

## **6. Thermochemistry and Hess's Law**

### **Introduction**

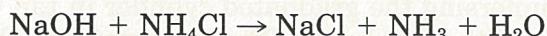
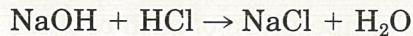
The energy changes that accompany chemical reactions are nearly always reflected by the release or absorption of heat. There are many practical and theoretical reasons for studying the quantitative aspects of this phenomenon. Each of these studies is an application of *thermochemistry* (Ebbing/Gammon,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

### **Purpose**

One-half of your class will measure the enthalpy change that occurs when solutions of sodium hydroxide ( $\text{NaOH}$ ) and hydrochloric acid ( $\text{HCl}$ ) are mixed. The other half will measure the enthalpy change that occurs when solutions of ammonia ( $\text{NH}_3$ ) and hydrochloric acid are mixed. Both groups will measure the enthalpy change that occurs when solutions of sodium hydroxide and ammonium chloride ( $\text{NH}_4\text{Cl}$ ) 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:



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:  $\text{NaOH}$  and  $\text{NH}_3$

Acids:  $\text{HCl}$  and  $\text{NH}_4\text{Cl}$

### A special note

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

## 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<sub>3</sub>-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<sub>3</sub> 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.

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  $\pm 0.2^\circ\text{C}$ . 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  $0.1^\circ\text{C}$  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  $q(\text{system})$  using  $4.184 \text{ J}/(\text{g} \cdot {}^\circ\text{C})$  and  $1.0 \text{ g/mL}$  for the specific heat and density of the solution, respectively, and  $1.0 \times 10^1 \text{ J}/{}^\circ\text{C}$  for the heat capacity of the calorimeter.

10. Calculate the enthalpy change,  $\Delta H$ , from  $q(\text{system})$  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.
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  $\Delta H$ .
12. Repeat Steps 1 through 11 for the  $\text{NH}_4\text{Cl}$ - $\text{NaOH}$  acid-base pair. Use a new piece of graph paper.



# ***Thermochemistry and Hess's Law***

Date: ..... Student name: .....  
Course: ..... Team members: .....  
Section: .....  
Instructor: .....

## 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)	Temperature (°C)
0	24.3
10	25.1
20	25.8
30	26.5
40	27.2
50	27.8
60	28.4
70	28.9
80	29.4
90	29.8
100	30.2

Time (s)	$t$ (°C)	Time (s)	$t$ (°C)
30	38.6	150	39.3
60	39.7	180	39.2
90	39.5	210	39.1
120	39.4	240	39.0

$t_f$ : .....

ic reaction? Why?

**130 Experiment 6**

- b. Is this an exothermic or an endothermic

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- c. Why does the temperature increase, re  
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## **Results**

### **1. Enthalpy change ( $\text{NaOH-HCl}$ or $\text{NH}_3\text{-HCl}$ )**

Concentration of HCl: .....

Concentration and identity of base: .....

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

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) ..... ....

$t_i$  ( $^{\circ}\text{C}$ ) ..... ....

*continued*

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	.....	.....
$\Delta H$ (kJ/mol)	.....	.....
Mean $\Delta H$ (kJ/mol)	.....	.....

Student name: ..... Course/Section: ..... Date: .....

**Calculations:****2. Enthalpy change ( $\text{NaOH-NH}_4\text{Cl}$ )**Concentration of  $\text{NH}_4\text{Cl}$ : .....Concentration of  $\text{NaOH}$ : .....

<b>Trial</b>	<b>1</b>	<b>2</b>
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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) ..... ....

*continued*

Trial	1	2
Volume added (mL)	.....	.....
$t_i$ ( $^{\circ}$ C)	.....	.....
Temperature ( $^{\circ}$ C) after		
30 s	.....	.....
60 s	.....	.....
90 s	.....	.....
120 s	.....	.....
150 s	.....	.....
180 s	.....	.....
210 s	.....	.....
240 s	.....	.....
$t_f$ ( $^{\circ}$ C)	.....	.....
$q$ (system) (J)	.....	.....
Moles of limiting reactant	.....	.....
$\Delta H$ (kJ/mol)	.....	.....
Mean $\Delta H$ (kJ/mol)	.....	.....

Calculations:

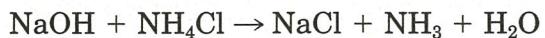
Student name: ..... Course/Section: ..... Date: .....

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

Reaction	$\Delta H$ (kJ/mol)	Mean $\Delta H$
NaOH-HCl	.....	.....
NH <sub>3</sub> -HCl	.....	.....
NaOH-NH <sub>4</sub> Cl	.....	.....

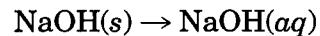
**Questions**

1. a. Use Hess's law and the measured mean enthalpy changes for the NaOH-HCl and NH<sub>3</sub>-HCl reactions to calculate the enthalpy change to be expected for the reaction



- b. Compare your experimental value with the one you have just calculated. The correct value is only  $-3.9 \text{ kJ/mol}$ . 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



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*	$\Delta H \text{ (kJ/mol)}$
$1/2\text{H}_2(g) + 1/2\text{Cl}_2(g) \rightarrow \text{HCl}(g)$	-92.3
$\text{Na}(s) + 1/2\text{O}_2(g) + 1/2\text{H}_2(g) \rightarrow \text{NaOH}(s)$	-426.8
$\text{Na}(s) + 1/2\text{Cl}_2(g) \rightarrow \text{NaCl}(s)$	-411.1
$\text{H}_2(g) + 1/2\text{O}_2(g) \rightarrow \text{H}_2\text{O}(l)$	-285.8
$\text{HCl}(g) \rightarrow \text{HCl}(aq)$	-75.2
$\text{NaCl}(s) \rightarrow \text{NaCl}(aq)$	4.0

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

Calculations:

Student name: ..... Course/Section: ..... Date: .....

3. Describe an experiment using only hot and cold water that would allow you to verify that the heat capacity of your coffee-cup calorimeter is about  $1.0 \times 10^1$  J/ $^{\circ}$ C. Be specific.

