

25. Hess's Law

Driving Questions

Is it possible to calculate the amount of energy released by the explosion of dynamite or during the formation of rust? These reactions cannot be easily or directly studied. How can you determine the enthalpy of a reaction indirectly when you cannot determine it directly?

Background

The heat released or absorbed by a chemical reaction is calculated by multiplying the mass m of the reactants, the specific heat capacity c of the solution, and the change in temperature ΔT produced when the reactants are mixed in a calorimeter.

$$q = m \times c \times \Delta T$$

The heat calculated is the heat change experienced by the calorimeter which is the surroundings. In chemistry, we are interested in the system that caused the change, generally a chemical reaction, which is the same in value as the heat calculated but opposite in sign.

q = heat absorbed or released by the surrounding

$-q$ = heat absorbed or released by the system

The change in enthalpy of a chemical reaction ΔH_{rxn} is the same as the heat produced by a system at constant pressure.

$$\Delta H_{\text{rxn}} = -q$$

The change in enthalpy of a chemical reaction can be determined two ways: directly and indirectly. The enthalpy of a reaction can be determined directly by performing the reaction in a calorimeter and calculating the enthalpy of the reaction using the equations given above. The enthalpy can be calculated indirectly by using the formulas above with Hess's law. Hess's law states that the energy change of the overall reaction is equal to the sum of the energy changes in alternative, individual steps that eventually make up the overall reaction.

$$\Delta H_{\text{rxn}} = \Delta H_{\text{step 1}} + \Delta H_{\text{step 2}} + \dots + \Delta H_{\text{step n}}$$

Hess's law is useful because it provides a method of determining the heat evolved or absorbed in a chemical process when direct measurement is not possible. Direct measurement of heat may not be possible if the reactants involved are toxic, expensive, or rare. Reactions that are too fast (like explosions) or occur too slowly are also able to be studied using Hess's law.

Materials and Equipment

For each student or group:

- ◆ Data collection system
- ◆ Temperature sensor
- ◆ Beaker, 250-mL
- ◆ Graduated cylinder, 50-mL
- ◆ Spatula
- ◆ Polystyrene cup (2)
- ◆ Lid for polystyrene cup
- ◆ Weighing paper (2)
- ◆ Wash bottle and waste container
- ◆ 1.0 M Hydrochloric acid (HCl), 25 mL
- ◆ 0.5 M Hydrochloric acid (HCl), 50 mL
- ◆ 1.0 M Sodium hydroxide (NaOH), 25 mL
- ◆ Sodium hydroxide (NaOH), pellets, 2.0 g
- ◆ Distilled (deionized) water, 50 mL

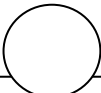
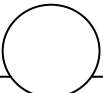
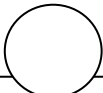
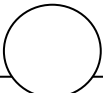
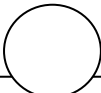
Safety

Add these important safety precautions to your normal laboratory procedures:

- ◆ Do not touch solid sodium hydroxide pellets with your hands. They are corrosive.
- ◆ Handle acids with care; they are corrosive.

Sequencing Challenge

The steps below are part of the Procedure for this lab activity. They are not in the right order. Determine the proper order and write numbers in the circles that put the steps in the correct sequence.

				
Use the data collected to calculate the molar enthalpy of the reaction directly and indirectly.	Dispose of the contents in the calorimeter. Repeat the experiment for the two remaining chemical reactions.	Measure and record the mass and volume of the starting materials.	Place the indicated starting material in the polystyrene calorimeter and begin collecting temperature data.	Add the second reactant and continue collecting data until the temperature decreases for 4 seconds.

Procedure

After you complete a step (or answer a question), place a check mark in the box () next to that step.

Note: When you see the symbol "◆" with a superscripted number following a step, refer to the numbered Tech Tips listed in the Tech Tips appendix that corresponds to your PASCO data collection system. There you will find detailed technical instructions for performing that step. Your teacher will provide you with a copy of the instructions for these operations.

