17.4 Calculating Heats of Reaction

Connecting to Your World
Emeralds are beautiful gemstones composed of the elements chromium, aluminum, silicon, oxygen, and beryllium. It is possible to break down an emerald into its component elements and measure the resulting enthalpy change—but then the gem would be destroyed. What if you wanted to determine the heat of reaction without actually performing the reaction? In this section you will see how you can calculate heats of reaction from known thermochemical equations and enthalpy data.

Guide for Reading

Key Concepts
• What are two ways that you can determine the heat of reaction when it cannot be directly measured?

Vocabulary
Hess’s law of heat summation
standard heat of formation

Reading Strategy
Outlining As you read, make an outline of the most important ideas in this section.

Hess’s Law
Sometimes it is hard to measure the enthalpy change for a reaction. For example, the reaction might take place too slowly to actually measure the enthalpy change. Or, the reaction might be an intermediate step in a series of reactions. Or, as mentioned above, you might not want to destroy the material that undergoes the reaction. Fortunately, it is possible to measure a heat of reaction indirectly. **Hess’s law of heat summation** states that if you add two or more thermochemical equations to give a final equation, then you can also add the heats of reaction to give the final heat of reaction.

Hess’s law allows you to determine the heat of reaction indirectly.

Figure 17.12 shows a diamond mine. Diamonds are a form of carbon that exists at 25°C. Another is graphite. Because graphite is more stable than diamond, you might predict the following reaction.

\[
\text{C(s, diamond)} \rightarrow \text{C(s, graphite)}
\]

Fortunately for people who own diamonds, the conversion of diamond to graphite takes millions and millions of years. This enthalpy change cannot be measured directly because the reaction is far too slow. Hess’s law, however, provides a way to calculate the heat of reaction.

Figure 17.12 This diamond mine is located in Mpumalanga Province, South Africa.

Guide for Reading

Build Vocabulary

Paraphrase Ask students why they think Hess’s law is called a law of heat summation. What does the word summation imply?

Reading Strategy

Using Prior Knowledge Have students recall how the overall enthalpy change for converting one mole of ice to water vapor can be calculated by summing the enthalpy changes for each step in the process. A similar strategy can be used for determining the enthalpy change for a chemical reaction.

INSTRUCT

Have students examine the photograph of emeralds. Ask, **Given that an emerald is too valuable to be destroyed, is there a way to determine the heat of reaction without actually performing the reaction?** (Yes. The heat of reaction might be determined indirectly by studying the enthalpy changes for related reactions. These reactions could involve less valuable forms of the structures found in an emerald crystal.)
**Hess’s Law**

**Use Visuals**

Figure 17.13 Have students study the diagram of enthalpy change. Ask, What is the enthalpy change of the reverse reaction—from graphite to diamond? (\(\Delta H = 1.9 \text{ kJ}\))

**Discuss**

Provide the following analogy. A group of hikers is attempting to reach the summit of a mountain. Two routes are possible: one is a short, steep path that goes directly to the top; the other is a long path that is less steep but involves a number of changes in direction. Although the distances covered by hikers using the two routes would be different, the final altitude would be the same. The change in altitude is analogous to the enthalpy change for a reaction. The distances traveled by the hikers on each path is analogous to the number of steps required to form a given set of products. No matter how one goes from a given set of reactants to a given set of products, in one step or in several, the overall enthalpy change is the same.

**Relate**

Made almost entirely of carbon, diamonds are the world’s oldest substance. At 3.3 billion years of age, they are almost as old as Earth itself. Diamonds only form under extremely intense temperature and pressure. The only place on Earth these conditions are found naturally is 100 miles underground. Volcanic eruptions lift diamonds and other minerals to the surface.

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**Facts and Figures**

The 1867 discovery of a diamond in South Africa radically changed the diamond industry. Until then, India and Brazil had been the world’s leading diamond producers, but by the 1880s, South Africa was producing 95% of the world’s diamonds. Today, South Africa is third in production in terms of value. Canada, Australia, Brazil, China and Russia now collectively account for more than half of world diamond mining.
Another case in which Hess’s law is useful is when reactions yield products in addition to the product of interest. Suppose you want to determine the enthalpy change for the formation of carbon monoxide from its elements. You can write the following equation for this reaction.

\[
\text{C(s, graphite)} + \frac{1}{2} \text{O}_2(g) \rightarrow \text{CO}(g) \quad \Delta H = ?
\]

