Spontaneity, Entropy, & Free Energy

Chapter 16

Review: Thermodynamics
- The study of energy and its conversions

First Law of Thermodynamics:
- The change in a systems internal energy (ΔE) is equal to the heat gained by the system (q) plus the work done on the system (w)

$$\Delta E = q + w$$

_____

Spontaneous Change
- A change that occurs at given conditions without outside intervention
- Could be fast changes or slow changes but change does occur

Entropy (S)
- A measure of a substance's randomness or disorder
- In nature, systems tend to change from more ordered to less ordered states
- One way to measure entropy is by considering "positional probability"
- The greater the number of positions that the particles can be in, the greater the entropy

Ex. Solid $\rightarrow$ Liquid $\rightarrow$ Gas
     $\rightarrow$ Entropy increases $\rightarrow$

16.1 (p783) Which has the highest positional entropy?
a) $CO_{2\,(s)}$ vs. $CO_{2\,(g)}$

b) $N_{2\,(g)}$ at 1 atm vs. $N_{2\,(g)}$ at 1.10×10^{-2} atm

16.2 (p783) What is the sign on the entropy change when:
a) sugar is dissolved in H_2O
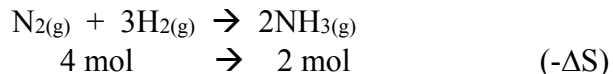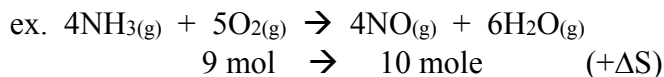
b) $I_{2\,(g)}$ condenses on a cold surface

Second Law of Thermodynamics
- In any spontaneous change, there is always an increase in the entropy of the universe.
  (The entropy of the universe is increasing)
- $\Delta S = \Delta S_{surroundings} + \Delta S_{system}$

- In truth, we really <u>do not</u> deal with this law in any problem solving. We will find ourselves mainly dealing with the entropy changes in chemical reactions. One note, to calculate the $\Delta S_{surroundings}$
  - $\Delta S_{surroundings} = -\Delta H/T$

Entropy Changes in Chemical Reactions
- For gaseous systems
  - if the number of moles of gases increases during the reaction, positional probability increases ($+\Delta S$)
  - because there are more particles, there are more different positions the particles could be in.

  ex. $4NH_{3(g)} + 5O_{2(g)} \rightarrow 4NO_{(g)} + 6H_2O_{(g)}$

               9 mol $\rightarrow$ 10 mole   ($+\Delta S$)

        $N_{2(g)} + 3H_{2(g)} \rightarrow 2NH_{3(g)}$

          4 mol $\rightarrow$ 2 mol   ($-\Delta S$)

Absolute Entropy (S^0)
- At a given temperature, every substance has a <u>measurable</u> entropy value
- many of these values are listed in appendix 4 in your textbook
- the <u>more organized</u> and <u>colder</u> a substance is, the <u>lower</u> its absolute entropy value
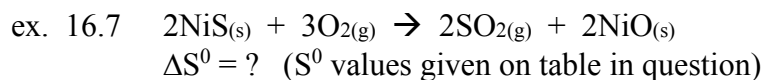
Third Law of Thermodynamics
        The entropy of a perfect crystal at 0 k is zero
- S^0 is measured in j/mol k
- S^0 is a "state function" (independent of path)
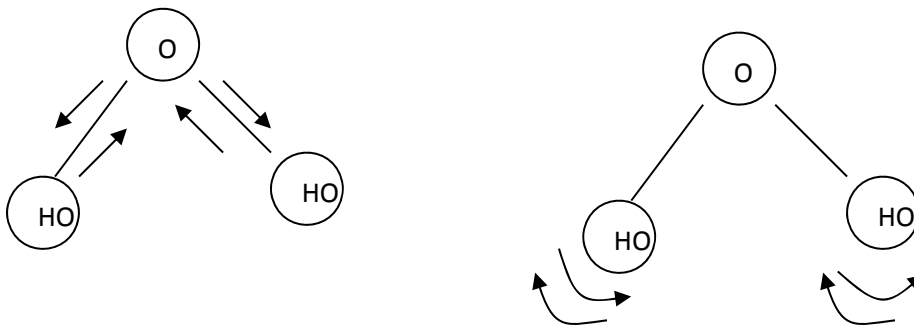- so: $\Delta S^0_{rxn} = \Sigma S^0_{products} - \Sigma S^0_{reactants}$

     or:

> $\Delta S^0_{rxn} = \Sigma S^0_P - \Sigma S^0_R$

ex. 16.7 $2NiS_{(s)} + 3O_{2(g)} \rightarrow 2SO_{2(g)} + 2NiO_{(s)}$

                  $\Delta S^0 = ?$ (S^0 values given on table in question)

ex. 16.8 $Al_2O_{3(s)} + 3H_{2(g)} \rightarrow 2Al_{(s)} + 3H_2O_{(g)}$

Entropy vs. Structure
- the more complex a molecule is, the higher its entropy value.
- the more complex the molecule the greater the types of motion in its atoms

ex.

