

Lab 7. Thermodynamic Prediction of Precipitation Reactions

Prelab Assignment

Before coming to lab:

- Read this lab handout thoroughly and then answer the pre-lab questions on the last page of this lab exercise and be prepared to hand them in at the start of your lab period. Background information for this lab can be found in [Chapter 20](#) in your textbook (*Silberberg 5th ed*).
- This lab exercise does not require a report in your lab notebook. The report for this exercise consists of completing the attached Report pages (pp. 5 – 6) as you carry out the procedure on [page 4](#).

Purpose

In this experiment you will calculate the free-energy changes of reaction, ΔG_{rxn} , for a variety of possible precipitation reactions, then use your calculated values to predict whether a precipitate will form when two solutions are mixed. In the last part of the experiment you will actually mix the reagents and attempt to confirm your predictions.

Introduction

A **spontaneous change** is one that occurs by itself, without the exertion of any outside force. A mixture of hydrogen and oxygen gas changes spontaneously (and explosively) into water after being ignited by a spark. Iron rusts spontaneously, albeit slowly, when it is exposed to air and water.

Many spontaneous chemical changes, such as combustion of hydrocarbons, are exothermic. However, there are many examples of endothermic processes that occur spontaneously. These include the melting of ice at temperatures above 0°C and the boiling of water at temperatures above 100°C (at 760 torr of pressure). In both of these cases, spontaneous change occurs in the direction of a **less ordered state**, that is, in the direction of **higher entropy**.

Two state functions have been defined to describe the tendency for a change to occur spontaneously. The first of these is ΔH , the **enthalpy change**. A negative value for ΔH denotes an exothermic process and is a factor that favors spontaneous change. The second state function is ΔS , the **entropy change**. Entropy is a measure of randomness. A **positive value for ΔS** denotes that the change will result in a more random (less ordered) system, a factor that also favors spontaneous change.

Very often the **temperature** determines the direction of spontaneous change. For instance, water changes spontaneously into ice when placed in the freezer ($t < 0^\circ\text{C}$), but ice cubes melt spontaneously when removed from the freezer ($t > 0^\circ\text{C}$). In these cases, the signs of ΔH and ΔS work in opposition (i.e., ΔH is favorable when water freezes—an exothermic process), but ΔS is unfavorable; ΔH is unfavorable when ice melts—an endothermic process), but ΔS is favorable—hence temperature is the factor that determines whether ΔH or ΔS will dominate. This information is incorporated into a single state function, the **Gibbs free energy change, ΔG** , defined in Equation 1.

$$\text{Equation 1.} \quad \Delta G = \Delta H - T\Delta S$$

It is easy to see that **ΔG must be negative if a process is spontaneous**, because a change for which **ΔH is negative** (exothermic) and **ΔS is positive** (increase in randomness) will surely be **spontaneous**. Endothermic processes that give positive entropy changes will be spontaneous at high temperatures (where $T\Delta S$ dominates). Exothermic processes that give negative entropy changes will be spontaneous at low temperatures (where ΔH dominates).

Many textbooks give tabulations of values for *standard free-energy changes of formation* (ΔG_f°), *standard enthalpy changes of formation* (ΔH_f°), and *standard entropies* (S°). The “o” symbol indicates that the values are for changes involving substances in their *standard state*, one atmosphere pressure and 298 Kelvin. The “f” subscript on ΔG and ΔH denotes formation; Hence, ΔG_f° and ΔH_f° are the free-energy and enthalpy change associated with a reaction in which *one mole of product is formed from its constituent elements in their standard states, 1 atm and 298 K*. Table 1 shows how to use tabulated values of ΔG_f° , ΔH_f° and S° for carbon, oxygen and carbon dioxide to calculate the free energy change in the combustion of carbon. Note that you can obtain the standard free energy change for any reaction, $\Delta G_{\text{rxn}}^\circ$ by subtracting the sum of the ΔG_f° for the reactants from the sum of ΔG_f° for the products as in Equation 2, below.

$$\text{Equation 2.} \quad \Delta G_{\text{rxn}}^\circ = \sum_{\text{products}} \Delta G_f^\circ - \sum_{\text{reactants}} \Delta G_f^\circ$$

Table 1. Calculation of the Free Energy Change for the Combustion of Carbon (Graphite)

