

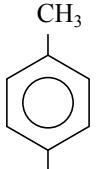
Unit 1 Organic Chemistry

ARE YOU READY?

(Page 4)

Understanding Concepts

1. (a) 3,3-dimethylpentane
(b) 1-methyl-4-propylcyclohexane
2. (a) $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$
(b)
$$\begin{array}{ccccccc} & \text{CH}_3 & & & & & \\ & | & & & & & \\ \text{CH}_3 & \text{C} & \text{H}_2 & \text{C} & \text{H}_2 & \text{C} & \text{H}_2 & \text{C} & \text{H}_3 \\ & | & & & & & & & \\ & \text{CH}_3 & & & & & & & \end{array}$$

(c)

(d)
$$\begin{array}{c} \text{CH}_3 \\ | \\ \text{CH}_2\text{CH}_3 \\ | \\ \text{CH}_3\text{CHCH}_2\text{CH}_2\text{CH}=\text{CH}_2 \end{array}$$

(e) $\text{CH}_3\text{CH}_2\text{C}\equiv\text{CH}$
3. $\text{C}_7\text{H}_{16} + 11\text{O}_2 \rightarrow 7\text{CO}_2 + 8\text{H}_2\text{O}$
4. Cyclohexane (a) and 2,3-dimethyl-2-butene (d) are structural isomers; cyclohexene (b) and hexyne (c) are structural isomers.
5. Pentane would have a higher boiling point because it has a long carbon chain allowing more van der Waals attractions between molecules. The 2,2-dimethylpropane has a more spherical shape, with fewer intermolecular attractions. More energy is required to separate molecules with stronger intermolecular attractions, and thus, these compounds have higher boiling points.
6. 2,2-dihydroxyethane, (a), will have a greater solubility in water than does methylbenzene, (b).
7. H, (C, S), (N, Cl), O
8. (a) intramolecular: single covalent bonds; intermolecular: van der Waals
(b) intramolecular: single covalent bonds; intermolecular: van der Waals forces and hydrogen bonds
(c) intramolecular: single covalent bonds; intermolecular: van der Waals forces and hydrogen bonds
9. Liquid 1 is 2-methylbutane; liquid 2 is 2-methyl-2-butene; liquid 3 is pentane.
10. (a) The safety precautions needed are as follows: wear eye protection and a lab apron; avoid direct contact with skin (if in contact with skin, wash with copious amounts of water); when diluting concentrated acids, add acid to water; handle concentrated acids in a fume hood; store in glass or plastic container in secure location.
(b) The safety precautions needed are as follows: wear eye protection and a lab apron; do not use with open flames; store in secure location.

CHAPTER 1 ORGANIC COMPOUNDS

Reflect on Your Learning

(Page 6)

1. (Sample response) Stain remover: nontoxic, soluble in water and fats and oils, not flammable, no unpleasant odours, liquid or solid at room temperatures, colourless, biodegradable.
2. (Sample response) They are similar in structure, similar in types of atoms, similar in size, similar in chemical reactivity.
3. • Solubility: “like dissolves like,” compounds that have large nonpolar components tend to be soluble in nonpolar solvents, and compounds that have small nonpolar components and polar groups such as C=O, OH, or NH groups tend to be soluble in polar solvents.
- Melting and boiling points: compounds with strong intermolecular attractions tend to have higher melting and boiling points as more energy is required to separate the molecules.
4. (Sample response) “Organic” means made by plants or animals; compounds that contain carbon atoms; grown without use of synthetic materials.

Try This Activity: How Do Fire-Eaters Do That?

(Page 7)

- (a) A relatively cool-burning fuel is used, and the fire-eater takes care always to stay below the flame, as the photograph shows.

1.1 FUNCTIONAL GROUPS

PRACTICE

Understanding Concepts

(Page 10)

1. A functional group is a structural arrangement of atoms that, because of their electronegativity and bonding type, imparts particular characteristics to the molecule.
2. Yes, C=C and C=C bonds are more reactive than C—C bonds because the second and third bonds formed are weaker than the first single bond formed, and are thus more readily broken, making the multiple bonds more reactive.
3. A polar molecule would have a boiling point higher than that of a less polar molecule; polar molecules have stronger intermolecular attractions, requiring more energy (higher temperatures) to separate them.
4. Functional groups can contain:
 - carbon–carbon multiple bonds, which are more reactive than single C—C bonds;
 - single bonds between carbon and more electronegative atoms (e.g., O, N, or a halogen atom), which result in polar bonds and consequently, hydrogen bonding;
 - carbon double-bonded to oxygen, making a strongly polarized bond.

SECTION 1.1 QUESTIONS

(Page 10)

Understanding Concepts

1. (a) The functional group raises the melting and boiling points of a compound because increased polarity of the molecule increases the intermolecular forces of attraction, requiring more energy to separate the molecules.
(b) The functional group increases the solubility in polar solvents because —OH and —NH groups allow increased hydrogen bonding with polar solvent.
2. (a) —OH group; high solubility in water
(b) carbon–carbon double bond; low solubility in water
(c) carbonyl group C=O; high solubility in water
(d) —OH group and carbonyl group C=O; high solubility in water

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(b) carbon–carbon double bond; low solubility in water
(c) carbonyl group C=O; high solubility in water
(d) —OH group and carbonyl group C=O; high solubility in water

3. (a) H_2O , NH_3 , CH_4
 (b) Water and ammonia are mutually soluble, methane is not soluble in the other two; electronegativity values of O, N, C, and H are 3.5, 3.0, 2.5, and 2.1, respectively. Thus, the O–H and N–H bonds in water and in ammonia are more polar than C–H bonds in methane. The polar bonds in water and ammonia allow them to form hydrogen bonds; thus, they are soluble in each other.
 (c) All three compounds are produced by living organisms (e.g., water by animals and plants, ammonia and methane by bacteria) and may be considered “organic” by the definition that a substance is organic if produced by a living organism. By the chemical definition of “organic” being compounds of carbon, only methane is organic.

