

CALORIMETRY

Thermal energy, usually called heat, is one of the most familiar forms of energy. We observe this form of energy when it is passed from an object of higher temperature to one at a lower temperature when the objects are in contact. Heat flow can be measured using a device called a **calorimeter**. A calorimeter is a device that is insulated from the surroundings so that essentially no heat can flow in or out of the device. Within the calorimeter, heat can be transferred from one system to another and this transfer causes a temperature change.

Specific Heat of an Unknown Metal

When heat flows into a substance, the temperature of the substance increases. The quantity of heat, **q**, required to cause a temperature change ΔT of any substance varies directly with the mass, **m**, of the substance such that:

$$\frac{q}{m \times \Delta T} = C = \text{specific heat of a substance}$$

The **specific heat, C**, can be considered the amount of heat required to raise the temperature of one gram of a pure substance by one degree Celsius. The calorie is a unit of heat as well as the joule. The **specific heat of water** is 1.000 calorie/g °C which equals **4.184 J/g °C**. The joule (J) is directly related to mechanical work and is the S.I. unit of energy; hence, we shall use the joule almost exclusively.

The specific heat of a metal can be easily measured with a calorimeter. A weighed amount of metal is heated to a specific temperature and is quickly added to a measured amount of water at a known temperature in a calorimeter. The metal loses heat to the water and eventually the metal and water equilibrate at a temperature above the original temperature of the water but below that of the hot metal. If we assume no heat loss to the surroundings or the walls of the container, the heat lost by the hot metal should equal the heat gain of the water. For heat flow q ,

$$q_{\text{water}} = -q_{\text{metal}} \quad (\text{the negative sign indicates the opposite flow of the heat})$$

If we now express the heat flow in terms of specific heat (C) for both the metal as well as the water we get:

$$(C_{\text{water}})(m_{\text{water}})(\Delta T_{\text{water}}) = -(C_{\text{metal}})(m_{\text{metal}})(\Delta T_{\text{metal}})$$

Knowing the specific heat of water we can use this equation to solve for the specific heat of the metal. The specific heat of a metal is related to its molar mass by a simple relationship. Dulong and Petit discovered that 25 joules is required to raise the temperature of one mole of many metals by 1 °C. This relationship, shown below, is known as the Law of Dulong and Petit:

$$\text{Molar Mass (g / mol)} = 25 / C_{\text{metal}} (\text{J/g } ^\circ\text{C})$$

In part A of this lab you will determine the specific heat and molar mass of an unknown metal.

Heat of Reaction

When a physical or chemical change occurs, it is usually accompanied by a change in the heat content (**enthalpy**) of

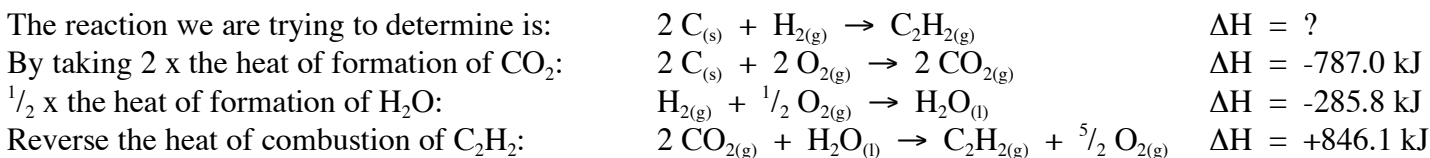
the material in question. Enthalpy (**H**) is defined as the heat content of a given set of conditions, called a **state**. Since there is only one value of enthalpy for any given state, the enthalpy is one of a number of thermodynamic variables called **state functions**. Because many factors internally contribute to the enthalpy of a substance there is no way to measure the enthalpy of a pure substance. Instead we can determine the change in the enthalpy (ΔH) when a chemical or physical change occurs. When a chemical reaction occurs in water solutions, the situation is similar to that which is present when a hot metal sample is put into water. As in the specific heat experiment the heat flow for the reaction mixture is equal in magnitude but opposite in sign to that for the water.

$$q_{\text{reaction}} = -q_{\text{water}} \quad \text{and} \quad \Delta H_{\text{reaction}} = q_{\text{reaction}} / \text{mol}$$

By measuring the mass of the water used as solvent, and by observing the temperature change that the water undergoes, we can find q_{water} and therefore $\Delta H_{\text{reaction}}$. An increase in water temperature indicates that heat is given off by the reaction; the reaction is **exothermic**, and $\Delta H_{\text{reaction}}$ is negative. Conversely if the temperature decreases, heat is absorbed by the reaction from the surroundings, the reaction is **endothermic**, and $\Delta H_{\text{reaction}}$ is positive.

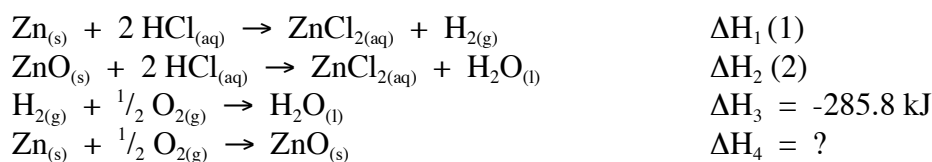
Hess's Law

Hess's law further states that when two or more chemical equations are *combined* to produce a balanced chemical equation, the enthalpy changes combined in the same manner will yield the enthalpy change of the new reaction. This will enable us to determine the enthalpy change for a reaction that may not be easily performed in the laboratory, i.e. the enthalpy of formation of acetylene gas (C_2H_2).



The **sum** of these enthalpies is **-226.7 kJ**, which is the enthalpy of formation of acetylene.

