



EXPERIMENT

Hess's Law

Hands-On Labs, Inc.
Version 42-0158-00-02

Review the safety materials and wear goggles when working with chemicals. Read the entire exercise before you begin. Take time to organize the materials you will need and set aside a safe work space in which to complete the exercise.

Experiment Summary:

You will compare exothermic and endothermic reactions and learn about the enthalpy of a reaction (H) and how it relates to Hess's Law. Using a student-made basic calorimeter, you will calculate the amount of heat gained or lost from three reactions (q_{rxn}) and calculate the change in enthalpy (ΔH) of three different reactions. Two of the chemical reactions are intermediate reactions for a third reaction. You will then compare the percent difference by measuring an experimental value directly and applying Hess's Law by using the data taken from the intermediate reactions.

Learning Objectives

Upon completion of this laboratory, you will be able to:

- State the difference between an exothermic and an endothermic reaction.
- Define enthalpy (H) and describe how it is related to exothermic and endothermic reactions.
- Describe the change in enthalpy (ΔH) of a reaction and the standard enthalpy of formation (ΔH°_f).
- Define Hess's law.
- Create a cooling trend based on data taken in a student-made calorimeter.
- Determine the amount of reactants and the amount of products that are in a solution based on molarity of the reactants.
- Calculate the amount of heat gained or lost (q_{rxn}) from three reactions and the change in enthalpy (ΔH) of the reactions.
- Evaluate the percent difference between change in enthalpy (ΔH) as calculated by Hess's law and measured temperature changes of chemical reactions.

Time Allocation: 2.5 hours



Materials

Student Supplied Materials

Quantity	Item Description
1	Bottle of distilled water
2	Coffee mugs
1	Pair of scissors
1	Roll of paper towels
1	Source of tap water
1	Timer, clock, or watch with second hand

HOL Supplied Materials

Quantity	Item Description
1	Digital thermometer
4	Foam cups, 8 oz.
1	Graduated cylinder, 25 mL
2	Pairs of gloves
1	Pair of safety goggles
1	Experiment Bag: Hess's Law 2 - Ammonium, NH_3 (labeled as aqueous Ammonia: NH_4OH), 2 M, 10 mL 2 - Ammonium chloride, NH_4Cl - 2 M - 10 mL 2 - Hydrochloric acid, HCl - 2 M - 20 mL 2 - Sodium hydroxide, NaOH - 2 M - 20 mL 1 - Long thin stem pipet, 4.5 mL

Note: To fully and accurately complete all lab exercises, you will need access to:

1. A computer to upload digital camera images.
2. Basic photo editing software such as Microsoft Word® or PowerPoint®, to add labels, leader lines, or text to digital photos.
3. Subject-specific textbook or appropriate reference resources from lecture content or other suggested resources.

Note: The packaging and/or materials in this LabPaq kit may differ slightly from that which is listed above. For an exact listing of materials, refer to the Contents List included in your LabPaq kit.

Background

Thermochemistry

Thermochemistry is the study of heat (thermal energy) that accompanies chemical reactions. Nearly all chemical reactions involve the release or absorption of heat energy which spontaneously transfers from warmer to cooler matter. If a chemical reaction occurs and heat is released to the surrounding environment, the reaction is considered **exothermic**. Therefore, in an exothermic reaction, the surrounding temperature increases. Alternatively, if a chemical reaction absorbs heat energy from its surrounding environment, the reaction is **endothermic**. In an endothermic reaction, the surrounding temperature decreases. For reactions that are happening in an aqueous solution, the water is surrounding the reactants and products. That means that the reactants and products will release or absorb energy to or from the water. See Figure 1.

