

Experiment 8 – Thermochemistry

Overview

Energy production, absorption, and flow through systems is of very high importance. For example, we want to know how to power our cell phones, laptops, cars, light our homes, etc. **Thermochemistry** is the study of how much energy is absorbed or produced by a chemical reaction. This experiment will focus on a few concepts in thermochemistry.

An important property of a substance is its **specific heat**. This measures how much **energy** (q) is required to affect a change in temperature (ΔT) of 1 °C per gram of substance. The specific heat of water, for example, is $4.18 \text{ J g}^{-1} \text{ }^\circ\text{C}^{-1}$.

Example: A 12.0 g sample of water ($C = 4.18 \text{ J/g}^\circ\text{C}$) absorbs heat changing its temperature from 19.2 °C to 36.0 °C. How much energy (q) did the water absorb?

Solution: This can be determined using the expression

$$\begin{aligned}q &= m C \Delta T \\&= (12.0 \text{ g}) \left(4.18 \frac{\text{J}}{\text{g}^\circ\text{C}} \right) (36.0 \text{ }^\circ\text{C} - 19.2 \text{ }^\circ\text{C}) \\&= 842.688 \text{ J} \\&= 843 \text{ J}\end{aligned}$$

Note: The water clearly absorbed the energy as evidenced by the fact that the temperature increased. Also note that ΔT is always calculated by taking the final temperature minus the initial temperature:

$$\Delta T = T_{\text{final}} - T_{\text{initial}}$$

Calorimetry

The **specific heat** of a substance is easily determined by comparing it to that of water. One way to do this is to place a sample of the substance in a known amount of water in a insulated container (such as a Styrofoam coffee cup) and measuring the temperature changes.

Example: A 30.0 g piece of metal, initially at 19.0 °C is placed in 55.0 g of water ($C = 4.18 \text{ J/g}^\circ\text{C}$) initially at 100.0 °C in an insulated cup. The final temperature of the metal and water are 95.2 °C once the system comes to thermal equilibrium. What is the specific heat of the metal?

Solution: Since the heat lost by the hot water must be equal to the heat gained by the cold metal,

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

and q can be calculated for either the water or the metal by

$$q = m C \Delta T$$

So

$$m_{\text{metal}} C_{\text{metal}} (T_f - T_{i,\text{metal}}) = -m_{\text{water}} C_{\text{water}} (T_f - T_{i,\text{water}})$$

$$(30.0 \text{ g})(C_{\text{metal}})(95.2^\circ\text{C} - 19.0^\circ\text{C}) = -(55.0 \text{ g}) \left(4.18 \frac{\text{J}}{\text{g}^\circ\text{C}}\right) (95.2^\circ\text{C} - 100^\circ\text{C})$$

Solving for C_{metal} gives

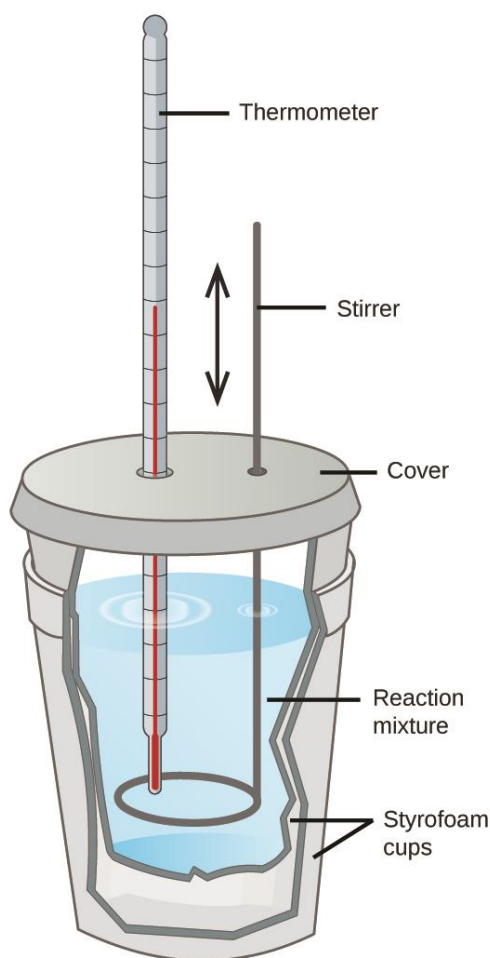
$$C_{\text{metal}} = 0.483 \frac{\text{J}}{\text{g}^\circ\text{C}}$$

The device used to measure heat flow is called a **calorimeter**. When the contents of the calorimeter are subjected to the constant pressure of the laboratory, the amount of heat transferred is measured at **constant pressure** and is equivalent to the change in **enthalpy** (ΔH). A very simple way to construct a constant pressure calorimeter is to use a Styrofoam coffee cup, fitted with a lid and a **thermometer** to measure **temperature** changes.

