



Thermochemistry

Experiment

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Thermochemistry is the study of the heat energy involved in chemical reactions and changes of physical state. Heat energy is always spontaneously transferred from hotter to colder matter. The *First Law of Thermodynamics* (Law of Energy Conservation) states that the total energy of the universe must remain constant. Therefore, all energy transferred between a system and its surroundings must be accounted for as either heat (q) or work (W). For example, the heat lost by a system is equal to the heat gain by the surroundings. The only difference between these two values is the sign.

$$-q_{\text{system}} = q_{\text{surroundings}}$$

The standard *S.I.* unit for heat energy is the joule (J). It takes 4.184 joules (1 calorie) to raise the temperature of one gram of water by 1° C. The quantity of heat needed to raise the temperature of one gram of a substance one degree Celsius is known as the *specific heat* (S). The *heat capacity* (C) of a substance is the amount of energy needed to raise the temperature of a substance or material one degree Celsius. Unlike specific heat, the heat capacity does not account for the mass of the material. The heat of fusion is the quantity of heat needed to melt one gram of a solid.

Calorimetry is a technique used to measure the amount of heat energy evolved or absorbed in some chemical process. In this technique an attempt is made to conserve all the evolved heat by carrying out the process in a *calorimeter*. The calorimeter usually contains a suitable liquid that makes good thermal contact with the process under investigation. If the process evolves heat energy, the energy transferred to the liquid and to the material of the calorimeter causes the temperature of the liquid to rise. The temperature change (ΔT) can be measured as the difference between the final and initial temperatures of the liquid in the calorimeter. The heat transfer in a calorimeter may be expressed with the following equation:

$$Q = m \times S \times \Delta T$$

The heat transferred is Q (joules or calories), the specific heat is S, and ΔT is the change in temperature.

Equipment and Reagents

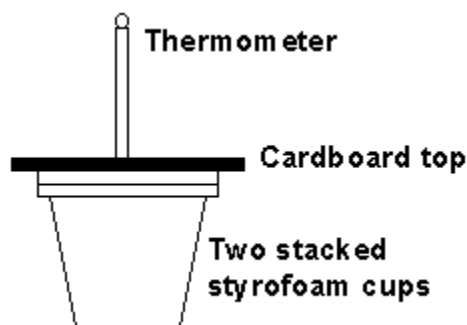
Styrofoam cups	Ice	100 mL graduated cylinder
Cardboard lid w/ hole	DI water	Burner or hot plate
Thermometer (-10 to 110 °C)	150 mL Beaker	Watch or Clock
Thermometer clamp	250 mL Beaker	centigram balance
Unknown Metals (day 2)	NH ₄ NO _{3(s)} (day 3)	3.0 M NaOH (day 3)
3.0 M HCl (day 3)	3.0 M acetic acid (day 3)	

Procedure

Day 1 - Calibration of the Calorimeter.

(Part I) – The Heat Capacity of the Calorimeter.

1. Assemble the Styrofoam coffee cup calorimeter by placing one cup into the other. The lid is made out of cardboard and has an opening for a thermometer. *See figure below.*



2. Place 60 mL of DI water into a beaker and chill in an ice bath to about 10 °C.
3. In another beaker, heat 60 mL of DI water between 60-80 °C using either a Bunsen burner or a hot plate. Use a ring stand and a thermometer clamp to position the thermometer. *Do not allow the thermometer to rest against the beaker.*
4. Using a 100 mL graduated cylinder, measure exactly 50 mL of the chilled DI water. Pour the chilled DI water into the calorimeter and place immediately place the cardboard top and thermometer over the top of the calorimeter. Record the temperature every 30 seconds for 4 minutes. The temperature should remain constant if the temperature of the water and the cup are at equilibrium.
5. When the temperature of the hot water is between 60 and 80 °C, measure 50 mL of the hot water in a 100 mL graduated cylinder and record the temperature.
6. Quickly add the heated water into the calorimeter containing the chilled water.
7. Swirl the calorimeter a record the temperature every 15 seconds for 4 minutes. The temperature should reach a maximum and then slowly decrease.
8. Repeat the above procedure two more times for a total of 3 trials.
9. Calculate the heat capacity of the calorimeter (see calculations).

Day 2 – Heat Capacity and Heat of Fusion.

(Part II) – Heat of Fusion of Ice.

1. Place about 100 mL of DI water into a 250 mL beaker and heat to a temperature between 60 and 70 °C on either a Bunsen burner or a hot plate.
2. Weigh an empty Styrofoam cup calorimeter on a centigram balance.
3. Add 40-50 grams of ice into the calorimeter and record the mass of the Styrofoam cup plus the ice.