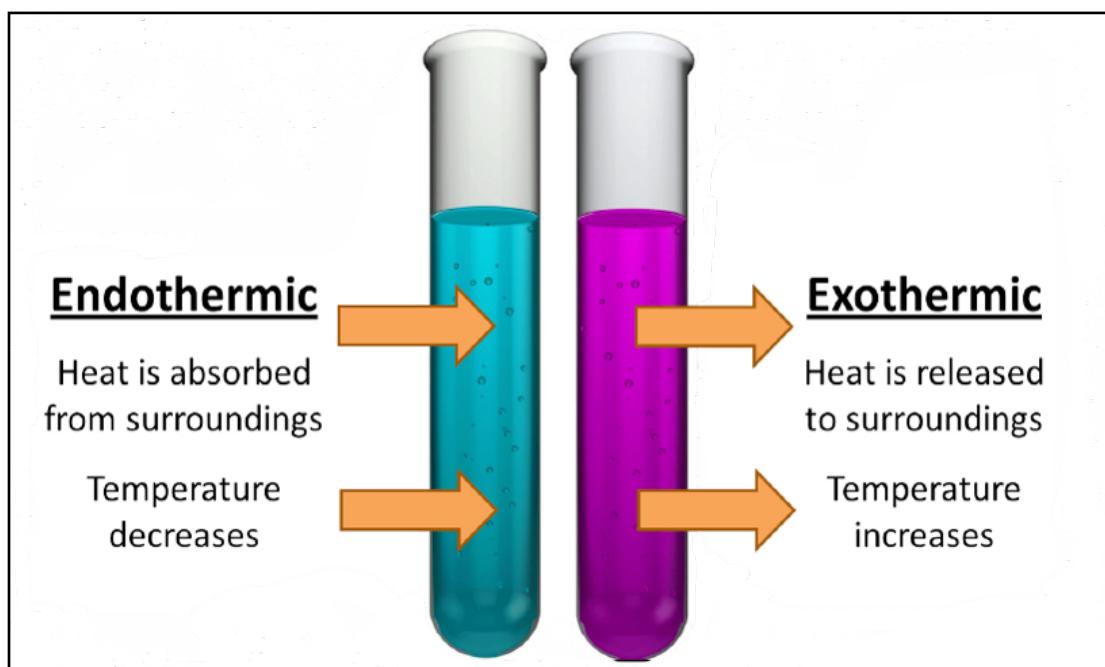


Figure 1. Qualities of endothermic and exothermic reactions. ©Aspect3D

The amount of energy that flows as heat during a chemical reaction can be measured. **Enthalpy** (H) is the sum of the internal energy of the system (E), which includes heat, and the product of the pressure (P) and volume (V). When a chemical reaction is at a constant pressure, the amount of heat given off or absorbed is called the **change in enthalpy** (ΔH) or the **heat of reaction**. The unit of measure for change in enthalpy, as identified by the International System of Units, is the **joule** (J). One thousand joules is equal to one kilojoule (1 kJ). When a change in enthalpy accompanies the formation of 1 mole of a compound under standard conditions from its pure elements, the enthalpy is denoted as (ΔH°_f), which represents the **standard enthalpy of formation**. The standard enthalpy of formation is known for a vast number of substances.

Thermodynamics

Thermodynamics is the study of how heat, energy, and work are interrelated. The First Law of Thermodynamics is the **Law of Conservation of Energy** which states that energy can neither be created nor destroyed but it can be converted from one form to another. Therefore, all energy transferred between a system and its surroundings during the conversion of reactants to products must be accounted for as **heat** or **work**. When the standard enthalpy of formation is known for all products and reactants in a reaction, then the change in the enthalpy of the reaction (ΔH) is equal to the enthalpy of the products (H_{products}) minus the enthalpy of the reactants ($H_{\text{reactants}}$).

$$\Delta H = H_{\text{products}} - H_{\text{reactants}}$$

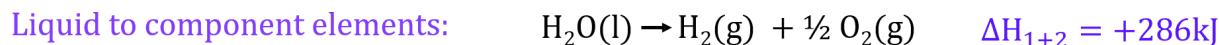
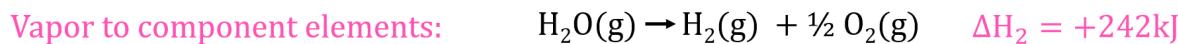
When a reaction releases heat energy and is exothermic, the enthalpy of the products is less than the reactants, and the ΔH will be a *negative number*. When the reaction absorbs energy from the surroundings and is endothermic, the products have greater enthalpy than the reactants, and ΔH is a *positive number*. For example, water (H_2O) is formed from the pure elements hydrogen (H_2) and oxygen (O_2). The reaction is exothermic, and 286 kJ of energy are released:



Hess's Law

Hess's law states that the total change in enthalpy is independent of the pathway. This means that if a reaction takes place in one step or in multiple steps, the ΔH for the overall process must be the sum of the ΔH values of the constituent reactions.

