

Exercises

Heat Capacity (Specific Heat Capacity)

- Calculate the quantity of heat, in kilojoules, (a) required to raise the temperature of 9.25 L of water from 22.0 to 29.4 °C; (b) associated with a 33.5 °C decrease in temperature in a 5.85 kg aluminum bar (specific heat capacity of aluminum = $0.903 \text{ J g}^{-1} \text{ }^\circ\text{C}^{-1}$).
- Calculate the final temperature that results when (a) a 12.6 g sample of water at 22.9 °C absorbs 875 J of heat; (b) a 1.59 kg sample of platinum at 78.2 °C gives off 1.05 kcal of heat ($c_p = 0.032 \text{ cal g}^{-1} \text{ }^\circ\text{C}^{-1}$).
- Refer to Example 7-2. The experiment is repeated with several different metals substituting for the lead. The masses of metal and water and the initial temperatures of the metal and water are the same as in Figure 7-3. The final temperatures are (a) Zn, 38.9 °C; (b) Pt, 28.8 °C; (c) Al, 52.7 °C. What is the specific heat capacity of each metal, expressed in $\text{J g}^{-1} \text{ }^\circ\text{C}^{-1}$?
- A 75.0 g piece of Ag metal is heated to 80.0 °C and dropped into 50.0 g of water at 23.2 °C. The final temperature of the Ag–H₂O mixture is 27.6 °C. What is the specific heat capacity of silver?
- A 465 g chunk of iron is removed from an oven and plunged into 375 g water in an insulated container. The temperature of the water increases from 26 to 87 °C. If the specific heat capacity of iron is $0.449 \text{ J g}^{-1} \text{ }^\circ\text{C}^{-1}$, what must have been the original temperature of the iron?
- A piece of stainless steel ($c_p = 0.50 \text{ J g}^{-1} \text{ }^\circ\text{C}^{-1}$) is transferred from an oven at 201 °C into 150 mL of water at 23.2 °C. The water temperature rises to 55.4 °C. What is the mass of the steel? How precise is this method of mass determination? Explain.
- A 1.00 kg sample of magnesium at 40.0 °C is added to 1.00 L of water maintained at 20.0 °C in an insulated container. What will be the final temperature of the Mg–H₂O mixture (specific heat capacity of Mg = $1.024 \text{ J g}^{-1} \text{ }^\circ\text{C}^{-1}$)?
- Brass has a density of 8.40 g/cm^3 and a specific heat capacity of $0.385 \text{ J g}^{-1} \text{ }^\circ\text{C}^{-1}$. A 15.2 cm^3 piece of brass at an initial temperature of 163 °C is dropped into an insulated container with 150.0 g water initially at 22.4 °C. What will be the final temperature of the brass–water mixture?
- A 74.8 g sample of copper at 143.2 °C is added to an insulated vessel containing 165 mL of glycerol, C₃H₈O₃(l) ($d = 1.26 \text{ g/mL}$), at 24.8 °C. The final temperature is 31.1 °C. The specific heat capacity of copper is $0.385 \text{ J g}^{-1} \text{ }^\circ\text{C}^{-1}$. What is the heat capacity of glycerol in $\text{J mol}^{-1} \text{ }^\circ\text{C}^{-1}$?
- A 69.0 g sample of gold at 127.1 °C is added to an insulated vessel containing 543.0 mL of water at 25.0 °C. The final temperature is 25.4 °C. What is the specific heat capacity of gold in $\text{J g}^{-1} \text{ }^\circ\text{C}^{-1}$? The specific heat capacity of water is $4.18 \text{ J g}^{-1} \text{ }^\circ\text{C}^{-1}$, and its density (at 25.0 °C) is 0.997 g mL^{-1} .
- In the form of heat, 6.052 J of energy is transferred to a 1.0 L sample of air ($d = 1.204 \text{ mg/cm}^3$) at 20.0 °C. The final temperature of the air is 25.0 °C. What is the heat capacity of air in J/K?
- What is the final temperature (in °C) of 1.24 g of water with an initial temperature of 20.0 °C after 6.052 J of heat is added to it?

Heats of Reaction

- How much heat, in kilojoules, is associated with the production of 283 kg of slaked lime, Ca(OH)₂?

$$\text{CaO(s)} + \text{H}_2\text{O(l)} \longrightarrow \text{Ca(OH)}_2\text{(s)}$$

$$\Delta_r H^\circ = -65.2 \text{ kJ mol}^{-1}$$
- The standard enthalpy of combustion of octane is $\Delta_c H^\circ = -548 \times 10^3 \text{ kJ/mol}$ C₈H₁₈(l). How much heat, in kilojoules, is liberated per gallon of octane burned? (Density of octane = 0.703 g/mL ; 1 gal = 3.785 L.)
- How much heat, in kilojoules, is evolved in the complete combustion of (a) 1.325 g C₄H₁₀(g) at 25 °C and 1 atm; (b) 28.4 L C₄H₁₀(g) at STP; (c) 12.6 L C₄H₁₀(g) at 23.6 °C and 738 mmHg? Assume that the enthalpy of reaction does not change significantly with temperature or pressure. The complete combustion of butane, C₄H₁₀(g), is represented by the equation

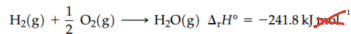
$$\text{C}_4\text{H}_{10}\text{(g)} + \frac{13}{2} \text{O}_2\text{(g)} \longrightarrow 4 \text{CO}_2\text{(g)} + 5 \text{H}_2\text{O(l)}$$

$$\Delta_r H^\circ = -2877 \text{ kJ mol}^{-1}$$
- Upon complete combustion, the indicated substances evolve the given quantities of heat. Write a balanced equation for the combustion of 1.00 mol of each substance, including the enthalpy of reaction, $\Delta_r H^\circ$, for the reaction.
 - 0.584 g of propane, C₃H₈(g), yields 29.4 kJ
 - 0.136 g of camphor, C₁₀H₁₆O(s), yields 5.27 kJ
 - 2.35 mL of acetone, (CH₃)₂CO(l) ($d = 0.791 \text{ g/mL}$), yields 58.3 kJ
- The combustion of methane gas, the principal constituent of natural gas, is represented by the equation

$$\text{CH}_4\text{(g)} + 2 \text{O}_2\text{(g)} \longrightarrow \text{CO}_2\text{(g)} + 2 \text{H}_2\text{O(l)}$$

$$\Delta_r H^\circ = -890.3 \text{ kJ mol}^{-1}$$
 - What mass of methane, in kilograms, must be burned to liberate $2.80 \times 10^7 \text{ kJ}$ of heat?
 - What quantity of heat, in kilojoules, is liberated in the complete combustion of $1.65 \times 10^4 \text{ L}$ of CH₄(g), measured at 18.6 °C and 768 mmHg?
 - If the quantity of heat calculated in part (b) could be transferred with 100% efficiency to water, what volume of water, in liters, could be heated from 8.8 to 60.0 °C as a result?

18. Refer to the Integrative Example. What volume of the synthesis gas, measured at STP and burned in an open flame (constant-pressure process), is required to heat 40.0 gal of water from 15.2 to 65.0 °C? (1 gal = 3.785 L.)
19. The combustion of hydrogen–oxygen mixtures is used to produce very high temperatures (approximately 2500 °C) needed for certain types of welding operations. Consider the reaction to be



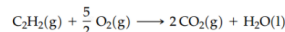
What is the quantity of heat evolved, in kilojoules, when a 180 g mixture containing equal parts of H₂ and O₂ by mass is burned?

