6. Thermochemistry and Hess's Law

Introduction

The energy changes that accompany chemical reactions are nearly always reflected by the release or absorption of heat. There are many practical and theoretical reasons for studying the quantitative aspects of this phenomenon. Each of these studies is an application of *thermochemistry* (Ebbing/Gammon, Chapter 6).

Purpose

One-half of your class will measure the enthalpy change that occurs when solutions of sodium hydroxide (NaOH) and hydrochloric acid (HCl) are mixed. The other half will measure the enthalpy change that occurs when solutions of ammonia (NH_3) and hydrochloric acid are mixed. Both groups will measure the enthalpy change that occurs when solutions of sodium hydroxide and ammonium chloride (NH_4Cl) are mixed. All of the data will be pooled. The mean enthalpy changes from the first two measurements will enable you to determine the accord between the mean enthalpy change from the third measurement and that predicted by Hess's law.

Concept of the Experiment

The chemical reactions that will occur during this experiment are given in the following equations:

$$NaOH + HCl \rightarrow NaCl + H_2O$$

$$NH_3 + HCl \rightarrow NH_4Cl$$

$$NaOH + NH_4Cl \rightarrow NaCl + NH_3 + H_2O$$

You may have noted that there is a relationship among these equations. If the first two equations are combined by addition in a particular way, the third equation is generated. This relationship provides the basis for using Hess's law of heat summation (Ebbing/Gammon, Section 6.7). You will find that you can predict the enthalpy change for the third reaction by combining the enthalpy changes for the first and second reactions.

The heat evolved or absorbed during these reactions will be measured with a coffee-cup calorimeter, whose use is described in Appendix B. This appendix also includes pertinent definitions of the system and its surroundings (Ebbing/Gammon, Section 6.2) in terms of this calorimeter.

The three chemical reactions that will occur in this experiment are examples of bases reacting with acids. Although you will learn much more about these terms during this course, it will be useful for us at least to identify the bases and the acids in this experiment.

Bases: NaOH and NH_3

Acids: HCl and NH_4Cl

A Special Note

By sharing your data with your classmates, you eliminate the need to observe all of the reactions yourself. Moreover, the accuracy of the measured enthalpy changes will be increased.

Copyright © Houghton Mifflin Company. All rights reserved.

Procedure

Getting Started

1. Work with a partner.

2. Obtain a coffee-cup calorimeter.

3. Ask your laboratory instructor which enthalpy change ($NaOH$–HCl or NH_3–HCl) you should measure.

Measuring the Evolution or Absorption of Heat

1. Obtain exactly 50 mL of the 2.0 *M* solution of HCl in a clean, dry graduated cylinder. Obtain exactly 50 mL of the 2.0 *M* solution of either NaOH or NH_3 in another clean, dry graduated cylinder.

   CAUTION: Hydrochloric acid, sodium hydroxide, and ammonia can cause chemical burns, in addition to ruining your clothing. If you spill one of these solutions on you, wash the contaminated area thoroughly and report the incident to your laboratory instructor. You may require further treatment. Always wear approved chemical splash goggles.

2. Measure the temperature of each of these solutions, using the same thermometer. However, rinse the thermometer and dry it after the first measurement. If the temperatures are not identical, cool the warmer solution by immersing the graduated cylinder in tap water, or warm the cooler solution with your hands. The temperatures should finally agree to within ±0.2°C. Record the mean temperature. This is the initial temperature, t_i.

3. Add the acid to the calorimeter. In order to account for incomplete draining, record the volume of the solution that remains in the graduated cylinder.

4. Add the base to the calorimeter. You will read the volume of any solution that remains in the cylinder in a subsequent step.

5. Immediately place the top on the calorimeter and begin stirring.

6. Record the temperature to the nearest 0.1°C after 30 s and every 30 s thereafter for 4 min.

7. During this time, measure and record the volume of the base remaining in the graduated cylinder from Step 4.

8. Plot the temperature against the time, using one of the pieces of graph paper that are available. Use a straight line to extrapolate your results to the time of mixing (time = 0 s). Record the extrapolated temperature. This is the final temperature, t_f.

