Chapter 16 - Spontaneity, Entropy, and Free Energy

16.1 Spontaneous Processes and Entropy

A. First Law
   1. "Energy can neither be created nor destroyed"
   2. The energy of the universe is constant

B. Spontaneous Processes
   1. Processes that occur without outside intervention
   2. Spontaneous processes may be fast or slow
      a. Many forms of combustion are fast
      b. Conversion of diamond to graphite is slow

C. Entropy (S)
   1. A measure of the randomness or disorder
   2. The driving force for a spontaneous process is an increase in the entropy of the universe
   3. Entropy is a thermodynamic function describing the number of arrangements that are available to a system
      a. Nature proceeds toward the states that have the highest probabilities of existing

D. Positional Entropy
   1. The probability of occurrence of a particular state depends on the number of ways (microstates) in which that arrangement can be achieved

$$S_{solid} < S_{liquid} << S_{gas}$$

16.2 Entropy and the Second Law of Thermodynamics

A. Second Law of Thermodynamics
   1. "In any spontaneous process there is always an increase in the entropy of the universe"
   2. "The entropy of the universe is increasing"
   3. For a given change to be spontaneous, ΔS_{univ} must be positive

$$\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr}$$

16.3 The Effect of Temperature on Spontaneity

A. Direction of Heat Flow
   1. Entropy changes in the surroundings are primarily determined by heat flow
      a. Exothermic reactions in a system at constant temperature increase the entropy of surroundings
      b. Endothermic reactions in a system at constant temperature decrease the entropy of surroundings
      c. The impact of the transfer of a given quantity of energy as heat to or from the surroundings will be greater at lower temperatures

16.4 Free Energy (G), also called "Gibbs Free Energy"

A. Calculating Free Energy Change (constant temperature and pressure)
   1. $\Delta G = \Delta H - T\Delta S$
      a. H is enthalpy
      b. T is Kelvin temperature

B. Free Energy and Spontaneity
  1. Reactions proceed in the direction that lowers their free energy ($-\Delta G$)

Value of DH	***Value of TDS***	***Value of DG***	***Spontaneity***
Negative	Positive	Negative	Spontaneous
Positive	Negative	Positive	Nonspontaneous
Negative	Negative	???	Spontaneous if the absolute value of ΔH is greater than the absolute value of $T\Delta S$ (low temperature)
Positive	Positive	???	Spontaneous if the absolute value of $T\Delta S$ is greater than the absolute value of ΔH (high temperature)

16.5 Entropy Changes in Chemical Reactions

A. Constant Temperature and Pressure
  1. Reactions involving gaseous molecules
    a. The change in positional entropy is dominated by the relative numbers of molecules of gaseous reactants and products

$$2C_2H_6(g) + 7O_2(g) \rightarrow 4CO_2(g) + 6H_2O(g)$$

9 molecules 10 molecules

ΔS increases

B. Third Law of Thermodynamics
  1. "The entropy of a perfect crystal at O K is zero" (NO disorder, since everything is in perfect position)

C. Calculating Entropy Change in a Reaction

$$\Delta S^0_{reaction} = \sum n_p S^0_{products} - \sum n_r S^o_{reactants}$$

  1. Entropy is an extensive property (a function of the number of moles)
  2. Generally, the more complex the molecule, the higher the standard entropy value

16.6 Free Energy and Chemical Reactions

A. Standard Free Energy Change
  1. ΔG^0 is the change in free energy that will occur if the reactants in their standard states are converted to the products in their standard states
  2. ΔG^0 cannot be measured directly
  3. The more negative the value for ΔG^0, the farther to the right the reaction will proceed in order to achieve equilibrium
    a. Equilibrium is the lowest possible free energy position for a reaction

B. Calculating Free Energy Change
  1. Method #1, for reactions at constant temperature:

$$\Delta G^0 = \Delta H^0 - T\Delta S^0$$

  2. Method #2, an adaptation of Hess's Law:

$$C_{diamond}(s) + O_2(g) \rightarrow CO_2(g) \qquad \Delta G^0 = -397 \text{ kJ}$$
$$\underline{C_{graphite}(s) + O_2(g) \rightarrow CO_2(g) \qquad \Delta G^0 = -394 \text{ kJ}}$$
$$C_{diamond}(s) \rightarrow C_{graphite}(s) \qquad \Delta G^0 = -397 \text{ kJ} - (-394 \text{ kJ}) = -3\text{kJ}$$

(Complete example is on page 798)

3. Method #3, using standard free energy of formation (ΔG_f^0)
    a. Standard Free Energy of Formation is the change in free energy that accompanies the formation of 1 mole of that substance from its constituent elements with all reactants and products in their standard states
    b. ΔG_f^0 of an element in its standard state is zero

$$\Delta G^0 = \sum n_p \Delta G^0_{f\,(products)} - \sum n_r \Delta G^0_{f\,(reac\tan ts)}$$

16.7 The Dependence of Free Energy on Pressure

A. Enthalpy, H
    1. enthalpy is not pressure dependent

B. Entropy, S
    1. entropy depends on volume, so it also depends on pressure

$S_{\text{large volume}} > S_{\text{small volume}}$
$S_{\text{low pressure}} > S_{\text{high pressure}}$

2. $G = G^0 + RTln(P)$
    a. G^0 is the free energy of the gas at a pressure of 1 atm
    b. G is the free energy of the gas at a pressure of P atm
    c. R is the universal gas constant, T is Kelvin temperature
3. $\Delta G = \Delta G^0 + RTln(Q)$
    a. Q is the reaction quotient (from the law of mass action, section 13.5)
    b. R is the gas constant (8.3145 J/K·mol)
    c. ΔG^0 is the free energy change for the reaction with all reactants and products at a pressure of 1 atm
    d. ΔG is the free energy change for the reaction for the specified pressures of reactants and products

16.8 Free Energy and Equilibrium

A. Thermodynamic View of Equilibrium
    1. Equilibrium point occurs at the lowest value of free energy available to the reaction system
    2. At equilibrium, $\Delta G = 0$ and Q = K

$$\Delta G^0 = -RTln(K)$$

DG^0	***K***
$\Delta G^0 = 0$	$K = 1$
$\Delta G^0 < 0$	$K > 1$
$\Delta G^0 > 0$	$K < 1$

B. Temperature Dependence of K
    1. $\Delta G^0 = -RT\ln(K) = \Delta H^0 - T\Delta S^0$
    2. $\ln(K) = -\dfrac{\Delta H^0}{RT} + \dfrac{\Delta S^0}{R} = -\dfrac{\Delta H^0}{R}\left(\dfrac{1}{T}\right) + \dfrac{\Delta S^0}{R}$ so *ln(K) µ 1/T*

16.9 Free Energy and Work

- A. Relationship to Work
  1. The maximum possible useful work obtainable from a process at constant temperature and pressure is equal to the change in free energy
     ("Free energy" is energy "free" to do work)

$$w_{\text{max}} = \Delta G$$

  2. The amount of work obtained is always less than the maximum
- B. Henry Bent's First Two Laws of Thermodynamics
  1. First law: You can't win, you can only break even
  2. Second law: You can't break even

The amount of available free energy of our system (Earth) is decreasing.