

Experiment A: Thermochemistry: Enthalpy of Reaction and Calorimetry

Introduction

Heat Transfer

By now you are probably already acquainted with some of the energy changes associated with chemical processes. For example, the reaction between copper metal and nitric acid is quite vigorous as well as *exothermic* (heat is evolved during the course of the reaction). On the other hand, the dehydration reaction that occurs when copper (II) hydroxide is heated is an *endothermic* process.

One branch of thermodynamics involves the study of energy changes in chemical reactions. Before embarking on the details of the experiment, there are a variety of conventions that must first be established. The ultimate goal of this experiment is to quantify the energy transferred during a chemical reaction. In this context “energy” includes both the capacity of a system (the subject under study) to do *work* or to transfer *heat* to the surroundings (everything else not included in “system”). This may suggest that there’s a lot to keep track of in experiments of this type, but one rule that simplifies this task states that *energy is conserved*. We simplify the situation further and consider only *heat* that is transferred during the experiment (neglecting *work*).

Heat transfer should also be familiar to you at some level. Heat transferred is assigned the symbol q . When $q > 0$, heat is absorbed by a system. When $q < 0$, heat is released from the system. The first step in quantifying the amount of heat transferred begins by considering the change in temperature, Δt , where $\Delta t = t_{\text{final}} - t_{\text{initial}}$ (this definition will ensure the correct sign for q).

One device for measuring heat transfer is called a *calorimeter*. Typically, this is an insulated container filled with water with an opening for a thermometer used to monitor the temperature change in the exchange process. A calorimeter is usually calibrated before use, in order to determine how well insulated it is as well as to correct for heat which might be lost.

Heat Capacity

When a substance, absorbs or loses heat energy, the quantity of heat transferred,

$$q = m \cdot c \cdot \Delta t, \quad (1)$$

is related to the mass and temperature by Eq. (1), where m is mass, Δt is temperature change and c is the *heat capacity*. Heat capacity can be expressed in a number of ways. On common form (and the one we will use in this experiment) is the *specific heat capacity* which is the heat exchanged when the temperature of one gram of a substance changes by 1° Celsius. Consider the case when 50.0 g copper ($c = 0.382 \text{ J/g}\cdot^\circ\text{C}$) at a temperature of 100.0 °C is placed in a calorimeter containing 50.0 g water ($c = 4.18 \text{ J/g}\cdot^\circ\text{C}$) at a temperature of 20.0°C. Later, the temperature of the water in the calorimeter was

determined to be 26.7 °C. We expect, if energy is conserved, the heat lost by the metal will be equal (in magnitude) to the heat gained by the water. The heat lost by the metal is given by

$$q_{\text{metal}} = (50.0\text{g})(0.382\text{ J/g}\cdot\text{°C})(26.7^\circ - 100.0^\circ) = -1.40 \times 10^3\text{ J} \quad (2)$$

where the negative sign is consistent with the fact that heat is *lost* from the metal. The heat gained by the water is

$$q_{\text{water}} = (50.0\text{g})(4.18\text{ J/g}\cdot\text{°C})(26.7^\circ - 20.0^\circ) = +1.40 \times 10^3\text{ J} \quad (3)$$

Note the positive sign means heat has been *gained* by the water. Consistent with our prediction,

$$q_{\text{metal}} = -q_{\text{water}} \quad (4)$$

We will exploit this fact to relate the heat gained by the water in our calorimeter to the heat evolved in a variety of chemical processes.

Law of Dulong and Petit

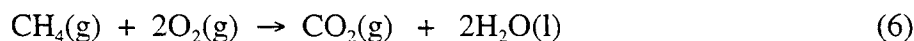
There is a trend that relates the specific heat per gram of an element (for those elements with atomic weights greater than 35 a.m.u.) to the atomic weight of the element. Dulong and Petit noted that for a series of heavier metals, the molar heat capacity of the element is approximately $25\text{ J}\cdot\text{mol}^{-1}\cdot\text{°C}^{-1}$. At room temperature, the internal energy of a metal is approximately $3RT$. Accordingly, the molar heat capacity can be determined by the relationship between changing internal energy and changing temperature (Eq. 5). It is useful for identifying a substance by its molar mass and is known as the *Law of Dulong and Petit*.

$$dU = \bar{C}_V dT \quad (5)$$

In the first part of this experiment, you will introduce a sample of an unknown metal into a calorimeter and measure the temperature increase in the calorimeter. You will relate this to the heat lost by the metal and determine the heat capacity and, ultimately, the atomic weight of the metal.

Enthalpy Changes during Chemical Reactions

As noted above, chemical reactions frequently occur with the gain or release of heat energy. For processes that occur at constant pressure, we speak of this heat energy as a quantity called *enthalpy* and give it the symbol H . In a sense, we can regard all substances as possessing a certain quantity of enthalpy. The heat gained or released during the course of a chemical reaction, then, can be described as the *change in enthalpy*, or ΔH . For example, the heat evolved during the combustion of one mole of methane, CH_4 , with sufficient oxygen as described in the following equation is 890 kJ. Here ΔH is the same as q for the reaction.



$$\Delta H = q_{\text{reaction}} = -890\text{ kJ} \quad (7)$$

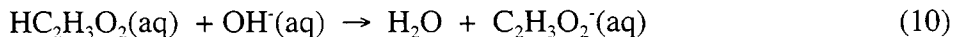
Other reactions with which you are acquainted, including *neutralization*, *vaporization*, *solution*, each have a ΔH associated with them. These are typically measured in a calorimeter. The temperature is measured before the reaction occurs. The reactants are added and, after the reaction is complete, the temperature is measured again. The change in temperature gives information about the heat absorbed (for exothermic reactions) or lost (for endothermic reactions) from the calorimeter. This is directly related to the enthalpy change for the reaction by the following expression.

