

Calorimetry and Coffee Cups

Objective:

In this experiment, we will investigate the exchange of energy as heat using a "coffee cup" calorimeter. Although primitive, this calorimeter can provide good results when used carefully.

Introduction:

According to the first law of thermodynamics, the total energy of an isolated system can neither be created nor destroyed. In other words, energy is conserved in any chemical reaction. In a mathematical sense,

$$(1.1) \quad E_{\text{initial}} = E_{\text{final}}$$

or equivalently,

$$(1.2) \quad \Delta E = 0.$$

Since chemical energy is usually defined as the sum of heat plus work ($E = \text{heat} + \text{work}$), many chemical reactions involve the evolution of heat or production of work. A common example would be a car engine, which converts the chemical energy stored in gasoline into heat and work. In many cases, the study of heat exchange is measured with an apparatus called a calorimeter. A diagram of a simple calorimeter is shown below.

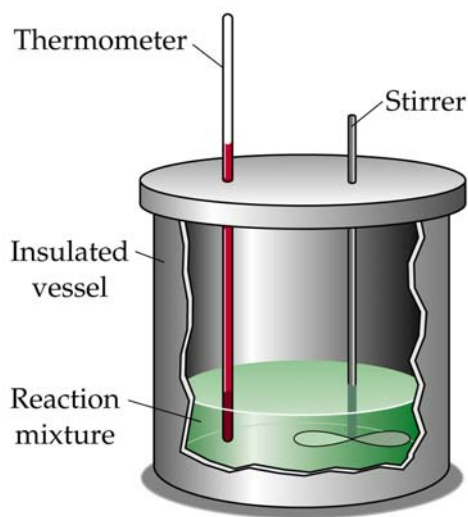


Figure 1: Inside a simple calorimeter

The major parts consist of an insulated vessel which prevents heat released by a reaction from escaping into the surroundings. The thermometer is used to measure any

temperature change and the stirrer is used to ensure that heat is uniformly distributed. All materials have some ability to absorb heat (q) and this heat is linearly related to the temperature change of the material by a constant called the heat capacity (C) as,

$$(1.3) \quad q = C \times \Delta T$$

where $\Delta T = T_{\text{final}} - T_{\text{initial}}$. Drinking hot coffee from Styrofoam cups without burning your hand can be better understood by analyzing the simple expression above. The heat transferred to your hand from the cup is accounted by,

$$(1.4) \quad q_{\text{transferred from the coffee cup}} = q_{\text{absorbed by your hand}}$$

The coffee cup has a large heat capacity and therefore it has the ability to "absorb" heat. Better insight to this idea can be found by solving Eq. 1.3 for the temperature change yielding,

$$(1.5) \quad \Delta T = \frac{q_{\text{transferred from the coffee cup}}}{C}$$

The larger the heat capacity (C) of the Styrofoam, the smaller the temperature change of the coffee cup. It follows from the preceding arguments that the temperature change experienced by your hand is minimized by the material of the coffee cup. This is why we use material like ceramic and Styrofoam for coffee cups instead of metals which typically have smaller heat capacities.

Part I: Finding the heat capacity of a coffee cup calorimeter

In the first part of the experiment, the heat capacity of the calorimeter will be found by analyzing the temperature change of tap water in the calorimeter when boiling tap water is added. The essential features of this experiment include the analysis of heat lost by the hot water and heat gained by water and the calorimeter.

The heat capacity (C_p) of the calorimeter will be determined calculating the heat exchange between the hot water, room temperature water, and calorimeter. The heat lost by the hot water is found by measuring the mass and temperature change of hot water. The heat given off by a sample of hot water is determined from the mass (m), specific heat capacity (C_{sp}), and temperature change (ΔT) as,

$$(1.6) \quad q = m \times C_{sp} \times \Delta T$$

Since q has units of Joules, m has units of g, and ΔT is measured in $^{\circ}\text{C}$, the specific heat capacity must have units of $\text{Jg}^{-1}\text{C}^{-1}$. Water has a specific heat capacity of $4.184 \text{ Jg}^{-1}\text{C}^{-1}$. If the coffee cup calorimeter has an initial mass of room temperature water and hot water is added to it, the following heat transfer spontaneously occurs,

$$(1.7) \quad q_{\text{lost by hot water}} = q_{\text{gained by room temperature water}} + q_{\text{gained by the calorimeter}}$$

