Chapter 19. Chemical Thermodynamics

SOURCE: Chemistry the Central Science: Prentice hall

I. Spontaneous Processes

- Thermodynamics is concerned with the question: **will** a reaction occur?

- **First Law of Thermodynamics:** energy is conserved.

- Any process which occurs without outside intervention is spontaneous.

- When two eggs are dropped they spontaneously break.

- The reverse reaction (two eggs leaping into your hand with their shells back intact) is not spontaneous.

- We can conclude that a spontaneous process has a direction.

- A process that is spontaneous in one direction is not spontaneous in the opposite direction.

- The direction of a spontaneous process can depend on temperature.

- Ice turning to water is spontaneous at $T > 0°C$.

- Water turning to ice is spontaneous at $T < 0°C$

• A reversible process is one which can go back and forth between states along the same path.

> When I mol of water is frozen at 1 atm at $0°C$ to form I mol of ice, $q = \Delta H_{vap}$ of heat is removed.
>
> To reverse the process, $q = \Delta H_{vap}$ must be added to the 1 mol of ice at $0°C$ and I atm to form 1 mol of water at $0°C$

Therefore, converting between 1 mol of ice and I mol of water at 0°C is a reversible processes.

Allowing 1 mol of ice to warm is an irreversible process. To get the reverse process to occur, the water temperature must be lowered to 0°C.

Chemical systems in equilibrium are reversible.
In any spontaneous process, the path between reactants and products is irreversible.

Thermodynamics gives us the direction of a process. It cannot predict the speed at which the process will occur.

Why are endothermic reactions spontaneous?

II. <u>Entropy and the Second Law of Thermodynamics</u>

• Why do spontaneous processes occur?

• Consider an initial state: two flasks connected by a closed stopcock. One flask is evacuated and the other contains I atm of gas.'

• The final state: two flasks connected by an open stopcock. Each flask contains gas at 0.5 atm.

• The expansion of the gas is isothermal (i.e. constant temperature). Therefore the gas does no work and heat is not transferred.
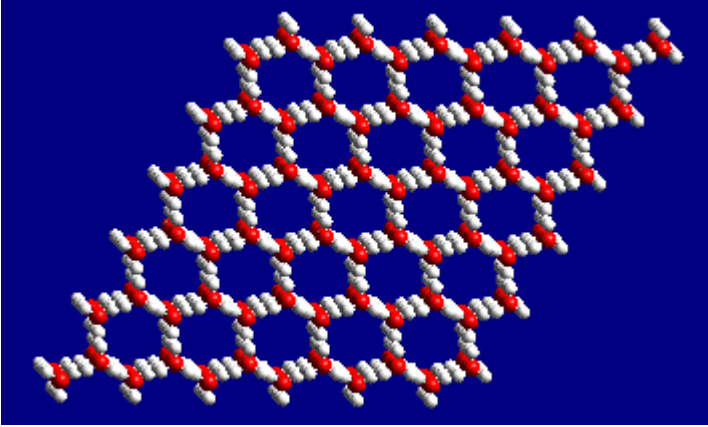
• Why does the gas expand?

A. Entropy

Entropy, S, is a measure of the disorder of a system.
Spontaneous reactions proceed to lower energy or higher entropy.
Consider a group of red and white balls placed at the top of a ramp.

When they are collected at the bottom there are two extremes for the arrangement of the balls: all the red sides face in one direction or the red sides are arranged randomly. Experience tells us that the red sides will be arranged randomly. That is, the system has moved to a state of higher entropy.

- In ice, the molecules are very well ordered because of the H-bonds.

   Therefore, ice has a low entropy.

- As ice melts, the intermolecular forces are broken (requires energy), but the order is interrupted (so entropy increases). Water is more random than ice, so ice spontaneously melts at room temperature.

- There is a balance between energy and entropy considerations.

- When an ionic solid is placed in water two things happen:

  1. the water organizes into hydrates about the ions (so the entropy decreases), and

  2. the ions in the crystal dissociate (the hydrated ions are less ordered than the crystal, so the entropy increases).

- Generally, when an increase in entropy in one process is associated with a decrease in entropy in another, the increase in entropy dominates.

- Entropy is a state function.

- For a system, $\Delta S = S_{final} - S_{initial}$

- If $\Delta S > 0$ the randomness increases, if $\Delta S < 0$ the order increases.

- Suppose a system changes reversibly between state I and state 2. Then, the change in entropy is given by

$$\Delta S = q_{rev}/T$$

   at constant T where q_{rev} is the amount of heat added reversibly to the system.

   (Example: a phase change occurs at constant T with the reversible addition of heat.)

   Consider the isothermal expansion of a gas from initial volume, V_1, to final volume, V_2

$$\Delta S = n\text{Rln}(V_2/V_1)$$

B. The Second Law of Thermodynamics

The second law of thermodynamics explains why spontaneous processes have a direction.

In any spontaneous process, the entropy of the universe increases.

$\Delta S_{univ} = \Delta S_{sys} + \Delta S_{Surr}$ the change in entropy of the universe is the sum of the change in entropy of the system and the change in entropy of the surroundings.

Entropy is not conserved: ΔS_{univ} is increasing.

For a reversible process: $\Delta S_{univ} = 0$.

For a spontaneous process (i.e. irreversible): $\Delta S_{univ} > 0$.

