

# Thermodynamics

## Introduction

Gibbs Free Energy,  $\Delta G$ , can be used to determine if a reaction is spontaneous or not. A negative value of  $\Delta G$  indicates that a given reaction is spontaneous at the measured conditions and will proceed in the forward direction.  $\Delta G$  can be calculated using the Gibbs-Helmholtz equation:  $\Delta G = \Delta H - T\Delta S$ . In this experiment,  $\Delta H$  (enthalpy) will be calculated from the temperature change of the reaction.  $\Delta S$  (entropy) will be calculated using standard entropy values from the textbook.

The reactions used in this lab will be the dissolution (dissociation) of two salts in water. It will be important to differentiate between the system (or reaction) and the surroundings in this experiment. The calorimeter used in this experiment is assumed to be a closed, isolated container that does not lose any heat to the environment. Therefore, all heat exchanges are assumed to take place between the system and the surroundings. The dissolution of each salt is the system; water is the surroundings. It is the temperature change of the water (the surroundings) that will be measured over time.

## Equations to use for the calculations:

Heat of solution:  $q_{\text{soln}} = mC\Delta T$

where mass ( $m$ ) = mass of solution

$C$  = specific heat of water = 4.184 J/g °C

$\Delta T = T_{\text{final}} - T_{\text{initial}}$

$T_{\text{final}}$  is the maximum or minimum temperature reached  $T_{\text{initial}}$  is the initial temperature of water before adding salt.

Law of Conservation of Energy:  $q_{\text{rxn}} + q_{\text{soln}} = 0 \rightarrow q_{\text{rxn}} = -q_{\text{soln}}$

Density of water: 1.00 g/mL (Use to find mass of measured volume.)

Free Energy of reaction:  $\Delta G_{\text{rxn}} = \Delta H_{\text{rxn}} - T\Delta S_{\text{rxn}}$  (where  $T = T_{\text{initial}}$  in Kelvin)

Enthalpy of Reaction:  $\Delta H_{\text{rxn}} = q_{\text{rxn}} / \text{moles of salt}$

Entropy of Reaction:  $\Delta S_{\text{rxn}}^{\circ} = \sum nS_{\text{(products)}}^{\circ} - \sum nS_{\text{(reactants)}}^{\circ}$

## Materials:

Styrofoam cup calorimeter

Timer

Digital thermometer

Distilled H<sub>2</sub>O

100 mL graduated cylinder

Solid calcium chloride, CaCl<sub>2</sub>

Plastic weighing cup

Solid ammonium chloride, NH<sub>4</sub>Cl

Name: \_\_\_\_\_

Date: \_\_\_\_\_

### **Thermodynamics Pre-Lab Questions & Calculations**

1. Calculate the mass of ammonium chloride required to prepare 25 mL of a 2.0 M solution. Show your work. **Record this value on your data table to reference during lab.**
2. Calculate the mass of calcium chloride required to prepare 25 mL of a 2.0 M solution. Show your work. **Record this value on your data table to reference during lab.**
3. Write the balanced equation for the dissolution of ammonium chloride in water.
4. Write the balanced equation for the dissolution of calcium chloride in water.
5. What does a negative value of  $\Delta H$  indicate about a reaction?
6. What does a negative value of  $\Delta S$  indicate about a reaction?
7. What does a negative value of  $\Delta G$  indicate about a reaction?
8. Calculate the heat of solution ( $q_{\text{soln}}$ ) if the mass of solution is 45.6 g, specific heat is 3.98 J/g $^{\circ}\text{C}$ , and  $\Delta T$  is  $-34.5^{\circ}\text{C}$ .
9. What is the heat of reaction ( $q_{\text{rxn}}$ ) for the above question?
10. If 0.612 moles of salt were used in the reaction, what is  $\Delta H_{\text{rxn}}$ ?

**Procedure:**

*Note: Thoroughly clean up any spilled salts.  $\text{CaCl}_2$  will corrode the metal on the balances. Use a brush to sweep off the metal surface of the balances **immediately**. Do NOT return excess reagent to the salt container. It must go into the designated waste container.*

1. Using a 100-mL graduated cylinder, measure about 25 mL of deionized (distilled) water and then add that to the Styrofoam cup. Record the exact volume of water used.
2. Tare out (zero) the mass of the weighing cup. Remove the weighing cup from the balance and use a spatula to add the appropriate mass of ammonium chloride (calculated in pre-lab). The mass should be within  $\pm 0.20$  grams of the calculated value.
3. Place a thermometer in the distilled water. This will be your initial temperature.
4. Add the salt to the water in the calorimeter and replace the lid. Stir the solution vigorously by swirling the beaker and contents, carefully holding the lid and thermometer in place, for two minutes. Record the temperature of the mixture every 10 seconds.
5. The highest (or lowest) temperature reached will be the final temperature,  $T_f$ . Note:  $T_f$  is NOT the temperature after 2 minutes, but the maximum (or minimum) temperature obtained.
6. Be sure to record your observations of the appearance of the salt solution in the calorimeter at the end of two minutes. Pour your salt solution in the sink and run some water to wash it down. Rinse, dry, and reuse the plastic weighing cup and the plastic coffee cup for your second trial.
7. Repeat all steps for a second trial of ammonium chloride. Repeat all steps for two trials of calcium chloride.
8. When complete graph the average for each compound in Google Sheets or SparkVUE.