Although it is easy to write the equation, carrying out the reaction in the laboratory as written is virtually impossible. Carbon dioxide (a “side product”) is produced along with carbon monoxide (the “desired product”). Therefore, any measured heat of reaction is related to the formation of both \(\text{CO}(g)\) and \(\text{CO}_2(g)\), and not \(\text{CO}(g)\) alone. However, you can calculate the desired enthalpy change by using Hess’s law and the following two reactions that can be carried out in the laboratory.

a. \(\text{C(s, graphite)} + \text{O}_2(g) \rightarrow \text{CO}_2(g) \quad \Delta H = -393.5 \text{ kJ}\)

b. \(\text{CO}(g) + \frac{1}{2} \text{O}_2(g) \rightarrow \text{CO}_2(g) \quad \Delta H = -283.0 \text{ kJ}\)

Writing the reverse of equation \(b\) and changing the sign of \(\Delta H\) yields equation \(c\).

c. \(\text{CO}_2(g) \rightarrow \text{CO}(g) + \frac{1}{2} \text{O}_2(g) \quad \Delta H = 283.0 \text{ kJ}\)

Adding equations \(a\) and \(c\) gives the expression for the formation of \(\text{CO}(g)\) from its elements. The enthalpy diagram for this heat summation is shown in Figure 17.14. Notice that only \(\frac{1}{2} \text{O}_2(g)\) cancels from each equation.

\[
\text{C(s, graphite)} + \frac{1}{2} \text{O}_2(g) \rightarrow \text{CO}(g) \quad \Delta H = -393.5 \text{ kJ}
\]

\[
\text{CO}_2(g) \rightarrow \text{CO}(g) + \frac{1}{2} \text{O}_2(g) \quad \Delta H = 283.0 \text{ kJ}
\]

The formation of \(\text{CO}(g)\) is exothermic; 110.5 kJ of heat is given off when 1 mol \(\text{CO}(g)\) is formed from its elements.

\[\text{Checkpoint}\] Why can’t you directly measure the heat of reaction for the formation of carbon monoxide from its elements?

\[\text{Figure 17.14}\] Hess’s law is used to determine the enthalpy change for the formation of \(\text{CO}(g)\) from its elements.

**Interpreting Diagrams** How does the diagram represent endothermic and exothermic reactions differently?

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**Differentiated Instruction**

**Less Proficient Readers**

If students are having trouble visualizing the application of Hess’s law, give them the following simplified equations.

\[1 + 2 \rightarrow 3\]

\[3 + 4 \rightarrow 5 + 2\]

Show students how 2 and 3 can be cancelled from both sides of the equations. The two equations can then be added together to produce \[1 + 4 \rightarrow 5\].

**Answers to...**

**Figure 17.13** The endothermic reaction \(\text{CO}_2(g) \rightarrow \text{C(s, graphite)} + \text{O}_2(g)\) is a decomposition reaction.

**Figure 17.14** The arrow points downward for an exothermic reaction and upward for an endothermic reaction.

\[\text{Checkpoint}\] The reaction in the laboratory is impossible because carbon dioxide is produced along with carbon monoxide.
Section 17.4 (continued)

Standard Heats of Formation

Use Visuals

Table 17.4 With Table 17.4 displayed on an overhead projector, define standard heat of formation (the change in enthalpy that accompanies the formation of 1 mole of a compound from its elements with all substances in their standard states at 25°C and 101.3 kPa.) Point out that the standard heat of formation of a free element in its standard state is defined as 0. Demonstrate how to use standard heats of formation to calculate heats of reaction at standard conditions.

Use Visuals

Figure 17.15 Have students study the enthalpy diagram. Ask, Does water have a lower or higher enthalpy than the elements from which it is formed? (lower) On what other basis can you account for your answer? (It takes energy to decompose water.)

Thermite Reaction

In this reaction, iron(III) oxide is reduced to metallic iron by aluminum.

\[
\text{Fe}_2\text{O}_3(s) + 2\text{Al}(s) \rightarrow 2\text{Fe}(s) + \text{Al}_2\text{O}_3(s) \\
\Delta H = -853.9 \text{ kJ}
\]

The reaction reaches a temperature of about 3000°C, meaning both reaction products are molten (mp_{\text{Fe}} = 1530°C; mp_{\text{Al}_2\text{O}_3} = 2030°C).
SAMPLE PROBLEM 17.7

Calculating the Standard Heat of Reaction
What is the standard heat of reaction ($\Delta H^\circ$) for the reaction of CO(g) with O$_2$(g) to form CO$_2$(g)?

