Measuring Enthalpy Changes

PURPOSE

To observe changes in enthalpy in chemical processes.

GOALS

- To identify exothermic and endothermic processes.

- To relate enthalpy changes and entropy changes to changes in free energy.

INTRODUCTION

Chemical processes occur spontaneously when they lower the free energy of the system. The free energy at constant temperature and pressure is the Gibbs free energy, ΔG, which is defined as follows:

$$\Delta G = \Delta H - T\Delta S \tag{1}$$

where ΔG is the change in **free energy**[1] of the system, ΔH is the change in **enthalpy**[2] of the system and ΔS is the change in **entropy**[3] of the system.

ΔG, the change in **free energy**, must be less than zero for a spontaneous process. This follows from the definition of a spontaneous process; it lowers the energy of the system. Free energy, given the symbol G in honor of the American chemist, J. Willard Gibbs, is the energy available from a spontaneous process to do work. For a nonspontaneous process, it is the amount of energy that must be supplied to cause the process to occur.

ΔH, the **enthalpy** change, is the amount of heat energy absorbed by a process that occurs at constant pressure ($-\Delta H$ is the heat given off). ΔH is often proportional to ΔT, the temperature change caused by the process. The proportionality constant between ΔH and ΔT is called the specific heat (s). The specific heat is a property of the substance being heated or cooled. For example, the specific heat of water is 4.18 J/(g · °C) meaning that 4.18 joules of heat energy are required to raise the temperature of 1 gram of water by 1.0°C.

Not all processes that involve a change in enthalpy are accompanied by a change in temperature. Phase changes, e.g. melting, boiling, and sublimation all absorb heat. However, the substance undergoing the phase change maintains a constant temperature. All the energy supplied to the substance is consumed in the phase change.

Processes that give off heat energy ($\Delta H < 0$) are **exothermic**[4]. Combustion is obviously an

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[1] http://en.wikipedia.org/wiki/Thermodynamic_free_energy
[2] http://en.wikipedia.org/wiki/Enthalpy
[3] http://en.wikipedia.org/wiki/Entropy
[4] http://en.wikipedia.org/wiki/Exothermic

exothermic chemical reaction. Condensation of steam to liquid water is also exothermic, although water maintains a constant temperature during the process. Processes that absorb heat energy ($\Delta H > 0$) are **endothermic**[5]. Sweat, liquid water that evaporates from your skin, cools you by absorbing heat from your body.

ΔS, the change in **entropy**, is related to the number of ways the energy of the system can be distributed. Entropy is commonly defined as disorder or randomness. Entropy is high in gases, because the molecules are free to move about in all directions, fill the space available, and adopt any orientation relative to each other. Entropy is low in solids, because the molecules cannot move much relative to each other, and their orientation is fixed.

With this information, one can see that a chemical process will certainly be spontaneous if it is exothermic ($\Delta H < 0$) and its entropy increases ($\Delta S > 0$). If the opposite holds ($\Delta H > 0$ and $\Delta S < 0$), the process cannot be spontaneous. What if both have the same sign?

If the process is exothermic, the process will be spontaneous below the temperature that satisfies the condition $\Delta H = T\Delta S$. It turns out that changes in entropy are small relative to changes in enthalpy in most processes. It is usually not possible to tell whether entropy has increased or decreased in spontaneous exothermic processes. The exceptions occur when gases are produced or consumed. Water will condense spontaneously if the temperature is below $100°$C; the process is sufficiently exothermic to offset the loss in entropy that accompanies the phase change.

If the process is endothermic, the process will be spontaneous above the temperature that satisfies the condition $\Delta H = T\Delta S$. As mentioned above, entropy changes are small relative to enthalpy changes when gases are not involved. Therefore, spontaneous endothermic processes are relatively uncommon. However, they must involve an increase in entropy.

When working with ΔG, ΔH, ΔT, ΔS, and in fact all chemical terms involving a Δ (change in) the quantity is calculated as final$-$initial. Thus, if a beaker containing water was originally at $22.5°$C and a chemical process caused its temperature to fall to $17.3°$C, the change in temperature would be

$$\Delta T = T_{\text{final}} - T_{\text{initial}} = 17.3°\text{C} - 22.5°\text{C} = -5.2°\text{C} \tag{2}$$

It is important to remember final$-$initial in order to get signs right. This can sometimes be confusing.

It is important to distinguish between **system** and **surroundings**[6], the two parts of the thermodynamic universe, when dealing with reaction energetics. The first line of this document stated that spontaneous processes lower the free energy of the system. The **system** is the part of the universe being studied. The first law of thermodynamics states that energy is neither created nor destroyed. The energy released by a system must be converted to some other form or transferred to some other place. Often, the energy is transferred to the **surroundings**, the part of the universe that interacts with the system being studied. In such studies, it is often practical to isolate a rather small "universe" of system and surroundings in which nearly all the energy is retained.

