

Thermodynamics—Enthalpy of Reaction and Hess's Law

Introduction

When we write chemical equations, we balance them so that all the atoms are accounted for. However, sometimes the amount of heat that is produced or consumed is of major importance. Thermochemical equations include the heat of the reaction as part of the equation. The heat released or absorbed in a reaction at constant pressure (open to the atmosphere) is the enthalpy change for the reaction.

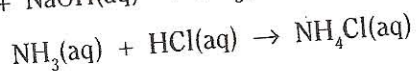
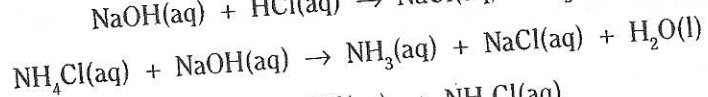
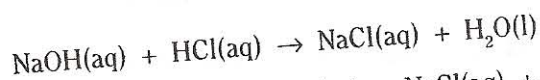
Concepts

- Enthalpy of reaction
- Heat of formation
- Hess's Law
- Calorimetry

Background

The release or absorption of heat energy is a unique value for every reaction. Were all these values experimentally determined? No, many were calculated using Hess's law. This lab demonstrates the principle of Hess's Law—if several reactions add up to produce an overall reaction, then the heat transfers of the reactions will add up to the value of the heat transfer for the overall reaction.

In this experiment, the enthalpy changes for the reaction of ammonia and hydrochloric acid will be determined using Hess's law. If the enthalpy change for the reaction between sodium hydroxide and hydrochloric acid and the reaction between sodium hydroxide and ammonium chloride are determined, the enthalpy change for the reaction between ammonia and hydrochloric acid can be calculated. The balanced equations for these reactions are as follows:



When Equation 2 is reversed and added to Equation 1, the result is Equation 3.

The heat or enthalpy change for a chemical reaction is called the *enthalpy of reaction*, ΔH_{rxn} . This energy change is equal to the amount of heat transferred, at constant pressure, in the reaction. This change represents the difference in enthalpy of the products and the reactants and is independent of the steps in going from reactants to products.

According to *Hess's Law*, if a reaction can be carried out in a series of steps, the sum of the enthalpies for each step equals the enthalpy change for the overall reaction. Another way of stating Hess's Law is: If a reaction is the sum of two or more other reactions, the ΔH_{rxn} for the overall reaction must be the sum of the ΔH_{rxn} values of the constituent reactions. In this laboratory experiment, the value of ΔH_{rxn} for Equation 1 minus the value of ΔH_{rxn} for Equation 2 will equal the value of ΔH_{rxn} for Equation 3. Unfortunately, there is no single instrument that can directly measure heat or enthalpy in the way a balance measures mass or a thermometer measures temperature. It is possible, however, to measure heat change when a chemical reaction occurs. If the reaction occurs in solution, the heat change is calculated from the mass, temperature change, and specific heat of the solution, according to Equation 4.

$$q = (\text{grams of solution}) \times (\text{specific heat of solution}) \times \Delta T \quad \text{Equation 4}$$

where q = heat energy gain or loss and ΔT is the temperature change in °C. Since ΔT equals the final temperature of the solution minus the initial temperature of solution, an increase in solution temperature

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results in a positive value for both ΔT and q . A positive value for q means the solution gains heat, while a negative value means the solution loses heat. If the solution gains heat, then the reaction “produces” heat and it is exothermic.

The three reactions in this experiment are all acid–base neutralizations. Acid–base neutralizations are exothermic processes. Combining solutions containing an acid and a base results in a rise of solution temperature. The heat given off by the reaction is calculated using Equation 4. This heat quantity can be converted to the enthalpy of reaction, in terms of kJ/mol, by using the concentrations of the reactants.