Set Up

- Start a new experiment on the data collection system. ◆^(1.2)
- Connect the temperature sensor to the data collection system. ◆^(2.1)
- Create a graph display of Temperature (°C) versus Time (s). ◆^(7.1.1)
- Place the polystyrene calorimeter (two polystyrene cups nested together) in the 250-mL beaker.
- Place the temperature sensor inside the calorimeter.



Collect Data

Part 1 – Direct Reaction, One Step

- Measure 50.0 mL of 0.50 M HCl in a clean graduated cylinder and carefully pour it into the calorimeter.
- Record the exact volume of HCl used in Table 1 below.

Table 1: Direct reaction, solid sodium hydroxide pellets + 0.50 M hydrochloric acid

Volume (mL) of 0.50 M hydrochloric acid (HCl)	
Mass (g) of sodium hydroxide (NaOH)	
Initial temperature (°C)	
Final temperature (°C)	

- Measure 1.0 g of solid sodium hydroxide (NaOH) and set it aside.

CAUTION: Do not touch the NaOH pellets. They burn your skin.

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9. Record the exact mass in Table 1 above.
10. Why is it necessary to record the exact mass of sodium hydroxide used?
-
-
11. Start recording data. $\diamond^{(6.2)}$
12. After 60 seconds, add the solid sodium hydroxide to the calorimeter.
13. Attach the lid to the calorimeter and swirl the apparatus until all the sodium hydroxide has dissolved.
14. Adjust the scale of the graph as necessary to see any changes taking place. $\diamond^{(7.1.2)}$
15. Continue to collect data until a maximum temperature is reached and the temperature decreases for 4 seconds.
16. Stop recording data. $\diamond^{(6.2)}$
17. Name the data run "direct". $\diamond^{(8.2)}$
18. Determine the initial temperature (minimum temperature) and the final temperature (maximum temperature) and record the values in Table 1 above. $\diamond^{(9.4)}$
19. What is the chemical equation for the process that just occurred in the calorimeter?
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20. Remove the temperature sensor from the calorimeter. Rinse and dry the sensor.
21. Dispose of the solution in the calorimeter according to the teacher's instructions.
22. Rinse and dry the calorimeter.
23. Clean the graduated cylinder by rinsing it several times with water.

Part 2 – Indirect Reaction, Step One of Two

24. Place the clean, dry calorimeter into the 250-mL beaker.
25. Place the temperature sensor inside the calorimeter.
26. Measure 50.0 mL of distilled water in a graduated cylinder and pour it into the calorimeter.
27. Let the water sit until it reaches room temperature.
28. Record the exact volume of water in Table 2 below.

Table 2: Indirect reaction, step 1, solid sodium hydroxide pellets + water

Volume (mL) of water (H₂O)	
Mass (g) of sodium hydroxide (NaOH)	
Initial temperature (°C)	
Final temperature (°C)	

29. Why does the volume of water need to be measured carefully?

30. Measure 1.0 g of solid sodium hydroxide (NaOH) and set it aside.
31. Record the exact mass in Table 2 above.
32. Collect temperature data as the reactants are mixed by following the steps you used earlier in the lab:
- Start recording data. ♦^(6.2)
 - After 60 seconds add the NaOH pellets.
 - Attach the lid and swirl the apparatus until all the NaOH is dissolved.
 - Continue to record data until a maximum temperature is reached and the temperature decreases for 4 seconds.
 - Stop recording data. ♦^(6.2)
33. Name the data run "indirect step 1". ♦^(8.2)

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34. Determine the initial temperature (minimum temperature) and the final temperature (maximum temperature) and record the values in Table 2 above. ♦^(9.4)

35. What is the chemical equation for the process that just occurred in the calorimeter?

36. Is dissolving sodium hydroxide an exothermic or endothermic process? How do you know?

37. Transition to the next stage of the activity by carefully cleaning and drying the temperature sensor and calorimeter.

