Thermodynamics

Introduction:

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

Refer to Sections 5.2, 5.3, 16.1, 16.2, and 16.4 of Openstax Chemistry for information on calorimetry and calculating q, enthalpy, spontaneity, entropy, and free energy.

Equations to use for the calculations:

Heat of solution: q_{soln} = mass x specific heat x ΔT, where

mass = mass of solution

specific heat = 4.184 J/g °C

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

T_{final} is the maximum or minimum temperature reached

$T_{initial}$ is the initial temperature of water before adding salt

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

Density of water: 1.00 g/mL; Use to find mass of measured volume

Enthalpy of reaction: $\Delta H_{rxn} = \dfrac{q_{rxn}}{\text{moles of salt}}$

Entropy of reaction: $\Delta S^o_{rxn} = \Sigma n\, S^o_{(products)} - \Sigma n\, S^o_{(reactants)}$

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

Materials:

Styrofoam cup calorimeter
Digital thermometer
100 mL graduated cylinder
plastic weighing cup
timer
DI H_2O
solid calcium chloride, $CaCl_2$
solid ammonium chloride, NH_4Cl

Procedure:

Note: Thoroughly clean up any spilled salts. $CaCl_2$ will corrode the metal on the balances. Use the brush to sweep off the metal surface of the balances immediately. Any spills left behind might result in points being deducted!

Do NOT return excess reagent to the salt container. It must go into the designated waste.

1. Place the nested Styrofoam cups into a 400-mL beaker. Use a 100-mL graduated cylinder to measure about 25 mL of deionized water and add to the blue plastic cup inside the Styrofoam cups. 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 ±0.20 grams of the calculated value. NOTE: DO NOT ADD SALT TO THE WEIGHING CUP WHILE IT IS ON THE BALANCE! Refer to the “Using an analytical balance”, “Transferring solids”, and “Preparing solutions” techniques.
3. Place a thermometer in the DI 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 **waste container** in the hood. 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.

Waste Disposal: Pour the salt solutions in the waste container. Clean-Up: Rinse everything well with tap water followed by a quick DI water rinse. Wipe your benchtop with a damp paper towel. Put all equipment back where you found it.

Thermodynamics Pre-Lab Questions and Calculations

You will complete this quiz in Canvas 1 hour before your lab period. This page will not be turned in or graded. You may use this page to set up your calculations before you take the Canvas quiz.

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 (page 4) 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 (page 4) 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 ΔH indicate about a reaction?

6. What does a negative value of ΔS indicate about a reaction?

7. What does a negative value of ΔG indicate about a reaction?

8. Calculate the heat of solution (q_{soln}) if the mass of solution is 45.6 g, specific heat is 3.98 J/g• ^{o}C, and ΔT is -34.5^{o}C.

9. What is the heat of reaction (q_{rxn}) for the above question?

10. If 0.612 moles of salt were used in the reaction, what is ΔH_{rxn}?

Name: ______________________________ Partners: _________________________

Thermodynamics Lab Report
Turn in pages 4-7 as your Lab Report.

Data and Calculations

Table 1: Mass, volume, and temperatures

	Ammonium Chloride			**Calcium Chloride**	
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_2O,T_i (°C)			Initial temp. of H_2O,T_i (°C)		
Time	**Temperature, ºC, Trial 1**	**Temperature, ºC, Trial 2**	**Time**	**Temperature, ºC, Trial 1**	**Temperature, ºC, Trial 2**
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:

Instructor Initials: __________

Calculations for NH_4Cl: Show a sample calculation for one trial for a) moles of salt, b) mass of solution, c) ΔT, d) q_{rxn}, e) ΔH, f) ΔS^o (Use values in Table 3 on page 6 for this calculation.), and g) ΔG. Refer to Results Table 4 for units of each quantity.

Instructor Initials: _________

Calculations for $CaCl_2$: Show a sample calculation for one trial for a) moles of salt, b) mass of solution, c) ΔT, d) q_{rxn}, e) ΔH, f) ΔS^o (Use values in Table 3 on page 6 for this calculation.), and g) ΔG. Refer to Results Table 4 for units of each quantity.

Instructor Initials: _________

Table 3: Thermodynamic data from textbook.

	ΔH_f^o (kJ/mol)	**ΔG_f^o (kJ/mol)**	**S^o (J/K·mol)**
NH_4Cl (s)	-314.4	-202.8	94.6
NH_4^+ (aq)	-132.5	-79.3	113.4
Cl^- (aq)	-167.2	-131.2	56.5
$CaCl_2$ (s)	-795.8	-748.1	104.6
Ca^{2+} (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_f (°C)				
ΔT (°C)				
q_{rxn} (J)				
ΔH_{rxn} (kJ/mol)				
ΔS^o_{rxn} (J/mol K) calculated from table 3				
ΔG_{rxn} (kJ/mol)				

Use values from Table 3 (top of this page) to calculate standard values of ΔH^o_{rxn} and ΔG^o_{rxn} for NH_4Cl.

$\Delta H°_{rxn}$:

$\Delta G°_{rxn}$:

How do your calculated ΔH_{rxn} and ΔG_{rxn} values using experimental data compare to the standard values?

Using your results for trial 1, calculate the temperature (in Kelvin) $CaCl_2$ becomes spontaneous.

Is the dissolution of $CaCl_2$ 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 ΔH, ΔS, and ΔG for each salt. Describe what the sign of each value tells you about the dissolution of that salt.

Post-Lab Questions – These questions will not be graded as part of your lab report grade. You will be responsible for the information in these questions and able to answer these or similar questions on the post-lab quiz at the start of next week's lab period.

Dissolution of ammonium chloride:

1. In the experiment, identify the system ______________ and the surroundings _______________.
2. Which one gains heat in this experiment? _______________
3. Is the system endothermic or exothermic? ___________________
4. Explain how the observed temperature change verifies your answer to #3.

5. From the temperature change obtained for the solution in the calorimeter, what must be the sign for ΔH_{rxn}? ______________________
6. a) Based on your observations at the end of the reaction, is the dissolution of ammonium chloride spontaneous or non-spontaneous at room temperature? _______________________

   b) Based on your observations at the end of the reaction, is $\Delta G > 0$ or < 0 for this process at room temperature? _______
7. Based on your calculated change in entropy, does the dissolution of ammonium chloride create more order or disorder? __________________
8. Is this salt soluble at all temperatures? **Explain based on the signs of the enthalpy change and entropy change for the dissolution of ammonium chloride.**

9. Calculate the temperature above or below which the salt will not dissolve, if applicable. Indicate if the solid will dissolve above or below this temperature.

Dissolution of calcium chloride:

1. In the experiment, identify the system _______________ and the surroundings ________________.
2. Which one gains heat in this experiment? ________________
3. From the temperature change obtained for the solution in the calorimeter, what must be the sign for ΔH_{rxn}? _______________
4. a) Based on your observations at the end of the reaction, is the dissolution of calcium chloride spontaneous or non-spontaneous at room temperature? ________________________

   b) Based on your observations at the end of the reaction, is $\Delta G > 0$ or < 0 for this process at room temperature? _______
5. Based on your calculated change in entropy, does the dissolution of calcium chloride create more order or disorder? ___________________
6. Is this salt soluble at all temperatures? **Explain based on the signs of the enthalpy change and entropy change for the dissolution of calcium chloride.**
7. Calculate the temperature above or below which the salt will not dissolve, if applicable. Indicate if the solid will dissolve above or below this temperature.

Discuss at least 2 sources of error. How did they affect your results and how would you correct them if you were to repeat the experiment?