Objective 12. Predict whether a reaction occurs using thermodynamics.

There are two driving forces for a reaction: enthalpy and entropy. These two thermodynamic quantities are related by the equation:

$$\Delta G = \Delta H - T\Delta S \qquad (1)$$

where ΔG is the change in free energy, ΔH is the change in enthalpy, and ΔS is the change in entropy.
Free energy is the energy that is freely available in a system to do work. For a physical process or chemical reaction, a net decrease in free energy, i.e., $\Delta G < 0$, means that the process or reaction occurs spontaneously.
For a reaction to occur spontaneously, $\Delta G < 0$. See Equation (1).
(i) If $\Delta H > 0$, does it help ΔG be less than 0? Answer: NO. If If so, ΔH is positive (right side of equation), it helps ΔG be positive. If $\Delta H < 0$, the reaction is favored by enthalpy.
(ii) If $\Delta S > 0$, does it help ΔG be less than 0? Answer: YES. If If so, ΔS is positive, then $-T\Delta S$ is negative (right side of equation), it helps ΔG be negative. If $\Delta S > 0$, the reaction is favored by entropy.
The sign and magnitude of ΔH and ΔS determines the sign of ΔG.

1. Predict the sign (> 0, = 0, or < 0; K is > 1 or < 1) of the specified quantities for the following processes. You will be able to predict the sign without doing a calculation for some reactions and quantities. Use a Table of thermodynamic values as needed. Give reasons for your answer.

	q	work	ΔH	ΔS	ΔG	K
Combustion of propane (used in bbq grills)						
CO_2 (s) ---> CO_2 (g) (sublmation of dry ice)						

2. You know salt, NaCl, dissolves in water. But limeston (calcium carbonate, $CaCO_3$) does not dissolve in water.
a. Write a chemical equation that represents the dissolution of each solid in water. (Hint: solid ---> aqueous ions)
b. Determine whether each reaction is exothermic or endothermic. What experimental observation tells you that this reaction is exothermic? Use Hess' law to calculate ΔH to confirm your answer. Is this reaction favored by enthalpy? (Answer: ΔH is approximately 4 kJ/mole for NaCl and between -10 and -15 kJ/mole for $CaCO_3$)
c. Determine ΔS for this reaction. Is this reaction favored by entropy? (Answer: ΔS is approximately 40 J/K mole for NaCl and between -200 and -210 J/K mole for $CaCO_3$)
d. Calculate ΔG at 25^{o}C. Does this calculation show NaCl is soluble in water? Does this calculation show $CaCO_3$ is not soluble in water?
e. There is a temperature at which NaCl (s) does not dissolve in water. ΔH and ΔS does not change with temperature but ΔG does. Use $\Delta G = \Delta H - T\Delta S$. Set $\Delta G = 0$ and substitute the numerical value for ΔH and ΔS into this equation and solve for T. Is it possible for NaCl not to dissolve at this T?
f. There is a temperature at which $CaCO_3$ (s) dissolves in water. Calculate this temperature. Is it possible for $CaCO_3$ to dissolve at this T?

3. You know water does not boil at 25^{o}C under normal atmospheric (P = 1 atm) conditions.

H_2O (l) --> H_2O (g)

a. Use Hess' law to calculate the numerical value of ΔH, ΔS, and ΔG for this reaction under standard state (298 K and 1 atm) conditions. (Answer: ΔH is greater than 0, ΔS is greater than 0, ΔG is greater than 0.)
(i) This reaction is not favored by enthalpy because _____.
(ii) This reaction is favored by entropy because _____.
(iii) Is this reaction spontaneous at 25^{o}C? What observation supports your answer?
(iv) As temperature increases, does ΔG increase, decrease, or stay the same?
b. Like you did in Question 2e, determine the temperature at which this reaction occurs. Use $\Delta G = \Delta H - T\Delta S$. (Answer: What is the boiling point of water?)