1.2 HYDROCARBONS

PRACTICE

(Page 15)

Understanding Concepts

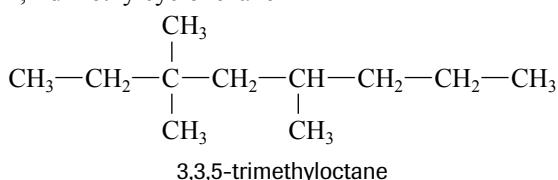
1. (a) 4-ethyl-2,3,5-trimethylheptane

(b) 3,7-dimethylnonane

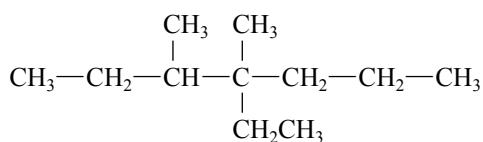
(c) 3,5,7-trimethyldecane

(d) 1,4-dimethylcyclohexane

2. (a)

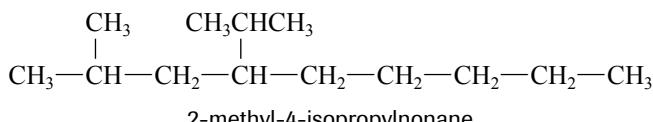


- (b)

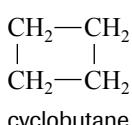


3,4-dimethyl-4-ethylheptane

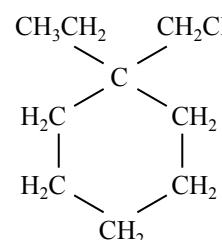
- (c)



- (d)



- (e)



1,1-diethylcyclohexane

3. (a) H_2O , NH_3 , CH_4
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PRACTICE

(Page 15)

Understanding Concepts

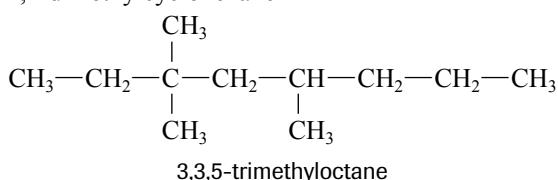
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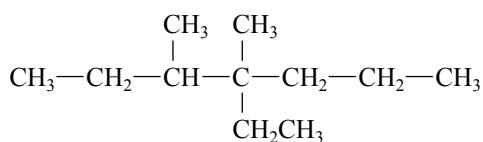
(c) 3,5,7-trimethyldecane

(d) 1,4-dimethylcyclohexane

2. (a)

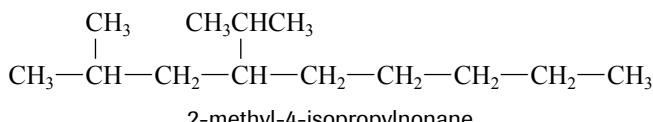


- (b)

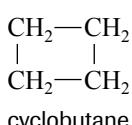


3,4-dimethyl-4-ethylheptane

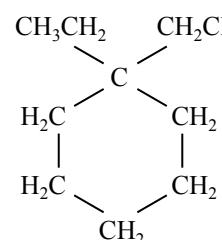
- (c)



- (d)



- (e)



1,1-diethylcyclohexane

PRACTICE

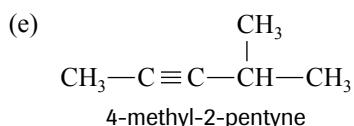
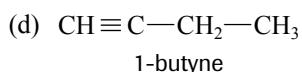
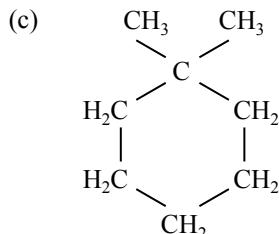
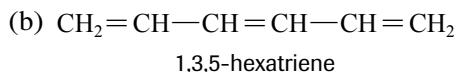
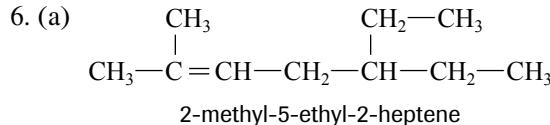
(Page 18)

Understanding Concepts

3. There is only one possible molecular structure for ethene and propene; the double bond in ethene can only be between the 2 C atoms, and the double bond in propene may be between C-1 and C-2, or between C-2 and C-3, both resulting in the same molecule.

4. The IUPAC name is ethyne; the common name is acetylene.

5. (a) 5-ethyl-4-methyl-2-heptyne
(b) 3-ethyl-2-hexene
(c) 1,4,7-nonatriene
(d) 5-methyl-1,3-octadiene
(e) 3,5-dimethylcyclohexene



Try This Activity: Building Hydrocarbons

(Page 20)

- (a) (Answers should include straight and branched chain alkanes with 6 carbons, such as hexane, 2-methylpentane, 3-methylpentane, 2,3-dimethylbutane, 2,2-dimethylbutane.)
- (b) (Answers should include straight and branched chain alkenes with 6 carbons and 1 double bond, and cycloalkanes with a total of 6 carbons, such as hexene; 2-methyl-1-pentene, 3-methyl-2-pentene; 2,4-dimethyl-2-butene; 2,3-dimethyl-1-butene; cyclohexane; methylpentane.)
- (c) (Answers should show an increasing number of double bonds or triple bonds.)
- (d) All the molecules in (a) are structural isomers, all in (b) are structural isomers, etc. Geometric isomers are also possible — *cis*- or *trans*- about a double bond.

