

Chemistry 12

Solutions Manual Part A

Unit 3 Energy Changes and Rates of Reaction

Answers to Unit 3 Preparation Questions (Student textbook pages 272-5)

- 1. a.** WHMIS symbol for flammable and combustible material. Precaution: Be aware of the location of the nearest fire extinguisher and type of fire for which the extinguisher can be used; ensure a fire blanket is available and a working fire alarm is nearby; Stop, Drop, Roll if clothing is ignited.
- b.** Safety symbol for thermal safety. Precaution: Check glassware for cracks before heating; do not allow a glass container to boil to dryness; when heating, point test tubes away from yourself and others; use thermal gloves to handle extremely hot or cold objects.
- c.** WHMIS symbol for corrosive material. Precautions: wear eye protection, a lab apron, and safety eyewear; use a safety shield; know location of eyewash station; report any spills and dispose of chemicals as directed by your teacher.
- d.** Safety symbol for chemical safety. Precautions: wear eye protection, gloves, and lab apron; use a safety shield; know location of eyewash station; report any spills and dispose of chemicals as directed by your teacher.
- 2. a.** Symbols c and d since hydrochloric acid is corrosive and even though it is dilute in this activity, it will irritate the skin and is dangerous to the eyes.
- b.** Symbol b as a reminder that the object is hot.
- 3.** A spill of sodium hydroxide should be washed from the skin with copious amounts of water. Adding hydrochloric acid will neutralize the base, but the acid is also corrosive. Having two corrosive chemicals on the skin increases the chance for injury. Also the reaction between hydrochloric acid and sodium hydroxide will generate some heat, which could result in a burn.

- 4. a.** To set up the Bunsen burner, you would do the following:
- place the burner to the side of the stand; do not try to light the burner when it is under the beaker
 - close the air inlet
 - make certain the lighting device is working to give a spark or flame
 - turn the gas source on full and ignite the gas with the lighter; the flame will be yellow.
 - open the air inlet to allow air to mix with the gas; continue this adjustment until the yellow disappears and the flame is blue.
- b.** To safely heat the water, you would do the following:
- Wear safety apron and protective eyewear.
 - Before beginning, check that the beaker has no cracks.
 - Do not leave the burner unattended during the heating.
 - Secure the burner to the stand.
 - Ensure the beaker is safely secured to the stand.
 - Ensure you are using a large enough beaker that you do not need to fill it much more than half full.
 - Unless specifically directed, do not boil the water; heat to the desired temperature using a thermometer to track the temperature.
 - Handle the hot beaker carefully with beaker tongs and thermal mitts if available.
- c.** To safely handle the accidental spill you would:
- Inform the teacher immediately.
 - Get treatment if anyone has been burned.
 - Avoid touching the broken glass with bare hands.
 - Collect broken glass with broom and dustpan.
 - Dispose of glass in “Broken Glass Container.” Do not mix broken glass with garbage.
- 5. e**
- 6.** A force is applied to the crate that sets it in motion; work is being done on the crate to move it. In other words, energy is transferred to the crate to move it; the person doing work on the crate caused the kinetic energy of the crate to increase

- 7. a.** *Gravitational potential energy:* A (the skier is at rest at the top of a hill)

Gravitational potential energy and kinetic energy: B (the skier is moving but has not yet reached the bottom of the hill)

- b.** In photo A, the skier is at the top of the hill and has high potential energy, given her position; gravitational potential does work to begin movement, causing an increase in kinetic energy; the kinetic energy of the skier increases and the gravitational potential energy decreases as she moves down the hill

- 8. a.** chemical energy: battery

- b.** electrical energy: energy that is transmitted via the wires from the battery to the light bulb
- c.** electromagnetic energy: light given off by the light bulb
- d.** thermal energy: when the light bulb is lit it releases thermal energy (begins to feel warm)
- e.** heat: as the light bulb warms up, thermal energy is transferred from it to the surroundings

- 9. d**

- 10.** *Sample answer:* Heat represents the quantity of thermal energy that is transferred between an object or area of higher temperature to one of lower temperature.

- 11.** Student presentations should include key points about the kinetic molecular theory; for example, the particle nature of matter, the differences in the energy of particles, the distance between particles, and the forces among particles in the three different states. Particles should be represented pictorially in the solid, liquid, and gas phases.

- 12.** According to the kinetic molecular theory of gases, air (a mixture of gases) is composed of particles that move in a random motion and can readily diffuse. Bees move their wings to cause drafts, allowing warm air to escape the hive and cooler air to enter. (Student research may also reveal that bees bring in water and move their wings to encourage evaporation by moving moist air out and dry air in. Evaporation is a process that absorbs thermal energy, cooling the hive.)

- 13. a**

- 14.** Graphic organizers should indicate the following key points: matter in all three states is composed of particles in motion; the behaviour of the particles differs in each state. Solids retain a constant shape and volume; particles are packed close together and in a fixed framework. Liquids have variable shape and constant volume; particles are less organized

and farther apart than in solids and are not in a fixed position (can slide over each other). Gases have variable shape and volume; particles are much less organized and much farther apart than in other states and bounce off each other and walls of container. In terms of motion, particles in solids vibrate; particles in liquids have primarily rotational motion; particles in gases have primarily translational motion.

- 15. b**

- 16.** A room temperature diagram will show particles moving randomly in straight lines at a speed of v_1 . At a lower temperature outside in the winter, the particles are again moving randomly but at a speed v_2 where $v_2 < v_1$. The number of collisions per unit area of the balloon surface is lower at v_2 resulting in a lower pressure and the balloon begins to deflate.

- 17. a.** As methanol cools to -97.7°C , its molecules, which previously moved with vibrational and rotational energy, lose kinetic energy. Their movement becomes predominantly vibrational as molecules form intermolecular bonds. The molecules form a rigid, crystalline structure as the methanol changes from a liquid to a solid.

- b.** As methanol heats up to 65°C , the kinetic energy of the molecules increase. The molecules begin to move with translational energy as they break away from the liquid state, overcoming intermolecular attractions. As more and more molecules gain sufficient energy to escape the liquid state and move with translational energy in the gas state, the methanol changes from a gas to a liquid.

- 18.** The rise is the vertical change between two points on the line ($y_2 - y_1$) and the run is the horizontal change between two points ($x_2 - x_1$). On this graph, rise represents a change in mass and run represents a change in volume.

- 19.** For the points indicated, the rise is 30 g and the run is 30 mL.

$$\text{slope} = \frac{\text{rise}}{\text{run}}; 1.0 \text{ g/mL}$$

$$y = 1.0x$$

- 22.** The graph represents a direct relationship; as mass increases the volume increases by the same factor.

- 23.** If the slope were steeper, there would be greater change in the y variable for the same change in the x variable. In other words, for every change in unit volume, there would be a greater change in unit mass.

24. a. Graph B represents $\frac{1}{x}$, an inverse relationship

Graph C represents x^n ($n > 1$), an exponential relationship

b. Graph A represents a direct relationship between variables.

25. a. $c_{\text{mean}} = \frac{0.54 \text{ mol/L} + 0.491 \text{ mol/L} + 0.51 \text{ mol/L}}{3}$

$$= 0.51366 \text{ mol/L}$$
$$= 0.51 \text{ mol/L}$$

b. $m = nM$

Find n :

$$n = cV$$
$$= 0.51366 \frac{\text{mol}}{\cancel{L}} \times 25 \cancel{\text{mL}} \times \frac{1 \cancel{L}}{1000 \cancel{\text{mL}}}$$
$$= 0.01284 \text{ mol}$$

Use n to find m .

$$m = nM$$
$$= 0.01284 \cancel{\text{mol}} \times 45.6 \frac{\text{g}}{\cancel{\text{mol}}}$$
$$= 0.58558 \text{ g}$$
$$= 0.59 \text{ g}$$

26. a. $y = 3$

b. $x = 2$

27. a. 0.583 L

b. $4.7 \times 10^3 \text{ cm/s}$

Chapter 5 Energy Changes

Answers to Learning Check Questions

(Student textbook page 283)

- Sample answer:* The heating element on an electric stove transfers heat to a metal pot, which transfers heat to the water inside; hot water in a wash basin transfers heat to your hands; a person exercising transfers body heat to the surrounding air.
- A closed system can exchange energy with its surroundings in forms such as thermal energy, mechanical energy, and chemical energy. For example, a hot object in a closed, metal container can transfer thermal energy to the metal container and then to the surroundings because the hot object, metal container, and surroundings are in thermal contact.
- Under conditions of constant pressure and volume, the enthalpy change of a system is equal to the heat exchanged between the system and the surroundings.
- The burning of fuel in an automobile occurs in an open system. It is not possible to isolate the combustion reaction that occurs in an automobile engine. Thermal energy is continually released to the surroundings

and dispersed. Under laboratory conditions, the combustion of a fuel could be studied in a controlled manner with all released thermal energy accounted for. The second law of thermodynamics would be shown to be valid. This tells us that when studying chemical reactions, the immediate surroundings must be isolated from the system for the results to be accurate.

5. An endothermic process is one in which the enthalpy or heat content of the system increases. Thermal energy is absorbed by the system. An exothermic process is one in which the enthalpy or heat content of the system decreases. Thermal energy is given off by the system.

- The products have greater potential energy.
- The enthalpy of the system is increasing; the reaction is endothermic; the enthalpy change is positive.

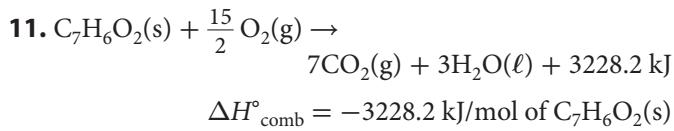
(Student textbook page 295)

7. The enthalpy term is a product in a thermochemical equation. The negative value for the enthalpy change means that energy is released.

8. Energy is released by the system, so the products have a lower potential energy than the reactants. The reactants, therefore, have more potential energy.



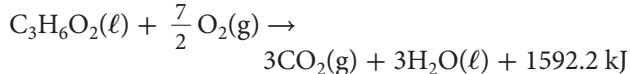
10. The diagram should indicate that the vertical scale measures potential energy in kilojoules per mole. The reactants, $\text{C}_3\text{H}_8(\ell) + \frac{9}{2} \text{O}_2(\text{g})$, are at a higher energy level than the products, $3\text{CO}_2(\text{g}) + 3\text{H}_2\text{O}(\ell)$, with an energy difference of 2091.3 kJ.



12. The equation for complete combustion of methyl methanoate is as written:



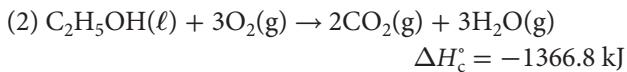
The equation for complete combustion of methyl ethanoate is as shown below (divide the given equation by 2):



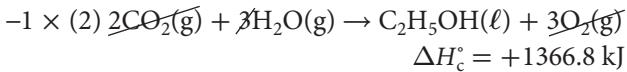
More heat is given off for $\text{C}_3\text{H}_6\text{O}_2(\ell)$ than for $\text{C}_2\text{H}_4\text{O}_2(\ell)$. The standard molar enthalpy of combustion for $\text{C}_3\text{H}_6\text{O}_2(\ell)$ is -1592.2 kJ/mol .

(Student textbook page 317)

13. For any physical or chemical process, the overall enthalpy change is the sum of the enthalpy changes of its individual steps and depends only on the initial and final conditions. The enthalpy change can thus be determined for reactions that are either very slow or are too dangerous to carry out under laboratory conditions.
14. The standard conditions are SATP (25°C or 298.15 K, and 100 kPa). For aqueous solutions, standard conditions assumes a concentration of 1 mol/L.
15. The pressure must be kept constant when comparing the enthalpy change between two reactions.
16. The enthalpy diagram should have the same overall appearance and labels as Figure 5.20, with these exceptions: Since the process is reversed, the arrows point upward to show the absorption of energy, an endothermic process. ΔH values should have their signs reversed so that they are all positive values.
17. Calorimetry experiments can be used to find the enthalpy of reaction for simpler steps. Data for a large number of simple reactions is known, so it may not be necessary to carry out each step experimentally. Any combination of reactions that total to the overall reaction can be used.
18. Hess's law is valid because the enthalpy change is determined only by the initial and final conditions of the system.
19. Adding the forward combustion reaction of ethene to the reverse combustion reaction of ethanol gives the target reaction, as shown below.



Add (1) to the reverse of (2)



The enthalpy of the reaction is $\Delta H_r^\circ = -74.4 \text{ kJ}$.

In the enthalpy diagram, the reactants, $\text{C}_2\text{H}_4(\text{g}) + \text{H}_2\text{O}(\ell)$, are 74.4 kJ higher in energy than the product, $\text{C}_2\text{H}_5\text{OH}(\ell)$.

(Student textbook page 332)

20. efficiency = $\frac{\text{energy output}}{\text{energy input}} \times 100\%$
21. *Sample answer:* In Canada, there are large reserves of natural gas, and the infrastructure to deliver and use this energy source is firmly established. It is more economical to look at how we can conserve use of energy, rather than to switch from this readily available source.
22. Hydrocarbons as a heating fuel have a low efficiency (as low as 30%) and there are serious environmental issues both in their production and use, such as the emissions of greenhouse gases that increase global warming and nitrogen oxides that contribute to the formation of acid rain and smog.
23. Advantages: use of nuclear energy produces no greenhouse gas emissions; once set up, the reactor is efficient to maintain; is reliable and long-term; produces radioactive isotopes as by-products that are important for treatment of some diseases.
Disadvantages: must store radioactive waste for thousands of years; has high initial set-up cost; requires uranium mines that are damaging to the environment; is susceptible to environmental disasters that can result in radioactive leaks into the air and water.
24. *Sample answer:* Four harmful effects from recovering or using a source of energy include deforestation (strip mining for coal); thermal pollution of natural habitats (warming of water in lakes and rivers used to cool power plants); hazards to birds (wind turbines); and air pollution (burning of fossil fuels).
25. A non-renewable energy source is effectively gone once it is used up; these sources include oil, natural gas, coal, and uranium. A renewable energy source can be replenished or is so large a source that it will not be used up; such sources include, wind, solar, geothermal, biomass.

Answers to Caption Questions

Figure 5.2 (Student textbook page 279): Three other examples of surroundings include equipment, air, and the water that will be added to the beaker. (The lab bench is another example of surroundings.)

Figure 5.3 (Student textbook page 279): An open system can exchange both energy and matter with its surroundings. Water vapour and heat escape into the air (surroundings) in the example shown. A closed system can exchange energy, but not matter, with its surroundings. The water and potatoes remain enclosed in the system,

but thermal energy is exchanged with the container and the surrounding air. An isolated system cannot exchange matter or energy with its surroundings. Since the pot is enclosed in a thermally insulated container, neither heat nor matter can escape to the surroundings.

Figure 5.16 (Student textbook page 301): Small holes minimize the loss of thermal energy to the surroundings.

Figure 5.18 (Student textbook page 306): The position of the flame should maximize the transfer of heat to the can rather than to the air around the can.

Figure 5.24 (Student textbook page 318): Graphite is the more stable form of carbon, because diamond has a greater potential energy, as shown by its higher standard molar enthalpy of formation.

Figure 5.30 (Student textbook page 331):
2010: coal + gas = 43%

Answers to Section 5.1 Review Questions

(Student textbook page 291)

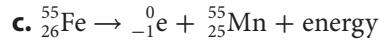
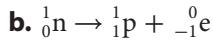
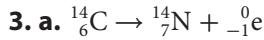
1. The system is the $\text{CaCl}_2(\text{s})$. The surroundings include the water, the beaker and anything in contact with the beaker. The surroundings are gaining energy since the temperature rises so the system must be losing thermal energy.

2. $Q = mc\Delta T$

$$= 350.0 \text{ g} \times 2.44 \frac{\text{J}}{\text{g} \cdot ^\circ\text{C}} \times 2.81^\circ\text{C}$$

$$= 23\,997.4 \text{ J}$$

$$= 2.40 \times 10^4 \text{ J}$$



4. Since the solvent molecules are only slightly polar, the attractions between the solvent molecules and ions from $\text{NaCl}(\text{s})$ would be small and there would be very low solubility. There would be greater solute-solvent attraction between molecules of ethanol and the solvent. The strength of the solute bonds in NaCl is very high and the strength of any solute-solvent bonds would be very low; therefore the enthalpy change would be positive. On the other hand, the intermolecular bonds in ethanol are much weaker than ionic bonds, and the solute-solvent bonds that would form would be significantly stronger than with NaCl . So the enthalpy change would be either much less positive than for NaCl or negative, depending on whether ethanol-ethanol bonds are stronger than ethanol-ethoxyethane bonds.

5. From Table 5.2, $\Delta H_{\text{melt}}^\circ(\text{O}_2(\text{s})) = 0.44 \text{ kJ/mol}$.

Therefore $\Delta H_{\text{fre}}^\circ(\text{O}_2(\ell)) = -0.44 \text{ kJ/mol}$

Heat removed to freeze 15.0 mol $\text{O}_2(\ell)$

$$\Delta H(\text{O}_2(\ell)) = n\Delta H_{\text{fre}}^\circ$$

$$= 15 \text{ mol} \left(-0.44 \frac{\text{kJ}}{\text{mol}} \right)$$

$$= -6.6 \text{ kJ}$$

6. $Q = mc(T_f - T_i)$

$$(T_f - T_i) = \frac{Q}{mc}$$

$$-T_i = \frac{Q}{mc} - T_f$$

$$T_i = T_f - \frac{Q}{mc}$$

$$= 14.7^\circ\text{C} - \frac{164.7 \text{ J}}{15.55 \text{ g} \times 0.129 \frac{\text{J}}{\text{g} \cdot ^\circ\text{C}}}$$

$$= 14.7^\circ\text{C} - 82.106^\circ\text{C}$$

$$= -67.4^\circ\text{C}$$

The initial temperature of the gold was -67.4°C

7. heat gained by air = heat lost by water

$$(mc\Delta T)_{\text{air}} = -(mc\Delta T)_{\text{water}}$$

$$(2.00 \text{ kg}) \left(\frac{1000 \text{ g}}{\text{kg}} \right) \left(1.01 \frac{\text{J}}{\text{g} \cdot ^\circ\text{C}} \right) \Delta T =$$

$$\left[-(1.00 \text{ kg}) \left(\frac{1000 \text{ g}}{\text{kg}} \right) \left(4.19 \frac{\text{J}}{\text{g} \cdot ^\circ\text{C}} \right) (-20.0^\circ\text{C}) \right]$$

$$\Delta T = \frac{\left[-(1.00 \text{ kg}) \left(\frac{1000 \text{ g}}{\text{kg}} \right) \left(4.19 \frac{\text{J}}{\text{g} \cdot ^\circ\text{C}} \right) (-20.0^\circ\text{C}) \right]}{(2.00 \text{ kg}) \left(\frac{1000 \text{ g}}{\text{kg}} \right) \left(1.01 \frac{\text{J}}{\text{g} \cdot ^\circ\text{C}} \right)}$$

$$= \frac{8.3800 \times 10^4}{2.02 \times 10^3 \frac{1}{^\circ\text{C}}}$$

$$= 41.48^\circ\text{C}$$

The air temperature will increase by 41.5°C .

8. Energy cannot be created or destroyed but can be transformed from one type to another or transferred from one object to another.

$$\Delta E_{\text{universe}} = E_{\text{system}} + E_{\text{surroundings}} = 0$$

or

$$E_{\text{system}} = -E_{\text{surroundings}}$$

9. $\Delta E = Q + W = (+500 \text{ J}) + (-500 \text{ J}) = 0 \text{ J}$

There is no net change to the energy of the system.

10. a. system is the burning natural gas; exothermic reaction, net energy given off to the surroundings; ΔH is negative.

- b. system is the water; net energy is absorbed by the water from the surrounding heat source; endothermic process; ΔH is positive.
- c. system is the body; potential energy of position is gained; reaction is endothermic; ΔH is positive.
- d. system is the wax; energy leaves the wax and goes to the surroundings; process is exothermic; ΔH is negative.
- e. system is the hydrogen atoms; fusion releases energy as helium forms; reaction is exothermic; ΔH is negative.

- 11.** The change is sublimation, represented by the following equation:



Enthalpy diagrams should show $\text{H}_2\text{O}(\text{g})$ on a straight line at a higher level than $\text{H}_2\text{O}(\text{s})$, also on a straight line. An arrow should point up from the lower line to the upper line and should be labelled ΔH .

- 12.** More energy is needed to vaporize or boil water than is required to melt an equivalent amount of ice. When ice changes to liquid water, the lattice structure is broken, but the water molecules are still attracted to one another. When liquid changes to gas, all intermolecular attractions, essentially, must be overcome; this requires far more energy. Student diagrams should show kinetic molecular theory representations of what is happening during melting and boiling.

13. Comparing Nuclear and Chemical Reactions

property	chemical reaction	nuclear reaction
a. identity of atoms	atoms do not change	atoms converted to a new element
b. atomic particles involved	electrons involved in bond breaking and bond making	protons and neutrons change
c. energy change	$10^2 - 10^3 \text{ kJ}$	$10^8 - 10^{10} \text{ kJ}$

Answers to Section 5.2 Review Questions

(Student textbook page 311)

- The calorimeter must be constructed to be a good thermal insulator so that you can assume all the heat is transferred from the system to the surroundings within the calorimeter.
- Polystyrene is a polymer made of low-density beads that contain air, which is very efficient at trapping heat. (It is also inexpensive.)

3.
$$Q = mc\Delta T$$

$$= 80.0 \text{ g} \times 4.19 \frac{\text{J}}{\text{g}\cdot^\circ\text{C}} \times (-1.5^\circ\text{C}) \\ = -502.8 \text{ J} \\ = -5.0 \times 10^2 \text{ J}$$

The thermal energy lost by the water is $5.0 \times 10^2 \text{ J}$.

- The concentration of the acid and the base must be recorded. As well, the volume of the two solutions and the initial and final temperatures of the solutions must be recorded. Assume that all of the heat from the neutralization is transferred to the solution in the calorimeter. Assume that the density of the solution is 1.0 g/mL and the specific heat capacity of the solution is $4.19 \text{ J/g}^\circ\text{C}$.
- In dilute solutions, the properties of the solute do not contribute significantly to the solution. In a concentrated solution, however, the attractions among the particles are significantly different than in pure water, and the properties of the solution (such as density and specific heat capacity) differ significantly as well.
- The temperature of the water increases. Since the enthalpy change of the reaction is negative, the dissolving process is exothermic. Heat must be absorbed by the surroundings, which, in this case, is water.

7. The triple Venn diagram should show:

- A: Polystyrene calorimeter: description—2 stacked cups; for reactions in aqueous solution; thermometer inserted through lid records ΔT ; gas can escape so thermal energy change is measured at constant pressure. Assumptions—all thermal energy is absorbed by the solution and solutions have same properties as water. Sources of error—heat loss via absorption by polystyrene and other calorimeter components; heat loss through small holes in lid
- B: Flame calorimeter: description—reaction chamber is large can with air holes; thermal energy transferred to suspended, small can of water; ΔT measured with thermometer in water. Assumptions—thermal energy given off is absorbed by the small can and the water. Sources of error—significant heat loss to surrounding air
- C: Bomb calorimeter: description—enclosed container. Assumptions—thermal energy transfer is to water and calorimeter; thermometer measures ΔT ; heat capacity of calorimeter used to determine the thermal energy absorbed by the calorimeter using $Q = C\Delta T$. Sources of error—minimal heat

loss to calorimeter container and surroundings, but a correction factor should be used to take into account pressure changes

- A and B: heat transfer to water calculated using $Q = mc\Delta T$
- A and C: both use a stirrer to keep water at uniform temperature
- B and C: both are suitable for determining enthalpy of combustion reactions
- A, B, and C: calorimetry is based on the 1st and 2nd laws of thermodynamics; calorimeters are used to measure release or absorption of thermal energy, usually for the purpose of determining the enthalpy change associated with chemical and physical processes

- 8. a.** Equimolar amounts are used and the reaction requires 1:1 ratios of reactants. Therefore the amount of either reactant can be used to determine the molar enthalpy of neutralization.

$$\begin{aligned} Q &= mc\Delta T \\ &= 200.0 \text{ g} \times 4.19 \frac{\text{J}}{\text{g}\cdot^\circ\text{C}} \times 0.33^\circ\text{C} \\ &= 276.54 \text{ J} \\ &= 0.27654 \text{ kJ} \\ n &= cV \\ &= 0.0500 \frac{\text{mol}}{\text{L}} \times 100.00 \text{ mL} \times \frac{1 \text{ L}}{1000 \text{ mL}} \\ &= 0.00500 \text{ mol} \\ \Delta H_{\text{neut}} &= \frac{-0.27654 \text{ kJ}}{0.00500 \text{ mol}} \\ &= -55.3 \frac{\text{kJ}}{\text{mol}} \end{aligned}$$

- b.** $\text{KOH(aq)} + \text{HNO}_3(\text{aq}) \rightarrow \text{KNO}_3(\text{aq}) + \text{H}_2\text{O}(\ell) + 55.3 \text{ kJ}$

- 9.** The first and second laws of thermodynamics apply to calorimetry as follows: The first law of thermodynamics states that the energy of the universe is constant. This law applies to calorimetry calculations because we assume that the heat change to the system is equal and opposite compared with the heat change to the surroundings. (The first law holds true even if there is heat lost outside the immediate surrounding but the more heat transferred beyond the calorimeter, the greater the experimental error.) The second law of thermodynamics states that thermal energy spontaneously flows from an object at a higher temperature to one at a lower temperature, when they are in thermal contact. When objects at different temperatures are in contact, thermal energy is transferred from the warmer object to the cooler object

until they are both at the same temperature. The energy change from a chemical reaction, therefore, results in a predictable temperature change to the surroundings, and insulating material can be used to create small, measurable surroundings.

Student diagrams could show a simple calorimeter including the following labels: system; surroundings; effective surroundings, insulating material

- 10.** A flame calorimeter is an open system because both matter and energy can be exchanged with the surroundings.

- 11.** Thermal energy gained by the calorimeter

$$\begin{aligned} Q &= C\Delta T \\ &= 11.6 \frac{\text{kJ}}{\text{C}} \times 8.41^\circ\text{C} \\ &= 97.556 \text{ J} \end{aligned}$$

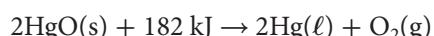
Thermal energy released by burning = -97.556 kJ

$$Q = \frac{-97.556 \text{ kJ}}{6.60 \text{ g}} = -14.7812 \text{ kJ/g}$$

The thermal energy released per gram of biscuit is 14.78 kJ/g

- 12.** Student reports should describe the design of the room, how it is insulated from outside energy changes, how changes in air temperature can be monitored, how $\text{O}_2(\text{g})$ uptake and $\text{CO}_2(\text{g})$ production are measured, how long the subject would stay in the room, what kind of food is used, what exercise is expected by the subject, and how is the mass of the person and/or changes in mass will be monitored. Reference(s) must be included.