Part 2 – Indirect Reaction, Step Two of Two

38. Place the clean, dry calorimeter into the 250-mL beaker.

39. Place the clean, dry temperature sensor into the calorimeter.

40. Why is it necessary to have the temperature sensor and calorimeter clean and dry?

41. Measure 25.0 mL of 1.0 M HCl in a graduated cylinder and carefully pour it into the calorimeter.

42. Allow the acid to stand until it reaches room temperature.

43. Record the exact volume of HCl used in Table 3 below.

Table 3: Indirect reaction, step 2, sodium hydroxide pellets + 1.0 M hydrochloric acid

Volume (mL) of 1.0 M hydrochloric acid (HCl)	
Volume (mL) of 1.0 M sodium hydroxide (NaOH)	
Initial temperature (°C)	
Final temperature (°C)	

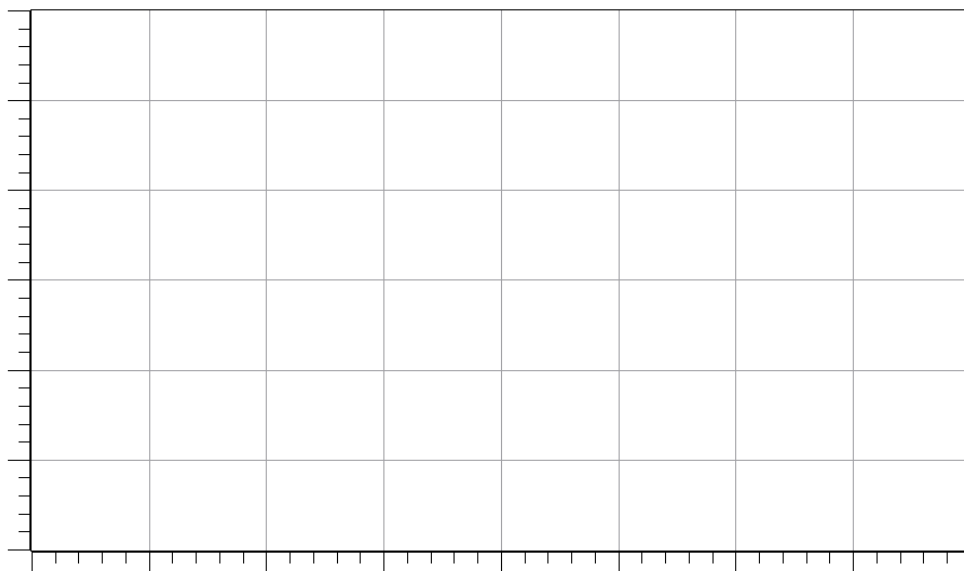
44. Clean the graduated cylinder by rinsing it several times with water.
45. Measure 25.0 mL of 1.0 M sodium hydroxide. Set it aside.
46. Record the exact volume of sodium hydroxide used in Table 3 above.
47. Collect temperature data as the reactants are mixed by following the steps you used earlier in the lab.
- Start recording data. ♦^(6.2)
 - After 60 seconds add the NaOH solution.
 - Attach the lid.
 - Continue to record data until a maximum temperature is reached and the temperature decreases for 4 seconds.
 - Stop recording data. ♦^(6.2)
48. Name the data run "indirect step 2". ♦^(8.2)
49. Determine the initial temperature (minimum temperature) and the final temperature (maximum temperature) and record the values in Table 3 above. ♦^(9.4)
50. What is the equation of the chemical reaction that just occurred in the calorimeter?
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51. Was this an exothermic or an endothermic process? How do you know?
-
52. Save your data file and clean up according to the teacher's instructions. ♦^(11.1)

Data Analysis

1. Create a graph with all three runs of data displayed on your data collection system. ♦^(7.1.3)

Note: Not all data collection systems will display three runs of data. If this is not possible, create one graph for the direct method and a second graph for the indirect method.

