Another shift in our study of chemistry in this chapter. We want to learn why some reactions proceed almost completely to products and others do not.

If the universe tends toward entropy, how can beautifully organized things like flower a butterflies exist?
I. Spontaneous Processes

A. A spontaneous process proceeds without any external influence (like energy inputs)

1. Physical change examples:

   a) Expansion of a gas into area of lower pressure (Fig. 16.1, p. 655).

   b) Water flowing down hill
2. Neither 1 a) nor b) proceeds spontaneously in the opposite direction. Can we force them to? (energy?)

a) Piston (Think of a car or syringe.)
b) Water tower (pump). A larger scale example?
B. A spontaneous reaction always moves a system toward equilibrium.

1. This is sometimes less clear than we might like.

Partially from Prob. 16.1, p. 656:

a) Do perfume molecules diffuse from areas of high concentration to low concentration spontaneously?

b) Does iron rust spontaneously?

c) Does CO$_2$ fixation (plants) occur spontaneously?

d) Does gas burn in a car engine spontaneously?

e) Does CaCO$_3$(s) spontaneously decompose to CaO and CO$_2$ at 25° C & 1 atm pressure? ($K_p = 1.4 \times 10^{-23}$)
2. It is important to be able to distinguish between kinetic & equilibrium aspects of a rxn.  (Fig. 16.2.)

   a) Kinetics depend on $E_a$.
   b) Equilibria depend on $\Delta E$ (been using $\Delta G$).

II. Enthalpy, Entropy, & Spontaneous Processes: Review

A. Can enthalpy alone tell us if a rxn. is spontaneous?

1. Consider burning (or explosion) of methane:

   \[
   \text{CH}_4(\text{g}) + 2 \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) + 2 \text{H}_2\text{O}(\text{l}) \quad \Delta H^\circ = -890.3 \text{ kJ}
   \]
It proceeds spontaneously (after the spark???). So do many other rxns. (1800's, M. Berthelot)
2. But some spontaneous processes don’t give off heat:

a) Evaporative cooling from sweat
b) Dissolving NH₄Cl
c) Decomposition of N₂O₄ to NO₂

This means that $\Delta H^\circ$ alone cannot predict spontaneity.
B. So, we’ll have to consider additional factors to predict whether or not a rxn. is spontaneous.


2. The term entropy ($S$) is used for randomness:

$$\Delta S = S_{\text{final}} - S_{\text{initial}}$$

3. $S$ is a state function (depends only on start and end, not the path taken).

4. If the system entropy increases, $\Delta S$ has a + value. If it decreases, $\Delta S$ has a negative value. (Figs. 16.1, 3 & 4.)
C. Be careful when thinking about $\Delta S$ to carefully examine initial and final states (all components).

1. Example: Dissolving crystalline solids:

$$\text{NaCl}_\text{(s)} \rightarrow \text{Na}^+_{\text{(aq)}} + \text{Cl}^-_{\text{(aq)}} \quad \Delta S = + 43 \text{ J/(K}\cdot\text{mol)}$$

$$\text{CaSO}_4\text{(s)} \rightarrow \text{Ca}^{2+}_{\text{(aq)}} + \text{SO}_4^{2-}_{\text{(aq)}} \quad \Delta S = -140 \text{ J/(K}\cdot\text{mol)}$$

*Draw a picture to look first at macroscopic issues.*

2. How (why?) can the $\Delta S$ be negative for CaSO$_4$? (Fig. 16.5, next page)
Comment on \((g)\) phase being simple, \((aq)\) being hard. Note: We are eventually going to get back to Chap 11.

Try Prob. 16.2, p. 659 & see next page.

16.2 Predict the sign of \(\Delta S\) for the following:

a) \(\text{H}_2\text{O}_{(g)} \rightarrow \text{H}_2\text{O}_{(l)}\) (Formation of rain droplets?)

b) \(\text{I}_2(g) \rightarrow 2 \text{I}_{(g)}\)

d) \(\text{Ag}^+_{(aq)} + \text{Br}^-_{(aq)} \rightarrow \text{AgBr}_{(s)}\)

e) deposition of frost (or dew???) on a cold morning?

a) Write a balanced equation for the rxn.

b) What is the sign of the $\Delta S$ for the rxn.?
III. Entropy and Probability
   (Relate to some “real life” experience.)