4. Record the temperature of the hot water. The temperature should be between 60-70 °C. Pour enough hot water into the cup to make the total mass of the hot water plus ice equal to 100 grams. Record the mass of the cup containing the hot water and ice.
5. Stir the ice-water mixture and record the final temperature when the last bit of the ice has melted. This should be when the temperature equilibrates.
6. Calculate the heat of fusion of ice (see calculations).

(Part III) – Specific Heat Capacity of an Unknown Metal.

1. In a 250 mL, place about 150 mL of DI water. Allow the water temperature to equilibrate to room temperature inside the beaker. This should take about 5 minutes.
2. Set up a Bunsen burner and a ring stand and wire gauze. Place a 600 mL beaker filled about 2/3 full with tap water on top of the iron ring and wire gauze.
3. Weigh a clean dry unknown metal sample on a centigram balance. The mass of the metal should be around 80 grams. The metal must also be dry. Carefully place the metal sample into a large test tube and stopper the tube. Record the unknown ID number of the metal.
4. Immerse the test tube in a 600 mL beaker and clamp to the ring stand. Heat the water in the beaker to a boil using the Bunsen burner. Boil the water for 15 minutes to ensure that the temperature of the metal reaches the temperature of the boiling water.
5. Measure 50 mL of the room temperature DI water from step 1 and pour into the calorimeter. Allow the water to equilibrate with the calorimeter for 5 minutes. Record the temperature (T_c) of the water.
6. Record the temperature of the boiling water (T_H). *Make sure to use the same thermometer for all temperature readings.*
7. Remove the test tube and metal from the boiling water bath. Wipe the outside of the test tube with a paper towel to remove the water on the outside of the tube. Quickly but carefully transfer the hot metal into the calorimeter and place the lid on top.
8. Stir the water in the calorimeter every 30 seconds for about 3 minutes or until the temperature remains constant. Record the temperature of the water (T_M).
9. Calculate the specific heat capacity of the unknown metal (see calculations).

Day 3 – Heats of Reactions.

(Part IV)- Heat of Solution.

1. Add 50 mL of DI water into the calorimeter and allow the temperature of the water to equilibrate with the calorimeter. Record the temperature after 5 minutes.
2. On a centigram balance, Tare a piece of weighing paper. Weigh approximately 2 grams of ammonium nitrate, NH_4NO_3 . Record the exact mass of the sample.
3. Add the ammonium nitrate to the calorimeter and swirl to dissolve. Record the temperature every 15 seconds for 5 minutes.
4. Calculate the heat of solution (see calculations).

(Part V) – Heat of Neutralization.

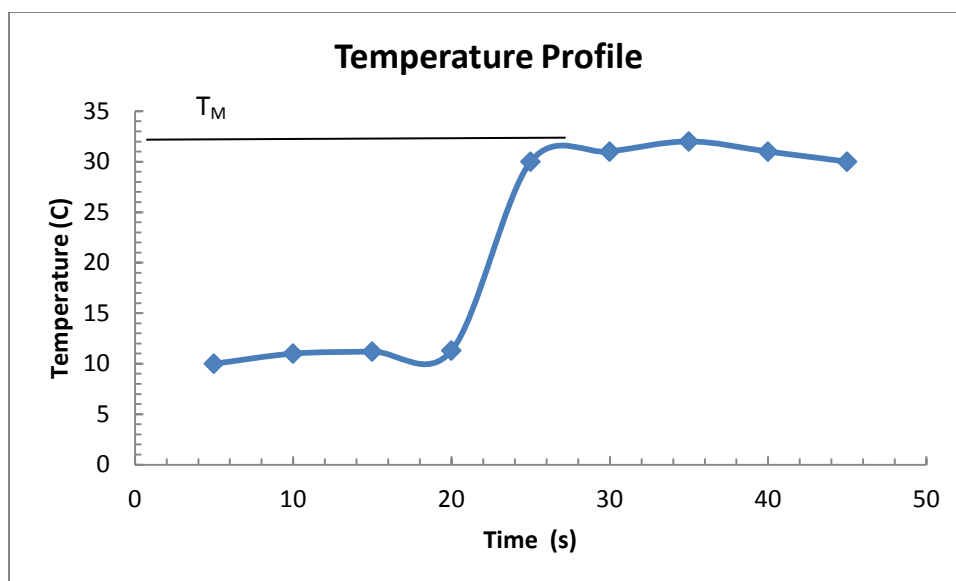
1. Using a graduated cylinder, add 50 mL of 3.0 M NaOH to the calorimeter. Cover it with the lid and let the solution temperature equilibrate for 5 minutes. Record the temperature after 5 minutes.
2. Measure 50 mL of 3.0 M HCl in a clean graduated cylinder. Allow to sit for 5 minutes and then record the temperature. The temperature of the HCl solution should be approximately the same as the NaOH solution.
3. Quickly but carefully add the HCl solution to the calorimeter. Put the lid on and swirl the solution. Record the temperature every 15 seconds for 5 minutes.
4. Repeat the above procedure using 3.0 M acetic acid instead of HCl.
5. Calculate the heat of neutralization (see calculations).

