

## Experiment 7

# Solution Calorimetry

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### PURPOSE

Measure the heats of two simple reactions and use Hess's Law to theoretically predict the heat of a third, difficult-to-carry-out, reaction.

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### CALORIMETRY

The basic principle of calorimetry is simple: chemicals are mixed together; a thermometer is used to measure the temperature change; and then the heat of the reaction is calculated. If the mixture gets hot, the chemical reaction produced kinetic energy which will be given off as heat and the reaction is said to be **exothermic** (heat exiting). If the mixture gets cold, heat will flow into the mixture and the reaction is **endothermic** (heat into).

Ideally, the reaction would be carried out in a **calorimeter** that neither absorbs any of the heat, nor leaks any to the surroundings. Although calorimeters costing over \$50,000 are commercially available, the styrofoam-cup calorimeter we will use is surprisingly effective.

### HOW IS HEAT FLOW RELATED TO $\Delta T$ ?

When a chemical reaction occurs, potential energy is converted into kinetic energy (exothermic) or *vice versa* (endothermic). This causes a temperature change in the reaction mixture. This temperature change is NOT due to heat flow. *The heat flow occurs when the reaction mixture slowly returns to the initial temperature.* However, since we already know the initial temperature, we do not need to wait for the heat flow to occur in order to determine  $\Delta T$ .

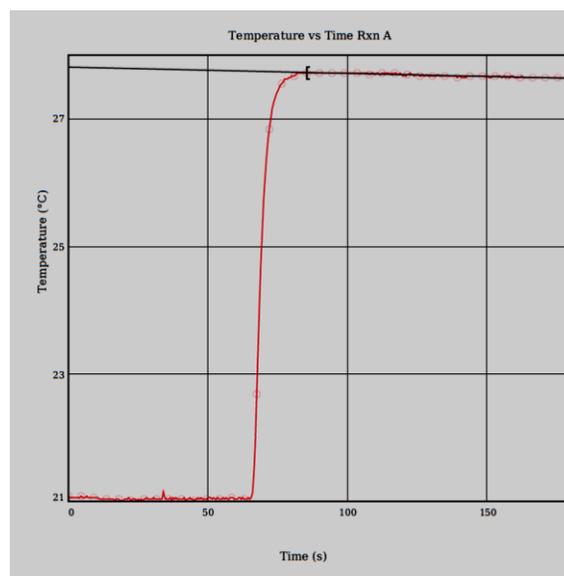


Figure 1. Temperature vs. time for an exothermic reaction.

During an exothermic reaction, kinetic energy is produced which *raises the temperature* of the calorimeter's contents, as shown in Figure 1. Heat will then flow out of the warm calorimeter (at 22°C) into the surroundings until the mixture returns to the initial (room) temperature (15°C).

So, technically,  $\Delta T$  should be  $15 - 22 = -7^\circ\text{C}$ . However, when we look at Figure 1, it looks like  $\Delta T$  should be  $+7^\circ\text{C}$  (which is the temperature change during the chemical reaction). So the fix, adopted by those who do calorimetry, is to let  $\Delta T$

be positive for an exothermic reaction, but then recognize that the  $q$  value they calculate,  $q_{\text{cal}}$ , is actually  $-q_{\text{rxn}}$ .

The fundamental equation of calorimetry, shows how  $q_{\text{cal}}$  depends on  $C$ , the system's heat capacity, and  $\Delta T$ :

$$q_{\text{cal}} = C\Delta T \quad (1)$$

The solution calorimeter used in this experiment is open to the atmosphere (at constant pressure), so  $q_{\text{rxn}} = \Delta H = -q_{\text{cal}}$ . Thus, we see for an exothermic reaction,  $\Delta T$  is positive, making  $q_{\text{cal}}$  positive and  $\Delta H$  negative, just as it is supposed to be.

## HEAT CAPACITIES

The heat capacity used in Equation 1 is the *total* heat capacity of the system. It is the amount of energy required to raise the temperature of the entire sample by one degree.