	C(graphite, 298) + O ₂ (g, 298) → CO ₂ (g, 298)		
<u>ΔH_f° of the reactants and products:</u>	ΔH_f°	0	$-393.5 \frac{\text{kJ}}{\text{mol}}$
<u>S° of the reactants and products:</u>	S°	$5.73 \frac{\text{J}}{\text{mol K}}$	$213.6 \frac{\text{J}}{\text{mol K}}$
<u>ΔG_f° of the reactants and products:</u>	ΔG_f°	0	$-394.3 \frac{\text{kJ}}{\text{mol}}$
<u>Calculation of $\Delta H_{\text{rxn}}^\circ$:</u>	$\Delta H_{\text{rxn}}^\circ = \Delta H_f^\circ (\text{CO}_2) - \Delta H_f^\circ (\text{O}_2) - \Delta H_f^\circ (\text{C})$ $\Delta H_{\text{rxn}}^\circ = -393.5 \frac{\text{kJ}}{\text{mol}}$		
<u>Calculation of $\Delta S_{\text{rxn}}^\circ$:</u>	$\Delta S_{\text{rxn}}^\circ = S^\circ (\text{CO}_2) - S^\circ (\text{O}_2) - S^\circ (\text{C})$ $\Delta S_{\text{rxn}}^\circ = 2.9 \frac{\text{J}}{\text{mol K}}$		
<u>Calculation of $\Delta G_{\text{rxn}}^\circ$:</u>	$\Delta G_{\text{rxn}}^\circ = \Delta H_{\text{rxn}}^\circ - T\Delta S_{\text{rxn}}^\circ = -394.4 \frac{\text{kJ}}{\text{mol}}$ $\Delta G_{\text{rxn}}^\circ = \Delta G_f^\circ (\text{CO}_2) - \Delta G_f^\circ (\text{O}_2) - \Delta G_f^\circ (\text{C})$ $\Delta G_{\text{rxn}}^\circ = -394.3 \frac{\text{kJ}}{\text{mol}}$		

The combustion of carbon to give carbon dioxide is, of course, a spontaneous process. This is confirmed by the fact that $\Delta G_{\text{rxn}}^\circ$ for the combustion process is -394.4 kJ/mol. This means that when one mole of graphite, the standard form of carbon, is combined with the mole of oxygen to produce one mole of CO₂, the free energy of the system decreases by 394.4 kJ. If the reaction is not performed with all materials in their standard states, if the reaction temperature is not 298K, or if more or less than one mole of carbon is consumed in the reaction, then a value of ΔG_{rxn} will differ from $\Delta G_{\text{rxn}}^\circ$. The relationship between ΔG_{rxn} and $\Delta G_{\text{rxn}}^\circ$ is shown in Equation 3, below.

$$\text{Equation 3.} \quad \Delta G_{\text{rxn}} = \Delta G_{\text{rxn}}^\circ + 2.303 RT \log Q \quad \text{or} \quad \Delta G_{\text{rxn}} = \Delta G_{\text{rxn}}^\circ + RT \ln Q$$

In Equation 3, R is the ideal gas constant (8.314 J/Kmol), and T is the temperature in *Kelvin*. The symbol “ Q ” denotes the reaction quotient, defined below.

$$aA + bB \rightleftharpoons cC + dD \quad Q = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

How to Calculate the Free Energy of a Reaction, ΔG_{rxn}

In this experiment, you calculate the ΔG_{rxn} for a variety of possible precipitation reactions. You will use your calculated values to predict whether a precipitate will form when two solutions are mixed. In the last part of the experiment, you will actually mix the reagents and attempt to confirm your predictions. *Table 2 lists the data you will use to make your calculations. The following paragraph explains how to use this data.*

The row and column headings of Table 2 show the standard free energies of formation of the various ions under consideration, with the standard state as a 1 M solution. Thus, ΔG_f° for Ag^+ is 77.107 kJ/mol and ΔG_f° for Cl^- is -131.228 kJ/mol. Entries within the body of the table show the standard free energies of formation for the crystalline solids that result from the combinations of the various ions whose rows and columns intersect to create the compound's cell. For instance, ΔG_f° for AgCl is -109.789 kJ/mol. The "W 10" entry in the cell corresponding to sodium sulfate indicates that the most likely precipitate is $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$. *When you write the equation for the precipitation of a hydrated salt, water will appear as a reactant. Therefore, in the calculation of ΔG_{rxn} , you will need to consider ΔG_f° for water (ΔG_f° of water = -237.129).*

Because you will not be working with 1 M solutions, the free-energy changes you will be calculating will not be standard free energies—therefore, equation 3 will be needed to convert ΔG_{rxn}° to ΔG_{rxn} . *See table 3 on page 4 for a sample calculation of the free-energy change, ΔG_{rxn} , for the possible reaction between Ag^+ and Cl^- to form the precipitate silver chloride, AgCl.*

Table 2. Gibbs Free Energies (kJ) of formation, ΔG_f° , for Ions in 1 M Solution and for Ionic Solids

Cations	Anions			
	Cl^- -131.228	I^- -51.57	NO_3^- -108.74	SO_4^{2-} -744.53
Ag^+ 77.107	-109.789	-66.19	-33.41	-618.41
Ba^{2+} -560.77	-1296.32 W2	-663.9	-796.59	-1362.2
Na^+ -261.905	-384.138	-286.06	-367.00	-3646.85 W10
Ca^{2+} -553.58	-748.1	-528.9	-743.07	-1797.28 W2