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[5]http://en.wikipedia.org/wiki/Endothermic
[6]http://en.wikipedia.org/wiki/System_(thermodynamics)

In Parts A - C of this lab, we will assume that the thermodynamic universe is the test tube or beaker in which the experiment is being conducted. Of course, some heat is transferred outside the test tube (you will be able to feel beakers heat up or cool down) but most is retained. The energy released or absorbed by the systems being studied (chemicals dissolving or reacting) will be transferred to or from the water in which the processes occur. Thus, water is a major component of the surroundings.

Returning to equation 2 and sign changes. In that example, the temperature of the **water** (the surroundings) decreased and heat was released. This means that a chemical **process** (the system) absorbed heat from the water. Since the process absorbed energy, it was endothermic. Now consider an exothermic example. If a chemical process (the system) releases heat to the water (the surroundings), the temperature of the water will increase as the water absorbs heat energy and the ΔT of the water will be positive.

In Part A of the lab, you will observe temperature changes that occur as compounds dissolve in water.
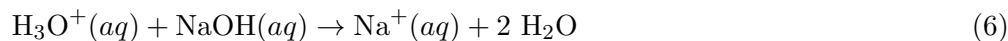
In Parts B and C, you will observe temperature changes that occur during chemical reactions. The reaction in Part C is a neutralization. Neutralization reactions (also known as acid-base reactions, which you will study in more detail later in the course) usually involve transfer of H^+ (a proton) from one chemical species to another. For example, the reaction of acetic acid and sodium hydroxide is shown below.

$$HC_2H_3O_2(aq) + NaOH(aq) \rightarrow NaC_2H_3O_2(aq) + H_2O \tag{3}$$
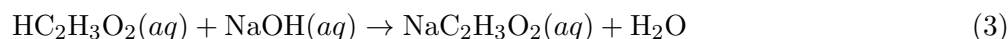
Strong acids, such as HCl and HNO_3, react with water as shown below.

$$HCl(aq) + H_2O \rightarrow Cl^-(aq) + H_3O^+(aq) \tag{4}$$

$$HNO_3(aq) + H_2O \rightarrow NO_3^-(aq) + H_3O^+(aq) \tag{5}$$
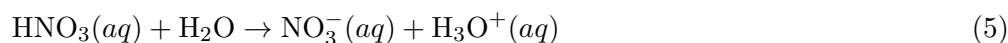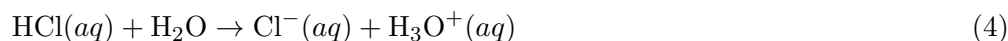
H_3O^+ is called the **hydronium**[7] ion. Whenever strong acids are placed in water, this is the species that reacts. For example, the reaction with sodium hydroxide is shown below.

$$H_3O^+(aq) + NaOH(aq) \rightarrow Na^+(aq) + 2\ H_2O \tag{6}$$

In these reactions, species are followed by "(aq)" to indicate that they are present in aqueous solution. This notation will be used frequently in the rest of this course.

In Part D of the lab, you will observe temperature changes that occur as energy is added to water in its solid and liquid phases.

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[7]http://en.wikipedia.org/wiki/Hydronium

EQUIPMENT

1 30 mL beaker

1 100 mL beaker

1 10 mL graduated cylinder

1 digital thermometer

4 small test tubes

1 test tube rack

1 ring stand and clamp

1 hot plate/stirrer

1 magnetic stir bar

1 deionized water squirt bottle

REAGENTS

~2 g $CaCl_2$(s, anydrous)

~2 g NH_4NO_3(s)

1 mL 1 M $NaOH$(aq)

1 mL 1 M $FeCl_3$(aq)

8 mL 0.1 M $NaOH$(aq)

3 mL 0.1 M HCl(aq)

3 mL 0.1 M HNO_3(aq)

3 mL 0.1 M $HC_2H_3O_2$(aq)

4 drops phenolphthalein indicator

60 g ice

13 mL deionized water

SAFETY

The solutions used in this experiment are diluted, but corrosive. They can attack the skin and cause permanent damage to the eyes. If any of the solutions splash into your eyes, flush them in the eyewash. Hold your eyes open or have someone assist you. If you spill any of the solutions on your skin or clothing, flush the area immediately with water. Have your lab partner notify your instructor about the accident.

You will be working with a hot plate. Keep flammable materials (papers, hair, clothing) away from it. It will stay hot for a long time after you have turned it off. Do not touch it until you have felt the air near it and are sure it will not burn you.

WASTE DISPOSAL

The waste from the experiments should be rinsed or scraped into the proper waste container provided by your instructor. Use water in a squeeze bottle to rinse the solid material out of the test tube and then wash the tube with soap and water.

