CHEMISTRY 206

Experiment 2: CALORIMETRY - THERMODYNAMICS OF THE OXIDATION OF ACETONE BY HYPOCHLORITE

Instructor's Informal Preamble

In this laboratory session, we will perform experiments that allow us to determine the enthalpy change for a chemical reaction. You should recall from class that *enthalpy (H)* is a state function that can be thought of as the potential energy stored in chemical bonds.
It is important to note that a system's enthalpy is not the same as its *internal energy (E)*, which is the system's total potential and kinetic energy. We cannot actually directly measure either the enthalpy or the internal energy of a sample of matter at any moment, but if our system undergoes some kind of physical or chemical *change*, we can begin to learn more about it. Because the energy of the universe is constant *(the First Law of Thermodynamics),* any changes in the system's internal energy (ΔE) must result from the transfer of heat (q) or the performance of work (w): **$\Delta E = q + w$.** Thus, if any energy enters or leaves our system, then we should be able to detect the opposite phenomenon occurring in the surroundings.

Imagine a very simple reaction that involves one bond breaking and a new bond forming. We know that breaking a bond *always* requires an energy input, and that forming a new bond *always* results in a release of energy. If the bond that forms is weaker than the bond that breaks, then the system will require a net input of energy for the reaction to occur; conversely, if the new bond in the product is stronger than the original bond in the reactant, then the reaction will result in energy being released from the system as heat.

It turns out that measuring heat flow is quite easy experimentally, and it forms the basis of *calorimetry*, the technique we will be using in this experiment. If we perform a reaction in a vessel open to the atmosphere, the pressure of the system will be constant even though its volume might change. Under constant pressure conditions, any heat that flows into or out of the system corresponds to, by definition, the enthalpy change (ΔH) for the reaction. By measuring the change in temperature of the matter immediately surrounding our reacting system, and then factoring in how much reactant was consumed in order to produce this change, we can determine the enthalpy of reaction.

The system's internal energy change will depend not only on heat flow such as this, but also on any work that is done. If the reaction involves gases, the system could lose energy if it expands (*e.g.,* net production of gas), or gain energy if work is done on the system by the surroundings (*e.g.,* if some gas disappears and the system contracts). If the reaction involves only liquids and solids, "PV work" will be negligible.

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Introduction

This experiment introduces the technique of calorimetry to measure the heat of a reaction (*i.e.,* the enthalpy change, ΔH, associated with the reaction). The chosen reaction is the oxidation of acetone, a common solvent, by hypochlorite ion, the active species in bleach (which is what you will use). The net reaction is:

$$3OCl^- + CH_3COCH_3 \rightarrow CH_3CO_2^- + CHCl_3 + 2OH^-$$

The products are acetate ion and chloroform (trichloromethane, a rather low-tech anesthetic).

By performing the reaction in an insulated container open to the atmosphere (thus, held at *constant pressure*) and measuring the temperature change, the amount of heat absorbed or released by the reaction can be determined. Thus, the enthalpy of reaction (ΔH_{rxn}) can be determined. The following principles and formulas are used:

- Energy, measured in joules (J), is conserved. Therefore, any heat lost by the system is gained by the surroundings (including our equipment), and vice versa.
- The heat energy (Q) needed to heat a homogeneous substance through a temperature change of ΔT is:

  $Q = m \times C \times \Delta T$ where m = mass and C = specific heat capacity

  For water, the specific heat capacity is approximately constant over small temperature ranges, with a value of 4.184 $J\ g^{-1}\ {}^oC^{-1}$ (or $J\ g^{-1}\ K^{-1}$) near room temperature. This value can also be used for dilute aqueous solutions, such as those involved in this experiment, since the major component in any dilute solution is water.

The calorimeter itself, notably the beaker and the thermometer, also have a significant capacity to hold heat. The mass of the calorimeter is constant, so the product of the mass × its specific heat capacity, if such a thing could be defined for such an inhomogeneous object, is constant. The first part of the experiment involves the determination of this constant, which is called the "heat capacity of the calorimeter" (without the word "specific"). It has units $J\ {}^oC^{-1}$. We will take this into account during our experiment.

Experiment Summary

The experiment is divided in to two parts: first, the heat capacity of the calorimeter is determined by mixing hot and cold water in it as a "blank", measuring the final temperature, and calculating how much heat is lost to the calorimeter. In the second part, the reagents themselves are mixed in the calorimeter, and the temperature change is used to obtain the heat of reaction.

Prelaboratory Assignment

Read the Introduction and Procedure sections carefully and answer the Prelaboratory Questions. Keep a copy of them for yourself, and have the TA sign your receipt record. Your TA will inspect and collect your prelab before you are permitted to begin working.