For example, the decomposition of liquid water into its component elements, $\text{H}_2(\text{g})$ and $\text{O}_2(\text{g})$, occurs in two reactions. In the first reaction, liquid water [$\text{H}_2\text{O}(\text{l})$] becomes gaseous water vapor [$\text{H}_2\text{O}(\text{g})$]. In the second reaction, water vapor [$\text{H}_2\text{O}(\text{g})$] decomposes into its component elements; $\text{H}_2(\text{g})$ and $\text{O}_2(\text{g})$. Each reaction has its own enthalpy, which are combined to obtain the total change in enthalpy. Note that as this reaction was reversed from formation to decomposition so the sign of the enthalpy changed; going from negative to positive.



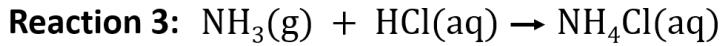
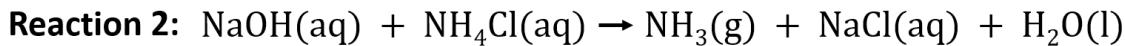
Notice that this reaction confirms Hess's law: the heat absorbed in the first reaction (+44 kJ) and the heat absorbed in the second reaction (+242 kJ) equals the total heat absorbed in the overall reaction (+286 kJ).



Dr. Germain Hess (1802 – 1850) was a Swiss-born Russian chemist who studied heat in chemical reactions which formed the foundation of thermochemistry. After leaving his career in medicine, Hess focused on chemistry through his early investigations of minerals and natural gas. In 1840, Hess announced the law of constant heat summation, which later became known as Hess's law. The experiments that led to Hess's law joined thermodynamics and chemistry, demonstrating that the law of conservation energy applied to chemical and physical changes.

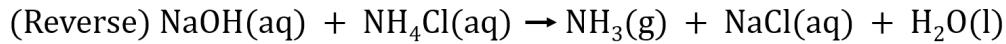
Hess' Law Laboratory

In this laboratory experience, you will measure ΔH for two reactions and use your findings to predict ΔH for a third reaction. More specifically, you will measure the temperature of a reaction that has the products $\text{NH}_3 + \text{NaCl} + \text{H}_2\text{O}$ and a reaction that has the products $\text{H}_2\text{O} + \text{NaCl}$. You will then use your findings to predict the temperature of a reaction that produces NH_4Cl . You will then perform the reaction for NH_4Cl and compare your predicted ΔH to temperatures you measure. The following chemical equations describe the three reactions:

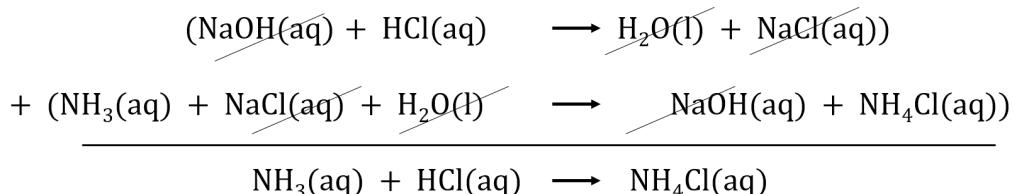


You will perform the third reaction as a tool to validate Hess's law; the ΔH for the third reaction should equal the sum of the ΔH values of the two constituent reactions.

Remember that the intermediate reactions can be reversed (and therefore, the sign will be reversed) when calculating the enthalpy change. For these intermediate reactions, they can be added together to get the overall reaction (when adding equations, you can cross out the effects of the same chemicals on the opposite side of the equation). You will reverse the second reaction:



The overall intermediate reactions will be added together to equal a third reaction:



Comparison of the calculated results will verify the generalization known as Hess's law. In this case, the target reaction $\text{NH}_3 + \text{HCl} \rightarrow \text{NH}_4\text{Cl}$ can also be performed directly and the results compared to the second two reactions.

Heat energy exchanges do not occur instantaneously and it takes time for energy to move from a hot object to a cold one. An acceptable solution to this problem is to obtain a cooling curve for the heat energy exchange and then extrapolate the data back to the exact time that the exchange began. You will create a cooling trend by taking the temperature of the solution every 20 seconds. Figure 2 shows a sample graph from hypothetical data.

