Protocol | Calorimetry of Reactions

Learning Objectives

1. Students will be able to measure the heat produced by a chemical reaction using calorimetry.
2. Students will be able to relate the thermochemical properties of a reaction to the temperature changes observed.
3. Students will be able to explain conservation of energy in terms of the calorimeter system and surroundings.
4. Students will be able to determine the overall enthalpy of a reaction by using Hess' Law and measured heat production of multiple reactions.

Introduction

Thermochemistry (Links to an external site.) is the study of heat evolved or absorbed during chemical reactions. Under conditions of constant pressure *P*, the first law of thermodynamics shows us that the heat given off or taken up by a reacting system is equal to the change in *enthalpy (Links to an external site.)*

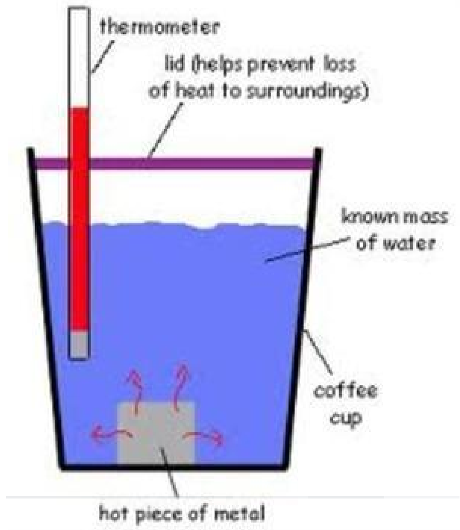
$(H = E + PV)$.

$\Delta E = q + w = q - P\Delta V$

$q = \Delta E + P\Delta V = \Delta H$

The second equation says that the change in enthalpy for a reaction is equal to the heat released or absorbed by the reacting species at constant pressure. Determining ΔH thus provides us with valuable information about the temperature changes the reaction will cause in the surroundings. In addition, the sign of ΔH tells us how the reaction will respond to small changes in temperature (that is, whether it will shift toward reactants or products when a temperature change is applied).

To determine ΔH, we need to measure the heat absorbed or released by the reaction run at constant pressure. To accurately measure the heat evolved in the process you wish to observe, you must minimize heat lost or gained by the system to the surroundings. Insulating materials are useful to isolate and contain the heat of the system. To illustrate the technique, Figure 1 shows a calorimeter setup. Imagine a hot (or cold) piece of metal (with known mass and initial temperature) is dropped into an insulated container



into a known volume and temperature of water. The temperature change of the water can be measured to determine the amount of heat absorbed by the water from the metal. As some heat will be lost to the surroundings (container walls and then to the air), we can determine this based on the actual temperature change compared to the theoretical temperature change in a perfectly isolated system. This is known as calibration! It is a way to account for the imperfect insulation in your consecutive measurements with an unknown amount of heat evolution, such as your reaction.

A calorimeter is nothing more than a well-insulated vessel containing the reacting species and a "bath" liquid that dissolves the reactants and products. The dissolved reactants can be thought of similarly to the block of metal in the previous illustration. (In this lab, we will use styrofoam coffee cups as calorimeters.) The atmosphere ensures that the external pressure is held constant at 1 atm. A thermometer measures the temperature of the bath liquid, which changes as the reacting species absorb or release heat. We treat the microscopic reacting species as the system and the bath liquid and calorimeter itself as the surroundings, ignoring heat flows to everything else (your hands, the lab bench, the air, etc.).

Given this division of system and surroundings, how is the heat of the reaction (q_{rxn}) related to the heat of the bath liquid (q_{bath}) and calorimeter walls (q_{cal})? *Write an equation using only these three variables.*

As the reaction occurs, the bath liquid and calorimeter walls will either increase or decrease in temperature. The temperature change of the bath liquid is related directly to the heat,

$q_{bath} = mc\Delta T$

where m is the mass of the liquid and c is the *specific heat* of the bath liquid in J/g·°C. The temperature change of the calorimeter walls, which we will assume to be equal to the temperature change of the bath liquid, is related similarly to the heat,

$q_{cal} = C_{cal}\Delta T$

where C_{cal} is the *heat capacity* of the calorimeter in J/°C.