**Clean-Up: Rinse everything well with tap water followed by a quick distilled water rinse. Wipe your bench-top with a damp paper towel. Put all equipment back where you found it.**

Name: \_\_\_\_\_

Date: \_\_\_\_\_

**Data & Calculations**

Table 1: Mass, volume and temperatures

	<b>Ammonium Chloride</b>			<b>Calcium Chloride</b>	
Calculated mass from pre-lab, g			Calculated mass from pre-lab, g		
Mass of salt, g			Mass of salt, g		
Volume of water, mL			Volume of water, mL		
Initial temp. of H <sub>2</sub> O, T <sub>i</sub> (°C)			Initial temp. of H <sub>2</sub> O, T <sub>i</sub> (°C)		
<b>Time</b>	<b>Temperature, °C, Trial 1</b>	<b>Temperature, °C, Trial 2</b>	<b>Time</b>	<b>Temperature, °C, Trial 1</b>	<b>Temperature, °C, Trial 2</b>
0:00			0:00		
0:10			0:10		
0:20			0:20		
0:30			0:30		
0:40			0:40		
0:50			0:50		
1:00			1:00		
1:10			1:10		
1:20			1:20		
1:30			1:30		
1:40			1:40		
1:50			1:50		
2:00			2:00		

Table 2: Observations of each salt after reaction and dissolution reaction in water.

Observation after reaction - ammonium chloride:	Observation after reaction – calcium chloride:
Balanced equation for dissolution of ammonium chloride:	Balanced equation for dissolution of calcium chloride:

Name: \_\_\_\_\_

Date: \_\_\_\_\_

**Calculations for  $\text{NH}_4\text{Cl}$ :** Show a sample calculation for one trial for a) moles of salt, b) mass of solution, c)  $\Delta T$ , d)  $q_{\text{rxn}}$ , e)  $\Delta H$ , f)  $\Delta S^\circ$  (Use values in Table 3 for this calculation.), and g)  $\Delta G$ . Refer to Results Table 4 for units of each quantity.

**Calculations for  $\text{CaCl}_2$ :** Show a sample calculation for one trial for a) moles of salt, b) mass of solution, c)  $\Delta T$ , d)  $q_{\text{rxn}}$ , e)  $\Delta H$ , f)  $\Delta S^\circ$  (Use values in Table 3 for this calculation.), and g)  $\Delta G$ . Refer to Results Table 4 for units of each quantity.

Name: \_\_\_\_\_

Date: \_\_\_\_\_

Table 3: Thermodynamic data.

	$\Delta H_f^\circ$ (kJ/mol)	$\Delta G_f^\circ$ (kJ/mol)	$S^\circ$ (J/K·mol)
NH <sub>4</sub> Cl (s)	-314.4	-202.8	94.6
NH <sub>4</sub> <sup>+</sup> (aq)	-132.5	-79.3	113.4
Cl <sup>-</sup> (aq)	-167.2	-131.2	56.5
CaCl <sub>2</sub> (s)	-795.8	-748.1	104.6
Ca <sup>2+</sup> (aq)	-542.9	-553.0	-55.2

**Results:**

Table 4: Results of salt dissolution calculations.

	Ammonium Chloride		Calcium Chloride	
	Trial 1	Trial 2	Trial 1	Trial 2
Moles of salt (mol)				
Mass of Water (g)				
Mass of Solution (g)				
Final temperature, T <sub>f</sub> (°C)				
$\Delta T$ (°C)				
q <sub>rxn</sub> (J)				
$\Delta H_{rxn}$ (kJ/mol)				
$\Delta S^\circ_{rxn}$ (J/mol K) calculated from table 3				
$\Delta G_{rxn}$ (kJ/mol)				

Use values from Table 3 (top of this page) to calculate standard values of  $\Delta H^\circ_{rxn}$  and  $\Delta G^\circ_{rxn}$  for NH<sub>4</sub>Cl.

$\Delta H^\circ_{rxn}$ :

$\Delta G^\circ_{rxn}$ :

Name: \_\_\_\_\_

Date: \_\_\_\_\_

How do your calculated  $\Delta H_{\text{rxn}}$  and  $\Delta G_{\text{rxn}}$  values using experimental data compare to the standard values? Calculate the %Error for each ( $\text{NH}_4\text{Cl}$  and  $\text{CaCl}_2$ ).

Using your results for Trial 1, calculate the temperature (in Kelvin)  $\text{CaCl}_2$  becomes spontaneous.

Is the dissolution of  $\text{CaCl}_2$  spontaneous above or below the temperature calculated above?  
Was this process spontaneous at room temperature?

**Conclusion:** In the space below, summarize your average calculated values for  $\Delta H$ ,  $\Delta S$ , and  $\Delta G$  for each salt. Describe what the sign of each value tells you about the dissolution of that salt.