Investigation 4: Calorimetry & Hess's Law

Focus Questions: *How much heat is absorbed or lost when solids are dissolved in water? How can you use calorimetry to determine the enthalpy of reactions? How can you use measured enthalpies to determine the enthalpy of formation of magnesium oxide?*

Pre-lab required reading

Chemistry; an Atoms-Focused Approach: Sections 9.3 – 9.6

Safety and Waste Disposal

- Eye protection should be worn at all times.
- Waste solutions produced in this investigation can be washed down the drain with copious amounts of water.

Part 1:

Background

Calorimetry is used to determine the amount of heat released or taken up during a chemical reaction or physical process. In the first part of this lab we will use simple solution calorimeters to determine the heat of reaction for three different solids dissolving, sodium chloride, potassium chloride and calcium chloride. Note that when these ionic solids dissolve they dissociate into ions. For example:

$$NaCl_{(s)} \longrightarrow Na^+_{(aq)} + Cl^-_{(aq)} \qquad (1)$$

We will use simple polystyrene coffee cups for a calorimeter. These cups have (to a very close approximation) a zero heat capacity. Thus no heat is transferred to the cups. However, the heat released or absorbed by the process of the solid dissolving IS released to the surrounding aqueous solution. We will assume that the aqueous solutions have the same heat capacity and density of pure water (i.e. c_{sol} = 4.184 J/g·C and a density of 1.00g/mL). We can measure the increase in temperature of the solution (ΔT) and calculate the amount of heat gained by the solution (q_{sol}) using our model for heat transfer:

$$q_{sol} = m_{sol} \cdot c_{sol} \cdot \Delta T \qquad (2)$$

Since the heat gained by the solution equals the heat lost by the reaction we find that the heat of the solution is related to the enthalpy change for the reaction (i.e. the process of the solid dissolving):

$$q_{rxn} = -q_{sol} \qquad (3)$$

And

$$\Delta H_{rxn} = \frac{q_{rxn}}{n} \qquad (4)$$

Procedure

Obtain a beaker with about 500 mL of distilled water, a thermometer and a "coffee-cup" calorimeter (consisting of two nested polystyrene cups, a lid, and stirrer).

Begin each trial by placing 50.0mL of water into the calorimeter. Record the temperature of the water. Precisely weigh 4-6 g of one of the salts (sodium chloride, potassium chloride or calcium chloride). Add the salt to the water in the calorimeter and place the lid on the calorimeter. Gently stir the reaction mixture, recording the temperature at 5-second intervals until the temperature reaches a plateau. Record the maximum or minimum temperature reached by the solution.

Dispose of the reaction mixture, rinse and dry the calorimeter, and repeat the procedure for the remaining two salts.

Part 2:

Background

In this part of the lab calorimetry is used to determine the amount of heat released or taken up during a chemical reaction. We will use simple solution calorimeters to determine the heat of reaction for two different reactions. We will use simple Styrofoam coffee cups for a calorimeter. These cups have (to a very close approximation) a zero heat capacity. Thus no heat is transferred to the cups. However, the heat released by the reactants IS released to the surrounding aqueous solution. One can assume that the aqueous solutions have a heat capacity of c_{sol} = 4.184 J/g·C and a density of 1.00g/mL. We can measure the increase in temperature of the solution (ΔT) and calculate the amount of heat gained by the solution (q_{sol}) using our model for heat transfer:

$$q_{sol} = m_{sol} \cdot c_{sol} \cdot \Delta T \qquad (5)$$

Where $\Delta T = T_F - T_I$. T_I is the initial temperature of the reactants and can be measure directly. T_F is the maximum temperature of the contents of the calorimeter during an exothermic reaction. The determination of a precise value for T_F is complicated by the fact that a very small heat exchange occurs between the surroundings and the contents of the calorimeter, both during the reaction and after its completion. The rate of exchange depends on the insulating properties of the calorimeter and on the rate of stirring. A correction for this heat loss is made by an extrapolation of a temperature vs. time curve (Figure 1). By extrapolating the linear portion of the curve back to zero time, T_F is obtained. The value of T_F obtained in this manner is the temperature of the product solution, had the reaction occurred instantaneously with no enthalpy loss to the surroundings.