Because it is not possible to know the size of every sample someone might use, published values of heat capacities are always given either as *molar* or *specific* heat capacities. We use the **specific heat**,  $c_s$ , in this experiment.  $c_s$  is the energy needed to raise the temperature of *one gram* of a substance by one degree.

$$C = (c_s)(\text{mass}) \quad (2)$$

The specific heats of the products are used since the heat flow occurs after the products are formed. These are given in Table I. The mass of products must equal the mass of the reactants (conservation of mass). The mass of liquid reactants can be determined from their densities and volumes. The densities of the reactant solutions used in this experiment are given in Table II. Thus, the *total* heat capacity of a solution can be calculated as

$$C = (c_s)[(V_1)(d_1) + (V_2)(d_2)] \quad (3)$$

for mixtures of two liquids

$$C = (c_s)[(V)(d) + \text{mass}_{\text{salt}}] \quad (4)$$

for mixtures of liquid and salt

The heat capacity of the *empty* calorimeter setup used *in this experiment* is negligible and assumed to be zero. However, with many calorimeters, or whenever extreme accuracy is required, allowance must be made for the heat capacity of both the calorimeter and its contents.

**Table I. Specific Heats at 298 K.**

solution	Reaction A		Reaction B	
	M (mol/L)	$c_s$ (J/g-°C)	M (mol/L)	$c_s$ (J/g-°C)
NH <sub>4</sub> Cl(aq)	0.5	4.04	0.9	3.93
NH <sub>4</sub> NO <sub>3</sub> (aq)	0.5	4.01	0.6	3.98

**Table II. Densities at 298 K.**

solution	M (mol/L)	density (g/ml)
H <sub>2</sub> O(l)	pure	0.997
HCl(aq)	1.0	1.02
HNO <sub>3</sub> (aq)	1.0	1.03
NH <sub>4</sub> OH(aq)	1.0	0.992

## DETERMINING THE TEMPERATURE CHANGE

Although there is little doubt about the temperature *at the start* of a reaction, the temperature *after the reaction* is more uncertain. This is because the reaction takes time, and the energy needs time to diffuse through the mixture, and the thermometer needs time to respond. During this time, our good-but-not-perfect calorimeter is leaking heat (the contents are returning to room temperature).

There is a clever graphical way to determine what the products' temperature *would have been* if the calorimeter had not leaked any heat: Temperature measurements are *continued after the reaction*, until only the slight, steady drift due to the heat leak is occurring. This drift line is *extrapolated back* to the time of mixing, and the temperature at that point is taken as the correct final temperature. Figure 2 illustrates this process.

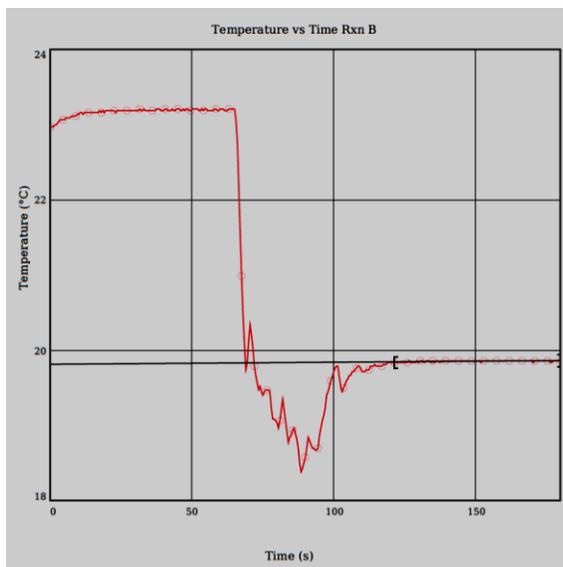
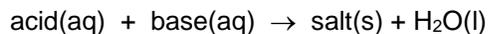


Figure 2. Temperature vs. time for an endothermic reaction. The square brackets enclose the points used to determine the line that is extrapolated to determine  $T_f$ .

