

Calorimetry and Hess's law

Objective: Use calorimetric measurements to determine heats of reaction and to demonstrate Hess's Law of combining reaction enthalpies.

Materials: 1 M HCl; 1 M NaOH; solid NaOH

Equipment: Styrofoam cup calorimeters; thermometers; 25-mL or 50-mL Erlenmeyer flasks; test tube with stopper; 100-mL graduated cylinder; stopwatch or timing device; spatula

Safety: The 1 M solutions of hydrochloric acid (HCl) and sodium hydroxide (NaOH) are caustic and corrosive, and should be handled with care. If these solutions make contact with skin, wash the affected area immediately. Solid NaOH pellets should not be handled, but measured or transferred using spatulas. Thermometers are fragile and should be handled gently. Wear safety goggles in the lab at all times.

Waste Disposal: All reagents and reaction solutions may be washed down the sink with plenty of water.

INTRODUCTION

One indication of a chemical reaction is the production of heat. The amount of heat gained or lost during a reaction is due to the breaking of bonds between atoms in the reactants, and the formation of bonds between atoms to form products. The heat of reaction is also called the **enthalpy** of reaction, or ΔH . For **endothermic** reactions, ΔH is positive and heat flows into the reaction. For **exothermic** reactions, ΔH is negative and heat is given off by the reaction.

Heats of reaction are measured by **calorimetry**, or the study of heat flow. For reactions that take place in solution, the total amount of heat flow in a reaction can be expressed as

$$q = S.H. \times m \times \Delta T \quad (1)$$

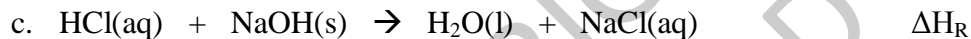
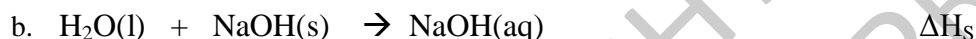
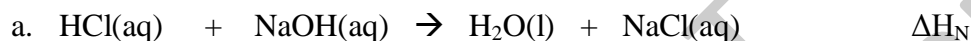
where q is the heat flow (in calories), *S.H.* stands for the **specific heat** of the reaction solution (in cal/g·°C), m is the mass of the solution (in g), and ΔT is the change in temperature (in °C). For an exothermic reaction, q_{reaction} is negative. The heat released by the reaction will increase the temperature of the solution in the calorimeter, and $q_{\text{calorimeter}}$ will be positive, or:

$$-q_{\text{reaction}} = q_{\text{calorimeter}} \quad (2)$$

A **calorimeter** is a device that can be used to measure heat flow. The main requirement for a calorimeter is that it be well insulated, so that there is no heat lost to the surroundings during the measurement. If this condition is met, then all the heat produced during a reaction will be retained within the calorimeter, and the temperature in the calorimeter will increase. A simple calorimeter can be constructed using Styrofoam cups with cardboard lids. While not perfectly insulated, it works well enough to give reasonably good results.

Enthalpies of reactions are **state functions**—the enthalpy change for a reaction depends only on the initial and final states and is independent of how the reaction is performed. **Hess's Law** demonstrates the concept of a state function. Hess's Law states that if a reaction can be expressed as the sum of two other reactions, then the enthalpy change for that reaction can be calculated as the sum of the enthalpies of the two other reactions.