PRACTICE

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Understanding Concepts

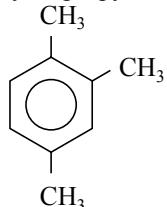
7. (a) 3-methyl-4-phenylhexane

(b) 2-phenyl-3-heptene

(c) 4-phenyl-1-pentyne

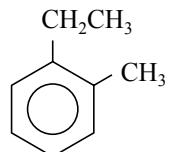
(d) 1-methyl-4-propylbenzene

8. (a)



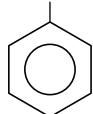
1,2,4-trimethylbenzene

(b)



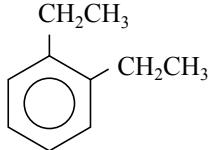
1-ethyl-2-methylbenzene

(c) CH₃—CH₂—CH—CH₂—CH₃



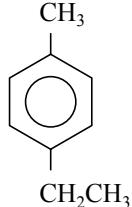
3-phenylpentane

(d)



o-diethylbenzene

(e)

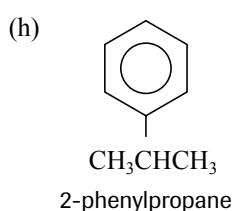
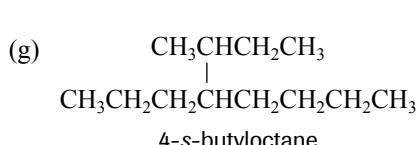
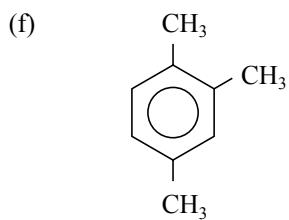
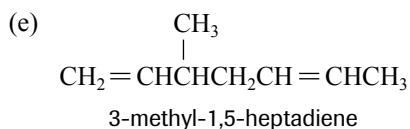
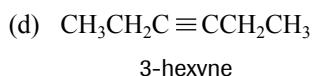
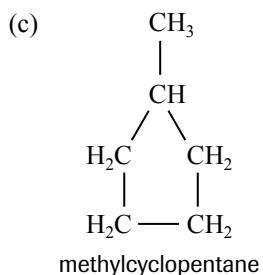
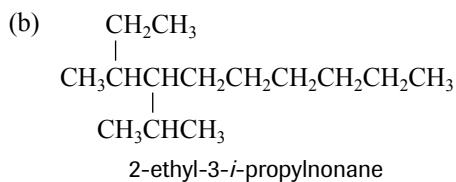
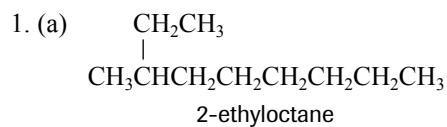


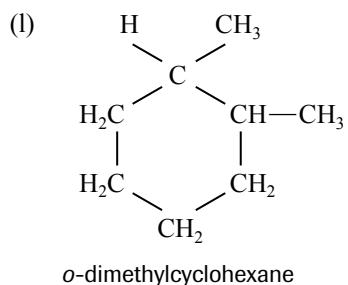
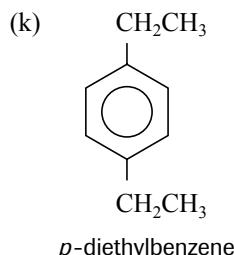
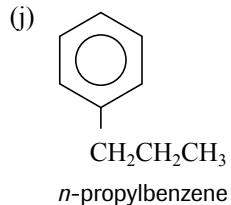
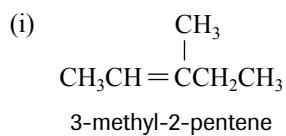
p-ethylmethylbenzene

SECTION 1.2 QUESTIONS

Understanding Concepts

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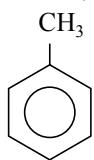


2. (a) 2-dimethylhexane: incorrect; does not indicate location of second methyl group. Possible correct name: 2,2-dimethylhexane
 (b) 3-methyl-1-pentyne: correct
 (c) 2,4-dimethylheptene: incorrect; does not indicate location of double bond. Possible correct name: 2,4-dimethyl-1-heptene
 (d) 3,3-ethylpentane: incorrect; should be diethyl. Possible correct name: 3,3-diethylpentane
 (e) 3,4-dimethylhexane: correct
 (f) 3,3-dimethylcyclohexene: correct (location of double bond in cyclohexene is understood to be position 1)
 (g) 2-ethyl-2-methylpropane: incorrect; the longest carbon chain is 4 carbons long. Possible correct name: 2,2-dimethylbutane
 (h) 2,2-dimethyl-1-butene: incorrect; compound does not exist because carbon-2 cannot form 5 bonds. Possible correct name: 3,3-dimethyl-1-butene
 (i) 1-methyl-2-ethylpentane: incorrect; the longest carbon chain is 6 carbons long. Correct name: 3-ethylhexane
 (j) 2-methylbenzene: incorrect; no numbering is needed for a single attached group. Correct name: methylbenzene
 (k) 1,5-dimethylbenzene: incorrect; use the lowest numbering system. Correct name: 1,3-dimethylbenzene
 (l) 3,3-dimethylbutane: incorrect; use the lowest numbering system. Correct name: 2,2-dimethylbutane
3. (a) 4-*i*-propyl-2,5-octadiene
 (b) 1-ethyl-3-methylbenzene
 (c) 3-methyl-2-phenylpentane
 (d) 1,2-diethylcyclopentane
 (e) 3,4-dimethyl-3-isopropyl-1-hexene
4. (a) ethylene
 $\text{CH}_2=\text{CH}_2$
 (b) propylene
 $\text{CH}_2=\text{CHCH}_3$

(c) acetylene

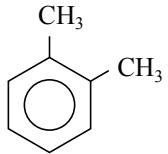


(d) toluene, the toxic solvent used in many glues

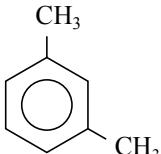


toluene

(e) the *o*-, *m*-, and *p*- isomers of xylene



i) *o*-xylene



ii) *m*-xylene



iii) *p*-xylene

Making Connections

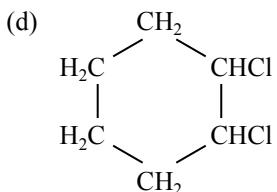
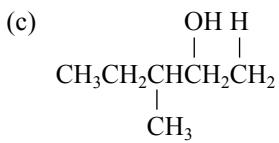
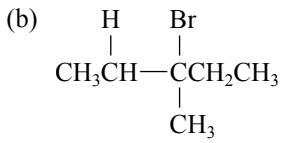
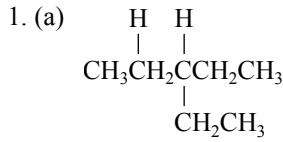
5. The graph shows a direct relationship between the number of carbon atoms and the boiling points of alkanes. This relationship is explained by the increasing number of van der Waals attractions between molecules, as the length of the carbon chain increases. As the intermolecular attraction increases, the amount of energy required to separate the molecules increases, resulting in a higher boiling point.