Possible Source of Unexpected Results

Take note that we are not considering possible deviations of the ions in solution from ideal behavior—we should be using “activity,” rather than molarity when calculating ΔG values. This omission/error will be **most serious when ions of high charge** (e.g. divalent ions) are involved. Highly charged ions (e.g. divalent ions) have a higher tendency to form **ion pairs** in solution than monovalent ions. The formation of ion pairs reduces the concentration of those ions in solution—that is, the formation of ion pairs reduces the “activity” of the ions involved. The term **activity** is used to explain the deviation in ionic properties of “real solutions” from “ideal solutions” and is related to the concentration and interaction of ions in solution, the more concentrated the solution the more the activity will deviate from the concentration, the difference usually being described in the form of an **activity coefficient**, i.e. **activity = coefficient \times concentration**. The activity coefficient depends on the identity of the ion and the magnitude of its charge. *The activity coefficient equals one for ideal solutions, hence the activity = concentration for ideal solutions.*

Table 3. Calculation of ΔG_{rxn}^o and ΔG_{rxn} for the formation of silver chloride, AgCl, when equal volumes containing silver ions and chloride ions are mixed.

$$\begin{aligned}
 & \text{Ag}^+ (0.1 \text{ M}) + \text{Cl}^- (0.1 \text{ M}) \rightarrow \text{AgCl} \\
 \Delta G_{rxn}^o &= \Delta G_f^o (\text{AgCl}) - \Delta G_f^o (\text{Ag}^+) - \Delta G_f^o (\text{Cl}^-) \\
 \Delta G_{rxn}^o &= -109.789 - (77.107) - (-131.228) \text{ kJ/mol} \\
 \Delta G_{rxn}^o &= -55.668 \text{ kJ/mol} \\
 \Delta G_{rxn} &= \Delta G_{rxn}^o + 2.303 RT \log Q \\
 \Delta G_{rxn} &= -55.668 \text{ kJ/mol} + 2.303 \frac{(8.314 \text{ J/molK})(298\text{K})}{1000 \text{ J/kJ}} \log \frac{1}{(0.1)(0.1)} \\
 \Delta G_{rxn} &= -44.250 \text{ kJ/mol}
 \end{aligned}$$

Procedure (Work in teams of two to four)

Special Equipment and Solutions:

- 0.20 M Solutions in dropper bottles of Ag^+ , Ba^{2+} , Na^+ , Ag^+ , Ca^{2+} , Cl^- , I^- , NO_3^- and SO_4^{2-}
- Spot plates

1. First calculate the standard free-energy change, ΔG_{rxn}^o , and then the free-energy change, ΔG_{rxn} , for each precipitate that *might* form when each of the 0.20 M solutions of cations listed in table 2 is mixed with an equal volume of each anion solution listed. Record your ΔG_{rxn} values at the **top** of the appropriate cells in table 4. *Sample Calculations:* Under question #1 on page 6 record sample calculations of the ΔG_{rxn}^o and the ΔG_{rxn} for the possible reaction between sodium ions and sulfate ions and for the possible reaction between barium ions and sulfate ions.
 - Note: The mixing equal volumes of 0.20 M solutions of cations and anions will result in 0.10 M solutions after mixing.
2. Use your ΔG_{rxn} values to predict which combinations will result in a precipitate (**ppt**) or will not form a precipitate (**no ppt**). Record your predictions below the ΔG_{rxn} values in table 4.
3. Mix the solutions and record in Table 4.....
 - a. the appearance and formula any precipitate the forms. If no precipitate forms, record **N.R.** (for no reaction).
 - b. whether your observations support (**S**) or refute (**R**) your predictions.
4. On the report sheet and separate paper if needed, discuss possible reasons for any discrepancies between your predictions and your observations.

Lab 7 Report Sheet
Thermodynamic Prediction of Precipitate Rxns

 Name _____
 Team No. ____ Date _____ Section ____

Experimental Results (Use a pen to record all experimental data and observations.)

Table 4. Calculated ΔG_{rxn} values, Predicted Results (*ppt* = precipitate; *NR* = no reaction) and Actual Results/Observations for the mixing of equal volumes of 0.20 M cation and anion solutions. *S* = observations support prediction; *R* = observations refute prediction

Cations	Anions			
	Cl^-	I^-	NO_3^-	SO_4^{2-}
Ag^+				
Ba^{2+}				
Na^+				
Ca^{2+}				

Section _____ Team # _____

1. a.) Write the chemical equation corresponding to ΔG_f° for AgCl.

b.) How does this equation differ from the net ionic equation that shows AgCl precipitating when solutions of $\text{Ag}^+_{(aq)}$ and $\text{Cl}^-_{(aq)}$ are mixed?

2. Under what conditions of temperature are endothermic processes spontaneous? Explain

3. The value of ΔG_f° for Mg^{2+} is -454.8 kJ/mol . The value for $\Delta G_{f,298}^\circ$ for $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ is -2114.64 kJ/mol . Will a precipitate form when 0.20 M Mg^{2+} is mixed with 0.20 M Cl^- ? Calculate ΔG for the reaction to determine if a precipitation reaction will occur or not.