

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:

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

where  $\Delta G$  is the change in free energy,  $\Delta H$  is the change in enthalpy, and  $\Delta S$  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  $\Delta G$  be less than 0? Answer: NO. If  $\Delta H$  is positive (right side of equation), it helps  $\Delta G$  be positive. If  $\Delta H < 0$ , the reaction is favored by enthalpy.

(ii) If  $\Delta S > 0$ , does it help  $\Delta G$  be less than 0? Answer: YES. If  $\Delta S$  is positive, then  $-T\Delta S$  is negative (right side of equation), it helps  $\Delta G$  be negative. If  $\Delta S < 0$ , the reaction is favored by entropy.

The sign and magnitude of  $\Delta H$  and  $\Delta S$  determines the sign of  $\Delta G$ .

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	$\Delta H$	$\Delta S$	$\Delta G$	K
Combustion of propane (used in bbq grills)						
$\text{CO}_2(\text{s}) \rightarrow \text{CO}_2(\text{g})$ (sublimation of dry ice)						

2. You know salt, NaCl, dissolves in water. But limestone (calcium carbonate,  $\text{CaCO}_3$ ) does not dissolve in water.

a. Write a chemical equation that represents the dissolution of each solid in water. (Hint: solid  $\rightarrow$  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  $\Delta H$  to confirm your answer. Is this reaction favored by enthalpy?

(Answer:  $\Delta H$  is approximately 4 kJ/mole for NaCl and between -10 and -15 kJ/mole for  $\text{CaCO}_3$ )

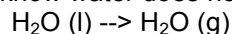
c. Determine  $\Delta S$  for this reaction. Is this reaction favored by entropy? (Answer:  $\Delta S$  is approximately 40 J/K mole for NaCl and between -200 and -210 J/K mole for  $\text{CaCO}_3$ )

d. Calculate  $\Delta G$  at 25°C. Does this calculation show NaCl is soluble in water? Does this calculation show  $\text{CaCO}_3$  is not soluble in water?

e. There is a temperature at which NaCl (s) does not dissolve in water.  $\Delta H$  and  $\Delta S$  does not change with temperature but  $\Delta G$  does. Use  $\Delta G = \Delta H - T\Delta S$ . Set  $\Delta G = 0$  and substitute the numerical value for  $\Delta H$  and  $\Delta S$  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  $\text{CaCO}_3$  (s) dissolves in water. Calculate this temperature. Is it possible for  $\text{CaCO}_3$  to dissolve at this T?

3. You know water does not boil at 25°C under normal atmospheric ( $P = 1$  atm) conditions.



a. Use Hess' law to calculate the numerical value of  $\Delta H$ ,  $\Delta S$ , and  $\Delta G$  for this reaction under standard state (298 K and 1 atm) conditions. (Answer:  $\Delta H$  is greater than 0,  $\Delta S$  is greater than 0,  $\Delta G$  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°C? What observation supports your answer?

(iv) As temperature increases, does  $\Delta G$  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 ( $\text{C}_8\text{H}_{18}$ , the main component of gasoline in your car) and hydrogen ( $\text{H}_2$ , thought by many to be the fuel for the 21<sup>st</sup> century).

Determine the sign (+ or -) of  $\Delta G$ ,  $\Delta H$ ,  $\Delta S$ , and w for each reaction.

a. Which fuel produces the most heat in kJ/g? Calculate  $\Delta H$  in kJ/g for each fuel to support your answer. (Answer: hydrogen)

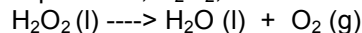
- Which fuel produces the most work? Write a balanced chemical equation and compare moles of gas reactants to moles of gas products to support your answer.
- Which reaction is favored by enthalpy?
- Which reaction is favored by entropy?
- Which fuel will combust at any temperature? For the other fuel, calculate the temperature at which combustion does not occur.
- Why is octane a better fuel to use in a car engine?
- 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.
- 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.

- When butane and air are mixed together at room temperature and pressure, nothing happens. Give reasons.
- Why is a spark needed for this combustion reaction to start?
- Based on your observations of any combustion reaction, would you expect the rate constant for this reaction to be large or small? Give reasons.
- Is the combustion of butane favored by entropy or enthalpy or both? Calculate  $\Delta H$  and  $\Delta S$  to support your answer.
- As the temperature increases, does  $\Delta G$  increase, decrease, or stay the same? Give reasons.
- 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 1<sup>st</sup> law of thermodynamics.
  - 1<sup>st</sup> 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  $= 0$ .
  - 1<sup>st</sup> law of thermodynamics:  $\Delta E = q + w$ . Since  $q = 0$  and  $w$  is \_\_\_\_\_, is  $\Delta E > 0$ ,  $< 0$ , or  $= 0$ ?
  - $\Delta E$  is \_\_\_\_\_ so temperature \_\_\_\_\_.
- 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.