20. Thermite mixtures are used for certain types of welding, and the thermite reaction is highly exothermic.
- $$\text{Fe}_2\text{O}_3(\text{s}) + 2 \text{Al}(\text{s}) \longrightarrow \text{Al}_2\text{O}_3(\text{s}) + 2 \text{Fe}(\text{s})$$
- $$\Delta_r H^\circ = -852 \text{ kJ mol}^{-1}$$
- 1.00 mol of granular Fe₂O₃ and 2.00 mol of granular Al are mixed at room temperature (25 °C), and a reaction is initiated. The liberated heat is retained within the products, whose combined specific heat capacity over a broad temperature range is about 0.8 J g⁻¹ °C⁻¹. (The melting point of iron is 1530 °C.) Show that the quantity of heat liberated is more than sufficient to raise the temperature of the products to the melting point of iron.
21. A 0.205 g pellet of potassium hydroxide, KOH, is added to 55.9 g water in a Styrofoam coffee cup. The water temperature rises from 23.5 to 24.4 °C. [Assume that the specific heat capacity of dilute KOH(aq) is the same as that of water.]
- (a) What is the approximate heat of solution of KOH, expressed as kilojoules per mole of KOH?
- (b) How could the precision of this measurement be improved *without* modifying the apparatus?
22. The heat of solution of KI(s) in water is +20.3 kJ/mol KI. If a quantity of KI is added to sufficient water at 24.3 °C in a Styrofoam cup to produce 175.0 mL of 2.50 M KI, what will be the final temperature? (Assume a density of 1.30 g/mL and a specific heat capacity of 2.7 J g⁻¹ °C⁻¹ for 2.50 M KI.)

Enthalpy Changes and States of Matter

29. What mass of ice can be melted with the same quantity of heat as required to raise the temperature of 3.50 mol H₂O(l) by 50.0 °C? [$\Delta_{\text{fus}}H^\circ = 6.01 \text{ kJ/mol H}_2\text{O}(\text{s})$]
30. What will be the final temperature of the water in an insulated container as the result of passing 5.00 g of steam, H₂O(g), at 100.0 °C into 100.0 g of water at 25.0 °C? ($\Delta_{\text{vap}}H^\circ = 40.6 \text{ kJ/mol H}_2\text{O}$)
31. A 125 g stainless steel ball bearing ($c_p = 0.50 \text{ J g}^{-1} \text{ °C}^{-1}$) at 525 °C is dropped into 75.0 mL of water at 28.5 °C in an open Styrofoam cup. As a result, the water is brought to a boil when the temperature reaches 100.0 °C. What mass of water vaporizes while the boiling continues? ($\Delta_{\text{vap}}H^\circ = 40.6 \text{ kJ/mol H}_2\text{O}$)

23. You are planning a lecture demonstration to illustrate an endothermic process. You want to lower the temperature of 1400 mL water in an insulated container from 25 to 10 °C. Approximately what mass of NH₄Cl(s) should you dissolve in the water to achieve this result? The heat of solution of NH₄Cl is +14.7 kJ/mol NH₄Cl.
24. Care must be taken in preparing solutions of solutes that liberate heat on dissolving. The heat of solution of NaOH is -44.5 kJ/mol NaOH. To what maximum temperature may a sample of water, originally at 24 °C, be raised in the preparation of 500 mL of 4.0 M NaOH? Assume the solution has a density of 1.08 g/mL and specific heat capacity of 4.00 J g⁻¹ °C⁻¹.
25. Refer to Example 7-4. The product of the neutralization is 0.500 M NaCl. For this solution, assume a density of 1.02 g/mL and a specific heat capacity of 4.02 J g⁻¹ °C⁻¹. Also, assume a heat capacity for the Styrofoam cup of 10 J/°C, and recalculate the heat of neutralization.
26. The heat of neutralization of HCl(aq) by NaOH(aq) is -55.84 kJ/mol H₂O produced. If 50.00 mL of 1.05 M NaOH is added to 25.00 mL of 1.86 M HCl, with both solutions originally at 24.72 °C, what will be the final solution temperature? (Assume that no heat is lost to the surrounding air and that the solution produced in the neutralization reaction has a density of 1.02 g/mL and a specific heat capacity of 3.98 J g⁻¹ °C⁻¹.)
27. Acetylene (C₂H₂) torches are used in welding. How much heat (in kJ) evolves when 5.0 L of C₂H₂ ($d = 1.0967 \text{ kg/m}^3$) is mixed with a stoichiometric amount of oxygen gas? The combustion reaction is



$$\Delta_r H^\circ = -1299.5 \text{ kJ mol}^{-1}$$

28. Propane (C₃H₈) gas ($d = 1.83 \text{ kg/m}^3$) is used in most gas grills. What volume (in liters) of propane is needed to generate 273.8 kJ of heat?



$$\Delta_r H^\circ = -2219.9 \text{ kJ mol}^{-1}$$

32. If the ball bearing described in Exercise 31 is dropped onto a large block of ice at 0 °C, what mass of liquid water will form? ($\Delta_{\text{fus}}H^\circ = 6.01 \text{ kJ/mol H}_2\text{O}$)
33. The enthalpy of sublimation (solid → gas) for dry ice (i.e., CO₂) is $\Delta_{\text{sub}}H^\circ = 571 \text{ kJ/kg}$ at -78.5 °C. If 125.0 J of heat is transferred to a block of dry ice that is -78.5 °C, what volume of CO₂ gas ($d = 1.98 \text{ g/L}$) will be generated?
34. The enthalpy of vaporization for N₂(l) is 5.56 kJ/mol. How much heat (in J) is required to produce 1.0 L of N₂(g) at 77.36 K and 1.0 atm?

292 Chapter 7 Thermochemistry

Calorimetry

35. A sample gives off 5228 cal when burned in a bomb calorimeter. The temperature of the calorimeter assembly increases by 4.39°C . Calculate the heat capacity of the calorimeter, in kilojoules per degree Celsius.
36. The following substances undergo complete combustion in a bomb calorimeter. The calorimeter assembly has a heat capacity of $5.136\text{ kJ}/^\circ\text{C}$. In each case, what is the final temperature if the initial water temperature is 22.43°C ?
- (a) 0.3268 g caffeine, $\text{C}_8\text{H}_{10}\text{O}_2\text{N}_4$ (heat of combustion = -1014.2 kcal/mol caffeine);
 (b) 1.35 mL of methyl ethyl ketone, $\text{C}_4\text{H}_8\text{O}$ (l), $d = 0.805\text{ g/mL}$ (heat of combustion = -2444 kJ/mol methyl ethyl ketone).
37. A bomb calorimetry experiment is performed with xylose, $\text{C}_5\text{H}_{10}\text{O}_5(\text{s})$, as the combustible substance. The data obtained are
- | | |
|----------------------------------|----------------------------------|
| mass of xylose burned: | 1.183 g |
| heat capacity of calorimeter: | $4.728\text{ kJ}/^\circ\text{C}$ |
| initial calorimeter temperature: | 23.29°C |
| final calorimeter temperature: | 27.19°C |
- (a) What is the heat of combustion of xylose, in kilojoules per mole? (b) Write the chemical equation for the complete combustion of xylose, and represent the value of $\Delta_r H$ in this equation. (Assume for this reaction that $\Delta U \approx \Delta_r H$.)
38. A coffee-cup calorimeter contains 100.0 mL of 0.300 M HCl at 20.3°C . When 1.82 g $\text{Zn}(\text{s})$ is added, the temperature rises to 30.5°C . What is the heat of reaction per mol Zn ? Make the same assumptions as in Example 7-4, and also assume that there is no heat lost with the $\text{H}_2(\text{g})$ that escapes.
- $$\text{Zn}(\text{s}) + 2\text{H}^+(\text{aq}) \longrightarrow \text{Zn}^{2+}(\text{aq}) + \text{H}_2(\text{g})$$
39. A 0.75 g sample of KCl is added to 35.0 g H_2O in a Styrofoam cup and stirred until it dissolves. The temperature of the solution drops from 24.8 to 23.6°C .
- (a) Is the process endothermic or exothermic?
 (b) What is the heat of solution of KCl expressed in kilojoules per mole of KCl ?
40. The heat of solution of potassium acetate in water is -15.3 kJ/mol KCH_3COO . What will be the final temperature when 0.241 mol KCH_3COO is dissolved in 815 mL water that is initially at 25.1°C ?
41. A 1.620 g sample of naphthalene, $\text{C}_{10}\text{H}_8(\text{s})$, is completely burned in a bomb calorimeter assembly and a temperature increase of 8.44°C is noted. If the heat of combustion of naphthalene is -5156 kJ/mol C_{10}H_8 , what is the heat capacity of the bomb calorimeter?
42. Salicylic acid, $\text{C}_7\text{H}_6\text{O}_3$, has been suggested as a calorimetric standard. Its heat of combustion is $-3.023 \times 10^3\text{ kJ/mol}$ $\text{C}_7\text{H}_6\text{O}_3$. From the following data determine the heat capacity of a bomb calorimeter assembly (that is, the bomb, water, stirrer, thermometer, wires, and so forth).
- | | |
|----------------------------------|-----------------------|
| mass of salicylic acid burned: | 1.201 g |
| initial calorimeter temperature: | 23.68°C |
| final calorimeter temperature: | 29.82°C |
43. Refer to Example 7-3. Based on the heat of combustion of sucrose established in the example, what should be the temperature change (ΔT) produced by the combustion of 1.227 g $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ in a bomb calorimeter assembly with a heat capacity of $3.87\text{ kJ}/^\circ\text{C}$?
44. A 1.397 g sample of thymol, $\text{C}_{10}\text{H}_{14}\text{O}(\text{s})$ (a preservative and a mold and mildew preventative), is burned in a bomb calorimeter assembly. The temperature increase is 11.23°C , and the heat capacity of the bomb calorimeter is $4.68\text{ kJ}/^\circ\text{C}$. What is the heat of combustion of thymol, expressed in kilojoules per mole of $\text{C}_{10}\text{H}_{14}\text{O}$?
45. A 5.0 g sample of NaCl is added to a Styrofoam cup of water, and the change in water temperature is 5.0°C . The heat of solution of NaCl is 3.76 kJ/mol . What is the mass (in g) of water in the Styrofoam cup?
46. We can determine the purity of solid materials by using calorimetry. A gold ring (for pure gold, specific heat capacity = $0.1291\text{ J g}^{-1}\text{K}^{-1}$) with mass of 10.5 g is heated to 78.3°C and immersed in 50.0 g of 23.7°C water in a constant-pressure calorimeter. The final temperature of the water is 31.0°C . Is this a pure sample of gold?