1.3 REACTIONS OF HYDROCARBONS

PRACTICE

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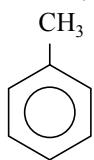
Understanding Concepts



(c) acetylene

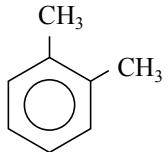


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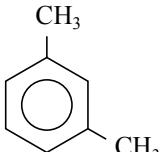


toluene

(e) the *o*-, *m*-, and *p*- isomers of xylene



i) *o*-xylene



ii) *m*-xylene



iii) *p*-xylene

Making Connections

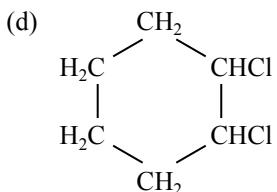
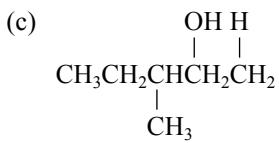
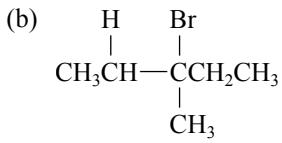
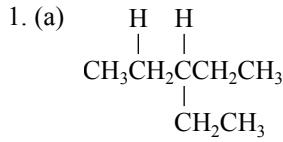
5. The graph shows a direct relationship between the number of carbon atoms and the boiling points of alkanes. This relationship is explained by the increasing number of van der Waals attractions between molecules, as the length of the carbon chain increases. As the intermolecular attraction increases, the amount of energy required to separate the molecules increases, resulting in a higher boiling point.

1.3 REACTIONS OF HYDROCARBONS

PRACTICE

(Page 27)

Understanding Concepts



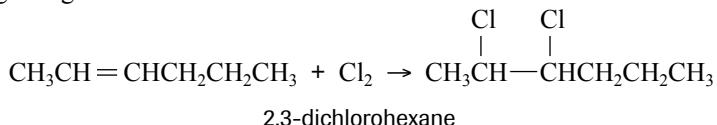
PRACTICE

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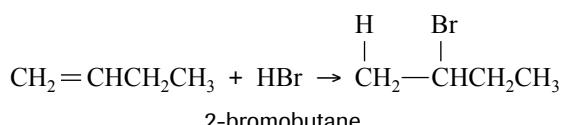
Understanding Concepts

2. When a double bond undergoes an addition reaction in which an H atom is added, the H atom adds to the C atom in the double bond that already bonds to more H atoms. Thus, the C atom that is already “rich” in H atoms, gets “richer” by gaining the additional H atom.

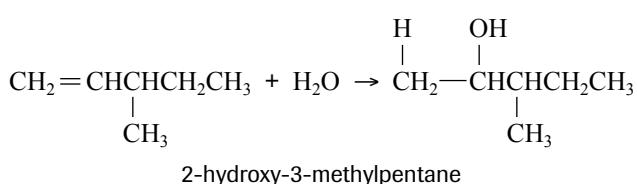
3. (a)



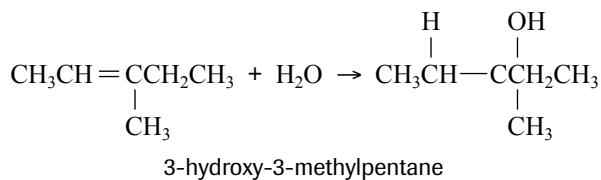
(b)



(c)



(d)

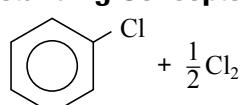


PRACTICE

(Page 30)

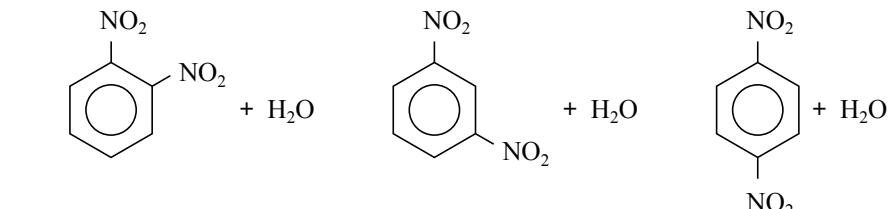
Understanding Concepts

4. (a)



chlorobenzene

(b)

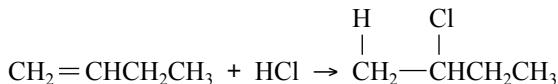


i) 1,2-dinitrobenzene

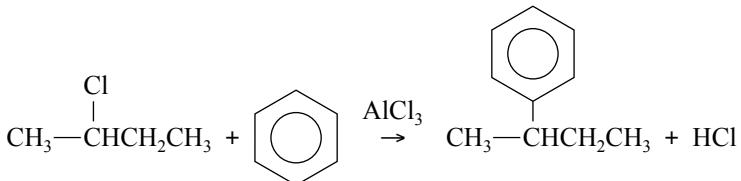
ii) 1,3-dinitrobenzene
(favoured product)

iii) 1,4-dinitrobenzene

5. (Sample answer) Step 1: Prepare 2-chlorobutane from 1-butene and HCl.



Step 2: Prepare 2-phenylbutane from 2-chlorobutane and benzene, in the presence of a catalyst.



6. The terms “substitution” and “halogenation” both describe the reaction between benzene and bromine; the term “addition” does not. In the reaction, a bromine atom is attached to the benzene ring, displacing an H atom, but no double bonds are broken. It is thus a substitution reaction and not an addition reaction. Since the reaction results in the presence of a halogen atom (Br) on the benzene structure, it is also a general halogenation reaction.