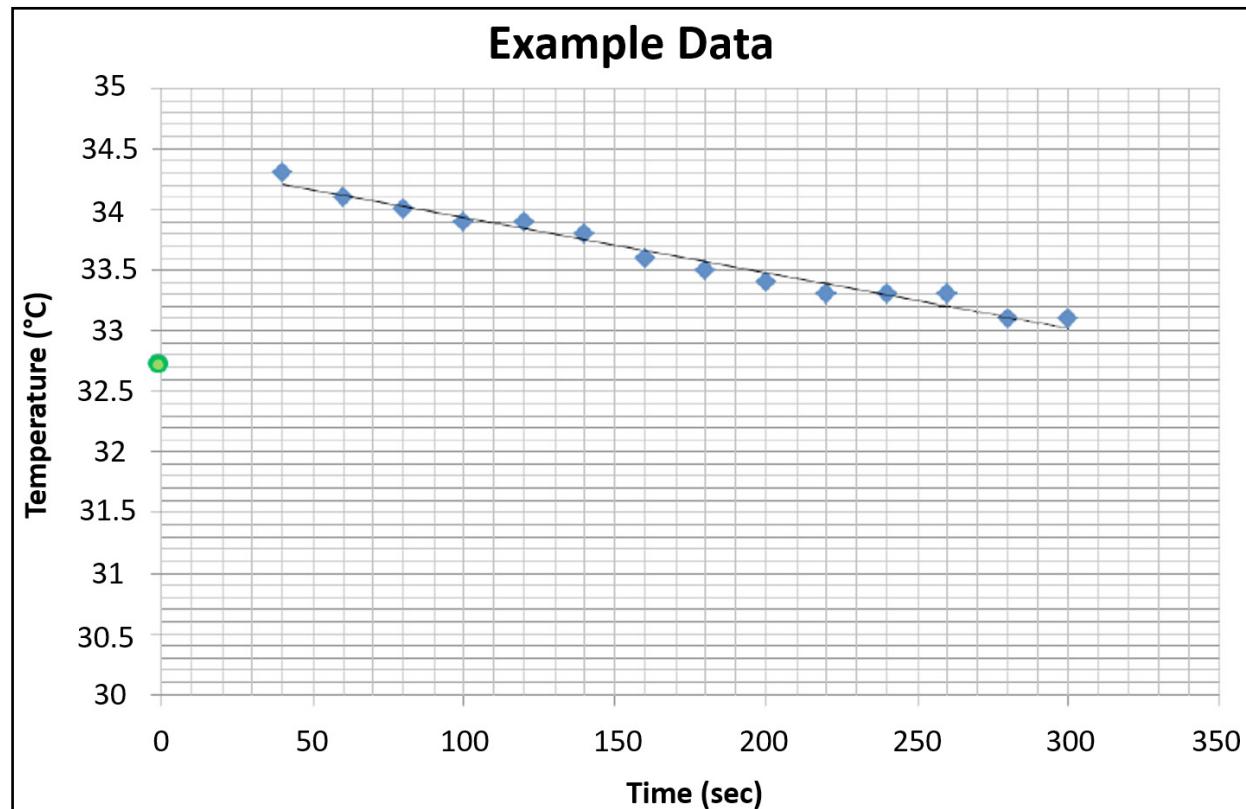


Figure 2. Example of a cooling trend. The green dot represents the temperature of the system before the reaction has begun.

You will create a cooling trend by taking data every 20 seconds. You cannot get the immediate change in heat from mixing the solutions, so you will extrapolate back to point "0" from the cooling curve. Using the same example data as in Figure 2, the extrapolation is done by extending the trend line from the cooling curve back to time "0." See Figure 3.

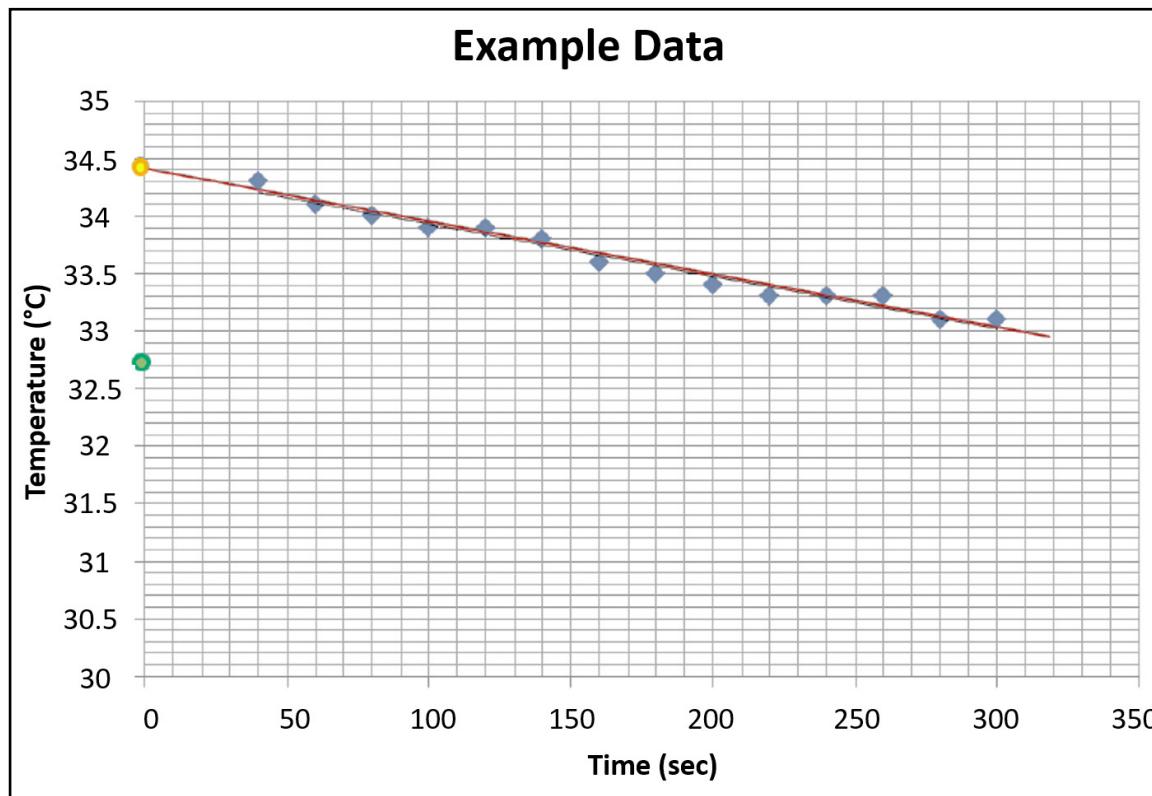


Figure 3. Example data for a cooling curve. The trend line has been extended to the “0” time point to predict the initial temperature as the reaction began. The yellow dot represents temperature at time “0”; the green dot represents temperature before the reaction began.

Calculations

Molarity (M or mol/L) is a measure of concentration that is calculated as number of moles of solute (mol) per volume of solution (L). The equation is stated as:

$$\text{Molarity} (M) = \text{moles of solute (mol)} / \text{volume of solution (L)}$$

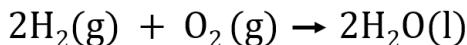
The **stoichiometry** (relative quantities of reactants and products) of a balanced chemical equation allows for the calculation of the amount of unknown reactants or products. In this experiment, you will calculate the amount of moles in the reactants to quantify the amount of moles produced in the product. To calculate the quantitative amount of product expected through a chemical reaction, one needs a balanced chemical equation and a known mass or molar amount for one of the reactants.

Step 1) Check to ensure that the chemical equation is balanced.

Step 2) Determine the number of moles of one of the reactants.

Step 3) Evaluate the molar ratio of the reactant and the product.

For example, consider the following equation:



Given 0.4 moles of H_2 , and 0.2 moles of O_2 (half the moles of H_2), the reaction produces 0.4 moles of H_2O (the same number of moles as H_2 , and double the number of moles of O_2).

After the moles of product are determined, the heat gained or lost from the reaction can be calculated. The equation used to calculate heat gained or lost (q_{rxn}) is:

$$q_{\text{rxn}} = (\text{mass of solution}) \times (\text{specific heat}) \times \Delta T$$

where:

$$\text{Density} = 1.02 \text{ g/mL}$$

Note: For all solutions in this experiment, use density to determine mass.

$$\text{Specific heat} = 4.184 \text{ J/g } ^\circ\text{C}$$

and:

$$\Delta T ({}^\circ\text{C}) = \text{Final temperature} - \text{Initial temperature}$$

Note: The heat of the reaction, q_{rxn} , could be determined by taking the negative of the heat gained by the solution, q_{soln} , plus that gained by the calorimeter, q_{cal} : $q_{\text{rxn}} = -(q_{\text{soln}} + q_{\text{cal}})$. A small amount of heat is absorbed by the calorimeter, which can be measured as the **calorimetry constant**, q_{cal} . However, the amount of heat lost to the calorimeter is so insignificant that it is often left off or simply assumed to be $1 \text{ J} \times \Delta T$. ($q_{\text{cal}} = c \times \Delta T$).

Once the total thermal energy transfer is known, the enthalpy of reaction can be determined using the following equation:

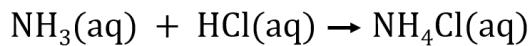
$$\Delta H = q_{\text{rxn}} / \text{moles of product in solution}$$

To find the percent difference, use the following equation (use the value collected directly from $\text{NH}_3 + \text{HCl} \rightarrow \text{NH}_4\text{Cl}$ as the “theoretical value” and the value obtained from the sum of the other two reactions as the “experimental value”):

$$\text{Percent Difference} = \frac{\text{Experimental value} - \text{Theoretical value}}{(\text{Theoretical value})} \times 100\%$$

Example:

Consider the following reaction:



Note: The numbers in this example are not intended to be the correct ΔH for this equation.

Using the example data shown in Figures 2 and 3, assume that 30 mL of NH_3 and 30 mL of HCl was used, and they were each a 3 M solution. Because you know the molarity and the amount of solution used, you can determine the amount of each chemical in moles:

$$3\text{M} = \frac{3\text{moles}}{1\text{Liter}} \times \frac{1\text{Liter}}{1000\text{mL}} \times 30\text{mL} = 0.09\text{moles}$$

Considering the stoichiometry of the chemical equation, the reactants and the product are each in a 1:1 ratio. Therefore, when the heat of the reaction is determined, it is for 0.09 moles of NH_4 .

When performing this experiment, you extrapolated the data to get an increase in temperature of 15 degrees within the calorimeter. You can determine the heat of the reaction:

$$\text{Density} = \frac{1.02\text{g}}{1\text{mL}} \times 60\text{mL} = 61.2\text{g} = \text{total mass}$$

$$q_{\text{rxn}} = (61.2\text{g}) \times (4.184\text{J/g }^\circ\text{C}) \times (-15^\circ\text{C}) = -3840.9\text{J} = -3.84\text{kJ}$$

$$\Delta H = -3.84\text{kJ}/0.09\text{mol} = -42.66\text{kJ/mol}$$

Finally, assume that when the ΔH of the intermediate equations were added together, they summed to -48.22 kJ/mol.

$$\text{Percent difference} = \frac{[(-48.22\text{kJ/mol}) - (-42.66\text{kJ/mol})]}{(-42.66\text{kJ/mol})} \times 100\% = 13.0\%$$

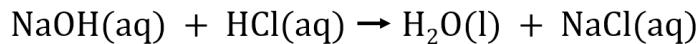
Exercise 1: Testing Hess's Law

In this laboratory experience, you will measure ΔH for two reactions and use your findings to predict ΔH for a third reaction.

Important: Wear safety goggles and gloves throughout this laboratory exercise.

Procedure

Part 1: First Reaction (NaOH + HCl)



1. Construct a calorimeter from 2 foam cups:

- Set a foam cup in a coffee mug. This will act as the base of the calorimeter and will hold the solution as the reaction proceeds.
- Trim the lip of a second foam cup, about 3 cm from the top using a pair of scissors. This will act as the lid of the calorimeter. Place the trimmed foam cup upside down in the top of the other foam cup, providing an insulated environment for monitoring temperature as shown in Figure 4.
- Using the digital thermometer, poke a hole in the top cup so a thermometer can be inserted. See Figure 4 again for complete setup.

Note: Use care when inserting the thermometer into the calorimeter since it has a pointed tip that could puncture the lower cup if inserted too forcefully. However, ensure that the thermometer can touch the bottom of the bottom cup. If not, trim a little more of the top "lid" of the calorimeter.



Figure 4. Calorimeter. **A.** Cutting off 3 cm of the top of a foam cup. **B.** Complete setup for calorimeter.