Pressure–Volume Work

47. Calculate the quantity of work associated with a 3.5 L expansion of a gas (ΔV) against a pressure of 748 mmHg in the units (a) atm L; (b) joules (J); (c) calories (cal).
48. Calculate the quantity of work, in joules, associated with the compression of a gas from 5.62 L to 3.37 L by a constant pressure of 1.23 atm .
49. A 1.00 g sample of $\text{Ne}(\text{g})$ at 1 atm pressure and 27°C is allowed to expand into an evacuated vessel of 2.50 L volume. Does the gas do work? Explain.
50. Compressed air in aerosol cans is used to free electronic equipment of dust. Does the air do any work as it escapes from the can?
51. In each of the following processes, is any work done when the reaction is carried out at constant pressure in a vessel open to the atmosphere? If so, is work done by the reacting system or on it? (a) Neutralization of $\text{Ba}(\text{OH})_2(\text{aq})$ by $\text{HCl}(\text{aq})$; (b) conversion of gaseous nitrogen dioxide to gaseous dinitrogen tetroxide; (c) decomposition of calcium carbonate to calcium oxide and carbon dioxide gas.
52. In each of the following processes, is any work done when the reaction is carried out at constant pressure in a vessel open to the atmosphere? If so, is work done by the reacting system or on it? (a) Reaction of nitrogen monoxide and oxygen gases to form gaseous nitrogen dioxide; (b) precipitation of magnesium hydroxide by the reaction of aqueous solutions of NaOH and MgCl_2 ; (c) reaction of copper(II) sulfate and water vapor to form copper(II) sulfate pentahydrate.

53. If 325 J of work is done by a system at a pressure of 1.0 atm and 298 K, what is the change in the volume of the system?

First Law of Thermodynamics

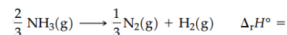
55. What is the change in internal energy of a system if the system (a) absorbs 58 J of heat and does 58 J of work; (b) absorbs 125 J of heat and does 687 J of work; (c) evolves 280 cal of heat and has 1.25 kJ of work done on it?
56. What is the change in internal energy of a system if the surroundings (a) transfer 235 J of heat and 128 J of work to the system; (b) absorb 145 J of heat from the system while doing 98 J of work on the system; (c) exchange no heat, but receive 1.07 kJ of work from the system?
57. The internal energy of a fixed quantity of an ideal gas depends only on its temperature. A sample of an ideal gas is allowed to expand at a constant temperature (isothermal expansion). (a) Does the gas do work? (b) Does the gas exchange heat with its surroundings? (c) What happens to the temperature of the gas? (d) What is ΔU for the gas?
58. In an *adiabatic* process, a system is thermally insulated—there is no exchange of heat between system and surroundings. For the adiabatic expansion of an ideal gas (a) does the gas do work? (b) Does the internal energy of the gas increase, decrease, or remain constant? (c) What

Relating ΔH and ΔU

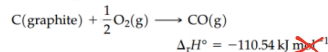
63. Only one of the following quantities is equal to the heat of a chemical reaction, *regardless of how the reaction is carried out*. Which one and why? (a) q_V ; (b) q_P ; (c) $\Delta U - w$; (d) ΔU ; (e) $\Delta_r H$.
64. Determine whether ΔH is equal to, greater than, or less than ΔU for the following processes. Keep in mind that “greater than” means more positive or less negative, and “less than” means less positive or more negative. Assume that the only significant change in volume during a constant pressure process is that associated with changes in the amounts of gases. (a) The complete combustion of one mole of butan-1-ol.

Hess's Law

67. The standard enthalpy of formation of $\text{NH}_3(\text{g})$ is -46.11 kJ/mol . What is $\Delta_r H^\circ$ for the following reaction?



68. Use Hess's law to determine $\Delta_r H^\circ$ for the reaction $\text{CO}(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) \longrightarrow \text{CO}_2(\text{g})$, given that



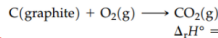
54. A movable piston in a cylinder holding 5.0 L $\text{N}_2(\text{g})$ is used to lift a 2.41 kg object to a height of 2.6 meters. How much work (in J) was done by the gas?

happens to the temperature of the gas? [Hint: Refer to Exercise 57.]

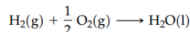
59. Do you think the following observation is in any way possible? An ideal gas is expanded isothermally and is observed to do twice as much work as the heat absorbed from its surroundings. Explain your answer. [Hint: Refer to Exercises 57 and 58.]
60. Do you think the following observation is in any way possible? A gas absorbs heat from its surroundings while being compressed. Explain your answer. [Hint: Refer to Exercises 55 and 56.]
61. There are other forms of work besides P - V work. For example, electrical work is defined as the potential \times change in charge, $w = \phi \Delta q$. If a charge in a system is changed from 10 C to 5 C in a potential of 100 V and 45 J of heat is liberated, what is the change in the internal energy? (Note: $1 \text{ V} = 1 \text{ J/C}$)
62. Another form of work is extension, defined as the tension \times change in length, $w = f \Delta l$. A piece of DNA has an approximate tension of $f = 10 \text{ pN}$. What is the change in the internal energy of the adiabatic stretching of DNA by 10 pm?

(b) The complete combustion of one mole of glucose, $\text{C}_6\text{H}_{12}\text{O}_6(\text{s})$.
(c) The decomposition of solid ammonium nitrate to produce liquid water and gaseous dinitrogen monoxide.

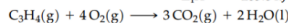
65. The heat of combustion of propan-2-ol at 298.15 K, determined in a bomb calorimeter, is -33.41 kJ/g . For the combustion of one mole of propan-2-ol, determine (a) ΔU , and (b) $\Delta_r H$. $\text{C}_3\text{H}_7\text{OH}$
66. Write an equation to represent the combustion of thymol referred to in Exercise 44. Include in this equation the values for ΔU and ΔH .



