

AP Chemistry Lab 7

Thermochemistry & Hess's Law

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PURPOSE

To determine the molar enthalpy of three reactions and to test Hess's Law that enthalpy is a state function.

INTRODUCTION

In this experiment you will determine the enthalpy change that occurs when sodium hydroxide and hydrochloric acid solutions are mixed. Next, the enthalpy change for the reaction between sodium hydroxide and ammonium chloride will be measured. Lastly, you will determine the enthalpy change for the reaction between ammonia and hydrochloric acid. An algebraic combination of the first two equations can lead to the third equation. Therefore, according to Hess's law, an algebraic combination of the enthalpy changes of the first two should lead to the enthalpy of the third reaction.

The molecular equations for the reactions are as follows:

- (1) $\text{NaOH}(aq) + \text{HCl}(aq) \rightarrow \text{NaCl}(aq) + \text{H}_2\text{O}(l)$
- (2) $\text{NH}_4\text{Cl}(aq) + \text{NaOH}(aq) \rightarrow \text{NH}_3(aq) + \text{NaCl}(aq) + \text{H}_2\text{O}(l)$
- (3) $\text{NH}_3(aq) + \text{HCl}(aq) \rightarrow \text{NH}_4\text{Cl}(aq)$

There is no single instrument that can directly measure heat in the way a balance measures mass or a thermometer measures temperature. However, it is possible to determine the heat change when a chemical reaction occurs. The change in heat is calculated from the mass, temperature change, and specific heat of the substance which gains or loses heat. The equation that is used to calculate heat gain or loss is:

$$q = (\text{grams of substance}) \times (\text{specific heat}) \times \Delta T$$

where q = the heat energy gained or lost and ΔT is the change in temperature. Since ΔT = (final temperature minus initial temperature), an increase in temperature will result in a positive value for both ΔT and q , and a loss of heat will give a negative value. A positive value for q means a heat gain, while a negative value means a heat loss.

Acid-base neutralization is an exothermic process. Combining solutions containing an acid and base results in a rise of solution temperature. The heat given off by the reaction (which will cause the solution temperature to rise) can be calculated from the specific heat of the solution, the mass of solution and the temperature change. This heat quantity can then be converted to the enthalpy change for the reaction in terms of kJ/mole by using the concentrations of the reactants.

According to Hess, if a reaction can be carried out in a series of steps, the sum of the enthalpies for each step should equal the enthalpy change for the total reaction. Another way of stating Hess's Law is if two chemical equations can algebraically be combined to give a third equation, the values of ΔH for the two equations can be combined in the same manner to give ΔH for the third equation. An examination of the acid-base equations above shows that if equation (2) is subtracted from equation (1), equation (3) will result. Therefore, if the value of ΔH for equation (2) is subtracted from that of equation (1), the enthalpy change for equation (3) should result. We will test this idea in this experiment.

DEFINITIONS

Hess's law, calorimetry, specific heat, heat capacity, ΔH , acid-base neutralization reaction.

MATERIALS

Hydrochloric acid, HCl 2.0M
Ammonia, NH_3 2.0M
Graduated cylinder, 50-mL
Two thermometers

Sodium hydroxide, NaOH 2.0M
Ammonium chloride, NH_4Cl 2.0M
Calorimeter and cover
Fume hood (optional)

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SAFETY

- You will be working with strong acids and bases in concentrated solutions. The ammonia and hydrochloric acid have strong odors. If you spill any on yourself, wash off with lots of water. Neutralize acid spills on the lab bench with baking soda. Neutralize ammonia and sodium hydroxide spills with vinegar, which is dilute acetic acid.
- Wear goggles.
- When NaOH and NH₄Cl solutions are mixed, ammonia gas is evolved. Work in a hood.

PROCEDURE

Find the Heat Capacity of the Calorimeter.

