

Calorimetry

INTRODUCTION

Heat is a form of energy, often called thermal energy. Energy can be transformed from one form to another (electric energy to heat and light in a light bulb, for example), but it cannot be created or destroyed; rather, energy is conserved. The higher the temperature of a material, the more thermal energy it possesses. In addition, at a given temperature, the more of a given substance there is, the more total thermal energy the material possesses.

On an atomic level, absorbed heat causes the atoms of a solid to vibrate, much as if they were bonded to one another through springs. As the temperature is raised, the energy of the vibrations increases. In a metal, this is the only motion possible. In a liquid or gas, absorbed heat causes the atoms in the molecule to vibrate, and the molecule to both rotate and move from place to place. Because there are more “storage” possibilities for energy in liquids and gases, their heat capacities are larger than in metals. Heat capacity, C_p , is the amount of heat required to change the heat content of 1 mole of a material by exactly 1°C . Specific heat, C_{sp} , is the amount of heat required to change the heat content of exactly 1 gram of a material by exactly 1°C .

Specific heat values can be determined in the following way. When two materials, each initially at a different temperature, are placed in contact with one another, heat always flows from the warmer material into the colder material until the two materials are at the same temperature. From the law of conservation of energy,

$$q_{\text{hot}} + q_{\text{cold}} = 0 \quad (1)$$

the heat gained by the initially colder material must equal to the heat lost by the initially warmer material:

$$-(\text{heat lost})_{\text{hot object}} = (\text{heat gained})_{\text{cold object}} \quad (2)$$

where q is used as the abbreviation for heat. The heat quantities in this equation would be calculated as (specific heat) \times (mass of the object) \times (the temperature change of the object), because specific heat has units of energy per (mass \times degrees). Equation 2 then becomes:

$$-[C_{sp} \cdot m \cdot \Delta T]_{\text{hot}} = [C_{sp} \cdot m \cdot \Delta T]_{\text{cold}} \quad (3)$$

A. Specific heat

In today's experiment, you will place hot metal into cold water. The specific heat of water is $4.2 \text{ J} \cdot \text{g}^{-1} \cdot \text{K}^{-1}$. Temperature changes are written in Kelvins. The water will be placed in a well-insulated coffee-cup with a thermometer. The cup and the thermometer will also absorb some heat. If the heat that the cup and thermometer absorb per degree is labeled C_{cup} , then equation 3 becomes:

$$-[(C_{sp} \cdot m) \cdot \Delta T]_{\text{hot}} = [(C_{sp} \cdot m + C_{\text{cup}}) \cdot \Delta T]_{\text{cold}} \quad (4)$$

In Part 1 of this experiment, you will pour hot water into cold water to determine the value of C_{cup} . In Part 2 of the experiment, you will place hot metal block into water to determine C_{sp} for the metal. For Part 1, equation 4 becomes:

$$-[(4.184 \text{ J} \cdot \text{g}^{-1} \cdot \text{K}^{-1}) \cdot m \cdot \Delta T]_{\text{hot}} = [(4.184 \text{ J} \cdot \text{g}^{-1} \cdot \text{K}^{-1}) \cdot m + C_{\text{cup}}] \cdot \Delta T]_{\text{cold}} \quad (5)$$

You will solve the equation for C_{cup} .

For Part 2, equation 4 becomes:

$$-[C_{sp} \cdot m_{\text{metal}} \cdot \Delta T]_{\text{hot}} = [(4.184 \text{ J} \cdot \text{g}^{-1} \cdot \text{K}^{-1}) \cdot m_{\text{water}} + C_{\text{cup}}] \cdot \Delta T]_{\text{cold}} \quad (6)$$

You will solve the equation (6) for C_{sp} , the specific heat of the metal.

B. Heat of reaction

When a chemical reaction occurs in water, there is an exchange of heat between the

reaction mixture and the solvent, water.

$$q_{\text{rxn}} + q_{\text{mixture}} = 0 \quad (7)$$

and equation 7 becomes

$$q_{\text{rxn}} + [(4.184 \text{ J.g}^{-1}.\text{K}^{-1}).m_{\text{mixture}} + C_{\text{cup}}] \cdot \Delta T = 0 \quad (8)$$

The heat flow associated with the reaction mixture is also equal to the enthalpy change, ΔH , for the reaction. By measuring the mass of the reaction mixture, and by observing the temperature change that the mixture undergoes, you can find ΔH_{rxn} . If the temperature of the mixture goes up, heat has been *given off* by the reaction, so the reaction is *exothermic*: q_{rxn} is *positive* and ΔH_{rxn} is *negative*. If the temperature of the mixture goes down, heat has been *absorbed* by the reaction, so the reaction is *endothermic*: q_{rxn} is *negative* and ΔH_{rxn} is *positive*.