69. Use Hess's law to determine $\Delta_r H^\circ$ for the reaction $\text{C}_3\text{H}_4(\text{g}) + 2 \text{H}_2(\text{g}) \longrightarrow \text{C}_3\text{H}_6(\text{g})$, given that



$$\Delta_r H^\circ = -285.8 \text{ kJ mol}^{-1}$$



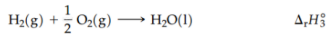
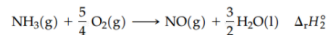
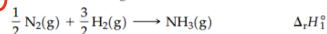
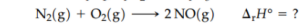
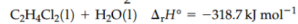
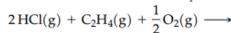
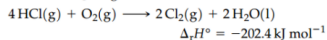
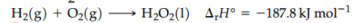
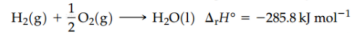
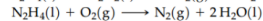
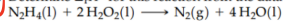
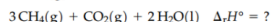
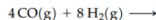
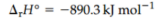
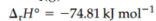
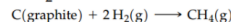
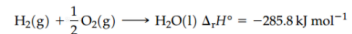
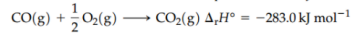
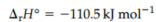
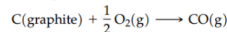
$$\Delta_r H^\circ = -1937 \text{ kJ mol}^{-1}$$



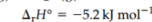
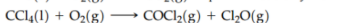
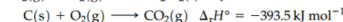
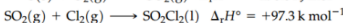
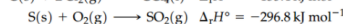
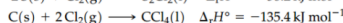
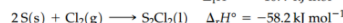
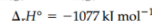
$$\Delta_r H^\circ = -2219.1 \text{ kJ mol}^{-1}$$

294 Chapter 7 Thermochemistry

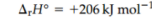
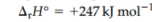
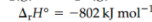
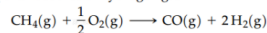
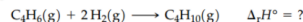
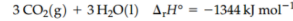
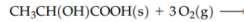
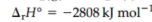
70. Given the following information:

Determine $\Delta_r H^\circ$ for the following reaction, expressed in terms of $\Delta_r H_1^\circ$, $\Delta_r H_2^\circ$, and $\Delta_r H_3^\circ$.71. For the reaction $\text{C}_2\text{H}_4(\text{g}) + \text{Cl}_2(\text{g}) \longrightarrow \text{C}_2\text{H}_4\text{Cl}_2(\text{l})$, determine $\Delta_r H^\circ$, given that72. Determine $\Delta_r H^\circ$ for this reaction from the data below.73. Substitute natural gas (SNG) is a gaseous mixture containing $\text{CH}_4(\text{g})$ that can be used as a fuel. One reaction for the production of SNG isUse appropriate data from the following list to determine $\Delta_r H^\circ$ for this SNG reaction.74. CCl_4 , an important commercial solvent, is prepared by the reaction of $\text{Cl}_2(\text{g})$ with a carbon compound. Determine $\Delta_r H^\circ$ for the reaction

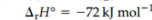
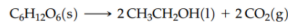
Use appropriate data from the following listing.



75. Use Hess's law and the following data

to determine $\Delta_r H^\circ$ for the following reaction, an important source of hydrogen gas76. The standard heats of combustion ($\Delta_r H^\circ$) of buta-1,3-diene, $\text{C}_4\text{H}_6(\text{g})$; butane, $\text{C}_4\text{H}_{10}(\text{g})$; and $\text{H}_2(\text{g})$ are -2540.2 , -2877.6 , and $-285.8 \text{ kJ mol}^{-1}$, respectively. Use these data to calculate the heat of hydrogenation of buta-1,3-diene to butane.*[Hint: Write equations for the combustion reactions. In each combustion, the products are $\text{CO}_2(\text{g})$ and $\text{H}_2\text{O}(\text{l})$.]*77. One glucose molecule, $\text{C}_6\text{H}_{12}\text{O}_6(\text{s})$, is converted to two lactic acid molecules, $\text{CH}_3\text{CH}(\text{OH})\text{COOH}(\text{s})$ during glycolysis. Given the combustion reactions of glucose and lactic acid, determine the standard enthalpy for glycolysis.

78. The standard enthalpy of fermentation of glucose to ethanol is



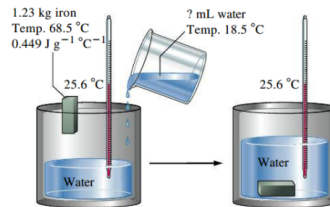
Use the standard enthalpy of combustion for glucose to calculate the enthalpy of combustion for ethanol.

Standard Enthalpies of Formation

79. Use standard enthalpies of formation from Table 7.2 and equation (7.22) to determine the standard enthalpy of reaction in the following reactions.
- (a) $\text{C}_3\text{H}_8(\text{g}) + \text{H}_2(\text{g}) \longrightarrow \text{C}_2\text{H}_6(\text{g}) + \text{CH}_4(\text{g})$;
 (b) $2\text{H}_2\text{S}(\text{g}) + 3\text{O}_2(\text{g}) \longrightarrow 2\text{SO}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l})$.
80. Use standard enthalpies of formation from Tables 7.2 and 7.3 and equation (7.22) to determine the standard enthalpy of reaction in the following reaction.
- $$\text{NH}_4^+(\text{aq}) + \text{OH}^-(\text{aq}) \longrightarrow \text{H}_2\text{O}(\text{l}) + \text{NH}_3(\text{g}).$$
81. Use the information given here, data from Appendix D, and equation (7.22) to calculate the standard enthalpy of formation per mole of $\text{ZnS}(\text{s})$.
- $$2\text{ZnS}(\text{s}) + 3\text{O}_2(\text{g}) \longrightarrow 2\text{ZnO}(\text{s}) + 2\text{SO}_2(\text{g})$$
- $$\Delta_r H^\circ = -878.2 \text{ kJ mol}^{-1}$$
82. Use the data in Figure 7-18 and information from Section 3-7 to establish possible relationships between the molecular structure of the hydrocarbons and their standard enthalpies of formation.
83. Use standard enthalpies of formation from Table 7.2 to determine $\Delta_r H^\circ$ at 25 °C for the following reaction.
- $$2\text{Cl}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l}) \longrightarrow 4\text{HCl}(\text{g}) + \text{O}_2(\text{g})$$
- $$\Delta_r H^\circ = ?$$
84. Use data from Appendix D to calculate $\Delta_r H^\circ$ for the following reaction at 25 °C.
- $$\text{Fe}_2\text{O}_3(\text{s}) + 3\text{CO}(\text{g}) \longrightarrow 2\text{Fe}(\text{s}) + 3\text{CO}_2(\text{g})$$
- $$\Delta_r H^\circ = ?$$
85. Use data from Table 7.2 to determine the standard heat of combustion of $\text{C}_2\text{H}_5\text{OH}(\text{l})$, if reactants and products are maintained at 25 °C and 1 bar.
86. Use data from Table 7.2, together with the fact that $\Delta_r H^\circ = -3509 \text{ kJ mol}^{-1}$ for the complete combustion of pentane, $\text{C}_5\text{H}_{12}(\text{l})$, to calculate $\Delta_r H^\circ$ for the reaction below.
- $$5\text{CO}(\text{g}) + 11\text{H}_2(\text{g}) \longrightarrow \text{C}_5\text{H}_{12}(\text{l}) + 5\text{H}_2\text{O}(\text{l})$$
- $$\Delta_r H^\circ = ?$$
87. Use data from Table 7.2 and $\Delta_r H^\circ$ for the following reaction to determine the standard enthalpy of formation of $\text{CCl}_4(\text{g})$ at 25 °C and 1 bar.
- $$\text{CH}_4(\text{g}) + 4\text{Cl}_2(\text{g}) \longrightarrow \text{CCl}_4(\text{g}) + 4\text{HCl}(\text{g})$$
- $$\Delta_r H^\circ = -397.3 \text{ kJ mol}^{-1}$$
88. Use data from Table 7.2 and $\Delta_r H^\circ$ for the following reaction to determine the standard enthalpy of formation of hexane, $\text{C}_6\text{H}_{14}(\text{l})$, at 25 °C and 1 bar.
- $$2\text{C}_6\text{H}_{14}(\text{l}) + 19\text{O}_2(\text{g}) \longrightarrow 12\text{CO}_2(\text{g}) + 14\text{H}_2\text{O}(\text{l})$$
- $$\Delta_r H^\circ = -8326 \text{ kJ mol}^{-1}$$
89. Use data from Table 7.3 and Appendix D to determine the standard enthalpy change in the following reaction.
- $$\text{Al}^{3+}(\text{aq}) + 3\text{OH}^-(\text{aq}) \longrightarrow \text{Al}(\text{OH})_3(\text{s}) \quad \Delta_r H^\circ = ?$$
90. Use data from Table 7.3 and Appendix D to determine $\Delta_r H^\circ$ for the following reaction.
- $$\text{Mg}(\text{OH})_2(\text{s}) + 2\text{NH}_4^+(\text{aq}) \longrightarrow \text{Mg}^{2+}(\text{aq}) + 2\text{H}_2\text{O}(\text{l}) + 2\text{NH}_3(\text{g}) \quad \Delta_r H^\circ = ?$$
91. The decomposition of limestone, $\text{CaCO}_3(\text{s})$, into quicklime, $\text{CaO}(\text{s})$, and $\text{CO}_2(\text{g})$ is carried out in a gas-fired kiln. Use data from Appendix D to determine how much heat is required to decompose $1.35 \times 10^3 \text{ kg CaCO}_3(\text{s})$. (Assume that heats of reaction are the same as at 25 °C and 1 bar.)
92. Use data from Table 7.2 to calculate the volume of butane, $\text{C}_4\text{H}_{10}(\text{g})$, measured at 24.6 °C and 756 mmHg, that must be burned to liberate $5.00 \times 10^4 \text{ kJ}$ of heat.
93. Ants release formic acid (HCOOH) when they bite. Use the data in Table 7.2 and the standard enthalpy of combustion for formic acid ($\Delta_r H^\circ = -255 \text{ kJ/mol}$) to calculate the standard enthalpy of formation for formic acid.
94. Calculate the enthalpy of combustion for lactic acid by using the data in Table 7.2 and the standard enthalpy of formation for lactic acid [$\text{CH}_3\text{CH}(\text{OH})\text{COOH}(\text{s})$]: $\Delta_r H^\circ = -694.0 \text{ kJ/mol}$.