A. Imagine playing draw poker. Would you try to draw to a straight if you were dealt 5♥, 6 ♦, 7 ♠, 9 ♦, K ♣?

1. What are the odds of drawing an inside straight?

\[
\text{odds} = \frac{\text{# of cards of the type you need}}{\text{# of cards total (sort of total?)}}
\]

2. Odds of drawing an outside straight? (5, 6, 7, 8, K)
B. Now let’s try coins.

1. How many possible outcomes for flipping 2 coins? 
   4 (HH, TT, HT, and TH) \(4 = 2^2\)

2. What are the odds of getting a given outcome?

   a) HH is 1/4. Same for TT.
   b) HT individually is also 1/4, but HT & TH is 2/4, or 1/2. Remind you of G. Mendel?

3. What about 3 coins? \(8 = 2^3\) Is the HHH flip very likely? Aside on offspring re. Mendel.
C. Boltzmann (~1900) proposed that the entropy (S) of a state is related to the number of different ways that state can be achieved.

\[ S = k \ln W \]

\( k = \text{Boltzmann’s constant} = \frac{R}{\text{Avogadro’s \#}} = 1.38 \times 10^{-23} \text{ J/K} \)

\( W = \text{# of ways the state can be achieved} \)

1. Because \( \ln W \) is dimensionless, units of S are J/K.
2. Back to the 3 coins. What is the entropy of HHH? There is only one way to achieve that state, so its entropy is:

\[ S = k \ln 1 = 0 \]

So, the S of a perfectly ordered state = zero.

Comment on absolute S vs. \( \Delta S \) (entropy changes).
3. What about 2 H and 1 T? There are three different ways to achieve this state (HHT, HTH, and THH), so

\[ S = 1.38 \times 10^{-23} \text{ J/K} \ln 3 \]

\[ S = 1.38 \times 10^{-23} \text{ J/K} \times (1.0986) = 1.516 \times 10^{-23} \text{ J/K} \]

A small number, but > zero. Note that in chemical systems we are usually dealing with much more than 8 possible outcomes.

What about 20 coins? \( 2^{20} = 1,048,576 \) different possible outcomes
Instead of coins, apply this to a crystal, where the 2 possibilities represent up or down orientation (vs. H or T)?
Back to: \( S = k \ln W \)

Instead of 20 molecules, imagine 1 mole of molecules \((6.022 \times 10^{23})\) & we consider only two possible orientations for each molecule, \( W = 2^{6.022 \times 10^{23}} \).

If we plug this into the Boltzmann equation, \( S = 5.76 \ \text{J/K} \)

The measured value for CO near 0 K is \( S = 5 \ \text{J/K} \), suggesting the CO molecules are arranged close to randomly.
However, for HCl near 0 K, $S \approx 0$: Almost all of the HCl molecules have the same orientation. Can you explain this difference between CO and HCl?

$CO \text{ dipole moment} = 0.11 \, D \quad HCl \text{ dipole moment} = 1.11 \, D$

Interplay between $\Delta H$ stuff and $\Delta S$ stuff (leads to $\Delta G$ stuff?)
D. Expansion of an Ideal Gas (Fig. 16.1)

1. Divide a volume up into a series of boxes of relatively smaller volume.

2. Arrangement of these molecules in these smaller boxes is clearly related to both our coin flipping and diatomic molecule arranging thoughts earlier.

3. Basically, the larger the volume, the more little boxes, and therefore the more ways to arrange the molecules. \( S \text{ bigger} \)

4. See text for details, outcome:  
   \[ \Delta S = nR \ln \left( \frac{V_{\text{final}}}{V_{\text{initial}}} \right) \]

   Employing \( PV = nRT \):
   \[ \Delta S = nR \ln \left( \frac{P_{\text{initial}}}{P_{\text{final}}} \right) \]

Prob. 16.4, p. 663.
IV. Entropy and Temperature (T)

A. Gas phase system at higher T will have a higher entropy than the same system at lower T. Logic:

1. View Boltzmann distributions as a function of T (see on next page, Fig. 16.7, p. 664, next page). Higher T curves are broader.

2. This means there are more ways to arrange the system components.

Relate to: \( S = k \ln W \)
B. Kinetic molecular theory can be partially applied to (l), but careful when applying it to (s).

