$$\begin{split} q_{\text{copper}} &= \textit{mc}\Delta T \\ &= 50.0 \text{ g} \times 0.385 \text{ J/(g} \cdot ^{\circ}\text{C}) \times (76.0 - 21.0) ^{\circ}\text{C} \\ q_{\text{copper}} &= 1.06 \text{ kJ} \\ \textit{n}\Delta H_{\text{reaction}} &= q_{\text{total}} \\ &= q_{\text{water}} + q_{\text{copper}} \\ \textit{n}\Delta H_{\text{reaction}} &= 47.0(4) \text{ kJ} \text{ [Digit in parentheses will be lost in rounding.]} \\ m_{\text{eicosane}} &= 8.567 - 7.357 \text{ g} \\ m_{\text{eicosane}} &= 1.21 \text{ g} \\ M_{\text{eicosane}} (C_{20}H_{42}) &= 282 \text{ g/mol} \\ n_{\text{eicosane}} &= 1.21 \text{ g} \times \frac{1 \text{ mol}}{282 \text{ g}} \\ n_{\text{eicosane}} &= 4.29 \times 10^{-3} \text{ mol} \\ \Delta H_{\text{comb}} &= \frac{47.0(4) \text{ kJ}}{4.29 \times 10^{-3} \text{ mol}} \\ &= \frac{47.0(4) \text{ kJ}}{4.29 \times 10^{-3} \text{ mol}} \end{split}$$

 $\Delta H_{\rm comb} = 1.10 \times 10^4 \, {\rm kJ/mol} \, {\rm C}_{20} {\rm H}_{42}$ Because the reaction is exothermic, $\Delta H_{\rm reaction}$ is -11.0 MJ/mol.

(b) The reaction was exothermic, because heat was released to the surroundings and the temperature increased.

(c)
$$C_{20}H_{42(s)} + 61/2 O_{2(g)} \rightarrow 20 CO_{2(g)} + 21 H_2O_{(g)} + 11.0 MJ$$

 $C_{20}H_{42(s)} + 61/2 O_{2(g)} \rightarrow 20 CO_{2(g)} + 21 H_2O_{(g)} \Delta H = -11.0 MJ$

Evaluation

(d) Percentage error =
$$\frac{(13.3 - 11.0)}{13.3} \times 100$$

= 17%

5.4 HESS'S LAW OF ADDITIVITY OF REACTION ENTHALPIES

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1. 1 × (1): 2 Al_(s) +
$$\frac{3}{2}$$
 O_{2(g)} \rightarrow Al₂O_{3(s)} $\Delta H = (1)(-1675.7)$ kJ
-1 × (2): Fe₂O_{3(s)} \rightarrow 2 Fe_(s) + $\frac{3}{2}$ O_{2(g)} $\Delta H = (-1)(-824.2)$ kJ
Fe₂O_{3(s)} + 2 Al_(s) \rightarrow Al₂O_{3(s)} + 2 Fe_(s) $\Delta H = -851.5$ kJ
2. $\frac{1}{2}$ × (1): C_(s) + $\frac{1}{2}$ O_{2(g)} \rightarrow CO_(g) $\Delta H = (\frac{1}{2})(-221.0)$ kJ
 $-\frac{1}{2}$ × (2): H₂O_(g) \rightarrow H_{2(g)} + $\frac{1}{2}$ O_{2(g)} $\Delta H = (-\frac{1}{2})(-483.6)$ kJ
 H_2 O_(g) + C_(s) \rightarrow CO_(g) + H_{2(g)} $\Delta H = 131.3$ kJ

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$$3. -\frac{1}{2} \times (1): CO_{(g)} \to C_{(s)} + \frac{1}{2} O_{2(g)} \qquad \Delta H = (-1/2)(-221.0) \text{ kJ}$$

$$\frac{1}{2} \times (3): H_{2(g)} + \frac{1}{2} O_{2(g)} \to H_2O_{(g)} \qquad \Delta H = (\frac{1}{2})(-483.6) \text{ kJ}$$

$$1 \times (2): C_{(s)} + O_{2(g)} \to CO_{2(g)} \qquad \Delta H = (1)(-393.5) \text{ kJ}$$

$$CO_{(g)} + H_{2(g)} + O_{2(g)} \rightarrow CO_{2(g)} + H_2O_{(g)} \quad \Delta H = -524.8 \text{ kJ}$$