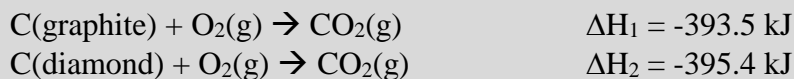
Reaction Enthalpy

Chemical **reaction enthalpies** (ΔH_{rxn}) are useful values as they indicate the amount of energy a chemical reaction will produce or use at constant pressure (q). For many reactions, measuring the reaction enthalpy involves a fairly simple experiment. But for some reactions, the experiment is not practical, for example, because the reaction of interest is very difficult to observe in the laboratory.

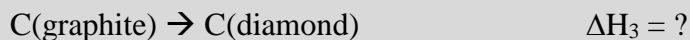
However, the tools of Thermodynamics give us a simple way to determine the reaction enthalpy for any reaction if we can express the reaction as the sum of reactions we have observed. This is typically how we describe **Hess' Law**.



Example: Suppose you want to know how much energy it takes to turn graphite into diamond. Based on the following reaction data



Determine the enthalpy of reaction (ΔH_3) for the reaction



Solution: The target reaction can be generated from the data reactions by flipping the second reaction front to back and then adding the reactions together. Flipping the second reaction will have the effect of changing the sign of the reaction enthalpy (ΔH_2).



Note: When adding the two reactions, $\text{O}_2(\text{g})$ and $\text{CO}_2(\text{g})$ cancel out, as one mole of each appears on both the reactants and products side of the sum of reactions 1 and 2.

Measuring a Reaction Enthalpy in a Coffee Cup Calorimeter

Since ΔH_{rxn} is given by q at **constant pressure**, and the laboratory is a constant pressure environment, one simply needs to measure q for a chemical reaction in order to get the enthalpy change (ΔH_{rxn}). This is done by carrying out the reaction in some medium (in the case of this experiment, an aqueous medium) and observing the temperature changes in the medium. These are then related to the amount of heat produced or absorbed by the chemical reaction.

$$q_{\text{rxn}} = -q_{\text{medium}}$$

Finding q is fairly strait forward. One uses the expression

$$q = m C \Delta T$$

Where m represents the mass of the medium in which the observation is being made, C is the **specific heat** of the medium, and ΔT is the change in temperature of the medium.

Example: A reaction takes place in a coffee cup calorimeter in which 50.0 mL of water ($C = 4.18 \text{ J g}^{-1} \text{ }^\circ\text{C}^{-1}$) is placed. The temperature of the water increases by $12.2 \text{ }^\circ\text{C}$. How much energy did the water absorb? Is the reaction endothermic or exothermic?

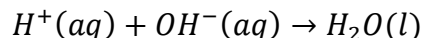
Solution: The heat (q) absorbed by the water is easily calculated:

$$\begin{aligned}q &= m C \Delta T \\&= (50.0 \text{ g}) \left(4.18 \frac{\text{J}}{\text{g}^\circ\text{C}} \right) (12.2^\circ\text{C}) \\&= 2550 \text{ J}\end{aligned}$$

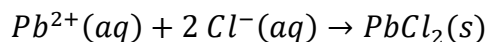
Clearly, the reaction is exothermic, as it is releasing the heat absorbed by the water in the calorimeter.

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

Calorimetry can also be used to calculate reaction enthalpies. In this calculation, the quantity of interest is the heat evolved per mol of one of the reactants or products. In a simple acid/base neutralization reaction with the net ionic reaction given by

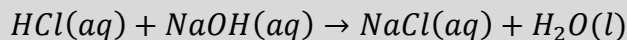


it doesn't matter if the reactant of interest is H^+ or OH^- since they both have unit stoichiometric coefficients. However, in a more complex reaction involving stoichiometric coefficients which are not unity, such as



care must be taken to properly account for the stoichiometric coefficients.