Gibbs Free Energy (G)
- this is a thermodynamic function used to predict whether or not a reaction is spontaneous
  - this is sometimes defined as the energy available to do useful work.
- $G = H - TS$
  - so:

$$\Delta G = \Delta H - T\Delta S \quad (T= \text{Kelvin})$$

  - if $-\Delta G$, the reaction is spontaneous
  - if $+\Delta G$, the reaction does not occur
  - if $\Delta G =)$, the system is at equilibrium

ex. For $Br_{2(l)} \rightarrow Br_{2(g)}$ $\Delta H^0 = 31.0$ kj/mol and $\Delta S^0 = 93.0$ j/mol k. Is this reaction spontaneous at 25°C?

$$\Delta G = \Delta H - T\Delta S$$
$$\Delta G = 31,000 \text{ j/mol} - (298k)(93 \text{ j/mol k})$$
$$= 31,000 - 27,714 = +3286 \text{ j/mol} \text{ No reaction } (+\Delta G)$$

Standard Free Energy Change (ΔG^0)
- This is the free energy change that occurs if the reactants, in their standard states, are converted to products, in their standard states.
- from section 6.4: Standard states: gases: P = 1atm, solutions = 1M, liquid or solid = liq. or sol.

Basically there are 2 ways to calculate ΔG^0

1. $\Delta G^0 = \Delta H^0 - T\Delta S^0$
   ex. 16.9 $2SO_{2(g)} + O_{2(g)} \rightarrow 2SO_{3(g)}$ at 25°C

Using the given values of ΔH^0_f and S^0, calculate ΔH^0, ΔS^0, and ΔG^0 for this reaction.

2. Manipulating reactions with known ΔG^0's to produce the desired reaction
   (we did this in Chapter 6 and Chapter 8 with ΔH's)
   Ex. For $2CO_{(g)} + O_2(g) \rightarrow 2CO_{2(g)}$ $\Delta G^0 =$
   Given: $2CH_{4(g)} + 3O_{2(g)} \rightarrow 2CO_{(g)} + 4H_2O_{(g)}$ $\Delta G^0 = -1088kj$
   $CH_{4(g)} + 2O_{2(g)} \rightarrow CO_{2(g)} + 2H_2O_{(g)}$ $\Delta G^0 = -801kj$

   Ex. 16.10 Given: $C_{diamond} + O_{2(g)} \rightarrow CO_{2(g)}$ $\Delta G^0 = -397kj$
                      $C_{graphite} + O_{2(g)} \rightarrow CO_{2(g)}$ $\Delta G^0 = -394kj$
   for $C_{diamond} \rightarrow C_{graphite}$ $\Delta G^0 = ?$

Standard free Energy of Formation (ΔG^0_f)
- this is th standard free energy change when 1 mole of a sutbstance is formed feom its elements
- it works the same as other Gibbs free energy problems

- $\Delta G^0_{rxn} = \Delta G^0_P - \Delta G^0_R$
- your references must be for ΔG^0_f

Ex. 16.11 & 16.12

- Sometimes you have to determine ΔG for a reaction at nonstandard conditions:
- to do this you use the equation: $\Delta G = \Delta G^0 + RT \ln Q$
    - where: ΔG = free energy change at nonstandard conditions
        - ΔG^0 = the standard free energy change
        - R = gas constant = 8.31 j/mol k
        - T = temperature, k
        - Q = reaction quotient (or mass action expression)
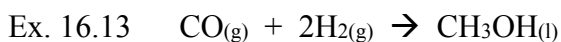
Ex. 16.13 $CO_{(g)} + 2H_{2(g)} \rightarrow CH_3OH_{(l)}$
        If CO = 5.0 atm and H₂ = 3.0 atm, (nonstandard conditions)
Calculate ΔG at 25°C
                    Appendix 4: Δ^0_f CH₃OH = -166kj   H₂ = 0   CO = -137kj
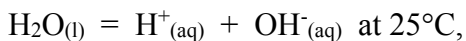
Free Energy and equilibrium
- at equilibrium $G_{products} = G_{reactants}$
    - ∴ΔG = 0

Here Comes a derivation:
- We know: $\Delta G = \Delta G^0 + RT \ln Q$
- but at equilibrium: ΔG = 0   and Q = K_{eq}
- so: $0 = \Delta G^0 + RT \ln Q$
- or: $\Delta G^0 = -RT \ln K$ **found on equation sheets**
- this means that you can use ΔG^0 to calculate K_{eq} at nonstandard conditions.

Ex. For the reaction
        $H_2O_{(l)} = H^+_{(aq)} + OH^-_{(aq)}$ at 25°C,
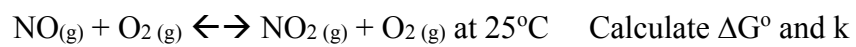 $\Delta G^0 = 79.83$ kj/mol
Calculate the value of k for this reaction
        $\Delta G^0 = -RT \ln k$

$$\ln k = \frac{\Delta G^\circ}{-RT} = \frac{79{,}830 \, ^j\!/_{mol}}{-(8.31 \, ^j\!/_{mol})(298K)} = -32.24$$

$$k = \text{anti ln} - 32.24 = 9.96 \times 10^{-15} = \boxed{1.0 \times 10^{-14}} \quad (= K_w)$$

Ex. For the reaction

$$NO_{(g)} + O_{2\ (g)} \longleftrightarrow NO_{2\ (g)} + O_{2\ (g)} \text{ at } 25^oC \quad \text{Calculate } \Delta G^o \text{ and k}$$

Given ΔG^o_f

NO	87kj/mol
NO_2	52 kj/mol
O_2	0
O_3	163 kj/mol