$$q_{\text{calorimeter}} + q_{\text{water}} = -q_{\text{reaction}} = -\Delta H_{\text{reaction}} \quad (8)$$

Note that the enthalpy change for the reaction corresponds to heat lost or gained both by the calorimeter and by the water. You will use this idea to determine the enthalpy changes for two classes of reactions. First, you will combine solutions of strong acid, HCl, and strong base, NaOH, and determine the ΔH for the reaction given by:



In addition, you will measure the enthalpy change for the neutralization of a weak acid, acetic acid, with NaOH, where the reaction is given by:



Experimental

Determination of heat capacity of the calorimeter

Pour 50.0 mL distilled water in the calorimeter and replace the cover. Allow the temperature to equilibrate for 5 minutes, and record the temperature (this is the initial temperature). Place 50.0 mL water in a 250 mL beaker and heat until the temperature is about 15 - 20° above room temperature. Then set the beaker on the bench top for a minute, record the temperature and quickly pour the water into the calorimeter and replace the cover. Record the temperature at 15 second intervals for three minutes. When you have finished recording the data, empty and dry out your calorimeter.

Enthalpy of neutralization: strong acid + strong base

Measure 50.0 mL 1.0 M NaOH into a graduated cylinder and pour it into your calorimeter. Then measure 50.0 mL 1.0 M HCl into a graduate cylinder. Allow the temperature to equilibrate for several minutes, and record the temperature. Wipe off the thermometer after measuring the temperature of each solution to ensure against any reaction taking place before you are ready. When the temperatures of the NaOH and HCl solutions are identical, quickly pour the HCl into the NaOH. Record the temperature at 15 second intervals for three minutes. When you have finished recording the data, empty and dry out your calorimeter.

Enthalpy of neutralization: weak acid + strong base

Follow the procedure from part 2, substituting 50.0 mL of 1.0 M acetic acid in place of HCl. Record the data as above and, when completed, empty and dry out your calorimeter.

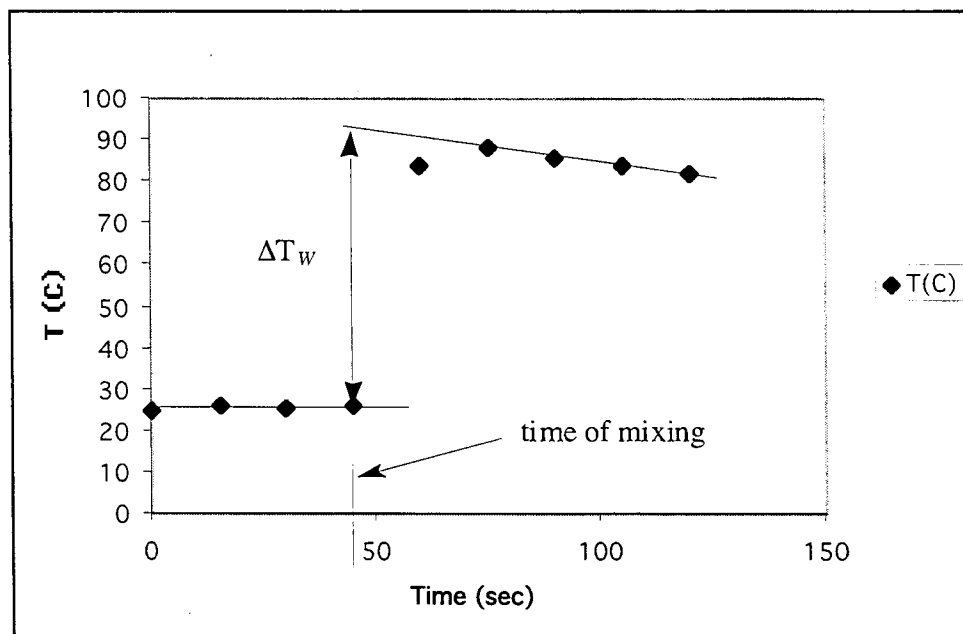
Heat capacity of an unknown metal

Place about 200 mL water in a 400 mL beaker. Weigh your metal sample in the vial to the nearest 0.01 g and carefully transfer your unknown metal into a large test tube. Then weigh the vial again (the mass of the metal sample is obtained by difference). Place the test tube in the beaker, add a few boiling chips to the water and heat the metal sample to the boiling temperature of water. While you are heating the metal sample, pour exactly 50.0 mL water into the calorimeter, allow the temperature to equilibrate for 5 minutes and record the temperature ($t = 0$ sec). After you have heated the metal sample near boiling for *a full 10 minutes*, record the temperature of the water and remove the test tube from the water. Quickly pour all of the metal into the calorimeter and record the temperature at 15 second intervals for three minutes. When you have finished recording the data, empty and dry out your calorimeter. Leave the metal sample to air dry while you are completing your calculations and return the sample to the vial it came in.

Data Workup

The temperature change in each experiment is determined graphically. For each set of data, plot time (x axis) versus (calorimeter + water) temperature (y axis). For the region of your plot prior to mixing and after the temperature has begun to fall, draw straight lines. The temperature change, determined at the point of mixing, is read directly from the difference between the two lines. Your plot might look something like Figure 1.

Figure 1. Plot of time versus temperature with extrapolation to zero time.



Results

For all runs, determine the temperature change using this method. Then calculate the heat capacity of the calorimeter, the enthalpy of neutralization (per mole of water released) for the two cases you examined, and the heat capacity, atomic mass, and identity of the metal.