7. The bonding structure in benzene is intermediate between that of single carbon–carbon bonds and double carbon–carbon bonds. All the carbon–carbon bonds around the benzene ring appear to be equivalent to each other. Evidence: Benzene is more reactive than hexane (with only single bonds) and less reactive than hexene (with a double carbon–carbon bond). Bond lengths between carbon atoms in a benzene ring are identical and are intermediate between the bond lengths of single and double carbon–carbon bonds.

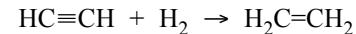
SECTION 1.3 QUESTIONS

(Page 31)

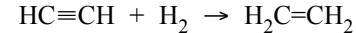
Understanding Concepts

1. (Sample answers)

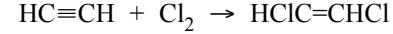
(a) addition



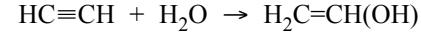
(b) hydrogenation



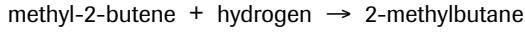
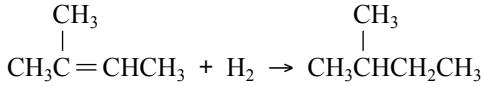
(c) halogenation



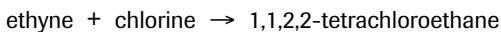
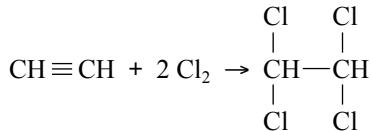
(d) hydration



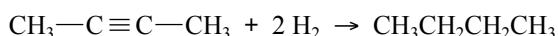
2. (a) addition, hydrogenation



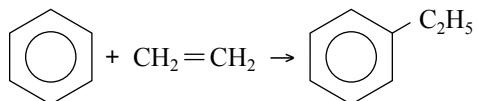
(b) addition, halogenation



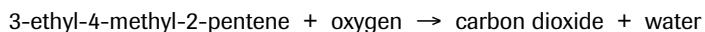
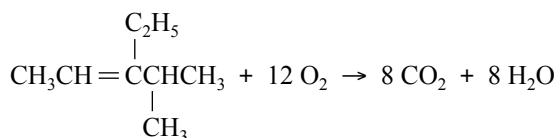
(c) addition, hydrogenation



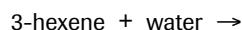
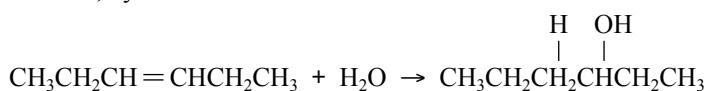
(d) substitution (for benzene), and addition (for ethene)



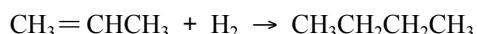
(e) combustion



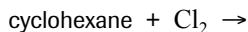
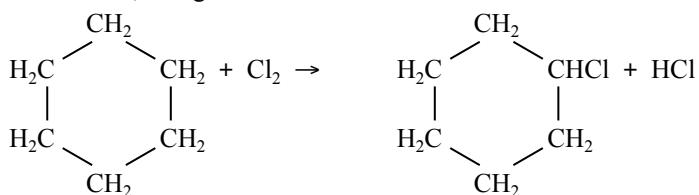
3. (a) addition, hydration



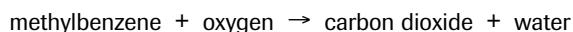
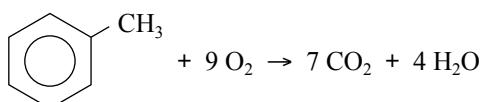
(b) addition, hydrogenation



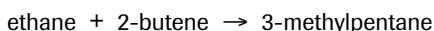
(c) substitution, halogenation



(d) combustion



(e) addition



Applying Inquiry Skills

4. (a) propene and water, in the presence of H_2SO_4 catalyst
- (b) cyclohexene and chlorine, at room temperature
- (c) 2-methyl-2-pentene and water, in the presence of H_2SO_4 catalyst
- (d) benzene and Cl_2 , in the presence of AlCl_3 catalyst

Making Connections

5. According to the balanced equation for the combustion of propane,
 $\text{CH}_3\text{CH}_2\text{CH}_3 + 5 \text{O}_2 \rightarrow 3 \text{CO}_2 + 4 \text{H}_2\text{O}$,
1 mol of propane reacts with 5 mol of oxygen to produce 3 mol of carbon dioxide and 4 mol of water vapour; that is, a total of 6 mol of gas reacts to produce a total of 7 mol of gas. The volume of gaseous product formed is greater than the volume of gaseous reactants, by a factor of 1 additional volume of product for each 6 volumes of reactants (17% increase).
6. Nonane would be the most effective solvent for removing oil stains because it is the least polar molecule, and would be most soluble with oil, which is nonpolar. The carbon–chlorine bonds and the carbon–oxygen bonds in the first two compounds are polar bonds (Cl and O are more electronegative than C), and thus, the molecules are more polar than nonane.
7. Trinitrotoluene (TNT) is a yellow, odourless solid produced by the substitution of three nitro (NO_2) groups for three hydrogen atoms in toluene ($\text{C}_6\text{H}_5\text{CH}_3$). The many nitro groups give the molecule excellent oxidizing properties, and allow it to react with the carbon atoms in the molecule to produce CO_2 and a large amount of energy. Consequently, TNT is one of the most stable of the high explosives and can be stored over long periods of time. It is the major component of dynamite. It does not attack metals, does not absorb moisture, and is practically insoluble in water.

Swedish chemist Alfred Nobel created TNT in 1867 as a safe alternative to nitroglycerin, a highly volatile substance. Nobel created a substance that would absorb the nitroglycerin into an inert, solid form (typically “diatomaceous earth”). This form of the compound requires a detonation device to explode.

TNT is used as an explosive in military shells, bombs, and grenades. It is also used for underwater blasting, blasting roads, demolishing buildings, mining, and creating tunnels.

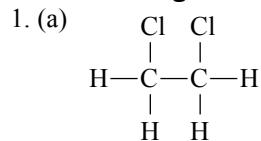
The misuse of TNT may result in environmental damage through waste waters and solid wastes caused from the manufacture of the compound, the processing and destruction of bombs and grenades, and the recycling of explosives.