Example: 50.0 mL of 3.00 M HCl are mixed with 50.0 mL of 3.00 M NaOH are mixed in a coffee cup calorimeter. The temperature of the mixture increases by 20.0 °C. Assuming a density of 1.01 g/mL, and the same specific heat as that for water ($C = 4.18 \text{ J/mol}^\circ\text{C}$), calculate the enthalpy of neutralization for the reaction



Solution: First, let's find the heat (q) absorbed by the chemical reaction mixture

$$\begin{aligned}q_{\text{obs}} &= m C \Delta T \\&= \left[(50.0 \text{ mL} + 50.0 \text{ mL}) \left(1.01 \frac{\text{g}}{\text{mL}} \right) \right] \left(4.18 \frac{\text{J}}{\text{g}^\circ\text{C}} \right) (20.0^\circ\text{C}) \\&= 8443.6 \text{ J}\end{aligned}$$

This is the heat that was released by the chemical reaction.

$$q_{\text{rxn}} = -q_{\text{obs}}$$

The reaction enthalpy can be calculated from

$$\Delta H_{rxn} = \frac{q_{rxn}}{n}$$

where n is the number of moles of the reactant of interest. For simplicity, let's use HCl as the reactant of interest, although the calculation would be unchanged if the reactant of interest was NaOH. The number of moles of the reactant of interest then is given by

$$n_{HCl} = 50.0 \text{ mL} \cdot \frac{L}{1000 \text{ mL}} \cdot \frac{3.00 \text{ mol}}{L} = 0.150 \text{ mol}$$

And then the reaction enthalpy (ΔH_{rxn}) is given by

$$\Delta H_{rxn} = \frac{-8443.6 \text{ J}}{0.150 \text{ mol}} \cdot \frac{\text{kJ}}{1000 \text{ J}} = -56.291 \frac{\text{kJ}}{\text{mol}}$$

Or

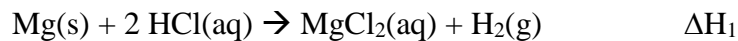
$$\Delta H_{rxn} = -56.3 \frac{\text{kJ}}{\text{mol}}$$

In this experiment, you will

- Measure the specific heat of piece metal and use your result to determine the identity of metal, and
- use Hess' Law to determine the reaction enthalpy for the difficult to observe reaction



by observing the reactions



Experimental description

Part A – Specific Heat of a Metal

In this part of the experiment, you are going to determine the identity of an unknown metal by determining its specific heat.

1. Make sure to record the unknown number of your sample!
2. Determine and record the mass of your metal sample. You may have to use a top-loading balance, as the mass of the sample may exceed the capacity for an analytical balance.
3. Record the mass of your **dry** calorimeter. Add about 40 mL of water, and record the mass again. The mass of water added will be determined by the difference.
4. Place the metal sample in a beaker of water (about 2/3 full), by hooking the wire over the side of the beaker.
5. Heat this on a hot-plate, allowing the metal to equilibrate for 10 minutes after the water has come to a boil. (until the metal is at the same temperature as the water.) Record the temperature of the hot water in the beaker, as this is the initial temperature of the metal.
6. Determine and record the initial temperature of the water immediately before adding the metal sample.
7. Add the metal sample, and monitor the temperature of the water in the calorimeter, until the temperature reaches a maximum. Continue to monitor the temperature for at least 1 minute after the maximum temperature is observed. The maximum temperature is the final temperature for both the water and the metal!
8. The specific heat of the metal is found from the relationship

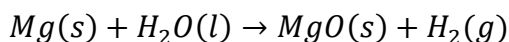
$$-q_{\text{metal}} = q_{\text{water}}$$

so

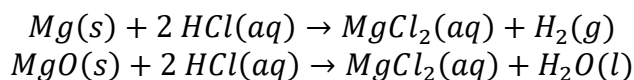
$$-m_{\text{metal}} C_{\text{metal}}(T_f - T_{i,\text{metal}}) = m_{\text{water}} C_{\text{water}}(T_f - T_{i,\text{water}})$$

Part B – Hess' Law

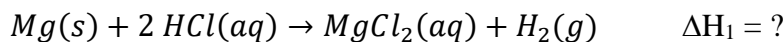
In this part of the experiment, you will determine the enthalpy of a reaction that is difficult to observe in the laboratory



using observations for the easier-to-observe reactions



1. For Reaction 1



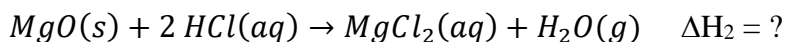
measure approximately 0.15 g Mg(s) and 25 mL of 1.0 M HCl. (Record the exact quantities used.)

2. Measure and record the initial temperature of the HCl in the calorimeter.
3. Add the Mg(s) and record the temperature until it reaches a maximum. Continue reading for another minute after the maximum temperature is achieved. Determine ΔT as the maximum temperature minus the initial temperature.

- Using your recorded data for the mass of Mg(s) and the mass of 1.0 M HCl, and assuming a specific heat of 4.18 J/g °C, calculate the heat (q) absorbed by the reaction mixture. From this data, determine the reaction enthalpy per mole of Mg.
- Use the following table to organize your observations.