In this experiment we will use calorimetry to verify Hess's Law for the three reactions below:



Since the reaction in step (c) can be written as the sum of a neutralization reaction [step (a)], and a dissolution process [step (b)], then

$$\Delta H_{\text{N}} + \Delta H_{\text{S}} = \Delta H_{\text{R}}$$

Pre-Lab Questions

1. Define the following terms:

a. Calorimetry :

b. Enthalpy:

c. Specific heat:

d. Exothermic:

e. Hess's Law:

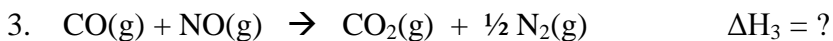
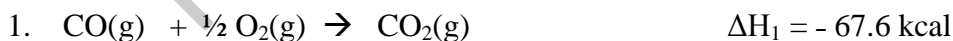
2. A piece of metal weighing 18.4 g is heated to raise its temperature from 21.7°C to 53.5°C. It is found that the metal absorbed 62.5 cal of heat in the process.

a. Calculate the specific heat of the metal. Include appropriate units.

b. Based on your results, identify the metal from the list below. Metal = _____

Element	Specific heat (cal/g·°C)
Aluminum	0.216
Copper	0.093
Iron	0.107
Silver	0.057

3. Determine the enthalpy change (ΔH_3) for the final reaction below.



PROCEDURE

Students should work in pairs. Each pair of students will require two Styrofoam cup calorimeters (see Figure 1), one thermometer, and one timing device (watch with second hand).

Part A: Heat of Neutralization (ΔH_N)

1. Measure 50.0 mL of 1.0 M HCl (to the nearest 0.1 mL) in a graduated cylinder and transfer to one of the calorimeters. Rinse and dry the graduated cylinder. Measure 50.0 mL of 1.0 M NaOH (to the nearest 0.1 mL) and transfer to the other calorimeter.
2. Place the thermometer in the cup containing the HCl solution and allow it to equilibrate for one minute. Record the temperature (to the nearest 0.1 °C) in one minute intervals for three minutes, and record these temperatures on Data Sheet 1. At the 4 minute mark, pour the 1.0 M NaOH solution into the HCl solution and mix thoroughly. You should pour and mix as quickly as possible while being careful to avoid spilling.
3. Replace the calorimeter cover and thermometer, and monitor the temperature. At this point, your calorimeter should resemble the example provided in Figure 1.
4. Note the solution temperature (to the nearest 0.1°C) at the 5, 6, and 7 minute marks and record these temperatures on Data Sheet 1.
5. Remove the thermometer from the calorimeter, taking care not to lose any of the solution. Take the calorimeter with the reaction solution to the analytical balance and record the mass (with solution) to the nearest 0.01 g on Data Sheet 1. Discard the solution down the sink, and rinse and dry the cup. Obtain the mass of the dry calorimeter cup, and record the mass on Data Sheet 1 to the nearest 0.01 g. By difference, calculate the mass of the reaction solution and record this value on Data Sheet 1.

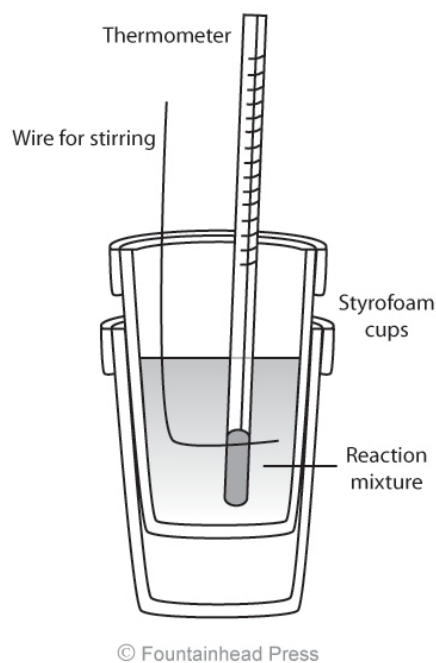


Figure 1. Styrofoam cup calorimeter assembly

6. Rinse and dry the other calorimeter, and perform a second determination by repeating Steps 1-4 of Part A.

Part B: Heat of Solution (ΔH_S)