1) Heat of solution: One of the simplest reactions that can be studied in solution occurs when a solid is dissolved in water. Example: the solvation of sodium hydroxide in water:



When this reaction occurs, the temperature of the solution becomes much higher than that of the NaOH and water that were used. If we dissolve a known amount of NaOH in a measured amount of water in a calorimeter, and measure the temperature change that occurs, we can use equation 8 to find ΔH_{sln} . Noting that ΔH_{sln} is directly proportional to the amount of NaOH used, you can calculate ΔH_{sln} of either a gram or a mole of NaOH. In the second part of this experiment you will measure ΔH_{sln} for an unknown ionic solid.

2) Heat of reaction: Chemical reaction often occurs when solutions are mixed. A very common reaction is the neutralization reaction when an acidic solution is mixed with a basic one. In the last part of this experiment, you will measure ΔH_{rxn} for a neutralization reaction between HCl (aq) and NaOH (aq). The heat effect is quite large, and is the result of the reaction between H^+ ions in the acidic solution with OH^- ions in the basic solution.

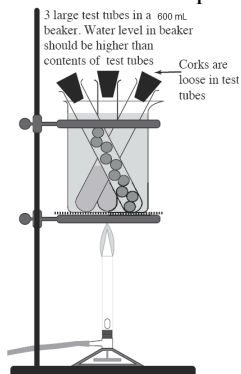


EXPERIMENTAL PROCEDURE

Read temperatures to the nearest 0.1°C. Use the balances to obtain masses.

A. Specific heat

1.) Set a 400-mL beaker on a ring stand as shown in the diagram below. Add about 450 mL of water. Turn on the burner to a hot flame so that the hot water bath will be heating while you are preparing the test tube for the experiment.



- 2.) Get an unknown metal block. Record the number of the metal in Part A2 of data table. Dry the metal block onto a paper towel. Immerse the metal block in the hot water bath.
- 3.) You will need two large test tubes and stoppers for Part A1. Into each test tube, add 30 ml of deionized water. *Loosely* stopper them, and place them into the hot water bath.
- 4.) When the water is boiling, turn the burner down to maintain a gentle boil in the beaker. The test tubes should reach the temperature in the water bath after 10 minutes of boiling. Assume that the temperature of the boiling water is 100.0°C.

1) Measuring C_{cup}

- 1.) Place 70 ml of deionized water into the coffee cup. Weigh the cup with lid and record the mass in Part A1 data table. Record the temperature of the water.
- 2.) Using test tube holder, pour the hot water from the test tube into the cup and quickly cover it with the lid. Stir with the thermometer and record the highest temperature reached. Now weigh the cup and record the mass as the final mass of cup and water.
- 3.) You will run two trials for Part A1 to see how consistent your data is. To begin the second trial, pour the water out of the cup, and shake out the last drops of water from the cup. Add 70 ml of deionized water to the cup, measure the mass as in the first trial, and record the temperature. Add the hot water, record the temperature again. Weigh the cup and record the mass. Empty the water from the cup.

2) Measuring C_{sp} of the metal

- 1.) You will do just one trial for Part A2. Add 100 ml of deionized water to the cup. Weigh the cup with the water and lid. Record the mass in Part A2 of data table. Record the temperature of the water in the cup. Quickly transfer the metal block from the water bath to the cup, and cover the cup immediately. Stir the cup with the thermometer and record the highest temperature reached. Now weigh the cup with water and metal block.
- 2.) Pour the water out of the cup. Blot the metal dry with paper towel, and place it in its container before returning the metal block to the instructor.

B. Heat of reaction

1) Heat of solution:

- 1.) Place 50 mL deionized water in the cup. Weigh the cup with the water and lid. Record the mass in Part B1 of data table. Record the temperature of the water in the cup.
- 2.) Get an unknown ionic solid sample. Record the number of the unknown in Part B1 of data table. In a small beaker, weigh about 5 g of the solid compound.
- 3.) Quickly transfer the compound from to the cup, and cover the cup immediately. Stir the cup continuously with the thermometer with occasional swirling. Record the highest temperature reached. Check to make sure that ALL the solid is dissolved.
- 4.) Weigh the cup with lid and solution, and record the mass in Part B1 data table.
- 5.) Pour the water out of the cup.

2) Heat of neutralization reaction:

- 1.) In a graduated cylinder, measure 25 mL of 1.00 M HCl (aq). Pour this acidic solution into the calorimetric cup. Measure the temperature of the solution and record it in Part B2 data table. Rinse and dry the thermometer.
- 2.) Rinse the cylinder with distilled water. Then measure 25 mL of 1.00 M NaOH (aq). Measure the temperature of this basic solution and record it in Part B2 data table.
- 3.) Place the clean and dry thermometer in the cup. Quickly pour the NaOH solution into the cup containing HCl solution. Cover the cup immediately. Stir the cup continuously with the thermometer with occasional swirling. Record the highest temperature reached.
- 4.) When you have completed the experiment, you may pour the neutralized solution down the sink. Rinse the calorimetric cup and thermometer with water, and return them to the instructor.