1. Construct a calorimeter of two nested Styrofoam cups with a cover that has a hole in it to accept a thermometer.
2. Measure 50.0 mL of water at room temperature into the calorimeter. Record temperature to the nearest 0.1°C.
3. Pour 50.0 mL of hot water (~60°C) into a graduated cylinder. Record its temperature to the nearest 0.1°C using a separate thermometer. Immediately after measuring its temperature, pour the hot water into the room temperature water in the calorimeter cup, cover, and mix the solutions by gently swirling the cup. Record the highest temperature of the mixture (after ~30 seconds after mixing.)

Find the Heat of the Reactions,

4. Determine the temperature change that occurs when 50.0 mL of 2.0M HCl solution reacts with 50.0 mL of 2.0M NaOH.
 - First, measure the temperature of each of the solutions. Be sure to rinse and dry the thermometer before transferring it to a second solution. The solution temperatures should agree to ±0.2°C. If they do not agree, you should use the average temperature as your initial temperature.
 - Put 50.0 mL of 2.0M HCl in the calorimeter. Measure 50.0 mL of 2.0M NaOH, add it to the acid, quickly cover and insert the thermometer. Gently swirl the cup to mix the solutions. Record the highest temperature of the mixture to the nearest 0.1°C (after ~30 seconds.)
5. Repeat the procedure, combining solutions of 2.0M NH₄Cl and 2.0M NaOH, and for the third reaction combining solutions of 2.0M NH₃ and 2.0M HCl. Be sure that containers and thermometers are rinsed and dried between reactions. *Caution:* ammonia has a very strong odor.
6. All solutions can be flushed down the drain with a 20-fold excess of water

ANALYSIS

Calculate the Heat Capacity of the Calorimeter.

1. Calculate the average temperature of the hot and cold water before mixing, T_{avg}.
2. The temperature of the hot/cold water after mixing, T_{mix}, is lower than T_{ave} because some heat was lost by the water and absorbed by the calorimeter. Calculate q_{water}, the heat lost by the water:

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

where q_{water} = heat lost by water and the specific heat of water is 4.18 J/(g°C). The heat absorbed by the calorimeter, q_{cal}, will be equal to that lost by the water.

$$q_{\text{cal}} = -q_{\text{water}}$$

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3. Calculate the heat capacity of the calorimeter, C_{cal} , which is the heat that the calorimeter absorbs each time the temperature of the solution changes by 1°C:

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

where T_{initial} is the initial temperature of the cool water.

Calculate ΔH for Each Reaction.

4. Calculate the amount of heat evolved in each reaction, q_{rxn} , by assuming that all of the heat is absorbed by the solutions and the calorimeter:

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

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

where $\Delta T_{\text{solution}} = (T_{\text{mix}} - T_{\text{initial}})$ for each reaction mixture. Assume that the density of the solutions is 1.03 g/mL, and that the specific heat of the solutions is the same as that of water.

5. Calculate the value of the enthalpy change, ΔH , in terms of kJ/mole for each of the reactions by dividing q_{rxn} by the number of moles of the limiting reactant.

Verify Hess's Law.

6. Write net ionic equations for the three reactions involved. Show how you must arrange the first two equations to algebraically find the third.
7. Calculate the value of ΔH for the third reaction from your ΔH values for the first two reactions using Hess's law. Do your experimental ΔH values support Hess's Law? Calculate the percent error, assuming the measured ΔH of the third reaction is the "accepted value."
8. Use Appendix 3 in your text, which lists standard heats of formation, to calculate ΔH for each of these net ionic equations. (Be sure to look up ΔH_f° values for the aqueous state of each species.) Show that the ΔH values calculated from Appendix 3 support Hess's law.
9. In the error analysis section of your report, calculate the percent error of your experimental ΔH values (from question 5) compared to the calculated ΔH values (based on Appendix 3) for all three reactions.

EXPERIMENTAL ERROR

The most likely source of experimental error comes measuring the final temperature of the reactions. For a given reaction, how is the calculated molar heat of reaction affected if the final temperature is measured too low?