### USE OF HESS'S LAW TO INDIRECTLY OBTAIN THE HEAT OF A REACTION

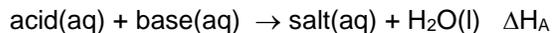
The change ( $\Delta$ ) in any extensive **state function** during a reaction is the sum of the  $\Delta$ 's for *any sequence* of reactions that adds up to the same overall reaction. This simple fact, when applied to **changes in the state function enthalpy**  $\Delta H$ , is known as **Hess's Law**.

In this experiment, Hess's Law will be used to determine the heat of an acid-base neutralization to produce a *solid* salt:

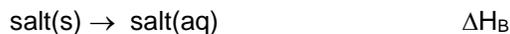


Note that an *aqueous salt solution*, rather than *the solid salt*, would normally result from acid-base neutralization. However, Hess's Law permits us to *indirectly* determine the heat of this reaction by carrying out *two other* more convenient reactions:

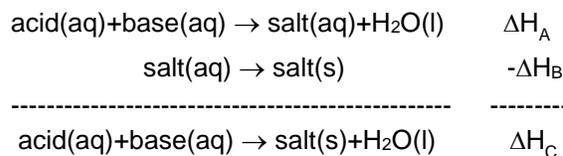
Reaction A, the "usual" neutralization of aqueous acid and base to give an aqueous salt solution,



and Reaction B, the dissolution of pure solid salt to give an aqueous salt solution,



Notice that if reaction B is reversed and then added to reaction A, the desired reaction (C) results:



When reaction B is reversed, the sign is changed in front of  $\Delta H_B$ . Then, by Hess's Law,  $\Delta H_C$  is the sum of  $\Delta H_A$  and  $(-\Delta H_B)$ .

Thus, with the help of Hess's Law, we can *predict* the heat of a reaction that may be *impossible* to actually carry out. Chemists use this trick a lot. Sometimes the information gained is of only theoretical interest; often it is useful for the calculation of other reaction heats.

### IN THIS EXPERIMENT

The  $\Delta H$  of two different reactions will be measured: (A) the neutralization of aqueous ammonia ( $\text{NH}_4\text{OH}$ ) with a strong acid ( $\text{HCl}$  or  $\text{HNO}_3$ ), and (B) the dissolution of the corresponding ammonium salt ( $\text{NH}_4\text{Cl}$  or  $\text{NH}_4\text{NO}_3$ ) in water. These results will be combined using Hess's Law to theoretically calculate the  $\Delta H$  of a third reaction (C) the aqueous ammonia - strong acid neutralization to produce the *pure ammonium solid salt* and water.

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## PRE-LABORATORY PREPARATION

1. **Read the procedure and data analysis sections of the experiment.**
  2. **Set up the DATA SHEET for the experiment.** Since all of the data will be collected by computer, the data sheet only needs to contain the actual concentrations and amounts of all of the reagents used.
  3. **Complete the prelab in Canvas.** You will be shown sample data for one calorimetric run, but you do not need to use any of the numbers in the data table provided. Some necessary data and equations are in the background section (page 2 of this experiment).
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## EXPERIMENTAL SECTION

### REAGENTS PROVIDED

**Standardized ammonia, 1 M.** Aqueous Ammonia bottles are sometimes labeled  $\text{NH}_3(\text{aq})$  and sometimes  $\text{NH}_4\text{OH}(\text{aq})$ . Record the exact concentration on your data sheet.

**Standardized hydrochloric acid, 1 M.** Record the exact concentration on your data sheet if this is your assigned acid.

**Standardized nitric acid, 1 M.** Record the exact concentration on your data sheet if this is your assigned acid.

**Ammonium chloride, solid.**

**Ammonium nitrate, solid.**

### Hazardous Chemicals

Be careful not to spill any solutions on your person, especially the acids and bases. Immediately wash off any spilled solution with lots of water.

### WASTE DISPOSAL

All of the chemicals used in this experiment may be safely disposed of by washing down the sink.