1. Look at entropy across the phases, Fig. 16.8, p. 664.

   a) Gradual $S$ changes within a phase.
   b) Large $S$ jumps between phases.
2. The 3\textsuperscript{rd} Law of Thermodynamics:

“The entropy of a perfectly ordered crystalline substance at 0 K is zero.”

3. So, we can measure absolute $S$ values, not just $\Delta S$. 
V. Standard Molar Entropies & Standard Entropies of Rxn. (How to use, not get them.)

A. Standard Molar Entropy ($S^\circ$)

1. By definition: the entropy of 1 mol of pure substance at 1 atm & a specified temp. (oft. 25°C)
2. See values Table 16.1 & Appendix B.

   a) Gas $S^\circ$ values are generally higher than liquids.
   b) Liquid values are generally higher than solids.
   c) What about $\text{H}_2\text{O}_{(l)}$ vs. $\text{H}_2\text{O}_{2(l)}$ (110) vs. $\text{Br}_2(l)$ (152.2)? p. A-9 & 11.

3. Units are J/K·mol (note: J, not kJ)
B. Standard Molar Entropies ($S^\circ$) of Rxn.

1. Subtract $S^\circ$ of all reactants from $S^\circ$ of all products:

$$\Delta S^\circ = S^\circ_{\text{products}} - S^\circ_{\text{reactants}}$$

2. You must take the number of moles of each component into account:

For the rxn.: $a \ A + b \ B \rightarrow c \ C + d \ D$

$$\Delta S^\circ = [c \ S^\circ_{(C)} + d \ S^\circ_{(D)}] - [a \ S^\circ_{(A)} + b \ S^\circ_{(B)}]$$

Units of $S^\circ$ are J/K·mol & units of the coefficients $a$-$d$ are mol, so the units of $\Delta S^\circ$ are J/K. Try Prob. 16.5, p. 667.
VI. Entropy & the 2\textsuperscript{nd} Law of Thermodynamics

A. First, review: What are the 1\textsuperscript{st} two Laws?

\textit{1st Law: In any process, the energy of the system + surroundings is constant. (Conservation of energy)}

\textit{2nd Law: In any spontaneous process, the entropy of the system + entropy of surroundings increases.}

\[ \Delta S_{\text{total}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}} \]

If \( \Delta S_{\text{total}} > 0 \), rxn. is spontaneous (goes toward products)
If \( \Delta S_{\text{total}} < 0 \), rxn. is not spontaneous (goes toward reactants)
If \( \Delta S_{\text{total}} = 0 \), rxn. is at equilibrium (no net change)
If we can get at \( \Delta S_{\text{total}} \), we can predict if a process is spontaneous.
B. Want $\Delta S_{\text{total}}$. Can we get $\Delta S_{\text{system}}$ & $\Delta S_{\text{surroundings}}$?

1. $\Delta S_{\text{system}}$ can be obtained as in sect. V B., above.

2. How do we get at $\Delta S_{\text{surroundings}}$?
   
   a) Recall our previous discussion on Entropy and Temp (sect. IV). Heat transfer from system to surroundings should increase the $\Delta S_{\text{surroundings}}$ in proportion to the heat transferred.
   b) The effect of this heat transfer is most “obvious” when molecular velocity is low. (re. T?) See rough water analogy on p. 661.
   c) Combining a & b above, we get:

   $$\Delta S_{\text{surr}} = -\Delta H/T$$

   The above relationship can be derived more rigorously. Try Prob. 16.6, p. 670, on your own.
VII. $\Delta G$, Free Energy & the Spontaneity of Chemical Rxns. $\Delta G$ tells if a rxn. goes to products.

A. The “G” is in honor of Willard Gibbs.

B. We have been using $\Delta G = \Delta H - T\Delta S$ without concern for its origin. Where does it come from?
1. Recall \[ \Delta S_{\text{total}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}} \]

We are usually more interested in the system, so \( \Delta S_{\text{system}} \) is usually just noted as \( \Delta S \).