1.4 ORGANIC HALIDES

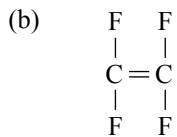
PRACTICE

(Page 33)

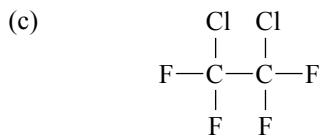
Understanding Concepts



1,2-dichloroethane



tetrafluoroethene



1,2-dichloro-1,1,2,2-tetrafluoroethane

Making Connections

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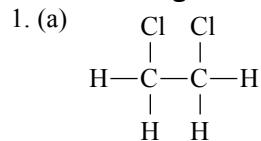
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1.4 ORGANIC HALIDES

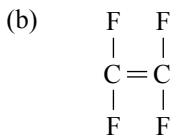
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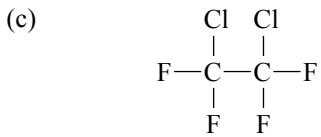
Understanding Concepts



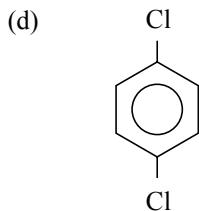
1,2-dichloroethane



tetrafluoroethene



1,2-dichloro-1,1,2,2-tetrafluoroethane



1,4-dichlorobenzene

2. (a) triiodomethane
 (b) 3-chloro-2-methylpropene
 (c) dichloromethane
 (d) 1,2,3-tribromopropane

PRACTICE

(Page 35)

Understanding Concepts

3. flow chart: Freon decomposed by UV radiation → reactive chlorine atoms → chlorine atoms react with ozone molecules in upper atmosphere → oxygen → ozone layer depleted, reducing protection from harmful UV radiation
 Reactions:
 $\text{CCl}_2\text{F}_{2(\text{g})} \rightarrow \text{CClF}_{2(\text{g})} + \text{Cl}_{(\text{g})}$ (reactive chlorine atoms)
 $\text{Cl}_{(\text{g})} + \text{O}_{3(\text{g})} \rightarrow \text{ClO}_{(\text{g})} + \text{O}_{2(\text{g})}$
 $\text{ClO}_{(\text{g})} + \text{O}_{(\text{g})} \rightarrow \text{Cl}_{(\text{g})} + \text{O}_{2(\text{g})}$
4. late 1800s: NH_3 , CH_3Cl , SO_2 used; leakage of these toxic refrigerants caused fatal accidents
 1930: Freon used; in 1970s, ozone holes in upper atmosphere discovered, attributed to reaction with Freon
 after 1970: HCFCs and HFCs studied for use as refrigerants, readily decomposed, less time to damage ozone layer
 1995: HFC-134a most commonly used refrigerant; contains no chlorine, the atom responsible for damage to ozone layer
5. (a) $\text{HCF}_2\text{Cl} + \text{OH} \rightarrow \text{CF}_2\text{Cl} + \text{H}_2\text{O}$
 $\text{HCF}_3 + \text{OH} \rightarrow \text{CF}_3 + \text{H}_2\text{O}$
 (b) The H atoms in these molecules react with OH^- ions in the air; CFCs contain no H atoms.
 (c) Since they decompose readily (because of their weaker bonds), they exist for a shorter time and thus, are less likely to cause damage.

Explore an Issue: Role Play: Can We Afford Air Conditioning?

(Page 35)

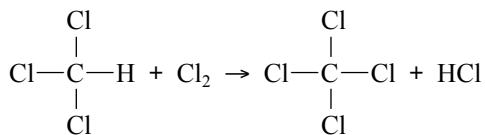
- (a) (Sample answers)
- financial cost: price of air conditioner to consumer, price of added gasoline required, cost to manufacturer, added taxes;
 - social: employment from manufacture and sale of air conditioners and cars;
 - environmental: cost of damage to air quality from coolants and added fuel consumption, raw materials used;
 - political: effect on revenue to shareholders, economy, pressure on government to manage environment, etc.
- (b) (Sample answers)
- union representative: more production means more employment for members;
 - local MP: increased employment means better economy, more votes;
 - environmentalist: air conditioning an unnecessary consumption of fossil fuel as well as possible damage by coolant to environment;
 - reporter from car magazine: debate on issue provides material for articles;
 - physician: air quality directly related to health, particularly elderly or people with respiratory problems; air conditioning offers relief in very hot temperatures;
 - shareholders in car company: give consumers what they want, responsibility is to make a profit.

PRACTICE

(Page 37)

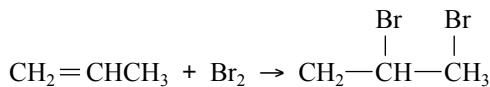
Understanding Concepts

6. (a) substitution



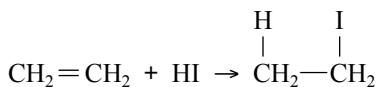
trichloromethane + chlorine \rightarrow tetrachloromethane + hydrogen chloride

(b) addition



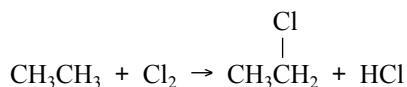
propene + bromine \rightarrow 1,2-dibromopropane

(c) addition



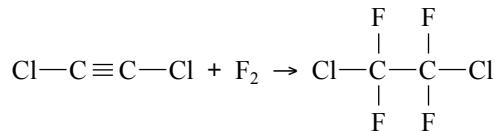
ethylene + hydrogen iodide \rightarrow iodoethane

(d) substitution



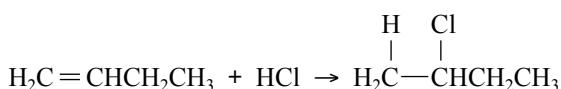
ethane + chlorine \rightarrow chloroethane + hydrogen chloride