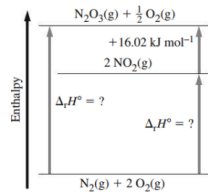
Integrative and Advanced Exercises

95. A British thermal unit (Btu) is defined as the quantity of heat required to change the temperature of 1 lb of water by 1 °F. Assume the specific heat capacity of water to be independent of temperature. How much heat is required to raise the temperature of the water in a 40-gal water heater from 48 to 145 °F in (a) Btu; (b) kcal; (c) kJ?
96. What volume of 18.5 °C water must be added, together with a 1.23 kg piece of iron at 68.5 °C, so that the temperature of the water in the insulated container shown in the figure remains constant at 25.6 °C?



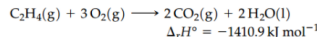
296 Chapter 7 Thermochemistry

97. A 7.26 kg shot (as used in the sporting event, the shot put) is dropped from the top of a building 168 m high. What is the maximum temperature increase that could occur in the shot? Assume a specific heat capacity of $0.47 \text{ J g}^{-1} \text{ } ^\circ\text{C}^{-1}$ for the shot. Why would the actual measured temperature increase likely be less than the calculated value?
98. An alternative approach to bomb calorimetry is to establish the heat capacity of the calorimeter, *exclusive* of the water it contains. The heat absorbed by the water and by the rest of the calorimeter must be calculated separately and then added together. A bomb calorimeter assembly containing 983.5 g water is calibrated by the combustion of 1.354 g anthracene. The temperature of the calorimeter rises from 24.87 to 35.63 $^\circ\text{C}$. When 1.053 g citric acid is burned in the same assembly, but with 968.6 g water, the temperature increases from 25.01 to 27.19 $^\circ\text{C}$. The heat of combustion of anthracene, $\text{C}_{14}\text{H}_{10}(\text{s})$, is -7067 kJ/mol $\text{C}_{14}\text{H}_{10}$. What is the heat of combustion of citric acid, $\text{C}_6\text{H}_8\text{O}_7$, expressed in kJ/mol ?
99. The method of Exercise 98 is used in some bomb calorimetry experiments. A 1.148 g sample of benzoic acid is burned in excess $\text{O}_2(\text{g})$ in a bomb immersed in 1181 g of water. The temperature of the water rises from 24.96 to 30.25 $^\circ\text{C}$. The heat of combustion of benzoic acid is -26.42 kJ/g . In a second experiment, a 0.895 g powdered coal sample is burned in the same calorimeter assembly. The temperature of 1162 g of water rises from 24.98 to 29.81 $^\circ\text{C}$. How many metric tons (1 metric ton = 1000 kg) of this coal would have to be burned to release $2.15 \times 10^9 \text{ kJ}$ of heat?
100. A handbook lists two different values for the heat of combustion of hydrogen: 33.88 kcal/g if $\text{H}_2\text{O}(\text{l})$ is formed, and 28.67 kcal/g if $\text{H}_2\text{O}(\text{g})$ is formed. Explain why these two values are different, and indicate what property this difference represents. Devise a means of verifying your conclusions.
101. Determine the missing values of $\Delta_r H^\circ$ in the diagram shown below.



102. A particular natural gas consists, in mole percents, of 83.0% CH_4 , 11.2% C_2H_6 , and 5.8% C_3H_8 . A 385 L sample of this gas, measured at 22.6 $^\circ\text{C}$ and 739 mmHg, is burned at constant pressure in an excess of oxygen gas. How much heat, in kilojoules, is evolved in the combustion reaction?

103. An overall reaction for a coal gasification process is $2 \text{C}(\text{graphite}) + 2 \text{H}_2\text{O}(\text{g}) \longrightarrow \text{CH}_4(\text{g}) + \text{CO}_2(\text{g})$. Show that this overall equation can be established by an appropriate combination of equations from Section 7-9.
104. Which of the following gases has the greater fuel value on a per liter (STP) basis? That is, which has the greater heat of combustion? [Hint: The only combustible gases are CH_4 , C_3H_8 , CO , and H_2 .]
 (a) coal gas: 49.7% H_2 , 29.9% CH_4 , 8.2% N_2 , 6.9% CO , 3.1% C_3H_8 , 1.7% CO_2 , and 0.5% O_2 , by volume.
 (b) sewage gas, 66.0% CH_4 , 30.0% CO_2 , and 4.0% N_2 , by volume.
105. A calorimeter that measures an exothermic heat of reaction by the quantity of ice that can be melted is called an ice calorimeter. Now consider that 0.100 L of methane gas, $\text{CH}_4(\text{g})$, at 25.0 $^\circ\text{C}$ and 744 mmHg, is burned at constant pressure in air. The heat liberated is captured and used to melt 9.53 g ice at 0 $^\circ\text{C}$ ($\Delta_{\text{fus}}H$ of ice = 6.01 kJ/mol).
 (a) Write an equation for the complete combustion of CH_4 , and show that combustion is incomplete in this case.
 (b) Assume that $\text{CO}(\text{g})$ is produced in the incomplete combustion of CH_4 , and represent the combustion as best you can through a single equation with small whole numbers as coefficients. ($\text{H}_2\text{O}(\text{l})$ is another product of the combustion.)
106. For the reaction



