Chapter 3

Page 183, Quick Check

1. a) a mole of liquid water has more disorder, or, entropy, and will occur spontaneously.
   b) the solution has more entropy and will occur spontaneously.
   c) the collection of pieces will occur spontaneously.
   d) the raw rubber has more entropy and will occur spontaneously.
   e) The randomly shuffled deck therefore has higher entropy and will occur spontaneously.

Page 185, Quick Check

1. ΔS= 109 J/(K*mol)
2. a) Cl_2 has more layers of electrons (ie. more "shells") in which the electrons can position themselves than F_2. Therefore, there are more microstates and thus more entropy in Cl_2.
   b) CO_2 has more places where electrons can exist due to the bigger electron cloud and more total electron shells in CO_2 than CO. Therefore, there are more microstates and more entropy in CO_2.
   c) The right picture (pile of bricks) has more entropy since there is more disorder while the left brick wall is organized, thus low on entropy.

Page 186, Practice Problems

1. a) the gas particles have far more microstates than the liquid particles (the entropy change will be positive), and thus the entropy change is going to be positive and evaporation will be spontaneous.
   b) ΔS is going to be negative. The reaction will be non-spontaneous.
   c) ΔS is positive and the change is likely spontaneous.
   d) the entropy change is going to be positive and the dilution will be spontaneous.
2. a) $\Delta S = 174.51 - 413.61 = \frac{-239.1J}{mol\ rxn*K}$
   The reaction is non-spontaneous (not thermodynamically favourable) as ΔS<0. [This makes sense as the moles of gas have decreased.]
   b) The reaction is non-spontaneous as ΔS<0.

Page 187, Review Questions

1. a), ΔS is positive
   b) ΔS is negative
   c) ΔS is positive
   d) ΔS is negative
   e) ΔS is negative
   f) ΔS is negative
2. a) ΔS is negative
   b) ΔS is negative
   c) ΔS is positive
   d) ΔS is negative
   e). ΔS is positive
   f) ΔS is negative
3. S= 93.8 J/mol*K
4. $T = \frac{\Delta H°}{\Delta S°} == 373.8K$ =100.6°C. At room temperature is 25°C, formic acid is in liquid state at room temperature.
5. ΔS = -238 J/K
6. T = 150 °C
7. a) 229.6 J/mol$_{rxn}$ K
   b) -311.4 kJ/mol$_{rxn}$
   c) 1065 °C
8. a) Sign of ΔS° will be negative as the reaction goes from 3 moles of gas to 2 moles of gas, and gases have much higher entropy than solids that the 3 moles of solid's entropy is negligible.
   b) -186.74 J/mol$_{rxn}$ K
9. 205 J/mol O_2*K
10. a) -44.42 J/mol$_{rxn}$ K
    b) -137.56 J/mol$_{rxn}$ K
    c) -5.14 J/mol$_{rxn}$ K
    d) -206.16 J/mol$_{rxn}$ K
    e) 974 J/mol$_{rxn}$ K

Page 193, Quick Check

1. a) Vapourizing any substance requires heat energy. Therefore, it is logical that this is an endothermic process (thus ΔH is positive).
   b) Gases have more microstates (occupy far more positions in space) than liquids, so a transition from liquid to gas results in an increase in entropy.
   c) 60.°C
   d) This temperature represents the boiling point for bromine.

Page 197, Practice Problems

1. -1325.33 kJ/mol rxn

2. –5296.9 kJ of work is available from oxidation of 1 mol of octane.
3. Method 1:
$\Delta G° = \Delta H° - T*\Delta S° = 180.50$ kJ/mol - 298 K*(24.77 J/K*mol) = 173.12 kJ/mol$_{rxn}$
Method 2:
$\Delta G° = 2*\Delta G°_f$ NO = 2* (86.55 kJ/mol) = 173.10 kJ/mol$_{rxn}$
The values are very close.

Page 199, Practice Problems
1. a) $\Delta G° = 14.0$ kJ/mol rxn
b) $\Delta G° = -18.1$ kJ/mol rxn
c) The reaction becomes more favorable as temperature increases as $\Delta G°$ decreases as temperature increases.

Page 200, Review Questions
1. a) Change in enthalpy (ΔH) and change in entropy (ΔS) affect the spontaneity of a process
b) ΔH is the change in potential energy available to be converted to heat and ΔS is the change in the number of microstates the matter can occupy.
c) negative ΔH and positive ΔS are associated with spontaneity

2.