### SPECIAL EQUIPMENT

The following items are available on the front bench (and should be returned there after lab):

2 styrofoam cups with a cardboard cover

### PROCEDURE

Assume you will work with a partner, unless told otherwise.

### COMPUTER/TEMPERATURE PROBE SETUP

**1. Turn on the LabQuest2 by pressing the red power button on the top.**

It takes a minute to warm up.

**2. Attach a stainless steel temperature probe to CH 1 on the left end of the LabQuest2.**

**3. Check to be sure the readings make sense.**

It should start with the meter screen showing. There will be a large red box containing the temperature reading. On the right side, it should show that the *Mode*: is *Time Based*.

**REACTION A: AQUEOUS AMMONIA - STRONG ACID NEUTRALIZATION**

There are two strong acids available. Your instructor will assign you either HCl or HNO<sub>3</sub> which you will react with NH<sub>4</sub>OH. You will use 50.0 mL of both aqueous ammonia and your assigned acid.

**4. Record the exact concentrations of the two solutions you use on your data sheet.**

**5. Using a 50 mL graduated cylinder, carefully measure into the clean, dry styrofoam calorimeter (which consists of a pair of nested cups) 50.0 mL of whichever solution contains the limiting reactant.**

It is okay if the volume isn't exactly 50.0 mL. However, *record the actual volume used on your data sheet (to the nearest 0.1 mL).*

Because equal volumes of the solutions are to be used, you can decide which contains the limiting reactant simply by comparing the precise concentrations given on the labels (calculations are not required).

The limiting reactant is added first, because addition of the second reactant is a little more rushed and subject to error.

Keep the solution covered as much as possible to minimize evaporative cooling.

**6. Put the cardboard cover over the calorimeter and insert the temperature probe through the hole in the cover so that the end of the probe is in the solution.**

Be sure the probe will not tip over the calorimeter when you take your hand away. It will sometimes do this if the cord is twisted. If you are having trouble getting it to stay upright, wrap the cord around a buret stand.

**7. Add 50.0 mL of the second reactant to a graduated cylinder, but do not add it to the calorimeter yet.**

Keep it covered by inverting a small beaker over the top of the cylinder.

*Record the actual volume on your data sheet.*

**8. Begin data collection.**

Tap on the **Start** button in the lower left corner of the screen. It will change to the Graph screen and you should see data points appearing on the graph. The line on the graph should be flat.

The default values for Logger Pro work very well for this experiment and so we do not need to change them. We will sample 2 points per second for 180 seconds.

**9. Wait for 60 seconds after starting data collection. Then, WITHOUT stopping the data collection, slide the calorimeter cover over to one side and pour the solution from the graduated cylinder into the calorimeter.**

The temperature probe should remain in the solution for the entire time.

Replace the calorimeter cover and mix the contents by gently stirring with the temperature probe.

**10. After data has been collected for 180 seconds, data collection will stop automatically. Remove the temperature probe from the solution and dry it with a paper towel. Dispose of the solution down the drain. Rinse and dry the styrofoam cups.**

**DETERMINATION OF  $\Delta T$** 

**11. Switch to the Data Table screen by tapping on the Data Table icon in the upper right corner of the screen.**

It is the white icon with the X and Y at the top.

**12. Scroll down the data table to see the temperature of the mixture at 60 s (immediately before mixing). Record this as the initial temperature in the Table for Data Analysis question 1.**

**13. Switch back to the Graph screen by tapping on the Graph icon in the upper left.**

**14. Perform linear regression on the flat region of the graph after the reaction is over:**

a. Click-and-drag, using your finger or stylus, to select the flat region at the right end of the

graph. Use your best judgment as to which points to select. Typically, you will use points between 90 and 180 seconds. See Figure 2 for an example.

- Tap **Analyze** then **Curve Fit**.
- Tap on the box saying **Temperature** that appears.
- Tap on the **Fit Equation** box and select **Linear**.
- You do not need to record any of the values that appear.
- Tap **OK**.