(e) addition



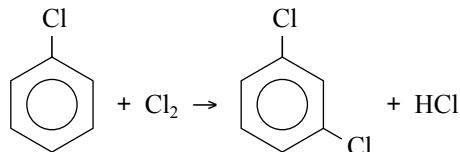
dichloroethyne + fluorine \rightarrow 1,2-dichloro-1,1,2,2-tetrafluoroethane

(f) addition



1-butene + hydrogen chloride \rightarrow 2-chlorobutane

(g) substitution



chlorobenzene + chlorine \rightarrow 1,3-dichlorobenzene + hydrogen chloride

Extension

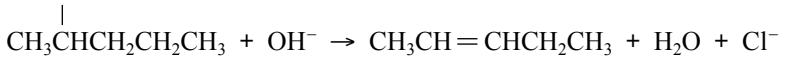
7. (Sample answer) DDT (dichloro, diphenyl trichloroethane) is a chlorinated hydrocarbon, a candidate for bioaccumulation. DDT has a half-life of 15 years, which means that it takes 15 years to reduce the amount of DDT by half. Since DDT has low solubility in water, it is not readily excreted by organisms that ingest it; it is thus stored in the fat tissues. The concentration of DDT is increased as these organisms are eaten by other organisms up the food chain.

SECTION 1.4 QUESTIONS

(Page 37)

Understanding Concepts

1.

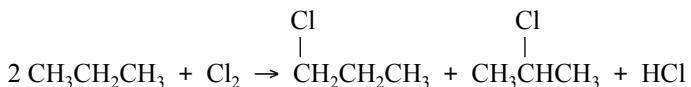


2-chloropentane + hydroxide ion \rightarrow 2-pentene + water + chloride ion

1-pentene, $\text{CH}_2=\text{CHCH}_2\text{CH}_2\text{CH}_3$, will also be formed.

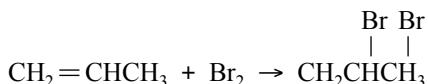
Conditions: presence of a base, OH^-

2. (a) substitution



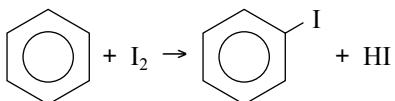
propane + chlorine \rightarrow 1-chloropropane + 2-chloropropane + hydrogen chloride

(b) addition



propene + bromine \rightarrow 1,2-dibromopropane

(c) substitution



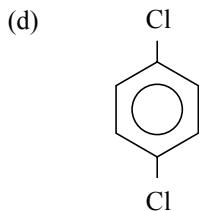
benzene + iodine \rightarrow iodobenzene + hydrogen iodide

Applying Inquiry Skills

3. (a) Begin with ethyne and Cl_2 , in a 1:1 ratio in amount (in moles); the addition reaction produces 1,2-dichloroethene. Then the product is reacted with HCl gas; the addition reaction produces 1,1,2-trichloroethane.
(b) A mixture of products may be formed, as a result of 2 molecules of Cl_2 being added to one molecule of ethyne, producing 1,1,2,2-tetrachloroethane. The components of such a mixture are difficult to separate.

Making Connections

4. (Answers will vary, but should include evidence of research into the health, safety, or environmental problems of the selected topic. References should be cited.)
5. Mustard gas is an alkyl halide (formula: $\text{ClCH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{Cl}$) that, when inhaled, reacts with water in the lungs to produce hydrochloric acid and other intermediate products, many of which damage lung and skin tissue.
Mustard gas causes mustard-coloured blisters, burns to mucous membranes, burning and swelling of the eyes, bronchitis, choking, and high levels can lead to death. During World War I, mustard gas could penetrate the materials used for clothing and masks. In more recent years, urethane has been discovered and used to resist exposure to mustard gas at a wide range of temperatures.
6. (a) HCFCs and HFCs are alternatives to CFCs that are still in use. They appear to be less damaging to the ozone layer than CFCs (although the “hole” in the ozone layer is still growing). However, HCFCs and HFCs may act as greenhouse gases, possibly leading to global warming.
(b) (Answers will vary, but should include a presentation of a product that will be sprayed under pressure, and a marketing strategy.)



1,4-dichlorobenzene

2. (a) triiodomethane
 (b) 3-chloro-2-methylpropene
 (c) dichloromethane
 (d) 1,2,3-tribromopropane

PRACTICE

(Page 35)

Understanding Concepts

3. flow chart: Freon decomposed by UV radiation → reactive chlorine atoms → chlorine atoms react with ozone molecules in upper atmosphere → oxygen → ozone layer depleted, reducing protection from harmful UV radiation
 Reactions:
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 $\text{Cl}_{(\text{g})} + \text{O}_{3(\text{g})} \rightarrow \text{ClO}_{(\text{g})} + \text{O}_{2(\text{g})}$
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 1930: Freon used; in 1970s, ozone holes in upper atmosphere discovered, attributed to reaction with Freon
 after 1970: HCFCs and HFCs studied for use as refrigerants, readily decomposed, less time to damage ozone layer
 1995: HFC-134a most commonly used refrigerant; contains no chlorine, the atom responsible for damage to ozone layer
5. (a) $\text{HCF}_2\text{Cl} + \text{OH} \rightarrow \text{CF}_2\text{Cl} + \text{H}_2\text{O}$
 $\text{HCF}_3 + \text{OH} \rightarrow \text{CF}_3 + \text{H}_2\text{O}$
 (b) The H atoms in these molecules react with OH^- ions in the air; CFCs contain no H atoms.
 (c) Since they decompose readily (because of their weaker bonds), they exist for a shorter time and thus, are less likely to cause damage.

Explore an Issue: Role Play: Can We Afford Air Conditioning?

(Page 35)

- (a) (Sample answers)
- financial cost: price of air conditioner to consumer, price of added gasoline required, cost to manufacturer, added taxes;
 - social: employment from manufacture and sale of air conditioners and cars;
 - environmental: cost of damage to air quality from coolants and added fuel consumption, raw materials used;
 - political: effect on revenue to shareholders, economy, pressure on government to manage environment, etc.
- (b) (Sample answers)
- union representative: more production means more employment for members;
 - local MP: increased employment means better economy, more votes;
 - environmentalist: air conditioning an unnecessary consumption of fossil fuel as well as possible damage by coolant to environment;
 - reporter from car magazine: debate on issue provides material for articles;
 - physician: air quality directly related to health, particularly elderly or people with respiratory problems; air conditioning offers relief in very hot temperatures;
 - shareholders in car company: give consumers what they want, responsibility is to make a profit.