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4. 1 × (1):
$$C_2H_{2(g)} + \frac{5}{2} O_{2(g)} \rightarrow 2 CO_{2(g)} + H_2O_{(l)}$$
 $\Delta H = (1)(-1299) \text{ kJ}$
2 × (2): $2 H_{2(g)} + O_{2(g)} \rightarrow 2 H_2O_{(l)}$ $\Delta H = (2)(-286) \text{ kJ}$
-1 × (3): $2 CO_{2(g)} + 3 H_2O_{(l)} \rightarrow C_2H_{6(g)} + \frac{7}{2} O_{2(g)}$ $\Delta H = (-1)(-1560) \text{ kJ}$

$$C_2H_{2(g)} + 2H_{2(g)} \rightarrow C_2H_{6(g)}$$
 $\Delta H = -311 \text{ kJ}$

Since the reaction is written for one mole of ethyne, the molar enthalpy of combustion of ethyne, ΔH_{comb} , is -311 kJ/mol.

amount of ethyne,
$$n = 200 \text{ g}$$
 ethyne $\times \frac{1 \text{ mol}}{26.0 \text{ g}}$

$$n = 7.69 \text{ mol}$$

$$\Delta H = n\Delta H_{\text{comb}}$$

= 7.69 mol × (-311 kJ/mol)

$$\Delta H = -2.39 \times 10^3 \text{ kJ}$$

$$5. -\frac{1}{2} \times (2): CO_{(g)} \rightarrow C_{(s)} + \frac{1}{2} O_{2(g)} \qquad \Delta H = (-\frac{1}{2})(-221.0) \text{ kJ}$$

$$-1 \times (3): CO_{2(g)} + 2 H_2 O_{(g)} \rightarrow CH_{4(g)} + 2 O_{2(g)} \qquad \Delta H = (-1)(-802.7) \text{ kJ}$$

$$1 \times (4): C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)} \qquad \Delta H = (1)(-393.5) \text{ kJ}$$

$$\frac{3}{2} \times (1): 3 H_{2(g)} + \frac{3}{2} O_{2(g)} \rightarrow 3 H_2 O_{(g)} \qquad \Delta H = (\frac{3}{2})(-483.6) \text{ kJ}$$

$$3 \text{ H}_{2(g)} + \text{CO}_{(g)} \rightarrow \text{CH}_{4(g)} + \text{H}_2\text{O}_{(g)}$$
 $\Delta H = -205.7 \text{ kJ}$

Since the reaction is written for one mole of carbon monoxide, the molar enthalpy of combustion, ΔH_{comb} , is -205.7 kJ/mol CO.

amount of CO,
$$n = 300 \text{ g} \times 1 \text{ mol}/28.0 \text{ g}$$

$$n = 10.7 \text{ mol}$$

$$\Delta H = n\Delta H_{\text{comb}}$$
$$= 10.7 \text{ mol} \times (-205.7 \text{ kJ/mol})$$

$$\Delta H = -2.20 \times 10^3 \text{ kJ}$$

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SECTION 5.4 QUESTIONS

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Understanding Concepts

1. (a) The reference thermochemical equations are:

(1)
$$C_8H_{18(l)} + \frac{25}{2}O_{2(g)} \rightarrow 8CO_{2(g)} + 9H_2O_{(l)}$$
 $\Delta H_1 = -5470 \text{ kJ}$
(2) $H_{2(g)} + \frac{1}{2}O_{2(g)} \rightarrow H_2O_{(l)}$ $\Delta H_2 = -285.8 \text{ kJ}$
(3) $C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)}$ $\Delta H_3 = -393.5 \text{ kJ}$

(b) Applying Hess's Law:

$$8 C_{(s)} + 9 H_{2(g)} \rightarrow C_8 H_{18(l)} \qquad \Delta H = -247.5 \text{ kJ}$$

$$2. -\frac{1}{2} \times (1): \text{HCl} + \frac{1}{2} \text{Na}_2 \text{O} \rightarrow \text{NaCl} + \frac{1}{2} \text{H}_2 \text{O} \qquad \Delta H = (-\frac{1}{2})(507) \text{ kJ}$$

$$-\frac{1}{2} \times (2): \text{NaNO}_2 \rightarrow \frac{1}{2} \text{NO} + \frac{1}{2} \text{NO}_2 + \frac{1}{2} \text{Na}_2 \text{O} \qquad \Delta H = (\frac{1}{2})(-427) \text{ kJ}$$

$$-\frac{1}{2} \times (4): \frac{1}{2} \text{N}_2 \text{O} + \frac{1}{2} \text{O}_2 + \frac{1}{2} \text{H}_2 \text{O} \rightarrow \text{HNO}_2 \qquad \Delta H = (-\frac{1}{2})(34) \text{ kJ}$$