When measuring the heat transfers for exothermic reactions using a calorimeter, most of the heat released is absorbed by the solution. A small amount of this heat will be absorbed by the calorimeter itself. The heat change for the reaction becomes

$$q_{\text{rxn}} = -(q_{\text{sol}} + q_{\text{cal}}) \quad \text{Equation 5}$$

where q_{rxn} is the amount of heat released by the reaction and q_{sol} and q_{cal} are the amounts of heat absorbed by the solution and calorimeter, respectively.

Typically, the specific heat ($J/^{\circ}\text{C}$) of the calorimeter is determined experimentally. This value is then multiplied by the change in temperature of the solution to calculate q_{cal} for the reaction.

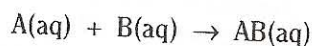
$$q_{\text{cal}} = \Delta T (^{\circ}\text{C}) \times \text{heat capacity } (J/^{\circ}\text{C}) \quad \text{Equation 6}$$

Experiment Overview

The purpose of this experiment is to verify Hess’s Law. Three acid–base reactions, chosen so that the third reaction equation equals the first reaction equation minus the second, are measured for temperature change by calorimetry. The values of heat change and enthalpy of reaction are calculated for each reaction. The measured value for the third reaction is then compared to the value calculated by subtracting the enthalpy of reaction for reaction two from the enthalpy of reaction of reaction one.

Pre-Lab Questions (Use a separate sheet of paper to answer the following questions.)

1. Define ΔH_{rxn} .
2. Define specific heat.
3. The specific heat of a solution is $4.18 \text{ J}/(\text{g}\cdot^{\circ}\text{C})$ and its density is 1.02 g/mL . The solution is formed by combining 25.0 mL of solution A with 25.0 mL of solution B, with each solution initially at $21.4 ^{\circ}\text{C}$. The final temperature of the combined solutions is $25.3 ^{\circ}\text{C}$. Calculate the heat of reaction, q_{rxn} , assuming no heat loss to the calorimeter. Use correct significant figures.
4. In problem 3 above, the calorimeter has a heat capacity of $8.20 \text{ J}/^{\circ}\text{C}$. If a correction is included to account for the heat absorbed by the calorimeter, what is the heat of reaction, q_{rxn} ?
5. If the reaction in question 3 is



and the molarity of A in solution A is 0.60 M and the molarity of B in solution B is 0.60 M , calculate the enthalpy of reaction, ΔH_{rxn} , for the formation of 1 mole of AB in solution. (Remember, ΔH_{rxn} is always written as kJ/mol.)

Materials

Chemicals

Ammonia solution, NH_3 , 2.0 M, 50 mL	Sodium hydroxide solution, NaOH , 2.0 M, 100 mL
Ammonium chloride solution, NH_4Cl , 2.0 M, 50 mL	Water, distilled or deionized
Hydrochloric acid solution, HCl , 2.0 M, 100 mL	

Equipment

Beaker, 250-mL	Graduated cylinder, 50-mL
Calorimeter and lid (2 Styrofoam® cups and cover)	Hot plate
Deionized or distilled water	Magnetic stirrer and stirring bar
Digital thermometer	Timer or stopwatch

Safety Precautions

The ammonia solution and its vapors are irritating, especially to the eyes. It is moderately toxic by ingestion or inhalation. Dispense in a fume hood. The hydrochloric acid solution is toxic by ingestion or inhalation; it is severely corrosive to skin and eyes. The sodium hydroxide solution is severely corrosive to skin and eyes. When NaOH and NH_4Cl solutions are mixed, ammonia gas is evolved. **Work in a fume hood or under a funnel attached to an aspirator.** Wear chemical splash goggles, chemical-resistant gloves, and a chemical-resistant apron. Wash hands thoroughly with soap and water before leaving the laboratory.