- 13. Sample answer:**



When 182 kJ of thermal energy is added to 2 mol of solid mercury(II) oxide, 2 mol of liquid mercury and 1 mol of oxygen gas are produced. Alternatively, you could say: To decompose 2 mol of mercury(II) oxide, 182 kJ of thermal energy must be added. 2 mol of liquid mercury and 1 mol of oxygen gas are produced.

Answers to Section 5.3 Review Questions (Student textbook page 324)

- 1.** The standard enthalpy change for a reaction in which a certain compound is a product is the enthalpy change for that reaction as written. It is applicable for production of that compound in the amount that corresponds to the stoichiometric coefficient in the chemical equation. The equation is:

$$\Delta H_r^\circ = [\Sigma(n\Delta H_f^\circ \text{products})] - [\Sigma(n\Delta H_f^\circ \text{reactants})]$$

The standard molar enthalpy of formation of a compound represents the enthalpy change when 1 mol of a compound is formed from its elements under standard conditions.

2. $\frac{1}{2} \text{N}_2(\text{g}) + \frac{5}{4} \text{H}_2(\text{g}) + \text{C}(\text{s}) + \frac{3}{2} \text{O}_2(\text{g}) \rightarrow (\text{NH}_4\text{HCO}_3)(\text{s}) + 849.4 \text{ kJ}$
3. $\text{H}_2(\text{g}) + \frac{1}{8} \text{S}_8(\text{s}) + 2\text{O}_2(\text{g}) \rightarrow \text{H}_2\text{SO}_4(\ell) + 814.0 \text{ kJ}$
4. (1) $\times -2: 2\text{NO}(\text{g}) \rightarrow \text{N}_2(\text{g}) + \text{O}_2(\text{g}) \quad \Delta H^\circ = -181.0 \text{ kJ}$
 (2) $\times -2: 2\text{NOCl}(\text{g}) \rightarrow 2\text{NO}(\text{g}) + \text{Cl}_2(\text{g}) \quad \Delta H^\circ = 78.0 \text{ kJ}$
-
- $$2\text{NOCl}(\text{g}) \rightarrow \text{N}_2(\text{g}) + \text{O}_2(\text{g}) + \text{Cl}_2(\text{g})$$
- $$\Delta H_r = (-181.0 \text{ kJ}) + (78.0 \text{ kJ}) = -103.0 \text{ kJ}$$
5. (1) $\times 1: \text{P}_4(\text{s}) + 6\text{Cl}_2(\text{g}) \rightarrow 4\text{PCl}_3(\ell) \quad \Delta H^\circ = -1272 \text{ kJ}$
 (2) $\times -1: \text{P}_4\text{O}_{10}(\text{s}) \rightarrow \text{P}_4(\text{s}) + 5\text{O}_2(\text{g}) \quad \Delta H^\circ = 2915 \text{ kJ}$
 (3) $\times -6: 6\text{PCl}_5(\text{s}) \rightarrow 6\text{PCl}_3(\ell) + 6\text{Cl}_2(\text{g}) \quad \Delta H^\circ = 750 \text{ kJ}$
 (4) $\times 10: 10\text{PCl}_3(\ell) + 5\text{O}_2(\text{g}) \rightarrow 10\text{Cl}_3\text{PO}(\text{g}) \quad \Delta H^\circ = -2670 \text{ kJ}$
-
- $$\text{P}_4\text{O}_{10}(\text{s}) + 6\text{PCl}_5(\text{s}) \rightarrow 10\text{Cl}_3\text{PO}(\text{g})$$
- $$\Delta H_r = (-1272 \text{ kJ}) + (2915 \text{ kJ}) + (750 \text{ kJ}) + (-2670 \text{ kJ}) = -277 \text{ kJ}$$

6. $n_{\text{Ba}} = \frac{5.48 \text{ g}}{137.33 \text{ g/mol}} = 0.03990 \text{ mol}$
 $\frac{-21.9 \text{ kJ}}{0.03990 \text{ mol}} = \frac{x}{1 \text{ mol}}$
 $x = -548.87 \text{ kJ}$

Ba(s) and BaO(s) are equimolar; therefore, the enthalpy of formation for BaO(s) is -549 kJ/mol

7. O₂(g) is the standard state of this element and is assigned a zero value. To produce O(g), energy must be added in order to break the strong covalent bonds in the oxygen molecules:



8. CaCl₂(s) ($\Delta H_f^\circ = -795.4 \text{ kJ/mol}$) >
 CrCl₃(s) ($\Delta H_f^\circ = -556.5 \text{ kJ/mol}$) >
 NaCl(s) ($\Delta H_f^\circ = -411.2 \text{ kJ/mol}$) >
 AgCl(s) ($\Delta H_f^\circ = -127.0 \text{ kJ/mol}$)

Decomposition is the reverse reaction of formation. The more negative the ΔH_f° , the more energy will be required to decompose the compound. The four compounds are ranked from the most negative ΔH_f° to the least negative.

9. a. $\Delta H_r^\circ = \Sigma(n\Delta H_f^\circ \text{ products}) - \Sigma(n\Delta H_f^\circ \text{ reactants}) = [(9 \text{ mol})(\Delta H_f^\circ \text{ Fe}(\text{s})) + (4 \text{ mol})(\Delta H_f^\circ \text{ Al}_2\text{O}_3(\text{s}))] - [(3 \text{ mol})(\Delta H_f^\circ \text{ Fe}_3\text{O}_4(\text{s})) + (8 \text{ mol})(\Delta H_f^\circ \text{ Al}(\text{s}))]$

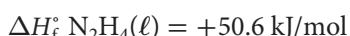
$$= [(9 \text{ mol})(0 \text{ kJ/mol})] + (4 \text{ mol})(-1675.7 \text{ kJ/mol}) - [(3 \text{ mol})(-1118.4 \text{ kJ/mol}) + (8 \text{ mol})(0 \text{ kJ/mol})]$$

$$= (-6702.8 \text{ kJ}) + (3355.2 \text{ kJ}) = -3347.6 \text{ kJ}$$

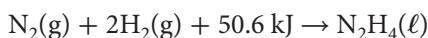
b. $n_{\text{Fe}(\text{s})} = \frac{1\ 000\ 000 \text{ g}}{55.85 \text{ g/mol}} = 1.7905 \times 10^4 \text{ mol}$
 $\frac{-3347.6 \text{ kJ}}{9 \text{ mol Fe}(\text{s})} = \frac{x}{1.7905 \times 10^4 \text{ mol Fe}(\text{s})}$
 $x = -6.659\ 86 \times 10^6 \text{ kJ}$

The quantity of heat given off would be
 $6.660 \times 10^6 \text{ kJ}$

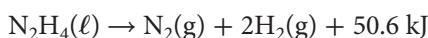
10. Sample answer: Hi. Is hydrazine a thermally stable compound? Let's look at the enthalpies involved:



The chemical equation for the formation of hydrazine is:



The equation for the thermal decomposition of hydrazine is the opposite:



What this means is that hydrazine releases thermal energy when it decomposes. This means that the bonds in hydrazine are not as strong as the bonds in nitrogen and hydrogen combined. So hydrazine is not very thermally stable.

11. $\Delta H_r^\circ = \Sigma(n\Delta H_f^\circ \text{ products}) - \Sigma(n\Delta H_f^\circ \text{ reactants})$

$$\Delta H_r^\circ = [(1 \text{ mol})(\Delta H_f^\circ \text{ N}_2(\text{g})) + (6 \text{ mol})(\Delta H_f^\circ \text{ HF}(\text{g})) + (1 \text{ mol})(\Delta H_f^\circ \text{ Cl}_2(\text{g}))] - [(2 \text{ mol})(\Delta H_f^\circ \text{ ClF}_3(\text{g})) + (2 \text{ mol})(\Delta H_f^\circ \text{ NH}_3(\text{g}))]$$

$$-1200 \text{ kJ} = [(1 \text{ mol})(0 \text{ kJ/mol}) + (6 \text{ mol})(-273.3 \text{ kJ/mol}) + (1 \text{ mol})(0 \text{ kJ/mol})] - [(2 \text{ mol})(\Delta H_f^\circ \text{ ClF}_3(\text{g})) + (2 \text{ mol})(-45.9 \text{ kJ/mol})]$$

$$-1200 \text{ kJ} = [(-1639.8 \text{ kJ})] - [(2 \text{ mol})(\Delta H_f^\circ \text{ ClF}_3(\text{g})) + (91.8 \text{ kJ})]$$

$$(2 \text{ mol})(n\Delta H_f^\circ \text{ ClF}_3(\text{g})) = -1731.6 \text{ kJ} + 1200 \text{ kJ}$$

$$(\Delta H_f^\circ \text{ ClF}_3(\text{g})) = -266 \text{ kJ/mol}$$

12. A positive ΔH_f° indicates that the system has gained energy in the formation of the compound. A greater amount of energy is absorbed in breaking bonds in the reactants than is liberated in the formation of bonds in the compound. Student diagrams should resemble Figure 5.13B on page 294 of the student textbook.

13. $n_{\text{CaCO}_3(\text{s})} = \frac{500.0 \text{ g}}{100.09 \text{ g/mol}} = 4.99550 \text{ mol}$
 $\Delta H_f^\circ \text{ CaCO}_3(\text{s}) = -1207.6 \text{ kJ/mol}$
 $\Delta H_f^\circ \text{ CaO}(\text{s}) = -634.9 \text{ kJ/mol}$
 $\Delta H_f^\circ \text{ CO}_2(\text{g}) = -393.5 \text{ kJ/mol}$

$$\Delta H_r = [(1 \text{ mol})(-634.9 \text{ kJ/mol}) + (1 \text{ mol})(-393.5 \text{ kJ/mol})] \\ - (1 \text{ mol})(-1207.6 \text{ kJ/mol})$$

$$= +179.2 \text{ kJ per mol CaCO}_3(\text{s})$$

$$\text{Heat required} = 4.995 \text{ mol} \times +179.2 \text{ kJ/mol} \\ = +895.2 \text{ kJ}$$

The quantity of heat required to decompose 500.0 g of $\text{CaCO}_3(\text{s})$ is +895.2 kJ.

Answers to Section 5.4 Review Questions

(Student textbook page 335)

1. In home use, there is only one energy conversion step, in which natural gas is burned in a high-efficiency furnace. The heat produced goes directly to the building. In a power plant, the thermal energy produced by burning natural gas is used to warm and boil water to generate steam, which turns a turbine, producing electrical power that then must be transported to homes. Energy is lost at each step in this process.

2. Polymers are important materials that are used in the manufacture of plastics and some clothing. The starting materials for these products come from fossil fuels. Some examples of plastics include the polyethylene used in plastic toys, bottles, garbage bags; and the polyester used to make clothing.

3. Negative issues:

- non-renewable resource
- emissions contribute to environmental problems—acid rain, global warming, smog
- strip mining for coal destroys the landscape
- deforestation

Ways to reduce the use of fossil fuels:

- use products that operate on different energy sources, such as hybrid cars
- advocate for alternative energy such as solar and wind power
- minimize use of fossil fuels through conservation, e.g., by walking instead of driving, or by turning down the thermostat at home.

4. Carbon dioxide emissions:

wood waste biomass: 93.32 kg/kJ

natural gas: 56.03 kg/kJ

$$\frac{\text{emission difference}}{\text{natural gas emission}} \times 100\% =$$

$$\frac{(93.32 - 56.03) \text{ kg/kJ}}{56.03 \text{ kg/kJ}} \times 100\% = 66.55\%$$

The emissions of $\text{CO}_2(\text{g})$ in kg/kJ are about 67% greater using wood waste biomass compared with natural gas.

5. Sample answer:

- Hibachi: lowest cost to purchase; inexpensive fuel; no on/off, need starter fuel to ignite; minimal control over burning, waste of fuel, high greenhouse gas emissions per kg (about 100 kJ/kg); also produces high levels of sulfur oxides and nitrogen oxides.
- Propane: high heat content; relatively inexpensive fuel; need to purchase in pressurized tanks; can control on/off and heat level; greenhouse gas emissions (about 66.61 kJ/kg); availability where you live may be a factor; non-renewable fuel source
- Natural gas: low cost; high heat content; reliable and convenient source; can control heat level and on/off; greenhouse gas emissions (about 56.08 kJ/kg); non-renewable fuel source

From a purely environmental perspective, the “best” barbecue would be the natural gas barbecue. Since its cost is not much greater than the propane barbecue, which is the second-best in terms of environmental concerns, it makes the best sense to purchase the natural gas barbecue if you are concerned about the environmental impact.

6. a. This is worse than the calculated fuel consumption since the gas consumption is higher.

b. Factors to explain the discrepancy may include: speeding, idling the engine, driving with under-inflated tires, accelerating quickly from a stop, not coasting to a stop, driving with windows open, or having a new car with an engine that is not yet “broken in.”

c. Fuel economy can be improved by changing your driving habits. Driving more slowly, not idling the car, accelerating slowly from a stop, keeping windows closed, and allowing a car to slow down by taking your foot off the gas rather than applying the brakes will all improve fuel economy.

7. Sample answer: To use the waste heat produced by any cooling system, which could include an air-conditioner as well as a refrigerator, you could build something similar to a solar heating system. The warm air exiting the air conditioner or refrigerator would have to be contained and circulated around piping containing water. The preheated water would then already be partially warmed before entering the hot water tank, reducing energy costs. Heated water could also be used as radiant floor heating.

8. You would look for information that tells you how much energy the appliance uses and how this compares to other, similar appliances. Specifically, you would examine the EnerGuide and/or ENERGY STAR®

stickers on the appliance. The EnerGuide label allows a consumer to quickly judge the energy efficiency of the appliance compared to others using a sliding scale. The ENERGYSTAR® label is an easy way to tell that this appliance is one of the most energy efficient in its category.

- 9.** *Sample answer:* A clean fuel is one that does not produce harmful emissions. There are some fuels that do not directly produce emissions at the point of generation (such as wind or hydro); however, in harnessing these forms of energy, other forms of energy are used (such as the gasoline used in the transportation of workers and to mine minerals used to build the machinery) that do not use clean fuels. Therefore, no energy source is perfectly “clean.”

- 10. a.** $\text{CO}_2(\text{g})$ (primarily)
b. $\text{CO}_2(\text{g}), \text{NO}_x(\text{g}), \text{SO}_x(\text{g})$
c. $\text{NO}_2(\text{g})$

- 11.** Heat content is measured in kJ/kg of fuel, whereas enthalpy of combustion is measured in kJ/mol of fuel. Heat content is more useful in evaluating fuels as consumers purchase and transport fuels using units of mass, not moles.

12. $m_{\text{octane}} = d \times V = 0.70 \text{ g/mL} \times 1.00 \text{ mL} = 0.70 \text{ g}$

$$n_{\text{octane}} = \frac{0.70 \text{ g}}{114.26 \text{ g/mol}} = 0.006126 \text{ mol}$$

input of heat from the burning of octane = $n\Delta H_c$

$$= 0.006126 \text{ mol} \times (-5470.3 \text{ kJ/mol})$$

$$= -33.5111 \text{ kJ}$$

$$= -33.5111 \text{ J}$$

output of heat absorbed by the water = $(m \times c \times \Delta T)$

$$= 250.00 \text{ g} \times 4.19 \text{ J/g°C} \times 22.7^\circ\text{C}$$

$$= 23778.25 \text{ J}$$

$$\text{Efficiency} = \frac{\text{Energy output}}{\text{Energy input}} \times 100\%$$

$$= 23778.25 \text{ J}/33511.1 \text{ J} \times 100\% = 71.956\%$$

The efficiency of the heating system is 72.0%.

- 13.** Select a convenient volume of fuel, say, 10.0 mL.

$$m_{\text{octane}} = d \times V = 0.70 \text{ g/mL} \times 10.0 \text{ mL} = 7.0 \text{ g}$$

heat given off during combustion = $7.0 \text{ g} \times 44.5 \text{ kJ/g}$
 $= 311.5 \text{ kJ}$

output of energy = $0.200 \times 311.5 \text{ kJ} = 62.3 \text{ kJ}$

$$m_{\text{ethanol}} = d \times V = 0.79 \text{ g/mL} \times 10.0 \text{ mL} = 7.9 \text{ g}$$

heat given off during combustion = $7.9 \text{ g} \times 29.7 \text{ kJ/g}$
 $= 234.63 \text{ kJ}$

output of energy = $0.250 \times 234.63 \text{ kJ} = 58.6 \text{ kJ}$

Given the rated efficiencies, octane gives off more energy per unit volume and is therefore a better fuel.

- 14.** Make the assumption that the enthalpy of complete combustion of methane is very close to the enthalpy of incomplete combustion of methane.

$$n_{\text{CH}_4(\text{g})} = \frac{100 \text{ g}}{16.05 \text{ g}} = 6.2305 \text{ mol}$$

Energy released on burning = $n\Delta H_c$

$$= 6.2305 \text{ mol} \times -802.5 \text{ kJ/mol}$$

$$= -5000.0 \text{ kJ}$$

$$= -5.000 \text{ MJ}$$

mass of $\text{CO}(\text{g})$ emitted = $5.000 \text{ MJ} \times 19.14 \text{ kg/MJ}$
 $= 95.7 \text{ kg}$

Answers to Practice Problems

For full solutions to Practice Problems, see Part B of this Solutions Manual.

(Student textbook page 281)

1. +4.06 kJ

2. +16.5 kJ

3. +6.10 kJ

- 4.** The liquid in beaker B absorbs twice as much heat because it has twice the mass.

5. $+2.14 \times 10^2 \text{ kJ}$

- 6.** Specific heat capacity is 0.790 J/g. $^\circ\text{C}$; it is granite.

7. 11.1 g

8. 1.95 $^\circ\text{C}$

9. +3.2 kJ

- 10. a.** ΔT for hydrogen is 3.49 $^\circ\text{C}$; the temperature change of the hydrogen gas is much less than the change for air.

- b.** The molecules that make up air have a greater mass than hydrogen molecules. There will be more molecules in 10.0 g of $\text{H}_2(\text{g})$ than in 10.0 g of air. The absorbed energy will be distributed among a larger number of $\text{H}_2(\text{g})$ molecules and each will gain less energy than in the air sample.

(Student textbook page 299)

11. a. -438.62 kJ

b. -701.80 kJ

c. -584.83 kJ

12. -136.7 kJ

13. a. -2742 kJ

b. $-6.51 \times 10^4 \text{ kJ}$

- c.** -1.126×10^6 kJ
- 14.** -55.5 kJ
- 15.** 12.43 g
- 16.** 23.8 kg
- 17. a.** -2058.0 kJ/mol
b. +244.5 kJ
- 18. a.** -2.2×10^3 kJ/mol
b. propane
- 19.** 20.2 g
- 20. a.** $\text{CH}_3\text{CH}(\text{OH})\text{CH}_3(\ell) + \frac{9}{2}\text{O}_2(\text{g}) \rightarrow 3\text{CO}_2(\text{g}) + 4\text{H}_2\text{O}(\ell) + 2006$ kJ
b. -695.8 kJ
- (Student textbook page 305)**
- 21.** -75.5 kJ/mol
- 22.** -55.0 kJ/mol
- 23.** -2.9×10^2 kJ/mol
- 24.** -27.4 kJ/mol
- 25.** The temperature increases by 0.853°C.
- 26.** -41.9 kJ/mol
- 27.** The temperature increases by 1.31°C.
- 28.** The initial temperature was 21.8°C.
- 29.** The temperature increases by 30.9°C.
- 30.** -54.47 kJ/mol KOH
- (Student textbook page 309)**
- 31.** 616°C
- 32.** -3.9×10^3 kJ/mol
- 33.** 2.00 g
- 34.** +20.3 kJ/g
- 35.** -24 kJ/g
- 36.** -617 kJ/mol
- 37. a.** -1.38×10^3 kJ/mol
b. $\text{C}_2\text{H}_4(\text{g}) + 3\text{O}_2(\text{g}) \rightarrow 2\text{CO}_2(\text{g}) + 2\text{H}_2\text{O}(\text{g}) + 1.38 \times 10^3$ kJ
- 38.** The temperature will increase by 8.81°C.
- 39.** 2.93 g
- 40.** -1780 kJ/mol
- (Student textbook page 316)**
- 41. a.** -55.3 kJ
b. $2\text{NO}_2(\text{g}) \rightarrow \text{N}_2\text{O}_4(\text{g}) + 55.3$ kJ
- 42.** -635.7 kJ
- 43.** -816.6 kJ
- 44.** -147.5 kJ
- 45.** -219.6 kJ
- 46.** -205.9 kJ
- 47.** -1124.0 kJ
- 48.** -395 kJ
- 49.** +52.6 kJ
- 50.** -128.8 kJ
- (Student textbook page 323)**
- 51. a.** $\text{C}_2\text{H}_5\text{OH}(\ell) + 3\text{O}_2(\text{g}) \rightarrow 2\text{CO}_2(\text{g}) + 3\text{H}_2\text{O}(\text{g})$
b. -1235 kJ/mol $\text{C}_2\text{H}_5\text{OH}(\ell)$
- 52.** -176.2 kJ
- 53. a.** -158.3 kJ
b. 52.3 g
- 54.** -902 kJ
- 55.** -102.7 kJ/mol
- 56.** -224.2 kJ/mol
- 57.** -130.8 kJ
- 58.** +20.4 kJ/mol
- 59.** -1857.3 kJ/mol $\text{C}_6\text{H}_{14}(\ell)$
- 60.** -478.8 kJ/mol
- (Student textbook pages 327-8)**
- 61.** 16%
- 62.** 69.5%
- 63.** 38.7%
- 64.** 0.812 g
- 65. a.** +13.4 kJ
b. +7363 kJ
- 66. a.** $+1.82 \times 10^4$ kJ
b. $+3.18 \times 10^4$ kJ; 36.4%
- 67.** +155.1 MJ
- 68. a.** 2.2×10^4 J
b. 3.6×10^4 J
c. 62%
- 69. a.** 2.78 g
b. +273 kJ
c. 4.92 g
- 70.** 77.9%

Answers to Chapter 5 Review Questions

(Student textbook pages 343-9)

- 1. b
- 2. c
- 3. b
- 4. c
- 5. c
- 6. e
- 7. a
- 8. d
- 9. b
- 10. d
- 11. a
- 12. c
- 13. c
- 14. d

15. Energy is the ability to generate heat or the capacity to move an object. The total energy of the universe is constant but can be changed from one form to another.

- 16. a.** This is an example of nuclear fission, in which a large nucleus absorbs a neutron and splits into two smaller nuclei.
b. There is less mass in the product nuclei than in the reactant nucleus plus the neutron. This “mass deficit” is converted to energy, which can be determined using the equation $E = mc^2$.

17. At 90.0°C, the water molecules have potential energy and kinetic energy. The kinetic energy reflects the degree of molecular movement and the potential energy is an indication of the position and attraction between molecules. From 90.0°C to 100.0°C, the kinetic energy increases as the molecular motion increases, mainly through the increase of the average speed of the molecules. At 100.0°C, the addition of thermal energy increases the potential energy of the molecules as intramolecular bonds are broken and molecules move farther apart. From 100.0°C to 110.0°C, once the molecules are all in the gas state, the addition of more thermal energy increases molecular motion as the kinetic energy increases.

18. a. The system is the part of the universe where an energy exchange originates, which is the wax candle in this example. Technically, the surroundings are the rest of the universe. For practical purposes, the surroundings include anything in the universe that

exchanges thermal energy with the system, which is the air and objects in the room in this example.

- b.** Any energy change in a system results in an equal and opposite energy change in the surroundings.

$$\Delta E_{\text{system}} = -\Delta E_{\text{surroundings}}$$

19. For a reaction at constant pressure, the change in potential energy of the system represents the change in thermal energy for the surroundings. Because the pressure is constant, the thermal energy change of the surroundings is equal and opposite to the enthalpy change for the reaction. For a reaction at constant volume, the change in potential energy of the system represents the change in thermal energy of the surroundings. Because the pressure changes, however, a correction factor would need to be used to determine the enthalpy.

20. Calorimetry is based upon the first and second laws of thermodynamics. The first law of thermodynamics, which states that the total energy in the universe is constant, means that any change in the energy of a system results in an equal but opposite energy change in the surroundings. The second law of thermodynamics, which states that thermal energy is spontaneously transferred from an object at a higher temperature to the one at a lower temperature if they are in thermal contact, ensures that the enthalpy change can be calculated based on the thermal energy change observed in the calorimeter.

21. The heat capacity of a bomb calorimeter takes into account all the heat that all parts of the calorimeter can gain or lose.

$$C_{\text{bomb calorimeter}} = C_{\text{water}} + C_{\text{thermometer}} + C_{\text{stirrer}} + C_{\text{container}}$$

The specific heat capacity would be different for each component and to use these values the mass of each component would need to be known. It is simpler to determine the heat capacity of the bomb calorimeter as a whole, by experiment, and use that value in subsequent experiments.

- 22. a.** The products have a greater potential energy.
b. The reaction is endothermic. More energy is required to break the bonds in $\text{N}_2(\text{g})$ and $\text{O}_2(\text{g})$ than is released in the formation of bonds in $\text{N}_2\text{O}_4(\text{g})$. There are more and/or stronger bonds in the reactants than in the products.

23. a. The black soot is carbon, indicating that combustion was incomplete. Not all of the carbon in the alcohol was burned. Less heat was produced than would be expected from complete combustion.