1. Obtain a stoppered test tube. Weigh it on the balance to the nearest 0.01 g, and record this mass on Data Sheet 2. Carefully add about 2.0 g of solid NaOH pellets. Solid NaOH is hygroscopic--keep the test tube stoppered when not transferring material to or from the test tube. Re-weigh the test tube to the nearest 0.01 g and record this mass on Data Sheet 2. By difference, calculate the mass of NaOH in the test tube.
2. Using a clean, dry graduated 100-mL graduated cylinder, carefully measure 50.0 mL of deionized water (to the nearest 0.1 mL) and transfer the water to one of the calorimeter cups. Insert the thermometer and allow it to equilibrate for 1 minute. Note the temperature of the water at the 1, 2, and 3 minute marks and record these temperatures on Data Sheet 2. At the 4 minute mark, transfer all of the NaOH pellets into the water in the calorimeter and stir gently until the pellets dissolve. Replace the calorimeter cover and insert the thermometer. Note the temperature of the solution at the 5, 6, and 7 minute marks and record these temperatures on Data Sheet 2.
3. Remove the thermometer carefully to avoid losing any of the solution. Weigh the cup with the NaOH solution to the nearest 0.01 g and record this mass on Data Sheet 2. Pour the solution down the sink with plenty of water. Rinse and dry the cup, and re-weigh it. Record this mass on Data Sheet 2. Calculate the mass of the NaOH solution by difference, and record this mass on Data Sheet 2.
4. Perform a second determination by repeating Steps 1-3 of Part B.

Part C: Heat of Reaction (ΔH_R)

1. Weigh about 2.0 g of NaOH pellets to the nearest 0.01 g following the same procedure as in Part B Step 1. Record these masses on Data Sheet 3.
2. Pour 55 mL of 1.0 M HCl into a clean, dry graduated cylinder, and add deionized water to a total volume of 100.0 mL.
3. Pour the HCl solution into a calorimeter cup. Replace the cover, insert the thermometer, and allow it to equilibrate for 1 minute. Note the temperature of the HCl solution at the 1, 2, and 3 minute marks, and record these temperatures on Data Sheet 3.
4. At the 4 minute mark, add the solid NaOH pellets and stir carefully with the thermometer to ensure that the pellets dissolve completely. Replace the cover and re-insert the thermometer. Note the temperature of the reaction solution at the 5, 6, and 7 minute marks, and record these temperatures on Data Sheet 3.
5. Remove the thermometer from the calorimeter, being careful not to lose any of the reaction solution. Weigh the cup and solution to the nearest 0.01 g, and record this mass on Data Sheet 3. Discard the reaction solution in the sink with plenty of water. Rinse and dry the

cup, and re-weigh it. Record this mass on Data Sheet 3. Calculate the mass of the reaction solution by difference and record this mass on Data Sheet 3.

6. Perform a second determination by repeating Steps 1–4 of Part C.
7. Clean and dry any borrowed equipment, and return them to the lab drawer or the equipment cart as instructed by the lab instructor or TA.

CALCULATIONS

Recall from the introduction that the heat associated with a reaction (q) can be calculated from Eq. (1)

$$q(\text{cal}) = \text{S.H.}(\text{cal/g}\cdot^{\circ}\text{C})\cdot m(\text{g})\cdot \Delta T(^{\circ}\text{C}) \quad (1)$$

The specific heat (S.H.) of the solutions in Parts A, B, and C can be estimated and have been provided in the Calculations sections on Data Sheets 1, 2, and 3. Knowing the mass of the reaction solution (m) and the change in temperature (ΔT), we can calculate the heat of the reaction.

We can calculate the temperature change for the reaction in the calorimeter as the difference between the initial and final calorimeter temperatures. Typically, the initial temperature measured during the first three minutes of each trial should be constant. If it is not, use the temperature at 3 minutes as the initial temperature. During reactions, heat may be released quickly, so that the last temperature reading may not reflect the true temperature change. The highest temperature reached during the reaction should be recorded as the final temperature for use in the calculations.