2. From sect. VI: \( \Delta S_{\text{surr}} = -\Delta H / T \)

3. Substitute into above equation: \( \Delta S_{\text{total}} = \Delta S - \Delta H / T \)

4. Multiply both sides by \(-T\): \(-T \Delta S_{\text{total}} = -T \Delta S + \Delta H \)

5. Rearrange: \(-T \Delta S_{\text{total}} = \Delta H - T \Delta S \)

6. Define \( \Delta G = -T \Delta S_{\text{total}} \) to get: \( \Delta G = \Delta H - T \Delta S \)
B. Relationship of $\Delta G$ to spontaneity ($\text{const } T \& P$):

If $\Delta G < 0$, rxn. is spontaneous (goes toward products)
If $\Delta G > 0$, rxn. is not spontaneous (goes toward reactants)
If $\Delta G = 0$, rxn. is at equilibrium (no net change)

Try Prob. 16.7-9, p. 672.
VIII. Standard Free-Energy changes for Rxns

A. The Standard State gives useful reference for understanding the thermodynamics of rxns. (Contrast with $\Delta G$, $\Delta H$, & $\Delta S$ for specific conditions.)
1. Standard State conditions:

   a) Solids, liquids, and gases in pure form at 1 atm,
   b) Solutes are 1 M (significant figures?)
   c) Specified temperature (usually 25°C)

2. Symbols: $\Delta G^\circ$, $\Delta H^\circ$, and $\Delta S^\circ$

3. Ex.: $\Delta G^\circ = \text{change when 1 mol Li reacts w/ 1 mol }$ 
$\text{H}_2\text{O to make 1 mol Li}^+, 1 \text{ mol OH}^-, \& 0.5 \text{ mol H}_2. $

$$\text{Li(s) + H}_2\text{O(l) \rightarrow } \frac{1}{2} \text{H}_2(g) + \text{Li}^+(aq) + \text{OH}^-(aq)$$

$\Delta G^\circ = -214 \text{ kJ}$   Meaning? Is product formation favored?
B. If you know $\Delta H^\circ$ & $\Delta S^\circ$ you can calc $\Delta G^\circ$ with

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \text{ if } T \text{ and } P \text{ are constant.}$$

C. Note that $\Delta G^\circ$ is conceptual. Re. actual rxns.:

1. it refers to separate (not mixed) reactants
2. it requires the rxn. to go completely to products
3. it assumes *large* quantities of components are present
   (so that $P$ change is $\approx 0$, see p. 674, States 1 & 2 figs.)

D. *Remember*, if $\Delta G^\circ$ is $-$, the rxn. proceeds toward products, if $\Delta G^\circ$ is $+$, the rxn. goes toward reactants.

Conceptual Problem 16.11, p. 675.
Consider the endothermic decomposition of AB$_2$:

a) What is the sign (+, −, 0) of ΔS for the rxn?
b) Is the rxn more likely to be spontaneous at high T or low T? Explain.

IX. Standard Free Energies of Formation (ΔG°$_f$)

(Table 16.3, p. 676)
A. $\Delta G^\circ_f$: free energy change for formation of 1 mol of substance in its standard state from its constituent elements in their standard states.

B. In addition to the approach used above to get values for $\Delta G^\circ_f$, you can use:

$$
\Delta G^\circ_f = \Delta G^\circ_f \text{ products} - \Delta G^\circ_f \text{ reactants}
$$

C. The value and sign of $\Delta G^\circ_f$ tell you whether it is a good idea to try to make a substance from its elements.

Why?
X. Free-Energy Changes Under Non-Standard Conditions

A. In the previous section we looked at changes under standard state conditions. Often, we are interested in other conditions. Can we apply these ideas then?

You betcha: \[ \Delta G = \Delta G^\circ + RT \ln Q \]

Q is the reaction quotient. Try Prob. 16.13, p. 679 on your own.
Consider the following gas-phase rxn. (A= red, B= blue):

\[ \text{A}_2 + \text{B}_2 \leftrightharpoons 2 \text{AB} \quad \Delta G^\circ = +15 \text{ kJ} \]

a) Which of the rxn mixtures has the largest \( \Delta G \) or rxn? Which the smallest?

b) If the partial pressure of each reactant and product in rxn mixture #1 = 1 atm, what is the numerical value of \( \Delta G \) for rxn #1?
XI. Free energy and Chemical Equilibrium

A. What happens to $\Delta G = \Delta G^\circ + RT \ln Q$ at equilibrium?

1. At equilibrium, $\Delta G = 0$ & $Q = K$, so:

$$\Delta G^\circ = -RT \ln K$$

2. This should complete the logic circuit needed for interpreting the kinetic and equilibrium aspects of the reaction progress diagrams we have been looking at this semester.

See Fig 16.11 & Table 16.4 (if needed) and try Prob. 16.17, p. 683.