- b.** The experimentally determined enthalpy of combustion will be too low.
- c.** The information needed includes: mass of water; mass of aluminum can; mass of alcohol; initial and final temperatures of the water (which will be same for the aluminum can); specific heat capacity of water and of aluminum.
- 24.** For an exothermic reaction, energy is released. Consider the complete combustion of methane:
- $$\text{CH}_4(\text{g}) + 2\text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) + 2\text{H}_2\text{O}(\text{g}) + 802.5 \text{ kJ}$$
- The total enthalpy of 1 mol $\text{CO}_2(\text{g})$ and 2 mol $\text{H}_2\text{O}(\text{g})$ is less than the total enthalpy of 1 mol $\text{CH}_4(\text{g})$ and 2 mol $\text{O}_2(\text{g})$. The enthalpy of combustion, $\Delta H^\circ_{\text{comb}}$, is -802.5 kJ because the system releases this amount of thermal energy to the surroundings. There must be more and/or stronger bonds in the products than in the reactants, because the formation of bonds releases thermal energy. More thermal energy is released when bonds form to make $\text{CO}_2(\text{g}) + 2\text{H}_2\text{O}(\text{g})$ than is absorbed when bonds are broken in $\text{CH}_4(\text{g}) + 2\text{O}_2(\text{g})$.
- 25.** *Sample answer:* Some activities that use fossil fuels include: showering and cooking breakfast in a warm home (natural gas to heat the water and space and to cook food, assuming a gas range), watching television (coal burned to create electricity), and driving to and from school (gasoline for the car).
- 26.** *Energy output:* energy delivered to consumer as heat or electricity; actual work done; expansion of a gas; movement of an object
- Energy input:* calculated energy in a fuel; energy used to extract and transport a fuel; solar energy used to create biomass; energy used to build and maintain a power plant
- 27.** A crop such as corn is considered biomass and is classed as a renewable energy resource. If corn were the only source of biomass, there would not be enough available land for it to be a practical energy source. Nevertheless, biomass is a source of energy that can be useful in the big picture of energy demand. To fully analyze the viability of this resource you would need to determine the energy used to grow the corn and convert it to ethanol and compare it with the energy content of the ethanol.
- 28.** The condensation that forms on the beaker is water from the air. The temperature of the solution is decreasing because the dissolving process is an endothermic reaction. Thermal energy is absorbed from the water in the beaker, which cools, along with the beaker itself. Water from the air condenses on the

cold beaker. Eventually the water temperature drops to, or below, 0°C and the condensed water droplets freeze.

- 29.** *Standard* indicates that ΔH_f° was determined at standard conditions of 25°C and 100 kPa ; *molar* indicates that ΔH_f° represents the formation of 1 mol of $\text{Cr}_2\text{O}_3(\text{s})$ (or whatever substance is specified); *enthalpy* refers to the thermal energy change associated with the formation reaction at constant pressure; *formation* indicates that ΔH_f° gives the enthalpy difference between the compound ($\text{Cr}_2\text{O}_3(\text{s})$) and the elements from which the compound is formed ($\text{Cr}(\text{s})$ and $\text{O}_2(\text{s})$) in their standard states.

Dividing the given equation by 2 and reversing it gives the formation reaction and enthalpy change:
 $\Delta H_f^\circ = -1128.4 \text{ kJ/mol}$

30. -96.7 kJ

- 31.** Since the temperature of the unknown liquid increased twice that of the same mass of water, its specific heat capacity must be half that of water, or $2.10 \text{ J/g}^\circ\text{C}$.



b. $n(\text{Cu}) = \frac{m}{M} = \frac{37.9 \text{ g}}{63.55 \text{ g/mol}} = 0.59638 \text{ mol}$

$$\frac{\Delta H}{Q} = \frac{302.9 \text{ kJ}}{Q} = \frac{1 \text{ mol}}{0.59638 \text{ mol}}$$

$$Q = 180.644 \text{ kJ}$$

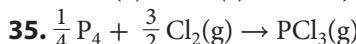
The thermal energy required to produce the copper is 181 kJ .

- 33.** The equation has been reversed and the sign of H_r° should now be negative, as shown. The given value of H_r° was for 1 mol of $\text{N}_2\text{O}_4(\text{g})$. Since there is now $\frac{1}{2}$ mol $\text{N}_2\text{O}_4(\text{g})$, H_r° must also be divided by 2. Therefore, the given equation is not correct. The correct equation is:

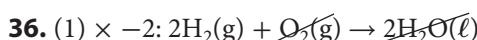


34. a. $n(\text{Pb}) = \frac{m}{M} = \frac{62.16 \text{ g}}{207.2 \text{ g/mol}} = 0.3000 \text{ mol}$

$$\Delta H_{\text{melt}}^\circ = \frac{Q}{n} = \frac{+98.1 \text{ kJ}}{0.3000 \text{ mol}} = +327 \text{ kJ/mol}$$



$$\Delta H_f^\circ = -71.9 \text{ kJ}$$



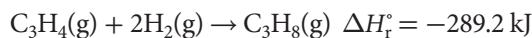
$$\Delta H^\circ = -571.6 \text{ kJ}$$



$$\Delta H^\circ = -1936.8 \text{ kJ}$$



$$\Delta H^\circ = 2219.2 \text{ kJ}$$



37. $\Delta H_r^\circ = [\Sigma(n\Delta H_f^\circ \text{ products})] - [\Sigma(n\Delta H_f^\circ \text{ reactants})]$

$$-159.6 \text{ kJ} = [(1 \text{ mol})(\Delta H_f^\circ \text{ Ni(CO)}_4(\text{g}))] - [(1 \text{ mol})(\Delta H_f^\circ \text{ Ni}) + (4 \text{ mol})(\Delta H_f^\circ \text{ CO(g)})]$$

$$-159.6 \text{ kJ} = [(1 \text{ mol})(\Delta H_f^\circ \text{ Ni(CO)}_4(\text{g}))] - [(1 \text{ mol})(0 \text{ kJ/mol}) + (4 \text{ mol})(-110.5 \text{ kJ/mol})]$$

$$\Delta H_f^\circ \text{ Ni(CO)}_4(\text{g}) = -159.6 \text{ kJ} - 442.0 \text{ kJ} = -601.6 \text{ kJ}$$

The standard molar enthalpy of formation is
-601.6 kJ/mol.

38. $\Delta H_r^\circ = [\Sigma(n\Delta H_f^\circ \text{ products})] - [\Sigma(n\Delta H_f^\circ \text{ reactants})]$

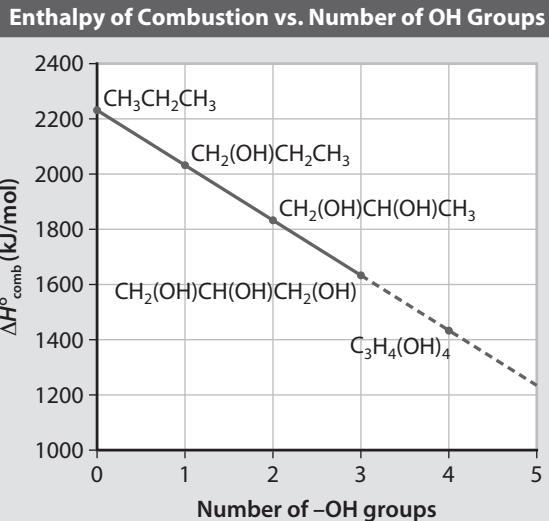
$$= [(1 \text{ mol})(\Delta H_f^\circ \text{ C}_4\text{H}_6(\text{g})) + (2 \text{ mol})(\Delta H_f^\circ \text{ H}_2\text{O(g)}) + (1 \text{ mol})(\Delta H_f^\circ \text{ H}_2(\text{g}))] - [(2 \text{ mol})(\Delta H_f^\circ \text{ C}_2\text{H}_5\text{OH}(\ell))]$$

$$= [(1 \text{ mol})(-391.1 \text{ kJ/mol}) + (2 \text{ mol})(-241.8 \text{ kJ/mol}) + (1 \text{ mol})(0 \text{ kJ/mol})] - [(2 \text{ mol})(-277.6 \text{ kJ/mol})]$$

$$= -319.5 \text{ kJ}$$

The standard enthalpy of reaction for the reaction as written is -319.5 kJ.

39. a. Graphs should show “Enthalpy of Combustion in kJ/mol” on the *y*-axis and “Number of -OH groups” on the *x*-axis. The shape of the graph should be a straight line sloping downward from left to right. The graph should have a reasonable title, such as “Enthalpy of Combustion vs. Number of OH Groups.”



- b.** There appears to be an inverse relationship between the number of -OH groups and the enthalpy of combustion. The more -OH groups on the chain, the lower the enthalpy of combustion.
- c.** Extending the straight line of the graph to the value of 4 on the *x*-axis, the enthalpy of combustion for $\text{C}_3\text{H}_4(\text{OH})_4(\text{s})$ is predicted to be 1450 kJ/mol.

40. $Q = 1377.65 \text{ kJ}$, $C = 15.6 \frac{\text{kJ}}{\text{C}^\circ}$

$$Q = C\Delta T$$

$$\Delta T = \frac{Q}{C}$$

$$= \frac{1377.65 \text{ kJ}}{15.6 \frac{\text{kJ}}{\text{C}^\circ}}$$

$$= 88.3 \text{ C}^\circ$$

The calorimeter will change temperature by 88.3°C.

41. a. $m_{\text{Zn}} = 1.20 \text{ g}$, $V_{\text{dil HCl}} = 90.0 \text{ mL}$, $T_i = 22.44^\circ\text{C}$, $T_f = 24.65^\circ\text{C}$

Heat gained by solution when Zn reacted with HCl:

$$Q = mc\Delta T$$

$$= 90.00 \text{ g} \times 4.19 \frac{\text{J}}{\text{g} \cdot {}^\circ\text{C}} \times 2.21^\circ\text{C}$$

$$= 833.39 \text{ J}$$

$$= 0.83339 \text{ kJ}$$

Heat entering solution is the amount of heat lost by the reaction.

$$\Delta H_r = -Q$$

$$\Delta H_r = -0.83339 \text{ kJ}$$

Find the number of moles of Zn used in reaction.

$$n_{\text{Zn}} = \frac{m}{M}$$

$$= \frac{1.20 \text{ g}}{65.38 \frac{\text{g}}{\text{mol}}}$$

$$= 0.018354 \text{ mol}$$

Heat of reaction per mole:

$$\Delta H_r = \frac{-0.83339 \text{ kJ}}{0.018354 \text{ mol}}$$

$$= -45.406 \frac{\text{kJ}}{\text{mol}}$$

The enthalpy of reaction in terms of zinc is -45.4 kJ/mol.

- b.** A paper cup was used as a calorimeter and paper is not as good an insulator as polystyrene. Significant heat would have been lost to the surroundings beyond the calorimeter.

c. efficiency = $\frac{45.4 \frac{\text{kJ}}{\text{mol}}}{155 \frac{\text{kJ}}{\text{mol}}} \times 100\%$

$$= 29.3\%$$

The efficiency of the experimental set-up is 29.3%.

42. $m_{\text{H}_2\text{O}} = 1.00 \text{ kg}$, $\Delta T = 15.5^\circ\text{C}$

$$Q = 1.00 \frac{\text{kg}}{\text{kg}} \times 1000 \frac{\text{g}}{\text{kg}} \times 4.19 \frac{\text{J}}{\text{g} \cdot {}^\circ\text{C}} \times 15.5^\circ\text{C}$$

$$= 64945 \text{ J}$$

$$= 64.945 \text{ kJ}$$

$$\Delta H = -64.945 \text{ kJ}$$

$$\frac{1 \text{ mol CS}_2}{-1077 \text{ kJ}} = \frac{x}{-64.945 \text{ kJ}}$$

$$x = 0.06030 \text{ mol CS}_2(\ell)$$

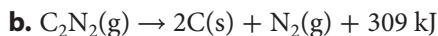
$$m = nM$$

$$m_{\text{CS}_2} = 0.06030 \text{ mol} \times 76.15 \frac{\text{g}}{\text{mol}} = 4.59 \text{ g}$$

43. a.

$$\begin{aligned}\Delta H_c^\circ &= [\Sigma(n\Delta H_f^\circ \text{products})] - [\Sigma(n\Delta H_f^\circ \text{reactants})] \\ &= [(2 \text{ mol})(\Delta H_f^\circ \text{CO}_2(\text{g})) + (1 \text{ mol})(\Delta H_f^\circ \text{N}_2(\text{g}))] - [(1 \text{ mol})(\Delta H_f^\circ \text{C}_2\text{N}_2(\text{g})) + (2 \text{ mol})(\Delta H_f^\circ \text{O}_2(\text{g}))] \\ -1096 \text{ kJ} &= [(2 \text{ mol})(-393.5 \text{ kJ/mol}) + (1 \text{ mol})(0 \text{ kJ/mol})] - [(1 \text{ mol})(\Delta H_f^\circ \text{C}_2\text{N}_2(\text{g})) + (2 \text{ mol})(0 \text{ kJ/mol})]\end{aligned}$$

$$\Delta H_f^\circ \text{C}_2\text{N}_2(\text{g}) = 309 \text{ kJ/mol}$$



44. a. Before calculating, ΔH_r , the limiting reactant must be determined and the amount, n , must represent the actual number of moles of limiting reactant that react. (Also, the sign of Q would need to be reversed so it reflects the change in the system, not the surroundings.)

b. The $\text{HCl}(\text{aq})$ is in excess. If the total number of moles of $\text{HCl}(\text{aq})$ is used, the value of ΔH_r calculated will be too small. (If the sign of Q is not reversed, the sign of the answer will be wrong.)

45. Heat lost by surroundings:

$$\begin{aligned}Q &= mc\Delta T \\ &= 50.0 \frac{\text{g}}{\text{g}} \times 4.19 \frac{\text{J}}{\text{g} \cdot {}^\circ\text{C}} \times (-1.6^\circ\text{C}) \\ &= -335.20 \text{ J}\end{aligned}$$

$$\text{Heat absorbed by system} = 0.3352 \text{ kJ}$$

$$n(\text{NH}_4\text{Br}) = \frac{1.00 \text{ g}}{97.95 \text{ g/mol}} = 0.010209 \text{ mol}$$

$$\Delta H_{\text{soln}} = \frac{0.3352 \text{ kJ}}{0.010209 \text{ mol}} = 32.833 \text{ kJ/mol}$$

The molar enthalpy of solution is 32.8 kJ/mol.

46. energy input = $41.0 \text{ kJ/g} \times 0.68 \text{ g} = 27.88 \text{ kJ}$

$$\text{energy output} = 8.7 \text{ kJ/}^\circ\text{C} \times 2.9^\circ\text{C} = 25.23 \text{ kJ}$$

$$\begin{aligned}\text{Efficiency} &= \frac{\text{energy output}}{\text{energy input}} \times 100\% \\ &= \frac{25.23 \text{ kJ}}{27.88 \text{ kJ}} \times 100\% = 90.49\%\end{aligned}$$

The efficiency is 90.5%.

47. The enthalpy diagram should show

" $\text{C}_2\text{H}_6(\text{g}) + \frac{7}{2}\text{O}_2(\text{g})$ " on a horizontal line with " $2\text{CO}_2(\text{g}) + 3\text{H}_2\text{O}(\ell)$ " on a horizontal line directly below. An arrow points from the top line to the bottom line. The arrow should have the following label: " $\Delta H_{\text{comb}}^\circ = -1560.7 \text{ kJ}$." The y -axis should be labelled " $H(\text{kJ})$ ".

48. Sample answer: Temperature measures the average kinetic energy of the particles in a sample. Heat refers to the transfer of thermal energy between two objects at different temperatures. To illustrate these terms, use a thermometer to take the temperature of warm water in a beaker. Since it is warm water, its temperature will be greater than the air temperature. The molecules of water have more thermal energy than the particles in the air. When the beaker is touched, it feels warm because heat is transferred from the beaker to the hand.

49. Sample answer:

PMI Chart for Data Regarding New Fuel Source

P	M	I
<ul style="list-style-type: none"> cost saving over using coal, since a municipality wants to get rid of this product estimation that $\text{CO}_2(\text{g})$ emission would be reduced 30% compared with coal company will be seen as environmentally friendly, leading to potential increased sales diversion of waste from landfills 	<ul style="list-style-type: none"> new equipment must be purchased and installed unknown costs to monitor emissions health risk of using a fuel containing plastics including polyvinyl chlorides (PVCs) waste is not of uniform and consistent energy content 	<ul style="list-style-type: none"> estimated energy content of coal is 26 kJ/g estimated energy content from current waste is 13 kJ/g

50. Sample answer: Some points to stress to make the food warmer seem appealing would be that it:

- is compact
- uses a low cost solid fuel
- emits no or few harmful gases
- is efficient

51. ΔH_{melt} for ice (snow) is +6.01 kJ/mol. The energy to melt the snow comes from your body heat. Therefore you are going to get colder if you eat snow.

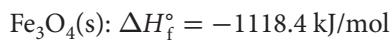
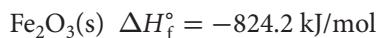
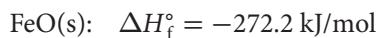
- 52. a.** Some of the technologies could include: hydrogen fuel cells and the catalysts used, solid oxide fuel cells, bacteria and solar hydrogen stations.
- b.** Some cons include that there are problems of storage and transportation. Also, there does not yet exist infrastructure for widespread use of hydrogen as a fuel. In addition, on metal surfaces, $\text{H}_2(\text{g})$ decomposes to atoms that can migrate into the metal, making it brittle.
- For the diagram, the main topic, the “backbone” of the “fish”, is the use of hydrogen gas as a fuel. Pros or supporting points might include the safety of waste material produced, the lack of radioactive waste, and the inexhaustible supply of starting material. Cons include the high start-up costs and problems of production, storage, and transportation. There is also a lack of infrastructure for delivery to the consumer. In addition, on metal surfaces, $\text{H}_2(\text{g})$ decomposes to atoms that can migrate into the metal, making it brittle.
- 53. Sample answer:**
- a. Positive aspects to emphasize:** Nuclear energy supplies large amounts of energy for amount of fuel used; can meet the growing global energy demands; produces no greenhouse gases; nuclear isotopes are a by-product of the fission process and some of these are used for medical treatments and industrial uses that are of benefit to society; new technology and innovations create new job opportunities; while there is a finite amount of nuclear fuel, there is ample for the foreseeable future, giving scientists and engineers time to work on the alternative source of nuclear energy, which is the process of nuclear fusion.
- Negative aspects to minimize:* nuclear waste is radioactive for many years and is difficult to store safely, but new technologies have improved storage of nuclear waste; nuclear accidents can be catastrophic, but new designs place nuclear plants at low risk for accidents.
- b.** A Main Idea Web could be used to concentrate on the positive aspects. Other reasonable answers are equally acceptable.
- 54. a.** Refer to Appendix A, page 712, for graphic organizer references. A Main Idea Web or a Concept Map are two possible ways to organize the information into essential and non-essential transportation needs as well as efficient and less-efficient heating methods.
- b.** The student will need to decide on a way to compare “dependency.” Dollars spent on each area is one possibility for comparison.
- 55.** Students should use a graphic organizer such as a Concept Map to categorize questions such as the following:
- What does the fuel cost per unit?
 - What factors (transportation, recovery, technology required for extraction) affect the cost?
 - What emissions come from burning the fuel?
 - Is the source renewable?
 - What is needed to use the fuel (furnace, wind turbine, solar panels)?
- 56. Sample answer:**
- The first law ($\Delta E_{\text{system}} = -\Delta E_{\text{surroundings}}$) tells us that energy released by a system is gained by the surroundings, and vice versa; the second law states that heat is always transferred from the hotter to the colder object when two objects are in thermal contact. The heat from the hot sand is transferred to our feet whereas the heat from a warm body will be transferred to the cooler water, which is why the sand feels hot and the water feels cool.
- Whether the day is sunny or cloudy affects the difference in sand and water temperature. Solar energy can penetrate into the water and therefore be dispersed more than in solid sand. The surface of the sand will absorb most of the energy. The temperature of this sand will rise more than the water because the greater volume of water can absorb more heat. More energy will be absorbed when the day is sunny rather than cloudy.
 - The specific heat capacity is the quantity of heat that will raise the temperature of a substance by 1°C . The specific heat capacity of water is $4.2 \text{ J/g}^{\circ}\text{C}$, while sand is in the range of $0.2 - 0.8 \text{ J/g}^{\circ}\text{C}$. The quantity of heat gained is given by $Q = mc\Delta T$. Since sand has a significantly lower value for c , given equal masses of sand and water gaining the same amount of energy, the ΔT will be greater for sand.
- 57. a. Sample answer:**
- i. Would you briefly outline the nature of your alternative energy source?
 - ii. Is this a renewable energy source?
 - iii. In using this source of energy, are there any by-products that are harmful to the environment?
 - iv. Can the source of energy be obtained without harming the environment?

- v. Is the source of energy readily available or are there steps in its preparation before use?
 - vi. What type of efficiency can be expected in the recovery and distribution of energy from this source?
 - vii. Are there large capital costs to using this energy source?
 - viii. Are there significant maintenance costs to using this energy source?
 - ix. What advantages are gained from using this energy source?
 - x. Are there any disadvantages to using this energy source?
- b. Sample answer:**
- i. Earth's geothermal energy originates from the original formation of the planet and from the radioactive decay of minerals: the inner core of Earth is molten and heat continues to radiate toward the surface. Geothermal energy is literally "Earth energy." The recovery of this thermal energy from Earth just 1–2 m below the surface is now a practical and efficient energy industry.
 - ii. The source is effectively inexhaustible but localized sites may cool down over time.
 - iii. Use of geothermal energy may result in low levels of hydrogen sulfide being released from the ground. The fluid used to absorb and radiate the energy may contain low levels of toxins.
 - iv. Care in choosing sites and disposing of used fluid will minimize harm to the environment.
 - v. Recovery of this thermal energy is achieved through heat exchange between water or another fluid circulating in plastic coils buried in the ground. Installation of a heat exchange system is required in the house.
 - vi. Data from geothermal power plants estimate a 16% efficiency rate of recovery of energy. The efficiency of a house heating system has too many variables to accurately estimate the overall efficiency.
 - vii. The capital costs include purchase and installation of a heat pump system, and construction costs to distribute the heat throughout the house. Switching to this system from a traditional heating system would incur additional capital costs.
 - viii. For any mechanical system there will some maintenance. There are few moving parts to wear out and plastic parts underground will not corrode. There are therefore no significant maintenance costs.

- ix. Advantages: once set up it is an inexpensive source; few or no emissions are produced; there are no transportation costs; the source has a high reliability; the source is unlikely to run out for a long time.
- x. There are no long-term disadvantages. High capital start-up costs are estimated to be recoverable in 10 years. The heat pump will rely on electricity which will shut down in a power interruption, just as with any furnace.

58. Student answers should include the key terms (see pages 278, 292, 312, and 325), as well as concepts shown on page 402. The graphic organizer could be a main idea web, a spider map, or a concept map.

59. The three oxides of iron listed are:



The reverse of a formation reaction is a decomposition reaction. The reverse of the enthalpy of formation is the enthalpy of decomposition. The greater the enthalpy of decomposition, the more heat is required to decompose the compound into its elements. The greater the enthalpy of decomposition, the greater the thermal stability. $\text{Fe}_3\text{O}_4(\text{s})$ has the most negative ΔH_f° and will therefore have the most positive enthalpy of decomposition. It is the most thermally stable.

$$\text{60. a. } Q(\text{CH}_4) = \frac{890.8 \text{ kJ}}{1 \text{ mol}} = \frac{890.8 \text{ kJ}}{16.05 \text{ g}} = 55.50 \text{ kJ/g}$$

$$Q(\text{H}_2) = \frac{285.8 \text{ kJ}}{1 \text{ mol}} = \frac{285.8 \text{ kJ}}{2.02 \text{ g}} = 141.5 \text{ kJ/g}$$

In terms of kJ/g, methane has only 39% of the energy content of hydrogen.

b. Assume STP conditions:

$$Q(\text{CH}_4) = \frac{890.8 \text{ kJ}}{1 \text{ mol}} = \frac{890.8 \text{ kJ}}{22.4 \text{ L}} = 39.8 \text{ kJ/L}$$

$$Q(\text{H}_2) = \frac{285.8 \text{ kJ}}{1 \text{ mol}} = \frac{285.8 \text{ kJ}}{22.4 \text{ L}} = 12.8 \text{ kJ/L}$$

In terms of kJ/L, hydrogen has only 32% of the energy content of methane.

61. For a 1.00 g sample of fuel:

$$n(\text{C}_4\text{H}_9\text{OH}(\ell)) = \frac{0.30 \text{ g}}{74.14 \text{ g/mol}} = 0.004046 \text{ mol}$$

$$\begin{aligned} \Delta H^\circ &= n\Delta H_f^\circ \\ &= 0.004046 \text{ mol} \times (-2758.6 \text{ kJ/mol}) \\ &= -11.1612 \text{ kJ} \end{aligned}$$

$$n(\text{C}_2\text{H}_5\text{OH}(\ell)) = \frac{0.70 \text{ g}}{46.08 \text{ g/mol}} = 0.0151909 \text{ mol}$$

$$\begin{aligned}
 \Delta H^\circ &= n\Delta H_c^\circ \\
 &= 0.0151909 \text{ mol} \times (-1366.8 \text{ kJ/mol}) \\
 &= -20.762 \text{ kJ} \\
 \text{total heat released} &= (-11.1612 \text{ kJ}) + (-20.762 \text{ kJ}) \\
 &= -31.9 \text{ kJ}
 \end{aligned}$$

The enthalpy of combustion is -31.9 kJ/g .

62. a. Electrical energy input

$$\begin{aligned}
 &= 1.100 \times 10^3 \text{ J/s} \times 2.00 \text{ min} \times 60.0 \text{ s/min} \\
 &= 1.32 \times 10^5 \text{ J} \\
 \text{microwave energy output} &= 81.02\% \text{ of } 1.32 \times 10^5 \text{ J} \\
 &= 0.8102 \times 1.32 \times 10^5 \text{ J} \\
 &= 1.0694 \times 10^5 \text{ J}
 \end{aligned}$$

$$\begin{aligned}
 \text{microwave energy absorbed by water} \\
 &= 98.3\% \text{ of } 1.0694 \times 10^5 \text{ J} \\
 &= 0.983 \times 1.0694 \times 10^5 \text{ J} \\
 &= 1.0512 \times 10^5 \text{ J}
 \end{aligned}$$

$$\begin{aligned}
 Q &= mc\Delta T \\
 1.0512 \times 10^5 \text{ J} &= 500.0 \text{ g} \times 4.19 \text{ J/g°C} \times \Delta T \\
 \Delta T &= 50.2^\circ\text{C}
 \end{aligned}$$

The temperature of the water is expected to increase by 50.2°C .

b. Some of the thermal energy absorbed by the water would be transferred to the Pyrex™ bowl and to the air inside the oven.

c. Some of the electrical energy is dissipated as heat in the electrical circuitry; also, electrical components use some of this energy—for example, the transformer, the light inside the oven, the fan, and the rotating turntable.

63. All the descriptions will affect the calculation of the heat, Q , absorbed by the surroundings.

$$Q = mc\Delta T$$

a. If the solution was not constantly stirred the heat would dissipate slowly and the expected final temperature would be too low or too high, depending on the part of the mixture measured. If too low, ΔT would be too small and the calculated value of Q would be smaller than expected. (If too high, the opposite would occur.)

b. Using 16.9°C rather than 19.6°C as the initial temperature will make ΔT too large and the calculated value of Q will be larger than expected.

c. The result of this description is that the values used for the mass and specific heat capacity are too low. This will give a calculated value of Q that is lower than expected.