2. Sketch or print a copy of your Temperature (°C) versus Time (s) graph with all three data runs on one set of axes. Label each data run as well as the overall graph, the x-axis, the y-axis, and include units on the axes. ♦^(11.2)



Indirect Method

The steps below guide you through the process of calculating the molar enthalpy of reaction for the reaction between solid sodium hydroxide and aqueous hydrochloric acid. Through this indirect method, you calculate the molar enthalpy of each step and add the two steps together.

3. Calculate the temperature change for each step in the indirect method. Record your answers in Table 4 below.

Table 4: Indirect reactions, change in temperature

Temperature	Step 1: Dissolving NaOH	Step 2: 1.0 M Sodium Hydroxide + 1.0 M Hydrochloric Acid
Final temperature (°C)		
Initial temperature (°C)		
Change in temperature, ΔT (°C)		

4. Calculate the mass of solution for each step. Use the density of water (1.00 g/mL) to convert between volume and mass. Assume solutions have a density equal to that of water.

Table 5: Indirect reactions, total mass of solutions

Step 1: Dissolving NaOH		Step 2: 1.0 M Sodium Hydroxide + 1.0 M Hydrochloric Acid	
Mass of H ₂ O (g)		Mass of NaOH (g)	
Mass of NaOH (g)		Mass of HCl (g)	
Total mass of solution (g)		Total mass of solution (g)	

5. Calculate the heat q absorbed by the solution in each step using the formula below. Show your work, including the units involved. Convert joules to kilojoules in your final answer.

$$q = m \times c \times \Delta T$$

q = heat lost or gained by the solution

m = mass of the solution

c = specific heat of water = 4.184 J/(g·°C)

ΔT = change in temperature of the solution

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Table 6: Indirect reactions, heat absorbed by the solution

	Step 1: Dissolving NaOH	Step 2: 1.0 M Sodium Hydroxide + 1.0 M Hydrochloric Acid
$q = m \times c \times \Delta T$ Show your work		
q (J)		
q (kJ)		

6. Find the molar enthalpy of reaction ΔH for each step. The amount of heat absorbed by the solution is the opposite of the amount of heat generated by the change.

$$\Delta H = -q$$

$$\text{moles} = (\text{mass})/(\text{molar mass}) \quad \text{or} \quad \text{moles} = (\text{volume})(\text{molarity})$$

$$\text{molar enthalpy} = \frac{\Delta H}{\text{moles of substance}}$$

Table 7: Indirect reactions, molar enthalpy of reaction

	Step 1: Dissolving NaOH	Step 2: 1.0 M Sodium Hydroxide + 1.0 M Hydrochloric Acid
ΔH (kJ)		
Moles of NaOH		
$\Delta H/\text{mol}$ (kJ/mol)		

7. Calculate the molar enthalpy for the overall reaction between solid sodium hydroxide and aqueous hydrochloric acid by adding the molar enthalpy of reaction for each step.

Direct Method

8. Calculate the molar enthalpy for the reaction between solid sodium hydroxide and aqueous hydrochloric acid. Use the temperature data you collected by directly reacting the two reactants. Use the steps for the indirect method in this section to guide you if you get stuck. Record your answer to the correct number of significant figures.

Table 8: Direct reaction, molar enthalpy for the reaction between NaOH and HCl

Heat of Reaction Calculations	Direct Reaction: Solid Sodium Hydroxide + 0.50 M Hydrochloric Acid	
	Show your work in this column.	Record your answer here.
Change in Temperature, ΔT ($^{\circ}\text{C}$)		
Total mass of solution, solvent + solute (g)		
q (J)		
q (kJ)		
ΔH (kJ)		
moles of NaOH		
ΔH mol (kJ/mol)		

Analysis Questions

1. How do the enthalpies of reaction for the indirect method compare with the direct method? Are they the same?

2. What is the percent error for the results produced in this experiment? (In this case, let the actual yield equal the enthalpy calculated indirectly and the theoretical yield equal the enthalpy calculated directly.)

$$\text{percent error} = \left| \frac{\text{accepted value} - \text{experimental value}}{\text{accepted value}} \right| \times 100$$

Synthesis Questions

Use available resources to help you answer the following questions.