Reaction 1	Run 1	Run 2 (if needed)
Mass Calorimeter (g)		
Mass Calorimeter + HCl (g)		
Mass Mg (g)		
T _{initial} (°C)		
T _{max} (°C)		

- For Reaction 2

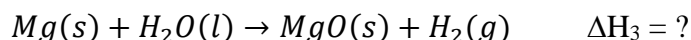


measure approximately 0.25 g MgO(s) and 25 mL of 1.0 M HCl. (Record the exact quantities used.)

- Measure and record the initial temperature of the HCl in the calorimeter.
- Add the MgO(s) and record the temperature until it reaches a maximum. Continue reading for another minute after the maximum temperature is achieved. Determine ΔT as the maximum temperature minus the initial temperature.
- Using your recorded data for the mass of MgO(s) and the mass of 1.0 M HCl, and assuming a specific heat of 4.18 J/g °C, calculate the heat (q) absorbed by the reaction mixture. From this data, determine the reaction enthalpy per mole of MgO.
- Use the table on the next page to organize your data.

Reaction 2	Run 1	Run 2 (if needed)
Mass Calorimeter (g)		
Mass Calorimeter + HCl (g)		
Mass MgO (g)		
T _{initial} (°C)		
T _{max} (°C)		

11. Combine your results to determine the enthalpy of the reaction



Vocabulary and Concepts

calorimeter	2	reaction enthalpy	2
constant pressure	2, 3	specific heat	1, 3
energy	1	temperature	2
enthalpy	2	thermochemistry	1
Hess' Law	2	thermometer	2

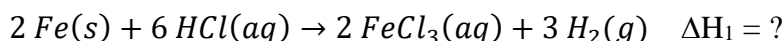
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Pre-Laboratory Assignment – Thermochemistry

Name _____ Section _____

1. A 34.6 g piece of metal, initially at 96.0 °C is placed in 50.0 g of water ($C = 4.18 \text{ J/g}^\circ\text{C}$) initially at 21.0 °C in an insulated container. The system comes to thermal equilibrium (the metal and the water are at the same temperature) at 23.1 °C. Calculate the specific heat of the metal.
2. When 1.104 grams of iron metal are mixed with 26.023 grams of hydrochloric acid in a coffee cup calorimeter, the temperature rises from 25.2 °C to a maximum of 33.5 °C. The reaction that occurs is given below.



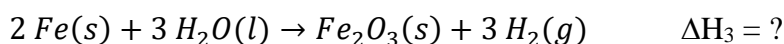
- a. Assuming a specific heat equivalent to that of pure water ($C = 4.18 \text{ J/g}^\circ\text{C}$), calculate the amount of heat absorbed by the reaction mixture in the calorimeter.
- b. What is the amount of heat that was released by the reaction?
- c. Calculate the reaction enthalpy:

$$\Delta H_1 = \frac{q_{rxn}}{2 \cdot \# \text{ mol Fe}}$$

- d. Using the reaction enthalpy for the reaction



and your result for part d. above, calculate the reaction enthalpy for the reaction



Report Sheet - Thermochemistry

Name _____ Date _____

Lab Partner(s) _____

Part A - Specific Heat of a Metal

Unknown number: _____

Mass metal _____ g

Mass water in Calorimeter _____ g

Initial temperature of metal _____ °C

Initial temperature of water _____ °C

Final temperature _____ °C

In the space below, calculate the specific heat of the metal. Use the table of specific heats to determine the identity of your unknown.

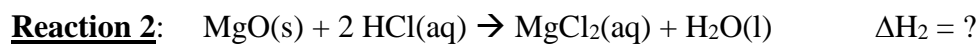
Specific Heat of Metal _____ J/g °C

Identity of unknown _____

Part B – Hess' Law



$\Delta T =$ _____ $^{\circ}\text{C}$
Mass Mg(s) = _____ g
Mol Mg(s) = _____ mol
Total mass of reaction mixture = _____ g
Heat absorbed by reaction mixture = _____ J
Heat released by the reaction = _____ J
Reaction Enthalpy (ΔH_1) = _____ kJ/mol



$\Delta T =$ _____ $^{\circ}\text{C}$
Mass MgO(s) = _____ g
Mol MgO(s) = _____ mol
Total mass of reaction mixture = _____ g
Heat absorbed by reaction mixture = _____ J
Heat released by the reaction = _____ J
Reaction Enthalpy (ΔH_2) = _____ kJ/mol



Reaction Enthalpy (ΔH_3) = _____ kJ/mol