For an exothermic process ($q_{\text{reaction}} = \text{negative}$), the heat generated by reaction is absorbed by solution and results in a temperature increase in the calorimeter ($q_{\text{calorimeter}} = \text{positive}$). Thus,

$$-q_{\text{reaction}} = q_{\text{calorimeter}}$$

Finally, enthalpies of reactions are expressed in cal/mol. Therefore, we must calculate the moles of reactants in each trial. In Part A, the moles of HCl neutralized in the reaction can be calculated as:

$$\# \text{ mol HCl} = (\text{Volume HCl, L})\cdot (\text{Molarity HCl, mol/L}) \quad (3)$$

For Parts B and C, the critical reactant is the NaOH. We can calculate the moles of NaOH as

$$\# \text{ mol NaOH} = (\text{Mass NaOH, g}) / (\text{MW NaOH, g/mol}) \quad (4)$$

From the heat of reaction (q) and the moles of reactant we can calculate the enthalpies of reaction for Parts A, B, and C

$$\Delta H_{\text{reaction}} = q(\text{cal}) / [\text{moles reactant, (mol)}] \quad (5)$$

According to Hess's Law: $\Delta H_R = \Delta H_S + \Delta H_N$ You can verify Hess's Law by using your experimentally determined values of ΔH_S and ΔH_N from Parts B and C to calculate a value of ΔH_R . The calculated value can then be compared to the value determined by experiment in Part A.

The % error in your experiment can be calculated as:

$$\% \text{ error} = \frac{(\Delta H_N + \Delta H_S) - \Delta H_R}{H_R} \times 100 \quad (6)$$

Data Sheet 1: Heat of Neutralization (ΔH_N)

Molarity of HCl: _____

		<i>Trial 1</i>	<i>Trial 2</i>
	Volume of HCl (mL)	_____	_____
Temperature ($^{\circ}\text{C}$):	1 min:	_____	_____
	2 min:	_____	_____
	3 min:	_____	_____
	4 min (MIX)	_____	_____
	5 min:	_____	_____
	6 min:	_____	_____
	7 min:	_____	_____
	$\Delta T = (T_{\text{final}} - T_{\text{initial}})$:	_____	_____
	Mass of Calorimeter + Solution (g)	_____	_____
	Mass of Calorimeter empty (g):	_____	_____
	Mass of Solution (g):	_____	_____

Calculations Part A:

	<i>Trial 1</i>	<i>Trial 2</i>
$q_{\text{calorimeter}} \text{ (cal)} = (0.961 \text{ cal/g}^{\circ}\text{C}) \cdot (m) \cdot (\Delta T)$:	_____ (cal)	_____ (cal)
$-q_{\text{reaction}} = q_{\text{calorimeter}}$:	_____ (cal)	_____ (cal)
# moles HCl = $V_{\text{HCl}}(\text{L}) \cdot M_{\text{HCl}}(\text{mol/L})$:	_____ (mol)	_____ (mol)
$\Delta H_N = (q_{\text{reaction}} / \text{moles HCl})$:	_____ (cal/mol)	_____ (cal/mol)
Average ΔH_N :	_____ (cal/mol)	

Data Sheet 2: Heat of Solution (ΔH_S)

	<i>Trial 1</i>	<i>Trial 2</i>
Mass of stoppered test tube + NaOH pellets:	_____ (g)	_____ (g)
Mass of empty stoppered test tube:	_____ (g)	_____ (g)
Mass of NaOH:	_____ (g)	_____ (g)
Temperature ($^{\circ}\text{C}$):		
1 min:	_____	_____
2 min:	_____	_____
3 min:	_____	_____
4 min (MIX)	_____	_____
5 min:	_____	_____
6 min:	_____	_____
7 min:	_____	_____
$\Delta T = (T_{\text{final}} - T_{\text{initial}})$:	_____	_____
Mass of Calorimeter + Solution (g)	_____	_____
Mass of Calorimeter empty (g):	_____	_____
Mass of Solution (g):	_____	_____