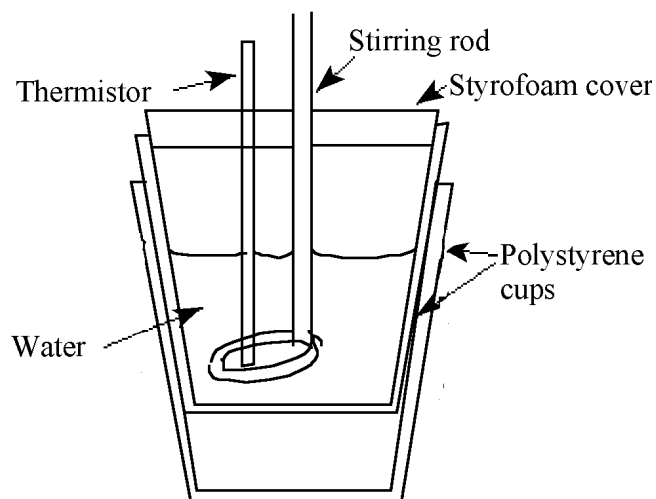
In this experiment we will measure the enthalpy change for the reaction of a metal, zinc, with acid to produce a zinc salt. We will then measure the enthalpy change for zinc oxide reacting with the same acid. From these two reactions along with the value for the reaction of hydrogen with oxygen, one can determine the heat of combustion of zinc metal.



Using a setup similar to the last experiment you can use a coffee cup calorimeter to determine the heats (q) of reaction and enthalpies for reactions **1** and **2**, above. Combining these enthalpy values with the enthalpy of formation for water (equation **3**, above), you can use Hess's Law to calculate the heat of formation for Zinc Oxide (equation **4**.)

PROCEDURE:**Part A: SPECIFIC HEAT of an UNKNOWN METAL**

1. Assemble the calorimeter as diagrammed. The calorimeter consists of two nested expanded polystyrene coffee cups with a Styrofoam cover. There are two holes in the cover, one for the thermometer and one for the glass stirrer provided for this experiment. Weigh the dry calorimeter to 0.001 g. Add about 40 mL of tap water and reweigh the calorimeter and water.



2. Fill a 600 mL beaker 2/3 full with tap water and heat it to boiling. While waiting for the water to boil, weigh a sample of dry metal to the nearest 0.001 g. Return the metal to the dry test tube and clamp the test tube in the boiling water bath so that the metal is below the water line.
3. Record the temperature of the boiling water bath to 0.01 °C. (You will need to obtain a mercury thermometer from your instructor; the thermometers at your lab desks are not as accurate). Remove the thermometer from the boiling water bath and wipe off all the hot water before placing it in the calorimeter. Record the temperature of the water in the calorimeter.
4. Remove the test tube from the boiling water bath, quickly wipe excess water off the outside of the test tube. Pour the hot metal into the calorimeter without causing the water to splash (tilt the calorimeter). While stirring the water in the calorimeter, monitor the temperature until it remains steady or begins to fall. Record the temperature when it has stabilized.
5. Dry the metal sample, return it to the large test tube and heat it again in the boiling water bath. Repeat the experiment.

CALCULATIONS for Part A:

1. For each trial, calculate the specific heat of the metal.
2. Determine the **average** specific heat and deviation in **parts per thousand**.
3. **Estimate the molar mass** using the law of Dulong and Petit. What is the identity of your metal?

Part B: HEAT of REACTION: HESS'S LAW**Zinc Reaction**

- 1) Add 75.0 mL 6.00 M HCl in the dry calorimeter. Record the temperature.
- 2) Weigh about 0.65 g of Zn to the nearest 0.001 g.
- 3) Add the metal to the calorimeter, stir and record the temperature when it stabilizes.

Zinc Oxide Reaction

- 4) Perform a similar experiment using 75.0 mL of 6.00 M HCl and 1.2 g zinc oxide.

CALCULATIONS for Part B:

1. Calculate the heat change (q) for the Zn and ZnO reactions.

Example for q_{Zn} : $q_{Zn} = -(\text{Heat capacity of HCl})(g \text{ HCl solution})(\Delta T)$

***Heat capacity** for HCl is 3.86 J/g \cdot °C. Assume the **density** of the HCl solution is 1.00 g/mL.

2. Calculate the heat of reaction (ΔH) for the Zn and ZnO reactions. Watch the sign of your value!

Example for Zn: $\Delta H = q_{Zn} / \text{mol Zn}$

3. Write balanced equations for the two reactions performed in lab, including your experimentally determined ΔH .
4. Use Hess's Law to determine the enthalpy change for the reaction: $Zn_{(s)} + \frac{1}{2} O_{2(g)} \rightarrow ZnO_{(s)}$
5. Look up the value for the heat of formation of $ZnO_{(s)}$ in your text. Calculate your **percent error**.
Percent error = absolute value{(actual - experimental)/ actual}*100%. Remember to explain (in your conclusion) any discrepancies.

POSTLAB QUESTIONS: *Note:* Use SI Units (i.e. joules) for **all** problems.

1. A metal sample weighing 45.23 g is heated to 100.00 °C. It is placed in 38.64 g of water in a calorimeter at 25.25 °C. At equilibrium, the temperature of the water and metal is 33.05 °C.
 - a. Calculate the q_{water} .
 - b. Calculate the specific heat of the metal.
 - c. Calculate the estimated molar mass of the metal.
2. When 0.5000 g of Zn are added to 50.00 mL of 6.00 M HCl in the coffee cup calorimeter that was used in question 1, the temperature of the solution rises from 20.00 °C to 32.56 °C. Using the assumptions recommended in the text concerning the HCl density and specific heat:
 - a. Calculate q_{Zn} .
 - b. Calculate ΔH for the reaction.

3. Calculate the enthalpy change for the allotropic transformation of graphite into diamond:

