

# Calorimetry and Hess's Law

A man working for a cleaning firm was told by his employer to pour some old cleaning supplies into a glass container for disposal. Some of the supplies included muriatic (hydrochloric) acid,  $\text{HCl}(aq)$ , and a drain cleaner containing lye,  $\text{NaOH}(s)$ . When the substances were mixed, the container shattered, spilling the contents onto the worker's arms and legs. The worker claims that the hot spill caused burns, and he is, therefore, suing his employer. The employer claims that the worker is lying because the solutions were at room temperature before they were mixed. The employer says that a chemical burn is unlikely because tests after the accident revealed that the mixture had a neutral pH, indicating that the  $\text{HCl}$  and  $\text{NaOH}$  were neutralized. The court has asked you to evaluate whether the worker's story is supported by scientific evidence.

Chemicals can be dangerous because of their special storage needs. Acids cannot be stored in metal containers, and organic solvents cannot be kept in plastic containers. Chemicals that are mixed and react are even more dangerous because many reactions release large amounts of heat. Glass, although relatively nonreactive with solutions of pure substances, is heat-sensitive and can shatter if there is a sudden change in temperature due to a reaction. Some glassware, such as Pyrex, is heat-conditioned but can still fracture under extreme heat conditions, especially if scratched.

You will measure the amount of heat released by mixing the chemicals in two ways. First you will break the reaction into steps and measure the heat change of each step. Then you will measure the heat change of the reaction when it takes place all at once. When you are finished, you will be able to use the calorimetry equation from the chapter "Causes of Change" to determine the following:

- the amount of heat evolved during the overall reaction
- the amount of heat for each step
- the amount of heat for the reaction in kilojoules per mole
- whether this heat could have raised the temperature of the water in the solution high enough to cause a burn

## OBJECTIVES

**Demonstrate** proficiency in the use of calorimeters and related equipment.

**Relate** temperature changes to enthalpy changes.

**Determine** the heat of reaction for several reactions.

**Demonstrate** that the heat of reaction can be additive.



**Always wear safety goggles and lab apron to protect your eyes and clothing.** If you get a chemical in your eyes, immediately flush the chemical out at the eyewash station while calling to your teacher. Know the location of the emergency lab shower and eyewash station and the procedures for using them.

**Calorimetry and Hess's Law** *continued*

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**Do not touch any chemicals.** If you get a chemical on your skin or clothing, wash the chemical off at the sink while calling to your teacher. Make sure you carefully read the labels and follow the precautions on all containers of chemicals that you use. If there are no precautions stated on the label, ask your teacher what precautions to follow. Do not taste any chemicals or items used in the laboratory. Never return leftovers to their original container; take only small amounts to avoid wasting supplies.



**Call your teacher in the event of a spill.** Spills should be cleaned up promptly, according to your teacher's directions.

**Acids and bases are corrosive.** If an acid or base spills onto your skin or clothing, wash the area immediately with running water. Call your teacher in the event of an acid spill. Acid or base spills should be cleaned up promptly.



**Do not heat glassware that is broken, chipped, or cracked.** Use tongs or a hot mitt to handle heated glassware and other equipment because hot glassware does not always look hot.

**When using a Bunsen burner, confine long hair and loose clothing.** If your clothing catches fire, WALK to the emergency lab shower and use it to put out the fire.

**MATERIALS**

- balance
- distilled water
- glass stirring rod
- graduated cylinder, 100 mL
- HCl solution, 0.50 M
- HCl solution, 1.0 M
- NaOH pellets
- NaOH solution, 1.0 M
- plastic-foam cups (or calorimeters)
- spatula
- thermometer
- watch glass

**Optional Equipment**

- CBL unit
- graphing calculator with link cable
- Vernier temperature probe

**Calorimetry and Hess's Law** *continued*

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**Procedure****ADVANCE PREPARATION**

1. Put on safety goggles, gloves, and lab apron.
2. If you are not using a plastic-foam cup as a calorimeter, ask your teacher for instructions on using the calorimeter. At various points in the procedure, you will need to measure the temperature of the solution within the calorimeter.

**Thermometer Procedure continues on page 39.**

**CBL AND SENSORS PROCEDURE**

3. Connect the CBL to the graphing calculator with the unit-to-unit link cable using the I/O ports located on each unit. Connect the temperature probe to the CH1 port. Turn on the CBL and the graphing calculator. Start the program CHEMBIO on the graphing calculator.
  - a. Select option *SET UP PROBES* from the MAIN MENU. Enter 1 for the number of probes. Select the temperature probe from the list. Enter 1 for the channel number. Select *USE STORED* from the CALIBRATION menu.
  - b. Select the *COLLECT DATA* option from the MAIN MENU. Select the *TRIGGER* option from the DATA COLLECTION menu.
4. Measure the temperature by gently inserting the Vernier temperature probe into the hole in the calorimeter lid.

**Reaction 1: Dissolving NaOH**

5. Pour about 100 mL of distilled water into a graduated cylinder. Measure and record the volume of the water to the nearest 0.1 mL. Pour the water into your calorimeter.
6. Using the temperature probe, measure the temperature of the water. Press TRIGGER on the CBL to collect the temperature reading. Record this temperature in your data table. Select *STOP* from the TRIGGER menu on the graphing calculator. Leave the probe in the calorimeter.
7. Select the *COLLECT DATA* option from the MAIN MENU. Select the *TIME GRAPH* option from the DATA COLLECTION menu. Enter 6 for the time between samples, in seconds. Enter 99 for the number of samples (the CBL will collect data for 9.9 min). Press ENTER. Select *USE TIME SETUP* to continue. If you want to change the number of samples or the time between samples, select *MODIFY SETUP*. Enter 0 for *Ymin*, enter 100 for *Ymax*, and enter 5 for *Yscl*.
8. Determine and record the mass of a clean and dry watch glass to the nearest 0.01 g. Remove the watch glass from the balance. While wearing gloves, obtain about 2 g of NaOH pellets, and put them on the watch glass.

**Calorimetry and Hess's Law** *continued*

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Use forceps when handling NaOH pellets. Measure and record the mass of the watch glass and the pellets to the nearest 0.01 g. **It is important that this step be done quickly because NaOH is hygroscopic. It absorbs moisture from the air, and its mass increases as long as it remains exposed to the air.**

9. Press ENTER on the graphing calculator to begin collecting the temperature readings for the water in the calorimeter.
10. Immediately place the NaOH pellets in the calorimeter cup, and gently stir the solution with a stirring rod. Place the lid on the calorimeter.
11. When the CBL displays DONE, use the arrow keys to trace the graph. Time in seconds is graphed on the  $x$ -axis, and the temperature readings are graphed on the  $y$ -axis. Record the highest temperature reading from the CBL in your data table.
12. When the reaction is finished, pour the solution into the container designated by your teacher for disposal of basic solutions.
13. Be sure to clean all equipment and rinse it with distilled water before continuing with the next procedure.

**Reaction 2: NaOH and HCl in solution**

14. Pour about 50 mL of 1.0 M HCl into a graduated cylinder. Measure and record the volume of the HCl solution to the nearest 0.1 mL. Pour the HCl solution into your calorimeter.
15. Select the *COLLECT DATA* option from the MAIN MENU. Select the *TRIGGER* option from the DATA COLLECTION menu. Using the temperature probe, measure the temperature of the HCl solution. Press TRIGGER on the CBL to collect the temperature reading. Record this temperature in your data table.
16. Pour about 50 mL of 1.0 M NaOH into a graduated cylinder. Measure and record the volume of the NaOH solution to the nearest 0.1 mL. **For this step only, rinse the temperature probe in distilled water.** Using the temperature probe, measure the temperature of the NaOH solution. Press TRIGGER on the CBL to collect the temperature reading. Record this temperature in your data table. Select *STOP* from the TRIGGER menu on the graphing calculator. Put the probe in the calorimeter.
17. Select the *COLLECT DATA* option from the MAIN MENU. Select the *TIME GRAPH* option from the DATA COLLECTION menu. Enter 6 for the time between samples, in seconds. Enter 99 for the number of samples. Press ENTER. Select *USE TIME SETUP* to continue. If you want to change the number of samples or the time between samples, select *MODIFY SETUP*. Enter 0 for  $Y_{min}$ , enter 100 for  $Y_{max}$ , and enter 5 for  $Y_{scl}$ . Press ENTER on the calculator to begin collecting temperature readings.
18. Pour the NaOH solution into the calorimeter cup, and stir gently. Place the lid on the calorimeter.

**Calorimetry and Hess's Law** *continued*

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- When the CBL displays DONE, use the arrow keys to trace the graph. Time in seconds is graphed on the  $x$ -axis, and the temperature readings are graphed on the  $y$ -axis. Record the highest temperature reading from the CBL in your data table.
- Pour the solution into the container designated by your teacher for disposal of mostly neutral solutions. Clean and rinse all equipment before continuing with the next procedure.

**Reaction 3: Solid NaOH and HCl in solution**

- Pour about 100 mL of 0.50 M HCl into a graduated cylinder. Measure and record the volume to the nearest 0.1 mL. Pour the HCl solution into your calorimeter.
- Select the *COLLECT DATA* option from the MAIN MENU. Select the *TRIGGER* option from the DATA COLLECTION menu. Using the temperature probe, measure the temperature of the HCl solution. Press TRIGGER on the CBL to collect the temperature reading. Record this temperature in your data table. Select *STOP* from the TRIGGER menu on the graphing calculator.
- Select the *COLLECT DATA* option from the MAIN MENU. Select the *TIME GRAPH* option from the DATA COLLECTION menu. Enter 6 for the time between samples, in seconds. Enter 99 for the number of samples. Press ENTER. Select *USE TIME SETUP* to continue. If you want to change the number of samples or the time between samples, select *MODIFY SETUP*. Enter 0 for  $Y_{min}$ , enter 100 for  $Y_{max}$ , and enter 5 for  $Y_{scl}$ . Press ENTER on the calculator to begin collecting temperature readings.
- Measure the mass of a clean and dry watch glass, and record it in your data table. Obtain approximately 2 g of NaOH. Place it on the watch glass, and record the total mass to the nearest 0.01 g. **It is important that this step be done quickly because NaOH is hygroscopic.**
- Press ENTER on the graphing calculator to begin collecting the temperature readings for the water in the calorimeter.
- Immediately place the NaOH pellets in the calorimeter, and gently stir the solution. Place the lid on the calorimeter.
- When the CBL displays DONE, use the arrow keys to trace the graph. Time in seconds is graphed on the  $x$ -axis, and the temperature readings are graphed on the  $y$ -axis. Record the highest temperature reading from the CBL in your data table.
- When the reaction is finished, pour the solution into the container designated by your teacher for disposal of basic solutions.
- Clean all apparatus and your lab station. Check with your teacher for the proper disposal procedures. Any excess NaOH pellets should be disposed of in the designated container. Always wash your hands thoroughly after cleaning up the lab area and equipment.

**Calorimetry and Hess's Law** *continued*

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**THERMOMETER PROCEDURE**

3. Measure the temperature by gently inserting the thermometer into the hole in the calorimeter lid. The thermometer takes time to reach the same temperature as the solution inside the calorimeter, so wait to be sure you have an accurate reading. **Thermometers break easily, so be careful with them, and do not use them to stir a solution.**

**Reaction 1: Dissolving NaOH**

4. Pour about 100 mL of distilled water into a graduated cylinder. Measure and record the volume of the water to the nearest 0.1 mL. Pour the water into your calorimeter. Measure and record the water temperature to the nearest 0.1°C.
5. Determine and record the mass of a clean and dry watch glass to the nearest 0.01 g. Remove the watch glass from the balance. While wearing gloves, obtain about 2 g of NaOH pellets, and put them on the watch glass. Use forceps when handling NaOH pellets. Measure and record the mass of the watch glass and the pellets to the nearest 0.01 g. **It is important that this step be done quickly because NaOH is hygroscopic. It absorbs moisture from the air, and increases its mass as long as it remains exposed to the air.**
6. Immediately place the NaOH pellets in the calorimeter cup, and gently stir the solution with a stirring rod. **Do not stir with a thermometer.** Place the lid on the calorimeter. Watch the thermometer, and record the highest temperature in the data table. When the reaction is finished, pour the solution into the container designated by your teacher for disposal of basic solutions.
7. Be sure to clean all equipment and rinse it with distilled water before continuing with the next procedure.

**Reaction 2: NaOH and HCl in solution**

8. Pour about 50 mL of 1.0 M HCl into a graduated cylinder. Measure and record the volume of the HCl solution to the nearest 0.1 mL. Pour the HCl solution into your calorimeter. Measure and record the temperature of the HCl solution to the nearest 0.1°C.
9. Pour about 50 mL of 1.0 M NaOH into a graduated cylinder. Measure and record the volume of the NaOH solution to the nearest 0.1 mL. **For this step only, rinse the thermometer in distilled water, and measure the temperature of the NaOH solution in the graduated cylinder to the nearest 0.1°C. Record the temperature in your data table, and then replace the thermometer in the calorimeter.**
10. Pour the NaOH solution into the calorimeter cup, and stir gently. Place the lid on the calorimeter. Watch the thermometer, and record the highest temperature in the data table. When finished with this reaction, pour the solution into the container designated by your teacher for disposal of mostly neutral solutions.
11. Clean and rinse all equipment before continuing with the next procedure.

**Calorimetry and Hess's Law** *continued***Reaction 3: Solid NaOH and HCl in solution**

- 12.** Pour about 100 mL of 0.50 M HCl into a graduated cylinder. Measure and record the volume to the nearest 0.1 mL. Pour the HCl solution into your calorimeter, as shown in Figure B. Measure and record the temperature of the HCl solution to the nearest 0.1°C.
- 13.** Measure the mass of a clean and dry watch glass, and record it in your data table. Obtain approximately 2 g of NaOH. Place it on the watch glass, and record the total mass to the nearest 0.01 g. **It is important that this step be done quickly because NaOH is hygroscopic.**
- 14.** Immediately place the NaOH pellets in the calorimeter, and gently stir the solution. Place the lid on the calorimeter. Watch the thermometer, and record the highest temperature in the data table. When finished with this reaction, pour the solution into the container designated by your teacher for disposal of mostly neutral solutions.
- 15.** Clean all apparatus and your lab station. Check with your teacher for the proper disposal procedures. Any excess NaOH pellets should be disposed of in the designated container. Always wash your hands thoroughly after cleaning up the lab area and equipment.

**TABLE 1 TEMPERATURE DATA FOR EACH REACTION**

	Reaction 1	Reaction 2	Reaction 3
Mass of empty watch glass			
Mass of watch glass with NaOH			
Total volumes of liquid(s)			
Initial temperature			
Final temperature			

**Analysis**

- 1. Organizing Data** Write a balanced chemical equation for each of the three reactions that you performed. (Hint: Be sure to include states of matter for all substances in each equation.)

**Calorimetry and Hess's Law** *continued*

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**2. Analyzing Results** Find a way to get the equation for the total reaction by adding two of the equations from Analysis item 1 and then canceling out substances that appear in the same form on both sides of the new equation. (Hint: Start with the equation whose product is a reactant in a second equation. Add those two equations together.)

**3. Explaining Events** Explain why a plastic-foam cup makes a better calorimeter than a paper cup does.

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**4. Organizing Data** Calculate the change in temperature ( $\Delta t$ ) for each of the reactions.

**5. Organizing Data** Assuming that the density of the water and the solutions is 1.00 g/mL, calculate the mass,  $m$ , of liquid present for each of the reactions.

**6. Analyzing Results** Using the calorimeter equation ( $\text{Heat} = m \times \Delta t \times c_{p,\text{H}_2\text{O}}$ ), calculate the heat released by each reaction. (Hint: Use the specific heat capacity of water in your calculations;  $c_{p,\text{H}_2\text{O}} = 4.180 \text{ J/g}\cdot^\circ\text{C}$ .)

## Calorimetry and Hess's Law *continued*

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**7. Organizing Data** Calculate the moles of NaOH used in each of the reactions. (Hint: To find the number of moles in a solution, multiply the volume in liters by the molar concentration.)

**8. Analyzing Results** Calculate the  $\Delta H$  value in terms of kilojoules per mole of NaOH for each of the three reactions.

**9. Analyzing Results** Using your answer to Analysis item 2 and your knowledge of Hess's law from the chapter "Causes of Change," explain how the enthalpies for the three reactions should be mathematically related.

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**10. Analyzing Results** Which of the following types of heat of reaction apply to the enthalpies calculated in Analysis item 8: heat of combustion, heat of solution, heat of reaction, heat of fusion, heat of vaporization, and heat of formation?

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## Conclusions

**11. Evaluating Methods** Use your answers from Analysis items 7 and 8 to determine the  $\Delta H$  value for the reaction of solid NaOH with HCl solution by direct measurement and by indirect calculation.

**Calorimetry and Hess's Law** *continued*

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**12. Drawing Conclusions** Third-degree burns can occur if skin comes into contact for more than 4 s with water that is hotter than  $60^{\circ}\text{C}$  ( $140^{\circ}\text{F}$ ). Suppose someone accidentally poured hydrochloric acid into a glass-disposal container that already contained the drain cleaner NaOH and the container shattered. The solution in the container was approximately 55 g of NaOH and 450 mL of hydrochloric acid solution containing 1.35 mol of HCl (a 3.0 M HCl solution). If the initial temperature of the solutions was  $25^{\circ}\text{C}$ , could a mixture hot enough to cause burns have resulted?

**13. Applying Conclusions** For the reaction between the drain cleaner and HCl described in item 12, which chemical is the limiting reactant? How many moles of the other reactant remained unreacted?

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**14. Evaluating Results** When chemists make solutions from NaOH pellets, they often keep the solution in an ice bath. Explain why.

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**15. Evaluating Methods** You have worked with heats of solution for exothermic reactions. Could the same type of procedure be used to determine the temperature changes for endothermic reactions? How would the procedure stay the same? What would change about the procedure and the data?

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## Calorimetry and Hess's Law *continued*

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- 16. Drawing Conclusions** Which is more stable, solid NaOH or NaOH solution? Explain your answer.

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### Extensions

- 1. Applying Conclusions** When a strongly acidic or basic solution is spilled on a person, the first step is to dilute it by washing the area of the spill with a lot of water. Explain why adding an acid or a base to neutralize the solution immediately is not a good idea.

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- 2. Designing Experiments** A chemical supply company is going to ship NaOH pellets to a very humid place, and you have been asked to give advice on packaging. Design a package for the NaOH pellets. Explain the advantages of your package's design and materials. (Hint: Remember that the reaction in which NaOH absorbs moisture from the air is exothermic and that NaOH reacts exothermically with other compounds as well.)

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