**15. Determine the final temperature:**

- Choose **Analyze** from the top menu.
- Next, tap on **Interpolate** from the submenu. Now, when you move your finger or stylus across the graph, you should see the temperature and time readings change (which are located in the boxes on the right side of the screen).
- Move your finger/stylus so the Time value is approximately what it was when you added the second reactant to the calorimeter (around 60 seconds).
- Read the Temperature value in the box. Record this value as the final temperature in the Table for Data Analysis question 1.

**16. Print out a copy of the graph.**

- Tap **File** from the top menu.
- Tap **Print** and then **Graph**.
- Tap on **Print Graph Title**.
- Enter an appropriate graph title. Usually, the title tells what is graphed in the format "Y" vs "X" (e.g., Temperature vs Time Rxn A).
- Tap **Print**.

Do **not** bother printing out the data table.

**REACTION B: DISSOLUTION OF AMMONIUM SALT IN WATER.**

Here you will repeat the calorimetric procedure, except, as the first reactant, use 100 mL distilled water, and, as the second reactant, use 5 grams of the ammonium salt which corresponds to the acid used in REACTION A.

Use  $\text{NH}_4\text{Cl(s)}$  if you used  $\text{HCl(aq)}$  and use  $\text{NH}_4\text{NO}_3\text{(s)}$  if you used  $\text{HNO}_3\text{(aq)}$ .

**17. Weigh out onto glassine weighing paper about 5 grams of your assigned salt.**

Break up the solid with your spatula so that it is not in chunks before weighing it. If the solid is in chunks it will cause erratic temperature changes as it dissolves. Glassine paper is preferred as no sample will stick to the paper.

Any amount close to 5 grams is okay, but you need to know exactly what the actual weight is. Record on your DATA SHEET the exact amount weighed out (to the nearest 0.001 g).

**18. Using a 50 mL graduated cylinder, add 100 mL of distilled water to the clean and dry styrofoam calorimeter cup.**

Record the actual volume used (to the nearest 0.1 mL) on your data sheet.

**19. Cover the calorimeter and place the temperature probe in the solution, as before.**

**20. Tap the Start button to begin data collection.**

The program should ask you what to do with the previously-collected data. If you have determined  $\Delta T$  and printed out the graph for Reaction A, you should choose **Discard**, which will cause data collection to begin. Otherwise, choose **Cancel** to go back and finish before erasing your data.

**21. After data has been collected for 60 seconds, slide the calorimeter cover over to one side and pour the salt into the calorimeter. Replace the cover and stir fairly vigorously using the temperature probe.**

The temperature probe should remain in the solution for the entire time.

*It is essential that the sample be stirred enough to dissolve all of the salt.* If it dissolves too slowly, the temperature change will be slow and erratic. After the run, look closely to see if all of the salt has dissolved; if it has not, the run must be repeated

**22. After data has been collected for 180 seconds, data collection will end. Remove the temperature probe from the solution, rinse it with some distilled water, and dry it with a paper towel. Dispose of the solution down the drain. Rinse and dry the styrofoam cups. Return them to the front bench.**

**23. Determine  $\Delta T$  for this reaction and print the graph following the same procedure described in steps 11-16.**

*Again, record your results for the initial and final temperatures in the Table for Data Analysis question 1.*

Print out the Temperature vs. Time graph for this reaction, as well. For the title enter *Temperature vs Time Rxn B*.

**24. Shut down the LabQuest2 by first tapping *File – Quit*. Choose to *Discard* the data. Next,**

**tap on the *System* folder and then *Shut Down* and, finally, tap *OK*.**

When you exit the app, you should not need to save your data. *You should have your two graphs printed and the values for the initial and final temperatures for both calorimetric runs.*

USE A BRUSH AND TAP WATER TO CLEAN YOUR GLASSWARE. RINSE IT WITH DISTILLED WATER AND DRY IT BEFORE RETURNING IT TO THE DRAWER.

