Thermochemistry II: Hess's Law

OBJECTIVES:

- Explore quantitative aspects of constant-pressure calorimetry
- Check the validity of Hess's law

DISCUSSION:

In this part of the experiment, you will use your calorimeter to measure the heat released by three related reactions. Because two of the reactions sum up to give the third reaction, you can use the set of measurements to check Hess's law of heat summation.

In the first reaction, solid sodium hydroxide dissolves in water:

$$NaOH_{(s)} \rightarrow Na^{+}_{(aq)} + OH^{-}_{(aq)} \qquad \Delta H_1 = ?$$

In the second reaction, aqueous solutions of sodium hydroxide and hydrochloric acid react to form water and aqueous sodium chloride:

$$Na^{+}_{(aq)} + OH^{-}_{(aq)} + H^{+}_{(aq)} + Cl^{-}_{(aq)} \rightarrow H_2O_{(l)} + Na^{+}_{(aq)} + Cl^{-}_{(aq)} \qquad \Delta H_2 = ?$$

In the third reaction, solid sodium hydroxide reacts with aqueous hydrochloric acid to form water and aqueous sodium chloride:

$$NaOH_{(s)} + H^{+}_{(aq)} + Cl^{-}_{(aq)} \rightarrow H_2O_{(l)} + Na^{+}_{(aq)} + Cl^{-}_{(aq)} \qquad \Delta H_3 = ?$$

As in the first part of the Thermochemistry lab, you will use an EPS cup supported in a beaker as the calorimeter. Although this assembly is not a perfect insulator, if we assume that the heat losses are not significantly different from one trial to the next, we can expect valid comparisons.

PROCEDURE: Be sure to read the Safety and Disposal section at the end.

Reaction 1

1. Insert the thermometer through a slit rubber stopper. Clamp the stopper to a ring-stand to suspend the thermometer in a vertical position.
2. Measure 100.0 mL of DI water into the cup. Place the thermometer in the water.
3. Weigh the provided vial of NaOH pellets. Because sodium hydroxide readily picks up moisture from the air, you should weigh it quickly and go on to the next step without delay.

> **CAUTION:** *Solid sodium hydroxide and NaOH solutions are quite caustic. Avoid skin contact, and wash thoroughly in the event of an accidental exposure.*

4. As it may take some time for the thermometer to come into thermal equilibrium with the solution, wait until you have at least three subsequent readings (at 15 second intervals) at the same temperature before adding the solid NaOH to the water in the calorimeter cup. Be sure to stir the pellets in the solution with a glass stirring-rod, to encourage complete dissolving. Collect data for a full 225 s, or at least until the temperature readings begin to drop after passing through a maximum value.
5. After collecting the temperature data, weigh the empty vial (with its cap) and record the mass of NaOH used in your experiment. Dispose of the solution into the proper waste container. Rinse the thermometer, the cup, and the stirring rod with DI water, then dry them in preparation for the next reaction.

6. Read through the data to find the initial solution temperature, T_1, and the maximum solution *equilibrium* temperature, T_2.. Record T_1 and T_2 on your data sheet. **Note**: You may want to graph the data to determine the maximum *equilibrium* temperature.

Reaction 2

1. Repeat steps 1-6, initially measuring out 50.0 mL of 1.0*M* HCl (not water) into the calorimeter cup. In step 3, measure 50.0 mL of 1.0*M* NaOH solution (not solid NaOH) into a clean dry graduated cylinder. After the temperature readings reach a steady value in the HCl solution, add the 1.0*M* NaOH solution to the calorimeter.

Reaction 3

1. Repeat steps 1-6, using solid NaOH again, but measuring out 100.0 mL of 0.5*M* HCl solution instead of water.

Data Analysis

1. Calculate the total mass of solution, *m*, for each of the reactions. Assume a density of 1.00 g/mL for water and 1.02 g/mL for the HCl and the NaOH solutions and be sure to add the mass of the solid NaOH when needed.
2. Calculate the temperature change, ΔT, for each of the reactions.
3. Calculate the heat, *q* (in kJ), absorbed by the solution in each reaction, using:

   $$q = m \cdot C_P \cdot \Delta T$$

   Assume that the 3 dilute solutions have the same specific heat as H_2O (*i.e.* C_P = 4.18 J/g·°C).
4. Assuming negligible heat losses to the calorimeter or the surroundings, we have (by the first law of thermodynamics) $\Delta H_{rxn} + q = 0$. Find ΔH_{rxn} for each reaction.
5. Calculate the amount (in moles) of NaOH used for each reaction. Use your NaOH mass data for the first and third reactions, and NaOH solution concentration and volume data for the second reaction.
6. Combine results from calculations 4 & 5 to find the enthalpy change per mole of NaOH for each reaction.
7. To verify Hess's Law, compare the molar value of ΔH_{rxn3} to the sum of the molar values of $\Delta H_{rxn\ 1} + \Delta H_{rxn\ 2}$. Calculate the percent difference for the experiment.