9. Calculate q(system) using 4.184 J/(g • °C) and 1.0 g/mL for the specific heat and density of the solution, respectively, and 1.0×10^1 J/°C for the heat capacity of the calorimeter.

10. Calculate the enthalpy change, ΔH, from q(system) and the number of moles of the acid or base. If you used unequal volumes of the acid and base solutions, use the number of moles of the limiting reactant.

Copyright © Houghton Mifflin Company. All rights reserved.

11. If time permits, repeat the measurement using the same acid and base and the same piece of graph paper to obtain t_f. Obtain the mean value of ΔH.
12. Repeat Steps 1 through 11 for the NH_4Cl–NaOH acid–base pair. Use a new piece of graph paper.

Copyright © Houghton Mifflin Company. All rights reserved.

Date: ______________ Student name: ______________

Course/Section: ______________ Team members: ______________

Instructor: ______________

Thermochemistry and Hess's Law

Prelaboratory Assignment

1. Give chemical equations for the reactions that will occur during this experiment.

2. Define the system and the surroundings for these reactions. If water is one of the products, does it belong in the system or in the surroundings?

3. a. When solutions of two reactants were mixed in a coffee-cup calorimeter, the following temperatures were recorded as a function of time. Plot the data on one of the available pieces of graph paper. Obtain t_f, the final temperature, by extrapolating to the time of mixing (time = 0 s) with a straight line. The initial temperature, t_i, was 24.3°C.

Time (s)	*t* (°C)	Time (s)	*t* (°C)
30	40.4	150	40.5
60	40.8	180	40.4
90	40.7	210	40.3
120	40.6	240	40.2

t_f: ______________

Copyright © Houghton Mifflin Company. All rights reserved.

b. Is this an exothermic or an endothermic reaction? Why?

c. Why does the temperature increase, reach a maximum, and then decrease?

4. What special safety precautions must be observed during this experiment?

Copyright © Houghton Mifflin Company. All rights reserved.

Date: ____________________ Student name: ____________________

Course/Section: ____________________ Team members: ____________________

Instructor: ____________________ ____________________

Thermochemistry and Hess's Law

Results

1. *Enthalpy change (NaOH–HCl or NH_3–HCl)*

Concentration of HCl: ____________________

Concentration and identity of base: ____________________

____

Trial	1	2
	________	________
Volume of acid in cylinder:		
Before pouring (mL)	________	________
After pouring (mL)	________	________
Volume added (mL)	________	________
Volume of base in cylinder:		
Before pouring (mL)	________	________
After pouring (mL)	________	________
Volume added (mL)	________	________
t_i (°C)	________	________

continued

Copyright © Houghton Mifflin Company. All rights reserved.

Trial	1	2
Temperature (°C) after		
30 s		
60 s		
90 s		
120 s		
150 s		
180 s		
210 s		
240 s		
t_f (°C)		
q(system) (J)		
Moles of limiting reactant		
ΔH (kJ/mol)		
Mean ΔH (kJ/mol)		

Copyright © Houghton Mifflin Company. All rights reserved.

Student name: __________ Course/Section: __________ Date: __________

Calculations:

2. *Enthalpy change (NaOH–NH_4Cl)*

Concentration of NH_4Cl: __________

Concentration of NaOH: __________

Trial	1	2
Volume of acid in cylinder:		
Before pouring (mL)		
After pouring (mL)		
Volume added (mL)		
Volume of base in cylinder:		
Before pouring (mL)		
After pouring (mL)		

Copyright © Houghton Mifflin Company. All rights reserved.