Procedure

Part 1. Determine the Heat Capacity of the Calorimeter

- Set up a calorimeter of two nested Styrofoam® cups with a cover having a hole in it to accept a thermometer. (Figure 1.)
- Measure 50.0 mL of distilled or deionized water in a 50-mL graduated cylinder and transfer the water into the calorimeter.
- Place the calorimeter assembly on a magnetic stirrer, add a magnetic stirring bar, and set the bar spinning slowly.
- Measure and record the temperature of the water in the Part 1 Data Table.
- Heat approximately 75 mL of distilled or deionized water to about 70 °C in a 250-mL beaker.
- Measure 50.0 mL of the 70 °C distilled water in a 50-mL graduated cylinder.
- Measure and record the temperature of the hot water in the Part 1 Data Table.
- Immediately pour the hot water into the room temperature water in the calorimeter.
- Cover the calorimeter, insert the thermometer, and stir the water.
- Record the temperature every 20 seconds for a total of 3 minutes in the Part 1 Data Table.
- Empty the calorimeter and dry the inside of calorimeter when finished.

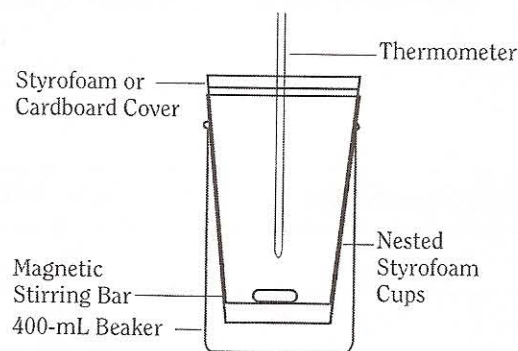
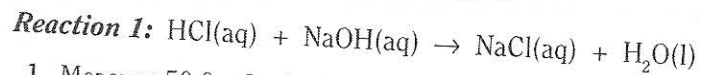


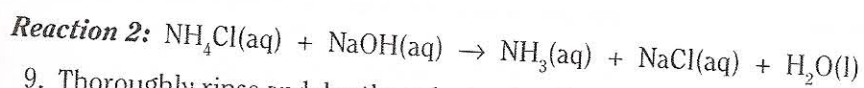
Figure 1.

Experiment 6

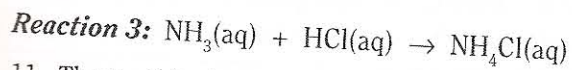
Part 2. Determine the Heats of Reaction



1. Measure 50.0 mL of a 2.0 M HCl solution in a 50-mL graduated cylinder and transfer to the calorimeter.
2. Record the temperature of the HCl solution in the Part 2 Data Table.
3. Rinse the 50-mL graduated cylinder with distilled water.
4. Measure 50.0 mL of a 2.0 M NaOH solution in a 50-mL graduated cylinder.
5. Record the temperature of the NaOH solution in the Part 2 Data Table.
6. Put a magnetic stirring bar into the calorimeter and start the bar spinning slowly in the HCl solution.
7. Quickly add the 50.0 mL of 2.0 M NaOH solution to the calorimeter, cover, and insert the thermometer.
8. Record the temperature after 20 seconds, and then every 20 seconds for a total of 3 minutes, in the Part 2 Data Table.



9. Thoroughly rinse and dry the calorimeter, thermometer, stirrer bar, and graduated cylinder used for Reaction 1.
10. Repeat steps 1–8 of Part 2 using 2.0 M NH_4Cl solution and 2.0 M NaOH solution. Be sure to perform this procedure in the fume hood.



11. Thoroughly rinse and dry the calorimeter, thermometer, stirrer bar, and graduated cylinder used for reaction 2.
12. Repeat steps 1–8 of Part 2 using 2.0 M NH_3 solution and 2.0 M HCl solution. Be sure to perform this procedure in the fume hood.

Disposal and Cleanup

Your teacher will provide disposal and cleanup information.