C. Molecular Interpretation of Entropy

- A gas is less ordered than a liquid which is less ordered than a solid.

- Any process which increases the number of gas molecules leads to an increase in entropy.

- When NO(g) reacts with O_2(g) (red) to form NO_2(g), the total number of gas molecules decreases. Therefore, the entropy decreases.

- There are three atomic modes of motion:

    1. **translation** (the moving of a molecule from one point in space to another),

    2. **vibration** (the shortening and lengthening of bonds, including the change in bond angles),

    3. **rotation** (the spinning of a molecule about some axis).

Energy is required to get a molecule to translate, vibrate or rotate.

- The more energy stored in translation, vibration and rotation, the greater the degrees of freedom and the higher the entropy.

- In a perfect crystal at 0 K there is no translation, rotation or vibration of molecules. Therefore, this is a state of perfect order.

III. Third Law of Thermodynamics

- The entropy of a perfect crystal at 0 K is zero.

- Entropy changes dramatically at a phase change.

- As we heat a substance from absolute zero, the entropy must increase.

• If there are two different solid state forms of a substance, then the entropy increases at the solid state phase change. (E.g. gray tin exists at T < 13C, white tin at T > 13C.)

• Boiling corresponds to a much greater change in entropy than melting.

• Entropy will increase when

  1. liquids or solutions are formed from solids,
  2. gases are formed from solids or liquids,
  3. the number of gas molecules increase,

  4. the temperature is increased.

IV. Calculation of Entropy Changes

• Absolute entropy can be determined from complicated measurements.

• **Standard molar entropy,** $S°$: entropy of a substance in its standard state. Similar in concept to $\Delta H°$

__Units: ΔS: J/mol-K. Note units of ΔH: kJ/mol.__

• **Standard molar entropies of elements are not zero.**

• For a chemical reaction which produces n products from m reactants:

$\Delta S° = \Sigma\, n\, S°_{(products)} - \Sigma\, n\, S°_{(reactants)}$

example: $N_2 + 3H_2 \quad 2NH_3$

$\Delta S° = 2S°_{(ammonia)} - [\ S°_{nitrogen} + 3\ S°_{hydrogen}]$

V. Gibbs Free Energy

• For a spontaneous reaction the entropy of the universe must increase.

• Reactions with large negative ΔH values are spontaneous.

• How to we balance ΔS and ΔH to predict whether a reaction is spontaneous?

• Gibbs free energy, G, of a state is

$$G = H - TS$$

• For a process occurring at constant temperature

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

There are three important conditions:

I . If $\Delta G < 0$ then the forward reaction is spontaneous.

2. If $\Delta G = 0$ then reaction is at equilibrium and no net reaction will occur.

3. If $\Delta G > 0$ then the forward reaction is not spontaneous. (However, the reverse reaction is spontaneous.) If $\Delta G > 0$, work must be supplied from the surroundings to drive the reaction.

For a reaction the free energy of the reactants decreases to a minimum (equilibrium) and then increases to the free energy of the products.

VI. Standard Free-energy Changes

• We can tabulate standard free-energies of formation, $\Delta G°_f$ (c.f. standard enthalpies of formation).

• Standard states are: pure solid, pure liquid, 1 atm (gas), 1 M concentration (solution), and $\Delta G° = 0$ for elements.

•   The standard free-energy change for a process is given by

$$\Delta G° = \Sigma \, n \, \Delta G_f°_{(products)} \; - \Sigma \, n \, \Delta G_f°_{(reactants)}$$

The quantity ΔG^O for a reaction tells us whether a mixture of substances will

spontaneously react to produce more reactants ($\Delta G^O > 0$) or products ($\Delta G^O < 0$).

VII. Free Energy and Temperature

• Focus on $\Delta G = \Delta H - T \Delta S$:

1. If $\Delta H < 0$ and $\Delta S > 0$, then ΔG is always negative.

2. If $\Delta H > 0$ and $\Delta S < 0$, then ΔG is always positive.

3. If $\Delta H < 0$ and $\Delta S < 0$, then ΔG is negative at low temperatures.

4. If $\Delta H > 0$ and $\Delta S > 0$, then ΔG is negative at high temperatures.

• Even though a reaction has a negative ΔG it may occur too slowly to be observed.

• *Thermodynamics gives us the direction of a spontaneous process, it does not give us*

   the rate of the process.

A. Driving Nonspontaneous Reactions

•   If $\Delta G > 0$, work must be supplied from the surroundings to drive the reaction.

VII. Relation between ΔG and the Equilibrium Constant

Remember that a reaction is spontaneous if ΔG is negative. A relationship exists between TG and K as follows:

$$\Delta G° = -RT \ln K$$

by substituting R= 8.31 x 10^{-3} and ln K = 2.30 $\log_{10}$ K we have

$$\Delta G° = -0.0191 \text{ T } \log_{10} K$$

We can then establish three possible situations:

1. $\Delta G°$ is negative, $\log_{10}$ K must be positive and therefore K is greater than 1. The forward reaction is spontaneous.
2. $\Delta G°$ is positive, $\log_{10}$ K must be negative and therefore K is less than 1. The reverse reaction is spontaneous.
3. If $\Delta G°$ is zero, $\log_{10}$K = 0 and k =1. The reaction is at equilibrium.

Note: K has been used to represent general equilibrium constants. We will be discussing K_w, K_a, K_b, K_{sp}, and K_f in future chapters.