- if the H_2O were obtained as a gas rather than a liquid, (a) would the heat of reaction be greater (more negative) or smaller (less negative) than that indicated in the equation? (b) Explain your answer. (c) Calculate the value of $\Delta_r H^\circ$ in this case.
107. Some of the butane, $\text{C}_4\text{H}_{10}(\text{g})$, in a 200.0 L cylinder at 26.0 $^\circ\text{C}$ is withdrawn and burned at a constant pressure in an excess of air. As a result, the pressure of the gas in the cylinder falls from 2.35 atm to 1.10 atm. The liberated heat is used to raise the temperature of 132.5 L of water in a heater from 26.0 to 62.2 $^\circ\text{C}$. Assume that the combustion products are $\text{CO}_2(\text{g})$ and $\text{H}_2\text{O}(\text{l})$ exclusively, and determine the efficiency of the water heater. (That is, what percent of the heat of combustion was absorbed by the water?)
108. The metabolism of glucose, $\text{C}_6\text{H}_{12}\text{O}_6$, yields $\text{CO}_2(\text{g})$ and $\text{H}_2\text{O}(\text{l})$ as products. Heat released in the process is converted to useful work with about 70% efficiency. Calculate the mass of glucose metabolized by a 58.0 kg person in climbing a mountain with an elevation gain of 1450 m. Assume that the work performed in the climb is about four times that required to simply lift 58.0 kg by 1450 m. ($\Delta_r H^\circ$ of $\text{C}_6\text{H}_{12}\text{O}_6(\text{s})$ is -1273.3 kJ/mol .)
109. An alkane hydrocarbon has the formula $\text{C}_n\text{H}_{2n+2}$. The enthalpies of formation of the alkanes decrease (become more negative) as the number of C atoms increases. Starting with butane, $\text{C}_4\text{H}_{10}(\text{g})$, for each additional CH_2 group in the formula, the enthalpy of

- formation, $\Delta_r H^\circ$, changes by about -21 kJ/mol. Use this fact and data from Table 7.2 to estimate the heat of combustion of heptane, $C_7H_{16}(l)$.
110. Upon complete combustion, a 1.00 L sample (at STP) of a natural gas gives off 43.6 kJ of heat. If the gas is a mixture of $CH_4(g)$ and $C_2H_6(g)$, what is its percent composition, *by volume*?
111. Under the entry H_2SO_4 , a reference source lists many values for the standard enthalpy of formation. For example, for pure $H_2SO_4(l)$, $\Delta_f H^\circ = -814.0$ kJ/mol; for a solution with 1 mol H_2O per mole of H_2SO_4 , -841.8 ; with 10 mol H_2O , -880.5 ; with 50 mol H_2O , -886.8 ; with 100 mol H_2O , -887.7 ; with 500 mol H_2O , -890.5 ; with 1000 mol H_2O , -892.3 ; with 10,000 mol H_2O , -900.8 ; and with 100,000 mol H_2O , -907.3 .
- (a) Explain why these values are not all the same.
 (b) The value of $\Delta_f H^\circ[H_2SO_4(aq)]$ in an infinitely dilute solution is -909.3 kJ/mol. What data from this chapter can you cite to confirm this value? Explain.
 (c) If 500.0 mL of 1.00 M $H_2SO_4(aq)$ is prepared from pure $H_2SO_4(l)$, what is the approximate change in temperature that should be observed? Assume that the $H_2SO_4(l)$ and $H_2O(l)$ are at the same temperature initially and that the specific heat capacity of the $H_2SO_4(aq)$ is about 4.2 J $g^{-1} \text{ } ^\circ\text{C}^{-1}$.
112. Refer to the discussion of the gasification of coal (page 283), and show that some of the heat required in the gasification reactions (equations 7.26 and 7.27) can be supplied by the *methanation* reaction. This fact contributes to the success of modern processes that produce *synthetic natural gas* (SNG).
113. A 1.103 g sample of a gaseous carbon-hydrogen-oxygen compound that occupies a volume of 582 mL at 765.5 Torr and 25.00 $^\circ\text{C}$ is burned in an excess of $O_2(g)$ in a bomb calorimeter. The products of the combustion are 2.108 g $CO_2(g)$, 1.294 g $H_2O(l)$, and enough heat to raise the temperature of the calorimeter assembly from 25.00 to 31.94 $^\circ\text{C}$. The heat capacity of the calorimeter is 5.015 kJ/ $^\circ\text{C}$. Write an equation for the combustion reaction, and indicate $\Delta_r H^\circ$ for this reaction at 25.00 $^\circ\text{C}$.
114. Several factors are involved in determining the cooking times required for foods in a microwave oven. One of these factors is specific heat capacity. Determine the approximate time required to warm 250 mL of chicken broth from 4 $^\circ\text{C}$ (a typical refrigerator temperature) to 50 $^\circ\text{C}$ in a 700 W microwave oven. Assume that the density of chicken broth is about 1 g/mL and that its specific heat capacity is approximately 4.2 J $g^{-1} \text{ } ^\circ\text{C}^{-1}$.
115. Suppose you have a setup similar to the one depicted in Figure 7-8 except that there are two different weights rather than two equal weights. One weight is a steel cylinder 10.00 cm in diameter and 25 cm long, the other weight produces a pressure of 745 Torr. The temperature of the gas in the cylinder in which the expansion takes place is 25.0 $^\circ\text{C}$. The piston restraining the gas has a diameter of 12.00 cm, and the height of the piston above the base of the gas expansion cylinder is 8.10 cm. The density of the steel is 7.75 g/ cm^3 . How much work is done when the steel cylinder is suddenly removed from the piston?
116. When one mole of sodium carbonate decahydrate (washing soda) is gently warmed, 155.3 kJ of heat is absorbed, water vapor is formed, and sodium carbonate heptahydrate remains. On more vigorous heating, the heptahydrate absorbs 320.1 kJ of heat and loses more water vapor to give the monohydrate. Continued heating gives the anhydrous salt (soda ash) while 57.3 kJ of heat is absorbed. Calculate ΔH for the conversion of one mole of washing soda into soda ash. Estimate ΔU for this process. Why is the value of ΔU only an estimate?
117. The oxidation of $NH_3(g)$ to $NO(g)$ in the Ostwald process must be very carefully controlled in terms of temperature, pressure, and contact time with the catalyst. This is because the oxidation of $NH_3(g)$ can yield any one of the products $N_2(g)$, $N_2O(g)$, $NO(g)$, and $NO_2(g)$, depending on conditions. Show that oxidation of $NH_3(g)$ to $N_2(g)$ is the most exothermic of the four possible reactions.
118. In the Are You Wondering 7-1 box, the temperature variation of enthalpy is discussed, and the equation $q_p = \text{heat capacity} \times \text{temperature change} = C_p \times \Delta T$ was introduced to show how enthalpy changes with temperature for a constant-pressure process. Strictly speaking, the heat capacity of a substance at constant pressure is the slope of the line representing the variation of enthalpy (H) with temperature, that is
- $$C_p = \frac{dH}{dT} \quad (\text{at constant pressure})$$
- where C_p is the heat capacity of the substance in question. Heat capacity is an extensive quantity and heat capacities are usually quoted as molar heat capacities $C_{p,m}$, the heat capacity of one mole of substance, which is an intensive property. The heat capacity at constant pressure is used to estimate the change in enthalpy due to a change in temperature. For infinitesimal changes in temperature,
- $$dH = C_p dT \quad (\text{at constant pressure})$$
- To evaluate the change in enthalpy for a particular temperature change, from T_1 to T_2 , we write
- $$\int_{H(T_1)}^{H(T_2)} dH = H(T_2) - H(T_1) = \int_{T_1}^{T_2} C_p dT$$
- If we assume that C_p is independent of temperature, then we recover equation (7.5)
- $$q_p = \Delta H = C_p \Delta T$$
- On the other hand, we often find that the heat capacity is a function of temperature; a convenient empirical expression is
- $$C_{p,m} = a + bT + \frac{c}{T^2}$$
- What is the change in molar enthalpy of N_2 when it is heated from 25.0 $^\circ\text{C}$ to 100.0 $^\circ\text{C}$? The molar heat capacity of nitrogen is given by
- $$C_{p,m} = \left(28.58 + 3.77 \times 10^{-3} T - \frac{0.5 \times 10^5}{T^2} \right) \text{J mol}^{-1} \text{K}^{-1}$$