Measuring the mass of the coffee cup calorimeter throughout the experiment is problematic. Instead of using Eq 1.6, the mass and specific heat capacity of the calorimeter are combined into the heat capacity C_p . This simplifies Eq 1.6 to,

$$(1.8) \quad q_{\text{gained by the calorimeter}} = C_p \times \Delta T.$$

Measuring the initial mass of the hot water, cold water, and the temperature change of the hot and cold water makes it possible to solve for C_p . Remember that there will be two temperature changes observed. The first temperature change is of the hot water initially near 100 °C and a final temperature of the hot and room temperature water mixture. The second temperature change is that of the water and calorimeter initially at 20-25 °C and the final temperature of the hot and room temperature water mixture. Since both hot and room temperature water are combined finding the correct temperature at the time of mixing may be problematic due to non uniform heat distribution. To overcome this experimental difficulty a plot of the cooling rate of the water mixture must be constructed. By tracking the cooling of the water in the calorimeter as a function of time, the temperature at the time of mixing can be accurately determined by constructing a calibration curve. Such a curve is shown in Figure 2.

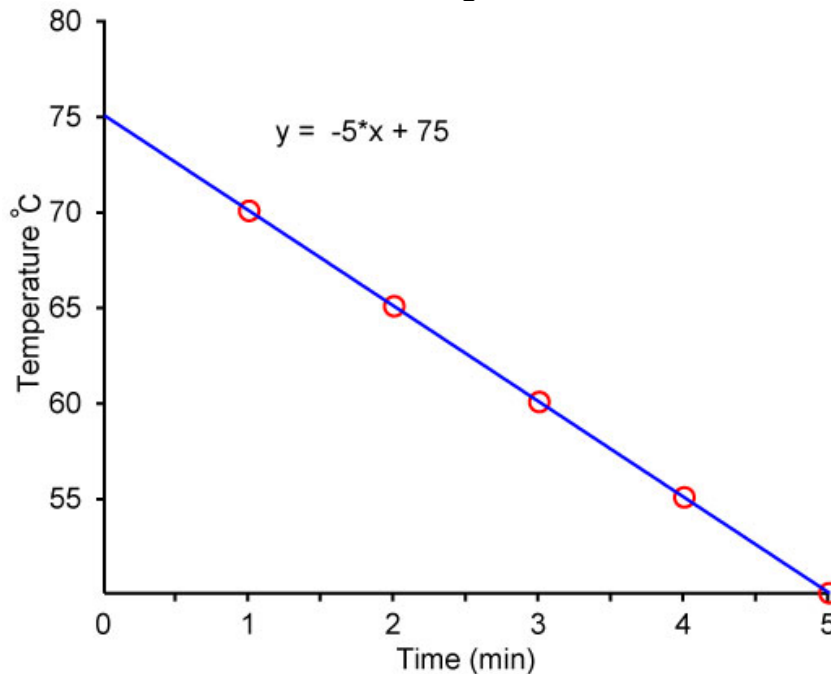


Figure 2: Cooling curve of water in the calorimeter

When the hot water is added to the cold water the resulting temperature of the mixture will be lower than the hot water. The heat of the hot water is not always distributed uniformly throughout the calorimeter despite gently swirling the mixture. The best way to measure the temperature at the time of mixing is to measure the temperature for 5 minutes in 1 minute intervals. Plotting the temperature as a function of time will give the cooling rate of the mixture. By fitting the data with a linear trend line using Excel it is possible to accurately measure the initial mixing temperature. In Figure 2, the initial

mixing temperature of 75 °C was determined from the y-intercept of the trend line. It is imperative that careful measurements are made for part I because the constant C_p is used throughout the entire experiment.

Part II: Finding the specific heat capacity of an unknown metal

In the second part of this experiment, we will be measuring the specific heat capacity of an unknown metal. This is accomplished by heating an unknown metal in boiling water for approximately 5 minutes. This hot metal is then transferred to the calorimeter and a temperature change is measured. The heat transferred from the boiling water to the metal causes the metal to have an initial temperature equal to that of the boiling water. When the hot piece of metal is placed into the coffee cup calorimeter containing room temperature water, a spontaneous heat transfer occurs from the hot metal to the room temperature water and the coffee cup calorimeter. This heat transfer is mainly accounted for by the equation,

$$(1.9) \quad q_{\text{lost by hot metal}} = q_{\text{gained by cold water}} + q_{\text{gained by the calorimeter}}$$

The C_{sp} of the unknown metal can be determined by precisely measuring the temperature change of the water in the calorimeter. A cooling curve must also be constructed as described in part I to measure the temperature at the time of mixing.

Parts III and IV: Finding the enthalpy of solvation for endothermic and exothermic reactions

The enthalpy of solvation will be determined by adding ammonium nitrate and hydrochloric acid to water and measuring the accompanying temperature change. The mixing of the reactants with water may be incomplete and the heat distribution non-uniform. Therefore it is necessary to construct a heating or cooling curve.