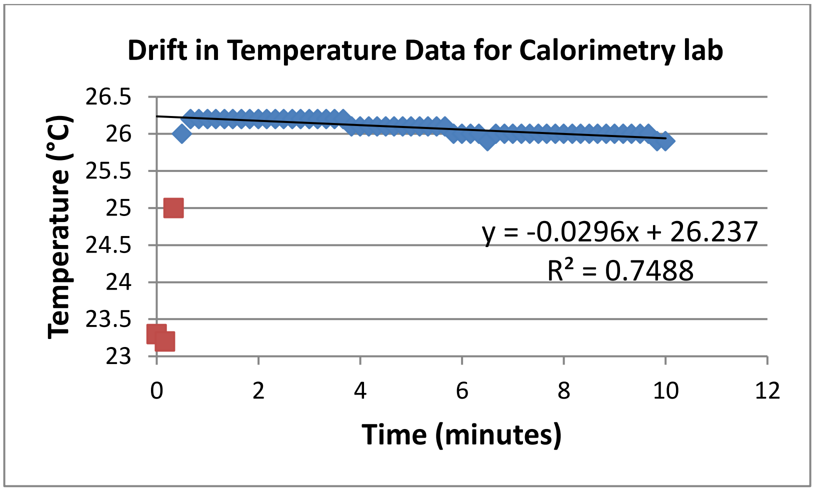

Figure 1: Demonstration of Drift in Temperature over Time. Note that only the linear portion (in blue) is included in the regression line. The y-intercept, 26.237°C, in this case would be the T_F for this trial.

Since the heat gained by the solution equals the heat lost by the reaction we find that the heat of the solution is related to the enthalpy change for the reaction:

$$q_{rxn} = -q_{sol} \qquad (6)$$

and

$$\Delta H_{rxn} = \frac{q_{rxn}}{n} \qquad (7)$$

The goal is to determine the ΔH_{rxn} experimentally for each of two reactions and use Hess's Law to combine these reactions together to find a target reaction, which corresponds to the $\Delta H_f°$ of MgO.

Target reaction: $Mg_{(s)} + \frac{1}{2} O_{2\,(g)} \rightarrow MgO_{(s)}$ (8)

In the first reaction magnesium metal is reacted with dilute hydrochloric acid to form hydrogen gas and magnesium chloride. In the second reaction, magnesium oxide is reacted with dilute hydrochloric acid to form water and magnesium chloride. The enthalpies of these two reactions will be determined experimentally using the average of several trials for each. Using these values and the enthalpy of formation of water (value found in the appendix 2A), one can use Hess's Law to determine the enthalpy of the target reaction.

Procedure

Reaction 1

In the first reaction magnesium metal is reacted with dilute hydrochloric acid to form hydrogen gas and magnesium chloride. Write the reaction for this process in your lab notebook. Begin each trial by carefully measuring 100mL of 1.0M HCl into a clean dry coffee cup calorimeter. Collect a 10-20cm strip of Mg . Be sure to use sand paper to remove any metal oxide to reveal the shiny metal if needed. Wrap the strip around a pencil to make a small spring. Then accurately weigh it. Just before you add the metal to the calorimeter, record the temperature of the HCl solution using the Vernier temperature probe. You can set-up the system to read and record the temperature every 10 seconds and then hit "start" to begin data collection. When you add the metal to the acid, continuously stir or swirl the heterogeneous solution to increase the rate (speed) of the reaction. Continue collecting data until the temperature has stabilized, about 5-10 minutes. From a plot of temperature vs. time, extrapolate back to the time of mixing, to determine the true value of T_2, the final temperature. You can do this most accurately using a linear regression. Dispose of your products down the drain with copious amounts of water. Repeat this step once for a total of two trials.

Reaction 2:

In the second reaction, magnesium oxide is reacted with dilute hydrochloric acid to form water and magnesium chloride. Write the reaction for this process in your lab notebook. Begin each trial by carefully measuring 100mL of 1.0M HCl into a clean dry coffee cup calorimeter. Accurately weigh a 0.5-1.0g sample of MgO. The MgO must be kept tightly covered to avoid adsorption and reaction with water in the air. Replace the cap and return to the desiccator when you are through. Do not weigh your sample until you are ready to add it to your calorimeter. When you add the MgO to the acid, continuously stir the heterogeneous solution to increase the rate (speed) of the reaction. Record the temperature at 30 second intervals for 10-15 minutes until a definite linear decrease in temperature is noted. From a plot of temperature vs. time, determine T_2. . Dispose of your products down the drain with copious amounts of water. Repeat this step once for a total of two trials.

References

Atkins, P.; Jones, L. "Chemical Principles: The Quest for Insight", 5th ed.; Freeman: New York. **2010**.
Vannatta, M. W.; Richards-Babb, M.; Sweeney, R. J. *J. Chem. Ed*., 87, 11, **2010**, pp. 1222 – 1224.
Davidovits, P. *Physics in Biology and Medicine*, 3rd ed.; Elsevier, Inc.; Oxford, UK, **2008**; pp 119.