1. **Analyze** List the knowns and the unknown.
   - Knowns
     - $\Delta H^\circ_{O_2(g)} = 0$ kJ/mol (free element)
     - $\Delta H^\circ_{CO(g)} = -110.5$ kJ/mol
     - $\Delta H^\circ_{CO_2(g)} = -393.5$ kJ/mol
   - Unknown
     - $\Delta H^\circ = ?$ kJ

   Balance the equation of the reaction of CO(g) with O$_2$(g) to form CO$_2$(g). Then determine $\Delta H^\circ$ using the standard heats of formation of the reactants and products.

2. **Calculate** Solve for the unknown.
   - First, write the balanced equation.
     $$2\text{CO(g)} + \text{O}_2(g) \rightarrow 2\text{CO}_2(g)$$
   - Next, find and add the $\Delta H^\circ$ of all of the reactants, taking into account the number of moles of each.
     $$\Delta H^\circ_{\text{reactants}} = 2 \text{ mol CO(g)} \times -110.5 \text{ kJ/mol} + 0 \text{ kJ} = -221.0 \text{ kJ}$$
   - Then, find the $\Delta H^\circ$ of the product in a similar way.
     $$\Delta H^\circ_{\text{product}} = 2 \text{ mol CO}_2(g) \times -393.5 \text{ kJ/mol} = -787.0 \text{ kJ}$$
   - Finally, solve for the unknown.
     $$\Delta H^\circ = \Delta H^\circ_{\text{products}} - \Delta H^\circ_{\text{reactants}}$$
     $$\Delta H^\circ = (-787.0 \text{ kJ}) - (-221.0 \text{ kJ})$$
     $$\Delta H^\circ = -566.0 \text{ kJ}$$

3. **Evaluate** Does the result make sense?
   - The $\Delta H^\circ$ is negative. Therefore, the reaction is exothermic. This makes sense because combustion reactions always release heat.

**Practice Problems**

32. Calculate $\Delta H^\circ$ for the following reactions.
   - a. Br$_2$(g) $\rightarrow$ Br$_2$(l)
   - b. CaCO$_3$(s) $\rightarrow$ CaO(s) + CO$_2$(g)
   - c. 2NO(g) + O$_2$(g) $\rightarrow$ 2NO$_2$(g)

33. With one exception, the standard heats of formation of Na(s), O$_2$(g), Br$_2$(l), CO(g), Fe(s), and He(g) are identical. What is the exception? Explain.

**Answers**

32. a. $-3.091 \times 10^1$ kJ
   b. $1.784 \times 10^2$ kJ
   c. $-1.130 \times 10^2$ kJ

33. CO is a compound and not an element in its standard state.
Section 17.2 (continued)

3 ASSESS

Evaluate Understanding L2
Have students explain two ways that scientists can determine the heat of a reaction indirectly. (1. Add two or more thermochemical equations to give the desired equation. 2. Find the difference between the standard heats of formation for all reactants and the standard heats of formation for all products in the reaction.)

Reteach L1
Work out a heat-of-reaction problem using both of the methods described above.

Elements Handbook

H₂O(g) + CH₄(g) → CO(g) + 3H₂(g)
ΔH = 206 kJ
H₂O(g) + CO(g) → CO₂(g) + H₂(g)
ΔH = −41 kJ
2H₂O(g) + CH₄(g) → CO₂(g) + 4H₂(g)
ΔH = 165 kJ

Figure 17.16 Standard heats of formation are used to calculate the enthalpy change for the reaction of carbon monoxide and oxygen. Interpreting Diagrams How does this diagram also demonstrate Hess's law?

Figure 17.16 is an enthalpy diagram that shows how the standard heat of reaction was calculated in Sample Problem 17.7.

2CO(g) + O₂(g) → 2CO₂(g)
The standard heat of formation of the product, CO₂(g), is −393.5 kJ/mol. The standard heats of formation of the reactants, CO(g) and O₂(g), are −110.5 kJ/mol and 0 kJ/mol, respectively. The diagram shows the difference between ΔH°(product) and ΔH°(reactants) after taking into account the number of moles of each.

17.4 Section Assessment

34. Key Concept What are two ways that the heat of reaction can be determined when it cannot be directly measured?
35. Calculate the enthalpy change (ΔH) in kJ for the following reaction.
   2Al(s) + Fe₂O₃(s) → 2Fe(s) + Al₂O₃(s)
   Use the enthalpy changes for the combustion of aluminum and iron:
   Al(s) + 3/2O₂(g) → Al₂O₃(g)  ΔH = −1669.8 kJ
   2Fe(s) + 3/2O₂(g) → Fe₂O₃(s)  ΔH = −824.2 kJ
36. What is the formula for calculating the standard heat of reaction?
37. What is the standard heat of reaction (ΔH°) for the decomposition of hydrogen peroxide?
   2H₂O₂(l) → 2H₂O(l) + O₂(g)

Sources of Hydrogen
Use Hess's law and two thermochemical equations on page R38 to calculate ΔH for the following reaction.
   2H₂O(g) + CH₄(g) → CO₂(g) + 4H₂(g)

Assessment 17.4 Test yourself on the concepts in Section 17.4.

