Reading: Chapter 11 up to end of 11.7

Goals:
- Motivate: Why do we use thermodynamics instead of merely compiling huge tables of equilibrium constants?
- Develop an intuitive grasp of the 2 opposing tendencies in nature: randomness and bonding
- See how when equilibrium occurs, there is a balance between these tendencies.
- Look at some practical examples of how these opposing tendencies work in nature
- Develop a mathematical framework for expressing them - entropy and enthalpy
- Use $\Delta S$ and $\Delta H$ as a way of determining stability
- Explore how $\Delta H$ is measured
- Define a standard state so that we have standard conditions for which we tabulate data
- Explore how $S$ is measured and calculated
- Show how $\Delta G$ is tabulated and used as a way of considering $H$ and $S$ simultaneously

1. What is the value of using thermodynamics? “We have successfully calculated equilibrium relationships using equilibrium constant we looked up in tables. Why can’t we just continue with that instead of learning all this abstract Thermodynamics stuff???”
   a. First, think about how large the table(s) would be if, for each reaction, they gave:
      i. The value of $K$ over the range of temperature occurring in geological environments
      ii. The value of $K$ over the range of pressure occurring in geological environments
   b. Then think about the number of different reactions we would need tables for:
      i. Example: If we consider only 10 elements, how many different compounds could be formed?
      ii. How many different chemical reactions could occur between all those many compounds?
      iii. The number is mind-boggling...too large to handle, and too large for us to measure all the possible equilibrium constants ($K$'s) in the laboratory.
   c. So then why is thermodynamics superior?
      i. It makes use of fundamental properties of the various compounds
      ii. There are simple relationships underlying these fundamental properties (and underlying the behavior of matter in general), and these simple relationships lead to simple formulae we can use to calculate equilibrium constants for a range of conditions (avoids the problem of unwieldy tables).
      iii. So this allows us to use a relatively small table of parameters that describe the fundamental properties of the compounds in our reactions
      iv. These parameters can be measured in the laboratory using methods that determine the amount of energy contained in the various compounds
         1. High energy means less stable
         2. Low energy means more stable

2. One way to approach this is to consider the competing tendencies of matter: Randomness versus bonding.
3. The drive to form bonds (creates ORDER)
   a. When atoms are bonded in neat rows, they are more stable than when they are in solution. So there is a general tendency for matter to forms bonds.
   b. Some bonds are more stable than others: Consider a chemical reaction
      i. Chamber containing $H_2$ and $O_2$ gases: $2H_2 + O_2 \Rightarrow 2H_2O$
      ii. Provide a spark to get the kinetics going and the reaction goes quickly- explosion.
      iii. If we make a specially designed chamber (a calorimeter), we can carefully measure the amount of energy given off by the reaction
      iv. Intuitively, we expect reactions that release large amounts of energy are favorable and will go forward
      v. The heat energy released is created as the new, more stable bonds are formed
      vi. Intuitively, we expect that a reaction with a small change in bonding can produce only a very small amount of heat when the reaction occurs
1. Accordingly, reactions that give off small amounts of heat involve only small increases in the stability of the components and have a lesser drive to proceed.

4. **Enthalpy**
   a. When we make measurements of the heat released by a reaction in a calorimeter, we are measuring **Enthalpy** changes.
   b. Calorimetry: Mix reactants at 298K (Kelvin) and 1 bar pressure, let the reaction occur (heat generated), then measure the amount of energy that must be removed to get the system back to 298K.
   c. This gives $-\Delta H_R^0$.
   d. So a reaction like $2H_2 + O_2 \Rightarrow 2H_2O$ has large NEGATIVE $\Delta H_R^0$.
   e. In other words, the products have much lower enthalpy.
   f. Rigorous Definition: "Enthalpy (also called heat content) is the sum of the internal energy of matter and the product of its volume multiplied by the pressure. Enthalpy is a quantifiable state function, and the total enthalpy of a system cannot be measured directly; the enthalpy change of a system is measured instead."
   g. Strictly speaking, bonding changes are not the only thing contributing to $\Delta H_R^0$; if the reaction involves a large change in volume, that enters into it also.
   h. We cannot measure enthalpy directly; we can only measure enthalpy change, $\Delta H$.
      i. Definition of $\Delta H$: The amount of heat liberated ($<0$) or gained ($>0$) when a reaction occurs at constant T and P.
      ii. We must pick an arbitrary zero point for our $\Delta H$.
         a. Let $H = 0$ for each element in its pure form at 25˚C and 1 bar.
         b. So all enthalpies will be relative to that.
   i. $\Delta H < 0 = \text{Exothermic}$; tends to make forward reaction more favorable.
   j. $\Delta H > 0 = \text{Endothermic}$; tends to make forward reaction less favorable.