298 Chapter 7 Thermochemistry

119. How much heat is required to convert 10.0 g of ice at -5.0°C to steam at 100.0°C ? The temperature-dependent constant-pressure specific heat capacity of ice is $c_p(T)/(\text{kJ kg}^{-1}\text{K}^{-1}) = 1.0187T - 1.49 \times 10^{-2}$. The temperature-dependent constant-pressure specific heat for water is $c_p(T)/(\text{kJ kg}^{-1}\text{K}^{-1}) = -1.0 \times 10^{-7}T^3 + 1.0 \times 10^{-4}T^2 - 3.92 \times 10^{-2}T + 8.7854$.
120. The standard enthalpy of formation of gaseous H_2O at 298.15 K is $-241.82\text{ kJ mol}^{-1}$. Using the ideas contained in Figure 7-16, estimate its value at 100.0°C given the following values of the molar heat capacities at constant pressure: $\text{H}_2\text{O}(\text{g})$: $33.58\text{ J K}^{-1}\text{ mol}^{-1}$; $\text{H}_2(\text{g})$: $28.84\text{ J K}^{-1}\text{ mol}^{-1}$; $\text{O}_2(\text{g})$: $29.37\text{ J K}^{-1}\text{ mol}^{-1}$. Assume the heat capacities are independent of temperature.
121. Cetane, $\text{C}_{16}\text{H}_{34}$, is a typical petrodiesel with a standard enthalpy of combustion of $-10,699.1\text{ kJ mol}^{-1}$. Methyl linoleate, $\text{C}_{19}\text{H}_{34}\text{O}_2$, is a biodiesel with a standard

enthalpy of combustion of $-11,690.1\text{ kJ mol}^{-1}$. What volume of methyl linoleate provides the same energy as one liter of cetane? The densities of cetane and methyl linoleate are 0.773 and 0.885 g mL^{-1} , respectively.

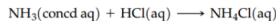
122. Carbon dioxide emissions have been implicated as a major factor in climate change. Which of the following liquid fuels, when burned completely in oxygen at 25°C , generates the smallest amount of CO_2 per kilojoule of energy output?
 Methanol, CH_3OH ($\Delta_f H^\circ = -238.7\text{ kJ mol}^{-1}$);
 cetane, $\text{C}_{16}\text{H}_{34}$ ($\Delta_f H^\circ = -456.3\text{ kJ mol}^{-1}$);
 methyl linoleate, $\text{C}_{19}\text{H}_{34}\text{O}_2$ ($\Delta_f H^\circ = -604.9\text{ kJ mol}^{-1}$);
 octane, C_8H_{18} ($\Delta_f H^\circ = -250.1\text{ kJ mol}^{-1}$).
 The $\Delta_f H^\circ$ values for $\text{CO}_2(\text{g})$ and $\text{H}_2\text{O}(\text{l})$ are -393.5 and $-285.8\text{ kJ mol}^{-1}$, respectively.

Feature Problems

123. James Joule published his definitive work related to the first law of thermodynamics in 1850. He stated that “the quantity of heat capable of increasing the temperature of one pound of water by 1°F requires for its evolution the expenditure of a mechanical force represented by the fall of 772 lb through the space of one foot.” Validate this statement by relating it to information given in this text.
124. Based on specific heat capacity measurements, Pierre Dulong and Alexis Petit proposed in 1818 that the specific heat capacity of an element is inversely related to its atomic weight (atomic mass). Thus, by measuring the specific heat capacity of a new element, its atomic weight could be readily established.
 (a) Use data from Table 7.1 and inside the front cover to plot a *straight-line* graph relating atomic mass and specific heat capacity. Write the equation for this straight line.
 (b) Use the measured specific heat capacity of $0.23\text{ J g}^{-1}\text{ }^\circ\text{C}^{-1}$ and the equation derived in part (a) to obtain an approximate value of the atomic mass of cadmium, an element discovered in 1817.
 (c) To raise the temperature of 75.0 g of a particular metal by 15°C requires 450 J of heat. What might this metal be?
125. We can use the heat liberated by a neutralization reaction as a means of establishing the stoichiometry of the reaction. The data in the table are for the reaction of 1.00 M NaOH with $1.00\text{ M citric acid}$, $\text{C}_6\text{H}_8\text{O}_7$, in a total solution volume of 60.0 mL .

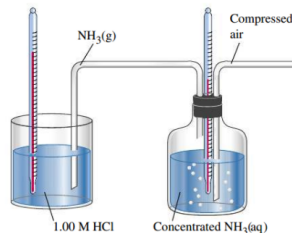
mL 1.00 M NaOH Used	mL 1.00 M Citric Acid Used	$\Delta T, ^\circ\text{C}$
20.0	40.0	4.7
30.0	30.0	6.3
40.0	20.0	8.2
50.0	10.0	6.7
55.0	5.0	2.7

- (a) Plot ΔT versus mL 1.00 M NaOH , and identify the exact stoichiometric proportions of NaOH and citric acid at the equivalence point of the neutralization reaction.
 (b) Why is the temperature change in the neutralization greatest when the reactants are in their exact stoichiometric proportions? That is, why not use an excess of one of the reactants to ensure that the neutralization has gone to completion to achieve the maximum temperature increase?
 (c) Rewrite the formula of citric acid to reflect more precisely its acidic properties. Then write a balanced net ionic equation for the neutralization reaction.
126. In a student experiment to confirm Hess’s law, the reaction



was carried out in two different ways. First, 8.00 mL of concentrated $\text{NH}_3(\text{aq})$ was added to 100.0 mL of 1.00 M HCl in a calorimeter. (The $\text{NH}_3(\text{aq})$ was slightly in excess.) The reactants were initially at 23.8°C , and the final temperature after neutralization was 35.8°C . In the second experiment, air was bubbled through 100.0 mL of concentrated $\text{NH}_3(\text{aq})$, sweeping out $\text{NH}_3(\text{g})$ (see sketch). The $\text{NH}_3(\text{g})$ was neutralized in 100.0 mL of 1.00 M HCl . The temperature of the concentrated $\text{NH}_3(\text{aq})$ fell from 19.3 to 13.2°C . At the same time, the temperature of the 1.00 M HCl rose from 23.8 to 42.9°C as it was neutralized by $\text{NH}_3(\text{g})$. Assume that all solutions have densities of 1.00 g/mL and specific heat capacities of $4.18\text{ J g}^{-1}\text{ }^\circ\text{C}^{-1}$.
 (a) Write the two equations and $\Delta_f H$ values for the processes occurring in the second experiment. Show that the sum of these two equations is the same as the equation for the reaction in the first experiment.

(b) Show that, within the limits of experimental error, $\Delta_r H$ for the overall reaction is the same in the two experiments, thereby confirming Hess's law.



127. When an ideal gas is heated, the change in internal energy is limited to increasing the average translational kinetic energy of the gas molecules. Thus, there is a simple relationship between ΔU of the gas and the change in temperature that occurs. Derive this relationship with the help of ideas about the kinetic-molecular theory of gases developed in Chapter 6. After doing so, obtain numerical values (in $\text{J mol}^{-1} \text{K}^{-1}$) for the following molar heat capacities.
- (a) the heat capacity, C_V , for one mole of gas under constant-volume conditions

(b) the heat capacity, C_p , for one mole of gas under constant-pressure conditions

128. Refer to Example 7-5 dealing with the work done by 0.100 mol He at 298 K in expanding in a single step from 2.40 to 1.20 atm. Review also the two-step expansion (2.40 atm \rightarrow 1.80 atm \rightarrow 1.20 atm) described on page 261 (see Figure 7-11).

(a) Determine the total work that would be done if the He expanded in a series of steps, at 0.10 atm intervals, from 2.40 to 1.20 atm.