Calculations

Day1.

Part I – Heat Capacity of Calorimeter.

Using Excel or some other computer graphing program, plot temperature (°C) on the y-axis vs time (s) on the x-axis. Determine the maximum temperature (T_M) from the graph.



Calculate the decrease in temperature of the hot water (ΔT_H) and the increase in temperature of the cold water.

$$\Delta T_H = T_M - T_H$$

and

$$\Delta T_C = T_M - T_C$$

The amount of heat lost by the hot water is equal to the heat gained by the cold water and the calorimeter. (The specific heat of water, S , is 4.184 J/g °C) Assume the density of water to be 1.00 g/mL.

$$-q_H = q_C$$

or

$$-(m_H)(S)(\Delta T_H) = (m_C)(S)(\Delta T_C) + (C_{cal})(\Delta T_C)$$

Solve for C_{cal} , the heat capacity of the calorimeter.

Day 2.

Part II - Heat of Fusion of Ice.

Ice melts at a constant temperature of 0 °C. The amount of energy needed to melt 1 g of ice is called the *heat of fusion*. When measuring the heat of fusion of ice in a calorimeter, the heat lost by the water is equal to the heat gained by the ice.

$$-q_{water} = q_{ice}$$

Solve for the heat lost by the water ($S = 4.184 \text{ J/g } ^\circ\text{C}$ and density of water = 1.00 g/mL):

$$q = -(m_{water})(S)(\Delta T_{water})$$

This value is equal to the heat gained by the ice. Divide this by the mass of the ice to obtain the heat of fusion of the ice.

$$\text{Heat of fusion} = \frac{q}{m_{ice}}$$

The known value for the heat of fusion of ice is 0.335 kJ/g. Calculate the percent difference between the experimental value and the known value.

Part III – Specific Heat Capacity of an Unknown Metal.

The heat energy lost by the hot metal is equal to the heat energy gained by the water.

$$-q_{metal} = q_{water}$$

$$-(m_m)(S_m)(\Delta T_m) = (m_w)(S)(\Delta T_w) + (C_{cal})(\Delta T_w)$$

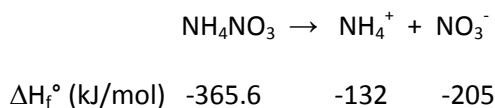
$\Delta T_m = T_{final} - T_{initial}$ where the $T_{initial}$ is equal to 100 °C.

$$\Delta T_w = T_{final} - T_{initial}$$

Solve for S_m , the specific heat capacity of the metal.

Day 3.

Part IV – Heat of Solution.



Theoretical heat of solution (calculated from standard heats of formation).

$$\Delta H_{\text{reaction}} = \sum \text{Products} - \sum \text{Reactants}$$

Experimental heat of solution (calculated from experimental measurements).

$$q_{\text{solution}} = -[(m_w)(S)(\Delta T_w) + (C_{\text{cal}})(\Delta T_w)]$$

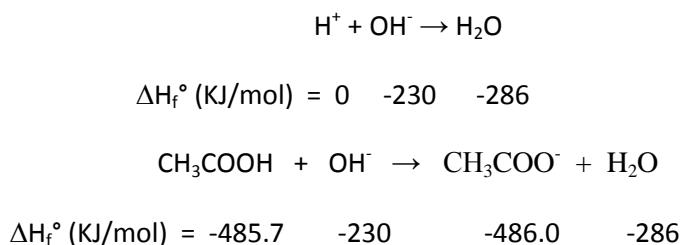
Assume the density of water to be 1.00 g/mL and $S = 4.184 \text{ J/g } ^\circ\text{C}$. Convert q to KJ before the next step.

$$\Delta H_{\text{solution}} = \frac{q_{\text{solution}}}{\text{moles of } \text{NH}_4\text{NO}_3}$$

Calculate the percent difference between the experimental value and the theoretical value.

Part V – *Heat of Neutralization*.

Neutralization Reactions (Net Ionic).



Theoretical heat of neutralization (calculated from standard heats of formation).

$$\Delta H_{\text{reaction}} = \sum \text{Products} - \sum \text{Reactants}$$

Experimental heat of solution (calculated from experimental measurements).

$$q_{\text{reaction}} = -[(m_w)(S)(\Delta T) + (C_{\text{cal}})(\Delta T)]$$

The mass of water is the combined mass of the acid and the base (100 g). Also assume the density of each solution to be 1.00 g/mL. Convert q to kJ before the next step. Calculate the moles of H_2O produced from the neutralization reaction.

$$\Delta H_{\text{reaction}} = \frac{q_{\text{reaction}}}{\text{moles of } \text{H}_2\text{O produced}}$$

Calculate the percent difference between the experimental value and the theoretical value.