Use the equations above to express q_{rxn} in terms of the measured temperature change ΔT.
Watch the [introduction and theory video (Links to an external site.)] to help with the derivations.

We will work with water as a bath liquid in this lab; the specific heat of water is readily available in your textbook. On the other hand, the heat capacity of the calorimeter (C_{cal}) must be measured for each unique calorimeter. Consider how you could use well defined heat flow from hot to cold water to measure C_{cal} without the need to run a chemical reaction.

The heat of reaction at constant pressure q_{rxn} is an extensive quantity equal to ΔH in Joules. We can convert this to an intensive value in Joules per mole by dividing by the number of moles of reaction events that took place. The molar (per-mole) $\Delta H°$ is useful for the determination of enthalpies of *other* reactions. Because enthalpy is a state function whose value depends only on the state of the system (*Hess's Law*), enthalpies of reactions can be scaled and added to calculate the enthalpy change of a "composite" reaction. We will apply Hess's law in this experiment to calculate the enthalpy of a related reaction (formation of metal oxide from its elements) from measured enthalpies of reactions of metal with hydrochloric acid and metal oxide with hydrochloric acid.

Hess' Law

The enthalpy of a process is equal to the sum of its individual steps. An analogous idea is that to know how much gasoline it takes to run all your errands for the day (grocery shopping, mailing a package, and buying a gift for a friend) is to know the amount of gas needed for each individual trip in the overall trip. This concept allows us to conveniently determine the enthalpy of processes that are difficult to measure directly. It is important to note that reverse reactions can also be used if necessary to obtain the desired overall reaction by using the negative of its enthalpy value. Similarly, stoichiometric alterations such as multiplication or division by a whole number are possible to allow the correct ratios of components to be incorporated in the overall reaction. Figure 2 below represents this concept for reactions that occur in multiple steps:

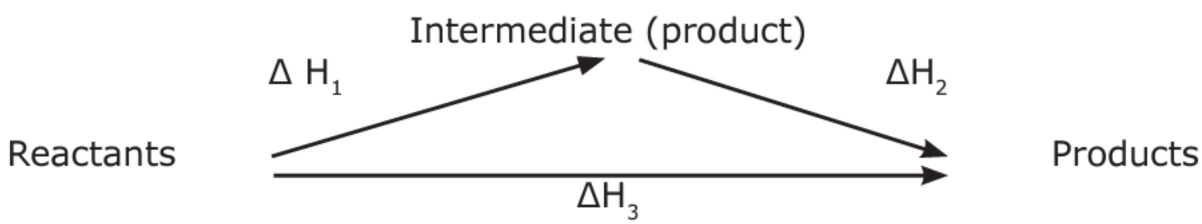


Figure 2. Enthalpy of product formation as the sum of two reaction steps.

Chemical Systems Under Study

We wish to know the enthalpy of formation of a metal oxide. This reaction is difficult to conduct directly. Using Hess' Law, we can determine the enthalpy of formation by combining measured enthalpies of other reactions if some form of reaction addition results in the desired remaining balanced equation.

Many metals are oxidized by aqueous hydrochloric acid to yield aqueous metal chloride salt and hydrogen gas. This exothermic reaction is accompanied by bubbling. We will use iron metal to illustrate the reactions involved:

$2\ Fe\ (s) + 6\ HCl\ (aq) \rightarrow 2\ FeCl_3\ (aq) + H_2\ (g)$

Although iron (III) oxide (Fe_2O_3) already contains iron in the +3 oxidation state, it undergoes a superficially similar process in aqueous hydrochloric acid to give aqueous iron (III) chloride and water.