Materials

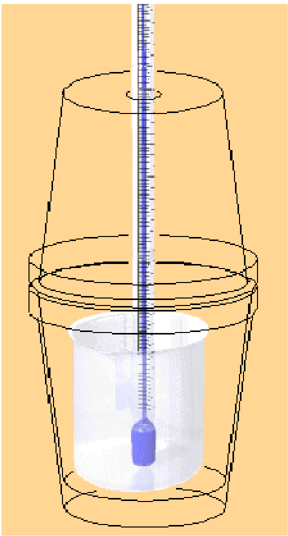
Apparatus

- Computer running Logger Pro 3
- Stainless steel temperature probe with USB connector
- Water bath thermostatted between 40 - 50°C
- Beakers: 1 × 50 mL, 1 × 250 mL
- Thermometer (for use in water bath)
- Graduated pipette, 5 mL (supplied with acetone solution)
- Graduated pipette, 20 mL (supplied with bleach solution)
- Graduated cylinder, 25 mL
- 3 styrofoam coffee cups

Reagents (prepared by the technical staff)

- Bleach (5.25% (w/v) sodium hypochlorite)
- Acetone (5% (**by volume**) in water)

Use stainless steel temp. probe here, not thermometer ↓



Procedure

Bleach is irritating to the skin and dangerous if it gets in your eyes. Clean up any spills immediately.

Preparation of the Calorimeter:

Build yourself a “coffee-cup calorimeter” as described here. *[The trimming & hole-boring may already be done for you.]* Place one styrofoam cup inside another to create a double-walled insulating container, and place the 50 mL beaker inside it. **Put these three items inside the 250 mL beaker to steady the apparatus.** Take the third styrofoam cup and trim off the rim with scissors so that it fits as a lid inside the innermost cup of the container. Then, with a cork borer, make a hole in the lid in which the probe fits snugly so that the tip will be immersed in the liquid that will go in the beaker. *Important: If you cannot clamp the probe so it rests without touching the bottom of the beaker, then gently rest it on the beaker bottom instead. Do not hold the probe in place with your hand, because your body heat and/or vibrations may affect the data.*

Part 1: Determining the heat capacity of the calorimeter.

1. On the computer: double click on the icon "CHEM 206 Experiment 2" to bring up the data acquisition window. *[The program is set up so that when the COLLECT button is pressed, the timer starts. Every few seconds, a temperature reading will be taken, displayed on the spreadsheet and plotted.]*
2. Measure 15.0 mL (15.0 g) of room temperature water with a graduated cylinder and transfer the water into the 50 mL beaker in the calorimeter.
3. Use a small clamp to secure the stainless steel temperature probe inside the calorimeter. Plug the temperature probe's cord into either one of the USB ports located on the front of the computer (the probe plugs directly into the computer; no other interface is required). The program will automatically identify the probe, at which point you are ready to begin collecting data.
4. Measure 15.0 mL of water into a graduated cylinder. Place this cylinder into the thermostatted hot water bath (40 to 50 ^{o}C) for at least 5 minutes so that the water can reach the temperature of the bath. The temperature of the bath should be measured with a thermometer to $\pm 0.1^{o}$C. Record this temperature in your lab report's data table ("T_h").
5. Click on COLLECT to begin recording the temperature of the room-temperature water in the calorimeter. Record the temperature for about one minute. You should see the readings appearing on both the graphical and spreadsheet display.
6. Leaving the program running, quickly open the calorimeter and pour the hot water into the room temperature water, then close the calorimeter again. This must be done quickly because the hot water will cool rapidly in air. Swirl the calorimeter gently to mix the water *(do not use the probe as a stirring rod!).* On the display, the temperature will rise sharply, level off, and then start to drift down.
7. Allow the data acquisition to continue until the downward trend in temperature is clearly established (about 3 minutes beyond the point of mixing). *[This is important. Later, you will need to extrapolate your cooling curve back to the moment of mixing, to correct for the constant loss of heat to the surroundings.]* Then press STOP.
8. Click on FILE, then SAVE AS, and save your data under a logical file name onto the computer's Desktop into the folder called *Chem 206 Expt 2 Data*. (If a folder like this does not yet exist: right click inside the Save As window, choose New, then Folder, then name the new folder as specified above). Your file name should include identifying details, *e.g.*, *jd-calibration-1*, the data file for John Doe's calorimeter calibration run #1. *Important: use a different file name for each run.*
9. Rinse and dry the sample beaker and probe, then reassemble the apparatus.
10. Print your graph, following the instructions given at the end of Part 2 (see below).
11. Repeat steps (2) – (10) two more times. To start a new acquisition, click on COLLECT while you still have the old run on the screen. A message will follow; choose "Erase and Continue". All the data points acquired in the previous run and the graph will disappear from view, and new data will begin appearing.