Name _____ Partner _____

Lab Report II

Data Sheet for Hydrochloric Acid + Sodium Hydroxide Calorimetry

RECORD TEMPERATURES TO THE THERMOMETER'S FULL AVAILABLE PRECISION. YOU MAY NOT HAVE TO USE ALL OF THE TIMES FOR EACH REACTION, BUT BE SURE TO THOROUGHLY STIR EACH MIXTURE SO THE REACTION GOES TO COMPLETION.

Reaction 1: $NaOH_{(s)} \rightarrow NaOH_{(aq)}$

time (s)	T (°C)	time (s)	T (°C)	time (s)	T (°C)
0		75		150	
15		90		180	
30		105		195	
45		120		210	
60		135		225	

Reaction 2: $NaOH_{(aq)} + HCl_{(aq)} \rightarrow NaCl_{(aq)} + H_2O_{(l)}$

time (s)	T (°C)	time (s)	T (°C)	time (s)	T (°C)
0		75		150	
15		90		180	
30		105		195	
45		120		210	
60		135		225	

Reaction 3: $NaOH_{(s)} + HCl_{(aq)} \rightarrow NaCl_{(aq)} + H_2O_{(l)}$

time (s)	T (°C)	time (s)	T (°C)	time (s)	T (°C)
0		75		150	
15		90		180	
30		105		195	
45		120		210	
60		135		225	

Name:_____ **Data**	**Reaction 1** $NaOH_{(s)} + H_2O_{(l)}$	**Reaction 2** $NaOH_{(aq)} + HCl_{(aq)}$	**Reaction 3** $NaOH_{(s)} + HCl_{(aq)}$
vial + NaOH mass	g	____M of NaOH _____M of HCl	g
empty vial mass	g	_____mL of HCl	g
NaOH used	g	mL	g
solution mass, *m*	g	g	g
maximum temperature, T_2	°C	°C	°C
initial temperature. T_1	°C	°C	°C
temperature difference, ΔT	°C	°C	°C

Calculations show details on separate sheet			
heat absorbed $q = m \cdot C_P \cdot \Delta T$	kJ	kJ	kJ
enthalpy change, ΔH	kJ	kJ	kJ
molar enthalpy of rxn, ΔH_{rxn}	kJ/mol NaOH	kJ/mol NaOH	kJ/mol NaOH
% difference	%		

1. Write net ionic equations for:

   a. Reaction 1 $\Delta H_1 =$ kJ/mol

   b. Reaction 2 $\Delta H_2 =$ kJ/mol

   c. Reaction 1 + Reaction 2 $\Delta H_{1+2} =$ kJ/mol

   d. Reaction 3 $\Delta H_3 =$ kJ/mol

2. Do your results agree with Hess's law to within 1%? 5%? 10%? Suggest reasons for any discrepancy.

Calculations: **Name:**_____

Reaction 1:

Solution mass:

heat absorbed $q = m \cdot C_P \cdot \Delta T$:

moles of NaOH:

molar enthalpy of rxn, ΔH_{rxn} (kJ/mole NaOH):

Reaction 2:

Solution mass:

heat absorbed $q = m \cdot C_P \cdot \Delta T$:

moles of NaOH:

molar enthalpy of rxn, ΔH_{rxn} (kJ/mole NaOH):

Reaction 3:

Solution mass:

heat absorbed $q = m \cdot C_P \cdot \Delta T$:

moles of NaOH:

molar enthalpy of rxn, ΔH_{rxn} (kJ/mole NaOH):

Saftey and Waste Disposal for Thermochemistry II: Hess's Law

PERSONAL PROTECTIVE EQUIPMENT

Chemical splash goggles are required. Latex or nitrile gloves are recommended.

HAZARDS IDENTIFICATION

Hydrochloric acid, $HCl_{(aq)}$ *Common name: muriatic acid*

Toxic. Corrosive. Contact with liquid can cause redness, pain and severe skin burns. Vapors can irritate and damage eye and lung tissue.

Sodium hydroxide, $NaOH_{(aq)}$ *Common names: lye, caustic soda*

Toxic. Corrosive, causes rapid tissue destruction upon contact. Irreversibly damages eyes. Solutions are hazardous in all dilutions. NaOH is an ingredient in drain-cleaners such as Drano™. The slippery feel of a sodium hydroxide solution on the skin is due to the saponification reaction: it transforms cell membranes and skin oils into soap.

Sodium hydroxide, $NaOH_{(s)}$

Toxic. Solid sodium hydroxide is extremely hygroscopic. Pellets dropped on lab bench tops or on the floor will rapidly absorb enough water to become very concentrated solutions which are very slippery and caustic (see $NaOH_{(aq)}$ hazards, above) . Pick up any dropped pellets immediately with Latex or nitrile gloves or paper towel and dispose of in the containers in the fume hood.