Trial	1	2
Volume added (mL)	______	______
t_i (°C)	______	______
Temperature (°C) after		
30 s	______	______
60 s	______	______
90 s	______	______
120 s	______	______
150 s	______	______
180 s	______	______
210 s	______	______
240 s	______	______
t_f (°C)	______	______
q(system) (J)	______	______
Moles of limiting reactant	______	______
ΔH (kJ/mol)	______	______
Mean ΔH (kJ/mol)	______	

Calculations:

Copyright © Houghton Mifflin Company. All rights reserved.

Student name: ______________ Course/Section: __________ Date: __________

3. *Pooled results* (Include your own.)

Reaction	ΔH (kJ/mol)	Mean ΔH
NaOH–HCl		
NH_3–HCl		
NaOH–NH_4Cl		

Questions

1. a. Use Hess's law and the measured mean enthalpy changes for the NaOH–HCl and NH_3–HCl reactions to calculate the enthalpy change to be expected for the reaction

$$NaOH + NH_4Cl \rightarrow NaCl + NH_3 + H_2O$$

Copyright © Houghton Mifflin Company. All rights reserved.

b. Compare your experimental value with the one you have just calculated. The correct value is only –3.9 kJ/mol. Try to explain any discrepancy between the experimental and calculated values and between these values and the correct value.

2. Calculate the enthalpy change to be expected for the reaction

$$NaCl(s) \rightarrow NaCl(aq)$$

where (s) and (aq) mean solid and aqueous, respectively. Use Hess's law, an enthalpy change that was measured in this experiment, and the data from the following table.

Reaction*	ΔH (kJ/mol)
$1/2H_2(g) + 1/2Cl_2(g) \rightarrow HCl(g)$	–92.3
$Na(s) + 1/2O_2(g) + 1/2H_2(g) \rightarrow NaOH(s)$	–426.8
$Na(s) + 1/2Cl_2(g) \rightarrow NaCl(s)$	–411.1
$H_2(g) + 1/2O_2(g) \rightarrow H_2O(l)$	–285.8
$HCl(g) \rightarrow HCl(aq)$	–75.2
$NaOH(s) \rightarrow NaOH(aq)$	–41.8

* (g) = gas, (l) = liquid, (s) = solid, and (aq) = aqueous.

Calculations:

Copyright © Houghton Mifflin Company. All rights reserved.

Student name: ______________ Course/Section: __________ Date: __________

3. Describe an experiment using only hot and cold water that would enable you to verify that the heat capacity of your coffee-cup calorimeter is about 1.0×10^1 J/°C. Be specific.

Copyright © Houghton Mifflin Company. All rights reserved.

b. Compare your experimental value with the one you have just calculated. The correct value is only –3.9 kJ/mol. Try to explain any discrepancy between the experimental and calculated values and between these values and the correct value.

2. Calculate the enthalpy change to be expected for the reaction

$$NaCl(s) \rightarrow NaCl(aq)$$

where (*s*) and (*aq*) mean solid and aqueous, respectively. Use Hess's law, an enthalpy change that was measured in this experiment, and the data from the following table.

Reaction*	ΔH (kJ/mol)
$1/2H_2(g) + 1/2Cl_2(g) \rightarrow HCl(g)$	–92.3
$Na(s) + 1/2O_2(g) + 1/2H_2(g) \rightarrow NaOH(s)$	–426.8
$Na(s) + 1/2Cl_2(g) \rightarrow NaCl(s)$	–411.1
$H_2(g) + 1/2O_2(g) \rightarrow H_2O(l)$	–285.8
$HCl(g) \rightarrow HCl(aq)$	–75.2
$NaOH(s) \rightarrow NaOH(aq)$	–41.8

* (*g*) = gas, (*l*) = liquid, (*s*) = solid, and (*aq*) = aqueous.

Calculations:

Copyright © Houghton Mifflin Company. All rights reserved.

Student name: ______________ Course/Section: __________ Date: __________

3. Describe an experiment using only hot and cold water that would enable you to verify that the heat capacity of your coffee-cup calorimeter is about 1.0×10^1 J/°C. Be specific.

Copyright © Houghton Mifflin Company. All rights reserved.