**RETURN EVERYTHING TO WHERE IT WAS AT THE START OF LAB. HAVE AN INSTRUCTOR CHECK YOUR STATION BEFORE LEAVING.**

It's always a good idea to wash your hands after handling glassware containing any chemicals.



## DATA ANALYSIS

1. Enter the relevant data into the table below and calculate  $\Delta T$  ( $T_{\text{final}} - T_{\text{initial}}$ ) for each reaction.

Reaction	T <sub>final</sub> (°C)	T <sub>initial</sub> (°C)	ΔT (°C)
A			
B			

### CALCULATION OF MOLAR REACTION ENTHALPIES

For each calculation below, show your work in the space provided. Show your calculation for each reaction, A and B, on its own side of the page.

2. Using the specific heat of the product solution from Table I (ammonium chloride if HCl was used, ammonium nitrate if HNO<sub>3</sub> was used) and the mass of product solution formed, calculate the heat capacity of the reaction products (using equation 3 for Reaction A and equation 4 for Reaction B). The densities provided are close enough, even if the concentrations are not exactly 1.0 M.

REACTION A.

C = \_\_\_\_\_

REACTION B

C = \_\_\_\_\_

**3. Calculate  $q_{\text{cal}}$  for both reactions in kJ (use equation 1). Then, give the value for  $\Delta H$  in kJ.** Since the reactions were carried out at constant pressure,  $\Delta H = -q_{\text{cal}}$  for each reaction. (Recall the minus sign appears because of how  $\Delta T$  is determined in calorimetry--see the background section entitled How is Heat Flow Related to  $\Delta T$ ?.)

REACTION A

 $q_{\text{cal}} =$  \_\_\_\_\_ $\Delta H =$  \_\_\_\_\_

REACTION B

 $q_{\text{cal}} =$  \_\_\_\_\_ $\Delta H =$  \_\_\_\_\_

**4. Calculate the moles of the limiting reactant for reaction A (from its molarity and volume), and the moles of salt added in reaction B. Molar masses:  $\text{NH}_4\text{Cl}$ , 53.49 g/mol;  $\text{NH}_4\text{NO}_3$ , 80.04 g/mol**

REACTION A

 $n =$  \_\_\_\_\_

REACTION B

 $n =$  \_\_\_\_\_

5. Convert the  $\Delta H$  values, calculated in question 3, into *molar* enthalpies of reactions, by using the moles of the limiting reactant (A) or moles of salt (B). A molar enthalpy is  $\Delta H$  per mole.

REACTION A

REACTION B

 $\Delta H =$  \_\_\_\_\_ $\Delta H =$  \_\_\_\_\_**USE OF HESS'S LAW TO INDIRECTLY DETERMINE  $\Delta H$  OF REACTION C.**

6. Write the *complete* balanced equations for both reactions studied in the calorimeter. Use  $\text{NH}_4\text{OH}(\text{aq})$  as the formula of the aqueous ammonia. Do NOT write net ionic reactions. Indicate the phase of each species in the reactions. [See the background section of the experiment on Hess's Law for general examples.]

REACTION A: Aqueous Ammonia – Strong Acid Neutralization

REACTION B: Dissolution of Ammonium Salt in Water

**7. Rewrite REACTIONS A and B, reversing directions as necessary, to show how they can be combined to give REACTION C, the reaction of aqueous ammonia with aqueous strong acid to produce the solid ammonium salt and water.**

Beside each reaction, write the molar enthalpy of reaction for that reaction. Because the reactions are balanced using stoichiometric coefficients, the corresponding molar enthalpies should be used. Be careful to use the proper sign for  $\Delta H$  based upon the direction the reaction is written.

**8. Calculate the molar enthalpy of reaction for REACTION C.**

$\Delta H$ , molar enthalpy of reaction for REACTION C = \_\_\_\_\_

**TURN IN your DATA SHEET, the DATA ANALYSIS pages, and your graphs for both calorimetric runs.**