4. Ideally, a fuel produces heat and work. Compare the combustion of octane (C_8H_{18}, the main component of gasoline in your car) and hydrogen (H_2, thought by many to be the fuel fo the 21st century).
Determine the sign (+ or -) of ΔG, ΔH, ΔS, and w for each reaction.
a. Which fuel produces the most heat in kJ/g? Calculate ΔH in kJ/g for each fuel to support your answer. (Answer: hydrogen)

b. Which fuel produces the most work? Write a balanced chemical equation and compare moles of gas reactants to moles of gas products to support your answer.
c. Which reaction is favored by enthalpy?
d. Which reaction is favored by entropy?
e. Which fuel will combust at any temperature? For the other fuel, calculate the temperature at which combustion does not occur.
f. Why is octane a better fuel to use in a car engine?
g. The operating conditions in a heat engine (car engine) are high temperature and high pressure. As more reactants (fuel and air) are added to the engine, products are removed. Using your knowledge of thermodynamics, equilibrium, and reaction rate, explain why these T and P conditions are used.
h. Why is hydrogen not a good fuel to use in a car engine? (We'll discuss hydrogen fuel cells to produce electricity later in Chem 1B.)

5. A stove designer decides to use a butane, C_4H_{10}, as a fuel for a stove. The butane is stored in a pressurized container and the pressurized butane is dispensed through a nozzle into the stove.
a. When butane and air are mixed together at room temperature and pressure, nothing happens. Give reasons.
b. Why is a spark needed for this combustion reaction to start?
c. Based on your observations of any combustion reaction, would you expect the rate constant for this reaction to be large or small? Give reasons.
d. Is the combustion of butane favored by entropy or enthalpy or both? Calculate ΔH and ΔS to support your answer.
e. As the temperature increases, does ΔG increase, decrease, or stay the same? Give reasons.
f. Some butane is released from the pressurized container (assume an adiabatic process). The temperature of the butane drops as it leaves the nozzle (goes to the lower pressure atmosphere from the high pressure container). Give reasons based on the 1st law of thermodynamics.

- 1st law of thermodynamics states the internal energy (E) can be converted to heat or work or both. Internal energy is the energy inside atoms and molecules due to the kinetic energy of the subatomic particles. If the internal energy increases ($\Delta E > 0$), the temperature increases.
- Adiabatic process means q = 0.
- As butane gas leaves the nozzle, the gas expands. Is $\Delta V > 0$, < 0, or $= 0$? Then, use $w = -p\,\Delta V$ to determine if $w > 0$, < 0, or $= 0$.
- 1st law of thermodynamics: $\Delta E = q + w$. Since q = 0 and w is _____, is $\Delta E > 0$, < 0, or $= 0$?
- ΔE is ____ so temperature ____.

g. As you know, a refrigerator is a heat engine that runs in reverse. Is the situation in part f a good way to run a refrigerator? Give reasons.

6. Use thermo to determine storage temperature.
Hydrogen peroxide, H_2O_2, is used as a disinfectant. H_2O_2 decomposes over time.

H_2O_2 (l) ----> H_2O (l) + O_2 (g)

a. Calculate _____ to support the statement "H_2O_2 decomposes".
b. At what temperature should be H_2O_2 be stored so it does not decompose? (Hint: ΔH = -197 kJ, ΔS = 126 J/K for this reaction)
c. You buy H_2O_2 at the store. Is the H_2O_2 decomposition reaction fast or slow?
d. Why is H_2O_2 stored in a brown bottle?