2. Use the clean 25 mL graduated cylinder to accurately measure 10.0 mL of 2M NaOH from the dropper bottle. When nearing 10.0 mL mark, add drops slowly to ensure a measurement of exactly 10.0 mL.
3. Remove the lid from the calorimeter and pour the 10.0 mL of NaOH into the foam base. Replace the lid with the digital thermometer in it.
4. Rinse and dry the graduated cylinder and accurately measure 10.0 mL of 2M HCl.
5. Pour the 10.0 mL of HCl into an unused foam cup. Set the foam cup in an empty coffee cup to prevent it from tipping over.
6. Turn on the digital thermometer and set it to record in Celsius (°C). Wait at least 1 minute to allow the temperature to equilibrate. Record the temperature of the NaOH solution in **Data Table 1** of your **Lab Report Assistant**.
7. Remove the thermometer, rinse the tip with distilled water, dry it with a paper towel, and place the thermometer in the HCl solution. Wait at least 1 minute and record the temperature of the solution in **Data Table 1**.
8. Calculate the average starting temperature by averaging the initial temperatures of NaOH and HCl and record the average in **Data Table 1**.
9. Remove the thermometer, rinse the tip with distilled water, and dry the thermometer with a paper towel.
10. Pour the contents of the foam cup containing HCl into the base of the calorimeter containing NaOH, combining the 2 solutions. Quickly place the foam lid on top of the cup containing the combined solutions and insert the thermometer through the hole in the lid. Be careful when inserting the thermometer to ensure its pointed tip does not puncture the lower foam cup. Immediately record the initial temperature of the mixed solutions in **Data Table 2** of your **Lab Report Assistant**.
11. Record temperature every 20 seconds for 5 minutes in **Data Table 2**.
12. Create a scatter plot using the data in **Data Table 2**. Plot time on the independent axis (x-axis) and temperature on the dependent axis (y-axis). Add a linear trendline that represents temperature change. Extend the trendline to the y-axis, time “0”. The extrapolation at the “0-second time” most likely represents the “highest change in temperature of the mixture.” Compare the extrapolated temperature to the initial recorded temperature of the mixture and record the greater temperature in **Data Table 1** as the highest temperature of the mixture. The graph should look similar to the sample cooling curve in Figure 3. **Resize** and insert an image of the graph into **Graph 1** of your **Lab Report Assistant**. Refer to the appendix entitled, “Resizing an Image” for guidance.
13. Subtract the greatest difference in temperature from the initial average temperature of the 2 separate solutions to get “ ΔT ,” and record it in **Data Table 1**.
14. Properly dispose of the solution in the calorimeter. Recall that the reaction of an acid (HCl) and base (NaOH) is a neutralization reaction that produces salt and water.
15. Rinse all equipment with distilled water in preparation for the second reaction. This includes the foam cups and the 25 mL graduated cylinder.

Part 2: Second Reaction (NaOH + NH₄Cl)

16. Place the calorimeter assembly into an empty coffee mug again to prevent it from tipping over. Make sure you are still wearing your safety goggles and gloves.
17. Use the clean 25 mL graduated cylinder to accurately measure 10.0 mL of 2M NaOH from the dropper bottle. When nearing 10.0 mL mark, add drops slowly to get the exact amount of 10.0 mL.
18. Pour the 10.0 mL of NaOH into the bottom cup of the foam calorimeter.
19. Rinse and dry the graduated cylinder and accurately measure 10.0 mL of 2M NH₄Cl.
20. Pour the 10.0 mL of NH₄Cl into another foam cup and place the cup into a second empty coffee cup to prevent it from tipping over.
21. Turn on the digital thermometer and place it into the NaOH solution. Wait at least 1 minute and record the temperature of the solution in **Data Table 3** of your **Lab Report Assistant**.
22. Remove the thermometer, rinse the tip with distilled water, dry it with a paper towel, and place the thermometer into the NH₄Cl solution. Wait at least 1 minute and record the initial temperature of the solution in **Data Table 3**.
23. Remove the thermometer, rinse the tip with distilled water, and dry it with a paper towel.
24. Pour the contents of one foam cup into the second one, combining the 2 solutions. Quickly place the foam lid on top of the cup containing the combined solutions and insert the thermometer through the hole in the lid. Be careful when inserting the thermometer to ensure its pointed tip does not puncture the lower foam cup. Record the initial temperature of the combined solutions as quickly as you see it in **Data Table 4** of your **Lab Report Assistant**.
25. Record the temperature every 20 seconds for 5 minutes in **Data Table 4**.
26. Create a scatter plot using the data in **Data Table 4**. Plot time on the independent axis (x-axis) and temperature on the dependent axis (y-axis). Add a linear trendline that represents temperature change. Extend the trendline to the y-axis, time 0. The extrapolation at the “0-second time” most likely represents the “highest temperature of the mixture.” Compare the extrapolated temperature to the initial recorded temperature of the mixture and record the greater temperature in **Data Table 3** as the highest temperature of the mixture. The graph should look similar to the sample cooling curve in Figure 3. Resize and insert an image of the graph into **Graph 2** of your **Lab Report Assistant**.
27. Subtract the greatest difference in temperature of the combined solutions from the initial average temperature of the 2 separate solutions to get “ ΔT ,” and record it in **Data Table 3**.
28. Properly dispose of the solution in the calorimeter.
29. Rinse all equipment with distilled water in preparation for the third reaction. This includes the foam cups, and the 25 mL graduated cylinder.