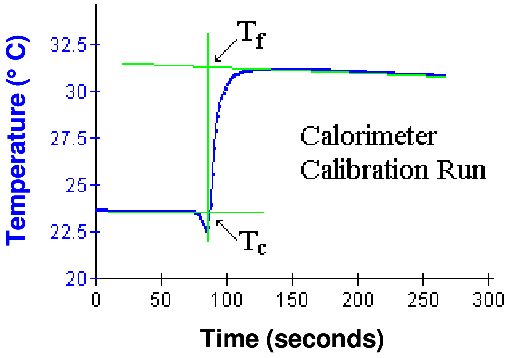
Part 2: Determining the heat of reaction of acetone with hypochlorite.

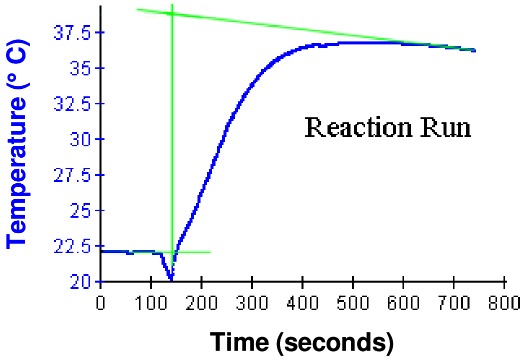
12. Using a volumetric pipette, add exactly 20.0 mL of sodium hypochlorite solution (bleach) to the 50 mL beaker from the calorimeter. Place it into the calorimeter.
13. Click on COLLECT to begin recording the temperature of the solution in the calorimeter. Record the temperature for about one minute. You should see the readings appearing on the display. *The time axis should extend to 1000 s; if not, click on Experiment, then Data Collection, then change the "length" entry to 1000 seconds, and click Done. To restart your run, click STOP, then COLLECT.*
14. In the meantime, measure out 4.0 mL of 5.0% aqueous acetone using a 5 mL graduated pipette, and add this solution to a 25 mL graduated cylinder.
15. Quickly open the calorimeter, pour the acetone solution into the bleach, and close the calorimeter. The temperature will slowly rise as the acetone reacts with the bleach. Swirl the calorimeter gently while the reaction takes place *(do not use the temperature probe as a stirring rod!)*. The temperature should reach its maximum about 3-4 minutes after mixing and then begin to drop gradually.
16. After the temperature has been dropping slowly for at least five minutes *(again, it is important that the linear downward trend is well established!)*, click on STOP. Save the data as before (see Part 1 step 8) under a new logical file name.
17. Pour the reaction mixture into a labeled waste beaker in the fume hood. Rinse and dry the sample beaker and probe, then reassemble the apparatus.
18. Repeat steps (12) – (17) two more times. Print out all three graphs - see below.

Printing Graphs

- Pick a file containing a graph you wish to print and open it using the FILE menu.
- Click on ANALYZE, then AUTOSCALE, then AUTOSCALE.
- Click on FILE in the menu bar and choose PRINT GRAPH. In the print window click on OK. Repeat this step so that both you and your lab partner have a copy.

The graphs should resemble the figures below. (Note that some lines have been added - see the Observations and Data section of the Lab Report.) Be sure to clearly label your graphs, including: your name, the experiment's title, a descriptive title of the graph, axis labels (including units), plus any important features of the graph (*e.g.,* time of mixing).





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Experiment 2: CALORIMETRY - THERMODYNAMICS OF THE OXIDATION OF ACETONE BY HYPOCHLORITE

Prelaboratory Questions

1. (3 marks) Write a brief summary, in your own words, describing the purpose of this experiment, and the steps you will follow. One page - maximum.
2. (1 mark) Bleach is made by reacting chlorine with sodium hydroxide. Write a balanced equation for the reaction of chlorine gas with hydroxide ion to produce hypochlorite and chloride ions. *[Review Chem 205, and/or search your text.]*
3. (1 mark) Think about the reaction of chlorine with sodium hydroxide and the reaction of acetone with hypochlorite ion. Classify each reaction as either: acid/base or oxidation/reduction. Explain your answer.

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Laboratory Report

Observations and Data

Space is provided to report data and calculations for three runs in both parts of the experiment. The following assumptions should be made in your calculations:

- The density of water and the solutions is 1.0 g mL^{-1}.
- The heat capacity of water and the solutions is 4.184 J g^{-1} $^{o}C^{-1}$.
- The limiting reagent in the reaction is the acetone.