The heat of solvation is found by using an equation that accounts for the most significant events of heat transfer for the reaction. Using equations that have a similar form to Eq. 1.9, we can determine the heat produced by the reaction. The enthalpy of reaction is found by dividing the heat of the reaction by the amount of moles of the reactant that caused it.

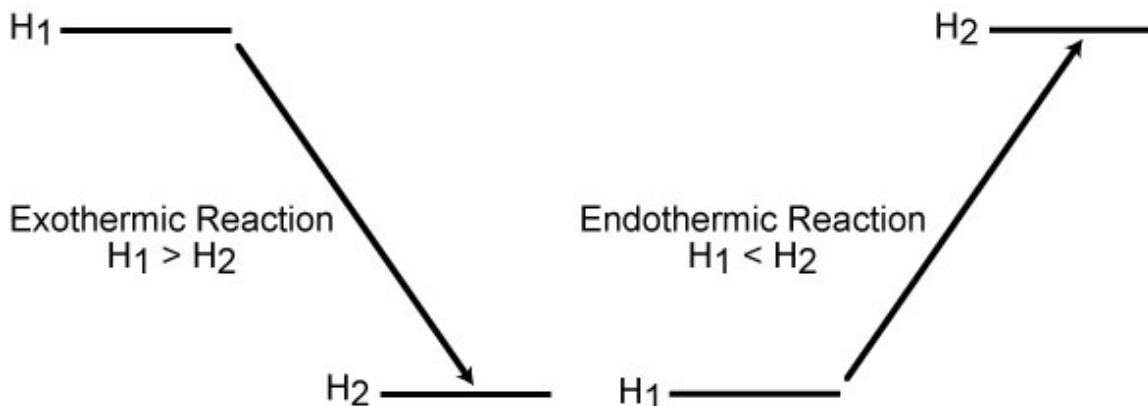


Figure 3: Relative enthalpies of reactants and products for exothermic and endothermic reactions

It is necessary to understand an additional concept, namely, what drives the reactions in the third and fourth parts of this experiment. Throughout this discussion it was assumed that heat spontaneously transfers from hot bodies to cold bodies. When the enthalpy of the reactants is larger than that of the products, the resulting heat transfer is exothermic. An exothermic reaction is one where the products have lower enthalpies than the reactants ($\Delta H < 0$). The difference of enthalpies is released as heat. An endothermic reaction occurs when the products have higher enthalpies than that of the reactants ($\Delta H > 0$). Both processes are shown in Figure 3. Since endothermic reactions need to absorb heat to proceed, what is the driving force to cause the products to have higher enthalpies than the reactants? The answer is entropy. Entropy is associated with the number and motion of particles in a system. For example, the entropy of a gas is higher than that of a liquid, because the molecules in a gas are more disordered compared to molecules in a liquid phase. The entropy has the effect of raising the enthalpy of the products higher than the reactants. Recall from last semester that the spontaneity of a chemical reaction is governed by the Gibbs free-energy change as,

$$(1.10) \quad \Delta G = \Delta H - T\Delta S.$$

This equation is a way to compare the effects of entropy and enthalpy. At a given temperature, if the change in entropy ΔS is greater than the change in enthalpy ΔH , the change in free energy ΔG will be a negative number. When ΔG is negative the reaction occurs spontaneously. For an endothermic reaction, a large ΔS drives the reaction, since the absorption of heat is not spontaneous.

Part IV: Measuring the enthalpy of fusion for water

The development of the procedure and the analysis of the data for this step are up to you. Come prepared with a procedure to determine the enthalpy of fusion of water.

Procedure:

Part I: Measurement of C_p

1. Use a hot plate to heat 200 mL of tap water to boiling in a 400 mL or larger beaker placed on a large ring stand.
2. Put two Styrofoam coffee cups in a 250 mL beaker.
3. Cut a 4" x 4" piece of cardboard, punch a hole in the center using a pencil and place on top of the coffee cups. Make sure that the hole is large enough to fit a thermometer through. If the hole is too big cover the hole with masking tape, and start another hole. Insert a thermometer through the hole.
4. Take the top Styrofoam cup from the calorimeter, place it on the balance, and calibrate to zero mass. Place approximately 40 g of tap water into the coffee cup and record the mass.
5. Place the cup back into the calorimeter. Using a buret holder, gently clamp the thermometer and lower it into the cup so that the whole bulb is covered with water but is not touching the bottom of the cup. Allow the thermometer to sit in the water a few minutes before recording the temperature.
6. Record the mass of a 100 mL clean beaker. Place about 40 mL of hot tap water into the beaker and record the mass. Measure the temperature of the hot water. Immediately after recording the temperature pour this water into the calorimeter. It's important to make sure that the lid and thermometer are in place on the calorimeter. The objective is to contain the heat in the calorimeter.
7. Gently swirl the calorimeter cup and measure the temperature every minute after mixing for five minutes. Use this data to determine the temperature at the time of mixing using a trend line in Excel.
8. Repeat steps 4 through 7 twice more. Make sure to dry the calorimeter and thermometer between each trial. Calculate the average heat capacity of your calorimeter.