7. A beverage is carbonated by dissolving CO_2 (g) into the drink:

CO_2 (g) ---> CO_2 (aq) (1).

a. Carbonated beverages are ____ (acidic or basic or neutral) because CO_2 reacts with water to form H^+ and HCO_3^-:

CO_2 (g) + H_2O (l) ---> H^+ (aq) + HCO_3^- (aq) (2).

b. Does more CO_2 (g) dissolve in water (Reaction 1) or react with water (Reaction 2)? Calculate ΔG and K_{eq} at 25°C for each reaction to confirm your answer. (Answer: at 25°C, ΔG = 8 kJ/mole for Reaction 1 and ΔG = 45 kJ/mole for Reaction 2)
c. One way to keep the soda from going flat is to ___ (raise or lower) the temperature. Calculate ΔH for Reaction (1) and apply Le Chatelier's principle to confirm your answer. (Answer: at 25°C, ΔH is between -19 and -22 kJ/mole for Reaction 1)
d. What happens to K_{eq} for Reaction (1) as the temperature changes? Calculate K_{eq} at 0°C for Reaction (1) and compare to K_{eq} at 25°C for Reaction (1) to confirm your answer. (What equations do you want to use?)
e. Another way to keep the soda from going flat is to ___ (raise or lower) the pressure. Give reasons based on Le Chatelier's principle.

f. If the CO_2 (g) pressure is 1 atm, calculate the pH of the soda. (Hint: use Reaction 2 and $K_{eq} = [H^+ (aq)][HCO_3^- (aq)]$/pressure of CO_2 (g). Answer: pH between 3.5 and 4.3)

8. One way to make a non-spontaneous reaction occur is to change the temperature. Another way to make a non-spontaneous reaction occur is to use the energy from a spontaneous reaction.
Lime stains ($Ca(OH)_2$) make your glasses and cups look dirty although they may be clean.
a. $Ca(OH)_2$ (s) <===> Ca^{2+} (aq) + 2 OH^- (aq) $K_{sp} = 4.7x10^{-6}$.
Calculate ΔG for this reaction. (Hint: use $\Delta G = -RT \ln K_{eq}$)
b. You can use acid, like HCl, to remove (dissolve) an insoluble hydroxide solid. Complete the chemical equation and then write a net ionic equation.
$Ca(OH)_2$ (s) + HCl ---->

c. Add Equation (1) to Equation (2) to get Equation (3). Equation (3) should be the same as your net ionic equation in part b.

$Ca(OH)_2$ (s) <===> Ca^{2+} (aq) + 2 OH^- (aq) $K_{sp} = 4.7x10^{-6}$ (1)
2 H^+ (aq) + 2 OH^- (aq) <===> 2 H_2O (l) $K = 1/K_w^2 = 1x10^{28}$ (2)

d. Calculate K for Equation (3). How does K show acid dissolves lime stains?
e. Calculate ΔG for Equation (3). How does ΔG show acid dissolves lime stains?

9. Biology: ATP is the universal currency of energy in biological systems. We use ATP in our bodies to supply energy for other reactions to occur. The hydrolysis of ATP to ADP and orthophosphate is a **spontaneous** reaction with a ΔG of -7.3 kcal/mole:

ATP + H_2O -----> ADP + P_i + H^+ $\Delta G = -7.3$ kcal/mole (1)
where P_i is orthophosphate, HPO_4^{2-}.

One of the ways metabolic energy is produced is by glycolysis. In glycolysis, glucose is converted into pyruvate in a 10 step process. In the first step, glucose is phosphorylated to glucose 6-phosphate:

glucose + P_i -----> glucose 6-phosphate + H_2O $\Delta G = 3.3$ kcal/mole (2).

a. Does the reaction that converts glucose to glucose 6-phosphate (Reaction 2) occur spontaneously? Give reasons.
b. (i) Add Reaction (1) to Reaction (2). Write the sum of the two reactions to give Reaction (3).
(Answer: glucose + ATP -----> glucose 6-phosphate + ADP + H^+)
(ii) Calculate the ΔG and K for Reaction (3). Does Reaction (3) occur spontaneously? Give reasons.
c. Explain why ATP is needed for the first step of glycolysis to occur.
d. Does Reaction (3) produce more products if the pH increases? Give reasons.