PRIOR TO CLASS

Please read the following section of Lab Safety and Practices: Preparing Graphs[8].

LAB PROCEDURE

Please print the worksheet for this lab. You will need this sheet to record your data.

Part A: Heat of Solution - $CaCl_2$ and NH_4NO_3

1   Use a spoon-type spatula to dispense anhydrous solid $CaCl_2$ into a dry 30 mL beaker. One spoonful, **not heaping,** is plenty.

2   Obtain 10 mL of deionized water in a graduated cylinder.

3   Measure the initial temperature of the water and record it in Table A.

4   Pour the water into the beaker containing the $CaCl_2$.

5   Place the thermometer in the beaker. Watch the temperature change on the thermometer. Record the maximum or minimum temperature reached in Table A.

6   When finished, dispose of your solution as directed by your instructor, rinse the beaker with deionized water and dry.

7   Repeat steps 1 through 6 with solid NH_4NO_3 in place of the solid $CaCl_2$.

8   Calculate the ΔT for each reaction and record them in Table A.

Part B: Heat of Reaction - $FeCl_3(aq) + NaOH(aq)$

1   Take two test tubes to the side shelf and obtain about 1 mL of 1 M $FeCl_3$ in one and about 1 mL of 1 M NaOH in the other.

2   Measure the temperature of the $FeCl_3$ solution, and note its color. Enter this information in Table B.

3   Add the 1 M NaOH to the $FeCl_3$ test tube.

4   Place the thermometer in the test tube containing the mixture. Watch the temperature change on the thermometer. Record the maximum or minimum temperature reached in Table B.

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[8]../graphs/manual.html

5 Record the appearance of the reaction mixture in Table B.

6 Calculate the ΔT for the reaction and record it in Table B.

7 When finished, dispose of your solution as directed by your instructor. Use water in a squeeze bottle to rinse the solid material out of the test tube and then wash the tube with soap and water.

Part C: Heat of Neutralization - NaOH + HCl, NaOH + HNO_3, NaOH + $HC_2H_3O_2$.

1 Add 2 mL of 0.1 M NaOH to **each** of 4 test tubes. Add 1 drop of phenolphthalein to each tube.

2 Measure the temperature of one of the NaOH solutions and record it in Table C. Note the appearance of the solutions in Table C. Assume that **all** the NaOH solutions in this experiment start out at this temperature.

3 Measure 3 mL of deionized water in a graduated cylinder and add it to the first test tube. Record the maximum or minimum temperature reached and any change in appearance in Table C.

4 Measure 3 mL of 0.1 M HCl in a graduated cylinder and add it to the second test tube. Record the maximum or minimum temperature reached and any change in appearance in Table C.

5 Measure 3 mL of 0.1 M HNO_3 in a graduated cylinder and add it to the third test tube. Record the maximum or minimum temperature reached and any change in appearance in Table C.

6 Measure 3 mL of 0.1 M $HC_2H_3O_2$ in a graduated cylinder and add it to the fourth test tube. Record the maximum or minimum temperature reached and any change in appearance in Table C.

7 Calculate the ΔT for each reaction and record them in Table C.

8 When finished, dispose of your solution as directed by your instructor, rinse the beaker with deionized water and dry.

Part D: Enthalpy and Phase Changes

1 Place a magnetic stir bar in a 100 mL beaker. Fill the beaker to the 60 mL mark with crushed ice and add tap water to the 60 mL mark.

2 Clamp your thermometer in the ring stand with a hot plate/stirrer on the base.

3 Place the beaker on the hot plate/stirrer and lower the thermometer into the ice slurry. The tip of the thermometer should be about a third of the way down in the slurry.

4 Start the stirrer; set the dial to about 6 for gentle stirring.

5 Read the temperature every 30 seconds for 3 minutes and record it in Table D.

6 Turn the hot plate to 100 and continue reading the temperature every 30 seconds.

7 After four more readings, turn the hotplate to 200.

8 Note the time when all the ice has melted in Table D and turn the heater to 400. Continue reading the temperature every 30 seconds.

9 As the water heats, record when you observe bubbles, steam, and true boiling in Table D.

10 Once boiling begins, read the temperature every 30 seconds for three minutes.

11 Plot your data points on a graph in your lab worksheet. Make sure to give your graph a title. Label the axes with the quantities being plotted and the units in which they are measured.

12 When you have completed your measurements, wash and dry all your equipment and return it neatly to the set-up area where you found it. Make sure the hot plate is turned off before you leave the lab.

13 Before leaving, go to a computer in the laboratory and enter your results in the In-Lab assignment. If all results are scored as correct, log out. If not all results are correct, try to find the error or consult with your lab instructor. When all results are correct, note them and log out of WebAssign. The In-Lab assignment must be completed by the end of the lab period. If additional time is required, please consult with your lab instructor.