Data Tables

Part 1 Data Table. Determination of the Heat Capacity of the Calorimeter

Initial temperature ($^{\circ}\text{C}$)

50.0 mL H_2O —room temperature _____

50.0 mL H_2O —heated _____

Mixing Data

Time (sec)	Temperature ($^{\circ}\text{C}$)	Time (sec)	Temperature ($^{\circ}\text{C}$)
20		120	
40		140	
60		160	
80		180	
100			

$T_{\text{mix}}, ^{\circ}\text{C}$ _____ q_{cal}, J _____

$T_{\text{ave}}, ^{\circ}\text{C}$ _____ $C_{\text{cal}}, \text{J}/^{\circ}\text{C}$ _____

Part 2 Data Table. Determination of Heats of Reaction

Reaction 1: $\text{HCl}(\text{aq}) + \text{NaOH}(\text{aq}) \rightarrow \text{NaCl}(\text{aq}) + \text{H}_2\text{O}(\text{l})$

Initial temperature ($^{\circ}\text{C}$)

50.0 mL 2.0 M HCl _____ $^{\circ}\text{C}$

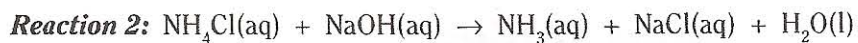
50.0 mL 2.0 M NaOH _____ $^{\circ}\text{C}$

Mixing Data

Time (sec)	Temperature ($^{\circ}\text{C}$)	Time (sec)	Temperature ($^{\circ}\text{C}$)
20		120	
40		140	
60		160	
80		180	
100			

$T_{\text{mix}}, ^{\circ}\text{C}$ _____ $\Delta H, \text{kJ/mol}$ _____

q_{rxn}, J _____



Initial temperature (°C)

50.0 mL 2.0 M NH_4Cl _____ °C

50.0 mL 2.0 M NaOH _____ °C

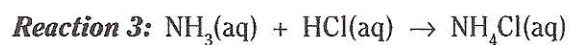
Mixing Data

Time (sec)	Temperature (°C)	Time (sec)	Temperature (°C)
20		120	
40		140	
60		160	
80		180	
100			

T_{mix} , °C _____

ΔH , kJ/mol _____

q_{rxn} , J _____



Initial temperature (°C)

50.0 mL 2.0 M NH_3 _____ °C

50.0 mL 2.0 M HCl _____ °C

Mixing Data

Time (sec)	Temperature (°C)	Time (sec)	Temperature (°C)
20		120	
40		140	
60		160	
80		180	
100			

T_{mix} , °C _____

ΔH , kJ/mol _____

q_{rxn} , J _____

Post-Lab Calculations and Analysis

(Use a separate sheet of paper to answer the following questions.)

Part 1. Calculate the Heat Capacity of the Calorimeter

1. Plot the Mixing Data with temperature on the vertical axis and time on the horizontal axis.

The first few data points may be erratic due to incomplete mixing and lack of equilibration with the thermometer. Draw a straight line through the subsequent points and extend the line back to the maximum temperature at time zero. Record this temperature as T_{mix} in the Part 1 Data Table.

Temperature versus Time After Mixing

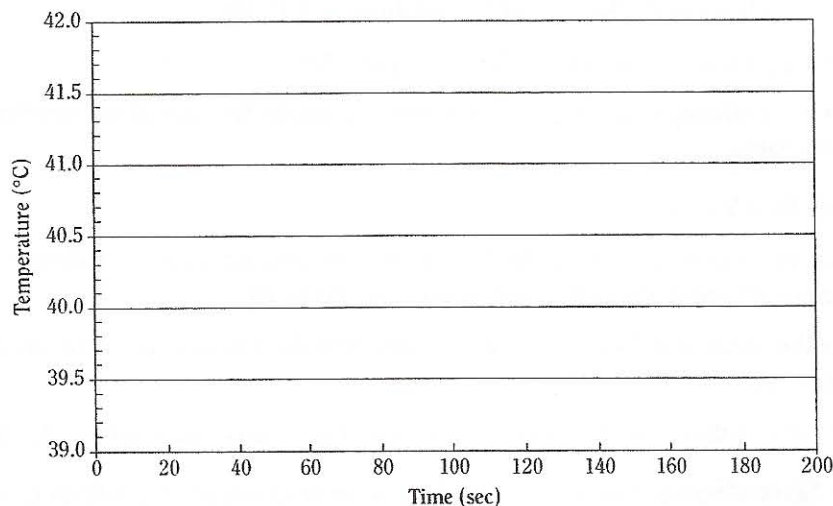


Figure 2.