Part II: Determination of the Specific Heat of a Metal

1. Using the same calorimeter built above, obtain a sample of metal from the supply area. The sample will be Sn, Cu, or Pb. Measure the mass of the sample using a wax weigh paper to protect it from contamination.
2. Use a test tube clamp to transfer the metal to the boiling water in the beaker. The test tube clamp should be held so that the sample is completely submerged (use a three pronged clamp to hold the test tube clamp). Let both metal and test tube

clamp sit in boiling water for 5 minutes to ensure that both objects are essentially the same temperature as the boiling water. Allow the test tube clamp and the metal to become the same temperature before transferring to the calorimeter.

3. When the metal is ready to be transferred, measure the temperature and mass of the water in the calorimeter (the mass should be approximately the same as part I). Next remove the metal from the boiling water by using a paper towel to grab the test tube clamp. Drop the metal object into the calorimeter and cover with cardboard and place the thermometer through the hole on top. Make sure that the thermometer is not touching the unknown metal.
4. Determine the mixing temperature using the same procedure as part I, step 7.
5. Repeat this procedure two additional times. Dry the calorimeter and thermometer between each trial. Calculate the specific heat capacity for trial for your unknown metal.

Part III: The Enthalpy of Solvation of an Endothermic Reaction

1. Accurately measure 24-26 g of tap water and 5 g of ammonium nitrate, perform this reaction in the calorimeter. Think carefully about what you will need to measure in order to calculate the enthalpy of reaction. Perform this experiment 3 times.
2. Using the molecular mass of ammonium nitrate and assuming all the heat is given by the water in the calorimeter and the calorimeter itself, calculate the enthalpy of reaction per mole of ammonium nitrate.

Part IV: The Enthalpy of Solvation of an Exothermic Reaction

1. Accurately measure 24-26 g of tap water using a balance. Use an auto-dispenser located in the hood to measure out 5 ml of 12 M concentrated hydrochloric acid into clean and dry 10 ml beaker. Think carefully what you will need to measure in order to calculate the enthalpy of reaction. Perform this experiment 3 times.
2. Using the molarity of concentrated HCl and assuming all heat is absorbed by the water in the calorimeter and by the calorimeter itself, calculate the enthalpy of reaction per mole of concentrated acid.

Part V: The Enthalpy of Fusion for Water

This is your chance to design an experiment that measures the enthalpy of fusion for water. Think carefully about the transfer of heat and what is necessary to measure in order to calculate this quantity. You will probably need some ice, your calorimeter,

water, and a balance. Make sure to plan ahead before coming to lab and design a procedure that can be repeated three times.

Results:

Summarize all results in a well organized table. Make sure to show a sample calculation for each part of this experiment.

Conclusions:

Part I: Why do we use Styrofoam cups to hold hot coffee? Justify your answer by making sense of the heat transfer process using the equations developed above. Make sense of why a cooling curve was used to determine the mixing temperature. What are the units of the slope of the linear trend line?

Part II: Why do we want the test tube clamp to be the same temperature as the unknown metal? Do you expect your value for the specific heat to be too high or too low? What is the physical significance of a negative heat capacity? What is your unknown metal? Use a CRC reference book to determine the C_{sp} for the possible unknown metals.

Part III: Is this reaction enthalpy favored? Is it entropy-favored? Write a chemical equation for this process and use it to justify your answers using the enthalpy/entropy concepts presented above.

Part IV: Pretend you are a chemistry instructor at a local high school. You are performing an experiment that mixes acid to water. Give safety instructions to your students about this experiment. Justify your reasoning by writing a chemical equation that indicates the evolution of heat. Is this reaction enthalpy favored? Is it entropy-favored? Justify your answers.

Part V: What is the heat of fusion for water determined from your results? Look up the accepted value for the enthalpy of fusion for water online at (<http://webbook.nist.gov/chemistry/>) or use a CRC reference book. Is this process exothermic or endothermic? Justify your answers. Report your average, standard deviation, and percent error. To calculate the percent error you will need the following equation,

$$(1.11) \quad \% \text{ error} = \frac{|\text{measured value} - \text{accepted value}|}{\text{accepted value}} \times 100\%.$$

References:

McMurry and Fay, Chemistry, Prentiss Hall, 2004, pgs. 326-327.

UC Davis general chemistry lab manual, in house publication, Spring 1996.

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