Part 1: Determining the heat capacity of the calorimeter

1. (2 marks) On each graph you printed, mark with a vertical line the time at which the warm water was mixed with the cold water. *[There will probably be an obvious discontinuity on the graph at this point.]* Next, draw a straight line through the points before mixing. Draw another straight line through the points that define the downward temperature trend observed when the mixture began to cool down. Extrapolate both lines until they intersect with the vertical line that marks the time of mixing. *[See the sample Calorimeter Calibration Run graph at the end of the procedure section.]*

   The point on the sample graph labeled "T_c" represents the initial temperature of the cold water at the time of mixing. The point labeled "T_f" represents the final temperature the mixture would have reached if (a) the mixing process had been truly instantaneous, and (b) the mixture had not lost any heat to the surroundings.

   Hand in your graphs with your report. On the graphs, clearly label T_c and T_f, and *explain exactly* how you determined these values.

The data table that follows will guide you through the calculations, although the exact calculations you must do are not specified. Refer to the assumptions listed at the top of this page 2-8 before calculating masses and heats. You should also assume that no heat was lost, *i.e.,* the total amount of heat gained by the cold water and calorimeter is the same as the amount of heat lost by the hot water. Some simple algebra will then allow you to calculate a value for the heat capacity of the calorimeter.

2. (2 marks) **Table 1: Determining the heat capacity of the calorimeter.**

	Run 1	**Run 2**	**Run 3**
Mass of the hot water, m_h (g):			
Initial temperature of the hot water, T_h (^oC):			
Mass of the cold water, m_c (g):			
Initial temperature of the cold water and calorimeter, T_c (^oC):			
Final temperature of the mixture, T_f (^oC):			
Heat lost by the hot water, Q_h (J):			
Heat gained by the cold water, Q_c (J):			
Heat gained by the calorimeter, Q_{cal} (J):			
Heat capacity of the calorimeter, C (J $^oC^{-1}$):			
Average heat capacity of calorimeter, C_{cal} (J $^oC^{-1}$):			

3. (1 mark) In this space, please show the full set of calculations for Part 1 Run 1.

Part 2: Heat of reaction of acetone with hypochlorite

3. (2 marks) On each graph you printed, mark with a vertical line the time at which the acetone solution was mixed with the sodium hypochlorite solution. Draw a straight line through the points before mixing and another line through the points that define the cooling trend after mixing, and then extrapolate them both to the line marking the time of mixing. Determine T_i and T_f the same way you calculated T_c and T_f in Part 1. Hand in your labeled graphs with your lab report.

The data table that follows will guide you through the calculations, although the exact calculations you must do are not specified. Refer to the assumptions listed at the top of page 2-8 before calculating masses and heats. You should assume that no heat was lost during the experiment, *i.e.,* the total amount of heat gained by the reaction mixture and calorimeter corresponds to the amount of heat released by the reaction. The molar heat of reaction (enthalpy of reaction, ΔH_{rxn}) is calculated as the heat released per mole of limiting reactant consumed.

4. (2 marks) **Table 2: Determining the heat of reaction of acetone with hypochlorite.**

	Run 1	**Run 2**	**Run 3**
Mass of the reactant mixture, m_{mix} (g):			
Initial temperature of the reactant solutions and calorimeter, T_i (^oC):			
Final temperature of reaction mixture, T_f (^oC):			
Heat gained by the reaction mixture, Q_{mix} (J):			
Heat gained by the calorimeter*, Q_{cal} (J):			
Heat released by the reaction, Q_{rxn} (J):			
Mass of acetone oxidized, m_{ac} (g): *(hint given!)* $m_{ac} = 4.0$ mL × 5/100 (% vol.) × 0.791 g mL^{-1}			
Moles of acetone oxidized, n_{ac} (mol):			
Molar heat of reaction, ΔH_{rxn} (J mol^{-1}):			
Average molar heat of reaction, ΔH_{rxn} (J mol^{-1}):			

* In this calculation, use the average heat capacity of the calorimeter, C_{cal}, from the previous table.

5. (1 mark) In this space, show the full set of calculations for Part 2 Run 1.

Additional Questions

1. (3 marks) What do you think were the most significant sources of error with the procedure used in this experiment? (Try to come up with at least three; think about the design of the experiment, and any assumptions made along the way, as well as the typical measurement limitations.)

2. (2 marks) In this experiment, is the enthalpy change you measured equal to the system's internal energy change? Explain your answer, using the equations for ΔH and ΔE from the text.