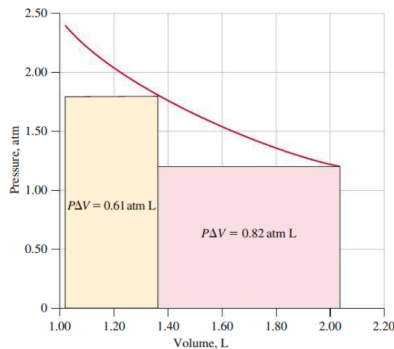
(b) Represent this total work on the graph below, in which the quantity of work done in the two-step expansion is represented by the sum of the colored rectangles.

(c) Show that the maximum amount of work would occur if the expansion occurred in an infinite number of steps. To do this, express each infinitesimal quantity of work as $dw = -P dV$ and use the methods of integral calculus (integration) to sum these quantities. Assume ideal behavior for the gas.

(d) Imagine reversing the process, that is, compressing the He from 1.20 to 2.40 atm. What are the maximum and minimum amounts of work required to produce this compression? Explain.

(e) In the isothermal compression described in part (d), what is the change in internal energy assuming ideal gas behavior? What is the value of q ?

(f) Using the formula for the work derived in part (c), obtain an expression for q/T . Is this new function a state function? Explain.



129. Look up the specific heat capacity of several elements, and plot the products of the specific heat capacities and atomic masses as a function of the

atomic masses. Based on the plot, develop a hypothesis to explain the data. How could you test your hypothesis?

Self-Assessment Exercises

130. In your own words, define or explain the following terms or symbols: (a) $\Delta_r H^\circ$; (b) $-P\Delta V$; (c) $\Delta_r H^\circ$; (d) standard state; (e) fossil fuel.
131. Briefly describe each of the following ideas or methods: (a) law of conservation of energy; (b) bomb calorimetry; (c) function of state; (d) enthalpy diagram; (e) Hess's law.
132. Explain the important distinctions between each pair of terms: (a) system and surroundings; (b) heat and work; (c) specific heat capacity and heat capacity; (d) endothermic and exothermic; (e) constant-volume process and constant-pressure process.
133. The temperature increase of 225 mL of water at 25 °C contained in a Styrofoam cup is noted when a 125 g sample of a metal at 75 °C is added. With reference to Table 7.1, the greatest temperature increase will be noted if the metal is (a) lead; (b) aluminum; (c) iron; (d) copper.
134. A plausible final temperature when 75.0 mL of water at 80.0 °C is added to 100.0 mL of water at 20 °C is (a) 28 °C; (b) 40 °C; (c) 46 °C; (d) 50 °C.
135. $\Delta U = 100$ J for a system that gives off 100 J of heat and (a) does no work; (b) does 200 J of work; (c) has 100 J of work done on it; (d) has 200 J of work done on it.
136. The heat of solution of NaOH(s) in water is -41.6 kJ/mol NaOH. When NaOH(s) is dissolved in water the solution temperature (a) increases; (b) decreases; (c) remains constant; (d) either increases or decreases, depending on how much NaOH is dissolved.
137. The standard molar enthalpy of formation of $\text{CO}_2(\text{g})$ is equal to (a) 0; (b) the standard molar heat of combustion of graphite; (c) the sum of the standard molar enthalpies of formation of $\text{CO}(\text{g})$ and $\text{O}_2(\text{g})$; (d) the standard molar heat of combustion of $\text{CO}(\text{g})$.
138. Write the formation reaction for each of the following compounds: (a) $\text{SnCl}_2(\text{s})$; (b) $\text{C}_6\text{H}_5\text{COOH}(\text{s})$; (c) $\text{COCl}_2(\text{g})$.
139. Compute $\Delta_r H^\circ$ for the following reactions. The value of $\Delta_r H^\circ$ in kJ mol^{-1} is given for each substance below its formula.
- | | | | | | | | |
|-----|--------------------------|---|--------------------------|-------------------|--------------------------|---|----------------------------------|
| (a) | $\text{SiO}_2(\text{s})$ | + | $4 \text{HF}(\text{g})$ | \longrightarrow | $\text{SiF}_4(\text{g})$ | + | $2 \text{H}_2\text{O}(\text{g})$ |
| | -910.9 | | -271.1 | | -1615.0 | | -241.8 |
| (b) | $2 \text{CuS}(\text{s})$ | + | $3 \text{O}_2(\text{g})$ | \longrightarrow | $2 \text{CuO}(\text{s})$ | + | $2 \text{SO}_2(\text{g})$ |
| | -53.1 | | 0.0 | | -157.3 | | -296.8 |
140. When dissolved in water, 1.00 mol LiCl produces 37.12 kJ of heat. What is the final temperature (in °C) when 5.00 g LiCl dissolves in 110.0 g of water at 20.00 °C? Assume that the solution produced has a specific heat capacity of $4.00 \text{ J g}^{-1} \text{ }^\circ\text{C}^{-1}$.
141. When an element is involved in a formation reaction, it does *not* have to be (a) pure; (b) at 1.00 M concentration; (c) at 1.00 bar pressure; (d) in its most stable form; (e) none of these.
142. The standard state of a substance is (a) the pure form at 1 bar; (b) the most stable form at 25 °C and 1 bar; (c) the most stable form at 0 °C; (d) the pure gaseous form at 25 °C; (e) none of these.
143. Which of the following statements is false? (a) $q_p = q_p$ for the reaction $\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \longrightarrow 2\text{NO}(\text{g})$; (b) $\Delta_r H^\circ > 0$ for an endothermic reaction; (c) By convention, the most stable form of an element must always be chosen as the reference form and assigned the value $\Delta_r H^\circ = 0$; (d) ΔU and $\Delta_r H^\circ$ for a reaction can never have the same value; (e) $\Delta_r H^\circ < 0$ for the neutralization of a strong acid by a strong base.
144. A 1.22 kg piece of iron at 126.5 °C is dropped into 981 g water at 22.1 °C. The temperature rises to 34.4 °C. What will be the final temperature if this same piece of iron at 99.8 °C is dropped into 325 mL of glycerol, $\text{HOCH}_2\text{CH}(\text{OH})\text{CH}_2\text{OH}(\text{l})$ at 26.2 °C? For glycerol, $d = 1.26 \text{ g/mL}$; $C_p = 219 \text{ J mol}^{-1} \text{ K}^{-1}$.
145. Write the balanced chemical equations for reactions that have the following as their standard enthalpy changes.
- (a) $\Delta_r H^\circ = +82.05 \text{ kJ/mol N}_2\text{O}(\text{g})$
 (b) $\Delta_r H^\circ = -394.1 \text{ kJ/mol SO}_2\text{Cl}_2(\text{l})$
 (c) $\Delta_r H^\circ = -1527 \text{ kJ/mol CH}_3\text{CH}_2\text{COOH}(\text{l})$
146. The standard molar heats of combustion of C(graphite) and $\text{CO}(\text{g})$ are -393.5 and -283 kJ/mol , respectively. Use those data and that for the following reaction
- $$\text{CO}(\text{g}) + \text{Cl}_2(\text{g}) \longrightarrow \text{COCl}_2(\text{g})$$
- $$\Delta_r H^\circ = -108 \text{ kJ mol}^{-1}$$
- to calculate the standard molar enthalpy of formation of $\text{COCl}_2(\text{g})$.
147. Can a chemical compound have a standard enthalpy of formation of zero? If so, how likely is this to occur? Explain.
148. Is it possible for a chemical process to have $\Delta U < 0$ and $\Delta H > 0$? Explain.
149. Use principles from this chapter to explain the observation that professional chefs prefer to cook with a gas stove rather than an electric stove.
150. Hot water and a piece of cold metal come into contact in an isolated container. When the final temperature of the metal and water are identical, is the total energy change in this process (a) zero; (b) negative; (c) positive; (d) not enough information.
151. A clay pot containing water at 25 °C is placed in the shade on a day in which the temperature is 30 °C. The outside of the clay pot is kept moist. Will the temperature of the water inside the clay pot (a) increase; (b) decrease; (c) remain the same?
152. Construct a concept map encompassing the ideas behind the first law of thermodynamics.
153. Construct a concept map to show the use of enthalpy for chemical reactions.
154. Construct a concept map to show the interrelationships between path-dependent and path-independent quantities in thermodynamics.