Answers to...

Figure 17.16 It shows the summation of thermochemical equations to give a final equation. It also shows the enthalpy change for each step.

34. Use Hess's law of heat summation or use standard heats of formation.
35. −8.456 × 10² kJ
36. ΔH° = ΔH°(products) − ΔH°(reactants)
37. −1.960 × 10² kJ
Heat of Combustion of a Candle

Purpose
To observe a burning candle and calculate the heat associated with the combustion reaction.

Materials
- candle
- aluminum foil
- safety matches
- ruler
- balance
- temperature probe (optional)

Procedure
Measure and record the length of a candle in centimeters. Place the candle on a small piece of aluminum foil and measure the mass of the foil-candle system. Note the time as you light the candle. Let the candle burn for about five minutes. **CAUTION** Keep clothing away from the flame. While you wait, begin answering the Analyze questions. After about 5 minutes, extinguish the candle and record the time. Measure the mass of the foil-candle system again. Do not try to measure the mass while the candle is burning.

Analyze
Using your experimental data, answer the following questions.
1. Observe the candle burn and draw a picture of what you see.
2. Examine the flame closely. Is it the wax or the wick that burns?
3. If you said the wax, how does the wax burn without touching the flame? If you said the wick, what is the function of the wick?
4. If you could measure the temperature near the flame, you would find that the air is much hotter above the flame than it is beside it. Why? Explain.
5. Scientists have often wondered if a candle would burn well in zero gravity. How would zero gravity change the shape of the flame?
6. How much length and mass did the candle lose? Are these data more consistent with the wax or the wick burning?
7. Keeping in mind that wick is also a verb, explain how a candle works.
8. The formula for candle wax can be approximated as \( \text{C}_20\text{H}_{42} \). Write and balance an equation for the complete combustion of the candle wax.
9. Calculate the number of moles of candle wax burned in the experiment.
10. Calculate the heat of combustion of candle wax in kJ/mol. The standard heat of formation of candle wax (\( \text{C}_20\text{H}_{42} \)) is \(-2230 \text{ kJ/mol}\). The standard heats of formation of carbon dioxide and water are \(-394 \text{ kJ/mol}\) and \(-242 \text{ kJ/mol}\), respectively. The heat of combustion of candle wax equals the sum of the heats of formation of the products minus the sum of the heats of formation of the reactants.
11. Calculate the amount of heat (in kJ) released in your reaction. (Hint: Multiply the number of moles of candle wax burned in the experiment by the heat of combustion of candle wax.)

You’re the Chemist
The following small-scale activities allow you to develop your own procedures and analyze the results.
1. **Design It!** Design an experiment to show that the candle wax does not burn with complete combustion.
2. **Design It!** Design an experiment to show that water is a product of the combustion of a candle.

### For Enrichment
Have students design an experiment to determine the heat of combustion of table sugar. This is a reaction that you might wish to demonstrate for the class.

### Address Misconceptions
Students have many misconceptions about the way candles burn. Questions 1 and 2 prompt students to wrongly conclude that the wick burns and the wax just slows the rate of burning. Questions 5 and 6 focus students on the key experiment, the determination of the mass loss of the candle, and allow them to revise their opinions.

### Prep Time
10 minutes

**Materials**
candle, metric ruler, aluminum foil, balance, safety matches, clock or watch, temperature probe (optional)

**Advance Prep**
Purchase or collect candles and a roll of aluminum foil.

**Class Time**
20 minutes

**Safety**
Remind students to wear safety glasses and to keep the flame away from any combustible material.

**Teaching Tips**
- For best results and greater safety, use short, stout votive candles.
- The day before the lab, remind students to tie long hair back and to avoid wearing loose-sleeved clothes.

**Expected Outcome**
The candle loses mass and length as it burns.

### Analyze
1. Acceptable drawings should show the wax melting.
2. Many students incorrectly choose the wick.
3. The wick draws melted wax to the flame. Those who think the wick burns may suggest that the wax just slows the rate of burning.
4. The hot gases expand and rise.
5. The flame might be round in zero gravity.

### Expected Results
- The flame might be round in zero gravity.
- The hot gases expand and rise.
- The flame might be round in zero gravity.
- The hot gases expand and rise.
- The flame might be round in zero gravity.