64. A constant volume calorimeter, such as a bomb calorimeter, is an isolated system calibrated to take

into account all of the parts and contents. For an open system at constant pressure using a flame calorimeter, there would be significant heat loss to the surrounding air. The data would be more reliable from a calorimeter at constant volume, especially if a correction factor is used to take the pressure change into account.

65. Needed information and assumptions:

Assume that natural gas is 100% methane, $\text{CH}_4(\text{g})$, and that the volume of gas is measured at SATP, giving a molar volume of 24.8 L/mol .

$$\Delta H^\circ_{\text{comb}} (\text{CH}_4) = 890.9 \text{ kJ/mol}$$

Express the volume of the given statistic in litres:

$$27 \text{ m}^3 = 2.7 \times 10^4 \text{ L}$$

Amount of CH_4 at SATP from the Internet statistic:

$$n = \frac{2.7 \times 10^4 \text{ L}}{24.8 \text{ L/mol}} = 1.1 \times 10^3 \text{ mol}$$

$$\text{Energy released} = n \times \Delta H^\circ_{\text{comb}} (\text{CH}_4)$$

$$= 1.1 \times 10^3 \text{ mol} \times 890.9 \text{ kJ/mol}$$

$$= 9.8 \times 10^5 \text{ kJ or about 1 GJ}$$

The statement is valid based on these calculations.

66. *Sample answer: Pros:* By using biomass, thermal energy is extracted from material that would otherwise be wasted. This saves on the use of non-renewable energy sources such as coal, oil and natural gas.

Cons: Burning of biomass fuels still contributes emissions that are linked to global warming and acid rain.

67. Sample answer:

Economic advantages: better fuel economy (gas mileage) because less gasoline is used; efficiencies give better fuel economy such as regenerative braking that reclaims mechanical energy and converts it to electrical energy to recharge batteries; electric motor boosts the power performance of gas engines at lower speed.

Environmental advantages: reduced dependency on fossil fuel; cleaner fuel with lower emission of greenhouse gases

Economic disadvantages: higher initial cost, especially for electric motor and batteries; lower acceleration rate; replacement parts more costly; repairs more costly

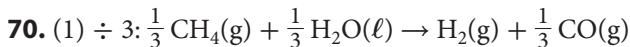
Environmental disadvantages: risk of exposure to high voltages in case of accident

68. The food would contain water. This would lead to erroneous data that would give a heat of combustion that was too low because the water would contribute non-combustible mass.

69. Sample answer:

For wind turbines: inexpensive, renewable, no polluting gases, low maintenance, no waste products to eliminate; new job opportunities.

Against wind turbines: weather dependent and therefore unreliable; unsightly and will lower land value and tourism income; long exposure to emitted inaudible infrasound waves suspected to be harmful to human and animal health; not cost efficient considering changes it makes to the landscape; will do nothing to change attitudes towards energy usage and conservation.



$$\Delta H_r^\circ = 68.6 \text{ kJ}$$

If reaction is 80.5% efficient, 68.6 kJ would produce 0.805 mol of $\text{H}_2(\text{g})$.

$$\frac{68.6 \text{ kJ}}{0.805 \text{ mol H}_2(\text{g})} = \frac{x}{1.000 \text{ mol H}_2(\text{g})}$$

$$x = 85.2 \text{ kJ}$$

85.2 kJ of thermal energy is required to produce 1 mol of $\text{H}_2(\text{g})$ by reaction (1).

If reaction (2) is 49.1% efficient, 285.8 kJ would produce 0.491 mol $\text{H}_2(\text{g})$.

$$\frac{285.8 \text{ kJ}}{0.491 \text{ mol H}_2(\text{g})} = \frac{x}{1.000 \text{ mol H}_2(\text{g})} = 582 \text{ kJ}$$

582 kJ of energy is required to produce 1 mol of $\text{H}_2(\text{g})$ by reaction (2).

Answers to Chapter 5 Self-Assessment Questions

(Student textbook pages 350-1)

1. d

2. c

3. d

4. $m = 10.0 \text{ g}$, $\Delta T = 1.00 \text{ }^\circ\text{C}$

$$Q = mc\Delta T$$

$$= 10.0 \text{ g} \times 4.19 \frac{\text{J}}{\text{g} \cdot {^\circ}\text{C}} \times 1.00 {^\circ}\text{C}$$

$$= 41.9 \text{ J}$$

The correct answer is b.

5. The mass of the sample does not affect the answer.

$$C = 2.337 \frac{\text{kJ}}{\text{°C}} \quad \Delta T = 3.03 \text{ }^\circ\text{C}$$

$$Q = C\Delta T$$

$$= 2.337 \frac{\text{kJ}}{\text{°C}} \times 3.03 {^\circ}\text{C}$$

$$= 7.08 \text{ kJ}$$

The correct answer is b.

6. % efficiency = $\frac{40.0 \text{ kJ}}{50.0 \text{ kJ}} \times 100\%$

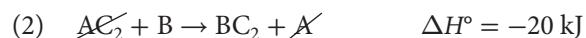
$$= 80.0\%$$

The correct answer is c.

7. e

8. Reverse equation (1) and add equation (2) to it.

Cancel compounds found on opposite sides of the equations.



The correct answer is a.

9. e

10. It takes 31.8 kJ to decompose 1 mol of Ag_2S .

Find the number of moles.

$$n = \frac{m}{M}$$

$$M = 2 \times 107.8 \frac{\text{g}}{\text{mol}} + 31.07 \frac{\text{g}}{\text{mol}}$$

$$= 247.67 \frac{\text{g}}{\text{mol}}$$

$$n = \frac{123.9 \text{ g}}{247.67 \frac{\text{g}}{\text{mol}}}$$

$$= 0.500 \text{ mol}$$

$$Q = n\Delta H_r$$

$$= 0.500 \text{ mol} \times 31.8 \frac{\text{g}}{\text{mol}}$$

$$= 15.9 \text{ kJ}$$

The correct answer is a.

11. Water molecules in the sample at 25°C have a lower average kinetic energy and are moving on average more slowly than the molecules in the 40°C sample. The total energy in each sample is unknown since the mass of each sample is unknown.

12. Lawn and garden equipment using gasoline include lawn mowers or riding lawn mowers, edgers, rototillers, hedge trimmers, and leaf blowers. To reduce environmental impact, use the tools less frequently or use electric or manual models of the equipment.

13. $n(\text{CH}_4(\text{g})) = \frac{2 \times 10^6 \text{ g}}{16.05 \text{ g/mol}} = 1.246 \times 10^5 \text{ mol}$

$$\text{latent heat} = 1.246 \text{ mol} \times 10^5 \text{ mol}$$

$$\times 802.5 \text{ kJ/mol} \times 0.97$$

$$= 1.0 \times 10^8 \text{ kJ}$$

14. $n_{\text{AlCl}_3} = \frac{6.85 \text{ g}}{133.33 \text{ g/mol}} = 0.051376 \text{ mol}$

$$\begin{aligned}\Delta H^\circ &= n\Delta H_{\text{soln}} \\ &= 0.051376 \text{ mol} \times (-373.8 \text{ kJ/mol}) \\ &= -19.2044 \text{ kJ}\end{aligned}$$

Heat absorbed by water = 19.2044 kJ = 19 204.4 J

$$Q = mc\Delta T$$

$$19\ 204.4 \text{ J} = 255.0 \text{ g} \times 4.19 \text{ J/g°C} \times \Delta T$$

$$\Delta T = 17.97^\circ\text{C}$$

$$T_f - T_i = 17.97^\circ\text{C}$$

$$48.7^\circ\text{C} - T_i = 17.97^\circ\text{C}$$

$$T_i = 30.7^\circ\text{C}$$



16. $\Delta H_r^\circ = [\sum(n\Delta H_f^\circ \text{products})] - [\sum(n\Delta H_f^\circ \text{reactants})]$

$$\begin{aligned}\Delta H_r^\circ &= [(1 \text{ mol})(\Delta H_f^\circ \text{C}_2\text{H}_2(\text{g})) + \\ &\quad (1 \text{ mol})(\Delta H_f^\circ \text{Ca(OH)}_2(\text{s}))] - \\ &\quad [(1 \text{ mol})(\Delta H_f^\circ \text{CaC}_2(\text{s})) + (2 \text{ mol})(\Delta H_f^\circ \text{H}_2\text{O}(\ell))] \\ -128.0 \text{ kJ} &= [(1 \text{ mol})(227.4 \text{ kJ/mol}) + \\ &\quad (1 \text{ mol})(-985.2 \text{ kJ/mol})] - [(1 \text{ mol})(\Delta H_f^\circ \text{CaC}_2(\text{s})) + \\ &\quad (2 \text{ mol})(-285.8 \text{ kJ/mol})]\end{aligned}$$

$$\Delta H_f^\circ \text{CaC}_2(\text{s}) = -58.2 \text{ kJ/mol}$$

17. $\Delta H_{\text{neutralization}} = -55.31 \text{ kJ/mol}$ of $\text{HNO}_3(\text{aq})$

$$n(\text{HNO}_3(\text{aq})) = 0.0500 \text{ mol/L} \times 0.400 \text{ L} = 0.0200 \text{ mol}$$

$$\Delta H_{\text{neut}} = \frac{Q}{n}$$

$$-55.31 \text{ kJ} = \frac{Q}{0.0200 \text{ mol}}$$

$$Q = 1.1062 \text{ kJ} = 1106.2 \text{ J}$$

Heat absorbed by solutions:

$$Q_{\text{soln}} = 1\ 106.2 \text{ J} = mc\Delta T$$

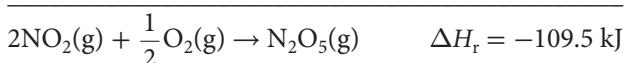
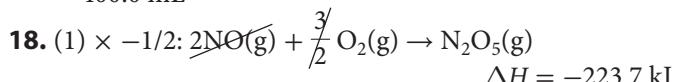
$$\Delta T = 19.00^\circ\text{C} - 18.67^\circ\text{C} = 0.33^\circ\text{C}$$

$$1106.2 \text{ J} = m \times 4.19 \text{ J/g°C} \times 0.33^\circ\text{C}$$

$$\text{Total mass of solutions} = m = 800.0289 \text{ g} = 800.0 \text{ g}$$

$$\begin{aligned}\text{Total volume of solutions} &= 800.0 \text{ g} \times 1.000 \text{ g/mL} \\ &= 800.0 \text{ mL}\end{aligned}$$

$$\begin{aligned}\text{Volume of KOH solution} &= 800.0 \text{ mL} - 400.0 \text{ mL} \\ &= 400.0 \text{ mL}\end{aligned}$$



19. Sample answer: For snow to form, water vapour must change to the solid state. This can occur in one step (sublimation) or it can condense first, then freeze. Energy is released when this happens. The energy goes into the air, resulting in a temperature increase. You could more simply explain in this way: "To make ice melt, you add heat. The opposite occurs when snow is made: water freezes. Since freezing is the opposite of melting, heat is given off into the air. The air heats up and the temperature rises."

20. Yes, it would because the enthalpy of formation for gaseous water differs from the enthalpy of formation for liquid water.

21. $1.245 \text{ kg} = 1245 \text{ g}$

$$Q = 1245 \text{ g} \times 4.19 \text{ J/g°C} \times 76^\circ\text{C}$$

$$= 3.96457 \times 10^5 \text{ J}$$

$$= 396.457 \text{ kJ}$$

$$\text{Efficiency} = \frac{\text{energy output}}{\text{energy input}} \times 100\%$$

$$34.5\% = \frac{-396.457 \text{ kJ}}{\text{energy input}} \times 100\%$$

$$\text{energy input from heat source} = 1.2 \times 10^3 \text{ kJ}$$

22. a. $Q = C\Delta T$

$$= 5923 \text{ J/g°C} \times 4.17^\circ\text{C}$$

$$= 24\ 698.91 \text{ J}$$

$$= 24.698 \text{ kJ}$$

$$\Delta H_c^\circ (\text{fat}) = \frac{-24.698 \text{ kJ}}{0.7450 \text{ g}} = -33.15 \text{ kJ/g}$$

b. Energy available for heat and activity =

$$(100\% - 9.48\%) \times 24.698 \text{ kJ}$$

$$= 22.36 \text{ kJ}$$

23. $Q = mc\Delta T = 5.000 \times 10^3 \text{ g} \times 0.46 \text{ J/g°C} \times 165^\circ\text{C}$

$$= 3.795 \times 10^5 \text{ J}$$

$$= 3.795 \times 10^2 \text{ kJ}$$

Heat required from burning of propane (heat output)

$$= -3.795 \times 10^2 \text{ kJ}$$

$$\text{Efficiency} = \frac{\text{energy output}}{\text{energy input}} \times 100\%$$

$$45\% = \frac{-3.795 \times 10^2 \text{ kJ}}{\text{energy input}} \times 100\%$$

$$\text{energy input} = -8.4333 \times 10^2 \text{ kJ}$$

$$\Delta H_c^\circ \text{C}_3\text{H}_8(\text{g}) = -2219.2 \text{ kJ/mol}$$

$$n(\text{C}_3\text{H}_8(\text{g})) = \frac{-8.4333 \times 10^2 \text{ kJ}}{-2219.2 \text{ kJ/mol}} = 0.3800 \text{ mol}$$

$$m(\text{C}_3\text{H}_8(\text{g})) = 0.3800 \text{ mol} \times 44.11 \text{ g/mol}$$

$$= 16.8 \text{ g or } 17 \text{ g}$$

24. $\Delta H_f^\circ = \Sigma(n\Delta H_f^\circ \text{ products}) - \Sigma(n\Delta H_f^\circ \text{ reactants})$

$$= [(2 \text{ mol})(\Delta H_f^\circ \text{ Fe}_2\text{O}_3(\text{s})) + (8 \text{ mol})(\Delta H_f^\circ \text{ SO}_2(\text{g}))]$$

$$- [(4 \text{ mol})(\Delta H_f^\circ \text{ FeS}_2(\text{s})) + (11 \text{ mol})(\Delta H_f^\circ \text{ O}_2(\text{g}))]$$

$$= [(2 \text{ mol})(-824.2 \text{ kJ/mol}) + (8 \text{ mol})(-296.8 \text{ kJ/mol})]$$

$$- [(4 \text{ mol})(-178.2 \text{ kJ/mol}) + (11 \text{ mol})(0 \text{ kJ/mol})]$$

$$= (-4022.8 \text{ kJ}) - (-712.8 \text{ kJ}) = -3.310 \times 10^3 \text{ kJ}$$

The reaction is exothermic; the reactants have $3.310 \times 10^3 \text{ kJ}$ more potential energy than the products.

- 25.** To determine the $\Delta H_{\text{comb}}^\circ$ data experimentally with even one alkane and its corresponding alkene, e.g. propane and prop-1-ene, would require a lengthy experiment and the availability of these hydrocarbons. The data is available in the Handbook of Chemistry and Physics or from Internet sources.

Draw up a table of $\Delta H_{\text{comb}}^\circ$ data for alkanes and the corresponding alkenes having a double bond between C₁ and C₂. For the alkanes and alkenes having from two to five carbon atoms, the data would be as shown below.

Alkane	$\Delta H_{\text{comb}}^\circ$ (kJ/mol)	Alkene	$\Delta H_{\text{comb}}^\circ$ (kJ/mol)
Ethane	1560	Ethene	1411
Propane	2219	Prop-1-ene	2058
Butane	2877	But-1-ene	2711
Pentane	3509	Pen-1-tene	3363

Analysis of the results will show that the enthalpy of combustion for each group of hydrocarbons increases as the number of carbon atoms increases and that alkenes with a double bond have a lower enthalpy of combustion than the corresponding alkane. A plot of H_{comb}° vs. number of carbon atoms in the alkane and in the alkene can be used to extrapolate to longer chain hydrocarbons in the same series.

Chapter 6 Rates of Reaction

Answers to Learning Check Questions

(Student textbook page 357)

- Measure the change in mass of the reactant, limestone, over a period of time or the volume of product, CO₂(g), generated over a period of time. The former is the more practical option.
- Sample answer:* A balanced chemical equation does not give information about the rate at which the chemical reaction occurs.

- Since the concentration increased from 0.25 mol/L to 0.420 mol/L over time, a product was measured.
- The graph should show that the tangent is a line drawn so it just touches the curve at one point. The instantaneous rate at the point where the tangent touches the curve is calculated by measuring the slope of the tangent. This is done by determining the rise and the run of the line and dividing the rise by the run. The rise is the change in concentration and the run is the change in time.

- a. Molecules of A that remain = 30; molecules of B that remain = 10
- The average rate of reaction can be determined using the number of molecules of A that are consumed or the number of molecules of B that are produced over a period of time.
$$\frac{\Delta A}{\Delta t} = \frac{30 \text{ molecules} - 40 \text{ molecules}}{10 \text{ s} - 0 \text{ s}}$$

$$= -1 \text{ molecule/s}$$

$$\frac{\Delta B}{\Delta t} = \frac{10 \text{ molecules} - 0 \text{ molecules}}{10 \text{ s} - 0 \text{ s}}$$

$$= +1 \text{ molecule/s}$$

- c. The average rate of change in the number of molecules of A and of B is the equal but opposite.
- The manager would be concerned about the average rate of spoilage. It represents how long the fruit could be left on the shelf. The instantaneous rate indicates only how fast the fruit was spoiling at one point in time.

(Student textbook page 367)

- The particles must collide with the proper orientation to one another and have sufficient kinetic energy to overcome the potential energy barrier (activation energy) between reactants and products.
- Many collisions have the wrong collision geometry, and only a fraction of the collisions have sufficient energy to overcome the potential energy barrier (activation energy).
- The angle at which the reactants collide must align with the angle at which the new bond or bonds in the products will form.
- Diagrams for exothermic reactions show reactants with a higher potential energy than the potential energy for the products. Diagrams for endothermic reactions show reactants with a lower potential energy than that for the products.

- 11.** **a.** The minimum kinetic energy required for a collision to result in a reaction between reactant particles.
- b.** Only the collisions with a kinetic energy equal to or greater than E_a will result in a reaction. For a reaction at room temperature with a high E_a , there will be few particles having sufficient energy to overcome the energy barrier when they collide.
- 12.** The enthalpy change, the activation energy, and whether the reaction is endothermic or exothermic are three characteristics of a reaction that you can determine from a potential energy diagram. The enthalpy change is the difference between the initial (reactant) and final (product) potential energies. The activation energy is the difference between the initial potential energy and the maximum potential energy. The relative values of the potential energy of the reactants and products indicate whether it is an endothermic or exothermic reaction.
- (Student textbook page 369)**
- 13.** The greater the activation energy, the slower the rate; the lower the activation energy, the faster the rate
- 14.** **a.** The flame increases the energy of a few reactant particles so that when collisions occur, the reactant particles have energy equal to or greater than the activation energy. After a few successful collisions occur, the reaction itself releases enough energy to provide energy for the rest of the particles to react.
- b.** Combustion reactions such as the burning of natural gas are exothermic processes. The thermal energy given off provides the energy for further particles to react.
- 15.** The thermochemical equation does not show the activation energy, which you would expect to be high, since graphite does not spontaneously change to diamond. Graphite and diamond have different arrangements of carbon atoms. Although the overall energy difference is small, to make the change, carbon–carbon bonds would need be broken and the atoms re-arranged.
- 16.** **a.** An activated complex is an unstable, temporary chemical species formed of the reactant and product; it will break apart either to form the product(s) or reform the reactants.
- b.** The nitrogen atom in the NO collides with an oxygen atom in the NO_3 . Student sketches should show dotted lines indicating new bonds forming between the N of NO and the O of NO_3 and dotted lines indicating the breaking of bonds between the O and N of NO_3 .
- 17.** Exothermic; $\Delta H = E_{\text{a}(\text{fwd})} - E_{\text{a}(\text{rev})} = 45 \text{ kJ} - 50 \text{ kJ} = -5 \text{ kJ}$
- 18.** Since the reverse of the reaction shown is endothermic, student sketches should indicate the product (carbon disulfide) with higher potential energy than the reactants (carbon and sulfur); the difference between the two values is 89 kJ.
- (Student textbook page 374)**
- 19.** Any change that increases the number of collisions between reactant particles will increase the rate of reaction. Any change that decreases the number of collisions between reactant particles will decrease the rate of reaction.
- 20.** Factors that can alter the rate of a chemical reaction include a change in the nature of the reactant(s); a change in the concentration of the reactant(s); a change in temperature; a change in pressure, if the reactants are gases; a change in the total surface area of the reactant material; and the introduction of a catalyst.
- 21.** Only collisions having kinetic energy equal to or exceeding the activation energy will lead to formation of product. At lower temperatures, there are fewer reactant particles with sufficient kinetic energy and the rate of reaction is slower.
- 22.** *Sample answer:* The rate of rusting would be slowed down by reducing the number of collisions between $\text{Fe}(\text{s})$ and $\text{O}_2(\text{g})$. Decreasing the temperature and covering the iron with a protective coating would be two ways to accomplish this.
- 23.** Sawdust and bulk plant material have a larger total exposed surface area than the pellets and there will be many more collisions between reactant particles. As successful collisions occur, heat is given off, which rapidly leads to more collisions between particles having kinetic energy greater than the activation energy. The result is a rapid, uncontrollable, and possibly explosive combustion. This is not desirable for a fuel. It is more important for fuels to burn slowly so that the heat from this burning can be distributed for a required use. Moreover, when the size and density of the pellets are consistent, the rate of the reaction will not only be smaller but also more predictable, so that the energy produced over time can be determined, assuming the materials of which the pellets are made burn at a consistent rate.
- 24.** *Sample answer:* Since the temperature is already high, an increase in temperature would not be expected to have much effect. The high temperature suggests that

there are sufficient collisions for a reaction to occur, so changing the concentration of the reactants would not be expected to have much effect. Introducing a catalyst would seem to have the best chance of changing the rate.

(Student textbook page 377)

- 25.** A catalyst will lower the activation energy of a reaction. This can make it possible for a reaction to occur at conditions that are safer and less costly to maintain. A catalyst may also speed up a very slow reaction to make a process more economical.
- 26.** To be suitable as a catalyst for an industrial process, a substance should allow a desired reaction to proceed at a reasonable rate under conditions that are economical to maintain.
- 27. a.** Diagrams should include the following: “Potential Energy” represented on the *y*-axis and “Reaction Progress” represented on the *x*-axis; products with lower potential energy than reactants; potential energy of products the same for catalyzed and uncatalyzed reactions; potential energy of reactants the same for catalyzed and uncatalyzed reactions; the transition state at a lower potential energy for the catalyzed reaction than for the uncatalyzed reaction.
- b.** For both the forward and reverse reactions, the activation energy is lower in the presence of a catalyst so that more of the collisions have the energy necessary to overcome the energy barrier and thus form products.
- c.** The catalyst has no effect on the potential energy of the reactants or products, so there is no change in ΔH .
- 28.** Petroleum refineries, pulp and paper mills, and steel mills are closely monitored for emissions because the by-products of their processes are harmful to the environment and threaten human health. Oxides of carbon, sulfur, and nitrogen produced by these industries lead to such problems as global warming, smog formation, acid rain, and ozone depletion, and they are can be major contributors to respiratory problems in humans.
- 29. a.** $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) + 92.6\text{ kJ}$
- b.** The reaction is slow at room temperature. A higher temperature increases the rate of reaction. A higher temperature increasingly favours the production of products, however, because the forward reaction is exothermic.

c. The catalyst is composed of iron and small amounts of potassium oxide and aluminum oxide. It provides an alternate path for the reaction that has a lower activation energy. Molecules of $H_2(g)$ and $N_2(g)$ form bonds with the metal catalyst, weakening the covalent bonds that hold the reactant molecules together. The reactant molecules split into atoms and recombine to form $NH_3(g)$. The $NH_3(g)$ quickly leaves the surface of the metal.

- 30.** A chemist studies why and how a reaction occurs. Fritz Haber was a chemist and was able to determine the temperature and type of catalyst for the conversion of $N_2(g)$ and $H_2(g)$ to $NH_3(g)$. A chemical engineer determines how a reaction can be made efficient and profitable on a large scale. Carl Bosch was a chemical engineer. Both scientists contributed to different aspects of this process. A team of researchers can contribute expertise from a variety of disciplines, resulting in a greater chance of developing a product.

(Student textbook page 383)

- 31.** The observed rate of a reaction is affected by the rate of the reverse reaction that may occur. The only accurate datum for the relationship between the concentration of a reactant and the forward reaction rate occurs at the point at which there is no product—at time zero.
- 32.** Initial rate is the reaction rate at a time at which there is no product present—time zero
- 33.** A graph of reactant concentration vs. time is plotted for a reaction. The initial rate of reaction is measured by drawing a line tangent to this curve at $t = 0$ and then determining the slope of this line.
- 34.** Carry out several experiments, each one starting with a different reactant concentration. Draw graphs of concentration vs. time for each experiment and determine the initial rate by measuring the slope of the tangent for each at $t = 0$. Plot a graph of initial rate vs. starting concentration.
- 35.** If the curve is linear, $\text{rate} = k[A]$; the reaction is first order. If the curve is parabolic, $\text{rate} = k[A]^2$; the reaction is second order.
- 36.** The meaning of the constants is as follows: m is the order of the reaction with respect to reactant A, n is the order of the reaction with respect to reactant B, and the proportionality constant, k , is called the *rate constant*. The order of the overall reaction is $m + n$. For a reaction, k , m , and n can be determined experimentally. Carry out several investigations, each one starting with a different concentration of

reactant. Draw graphs of concentration vs. time for each investigation and determine the initial rate by measuring the slope of the tangent for each at $t = 0$. Plot a graph of initial rate vs. starting concentration. The type of curve indicates if the reaction is first or second order with regards to that reactant.

Answers to Caption Questions

Figure 6.7 (Student textbook page 362): If cotton wool were not used, some of the aqueous solution could escape from the flask as the reaction proceeds, increasing the measured mass lost and making the reaction rate appear to be faster than it actually is.

Figure 6.8 (Student textbook page 365): The first four collisions shown are ineffective because the orientations of the reactants are not favourable for the new bonds in the product to form. In the effective collision, the reactants are oriented with approximately the same geometry that will exist in the products.

Figure 6.15 (Student textbook page 373): Under the T_1 curve is blue cross-hatching to indicate the area that represents the relative number of collisions with sufficient activation energy for a successful collision; under the T_2 curve is a red cross-hatched area to indicate the same.