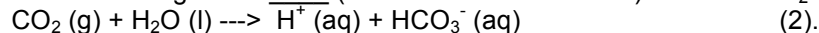


- Calculate \_\_\_\_\_ to support the statement " $H_2O_2$  decomposes".
- At what temperature should  $H_2O_2$  be stored so it does not decompose? (Hint:  $\Delta H = -197 \text{ kJ}$ ,  $\Delta S = 126 \text{ J/K}$  for this reaction)
- You buy  $H_2O_2$  at the store. Is the  $H_2O_2$  decomposition reaction fast or slow?
- Why is  $H_2O_2$  stored in a brown bottle?

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



- Carbonated beverages are \_\_\_\_\_ (acidic or basic or neutral) because  $CO_2$  reacts with water to form  $H^+$  and  $HCO_3^-$ :



- Does more  $CO_2(g)$  dissolve in water (Reaction 1) or react with water (Reaction 2)? Calculate  $\Delta G$  and  $K_{eq}$  at  $25^\circ C$  for each reaction to confirm your answer. (Answer: at  $25^\circ C$ ,  $\Delta G = 8 \text{ kJ/mole}$  for Reaction 1 and  $\Delta G = 45 \text{ kJ/mole}$  for Reaction 2)
- One way to keep the soda from going flat is to \_\_\_\_\_ (raise or lower) the temperature. Calculate  $\Delta H$  for Reaction (1) and apply Le Chatelier's principle to confirm your answer. (Answer: at  $25^\circ C$ ,  $\Delta H$  is between  $-19$  and  $-22 \text{ kJ/mole}$  for Reaction 1)
- What happens to  $K_{eq}$  for Reaction (1) as the temperature changes? Calculate  $K_{eq}$  at  $0^\circ C$  for Reaction (1) and compare to  $K_{eq}$  at  $25^\circ C$  for Reaction (1) to confirm your answer. (What equations do you want to use?)
- 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  $\text{CO}_2$  (g) pressure is 1 atm, calculate the pH of the soda. (Hint: use Reaction 2 and  $K_{\text{eq}} = [\text{H}^+ (\text{aq})][\text{HCO}_3^- (\text{aq})]/\text{pressure of } \text{CO}_2 (\text{g})$ . 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 ( $\text{Ca}(\text{OH})_2$ ) make your glasses and cups look dirty although they may be clean.

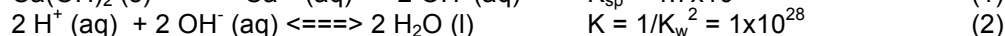
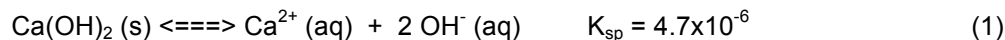
a.  $\text{Ca}(\text{OH})_2 (\text{s}) \rightleftharpoons \text{Ca}^{2+} (\text{aq}) + 2 \text{OH}^- (\text{aq})$   $K_{\text{sp}} = 4.7 \times 10^{-6}$ .

Calculate  $\Delta G$  for this reaction. (Hint: use  $\Delta G = -RT \ln K_{\text{eq}}$ )

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.

$\text{Ca}(\text{OH})_2 (\text{s}) + \text{HCl} \rightarrow$

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.



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

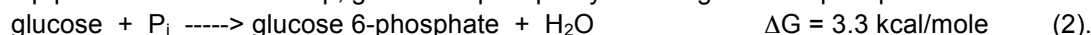
e. Calculate  $\Delta G$  for Equation (3). How does  $\Delta G$  show acid dissolves lime stains?

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  $\Delta G$  of -7.3 kcal/mole:



where  $\text{P}_i$  is orthophosphate,  $\text{HPO}_4^{2-}$ .

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:



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:  $\text{glucose} + \text{ATP} \rightarrow \text{glucose 6-phosphate} + \text{ADP} + \text{H}^+$ )

(ii) Calculate the  $\Delta G$  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.