Fe_2O_3 (*s*) + 6 HCl (*aq*) → 2 $FeCl_3$ (*aq*) + 3 H_2O (*l*)

We will study both reactions inside a coffee-cup calorimeter to determine their enthalpy changes. Together with the formation reaction of water, these two reactions can be scaled and added to produce the formation reaction of metal oxide:

2 Fe (*s*) + 1½ O_2(*g*) → Fe_2O_3 (*s*)

Because of its large Δ*H*°, this reaction is difficult to study directly. However, measurement of two related reaction enthalpies and application of Hess's Law enables the rigorous determination of the enthalpy of this process. Figure 3 demonstrates the use of Hess' Law in this type of experiment:

$$2\,\mathrm{Fe(s)} + 6\,\mathrm{HCl(aq)} \longrightarrow 2\,\mathrm{FeCl_3\,(aq)} + 3\,\mathrm{H_2\,(g)} \qquad \Delta H_A$$

$$\mathrm{Fe_2O_3\,(s)} + 6\,\mathrm{HCl(aq)} \longrightarrow 2\,\mathrm{FeCl_3\,(aq)} + 3\,\mathrm{H_2O(l)} \qquad \Delta H_B$$

$$2\,\mathrm{H_2\,(g)} + \mathrm{O_2\,(g)} \longrightarrow 2\,\mathrm{H_2O(l)} \qquad \Delta H_C$$

$$4\,\mathrm{Fe(s)} + 3\,\mathrm{O_2\,(g)} \longrightarrow 2\,\mathrm{Fe_2O_3\,(s)} \qquad \Delta H = ?$$

Figure 3. Addition of three reactions to obtain overall reaction. Note: Reaction B will be reversed to cancel appropriately!)

If Reaction B in Figure 3 is reversed, all bystanders (species not present in the overall reaction) can be eliminated similar to canceling terms in algebraic equations. If a reaction step is reversed in the problem, its enthalpy has the opposite sign (e.g., endothermic and positive becomes exothermic and negative). Reactions may also need to be multiplied or divided by a factor to achieve the same number of moles present in the overall balanced reaction. This operation is also applied to that reaction step's enthalpy value. Thus, for the example in Figure 3, the value of ΔH°_{rxn} can be calculated as follows:

$\Delta H^\circ_{rxn} = 2(\Delta H^\circ_A) + (-2(\Delta H^\circ_B)) + 3(\Delta H^\circ_C)$

Outline of Objectives

During this experiment, your team will develop the measurements and methods necessary to achieve a set of goals. There are three high-level goals of the experiment:

1. Measure the amount of heat absorbed by the walls of your coffee-cup calorimeter per degree Celsius change in temperature (C_{cal}).
2. Measure the molar enthalpy change for the oxidation steps (oxidation to metal cation and reversed oxide formation).

3. Determine an experimental value for the enthalpy of oxidation of a metal by hydrochloric acid.

Accomplishing Goal 1 will be necessary to achieve Goals 2 and 3, since heat flow to or from the calorimeter walls should be accounted for when determining ΔH. You will need the specific heat of water (the bath liquid): 4.184 J/g·°C.

Safety and Materials

The hydrochloric acid used in this experiment is corrosive; handle it with care. Exercise caution when using hot plates: ensure that plastic does not contact the hot surface and leave hot plates plugged in to cool. The aqueous metal chloride products of these reactions can be rinsed down the drain.

The following reagents will be available:

- 1.0 M hydrochloric acid solution
- 6.0 M hydrochloric acid
- Zinc metal (powder)
- Zinc oxide solid
- Aluminum metal (powder)
- Aluminum oxide solid
- Magnesium metal (ribbon)
- Magnesium oxide solid

Research Questions

1. What is the overall enthalpy of zinc oxide formation?
2. What is the overall enthalpy of magnesium oxide formation?
3. What is the overall enthalpy of aluminum oxide formation?
4. How do the standard reaction enthalpies for the oxidation of zinc, magnesium, and aluminum compare to one another?

Procedures

A. Calibration of the calorimeter

1. Obtain two nested styrofoam cups, a lid, and an alcohol thermometer to use as a calorimeter. *The total volume of solution in the calorimeter should always be <100 mL.*
2. Use a graduated cylinder to measure an exact volume of water accurately and place the same size water sample into each of three small beakers. Using a hot plate, heat the water to a desired temperature.

