu > 0 \Rightarrow \text{Reaction cannot/will not occur spontaneously} \)

\( \Delta \mu = 0 \Rightarrow \text{Reaction is at equilibrium} \)

( replace \( \Delta \mu \) by \( \Delta G \) - same thing )
Let's explore why.

Remember that for reversible process \( \Delta S = \frac{q_{\text{rev}}}{T} \)

and \( \Delta S > \frac{q_{\text{irrev}}}{T} \) for irreversible process (p. 80) (Spontaneous)

\[ \Delta S \geq \frac{q}{T} \quad \text{(both cases)} \]

From \( \Delta E = q + w \), we have \( q = \Delta E - w \)

\[ \geq \Delta S \geq \frac{\Delta E - w}{T} \]

if we allow only expansion/compression work (Const. P, but not V) then

\[ w = -P \Delta V \]

\[ \geq \Delta S \geq \frac{\Delta E + P \Delta V}{T} \quad \text{(Const. T and P)} \]

\[ \geq \frac{E_2 - E_1 + PV_2 - PV_1}{T} = \frac{(E_2 + PV_2) - (E_1 + PV_1)}{T} \quad \text{Eq. 212} \]

\[ \geq \frac{H_2 - H_1}{T} = \frac{\Delta H}{T} \]

(Remember \( H = E + PV \))

\[ \geq \Delta S \geq \frac{\Delta H}{T} \]

\[ \geq T \Delta S \geq \Delta H \]

\( \Delta G < 0 \) spontaneous

\( \Delta G = 0 \) equilibrium

\( \Delta G > 0 \) not spontaneous

\( \Delta H - T \Delta S \leq 0 \)

\( \Delta G \leq 0 \)
G is derived from state variables and so therefore is a state variable itself.

Consequently, all the familiar rules/games apply

\[ \Delta G^\circ = \sum C_{f}^{o} \text{ (prods)} - \sum C_{f}^{o} \text{ (reactants)} \]

Look things up in the tables.

(or look up \( H_f^{o} \) and \( S_f^{o} \) values and combine)

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Are proteins stable?

\[
\text{Glycylglycine}^{(ag)} + H_2O \rightarrow 2 \text{ Glycine}^{(ag)}
\]

\[ \Delta G_{298}^{o} = 2\Delta G^{o} \text{ (glycine, s)} - \Delta G^{o} \text{ (glycylglycine, s)} - \Delta G^{o} \text{ (H}_2\text{O)} \]

\[ \text{[we use } \Delta G^{o}(s) \text{ because we don't have } \Delta G^{o}(ag) \text{]} \]

Book says they're close

Result

\[ \Delta G_{298}^{o} = -27.6 \text{ kJ \cdot mol}^{-1} \]

Answer: No, the dipeptide (and proteins) are not stable and CAN spontaneously hydrolyze.

The converse of this is that amino acids will not spontaneously (even with a catalyst) assemble into proteins (we must couple to other spontaneous rxns).
Fortunately, KINETICS saves us!

Another implication:

Proteases can speed up the spontaneous reaction and so need no ATP, etc.

If (and this is NOT true for rxns like protein folding)

$\Delta H$ and $\Delta S$ are relatively independent of $T$,

then

$$\Delta G_T = \Delta H_{25\circ} - T_2 \Delta S_{25\circ}$$

Note that

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

Subtracting:

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

If $\Delta S < 0$ then $\Delta G$ increases (less spont) w/ $T \uparrow$

If $\Delta S > 0$ then $\Delta G$ decreases (more spont) w/ $T \uparrow$

From

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

and

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

Again if $\Delta H_{25\circ} \approx \Delta H_{T_2}$ and $\Delta S_{25\circ} \approx \Delta S_{T_2}$ (temp indep)

Then

$$\frac{\Delta G_{T_2}}{T_2} - \frac{\Delta G_{25\circ}}{298} = \left(\frac{1}{T_2} - \frac{1}{298}\right) \Delta H$$
If $\Delta H$ and $\Delta S$ are dependent on $T$, the calculations get more complicated.

One result:

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

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Phase Changes

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

$$\Delta G = 0 \quad \text{(equilibrium)}$$

To characterize $\Delta G$, phase change at other $T$'s use previous equations.