Figure 6.16 (Student textbook page 374): A catalyst does not have any effect on the enthalpy change, ΔH .

Figure 6.17 (Student textbook page 375): In part A the hydrogen and nitrogen molecules approach the surface of the catalyst; in part B the element molecules dissociate into H and N atoms, forming bonds with the catalyst; in part C the highly reactive H and N atoms react to form ammonia molecules.

Figure 6.18 (Student textbook page 376): It is important that the catalyst has a large surface area to increase reaction rate as much as possible. The greater the surface area, the more sites are available on which a reaction can occur.

Answers to Section 6.1 Review Questions

(Student textbook page 364)

1. *Sample answer:* Four applications in which an understanding of reaction rate benefit society are slowing the rate of corrosion, delaying the spoilage of foods, designing safety devices such as air bags in an automobile, and manufacturing a product in a process that involves chemical reactions.

2. a. The instantaneous rate of reaction is the rate of a chemical reaction at a particular point in time. The average rate of reaction is the change in the

concentration of a reactant or product over a specific time interval.

- b.** The data is plotted on a graph of concentration (y -axis) vs time (x -axis). The average rate of reaction is calculated by determining the slope of a line drawn between two points that define the time interval. The instantaneous rate is calculated by determining the slope of a line tangent to the curve at a particular point in time.
- c.** The units for instantaneous and average rate are mol/L·s.

$$3. \text{rate} = \frac{\Delta[\text{CuSO}_4]}{\Delta t} = \frac{0.42 \frac{\text{mol}}{\text{L}} - 0.50 \frac{\text{mol}}{\text{L}}}{280 \text{ s}} \\ = -2.857 \times 10^{-4} \frac{\text{mol}}{\text{L}\cdot\text{s}} \\ = -2.9 \times 10^{-4} \text{ mol/L}\cdot\text{s}$$

$$4. \Delta t = 2 \cancel{d} \frac{24 \cancel{K}}{\cancel{d}} \times \frac{60 \cancel{\text{min}}}{\cancel{K}} \times \frac{60 \text{ s}}{\cancel{\text{min}}} = 1.728 \times 10^5 \text{ s} \\ \text{rate} = \Delta m / \Delta t \\ = \frac{6.29 \text{ g} - 6.18 \text{ g}}{1.728 \times 10^5 \text{ s}} \\ = 6.37 \times 10^{-7} \text{ g/s}$$

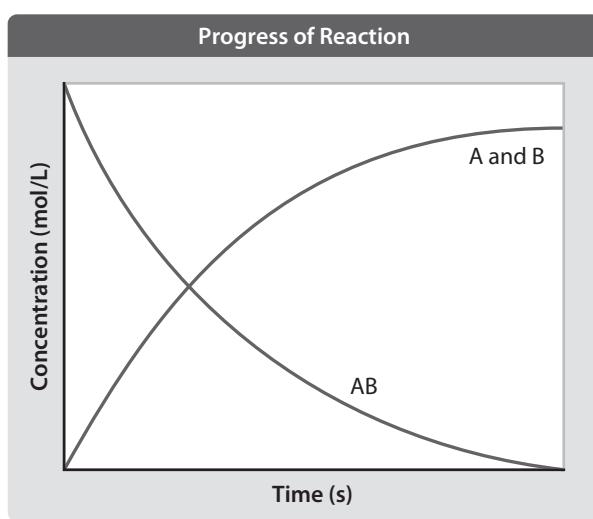
$$5. \text{rate} = \Delta V / \Delta t \\ \Delta \text{time} = \frac{\Delta V}{\text{rate}} = \frac{88.4 \frac{\text{mL}}{\text{min}}}{0.67 \frac{\text{mL}}{\text{s}}} = 131.94 \text{ s} = 132 \text{ s}$$

- 6. a.** The slope of the tangent represents the instantaneous rates of reaction at those times.
- b.** The rate at which product forms decreases as the reaction proceeds. The slope of smaller value would be what was measured at the later time. Therefore, the slope of $4.5 \times 10^{-2} \text{ mol/L}\cdot\text{min}$ must have been recorded at 5.0 minutes.
- c.** The reactant would be consumed and the slope of the graph at any time would be negative. Since both of the given slopes were positive, this data could not represent the consumption of a reactant.

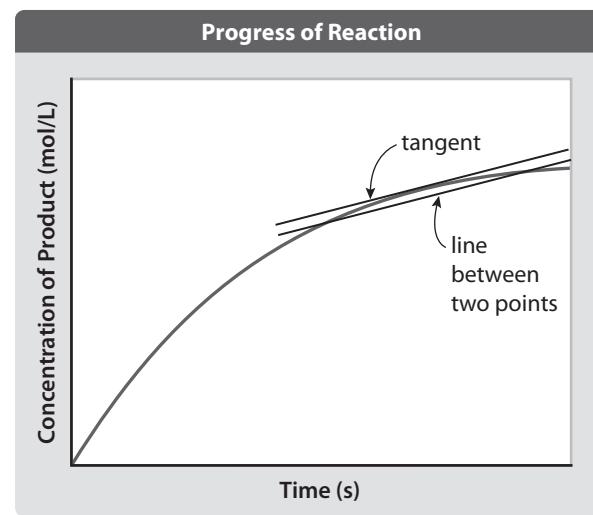
- 7. a.** Questions to be asked might include:

- (i)** What products are formed in the reaction?
- (ii)** Which quantity is easier to measure, change in mass of magnesium (reactant) or change in volume of hydrogen gas (product)?
- (iii)** Can the change in quantity be monitored throughout the reaction?
- (iv)** Can measurements be made before and after the reaction to determine either the total mass of magnesium used or the total volume of hydrogen collected?

- b.** The average rate can be determined from knowing the overall change in a quantity over a given time period. The instantaneous rate can be determined from data collected during the course of the reaction, plotting a graph of concentration *vs* time and finding the slope of a tangent to this graph at a point in time. It would be easier to determine the average rate of reaction.
- 8.** At that point in time, there is an equal concentration of reactant A and product B. The concentration of B is increasing and the concentration of A is decreasing.
- 9.** The curve representing the reactant AB must gradually reach a concentration of zero. The products A and B form in equal amounts measured in moles. The curve representing their formation will be the same for both.



- 10.** Referring to the graph of concentration *vs.* time, as the reaction slows down, the curve begins to level off. The slope of the tangent in this region approaches the slope of the line between two points. The instantaneous rate will be almost the same as the average rate of reaction. The statement is correct.



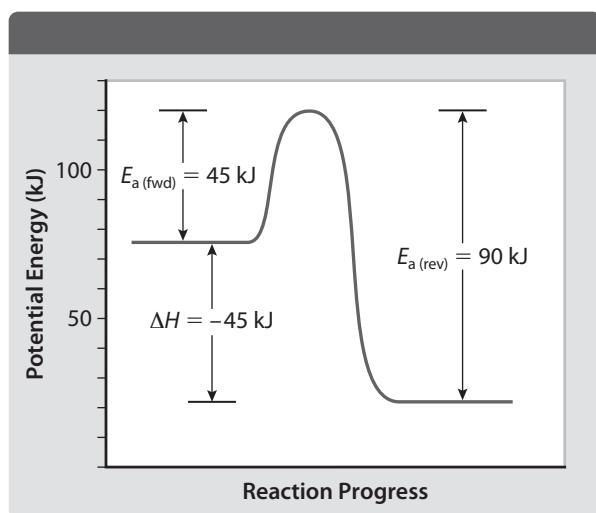
- 11.** The mole ratio between the substances as given in the balanced equation must be known in order to use the rate of change in the quantity of one substance in a reaction to determine the rate of change of another.

- 12.** Consumption of $\text{O}_2(\text{g})$: 0.10 mol/L·s
Formation of $\text{H}_2\text{O}(\text{g})$: 0.12 mol/L·s

Answers to Section 6.2 Review Questions (Student textbook page 379)

- In a chemical reaction, reactants approach each other. They have kinetic energy. During the collision, kinetic energy is converted to potential energy. If the collision occurred with sufficient energy (and with the right orientation), an activated complex will form. This is a temporary arrangement of atoms with partial bonds, in which reactant bonds are breaking and new bonds are forming. The activated complex then breaks down, either to form products or to reform the reactants.
- From a potential energy diagram, the following data can be obtained about a reaction: $E_{\text{a(fwd)}}$, $E_{\text{a(rev)}}$, and ΔH .
- For a collision to be successful, it must occur between particles with the proper orientation that have sufficient kinetic energy to equal or exceed the activation energy for the reaction.
- The activated complex is neither reactant nor product. The activated complex is a transitional compound that forms at the top of the activation barrier when a collision occurs between reactant particles. It may break apart and reform reactants or break apart and form products.
- The activated complex is the species in a reaction with the highest potential energy, which is why it is drawn at the “peak” of a potential energy diagram. However, like a boulder teetering at the top of a peak, it is highly unstable and could “fall” in either direction from that peak, meaning that it could either reform reactants or form products (both at lower potential energies than the activated complex).

6.



7. For a reaction to occur, collisions must take place between reactant particles. The surface area of the reactant material will vary with shape. A large piece of firewood cut into smaller pieces will have a larger exposed surface area than the original piece, allowing for more collisions between the wood and oxygen in the air, and consequently a faster burning rate. Students could make the explanation more quantitative by comparing the surface area of spherical and cylindrical shapes and so on. Student diagrams should clearly demonstrate this concept, for example by comparing the surface area of an intact cube with the surface area of the same cube divided into pieces.

8. Even though the combustion of long chain hydrocarbons, such as those found in kerosene, may have a high activation energy, it can still be used as a fuel. This is because, once ignited, the combustion reaction is exothermic and this energy provides the activation energy for the other reactant particles. This keeps the process going at a rapid rate.

9. The following factors must be controlled or held constant in order for a change in rate to be linked to the change in the acid concentration: total surface area of marble chips, total mass of marble chips, temperature of acid solution, volume of acid solution.

10. a. A decrease in temperature will decrease the number of reactant particles having kinetic energy equal to or greater than the activation energy. The rate of reaction will decrease.

b. Using magnesium in the form of a powder increases the total surface area exposed to the acid. More collisions can then occur between reactant particles and the rate of reaction will increase.

c. Increasing the pressure affects gases by moving the particles closer together and increasing the number of collisions. Neither reactant in this reaction is a gas. Therefore increasing the pressure will not affect the rate of reaction.

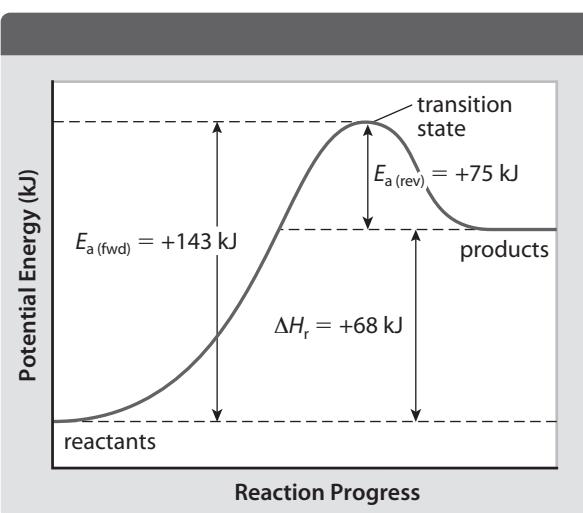
d. If the concentration of the $\text{H}_2\text{SO}_4(\text{aq})$ is increased, there will be more collisions between the metal and the acid particles and the rate of the reaction will increase.

11. -160 kJ

$$\begin{aligned}12. \text{a. } \Delta H_r &= E_{a(\text{fwd})} - E_{a(\text{rev})} \\&= +143 \text{ kJ} - (+75) \text{ kJ} \\&= +68 \text{ kJ}\end{aligned}$$

The reaction is endothermic in the forward direction.

b.



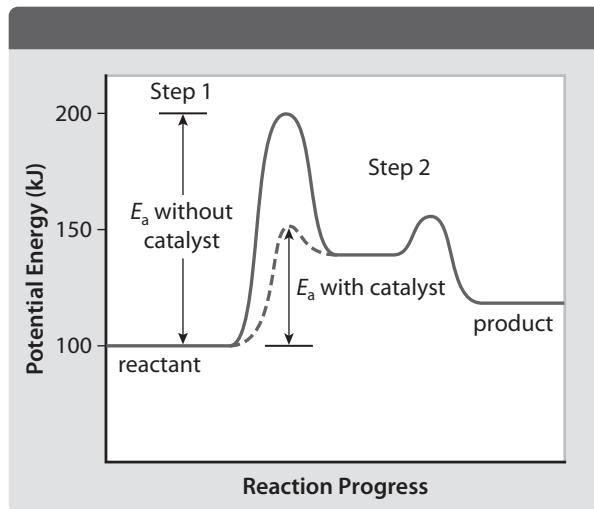
Answers to Section 6.3 Review Questions

(Student textbook page 387)

- The concentration of the reactants is the factor included quantitatively in the rate law expression.
- A balanced equation gives no information about the rate law. The rate law expression must be determined by experiment.
- Sample answer:* This is the potential energy diagram for the reaction between nitrogen monoxide and hydrogen gas to produce nitrogen gas and water vapour. The reaction consists of three elementary steps, each with its own activation energy and activated complex. The activated complexes are unstable species that have the highest energy of each step. Intermediates, such as N_2O_2 and N_2O in this example, are products that are formed in one step and consumed in a subsequent step.

- 4.** Initial rate is the rate of change in the concentration of the reactants at time zero, or the instant when reactants are mixed.
- 5.** Because the rate depends only on the concentration of A, according to the rate law, doubling the surface area of reactant B (all other factors remaining the same) would be expected to have no effect on the rate of the reaction.

6.



- 7.** The rate-determining step is the slowest elementary step in the reaction mechanism. This step determines the overall rate of the reaction.
- 8.** An activated complex cannot be an intermediate. The activated complex is a highly unstable species that exists for only femtoseconds before it decomposes into products or reactants. An intermediate is a more stable species that is formed as a product from one step but is then consumed in a subsequent step in the reaction. In some cases, the intermediate can be isolated but this is not possible for an activated complex.
- 9.** The collision of two particles is the simplest and the most likely event to occur in a reaction. More than two particles colliding with sufficient energy and the correct orientation for a reaction to occur is far less probable. A chemist is unlikely to propose as an elementary step a collision that is highly unlikely to take place.
- 10. a.** The overall equation can be determined by adding the elementary steps together:
- Step 1: $\text{Cl}_2(\text{g}) \rightarrow 2\text{Cl}(\text{g})$
- Step 2: $2\text{Cl}(\text{g}) + \text{CHCl}_3(\text{g}) \rightarrow \text{HCl}(\text{g}) + \text{CCl}_3(\text{g})$
- Step 3: $\text{Cl}(\text{g}) + \text{CCl}_3(\text{g}) \rightarrow \text{CCl}_4(\text{g})$
- $\text{Cl}_2(\text{g}) + \text{CHCl}_3(\text{g}) \rightarrow \text{CCl}_4(\text{g}) + \text{HCl}(\text{g})$

- b.** There is no catalyst in this reaction; it would be shown as a reactant in one of the steps and a product in a subsequent step.

- c.** There are two intermediates, $\text{Cl}(\text{g})$ and $\text{CCl}_3(\text{g})$, since both are produced in one step and consumed in a subsequent step.
- d.** Step 2 is the rate-determining step since it is the only step that includes CHCl_3 as a reactant.

- 11. a.** B, D and F represent activated complexes.

- b.** $+80.0 \text{ kJ}$

- c.** C and E represent reaction intermediates.

- d.** $+60.0 \text{ kJ}$

- e.** $+20.0 \text{ kJ}$

- f.** -30.0 kJ

Answers to Practice Problems

For full solutions to Practice Problems, see Part B of this Solutions Manual.

(Student textbook pages 360-1)

- The average rate of consumption of B is $-4.74 \times 10^{-5} \text{ mol/L}\cdot\text{s}$.
- $-7.0 \times 10^{-4} \text{ mol/L}\cdot\text{s}$
- a.** 0.165 mol
b. 0.165 mol $\text{Br}_2(\text{aq})$
- 1.4 mol/L
- $5.0 \times 10^{-4} \text{ L/s}$
- rate of formation of $\text{BrO}_3^-(\text{aq}) = 0.060 \text{ mol/L}\cdot\text{s}$; rate of consumption of $\text{BrO}^-(\text{aq}) = 0.18 \text{ mol/L}\cdot\text{s}$
- a.** The average rate of consumption of $\text{HBr}(\text{g})$ over 50.0 s is 0.0032 mol/L·s.
b. 0.080 mol/L
- $1.40 \times 10^2 \text{ mol/L}$
- a.** $2.42 \times 10^{-4} \text{ mol/s}$
b. $2.98 \times 10^{-3} \text{ L/s}$
- 0.70 mol/L·s $\text{Cl}_2(\text{g})$ consumption; $\text{NOCl}(\text{g})$ is produced at a rate of 1.4 mol/L·s

(Student textbook page 371)

- Diagrams should contain the following: “Potential Energy” on y-axis; “Reaction Progress” on x-axis; $E_{\text{a(fwd)}}$ is the energy between the reactants and the transition state; $E_{\text{a(rev)}}$ is the energy between the transition state and the products; ΔH_r is the energy between the reactants and the products.
 - Endothermic
 - Products

- 12.** Diagrams should indicate the following: the reactants have a lower potential energy than the products; $E_{a(fwd)}$ is the energy between the reactants and the transition state (+99 kJ); $E_{a(rev)}$ is the energy between the transition state and the products (+34 kJ); and ΔH_r is the enthalpy of reaction between the reactants and the products (+65 kJ).
- 13.** Diagrams should indicate the following: the reactants have a higher potential energy than the products; $E_{a(fwd)}$ is the energy between the reactants and the transition state (+61 kJ); $E_{a(rev)}$ is the energy between the transition state and the products (+150 kJ); and ΔH_r is the enthalpy of reaction between the reactants and the products (-89 kJ).
- 14.** $E_{a(fwd)} = +42 \text{ kJ}$; $E_{a(rev)} = +67 \text{ kJ}$; $\Delta H_r = -25 \text{ kJ}$; exothermic
- 15.** $E_{a(rev)} = +411 \text{ kJ}$; energy diagrams should indicate the reactants having higher potential energy than the products with $E_{a(fwd)}$ being the energy between the reactants and the transition state (+19.0 kJ); $E_{a(rev)}$ is the energy between the transition state and the products (+411 kJ); and ΔH_r is the enthalpy of reaction between the reactants and the products (-392 kJ).
- 16. a.** $E_a = 112 \text{ kJ} - 36 \text{ kJ} = +76 \text{ kJ}$
 $\Delta H = 78 \text{ kJ} - 36 \text{ kJ} = +42 \text{ kJ}$
- b.** Potential energy diagrams should indicate the reactants having lower potential energy than the products and the activated complex having the highest potential energy, positioned between the reactants and products.
- 17. a.** $\text{CH}_4(\text{g}) + 2\text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) + 2\text{H}_2\text{O}(\ell) + 890.8 \text{ kJ}$
- b.** Since $\text{CH}_4(\text{g})$ easily ignites with a spark, the activation energy for the combustion reaction would be expected to be small. The activated complex would be an unstable association of $\text{CH}_4(\text{g})$ and $\text{O}_2(\text{g})$.
- 18.** Diagrams should indicate the reactants having higher potential energy than the products and the activated complex having the highest potential energy, positioned between the reactants and products.
 $\Delta H_r = E_{a(fwd)} - E_{a(rev)}$; $E_{a(fwd)} = +49.5 \text{ kJ}$
- 19.** Diagrams should indicate the reactants having lower potential energy than the products and the activated complex having the highest potential energy, positioned between the reactants and products.
- 20.** $\Delta H_r = E_{a(fwd)} - E_{a(rev)}$; $E_{a(fwd)} = +320 \text{ kJ}$

Answers to Chapter 6 Review Questions

(Student textbook pages 392-7)

1. d

2. b

3. c

4. a

5. e

6. d

7. d

8. b

9. d

10. e

11. a

12. d

13. c

14. d

15. Rate of reaction is equal to the change in the quantity of a reactant or a product divided by the time during which the change occurs.

16. Sample answers:

a. mL/s

b. kPa/s

c. pH/s

17. a. The rate will increase since at a higher total pressure the particles are forced closer together and they will collide more often, resulting in a higher frequency of successful collisions.

b. The rate will not be affected because the particles in an aqueous solution cannot be forced any closer together and cannot be made to collide more often by increasing the pressure.

18. The reactant particles have strong bonds that require a high energy collision to break; the reactant particles have a shape that requires an exact orientation before a collision can be effective.

19. a. The initial rate of reaction occurs when the reactants are first mixed together and have just begun to react.

b. The initial rate of reaction can be determined graphically by determining the slope of the tangent to the reaction curve (concentration vs. time) at $t = 0$.

- c.** It is possible for the instantaneous rate to have the same value as the average rate of reaction. This would happen when a tangent to the reaction curve has the same slope as a line drawn between two points on the reaction curve. It occurs when the shape of the curve is straight between two points.
- 20. a.** A catalyst speeds up a reaction by providing an alternate path with a lower activation energy so that a greater percentage of the collisions occur with enough energy to get over the activation energy barrier.
- b.** A catalyst would not be expected to speed up this reaction. This reaction is between two oppositely charged ions in solution, and is therefore already a fast reaction. No simpler two-particle process is likely.
- 21.** The partial pressure of a gas is increased by adding more of that gas to the container, thus increasing its concentration. There will be more collisions between reactant particles as a result, and the rate will increase.
- 22.** Without stirring, the solid solute becomes surrounded by more and more concentrated solution as it dissolves, eventually becoming surrounded by a zone of saturated solution. This dissipates slowly by diffusion. By stirring, the solution is kept as dilute as possible, ensuring that many water molecules are available to surround solute particles. The effect is the same as increasing the surface area of a reactant. Stirring would have to be very vigorous to substantially increase the kinetic energy of the particles and this is not the major reason that stirring increases the rate of dissolving.
- 23.** The activation energy is the minimum energy that colliding reactant particles must have to allow them to reach a transitional state where they may break up into products. The activated complex is an unstable association of reactant particles formed temporarily at the transition state that will break apart either to reform the reactants or to form products.
- 24.** To determine the initial rates of reactions at different concentrations, several experiments are carried out, each with a different concentration of reactant. Data for each experiment is plotted as graphs of concentration vs. time. From these curves, the initial rates are determined for each experiment by measuring the slope of the tangent lines at time zero on each graph. These initial rates are plotted and the resulting graph of initial rate vs. initial concentration of reactant shows the relationship between reaction rate and concentration.
- 25.** For an effective collision to occur, particles must collide with sufficient energy to get over the activation energy barrier and at a favourable orientation. There is a relatively good probability of a collision between two particles meeting these criteria. For three or more particles to collide in this manner is much less probable.
- 26.** (i) For a solid catalyst, the more surface area exposed, the better the ability of the substance to catalyze the reaction. (ii) The state of the reactants compared to the state of the catalyst affects how the substance can catalyze the reaction. For reactions between gases, the catalyst is most often in the solid state since the gases can be easily passed over a solid. If the catalyst for a reaction between gases is also a gas, continual intimate mixing of the gases would be required. (iii) The purity of the catalyst is also a factor. Contaminants in the catalyst would result in less contact between particles that are involved in the reaction. Also, an impurity could interfere with the reaction. (iv) Temperature would be a factor for a biological catalyst (called an enzyme). At higher temperatures, this type of catalyst is destroyed because its action depends on its shape, and because it is a protein, it becomes denatured at high temperatures.
- 27. a.** The straight line represents a direct relationship between rate and concentration.
- b.** The slope of the graph represents the rate constant, k .
- c.** The reaction is first order and has the form rate = $k[A]$.
- 28. a.** The rate constant, k , will not be affected by a change in the concentration of the reactants.
- b.** NO_3 is a reaction intermediate because it is produced in step 1 and used up in step 2.
- 29.** $+5.0 \times 10^2 \text{ kJ}$
- 30.** $+3.1 \times 10^2 \text{ kJ}$
- 31.** The catalyzed reaction is faster because it has a lower activation energy.
- 32.** $+7 \times 10^2 \text{ kJ}$
- 33.** $+4.7 \times 10^2 \text{ kJ}$
- 34.** $-1.7 \times 10^2 \text{ kJ}$
- 35.** $+1.7 \times 10^2 \text{ kJ}$

36. rate of formation of A_2 = $\frac{\Delta \text{concentration}}{\Delta t}$

$$= \frac{c_f - c_i}{t_f - t_i} = \frac{0.68 \text{ mol/L} - 0.52 \text{ mol/L}}{5.6 \text{ min} - 4.4 \text{ min}}$$

$$= \frac{0.16 \text{ mol/L}}{1.2 \text{ min}} = 0.13 \text{ mol/L}\cdot\text{min}$$

The mole ratio AB: A_2 is 2:1. For every 2 mol of AB that decompose, 1 mol of A_2 is produced.

$$\frac{\text{rate of decomposition of AB}}{\text{rate of formation of } A_2} = \frac{n \text{ AB}}{n \text{ } A_2}$$

$$\frac{\text{rate of decomposition of AB}}{0.13 \text{ mol/L}\cdot\text{min}} = \frac{2 \text{ mol AB}}{1 \text{ mol } A_2}$$

$$= 2 \times 0.13 \text{ mol/L}\cdot\text{min} = 0.26 \text{ mol/L}\cdot\text{min}$$

37. change in amount of $HNO_3(aq)$ is 0.10 mol

$$\frac{\text{rate of change of Cu}}{\text{rate of change of } HNO_3} = \frac{n \text{ Cu}}{n \text{ } HNO_3} = \frac{1}{4}$$

change in the amount of copper

$$= 0.25 \times 0.10 \text{ mol} = 0.025 \text{ mol}$$

mass of copper used in this time

$$= 0.025 \text{ mol} \times 63.55 \frac{\text{g}}{\text{mol}} = 1.6 \text{ g}$$

$$\text{rate of change in mass of copper} = \frac{1.6 \text{ g}}{90.0 \text{ s}} = 0.018 \text{ g/s}$$

38. a. III

- b. IV
- c. III
- d. II

39. The coefficients in the chemical equation indicate the mole ratios for the components of the reaction. For every 4 mol of $HBr(g)$ that decompose, 2 mol of $Br_2(g)$ is formed. In other words, there is a 2:1 ratio of $HBr(g)$ decomposition to $Br_2(g)$ formation.

$$\frac{\text{rate of decomposition } HBr}{\text{rate of formation of } Br_2} = \frac{nHBr}{nBr_2} = \frac{4}{2} = \frac{2}{1}$$

40. rate in mol/s = $\frac{0.48 \text{ g}}{5.8 \text{ min}} \times \frac{1 \text{ mol}}{84.32 \text{ g}} \times \frac{1 \text{ min}}{60 \text{ s}}$

$$= 1.6 \times 10^{-5} \text{ mol/s}$$

41. Potential energy diagram A most accurately shows the catalytic action on the mechanism. Step 1 has the highest activation energy, and it will be the slowest or rate-determining step. The catalyst would be used to lower the activation energy of the rate-determining step 1.