5. So then, does $\Delta H$ tell us all we need to know to predict if a reaction will go forward or backward?
   a. No, there’s the entropy drive also.
   b. Example: $\text{NH}_4\text{Cl}(s) \Rightarrow \text{NH}_4^+ + \text{Cl}^-(aq)$.
      i. Used in some of those “chemical cold packs” used at sports events.
      ii. As the $\text{NH}_4\text{Cl}$ dissolves, the aqueous solution becomes cold.
   c. So clearly, $\Delta H_R^0$ is $>0$; energy absorbed.
   d. Does this mean the reaction cannot occur??? No the reaction goes forward strongly!
   e. The entropy drive is strong- the right side of the equation is less ordered, more random.

6. **The natural drive toward randomness**
   a. Experiment:
      i. Beaker with pure water in it. Add $\text{NH}_4\text{Cl}(s)$
      ii. Purely random motions will cause $\text{NH}_4^+(aq) + \text{Cl}^-(aq)$ to break free, move into solution.
      iii. MAJOR POINT: There is a strong drive toward randomness in nature.

7. **Quantitative measures of these competing tendencies**
   a. $S = \text{Entropy}$ is related to disorder (greater $S$ is favorable).
   b. $H = \text{Enthalpy}$. Formation of bonds decreases enthalpy (lesser $H$ is favorable).
   c. So consider a reaction:
      i. $\Delta H_R$ is the enthalpy change, $\Delta S_R$ is the entropy change of the reaction.
      ii. At equilibrium, there must be some balance between the drive toward disorder and the drive toward bonding (order).
      iii. **At equilibrium the balance is given by...** $\Delta H = T\Delta S$.
         a. This can be arrived at by rigorous mathematics.
         b. Why is entropy multiplied by temperature? Because as $T$ increases, the entropy drive takes on greater importance- makes sense.
   d. If we do not have equilibrium, then we can quantify how far away we are from equilibrium using $...\Delta H - T\Delta S$ gives the "imbalance" or
   e. We can define a function $G$ so that: $\Delta G = \Delta H - T\Delta S$.

8. **How can we get $\Delta H_R$?**
   a. Experiments give the $\Delta H$ of formation of compounds and other species from the pure elements; Symbol: $\Delta H_f^0$.
      a. The superscript 0 means that these values apply only at 298K and 1 bar (standard conditions).
      b. These are found in tables like Appendix B in Faure.
c. For compounds, the values are for one mole of the pure compound

d. For dissolved ions, one cannot have a mole of pure ions!
   i. It works out well if we specify that the standard state condition for dissolved ions is a state of having the activity = 1.00000, in addition to 25°C and 1 bar.

e. From the $\Delta H_f^0$ values for the compounds in a reaction, we can calculate $\Delta H_R^0$.
   $$\Delta H_R^0 = \Sigma \Delta H_f^0_{\text{products}} - \Sigma \Delta H_f^0_{\text{reactants}}$$
   This is the enthalpy of reaction when the appropriate number of moles of each reactant combine to form the product(s)

f. APPLIES WHEN ALL REACTANTS AND PRODUCTS ARE AT 25°C and 1 bar.

9. How can we get $\Delta H_R^0$ at temperatures other than 25°C, the standard state T?
   a. Correct the $\Delta H_f$ values for the change in T using the heat capacities of the reactants and products
   $$H(T) - H(298K) = \int_{298}^{T} dH = \int_{298}^{T} C_p dT$$

b. Note that $C_p$ changes with T

c. See Faure, section 11.5 for the function used to model $C_p$ changes with T

10. We can calculate $\Delta S_R$, the $\Delta S$ for a reaction, in similar ways.
   a. Unlike the $\Delta H_f$ case, we have a natural zero point: $S=0$ at absolute zero (makes sense)
   b. $S$ is related to the amount of energy needed to warm a substance to a given temperature
      i. Why? Because the warming of a substance is an increase in vibration, which is the same as an increase in entropy.
   c. Mathematically, we get $S$ by integrating the constant volume heat capacity divided by T:
      $$S(298K) = \int_{0}^{298} dS = \int_{0}^{298} C_v \frac{dT}{T}$$
      $C_v$ differs from $C_p$ in that volume is constant, not temperature. Can be determined experimentally.
   d. So we can calculate $S$ for any substance at any temperature if we know the $C_v$ function
      i. Note: we define $S^0 = S$ at 25°C and 1 bar
   e. And we can calculate $\Delta S_R = \Sigma S_{\text{products}} - \Sigma S_{\text{reactants}}$

11. We can tabulate values for $\Delta G_f^0$, the free energy of formation of various compounds and species
   a. $\Delta G_f^0 = \Delta H_f^0 - TS^0$
   b. Convenient: $\Delta G_R^0 = \Sigma \Delta G_f^0_{\text{products}} - \Sigma \Delta G_f^0_{\text{reactant}}$
   c. Note that Faure gives $\Delta G_f^0$ for all compounds and dissolved species in Appendix B, but does not tabulate $S^0$ (but you can get it using $\Delta G_f^0 = \Delta H_f^0 - TS^0$)