Calorimetry

Name _____

Date _____

Partner's Name _____

PART A1) C_{cup}

DATA	Trial 1	Trial 2
1) Mass of the coffee cup and lid (assumed to be constant during experiment)	_____ g	
2) Mass after addition of 70 mL water	_____ g	_____ g
3) Initial temperature of water in the cup	_____ $^{\circ}\text{C}$	_____ $^{\circ}\text{C}$
4) Final temperature of water in the cup after hot water is added	_____ $^{\circ}\text{C}$	_____ $^{\circ}\text{C}$
5) Final mass of cup, lid, and water	_____ g	_____ g

Calculations

6) Mass of hot water	_____ g	_____ g
7) ΔT for the hot water (a minus value)	_____ $^{\circ}\text{C}$	_____ $^{\circ}\text{C}$
8) Mass of cold water	_____ g	_____ g
9) ΔT for the cold water	_____ $^{\circ}\text{C}$	_____ $^{\circ}\text{C}$
10) C_{cup} Show your setup. Watch your algebra! Watch significant digits.	_____ J.K^{-1}	_____ J.K^{-1}

11) Average value of C_{cup} : _____ J.K^{-1}

PART A2) C_{sp} of unknown metal

DATA

- 1) Mass of the coffee cup, lid, and 100 mL water _____ g
- 2) Initial temperature of water in the cup _____ $^{\circ}\text{C}$
- 3) Final temperature of water in the cup
after hot metal is added _____ $^{\circ}\text{C}$
- 4) Final mass of cup, lid, water, and metal _____ g

Calculations

- 5) Mass of cold water in the cup _____ g
- 6) ΔT for the water _____ $^{\circ}\text{C}$
- 7) Mass of metal used _____ g
- 8) ΔT for the hot metal (a minus value) _____ $^{\circ}\text{C}$
- 9) C_{sp} (use the average value of C_{cup} from part I)
Show your setup. Watch your algebra! Watch significant digits. _____ $\text{J}\cdot\text{g}^{-1}\cdot\text{K}^{-1}$

- 10) Metal _____ $C_{sp}(\text{book})$ _____ $\text{J}\cdot\text{g}^{-1}\cdot\text{K}^{-1}$
(Get this value from a reference or a textbook)

11) % Deviation = $\frac{C_{sp(\text{exp})} - C_{sp(\text{book})}}{C_{sp(\text{book})}} \times 100 =$ _____ %

**PART B1) Heat of solution of an ionic salt
DATA**

- 1) Mass of the coffee cup, lid, and 50 mL water _____ g
- 2) Initial temperature of water in the cup _____ $^{\circ}\text{C}$
- 3) Final temperature of solution in the cup
after ALL solid is dissolved _____ $^{\circ}\text{C}$
- 4) Final mass of cup, lid, and solution _____ g

Calculations

- 5) Mass of water in the cup _____ g
- 6) ΔT for the solution _____ $^{\circ}\text{C}$
- 7) ΔH_{sol} (Eq. 8) _____ J
- 8) Mass of unknown solid in solution _____ g
- 9) ΔH_{sol} per gram of solid sample _____ J/g
- 10) The solution reaction is endothermic exothermic. (Circle the correct answer and explain).

Solid unknown #:

**PART B2) Heat of neutralization reaction
DATA**

- 1) Initial temperature of HCl solution _____ $^{\circ}\text{C}$
- 2) Initial temperature of NaOH solution _____ $^{\circ}\text{C}$
- 3) Average initial temperature of the 2 solutions _____ $^{\circ}\text{C}$
- 4) Final temperature of neutralized solution _____ $^{\circ}\text{C}$
- 5) Final mass of cup, lid, and solution _____ g

Calculations

- 6) Mass of solution in the cup _____ g
- 7) ΔT for the solution = $T_f - \text{Average } T_i$ _____ $^{\circ}\text{C}$
- 8) ΔH_{rxn} (Eq. 8) _____ J
- 9) ΔH_{rxn} per mole of H^+ and OH^- ions reacting _____ J/mol
- 9) The solution reaction is endothermic exothermic. (Circle the correct answer and explain).

Post-Lab Questions and Exercises

(All questions must be answered during the lab and submitted with your lab report at the end of the lab period).

Please answer the following questions and show all work and units. Express all answers to the correct number of significant digits.

1) Explain what the value of C_{cup} in Part I describes, and why it should be a small positive number.

2) The Law of Dulong and Petit states that for a metal, Atomic Mass = $\frac{25 J \cdot mol^{-1} \cdot K^{-1}}{C_{sp}}$.

Calculate the atomic mass of the metal from your experimental value of C_{sp} of the metal. Look up the book value for the atomic mass of the metal from the Periodic Table. Then calculate

$$\% \text{ Deviation} = \frac{AM_{(\text{exp})} - AM_{(\text{book})}}{AM_{(\text{book})}} \times 100 = \underline{\hspace{2cm}} \%$$

3) Recalculate the atomic mass of the metal, using the book value of C_{sp} in the Dulong and Petit relation. Comment on the accuracy of the Law of Dulong and Petit.

4) When 2.0 g of NaOH were dissolved in 49.0 g water in a calorimeter at 24.0 °C, the temperature of the solution went up to 34.5 °C. Is this solution reaction exothermic? Explain. Calculate ΔH_{rxn} of 1.00 mol NaOH in water.