42. a. +20 kJ

- b. No; the reverse reaction would have a greater activation energy than in (a).

$$E_{a(\text{rev})} = E_{a(\text{fwd})} - \Delta H$$

$$= +45 \text{ kJ} - (-25 \text{ kJ})$$

$$= 70 \text{ kJ}$$

43. a. There are two steps in the reaction.

- b. C + D = overall activation energy
- c. The overall reaction is exothermic.
- d. Quantity B represents the activation energy for step 1.
- e. Quantity E represents the difference between potential energy of the product(s) of step 1 and the potential energy of the final product(s).

44. a. Both reactions are second order.

- b. If the molar concentration of R is doubled, the rate of reaction A will quadruple (2^2) and the rate of reaction B will double (2^1).

45. a. catalyst

- b. intermediate
- c. intermediate
- d. reactant

46. When the volume is reduced to half the original volume, the concentration of the reactants will each be doubled. Since the rate law is first order only in gas $X_2(g)$, the rate of the reaction would be expected to double.

47. a. Step 2 is the rate-determining step since it is identified as a slow step.

- b. Intermediates are formed in one step and consumed in a subsequent step. The intermediates are $AlBr_4^-$, $C_2H_5^+$, and $C_6H_6C_2H_5^+$.
- c. $AlBr_3$ is a catalyst because it is part of the reaction as a reactant in step 1 and is regenerated in step 3.

48. The rate of reaction must be compared using samples that have the same number of particles. Equal masses of different metals will not contain the same number of particles because the molar masses are different.

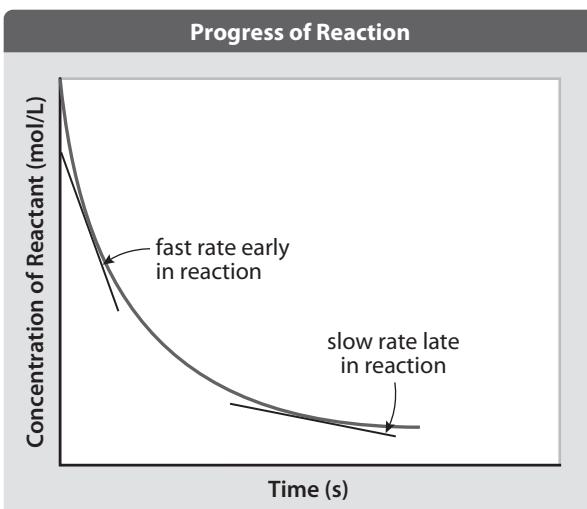
The mass of each metal used per unit of time must be converted to amount (in mol) per unit of time so that the comparison will be valid.

49. Units should include change in volume per unit time (mL/s, mL/min, mL/h, L/h); change in partial pressure per unit time (kPa/s, kPa/min); and change in the amount in moles per unit time (mol/min, mol/h).

50. This statement is incorrect. The frequency of collisions will affect the rate of reaction. The greater the number of collisions, the faster the rate. The value of the activation energy depends solely upon the nature of the reactants. Frequency of collisions does not affect this.

51. It is possible for these measurements to represent the same reaction. Early on in a reaction, the reaction proceeds relatively quickly. As the reaction proceeds,

the reactants become used up and the reaction rate slows down. The instantaneous rate of reaction is given by the slope of the curve of concentration vs. time at any particular time. The graph below shows the change in concentration of a reactant over time. The slope of the tangent to this graph early in the reaction is steep while the slope measured as the reaction nears its end is much less so.



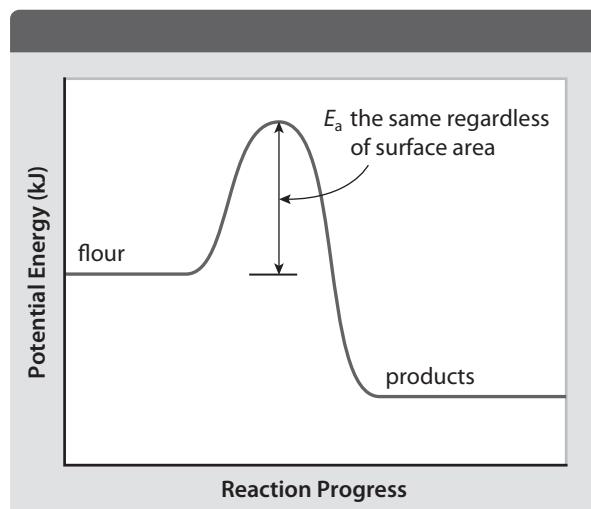
- 52.** A catalyst changes the rate of reaction by providing an alternate mechanism for the reaction that has a lower activation energy. The lower activation energy means that more particles have enough energy to react when a collision occurs. At a higher temperature the activation energy does not change. Instead, the distribution of kinetic energy of the reacting particles changes so that more colliding particles have energy equal to or greater than the activation energy. There are now more collisions that are effective and the rate of reaction increases.

- 53.** When it comes to reactions between a solid reactant and an aqueous or liquid reactant, it is the surface area of the solid that counts, not its total mass, when it comes to rate. Only the particles in the solid that are exposed to the solution can participate in collisions with the dissolved reactant. The doubling of the rate in this experiment is, in fact, due to the doubling of the surface area, not the doubling of the mass of the reactant. However, the design of the experiment is faulty because two variables were changed: mass and surface area. It would have been better to have used the same mass of magnesium and changed the surface area, either by cutting it into pieces or by using powdered metal. (Students' diagrams could show solute particles colliding only with the surface of a solid, or show how the surface area of a solid increases when it is divided into pieces or ground up.)

54. The reactants in both reactions likely have similar bond strengths and the orientation factor for both sets of reactants likely is similar. This would account for the fact that both reactions have the same activation energy. One reason that the rate of reaction could be different is that the endothermic reaction would need a continual source of activation energy while the exothermic reaction would, once started, produce energy to maintain the reaction. This thermal energy gives the particles more kinetic energy and the rate of reaction will continue to increase. The rates can also be different because of a difference in the rate constant.

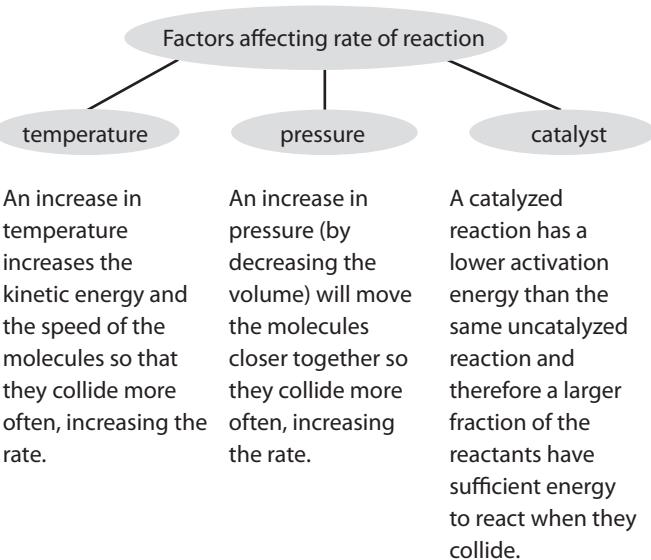
- 55.** A main idea web or a spider map may be used to summarize information related to a catalyst such as availability, cost, effectiveness, durability, recoverability, and state of matter.

- 56.** The flour blown into the flame has a greater surface area than the flour is in a pile. Each small particle of flour will burn in an instant. When in a pile, only the particles of flour on the outside of the pile collide with the oxygen in the air so few particles react at a given time. With few particles reacting, the heat given off by the combustion reaction will be a small and it will be difficult to maintain the burning. However, all of the flour particles have the same chemical bonds and it will require the same amount of energy to break these bonds. The activation energy for the flour particles will be the same regardless of whether the sample of flour burns in an instant or not. The potential energy diagram will therefore be the same for both burnings.



- 57.** Students' graphic organizers should show that the following factors would increase the rate of reaction between two gases: increasing the temperature, increasing the pressure, and adding a catalyst.

Sample concept map:



- 58.** Students should organize the following answers in a graphic display or concept map.
- A catalyst provides an alternate mechanism for the reaction that has a lower activation energy.
 - The catalyst affects the forward and reverse reactions by lowering the activation energy by the same quantity.
 - Only a small amount of catalyst is needed because it is regenerated in the reaction and can be used over and over.
 - The site where the catalytic action occurs must be able to interact in a specific way with the reactant or reactants. A catalyst is often specific for one reaction.
 - The Haber process for the production of ammonia and the Contact process for the production of sulfuric acid use catalysts.
- 59.** Graphic organizers should summarize key concepts related to rates of reaction, collision theory, factors affecting rates of reaction, and reaction mechanisms, using the correct vocabulary. The graphic organizer should also show how the four topics are related.
- Since $\text{FeS}_2(s)$ is in the solid state, its rate of decomposition could be measured in mol/s , g/s , mol/min , or g/min , to name a few.
 - Since $\text{SO}_2(g)$ is a gas, its rate of formation can be measured in mL/s , moL/s , mL/min , or mol/min to name a few.

- c.** The two rates can be compared using the balanced equation. The relative rate of change of a reactant or product is in proportion to their mole ratio in the balanced equation. The mole ratio $\text{FeS}_2(s):\text{SO}_2(g)$ is 4:8. For every 4 mol of $\text{FeS}_2(s)$ that decomposes, 8 mol of $\text{SO}_2(g)$ is produced.

$$\frac{\text{rate of decomposition FeS}_2}{\text{rate of formation SO}_2} = \frac{4\text{FeS}_2}{8\text{SO}_2} = \frac{1\text{FeS}_2}{2\text{SO}_2}$$

$$\text{rate of decomposition of FeS}_2 = 0.5 \times \text{rate of formation of SO}_2(g)$$

- 61.** The mole ratio $\text{Na}_3\text{AlF}_6(\ell):\text{F}_2(g)$ is 1 : 3. For every 1 mol of $\text{Na}_3\text{AlF}_6(\ell)$ that decomposes, 3 mol of $\text{F}_2(g)$ is produced.

$$\frac{\text{rate of decomposition Na}_3\text{AlF}_6(\ell)}{\text{rate of formation of F}_2(g)} = \frac{n \text{Na}_3\text{AlF}_6}{n \text{F}_2}$$

$$\frac{\text{rate of decomposition Na}_3\text{AlF}_6(\ell)}{0.85 \text{ mol/s}} = \frac{1 \text{ mol Na}_3\text{AlF}_6}{3 \text{ mol F}_2}$$

average rate at which $\text{Na}_3\text{AlF}_6(\ell)$ decomposes

$$= 1/3 \times 0.85 \text{ mol/s}$$

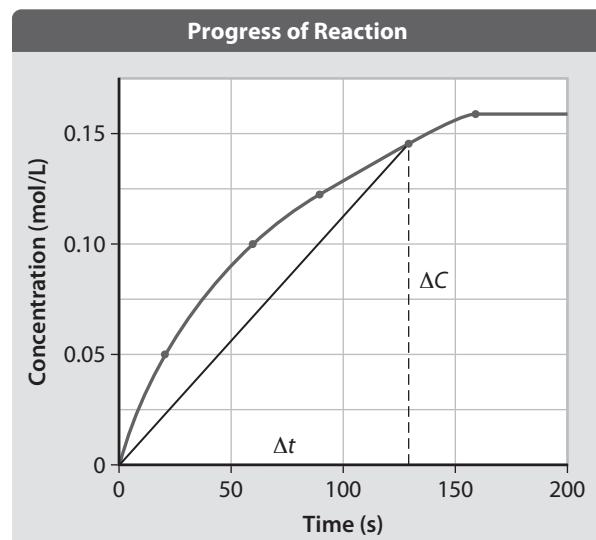
$$= 0.28 \text{ mol/s}$$

$$m \text{Na}_3\text{AlF}_6(\ell) = 0.28 \text{ mol} \times 209.95 \frac{\text{g}}{\text{mol}}$$

$$= 58.786 \text{ g}$$

average rate of decomposition of $\text{Na}_3\text{AlF}_6(\ell) = 59 \text{ g/s}$

- 62. a.**



Slope of line between 130 s and 0 s

$$= \frac{\Delta c}{\Delta t} = \frac{0.148 \frac{\text{mol}}{\text{L}} - 0.000 \frac{\text{mol}}{\text{L}}}{130 \text{ s} - 0.00 \text{ s}}$$

$$= 1.14 \times 10^{-3} \text{ mol/L·s}$$

Average rate of production of $\text{NH}_3(g)$ in 130 s is $1.14 \times 10^{-3} \text{ mol/L·s}$.

- b.** The change in concentration of $\text{N}_2(g)$ and $\text{H}_2(g)$ will not occur at the same average rate as the production of ammonia. The relative rate of change of a reactant

or product is in proportion to their mole ratio in the balanced equation.

The mole ratio $\text{N}_2(\text{g}) : \text{NH}_3(\text{g})$ is 1:2. For every 1 mol of $\text{N}_2(\text{g})$ consumed, 2 mol of $\text{NH}_3(\text{g})$ is produced.

$$\frac{\text{rate at which } \text{N}_2 \text{ used}}{\text{rate of formation } \text{NH}_3} = \frac{n\text{N}_2}{n\text{NH}_3}$$

$$\frac{\text{rate at which } \text{N}_2 \text{ used}}{1.14 \times 10^{-3} \frac{\text{mol}}{\text{L}\cdot\text{s}}} = \frac{1\text{N}_2}{2\text{NH}_3}$$

average rate of consumption of $\text{N}_2(\text{g})$

$$= 0.5 \times 1.14 \times 10^{-3} \text{ mol/L}\cdot\text{s}$$

$$= 5.69 \times 10^{-4} \text{ mol/L}\cdot\text{s}$$

The mole ratio of $\text{H}_2(\text{g}) : \text{NH}_3(\text{g})$ is 3:2. For every 3 mol of $\text{H}_2(\text{g})$ used, 2 mol of $\text{NH}_3(\text{g})$ is produced

$$\frac{\text{rate at which } \text{H}_2 \text{ used}}{\text{rate of formation } \text{NH}_3} = \frac{n\text{H}_2}{n\text{NH}_3}$$

$$\frac{\text{rate at which } \text{H}_2 \text{ used}}{1.14 \times 10^{-3} \frac{\text{mol}}{\text{L}\cdot\text{s}}} = \frac{1\text{H}_2}{2\text{NH}_3}$$

average rate of consumption of $\text{H}_2(\text{g})$

$$= 1.5 \times 1.14 \times 10^{-3} \text{ mol/L}\cdot\text{s}$$

$$= 1.71 \times 10^{-3} \text{ mol/L}\cdot\text{s}$$

$$63. n(\text{N}_2\text{O}_5) = \frac{5.00 \times 10^5 \cancel{\text{g}}}{108.02 \frac{\text{g}}{\text{mol}}} = 4.628 \times 10^4 \text{ mol}$$

$\text{N}_2\text{O}_5(\text{g})$ is used up at a rate of $4.628 \times 10^4 \text{ mol/h}$

$$= 4.628 \times 10^4 \text{ mol}/60 \text{ min}$$

$$= 7.715 \times 10^1 \text{ mol/min}$$

The mole ratio of $\text{NO}_2(\text{g}) : \text{N}_2\text{O}_5(\text{g})$ is 4:2. For every 4 mol of $\text{NO}_2(\text{g})$ produced, 2 mol of $\text{N}_2\text{O}_5(\text{g})$ is consumed.

$$\frac{\text{rate of formation } \text{NO}_2}{\text{rate of consumption } \text{N}_2\text{O}_5} = \frac{4 \text{ NO}_2}{2 \text{ N}_2\text{O}_5}$$

$$\frac{\text{rate of formation } \text{NO}_2}{7.715 \times 10^{-1} \frac{\text{mol}}{\text{min}}} = \frac{4 \text{ NO}_2}{2 \text{ N}_2\text{O}_5}$$

$$\text{rate at which } \text{NO}_2(\text{g}) \text{ forms} = 2 \times 7.715 \times 10^1 \text{ mol}/\text{min} = 1.54 \times 10^2 \text{ mol/min}$$

64. The percent conversion is low because only a fraction of the particles are in contact with the catalyst. To improve the percent conversion with the catalyst the process must increase the surface area available for contact with the reactant gases. The reactant gases could also be continually recycled until they make contact with the catalyst.

65. a. At the higher temperature, more particles have kinetic energy equal to or exceeding the activation energy. More of the collisions will result in reactants forming products. Students' diagrams should resemble Figure 6.15 in the student textbook.

b. The activation energy and enthalpy change do not change with temperature. There would be no change in the values of E_a and ΔH . Students' diagrams should resemble Figure 6.10A in the student textbook.

c. To run the process at a higher temperature will increase the energy cost. This would have to be factored into the overall cost.

66. Since the reaction is first order with respect to D and E, D and E both must take part in the rate-determining step. This means that Mechanism 1 is unlikely to be correct. Mechanism 2 is more likely to be correct since both D and E are reactants in the slow step. Just examining possible steps does not prove that a mechanism is correct; the mechanism must be tested by experiment.

67. The reaction involving the new material must have a high activation energy. The new material must have stronger bonds that require more energy to break and/or a shape requiring a specific orientation in order for the reaction to begin. If the reaction is highly exothermic, once the reaction starts, there should be sufficient energy to keep the reaction going. To allow the new reactant to be used, the reaction could be started at a higher temperature or a catalyst could be used to lower the activation energy.

68. All chemical reactions involve the interaction of electrons with other electrons and with the nuclei of the atoms involved. The atoms of transition metals have partially filled d orbitals. They can both share and donate electrons. These d orbitals provide a way for electrons to form transitional, partial bonds. The result is that the catalyzed transition state has a lower energy than an uncatalyzed transition state would have for the same process. A lower activation energy results in a faster reaction rate.

69. A reaction in which a single particle splits up into two or more smaller particles would not necessarily be collision dependent. The rate of reaction would depend upon the vibrational energy of the chemical bonds in the particles and therefore on the temperature. One example is the thermal decomposition of calcium carbonate, $\text{CaCO}_3(\text{s})$.



Answers to Chapter 6 Self-Assessment Questions (Student textbook pages 398-9)

1. a
2. e
3. b

4. d

5. d

6. e

7. c

8. d

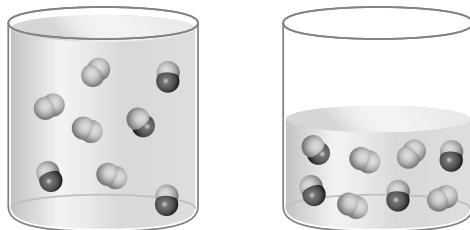
9. d

10. b

11. a. $E_{a(fwd)} = E_{a(rev)} + \Delta H$

b. For an endothermic reaction, $E_{a(fwd)} > E_{a(rev)}$

12. Use different symbols to represent the two types of reactant particles. One diagram, representing the container at a volume of V_1 , shows four particles of each reactant. Explain that over a period of time, there will be a number of collisions among the reactant particles. In a second diagram, the volume, V_2 , will be shown as half the original ($\frac{1}{2}V_1$). Now the same number of particles occupy half the space. On average there will be twice as many collisions and this should lead to an increase in the rate of reaction.



$$13. n\text{KClO}_3(\text{s}) = \frac{m}{M} = \frac{0.20 \text{ g}}{122.55 \frac{\text{g}}{\text{mol}}} = 1.6319 \times 10^{-3} \text{ mol}$$

The mole ratio of $\text{O}_2 : \text{KClO}_3$ is 3:2

$$\frac{\text{mol O}_2}{\text{mol KClO}_3} = \frac{3}{2}$$

$$n\text{O}_2(\text{g}) = \frac{3}{2} \times \text{mol KClO}_3(\text{s})$$

$$= \frac{3}{2} \times 1.6319 \times 10^{-3} \text{ mol}$$

$$= 2.4478 \times 10^{-3} \text{ mol}$$

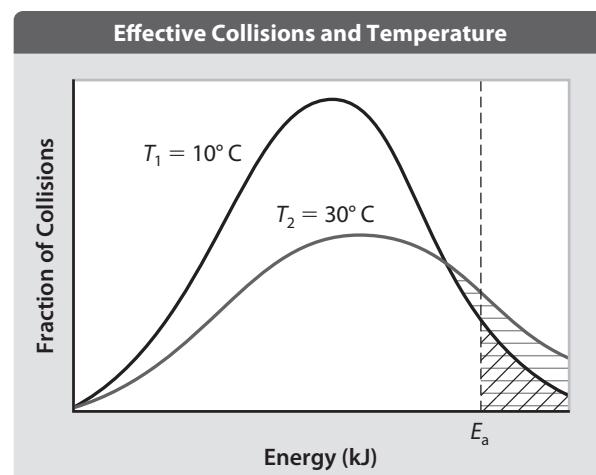
$$PV = nRT$$

$$V = \frac{nRT}{P} = \frac{2.4478 \times 10^{-3} \text{ mol} \times 8.314 \frac{\text{kPa}\cdot\text{L}}{\text{mol}\cdot\text{K}} \times 298.15 \text{ K}}{100.0 \text{ kPa}} = 6.0676 \times 10^{-2} \text{ L}$$

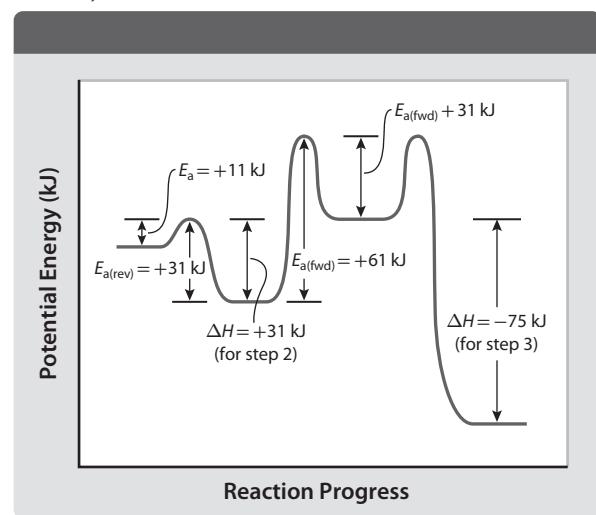
$$\text{Rate of formation of O}_2(\text{g}) = \frac{60.676 \text{ mL}}{2.8 \text{ s}} = 21.67 \frac{\text{mL}}{\text{s}} = 22 \frac{\text{mL}}{\text{s}}$$

14. An input of energy is needed to start the reaction associated with the explosion. This initial input of energy provides a few reactants with enough energy to overcome the activation barrier of the reaction. Explosive reactions are exothermic, so the initial successful collisions will generate energy to allow further reactions to occur.

15. Students' diagrams should resemble Figure 6.15 in the student textbook. They should change labels to show a 20°C difference. Even a modest increase in temperature can result in a significant increase in the number of collisions that occur with enough energy for a reaction to take place.



16. -64 kJ



17. The relative rate of change of a reactant or product is in proportion to their mole ratios in the balanced chemical equation.

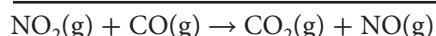
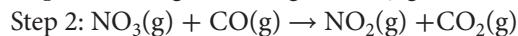
The mole ratio of $\text{NO:H}_2\text{O}$ is 4:6.

$$\frac{\text{rate of consumption}}{\text{rate of consumption of CO}_2} = \frac{n\text{NO}}{n\text{H}_2\text{O}}$$

$$\frac{0.050 \frac{\text{mol}}{\text{L}\cdot\text{s}}}{\text{rate of consumption of H}_2\text{O}} = \frac{4}{6}$$

$$\begin{aligned} \text{rate at which H}_2\text{O(g)} \text{ reacts} &= \frac{6}{4} \times 0.050 \frac{\text{mol}}{\text{L}\cdot\text{s}} \\ &= 7.5 \times 10^{-2} \frac{\text{mol}}{\text{L}\cdot\text{s}} \end{aligned}$$

18. One possible mechanism is shown below.



19. rate of change in $\text{AgNO}_3(\text{aq})$

$$\begin{aligned} \frac{\Delta C}{\Delta t} &= \frac{0.42 \frac{\text{mol}}{\text{L}} - 0.28 \frac{\text{mol}}{\text{L}}}{60.0 \text{ s} - 30.0 \text{ s}} \\ &= 4.667 \times 10^{-3} \frac{\text{mol}}{\text{L}\cdot\text{s}} \end{aligned}$$

The relative rate of change of a reactant or product is in proportion to the mole ratios in the balanced equation.

From the balanced equation, mole ratio $\text{AgNO}_3 : \text{Cl}^-$ is 2:2 (or 1:1). Therefore, the rate of reaction of chloride is equal to the rate of reaction of silver nitrate.

$$\begin{aligned} \text{rate of reaction of Cl}^- &= 4.667 \times 10^{-3} \frac{\text{mol}}{\text{L}\cdot\text{s}} \\ &= 4.7 \times 10^{-3} \frac{\text{mol}}{\text{L}\cdot\text{s}} \end{aligned}$$

20. The activation energy and the enthalpy change remain the same when the concentrations of the reactants are altered. Having a greater number of particles collide at a higher concentration does not affect the mechanism of the reaction or the nature of the bonds in the reactants. The reaction will proceed more quickly and more thermal energy will be generated more quickly, but the value of ΔH_r for the reaction as written in a thermochemical equation will not change.

21. It is a second-order reaction; for second-order reactions, the rate is proportional to the square of the reactant.

22. The number of effective collisions must be doubled to double the rate of reaction. This can be accomplished by increasing the temperature and/or, if the reactants are gases, by increasing the pressure.

23. a. Because there are three “peaks” representing three transition states, there are three steps involved in this reaction.

b. A: the reactants

B: transition state of Step 1

C: the products formed in Step 1, intermediates, and any unreacted reactants

D: the transition state of Step 2

E: the products formed in Step 2, intermediates, and any unreacted reactants

F: the transition state for Step 3

G: the products

H: the activation energy for the reverse of Step 1

I: the enthalpy change for Step 1

J: the activation energy for Step 2

K: the activation energy for Step 3

L: the enthalpy change for the overall reaction

c. A net quantity of energy is added because the products are higher in energy than the reactants, which means the overall reaction is endothermic.

24. Chemists use very short laser pulses to monitor chemical reactions. The durations of these pulses are in the range of femtoseconds. The first pulse provides the activation energy for the reaction. Chemists analyze the absorbance of the second pulse, and use the data to determine the absorbance characteristics of any activated complexes or chemical intermediates. This data allows chemists to identify the chemical species that are formed during a reaction and to provide evidence to support or refute a proposed reaction mechanism.

25. An increase in temperature will increase the rate of a reaction. As temperature increases, more particles will collide with enough energy to react. Student diagrams should resemble Figure 6.15 in the student textbook.

Answers to Unit 3 Review Questions

(Student textbook pages 403-9)

1. a

2. d

3. c

4. a

5. c

6. b

7. e

8. d

9. b

10. e

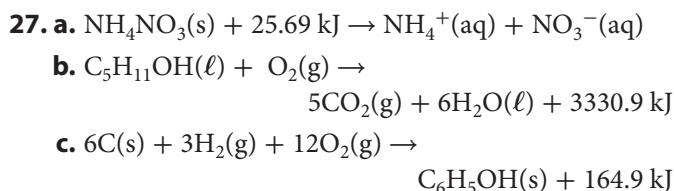
11. Since both water samples are at the same temperature, the average kinetic energy of the particles will be the same. Thermal energy is the sum of the kinetic energies of all the particles in a sample. Since there are more particles in the bathtub of water, the thermal energy will be greater in the bathtub sample.

- 12.** **a.** Thermal energy is removed from the air (the system).
- b.** The enthalpy change, ΔH_{cond} , is negative.
From Table 5.3, $\Delta H_{\text{vap}} = +40.7 \text{ kJ/mol}$.
Therefore $\Delta H_{\text{cond}} = -40.7 \text{ kJ}$.
- c.** $\text{H}_2\text{O(g)} \rightarrow \text{H}_2\text{O}(\ell) + 40.7 \text{ kJ}$
- 13.** Activation energy is the minimum collision energy between two particles that is required for a reaction to take place between the particles. For a reaction to occur, chemical bonds must be broken. The activation energy is primarily used for this process. The stronger the bonds, the greater the activation energy.
- 14.** The relative amount of energy required to break bonds in the reactants compared to the energy given off when new bonds form in the products determines whether the reaction is exothermic or endothermic. There is no relationship between this and the activation energy.
- 15.** **a.** three steps
b. Step 3
c. C to E
d. B, C, F
- 16.** **a.** To determine the average rate of reaction, one of the following can be determined before and after a period of time in the reaction: (i) the change in pH since HCl(aq) is an acid, (ii) the change in mass of $\text{LiCO}_3(\text{s})$, and (iii) the change in volume of $\text{CO}_2(\text{g})$.
- b.** To determine the instantaneous rate, one of these quantities must be measured over time. A graph of this quantity vs. time must be plotted and the slope of the tangent to the graph at some point in time must be measured.
- 17.** The kinetic molecular theory of gases describes the particles in constant motion, colliding with one another and with the walls of the container in elastic collisions. An increase in temperature adds kinetic energy so the particles move faster and collide more often. More of the collisions will be between particles having energy equal to or exceeding the activation energy and therefore more collisions will be effective. This will lead to an increase in the rate of the reaction.
- 18.**
- | catalyst | product | process |
|--|-------------------------|-------------|
| $\text{Fe}, \text{K}_2\text{O}, \text{Al}_2\text{O}_3$ | NH_3 | Haber-Bosch |
| V_2O_5 | H_2SO_4 | Contact |
| Pt/Ir | HNO_3 | Ostwald |
| xylanase | white paper | — |
| amylase | starch | — |
- 19.** A catalyst provides a site at which an alternate pathway of lower activation energy can occur. More of the colliding particles will have a kinetic energy equal to or exceeding the activation energy barrier. There will be more collisions that are effective and the rate of reaction will increase.
- 20.** **a.** An elementary step is a step in a series of simple reactions that represent the progress of a chemical reaction. The sum of the elementary steps gives the overall reaction.
- b.** The rate determining step is the slowest of the elementary steps in the reaction mechanism.
- c.** The rate determining step will have the highest activation energy of all the steps in the reaction mechanism.
- d.** The reactants in the rate determining step will be part of the rate law.
- 21.** The units for k will indicate the overall order of the reaction. The magnitude of k will give an indication of the rate of reaction. The larger the value of k , the faster the rate of reaction. Knowing the value of k when the concentration of the reactants is given allows you to predict the rate of reaction.
- 22.** The temperature change can be used but there are practical difficulties to control in order for results to be considered valid. The solution will absorb the heat change as the reaction proceeds. It will be necessary to have the solution stirred so that the heat change is uniform. It will be necessary to ensure that the volume of the solution is always the same for each trial so that any changes in temperature are solely because of the reaction. The reading of a thermometer must be done quickly for each reading.
- 23.** No, it cannot be stated with certainty. Reaction rates must be tested experimentally to determine exact relationships concerning rates. If the reaction is exothermic, once some particles react, the energy given off will give more particles sufficient kinetic energy to have effective collisions and the reaction will continue. For an endothermic reaction few particles are likely to combine initially and little energy will be available, or at least less energy than for the exothermic reaction, to give other particles kinetic energy to keep the reaction going. It could be expected that the average rate of the exothermic reaction will be faster over a given time period, but it cannot be stated with certainty.

24. In solution the molecules or ions are closer together and forces of attraction exist between the particles, which are not present in gases. Therefore, the 10°C increase in temperature would not increase the kinetic energy of particles in solution as much as gas particles. Therefore, it would not result in an increase in reaction rate to the same extent.

25. The diagram correctly shows the path of the reaction without a catalyst having a lower activation energy. The diagram is incorrect because the potential energy of the product must be the same with and without a catalyst.

$$\begin{aligned} \text{26. } \Delta H_f^\circ &= [\sum(n\Delta H_f^\circ \text{products})] - [\sum(n\Delta H_f^\circ \text{reactants})] \\ &= [(3 \text{ mol})(0.0 \text{ kJ/mol})] - [(2 \text{ mol})(+142.7 \text{ kJ/mol})] \\ &= -285.4 \text{ kJ} \end{aligned}$$



$$\begin{aligned} \text{28. } n(\text{NH}_3) &= \frac{6.46 \cancel{\text{g}}}{17.04 \frac{\cancel{\text{g}}}{\text{mol}}} = 0.3791 \text{ mol} \\ \Delta H_{\text{fre}} &= -5.66 \text{ kJ/mol} \\ \text{heat given off} &= n\Delta H_{\text{fre}} = 0.3791 \cancel{\text{mol}} \times -5.66 \frac{\text{kJ}}{\cancel{\text{mol}}} \\ &= -2.14 \text{ kJ} \end{aligned}$$



$$\begin{aligned} \text{b. } M(\text{CH}_4) &= 16.05 \text{ g/mol} \\ n(\text{CH}_4) &= \frac{100.0 \cancel{\text{g}}}{16.05 \frac{\cancel{\text{g}}}{\text{mol}}} = 6.230 \text{ mol} \\ Q &= n\Delta H_{\text{vap}} = 6.230 \cancel{\text{mol}} \times 8.19 \frac{\text{kJ}}{\cancel{\text{mol}}} = 51.0 \text{ kJ} \end{aligned}$$

30. For NH_3 : -226 kJ/mol; for O_2 : -181 kJ/mol; for NO : -226 kJ/mol; for H_2O : -151 kJ/mol

$$\begin{aligned} \text{31. } Q &= mc\Delta T = 324 \text{ g} \times 2.8 \frac{\text{J}}{\text{g} \cdot {}^\circ\text{C}} \times \Delta T \\ \Delta T &= \frac{2560 \cancel{\text{J}}}{324 \cancel{\text{g}} \times 2.80 \frac{\cancel{\text{J}}}{{}^\circ\text{C}}} = 2.82 {}^\circ\text{C} \end{aligned}$$

$$T_f - T_i = 2.82 {}^\circ\text{C}$$

$$T_f - 5.0 {}^\circ\text{C} = 2.82 {}^\circ\text{C}$$

$$T_f = 7.8 {}^\circ\text{C}$$

$$\begin{aligned} \text{32. a. } \frac{0.26 \text{ mol}}{355.4 \text{ kJ}} &= \frac{1 \text{ mol}}{x} \\ x &= 1366.9 \text{ kJ/mol} \end{aligned}$$

The molar heat of combustion is -1367 kJ/mol

b. ethanol

33. a. This thermochemical equation shows the decomposition of 1 mol of ammonium hydrogen sulfite, $\text{NH}_4\text{HSO}_3(\text{s})$, into its elements. It is the reverse of the formation equation for this compound.

$$\begin{aligned} \text{b. } \frac{\Delta H_1}{\Delta H_2} &= \frac{n_1 S(\text{s})}{n_2 S(\text{s})} \\ \frac{768.6 \text{ kJ}}{2690.1 \text{ kJ}} &= \frac{1 \text{ mol } S(\text{s})}{x \text{ mol } S(\text{s})} \\ x &= 3.500 \text{ mol} \\ \text{mass } S(\text{s}) &= nM = 3.500 \cancel{\text{mol}} \times 32.07 \frac{\text{g}}{\cancel{\text{mol}}} \\ &= 112.2 \text{ g} \end{aligned}$$

34. By using gasoline, there is $47.30 \text{ MJ/kg} - 44.80 \text{ MJ/kg} = 2.50 \text{ MJ/kg}$ more energy is available to heat the water.

$$\begin{aligned} 2.50 \cancel{\text{MJ}} \times 1 \times 10^3 \frac{\text{kJ}}{\cancel{\text{MJ}}} &= 2.5 \times 10^3 \text{ kJ} \\ Q &= n\Delta H_{\text{vap}} \\ n &= \frac{Q}{\Delta H_{\text{vap}}} = \frac{2.5 \times 10^3 \cancel{\text{kJ}}}{40.7 \frac{\cancel{\text{kJ}}}{\text{mol}}} = 61.425 \text{ mol} \\ m(\text{H}_2\text{O}) &= 61.425 \cancel{\text{mol}} \times 18.02 \frac{\text{g}}{\cancel{\text{mol}}} \\ &= 1.107 \times 10^3 \text{ g} = 1.11 \text{ kg} \end{aligned}$$

35. a, b, d, e, and f

$$\begin{aligned} \text{36. a. } Q &= mc\Delta T = 500.0 \cancel{\text{g}} \times 4.19 \frac{\text{J}}{\cancel{\text{g} \cdot {}^\circ\text{C}}} \times 12.3 {}^\circ\text{C} \\ &= 25768 \text{ J} = 25.8 \text{ kJ} \end{aligned}$$

$$\begin{aligned} \text{b. } n(\text{CH}_3\text{OH}) &= \frac{m}{M} = \frac{1.84 \cancel{\text{g}}}{32.05 \frac{\cancel{\text{g}}}{\text{mol}}} = 0.05741 \text{ mol} \end{aligned}$$

Heat given off during combustion = $n\Delta H_c^\circ$

$$\begin{aligned} &= 0.05741 \cancel{\text{mol}} \times -726.1 \frac{\text{kJ}}{\cancel{\text{mol}}} = -41.686 \text{ kJ} \\ &= -41.69 \text{ kJ} \end{aligned}$$

c. Energy input (the energy given off during combustion) = -41.69 kJ

Energy output (the thermal energy absorbed by the water) = 25.8 kJ

$$\begin{aligned} \text{d. Efficiency} &= \frac{\text{energy output}}{\text{energy input}} \times 100\% \\ &= \frac{25.768 \text{ kJ}}{41.686 \text{ kJ}} \times 100\% = 61.8\% \end{aligned}$$

37. $\Delta H_f^\circ = \Sigma(n\Delta H_f^\circ \text{products}) - \Sigma(n\Delta H_f^\circ \text{reactants})$

$$-1189.2 \text{ kJ} = [(2 \text{ mol})(\Delta H_f^\circ \text{CO}_2(\ell)) + (3 \text{ mol})(\Delta H_f^\circ \text{H}_2\text{O}(\ell))] - [(1 \text{ mol})(\Delta H_f^\circ \text{C}_2\text{H}_6\text{O}_2(\ell)) + (\frac{5}{2} \text{ mol})(\Delta H_f^\circ \text{O}_2(\ell))]$$

$$-1189.2 \text{ kJ} = [(2 \text{ mol})(-393.5 \text{ kJ/mol}) + (1 \text{ mol})(-285.8 \text{ kJ/mol})] - [(1 \text{ mol})(\Delta H_f^\circ \text{C}_2\text{H}_6\text{O}_2(\ell)) + (\frac{5}{2} \text{ mol})(0 \text{ kJ/mol})]$$

$$-1189.2 \text{ kJ} = (-1644.4 \text{ kJ/mol}) - (\Delta H_f^\circ \text{C}_2\text{H}_6\text{O}_2(\ell))$$

$$\Delta H_f^\circ \text{C}_2\text{H}_6\text{O}_2(\ell) = -455.2 \text{ kJ}$$

The heat of formation of ethylene glycol is
-455.2 kJ/mol

38. energy given off when 1.00 kg of natural gas burns

$$= 54.0 \frac{\text{kJ}}{\text{kg}} \times 1000 \frac{\cancel{\text{g}}}{\text{kg}}$$

$$= 5.40 \times 10^4 \frac{\text{kJ}}{\text{kg}}$$

$$= 5.40 \times 10^4 \frac{\cancel{\text{kJ}}}{\text{kg}} \times 0.00100 \frac{\text{MJ}}{\cancel{\text{kJ}}} = 54.0 \frac{\text{MJ}}{\text{kg}}$$

Energy given off when 1.00 kg of natural gas burns is
54.0 MJ.

$$\text{particulate emission level} = 3.35 \frac{\text{kg}}{\text{MJ}}$$

mass of particulate matter emitted

$$= 3.35 \frac{\text{kg}}{\text{MJ}} \times 54.0 \text{ MJ} = 1.809 \times 10^2 \text{ kg} = 181 \text{ kg}$$

39. (1) $\times 2 \quad 2S(s) + 2O_2(g) \rightarrow 2SO_2(g) \quad \Delta H_c^\circ = -593.6 \text{ kJ}$

(2) $\times -2 \quad SO_3(g) \rightarrow 2S(s) + 3O_2(g) \quad \Delta H_c^\circ = +791.4 \text{ kJ}$

$$2SO_3(g) \rightarrow 2SO_2(g) + O_2(g) \quad \Delta H = +197.8 \text{ kJ}$$

40. a. $M(C_{12}H_{22}O_{11}) = 342.34 \text{ g/mol}$

$$n(C_{12}H_{22}O_{11}) = \frac{m}{M} = \frac{3.00 \cancel{\text{g}}}{342.34 \frac{\cancel{\text{g}}}{\text{mol}}} = 0.008763 \text{ mol}$$

Heat given off during combustion

$$= n\Delta H_c^\circ = 0.008763 \text{ mol} \times -5650 \frac{\text{kJ}}{\text{mol}} = -49.512 \text{ kJ} = -49.5 \text{ kJ}$$

b. The calorimeter will absorb the heat given off by the combustion reaction, or $Q = +49.5 \text{ kJ}$.

c. Heat capacity of bomb calorimeter = $1284 \frac{\text{J}}{\text{°C}}$

$$\Delta T = \frac{49512 \cancel{\text{J}}}{1284 \frac{\cancel{\text{J}}}{\text{°C}}} = 38.6 \text{ °C}$$

d. rate of burning = $\frac{n}{\Delta t}$

$$= \frac{0.008763 \text{ mol}}{38.0 \text{ s}} = 2.31 \times 10^{-4} \frac{\text{mol}}{\text{s}}.$$

41. a. mol ratio $\text{Ag}^+(\text{aq}):\text{AgNO}_3(\text{aq}) = 1:1$

$$\Delta C(\text{AgNO}_3) = c_f - c_i = 0.185 \frac{\text{mol}}{\text{L}} - 0.200 \frac{\text{mol}}{\text{L}}$$

$$= 0.015 \frac{\text{mol}}{\text{L}}$$

$$\Delta \text{Ag}^+(\text{aq}) = \frac{\Delta C}{\Delta t} = \frac{0.015 \frac{\text{mol}}{\text{L}}}{25.0 \frac{\text{min}}{\text{min}} \times \frac{60 \text{ s}}{\text{min}}}$$

$$= 1.0 \times 10^{-5} \frac{\text{mol}}{\text{L}\cdot\text{s}}$$

b. mol ratio $\text{Ag}^+(\text{aq}):\text{AgNO}_3(\text{aq}) = 1:1$

mol ratio $\text{Fe}^{2+}(\text{aq}):\text{Fe}(\text{NO}_3)_2(\text{aq}) = 1:1$

The relative rate of change of a reactant or product is in proportion to their mole ratio in the balanced equation.

From the balanced equation, the mole ratio $\text{Ag}^+(\text{aq}):\text{Fe}^{2+}(\text{aq})$ is 2:1

$$\frac{\text{rate of formation of } \text{Fe}^{2+}}{\text{rate of consumption of } \text{Ag}^+} = \frac{n \text{ Fe}^{2+}}{n \text{ Ag}^+} = \frac{1}{2}$$

$$\frac{\text{rate of formation of } \text{Fe}^{2+}}{1.0 \times 10^{-5} \frac{\text{mol}}{\text{L}\cdot\text{s}} \text{ Ag}^+} = \frac{1}{2}$$

$$\text{Rate of formation of } \text{Fe}^{2+}(\text{aq}) = \frac{1}{2} \times 1.0 \times 10^{-5} \frac{\text{mol}}{\text{L}\cdot\text{s}}$$

$$= 5.0 \times 10^{-6} \text{ mol/L}\cdot\text{s}$$

42. instantaneous rates are $0.0050 \text{ mol/L}\cdot\text{s}$ ($t = 0 \text{ s}$)

and $0.00020 \text{ mol/L}\cdot\text{s}$ ($t = 30.0 \text{ s}$); average rate is $0.00075 \text{ mol/L}\cdot\text{s}$

43. For reaction 1: $E_{a(\text{rev})} = E_{a(\text{fwd})} + \Delta H$

$$= 25 \text{ kJ} + 50 \text{ kJ} = 75 \text{ kJ}$$

For reaction 2: $E_{a(\text{rev})} = E_{a(\text{fwd})} - \Delta H$

$$25 \text{ kJ} = E_{a(\text{fwd})} - 50 \text{ kJ}$$

$$E_{a(\text{fwd})} = 75 \text{ kJ}$$

$E_{a(\text{fwd})}$ and $E_{a(\text{rev})}$ are both 75 kJ

44. $M(\text{BrO}_3^-) = 127.9 \text{ g/mol}$

$$1.28 \frac{\text{g}}{\text{L}\cdot\text{s}} = \frac{\frac{1.28 \cancel{\text{g}}}{127.9 \frac{\cancel{\text{g}}}{\text{mol}}}}{\frac{\text{L}\cdot\text{s}}{0.0100 \text{ mol}}} = \frac{0.0100 \text{ mol}}{\text{L}\cdot\text{s}}$$

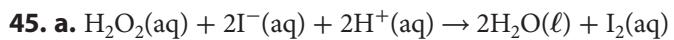
$$\frac{\text{rate of consumption } \text{BrO}_3^-(\text{aq})}{\text{rate of formation } \text{Br}_2(\ell)} = \frac{n \text{ BrO}_3^-(\text{aq})}{n \text{ Br}_2(\ell)}$$

$$\frac{0.0100 \frac{\text{mol}}{\text{L}\cdot\text{s}}}{\text{rate of formation } \text{Br}_2(\ell)} = \frac{1}{3}$$

$$\text{rate of formation of } \text{Br}_2(\ell) = 3 \times 0.0100 \frac{\text{mol}}{\text{L}\cdot\text{s}}$$

$$= 0.0300 \frac{\text{mol}}{\text{L}\cdot\text{s}}$$

$$= 3.00 \times 10^{-2} \text{ mol/L}\cdot\text{s}$$

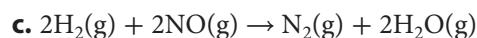


b. (i) Change in pH. As $\text{H}^+(\text{aq})$ is consumed the pH will rise.

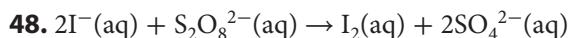
(ii) Both reactants are clear and colourless in aqueous solution. As $\text{I}_2(\text{aq})$ forms the solution will gradually turn reddish-brown as $\text{I}_2(\text{s})$ dissolves in the alcohol. This colour change could be used to monitor the rate of reaction with the use of a spectrophotometer.

46. a. No, a catalyst is not present. If a catalyst was present it would be shown as a reactant in one step and as a product in a later step.

b. $\text{N}(\text{g})$ and $\text{N}_2\text{O}(\text{g})$



47. $\frac{\text{mol}^{\frac{2}{3}}}{\text{L}^{\frac{2}{3}} \cdot \text{s}}$

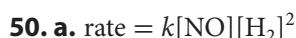


49. The relative rate of change of a reactant or product is in proportion to their mole ratio in the balanced equation.

The mole ratio $\text{H}_2(\text{g}) : \text{PH}_3(\text{g})$ is $\frac{3}{2} : 1$. For every $\frac{3}{2}$ mol of $\text{H}_2(\text{g})$ produced, 1 mol of $\text{PH}_3(\text{g})$ decomposes.

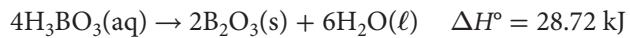
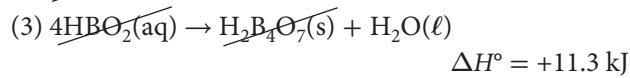
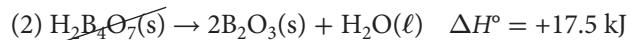
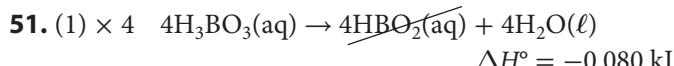
$$\frac{\text{rate of decomposition of } \text{PH}_3(\text{g})}{\text{rate of formation of } \text{H}_2(\text{g})} = \frac{n \text{ PH}_3(\text{g})}{n \text{ H}_2(\text{g})} = \frac{\frac{2}{3}}{\frac{3}{2}}$$

$$\begin{aligned} \text{rate of decomposition of } \text{PH}_3(\text{g}) &= \text{rate of formation } \text{H}_2(\text{g}) \times \frac{2}{3} \\ &= 4.8 \times 10^{-3} \frac{\text{mol}}{\text{L} \cdot \text{s}} \times \frac{2}{3} \\ &= 3.2 \times 10^{-3} \frac{\text{mol}}{\text{L} \cdot \text{s}} \end{aligned}$$

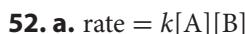
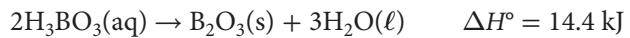


b. $\frac{\text{rate}_1}{\text{rate}_2} = \frac{k[\text{NO}(\text{g})][\text{H}_2(\text{g})]^2}{k[2\text{NO}(\text{g})][2\text{H}_2(\text{g})]^2} = \frac{1}{8}$

When both occur together the rate will increase by a factor of 8 times.

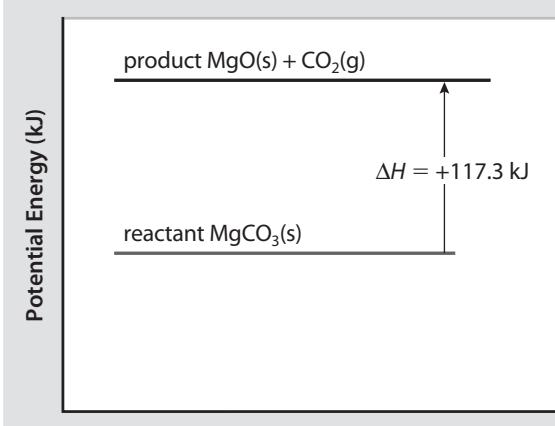


divide equation and enthalpy by 2



b. 2

53.



54. Energy is the ability to do work or produce heat.

Potential energy is stored energy. Kinetic energy is energy due to movement of particles. Compare these energies before and after lighting the gas. When unlit, the natural gas by itself is not doing work or producing heat. Its energy is stored in the chemical bonds of methane gas. When lit, bonds are broken and new bonds are formed, releasing thermal energy that heats the surroundings. The thermal energy increases movement of particles, which results in an increase in kinetic energy.

55. The symbol for *a change in value* is the Greek letter, lower case delta, Δ . By convention, this is understood to mean the final state minus the initial state for whatever variable is described.

ΔH_{fre} represents the difference in total energy between the liquid and solid.

$$\Delta H_{\text{fre}} = \text{energy of solid (final state)} - \text{energy of liquid (initial state)}$$

Since energy must be taken away from the liquid for freezing to occur, the energy of the solid is a smaller quantity than the energy of the liquid. ΔH_{fre} will be a negative quantity.

56. Answer should include the following: ΔH_r , ΔH_f , ΔH_{comb} , ΔH_{vap} , ΔH_{cond} , ΔH_{fre} , ΔH_{melt} , ΔH_{neut} , ΔH_{soln} .

ΔH_r is the enthalpy change of a reaction.

ΔH_f is the enthalpy change of a reaction that is the formation of a compound from its elements.

ΔH_{comb} is the enthalpy change of a combustion reaction.

ΔH_{vap} , ΔH_{cond} , ΔH_{fre} , and ΔH_{melt} represent the change in enthalpy that is associated with phase changes.

ΔH_{neut} is the enthalpy change of a neutralization reaction.

ΔH_{soln} is the enthalpy change associated with a solute dissolving in a solvent.

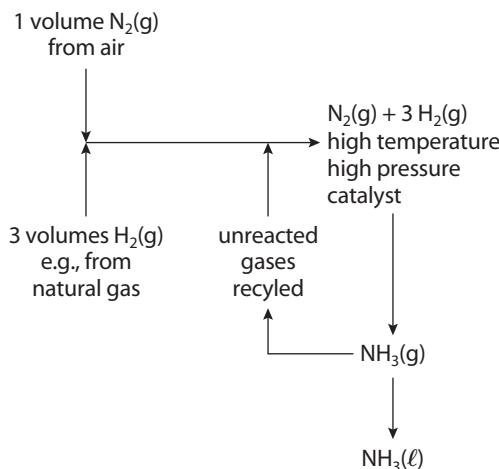
- 57.** Student reports should be one-page in length, with a clear outline of the different processes. The following information could be included:

Catalytic cracking breaks complex hydrocarbons into simpler molecules in order to increase the quality and quantity of lighter, more desirable products such as kerosene, gasoline, and heating oil. Use of a zeolite catalyst (aluminosilicates) increases the yield of products under much less severe operating conditions than in thermal cracking.