2. Calculate the average initial temperature, T_{ave} , of the hot and cold water. Record this temperature as T_{ave} in the Part 1 Data Table.
3. The difference between T_{ave} and T_{mix} is due to the heat lost by the water and absorbed by the calorimeter. The heat lost by the water, q_{water} , is:

$$q_{\text{water}} = (\text{grams of water}) \times (\text{specific heat of water}) \times (T_{\text{mix}} - T_{\text{ave}})$$

where the specific heat of water is $4.18 \text{ J}/(\text{g}\cdot^{\circ}\text{C})$.

The heat gained by the calorimeter, q_{cal} , is equal to that lost by the water, but opposite in sign.

Calculate q_{cal} for the calorimeter and enter this value in the Part 1 Data Table.

4. Calculate the heat capacity of the calorimeter, C_{cal} . This is equal to the heat the calorimeter absorbs when 100 mL of solution changes 1°C in temperature.

$$C_{\text{cal}} = \frac{q_{\text{cal}}}{(T_{\text{mix}} - T_{\text{initial}})}$$

where T_{initial} is the initial temperature of the cool water. Record the heat capacity, C_{cal} , in the Part 1 Data Table.

Part 2. Calculate the Enthalpy of Reaction, ΔH_{rxn}

1. Graph the temperature versus time on a separate sheet of graph paper for each of the three reactions tested. Extrapolate the line back to find the instantaneous mixing temperature, T_{mix} , for each reaction. Record this value for each reaction in the Part 2 Data Table.
2. Calculate the amount of heat evolved in each reaction, q_{rxn} . If it is assumed that all the heat of reaction is absorbed by the solution and calorimeter, then:

$$q_{\text{rxn}} = -[\text{heat absorbed by solution} + \text{heat absorbed by calorimeter}]$$

$$q_{\text{rxn}} = -[(\text{grams of solution} \times \text{specific heat of solution} \times \Delta T_{\text{solution}}) + (C_{\text{cal}} \times \Delta T_{\text{solution}})]$$

where $\Delta T_{\text{solution}} = (T_{\text{mix}} - T_{\text{initial}})$ for each reaction mixture. Assume the density of the final solutions is 1.03 g/mL and the specific heat of all the solutions is 4.18 J/g \cdot °C.

Record the q_{rxn} for each reaction in the Part 2 Data Table.

3. Calculate the enthalpy change, ΔH_{rxn} , in terms of kJ/mole, for each of the reactions. Record the values in the Part 2 Data Table.

Part 3. Verify Hess's Law

1. Write the net ionic equations for the three reactions involved in the experiment. Show how the first two reactions are arranged algebraically to determine the third.
2. Calculate the value of ΔH for the third reaction from the values of ΔH determined for the first two reactions using Hess's Law.
3. Find the percent difference between the calculated and measured values of ΔH for the third reaction.

Post-Lab Questions (Use a separate sheet of paper to answer the following questions.)

1. What is meant by calorimetry?
2. How does graphical analysis improve the accuracy of the data?
3. The equation for calculating the heat evolved in each reaction is:
$$q_{\text{rxn}} = -[(\text{grams of solution} \times \text{specific heat of solution} \times \Delta T_{\text{solution}}) + (C_{\text{cal}} \times \Delta T_{\text{solution}})]$$

What is the meaning of the negative sign in front of the brackets?
4. Do the lab results support Hess's Law?
5. How could the procedure be modified to achieve greater accuracy?
6. Find a table in a reference that lists standard heats of formation for the species included in your net ionic equations. Use them to calculate ΔH_{rxn} for each of the three net ionic equations. Do these values support Hess's Law?