Calculations Part B:

	<i>Trial 1</i>	<i>Trial 2</i>
$q_{\text{calorimeter}} \text{ (cal)} = (0.939 \text{ cal/g}^{\circ}\text{C}) \cdot (m) \cdot (\Delta T)$:	_____ (cal)	_____ (cal)
$- q_{\text{solution}} = q_{\text{calorimeter}}$:	_____ (cal)	_____ (cal)
# moles NaOH = $g_{\text{NaOH}} / (40.0 \text{ g/mol})$:	_____ (mol)	_____ (mol)
$\Delta H_S = (q_{\text{solution}} / \text{moles NaOH})$:	_____ (cal/mol)	_____ (cal/mol)
Average ΔH_S :	_____ (cal/mol)	

Data Sheet 3: Heat of Reaction (ΔH_R)

	<i>Trial 1</i>	<i>Trial 2</i>
Mass of stoppered test tube + NaOH pellets:	_____ (g)	_____ (g)
Mass of empty stoppered test tube:	_____ (g)	_____ (g)
Mass of NaOH:	_____ (g)	_____ (g)
Temperature ($^{\circ}\text{C}$):		
1 min:	_____	_____
2 min:	_____	_____
3 min:	_____	_____
4 min (MIX)	_____	_____
5 min:	_____	_____
6 min:	_____	_____
7 min:	_____	_____
$\Delta T = (T_{\text{final}} - T_{\text{initial}})$:	_____	_____
Mass of Calorimeter + Solution (g)	_____	_____
Mass of Calorimeter empty (g):	_____	_____
Mass of Solution (g):	_____	_____

Calculations Part C:

	<i>Trial 1</i>	<i>Trial 2</i>
$q_{\text{calorimeter}} \text{ (cal)} = (0.961 \text{ cal/g}^{\circ}\text{C}) \cdot (m) \cdot (\Delta T)$:	_____ (cal)	_____ (cal)
- $q_{\text{reaction}} = q_{\text{calorimeter}}$:	_____ (cal)	_____ (cal)
# moles NaOH = $g_{\text{NaOH}} / (40.0 \text{ g/mol})$:	_____ (mol)	_____ (mol)
$\Delta H_R = (q_{\text{reaction}} / \text{moles NaOH})$:	_____ (cal/mol)	_____ (cal/mol)
Average ΔH_R :	_____ (cal/mol)	

Hess's Law Calculations

According to Hess's Law:

$$\Delta H_{\text{Reaction}} = \Delta H_{\text{Solution}} + \Delta H_{\text{Neutralization}}$$

Verify Hess's Law:

$$\text{Average } \Delta H_S = \text{_____ (cal/mol)}$$

$$\text{Average } \Delta H_N = \text{_____ (cal/mol)}$$

$$\text{Calculated } \Delta H_R = \text{_____ (cal/mol)}$$

This can be compared to your experimentally determined value of ΔH_R :

$$\text{Average } \Delta H_R = \text{_____ (cal/mol)}$$

$$\text{Percent error (from Eq. (6)): _____ \%}$$

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Post-Lab Questions

1. In the Calculations section you were asked to calculate the percent error in your Hess's Law determination. Discuss at least two possible sources of error that could contribute to your percent error.
2. A student is performing Part C and does not completely dissolve the NaOH pellets before acquiring the final temperature. How will this affect his value for ΔH_R and his percent error calculations?
3. In a different experiment it is observed that 322 cal of heat is absorbed as the temperature of 58.2 g of Cu(s) is raised from 21.6°C to 79.5°C. Calculate the specific heat of Cu in cal/g·°C, and the % error in your calculated value. The S.H. for Cu is 0.093 cal/g·°C.
4. For the three reactions studied in this experiment, demonstrate how the third reaction is the sum of the first two reactions. Which species "cancel out"?