Sign of $\Delta H°$	Sign of $\Delta S°$	Temp	Sign of $\Delta G°$	Spontaneous/ Non-spontaneous
-	+	Low	-	Spontaneous
-	+	High	-	Spontaneous
+	-	Low	+	Non-spontaneous
+	-	High	+	Non-spontaneous
-	-	Low	-	Spontaneous
+	+	High	-	Spontaneous
-	-	High	+	Non-spontaneous
+	+	Low	+	Non-spontaneous

3. Circle A:
i) ΔH is positive, ΔS is also positive
ii) spontaneous only at high temperatures as ΔG is negative only when T*ΔS is bigger than ΔH.

Circle B:
i) ΔH is negative, ΔS is also negative
ii) spontaneous only at low temperatures as ΔG is negative only when T*ΔS is smaller than ΔH.

4. a) $\Delta S°$ is positive as there are more gas molecules (and thus more microstates) on the product side. $\Delta G°$ is negative as $\Delta G° = \Delta H° - T*\Delta S°$ and $\Delta H°$ is negative while $\Delta S°$ is positive, hence $\Delta G° = (-) - T(+)$ gives a negative value.
b) This process is spontaneous at all temperatures - $\Delta G° = (-) - T(+)$ gives a negative answer no matter what the T value.
5. a) 3 H_2 (g) + N_2 (g) → 2 NH_3 (g)
b) -92.22 kJ/mol$_{rxn}$
c) $\Delta S°_{rxn}$ is negative.
d) As $\Delta H°_{rxn}$ is negative and $\Delta S°_{rxn}$ is also negative, and $\Delta G° = \Delta H° - T*\Delta S°$, this process will be spontaneous only if temperature is low. Otherwise, $-T*\Delta S°$ will make $\Delta G°$ positive.
e) The spontaneity of this reaction changes when $\Delta G°=0$, so $\Delta G° = 0 = \Delta H° - T*\Delta S°$, or, when T = $\Delta H°/\Delta S°$.
$\Delta S° = -198.75$ J/K*mol$_{rxn}$
T = 191.0 °C
6. a) I_2 (g) → I_2 (s)
b) T = 159.0°C
7. a) $\Delta S°_{rxn}$ will be positive
b) $\Delta S°_{rxn} = 137.56$ J/K*mol
$\Delta G°_{rxn} = -326.4$ kJ/mol
The predicted signs match the calculated signs, hence the predictions were accurate.
8. a) = -91.12 kJ/mol$_{rxn}$
b) -91.73 kJ/mol$_{rxn}$
c) 13374.0 kJ/mol$_{rxn}$
9. a) -74 kJ/mol$_{rxn}$
b) 536 J/mol$_{rxn}$
c) -326.6 kJ/mol$_{rxn}$
d) Since the enthalpy change is negative and the entropy change is positive, the free energy change will be negative (and hence the reaction will be thermodynamically favourable - that is spontaneous) under all temperature conditions.
e) The ability to produce fuel over a wide range of temperature conditions improves the economic feasibility. It is particularly expensive to maintain high temperatures during a chemical process, so being able to produce fuels without this necessity makes the process very attractive to a company trying to make money.
10. a) -47 J/K*mol$_{rxn}$
b) As $\Delta S°$ is negative and $\Delta H°$ is also negative, $\Delta G°$ will be negative only when the temperature is low enough.
c) -187 kJ/mol$_{rxn}$. The reaction is *still* spontaneous at this high temperature (though as expected, it is less spontaneous).

Page 207, Practice Problems
1. -36.31 kJ/mol$_{rxn}$
2. 1.26 kJ/mol$_{rxn}$

3. -33.38/ kJ/mol$_{rxn}$

Page 209, Practice Problems
1. 110 kJ/mol$_{rxn}$
2. a) 1×10^6
    b) 7×10^{-7}
    c) The K value for a) is much bigger than K value for b). This means the reaction in a) is very spontaneous in the forward direction while the reaction in b) is very spontaneous in the reverse direction. This is well suported by the values of $\Delta G°$, as negative value of $\Delta G°$ in a) indicates that the reaction is spontaneous while the positive value of $\Delta G°$ in b) indicates that the reaction is non-spontaneous or spontaneous in the reverse reaction.