Part 3: Third Reaction (NH₃ + HCl)

30. Place the calorimeter assembly into an empty coffee mug again to prevent it from tipping over.
31. Use the clean 25 mL graduated cylinder to accurately measure 10.0 mL of 2M NH₃ from the dropper bottle. When nearing the 10.0 mL mark, add drops slowly to get the exact amount of 10.0 mL.
32. Pour the 10.0 mL of NH₃ into the bottom cup of the foam calorimeter.
33. Rinse and dry the graduated cylinder and accurately measure 10.0 mL of 2M HCl.
34. Pour the 10.0 mL of HCl into another foam cup and place the cup into a second empty coffee cup to prevent it from tipping over.
35. Turn on the digital thermometer and place it into the NH₃ solution. Wait at least 1 minute and record the temperature of the solution in **Data Table 5** of your **Lab Report Assistant**.
36. Remove the thermometer, rinse the tip with distilled water, dry it with a paper towel, and place the thermometer into the HCl solution. Wait at least 1 minute and record the temperature of the solution in **Data Table 5**.
37. Remove the thermometer, rinse the tip with distilled water, and dry it with a paper towel.
38. Pour the contents of one foam cup into the second one, combining the 2 solutions. Quickly place the foam lid on top of the cup containing the combined solutions and insert the thermometer through the hole in the lid. Be careful when inserting the thermometer to ensure its pointed tip does not puncture the lower foam cup. Record the initial temperature as quickly as you see it in **Data Table 6** of your **Lab Report Assistant**.
39. Record the temperature that you see every 20 seconds for 5 minutes in **Data Table 6**.
40. Create a scatter plot using the data in **Data Table 6**. Plot time on the independent axis (x-axis) and temperature on the dependent axis (y-axis). Add a linear trendline that represents temperature change. Extend the trendline to the y-axis, time 0. The extrapolation at the “0-second time” most likely represents the “highest temperature of the mixture.” Compare the extrapolated temperature to the initial recorded temperature of the mixture and record the greater temperature in **Data Table 5** as the highest temperature of the mixture. The graph should look similar to the sample cooling curve in Figure 3. Resize and insert an image of the graph into **Graph 3** of your **Lab Report Assistant**.
41. Subtract the greatest difference in temperature of the combined solutions from the initial average temperature of the 2 separate solutions to get “ ΔT ,” and record it in **Data Table 5**.

Cleanup:

42. Properly dispose of the solution in the calorimeter.
43. Rinse all equipment with distilled water. This includes the foam cups, and the 25 mL graduated cylinder.
44. Dry and return all equipment to the lab kit for future use.
45. When you are finished uploading photos and data into your **Lab Report Assistant**, save and zip your file to send to your instructor. **Refer** to the appendix entitled “Saving Correctly,” and the appendix entitled “Zipping Files,” for guidance with saving the **Lab Report Assistant** in the correct format.

Questions

- A. What were the starting temperatures for each of the reactions? Use the scatter plots in Graph 1, Graph 2, and Graph 3 to support your answers.
- B. Calculate the heat loss or heat gain of the 3 solution mixtures (q_{rxn}). Then calculate the ΔH for each reaction. Show your calculations.
- C. Use Hess's law to determine ΔH for the first 2 reactions and then add them together to determine ΔH for the third reaction: $\text{NH}_3 + \text{HCl} \rightarrow \text{NH}_4\text{Cl}$.
- D. Compare the results of question “C” with the experimental results of the reaction:
$$\text{NH}_3 + \text{HCl} \rightarrow \text{NH}_4\text{Cl}$$
 (calculate the percent difference).
- E. Use the thermodynamic quantities given below to calculate the theoretical ΔH for this reaction: $\text{NH}_3 + \text{HCl} \rightarrow \text{NH}_4\text{Cl}$
 - ΔH°_f for NH_3 (aq) = - 80.29 kJ/mol
 - ΔH°_f for HCl (aq) = - 167.2 kJ/mol
 - ΔH°_f for NH_4^+ (aq) = - 132.5 kJ/mol
 - ΔH°_f for Cl^- (aq) = - 167.2 kJ/mol
- F. What was the percent difference of the various methods used when comparing the results of Hess's law method and the experimental results to the theoretical value?
- G. Were the reactions performed in this laboratory exercise exothermic or endothermic? How could you determine this?
- H. Define Hess's law. Did your experimental results support Hess's law? Use your data to explain your answer.
- I. What are some possible sources of error in this experiment?