Catalytic reforming is the reuniting of smaller hydrocarbons to make larger ones using a platinum and platinum-rhenium mix for a catalyst. For example, low weight naphtha fraction can be combined into aromatics, which are used in blending gasoline.

Catalytic isomerization rearranges molecules into structural forms of the same molar mass but different molecular structure. For example, low octane number saturated hydrocarbons are converted to high octane number hydrocarbons. Catalysts are specific for a reaction but can include $\text{Pt}/\text{Al}_2\text{O}_3$, $\text{MoO}_3/\text{TiO}_2$, and $\text{Re}(\text{CO})$ compounds.

- 58.** A schematic similar to the following should be provided; more detail can be included.

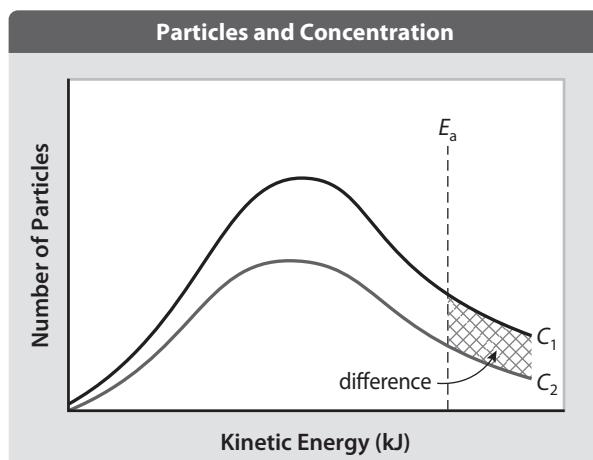


- 59.** Possible examples include: catalytic converters, fuel cells, formation of formaldehyde from methanol

- 60.** List the two requirements that must be met in order for a reaction to occur when particles collide, namely correct orientation and sufficient kinetic energy to equal or exceed the activation energy for the reaction. For the reaction to occur as shown in the balanced equation, 2 particles of X and 3 particles of Y must collide at one instant and meet the two requirements. Demonstrate models of the two types of reactants. This possibility has a very low probability of happening. There is a need for a reaction mechanism made up of bimolecular or two-particle collisions that will result in the equivalent overall reaction.

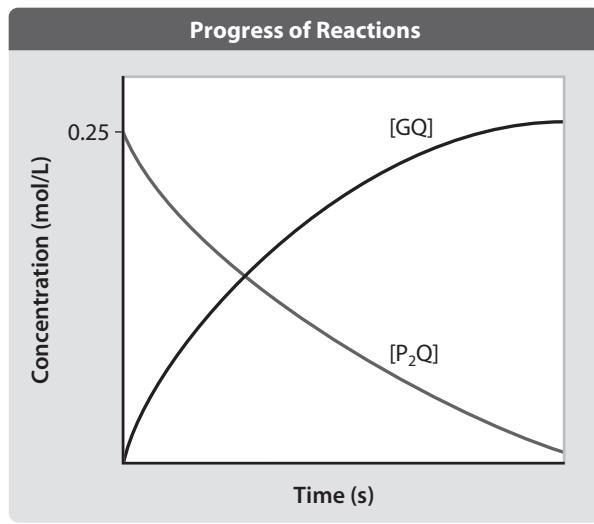
- 61.** Graphic organizers should provide the definition of each term and indicate how they relate to rates of reaction and, when applicable, each other.

- 62.**



In the graphic, concentration $c_1 >$ concentration c_2 . The total number of collisions and the total number of collisions with energy greater than the activation energy are both greater at concentration c_1 . The shaded area represents the difference in the number of particles at concentration c_1 having energy greater than the activation energy, E_a . This increase in the number of collisions with energy greater than E_a results in an increase in the reaction rate.

- 63.** Since all of $\text{P}_2\text{Q}(\text{aq})$ is used up, and in the balanced equation, the mole ratio $\text{P}_2\text{Q}(\text{aq}):G\text{Q}(\text{aq})$ is 1:1, the concentration of $\text{GQ}(\text{aq})$ at the completion of the reaction is 0.25 mol/L. $\text{G}(\text{s})$ and $\text{P}(\text{s})$ are not shown on this graph because they are solids and their amounts are not expressed in concentration units.



64. The layer of $\text{Al}_2\text{O}_3(s)$ is very thin and very little heat is actually given off per unit area of aluminum. In addition, the heat is quickly conducted away by the metal.

65. a. Each metal has a different specific heat capacity. This means that it takes a different quantity of heat to change its temperature by 1°C .

b. metal 1

$$\begin{aligned} \text{heat lost by metal} &= \text{heat gained by water} \\ mc\Delta T &= mc\Delta T \end{aligned}$$

$$\begin{aligned} 12.5 \text{ g} \times c \times (150.0^\circ\text{C} - 21.5^\circ\text{C}) &= \\ 100.0 \text{ g} \times 4.19 \frac{\text{J}}{\text{g}^\circ\text{C}} \times (21.5^\circ\text{C} - 20.0^\circ\text{C}) \\ c &= 0.391 \frac{\text{J}}{\text{g}^\circ\text{C}} \end{aligned}$$

metal 2

$$\begin{aligned} \text{heat lost by metal} &= \text{heat gained by water} \\ mc\Delta T &= mc\Delta T \end{aligned}$$

$$\begin{aligned} 12.5 \text{ g} \times c \times (150.0^\circ\text{C} - 23.4^\circ\text{C}) &= \\ 100.0 \text{ g} \times 4.19 \frac{\text{J}}{\text{g}^\circ\text{C}} \times (23.4^\circ\text{C} - 20.0^\circ\text{C}) \\ c &= 0.900 \frac{\text{J}}{\text{g}^\circ\text{C}} \end{aligned}$$

metal 3

$$\begin{aligned} \text{heat lost by metal} &= \text{heat gained by water} \\ mc\Delta T &= mc\Delta T \end{aligned}$$

$$\begin{aligned} 12.5 \text{ g} \times c \times (150.0^\circ\text{C} - 21.7^\circ\text{C}) &= \\ 100.0 \text{ g} \times 4.19 \frac{\text{J}}{\text{g}^\circ\text{C}} \times (21.7^\circ\text{C} - 20.0^\circ\text{C}) \\ c &= 0.444 \frac{\text{J}}{\text{g}^\circ\text{C}} \end{aligned}$$

Referring to Table 5.1, metal 1 is Cu, metal 2 is Al, and metal 3 is Fe.

66. Sample answers: cold temperature of a refrigeration unit to reduce the rate of food spoilage; application of a paint to a surface to prevent corrosion; vacuum packaging of food to exclude air and water to reduce the rate of spoilage; package with an inactive gas such

as nitrogen to keep food out of contact with air and prevent drying out and spoilage; a solution of hydrogen peroxide will include an inhibitor to reduce the rate of decomposition of H_2O_2 .

67. a. heat gained by surroundings

$$\begin{aligned} &= (mc\Delta T)_{\text{water}} + (mc\Delta T)_{\text{iron}} \\ &= 882 \text{ g} \times 4.19 \frac{\text{J}}{\text{g}^\circ\text{C}} \times 85.0^\circ\text{C} + \\ &\quad 1208 \text{ g} \times 0.449 \frac{\text{J}}{\text{g}^\circ\text{C}} \times 85.0^\circ\text{C} \\ &= 314\,124 \text{ J} + 46\,103 \text{ J} \\ &= 360\,227 \text{ J} = 3.602 \times 10^5 \text{ kJ} \end{aligned}$$

The transfer of heat from the burner to the pot of water is 45% efficient.

$$\text{Efficiency} = \frac{\text{Energy output}}{\text{Energy input}} \times 100\%$$

$$45.0\% = \frac{-3.602 \times 10^5 \text{ kJ}}{\text{Energy input}} \times 100\%$$

$$\text{Energy input} = 8.0044 \times 10^5 \text{ kJ}$$

$$\text{Heat given off from burning butane} = \Delta H$$

$$= -8.0044 \times 10^5 \text{ kJ}$$

$$\Delta H_c \text{ butane} = -2877.6 \text{ kJ/mol}$$

$$n = \frac{\Delta H}{\Delta H_c} = \frac{-8.0044 \times 10^5 \text{ kJ}}{-2877.6 \frac{\text{kJ}}{\text{mol}}} = 278.16 \text{ mol}$$

$$\begin{aligned} \text{mass of C}_4\text{H}_{10} &= n \times M = 278.16 \text{ mol} \times 58.14 \frac{\text{g}}{\text{mol}} \\ &= 1.6172 \times 10^4 \text{ g or } 16.2 \text{ kg} \end{aligned}$$

$$\text{b. Rate of burning butane} = \frac{\Delta Q}{\Delta t}$$

$$= \frac{278.16 \text{ mol}}{75.0 \text{ min}} = 3.71 \frac{\text{mol}}{\text{min}}$$

68. a. Incomplete combustion occurs when the fuel is first lit and burns with an orange flame. Complete combustion occurs when there is more oxygen present and the flame burns blue.

$$\text{b. } \Delta H_f^\circ = \Sigma(n\Delta H_f^\circ \text{ products}) - \Sigma(n\Delta H_f^\circ \text{ reactants})$$

$$\begin{aligned} \Delta H_{\text{comb}}^\circ &= [(2 \text{ mol})(\Delta H_f^\circ \text{ CO}_2(\text{g})) + \\ &\quad (1 \text{ mol})(\Delta H_f^\circ \text{ H}_2\text{O}(\text{g}))] - [(1 \text{ mol})(\Delta H_f^\circ \text{ C}_2\text{H}_2(\text{g})) \\ &\quad + (\frac{5}{2} \text{ mol})(\Delta H_f^\circ \text{ O}_2(\text{g}))] \\ &= [(2 \text{ mol})(-393.5 \text{ kJ/mol}) + (1 \text{ mol})(-241.8 \text{ kJ/mol})] \\ &\quad - [(1 \text{ mol})(227.4 \text{ kJ/mol}) + (\frac{5}{2} \text{ mol})(0 \text{ kJ/mol})] \\ &= (-1028.8 \text{ kJ/mol}) - (227.4 \text{ kJ/mol}) \\ &= -1256.2 \text{ kJ/mol} \end{aligned}$$

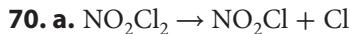
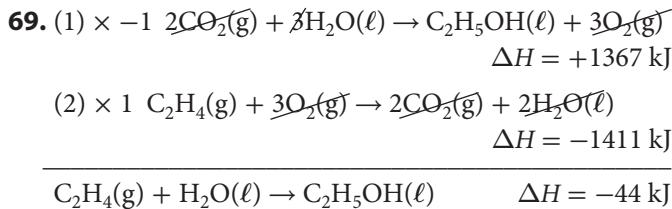
The enthalpy of combustion for complete combustion of acetylene is -1256.2 kJ/mol .

$$\begin{aligned}\Delta H_r^\circ &= \Sigma(n\Delta H_f^\circ \text{ products}) - \Sigma(n\Delta H_f^\circ \text{ reactants}) \\ \Delta H_{\text{comb}}^\circ &= [(\frac{1}{2} \text{ mol})(\Delta H_f^\circ \text{ CO}_2(\text{g})) + \\ &\quad (\frac{3}{2} \text{ mol})(\Delta H_f^\circ \text{ C(s)}) + (1 \text{ mol})(\Delta H_f^\circ \text{ H}_2\text{O(g)})] - \\ &\quad [(1 \text{ mol})(\Delta H_f^\circ \text{ C}_2\text{H}_2(\text{g})) + (1 \text{ mol})(\Delta H_f^\circ \text{ O}_2(\text{g}))] \\ &= [(\frac{1}{2} \text{ mol})(-393.5 \text{ kJ/mol}) + (\frac{3}{2} \text{ mol})(0 \text{ kJ/mol}) + \\ &\quad (1 \text{ mol})(-241.8 \text{ kJ/mol})] - \\ &\quad [(1 \text{ mol})(227.4 \text{ kJ/mol}) + (1 \text{ mol})(0 \text{ kJ/mol})] \\ &= (-438.55 \text{ kJ/mol}) - (227.4 \text{ kJ/mol}) \\ &= -665.95 \text{ kJ/mol}\end{aligned}$$

The enthalpy of combustion for the incomplete combustion of acetylene is -660.0 kJ/mol .

$$\begin{aligned}\text{c. } \frac{\Delta H_{\text{comb incomplete}}^\circ}{\Delta H_{\text{comb complete}}^\circ} \times 100\% &= \frac{-665.95 \text{ kJ}}{-1256.2 \text{ kJ}} \times 100\% \\ &= 53.01\%\end{aligned}$$

About half as much energy is available when acetylene burns in the manner shown by incomplete combustion.



- b.** An intermediate is a product in one step that is a reactant in a subsequent step. In this mechanism, NO_2Cl and Cl are intermediates.
- c.** In step 2, NO_2Cl_2 is the reactant. This species is an intermediate in the mechanism. An intermediate will not be part of the rate law. The rate law is most closely related to the rate determining or slow step. Step 2 is not likely the slow step.

- d.** Answers should include harmful effects (if any) related to water, soil, and air, and all life forms. Arguments related to use of the chemical should detail potential benefits as well as harms, and can look at economic impact as well as short- and long-term environmental effects. Answers should show evidence of risk/benefit analysis.

- 71. a.** The rate law depends on both the concentration of A and B. For the rate to be unchanged, if $[A]$ is changed, $[B]$ must also change.

- b.** For the rate to remain unchanged when $[A]$ is doubled, $[B]$ must be reduced to half the original amount.

$$\text{c. } k = \frac{\text{rate}}{[\text{A}][\text{B}]} = \frac{4.5 \times 10^{-2} \frac{\text{mol}}{\text{L}\cdot\text{s}}}{(0.40 \frac{\text{mol}}{\text{L}})(0.60 \frac{\text{mol}}{\text{L}})}$$

$$= 0.1875 \frac{\text{L}}{\text{mol}\cdot\text{s}} = 0.19 \frac{\text{L}}{\text{mol}\cdot\text{s}}$$

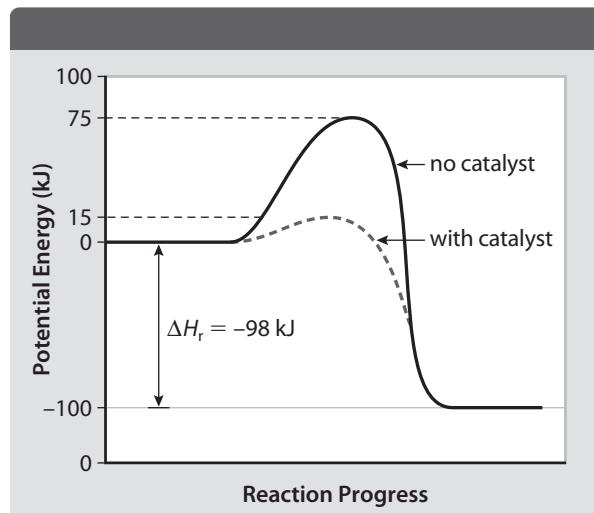
$$\begin{aligned}\text{d. rate} &= k[\text{A}][\text{B}] \\ &= 0.1875 \frac{\text{L}}{\text{mol}\cdot\text{s}} \times 0.80 \frac{\text{mol}}{\text{L}} \times 0.30 \frac{\text{mol}}{\text{L}} \\ &= 4.5 \times 10^{-2} \frac{\text{mol}}{\text{L}\cdot\text{s}}\end{aligned}$$

- 72.** Both reactions are first order. The reaction represented by the graph with the steeper slope occurs faster than the other.

- 73. a.** The reason why it foams is because blood and cells contain an enzyme called catalase. Since a cut or scrape contains both blood and damaged cells, there is catalase present. When the catalase comes in contact with hydrogen peroxide, it speeds up the breakdown of hydrogen peroxide (H_2O_2) into water (H_2O) and oxygen gas (O_2).

$$\begin{aligned}\text{b. } \Delta H_r^\circ &= \Sigma(n\Delta H_f^\circ \text{ products}) - \Sigma(n\Delta H_f^\circ \text{ reactants}) \\ &= [(1 \text{ mol})(\Delta H_f^\circ \text{ H}_2\text{O}(\ell))] + (1/2 \text{ mol}) \\ &\quad (\Delta H_f^\circ \text{ O}_2(\text{g})) - [(1 \text{ mol})(\Delta H_f^\circ \text{ H}_2\text{O}_2(\ell))] \\ &= [(-285.8 \text{ kJ}) + (0 \text{ kJ}) - [(-187.8 \text{ kJ})]] \\ &= -98 \text{ kJ}\end{aligned}$$

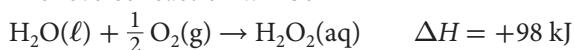
c.



If there are 80% more collisions leading to a reaction, it would be reasonable to estimate that the activation energy with the catalyst is 20% of the activation energy without a catalyst. The exact value of the activation energy must be determined experimentally.

Estimating: 20% of 75 kJ = 15 kJ

- d.** The reverse reaction will be



A heat of formation equation shows the elements as reactants and one mole of compound as product. This is not a heat of formation equation because the reactants include a compound, $\text{H}_2\text{O}(\ell)$.

- 74.** The rate of reaction is directly proportional to the concentration of reactant X. The rate is independent of the concentration of Y. If the volume of the container is doubled, the concentration of all reactants will be halved. Only the change in the concentration of X will affect the rate. Since the concentration of X is half the original concentration, the rate will be reduced to half the original rate.

Answers to Unit 3 Self-Assessment Questions

(Student textbook pages 410-11)

1. e

2. d

3. c

4. b

5. a

6. d

7. b

8. d

9. b

10. c

- 11.** This is a formation reaction for the compound copper(II) chloride from its elements. The compound $\text{CuCl}_2(\text{s})$ forms from its elements in an exothermic reaction. Measured at the standard state of 25°C and 100 kPa pressure, 1 mol of $\text{Cu}(\text{s})$ and 1 mol of $\text{Cl}_2(\text{g})$ react to release 220.1 kJ of energy and form $\text{CuCl}_2(\text{s})$.

- 12.** (1) $6\text{C}(\text{s}) + 3\text{H}_2(\text{g}) \rightarrow \text{C}_6\text{H}_6(\ell) \quad \Delta H_f^\circ = +49.1 \text{ kJ/mol}$
 (2) ~~$6\text{C}(\text{s}) + 3\text{H}_2(\text{g}) \rightarrow \text{C}_6\text{H}_6(\text{g}) \quad \Delta H_f^\circ = +82.91 \text{ kJ/mol}$~~
 (1) $\times -1 \quad \text{C}_6\text{H}_6(\ell) \rightarrow \text{C}_6\text{H}_6(\text{g}) \quad \Delta H_f^\circ = -49.1 \text{ kJ/mol}$



- 13.** The system is isolated so that any thermal energy exchanged with the surroundings outside the calorimeter is small and can be ignored. The thermal energy that is exchanged with the calorimeter (cup, lid, stirring rod) is small enough to be ignored. The density and specific heat capacity of any solutions are the same as for water.

- 14.** H_f° reactions show the elements as reactants in the correct mole ratio as they appear in the product, 1 mol of compound. In the equation as written, one of the reactants is a compound, $\text{CO}(\text{g})$. The correct equation for the heat of formation of $\text{CO}_2(\text{g})$ is $\text{C}(\text{s}) + \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g})$.

$$15. n(\text{H}_2\text{O}) = \frac{9.83 \times 10^{13} \text{ g}}{18.02 \frac{\text{g}}{\text{mol}}} = 5.4550 \times 10^{12} \text{ mol}$$

$$= (5.4550 \times 10^{12} \text{ mol}) \times (-40.7 \frac{\text{kJ}}{\text{mol}})$$

$$= -2.22 \times 10^{14} \text{ kJ}$$

$$16. \Delta H_r^\circ = [\Sigma(n\Delta H_f^\circ \text{ products})] - [\Sigma(n\Delta H_f^\circ \text{ reactants})]$$

$$= [(1 \text{ mol})(\Delta H_f^\circ \text{ CO}_2(\text{g})) + (2 \text{ mol})(\Delta H_f^\circ \text{ SO}_2(\text{g}))] -$$

$$[(1 \text{ mol})(\Delta H_f^\circ \text{ CS}_2(\ell)) + (3 \text{ mol})(\Delta H_f^\circ \text{ O}_2(\text{g}))]$$

$$= [(1 \text{ mol})(-393.5 \text{ kJ/mol}) + (2 \text{ mol})(-269.8 \text{ kJ/mol})] -$$

$$[(1 \text{ mol})(+89 \text{ kJ/mol}) + (3 \text{ mol})(0 \text{ kJ/mol})]$$

$$= -1022.1 \text{ kJ}$$

This is the heat given off when 2 mol of $\text{SO}_2(\text{g})$ is produced.

The heat of reaction per mol $\text{SO}_2(\text{g})$ is -511.0 kJ/mol .

- 17.** heat gained by ethanol = $mc\Delta T$

$$= 250.0 \text{ g} \times 2.44 \frac{\text{J}}{\text{g} \cdot ^\circ\text{C}} \times 30.0 \text{ }^\circ\text{C}$$

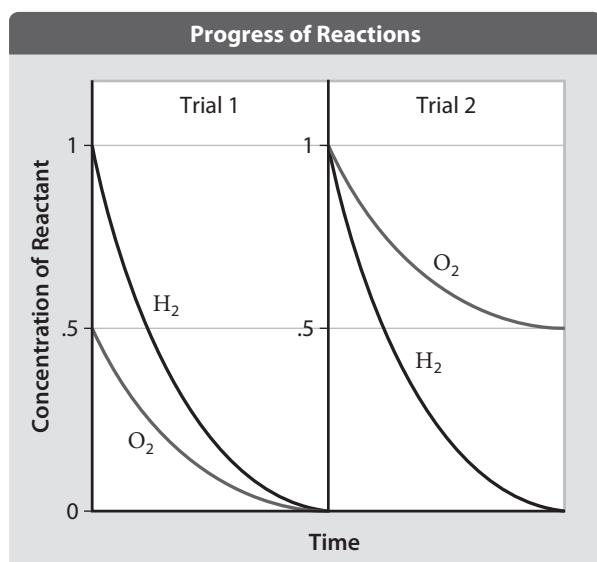
$$= 1.830 \times 10^4 \text{ J} = 18.30 \text{ kJ}$$

$$\text{Efficiency} = \frac{\text{Energy output}}{\text{Energy input}} \times 100\%$$

$$= \frac{18.30 \text{ kJ}}{27.3 \text{ kJ}} \times 100\% = 67.0 \%$$

- 18.** From the balanced equation, the gases react as

$\text{H}_2(\text{g}) : \text{O}_2(\text{g}) = 2:1$. In the first trial, there will be no reactant gases remaining after the reaction. In the second trial, the $\text{O}_2(\text{g})$ is in excess and half of the original amount of this gas will remain.



- 19.** Since the reaction occurs only when the heat is supplied, the reaction must be endothermic. Thermal energy must be supplied to the particles of HgO(s) that equals or exceeds the activation energy barrier for the reaction.
- 20.** Every reaction will have an activation energy. The activation energy for these reactions is not zero. The collision necessary to cause a reaction will occur between two ions that are opposite in charge. The attractions that must be overcome in aqueous solution are solvent-solvent and solvent-solute attractions, both of which will be small in magnitude. The thermal energy in the solutions at room temperature is sufficient to supply this small amount of energy.
- 21.** The steps associated with using Hess's law and enthalpies of formation is given as an example. Flowcharts should include the following key components.
1. Write the balanced chemical equation.
for example:
 $\text{CH}_4(\text{g}) + 2\text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) + 2\text{H}_2\text{O}(\text{g})$
 2. Use the following equation and standard molar enthalpies of formation data from a reference source.
- $$\Delta H_r^\circ = \Sigma(n\Delta H_f^\circ \text{ products}) - \Sigma(n\Delta H_f^\circ \text{ reactants})$$
- $$\Delta H_{\text{comb}}^\circ = [(1 \text{ mol})(\Delta H_f^\circ \text{ CO}_2(\text{g})) + (2 \text{ mol})(\Delta H_f^\circ \text{ H}_2\text{O}(\text{g}))] - [(1 \text{ mol})(\Delta H_f^\circ \text{ CH}_4(\text{g})) + (2 \text{ mol})(\Delta H_f^\circ \text{ O}_2(\text{g}))]$$
- $$= [(1 \text{ mol})(-393.5 \text{ kJ/mol}) + (2 \text{ mol})(-241.8 \text{ kJ/mol})] - [(1 \text{ mol})(-74.6 \text{ kJ/mol}) + (2 \text{ mol})(0 \text{ kJ/mol})]$$
- $$= [(-393.5 \text{ kJ}) - (483.6 \text{ kJ/mol})] - (-74.6)$$
- $$= -802.5 \text{ kJ}$$
- 22. a.** $2\text{NO}_2(\text{g}) + \text{Br}_2(\text{g}) \rightarrow 2\text{NO}_2\text{Br}(\text{g})$
- b.** step 2
- c.** 1
- 23.** The reactants in the rate determining step will be present in the rate law. The rate determining step is the slow step in the mechanism. In the proposed mechanism, the rate determining step shows an intermediate in the reaction mechanism. An intermediate is produced in one step and used up in a subsequent step. An intermediate will not be a component in a rate law. The mechanism is not consistent with the rate law.
- 24.** Enthalpy changes associated with nuclear changes are much greater than those of physical and chemical changes. An example of a nuclear change is the $2 \times 10^{10} \text{ kJ}$ of energy released when 1 mol of uranium-235 undergoes nuclear fission. Enthalpy changes of chemical changes are greater than enthalpy changes of physical changes. An example is the enthalpy of combustion of methane, which is -890 kJ . An example of enthalpy change associated with physical changes is the enthalpy of melting for water, which is approximately 6 kJ/mol .
- 25.** The projected use of energy resources by 2015 is 40%. These projections include 15% for wind energy and up to 5% for solar energy. Advantages of wind energy include low operating costs and no chemical pollutants. Disadvantages include noise pollution and potential danger to birds near the wind farms. Advantages to solar energy are that the source is free and unlimited. However, the technology is still expensive.
- The majority of the remaining renewable energy is hydroelectric power. Advantages of hydroelectric power include no combustion emissions and high efficiency. Disadvantages include flooding of land and damage to habitats in the region that the dam is built.