$$\frac{1}{2} \times (3): \frac{1}{2} \text{NO} + \frac{1}{2} \text{NO}_2 \rightarrow \frac{1}{2} \text{N}_2 \text{O} + \frac{1}{2} \text{O}_2 \qquad \Delta H = (\frac{1}{2})(-43) \text{ kJ}$$

$$HC1 + NaNO_2 \rightarrow HNO_2 + NaC1$$
 $\Delta H = -78.5 \text{ kJ}$

3. The reference equations are:

$$(1) C_{2}H_{5}OH_{(1)} + 3 O_{2(g)} \rightarrow 2 CO_{2(g)} + 3 H_{2}O_{(1)} \qquad \Delta H_{1} = -1367 \text{ kJ}$$

$$(2) CH_{3}COOH_{(1)} + 2 O_{2(g)} \rightarrow 2 CO_{2(g)} + 2 H_{2}O_{(1)} \qquad \Delta H_{2} = -875 \text{ kJ}$$
Applying Hess's Law:
$$1 \times (1): C_{2}H_{5}OH_{(1)} + 3 O_{2(g)} \rightarrow 2 CO_{2(g)} + 3 H_{2}O_{(1)} \qquad \Delta H = (1)(-1367) \text{ kJ}$$

$$-1 \times (2): 2 CO_{2(g)} + 2 H_{2}O_{(1)} \rightarrow CH_{3}COOH_{(1)} + 2 O_{2(g)} \qquad \Delta H = (-1)(-875) \text{ kJ}$$

$$C_{2}H_{5}OH_{(1)} + O_{2(g)} \rightarrow CH_{3}COOH_{(1)} + H_{2}O_{(1)} \qquad \Delta H = 492 \text{ kJ}$$

Applying Inquiry Skills

4. (a) When reference equations (1) and (2) are added together, the result is reference equation (3).

$$\begin{array}{l} \textbf{1} \times \textbf{(1):} \ \text{HBr}_{(\text{aq})} \ + \ \text{KOH}_{(\text{aq})} \ \rightarrow \ \text{H}_2\text{O}_{(\text{l})} \ + \ \text{KBr}_{(\text{aq})} \\ \textbf{1} \times \textbf{(2):} \ \text{KOH}_{(\text{s})} \ \rightarrow \ \text{KOH}_{(\text{aq})} \\ \end{array}$$

(3)
$$KOH_{(s)} + HBr_{(aq)} \rightarrow H_2O_{(1)} + KBr_{(aq)}$$
 $\Delta H_3 = \Delta H_1 + \Delta H_2$

(b) In all three experiments, assume 200.0 mL of solution is 200.0 g water.

Experiment 1:

$$q_{\text{water}} = mc\Delta T$$

 $= 200.0 \text{ g} \times 4.18 \text{ J/g} \cdot ^{\circ}\text{C} \times (22.5 - 20.0) ^{\circ}\text{C}$
 $q_{\text{water}} = 2.09 \text{ kJ}$
 $n\Delta H_1 = q_{\text{water}}$
 $= 2.09 \text{ kJ}$
amount of KOH, $n = CV$
 $= 1.00 \text{ mol/L} \times 0.100 \text{ L}$
 $n = 0.100 \text{ mol}$
 $\Delta H_1 = \frac{q}{n}$
 $= \frac{2.09 \text{ kJ}}{0.100 \text{ mol}}$

Because the reaction is exothermic and is written for one mole of KOH, ΔH_1 is -20.9 kJ.

Experiment 2:

 $\Delta H_1 = 20.9 \text{ kJ/mol KOH}$

$$q_{\text{water}} = mc\Delta T$$

= 200.0 g × 4.18 J/g•°C × (24.1 – 20.0)°C
 $q_{\text{water}} = 3.43 \text{ kJ}$
 $n\Delta H_2 = q_{\text{water}}$
= 3.43 kJ
molar mass of KOH, $M = 56.1 \text{ g/mol}$
amount of KOH, $n = 5.61 \text{ g} \times \frac{1 \text{ mol}}{56.1 \text{ g}}$
 $n = 0.100 \text{ mol}$
 $\Delta H_2 = \frac{q}{n}$
= $\frac{3.43 \text{ kJ}}{0.100 \text{ mol}}$

 $\Delta H_2 = 34.3 \text{ kJ/mol KOH}$

 $\Delta H_3 = 56.0 \text{ kJ/mol KOH}$

Because the reaction is exothermic and is written for one mole of KOH, ΔH_2 is -34.3 kJ.