3. Add an exact volume of room temperature distilled water to the calorimeter and record the initial temperature through the hole in the lid.
4. Once your heated water temperature is recorded, prepare to transfer one of the hot water samples into the calorimeter. Quickly but without spilling, transfer the hot water to the calorimeter.
5. Record the temperature of the mixture every five seconds or so until it stabilizes. The stabilized temperature is the equilibrium temperature of the mixture T_f; make sure to record it.
6. Empty and dry the calorimeter. Repeat the steps above with the remaining two samples of hot water to obtain three sets of measurements of hot water temperature, cool water temperature, and equilibrium (final) temperature.

Concept Check! In your lab notebook, draw a representation of the apparatus in this part of the experiment that includes the calorimeter walls, the solvent, and the reactant molecules. Use arrows to depict the directions of heat flows between these components as the reaction occurs. Identify the reaction as exothermic or endothermic and record this in your notebook.

B. Calorimetry of the reaction of metal with hydrochloric acid

1. Weigh out a sample of approximately 0.1 g of your **metal**. Record the exact mass used.
2. Using a 250 mL beaker and graduated cylinder, transfer 30.0 mL of **1.0 M (for Mg) or 6.0 M (for Zn or Al) hydrochloric acid** into the calorimeter. Record the initial temperature through the lid.
3. Add the metal sample to the calorimeter.
4. Monitor the temperature as the reaction occurs. Use the thermometer to gently swirl the solution, *but do not spill!!* Record the temperature every 30 seconds until it appears to plateau.
5. Rinse the calorimeter with deionized water and dry with a paper towel. The reaction mixture and rinsate can be discarded in the sink.

C. Calorimetry of the reaction of metal oxide with hydrochloric acid

1. Replication part B with approximately 0.4 g of your metal oxide. Record all the same data points.

D. Applying Hess's Law: Enthalpy of Oxidation of a Metal

Work together with your lab partner to determine an experimental value (i.e., one *derived from* your mean $\Delta H_{ox,1}$ *and* $\Delta H_{ox,2}$) for the enthalpy of oxidation of your metal.

Metal	**Metal Oxide**
Zn	ZnO
Mg	MgO
Al	Al_2O_3

Write a balanced chemical equation for the reaction of the solid metal with $O_2(g)$, which forms the solid metal oxide (the "metallic oxidation" reaction). *Make sure the equation is balanced.* Determine how the oxidation of the metal with HCl can be combined with the metal oxide and HCl reaction to produce your balanced metallic oxidation reaction, then calculate ΔH for the metallic oxidation in kilojoules per mole.

Process

Prelab - online	**Read** (this document) learning objectives, conceptual background, safety and chemical info. **Take the prelab quiz** over all content associated with learning objectives (from this document). Select a research question option from within the prelab quiz/this document and **write down the question in your lab notebook**.
Planning investigation (15 min)	Your TA will briefly discuss background. Groups of ~4 will form **based on the selected research question**. Groups will **determine the appropriate procedure(s)** to answer the research question and **determine a plan** to carry out the necessary experiment. This plan must be written in the lab notebook along with any data tables needed for the investigation. What amounts will be used? Who will do what? How will you collect and organize data in your notebooks?
Carrying out investigation (1 hour)	The groups will **follow their plan** to address the research question. Fill in your data tables and add annotations to note any unexpected results, obstacles, or changes. Once groups have collected all data, they will clean up and move on to the next phase.
Investigation analysis	Groups will **return to their original research question** then discuss and analyze their data with that in mind.

(30 min)	Groups will decide how to present their results **visually**. Groups will **create an argument from evidence** to answer their research question following argumentation guidelines. They will debate amongst themselves **alternative explanations** as applicable.
Results and conclusions (30 min)	Groups will **create some form of presentation** to share. This can be on a white board, poster board, or digitally (PowerPoint, Google slides, etc). They must include their research question, results in some sort of figure, graph, or table, as well as their written argument.
Class discussion of findings (30 min)	Each group will take turns **sharing their presentations with the class**. Other groups can **ask questions, critique, suggest future investigation ideas, or give positive feedback**. (TA's can also contribute positively to the discussion, allowing students to primarily speak)
Post-lab - online	You will individually **submit your notebook pages** as well as a **written summary** of the methods, results, and conclusions including any relevant data and figures. You must make references to your data and background information to support your conclusion. Use the abbreviated report template to complete the postlab report and upload to Canvas by the due date.