1. In your own words, what is Hess's law?

2. In what circumstances would Hess's law be useful?

3. What is the heat of reaction for the formation of “water gas” (a mixture of CO and H₂ gases)? Is this reaction endothermic or exothermic? Use the note and the data in Table 9 below to answer this question.

Note: The following formula shows the formation of water gas, which is a mixture of CO and H₂ gases:
 $C(s) + H_2O(g) \rightarrow CO(g) + H_2(g)$.

Table 9: Calculations for three reactions

Reaction 1:	$C(s) + O_2(g) \rightarrow CO_2(g)$	$\Delta H = -394 \text{ kJ/mol}$
Reaction 2:	$CO_2(g) \rightarrow CO(g) + \frac{1}{2}O_2(g)$	$\Delta H = 283 \text{ kJ/mol}$
Reaction 3:	$H_2O(g) \rightarrow H_2(g) + \frac{1}{2}O_2(g)$	$\Delta H = 242 \text{ kJ/mol}$

Multiple Choice Questions

Select the best answer or completion to each of the questions or incomplete statements below.

- 1. What data does NOT need to be collected in order to determine the enthalpy of a chemical reaction?**
 - A. Mass of the solution
 - B. Change in temperature of the solution
 - C. The specific heat capacity of the solution
 - D. Volume of the solution

- 2. How does the enthalpy of the overall reaction compare with the sum of the enthalpies of the intermediate steps?**
 - A. Greater than
 - B. Less than
 - C. Equal to
 - D. Either A or B depending on the reaction

- 3. How can the enthalpy of a particular reaction be determined?**
 - A. By measuring the change in temperature of the reaction directly
 - B. By measuring the change in temperature of a series of reactions that, when added together, give the particular reaction
 - C. Both A and B are possible depending on the reaction
 - D. Enthalpies of reactions cannot be determined experimentally

- 4. What circumstances may require the use of Hess's law to find the enthalpy of a reaction?**
 - A. Reactions that take millions of years
 - B. Reactions involving toxic chemicals
 - C. Reactions that are explosive
 - D. All of the above

- 5. What does Hess's law state?**
 - A. The enthalpy change of the overall reaction is equal to the sum of the enthalpy changes in the individual steps
 - B. The enthalpy change of the overall reaction is equal to the product of the enthalpy changes in the individual steps
 - C. The enthalpy change of the overall reaction is greater than the sum of the enthalpy changes in the individual steps
 - D. The enthalpy change of the overall reaction is less than the product of the enthalpy changes in the individual steps

Key Term Challenge

Fill in the blanks from the list of words in the Key Term Challenge Word Bank.

1. Chemical and physical processes often involve changes in _____.
Processes that produce heat are _____ and those that absorb heat are _____. Changes in _____ can be measured by performing the chemical reaction or physical process in an insulated container called a _____. The heat of the process is then calculated by multiplying the _____, the _____, and change in temperature ΔT together ($q = m \times c \times \Delta T$).
2. _____ is the term chemists use to express the heat content of a system at constant pressure. The enthalpy of some chemical reactions can be calculated directly by mixing the reactants and measuring the change in _____. Some chemical reactions take too long (millions of years) or occur too _____ to get an accurate temperature reading. Other chemical reactions may involve toxic chemicals or chemicals that are too expensive or rare to be obtained. In these situations an _____ using a series of chemical reactions that _____ together to give the overall reaction can be used in accordance with Hess's law. _____ states that the enthalpy change of the overall reaction is equal to the sum of the enthalpy changes in the _____ that make up the _____.

Key Term Challenge Word Bank

Paragraph 1

calorimeter
endothermic
exothermic
heat
mass
pressure
specific heat capacity
temperature
volume

Paragraph 2

add
enthalpy
Hess's law
indirect method
individual steps
long
multiply
overall reaction
quickly
temperature
volume