Experiment 3:

$$q_{\text{water}} = mc\Delta T$$

= 200.0 g × 4.18 J/g•°C × (26.7 - 20.0)°C
 $q_{\text{water}} = 5.60 \text{ kJ}$
 $n\Delta H_{\text{reaction}} = q_{\text{water}}$
= 5.60 kJ
amount of KOH, $n = 5.61 \text{ g} \times \frac{1 \text{ mol}}{56.1 \text{ g}}$
 $n = 0.100 \text{ mol}$
 $\Delta H_3 = \frac{q}{n}$
= $\frac{5.60 \text{ kJ}}{0.100 \text{ mol}}$

Because the reaction is exothermic and is written for one mole of KOH, ΔH_3 is -56.0 kJ/mol.

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(c) Experimental percentage error =
$$\frac{|(\Delta H_1 + \Delta H_2) - \Delta H_3|}{\Delta H_3} \times 100\%$$
$$= \frac{|(20.9 + 34.3) - 56.0|}{56.0} \times 100\%$$
$$= 1.4 \%$$

STANDARD ENTHALPIES OF FORMATION 5.5

PRACTICE

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Understanding Concepts

1. (a)
$$6 C_{(s)} + 3 H_{2(g)} \rightarrow C_6 H_{6(l)}$$

(b) $K_{(s)} + \frac{1}{2} Br_{2(l)} + 3/2 O_{2(g)} \rightarrow KBrO_{3(s)}$
(c) $6 C_{(s)} + 6 H_{2(g)} + 3 O_{2(g)} \rightarrow C_6 H_{12} O_{6(s)}$
(d) $Mg_{(s)} + H_{2(g)} + O_{2(g)} \rightarrow Mg(OH)_{2(s)}$

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Jnderstanding Concepts
2. (a)
$$C_5H_{12(1)} + 8O_{2(g)} \rightarrow 5CO_{2(g)} + 6H_2O_{(1)}$$

$$\Delta H^{\circ}_{f(C_5H_{12(1)})} = -173.5 \text{ kJ/mol}$$

$$\Delta H^{\circ}_{f(C_0_{2(g)})} = 0 \text{ kJ/mol}$$

$$\Delta H^{\circ}_{f(C_0_{2(g)})} = -393.5 \text{ kJ/mol}$$

$$\Delta H^{\circ}_{f(H_2O_{(1)})} = -285.8 \text{ kJ/mol}$$

$$\Delta H = 5 \Delta H^{\circ}_{f(CO_{2(g)})} + 6 \Delta H^{\circ}_{f(H_2O_{(1)})} - 1 \Delta H^{\circ}_{f(C_5H_{12(1)})} - 8 \Delta H^{\circ}_{f(O_{2(g)})}$$

$$= 5 (-393.5) + 6 (-285.8) - 1 (-173.5) - 8 (0)$$

$$\Delta H = -3509 \text{ kJ}$$
(b) Fe₂O_{3(s)} + 3 CO_(g) → 2 Fe_(s) + 3 CO_{2(g)}

$$\Delta H^{\circ}_{f(Fe_2O_{3(s)})} = -824.2 \text{ kJ/mol}$$

$$\Delta H^{\circ}_{f(CO_{(g)})} = -110.5 \text{ kJ/mol}$$

$$\Delta H^{\circ}_{f(CO_{2(g)})} = 0 \text{ kJ/mol}$$

$$\Delta H^{\circ}_{f(CO_{2(g)})} = -393.5 \text{ kJ/mol}$$

$$\Delta H = 2 \Delta H^{\circ}_{f(Fe_{(s)})} + 3 \Delta H^{\circ}_{f(CO_{2(g)})} - 1 \Delta H^{\circ}_{f(Fe_2O_{3(s)})} - 3 \Delta H^{\circ}_{f(CO_{(g)})}$$

$$= 2 (0) + 3 (-393.5) - 1 (-824.2) - 3 (-110.5)$$

$$\Delta H = -24.8 \text{ kJ}$$
3. C₆H₁₂₍₁₎ + 9 O_{2(g)} → 6 CO_{2(g)} + 6 H₂O₍₁₎

$$\Delta H^{\circ}_{comb(C_6H_{12(1)})} = -3824 \text{ kJ/mol}$$

$$\Delta H^{\circ}_{f(CO_{2(g)})} = 0 \text{ kJ/mol}$$

$$\Delta H^{\circ}_{f(CO_{2(g)})} = -393.5 \text{ kJ/mol}$$

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