Page 211, Review Questions
1. 163 kJ/mol
2. a) 48.3 kJ/mol$_{rxn}$ > 0
    Therefore, the forward reaction is not spontaneous at room temperature.
    b) $\Delta S° = 175.0$ J/K*mol$_{rxn}$ > 0
    Entropy drives the reaction forward.
    $\Delta H° = 100.6$ kJ/mol$_{rxn}$ > 0
    Enthalpy drives the reaction in the reverse direction. Therefore, only entropy drives the reaction forward.
    c) 3×10^{-9}
    d) 301.9°C
    e) $\Delta G = \Delta H° - T*\Delta S°$ thus (+) - T(+) only becomes negative when T exceeds 299.9. As T increases further, ΔG becomes more negative and the reaction becomes more spontaneous.
3. a) When the barrel is wide open, CH_4 (g) + 2 O_2 (g) $\rightarrow$ CO_2 (g) + 2 H_2O (g).
    $\Delta G° = -800.78$ kJ/mol$_{rxn}$
    When the barrel is nearly closed, CH_4 (g) + 2 O_2 (g) $\rightarrow$ CO_2 (g) + 2 H_2O (l).
    $\Delta G° = -817.90$ kJ/mol$_{rxn}$
    b) When the barrel is wide open,
    $K = 2 \times 10^{140}$
    When the barrel is nearly closed,
    $K = 2 \times 10^{143}$
    c) As evidenced by larger K value and more negative $\Delta G°$, the combustion of methane is more spontaneous when the barrel is nearly closed.
    d) Opening barrel allows more O_2 gas to react to force reaction right.
4. a) $\Delta H° = -41.16$ kJ/mol$_{rxn}$
    b) $\Delta S° = -42.08$ J/K*mol$_{rxn}$
    c) $\Delta G° = -28.62$ kJ/mol$_{rxn}$
    d) $K = 1*10^5$
    e) $K = 1.0*10^3$

f) As temperature increased, the K value decreased. This means the reaction was exothermic - as temperature increases, the reaction shifts left to offset the additional heat energy, decreasing the K value.
This agrees with the answer to part (a) as $\Delta H° = -41.16$ kJ/mol$_{rxn}$ < 0
5. a) The graphs are similar in that they show potential energy changes as reactants convert to products. Also both graphs represent reactions in which the products have less available energy than the reactants ("exo").
    b) The graphs are different in that the first graph shows changes in free energy as the reaction proceeds while the second graph shows changes in enthalpy. The second graph shows the activated complex while the first graph shows equilibrium point.
6. A: a) The sign of $\Delta H°$ is positive, as ice melts into water by absorbing heat from its surroundings.
    b) The sign of $\Delta S°$ is positive, as the state of water changes from solid to liquid (which has more microstates).
    c) Both $\Delta H°$ and $\Delta S°$ are positive, so at high temperatures, $\Delta G°$ is negative while at low temperatures it is positive.
    B: a) The sign of $\Delta H°$ is positive as the reverse reaction, the combustion of hydrogen, is exothermic.
    b) The sign of $\Delta S°$ is positive, as the reaction goes from 2 moles of gas to 3 moles of gas.
    c) $\Delta H°$ and $\Delta S°$ are both positive, so $\Delta G°$ will be negative at low temperatures and positive at high temperatures.
7. a) $\Delta G° = 4.73$ kJ/mol$_{rxn}$
    b) $\Delta G = -1.53$ kJ/mol$_{rxn}$
    c) As ΔG < 0, the equilibrium will shift right, producing more NO_2 from N_2O_4. Therefore, the representation will have more NO_2 molecules and less N_2O_4 molecules.
8. a) = -60.3 kJ/mol$_{rxn}$
    b) The reaction is less spontaneous under these pressure conditions as $\Delta G° = -71.2$ kJ/molrxn < -60.3 kJ/molrxn = ΔG
9. a) -4.0 kJ/mol$_{rxn}$
    b) The reaction is more spontaneous under these conditions than under standard conditions as $\Delta G = -14.02$ kJ/mol$_{rxn}$ < 20.21 kJ/mol$_{rxn}$ = $\Delta G°$
10. a) 27 kJ/mol$_{rxn}$
    b) -13. kJ/mol$_{rxn}$
    c) The reaction becomes thermodynamically favorable as ΔG is now negative.