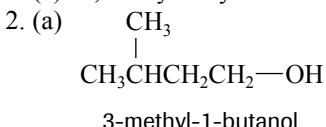
1.5 ALCOHOLS AND ETHERS

PRACTICE

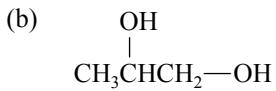
(Page 41)

Understanding Concepts

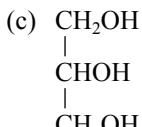
1. (a) 2-butanol
(b) 1,4-pentanediol
(c) 1,3-dihydroxybenzene



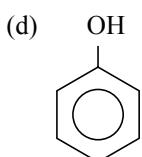
3-methyl-1-butanol



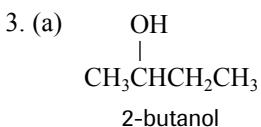
1,2-propanediol



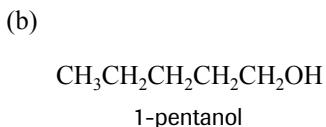
glycerol



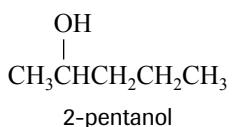
phenol



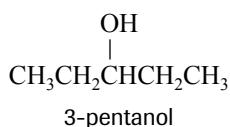
2-butanol



1-pentanol



2-pentanol



3-pentanol

PRACTICE

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Understanding Concepts

A longer carbon chain allows more intermolecular attractions such as van der Waals forces; thus, octane has a higher boiling point than does butane. The alcohols generally have higher boiling points than the alkanes because of the presence of the hydroxyl groups. Octanol has a higher boiling point than does butanol, also because of its longer carbon chain.

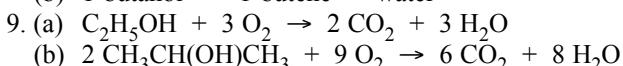
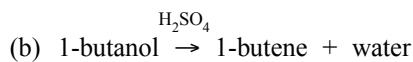
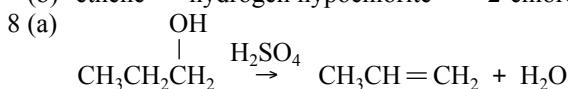
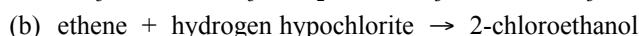
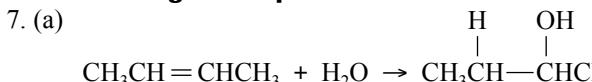
Making Connections

6. Each molecule of glycerol contains three hydroxyl groups which can hydrogen bond with water, interfering with the attractions between water molecules, and thus interfering with the freezing of water. When water in tissues does not freeze, there is less damage to the tissues.

PRACTICE

(Page 44)

Understanding Concepts



PRACTICE

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Making Connections

10. (a) Fuel cell technology – in the direct methanol fuel cell chamber, a catalyst-coated membrane separates two chambers: a negatively charged chamber containing methanol/water solution, and a positively charged chamber containing air. Hydrogen ions pass through the membrane, creating an electric current.
 (b) Advantages: cleaner burning, CO_2 emissions half those of burning gasoline; methanol is readily broken down by microorganisms; methanol can be produced from renewable sources such as wood and sewage.
 Disadvantages: less energy per litre; higher fuel cost per kilometre; methanol refuelling stations not readily available.
 (c) For: environmental benefits; renewable resource.
 Against: cost to manufacturers and consumers; low-energy fuel; building system of refuelling stations.

PRACTICE

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Making Connections

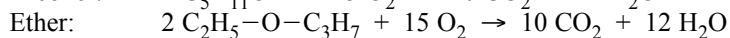
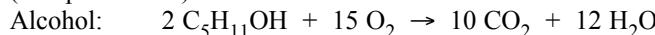
11. (a) methoxyp propane
 (b) ethoxypropane

PRACTICE

(Page 48)

Understanding Concepts

12. (Sample answer)



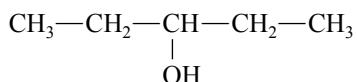
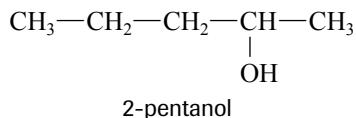
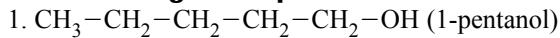
13. (a) $\text{CH}_3-\text{CH}_2-\text{O}-\text{CH}_2-\text{CH}_3$ and $\text{CH}_3-\text{O}-\text{CH}_2-\text{CH}_2-\text{CH}_3$
 Yes, they are structural isomers.



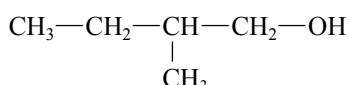
SECTION 1.5 QUESTIONS

(Page 48)

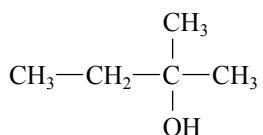
Understanding Concepts



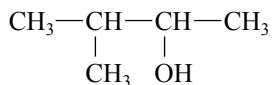
3-pentanol



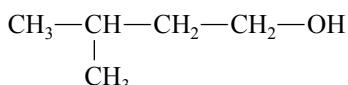
2-methyl-1-butanol



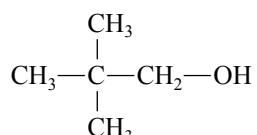
2-methyl-2-butanol



3-methyl-2-butanol



3-methyl-1-butanol

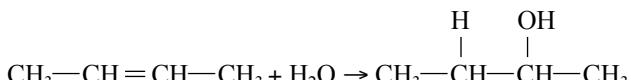


2,2-dimethyl-1-propanol

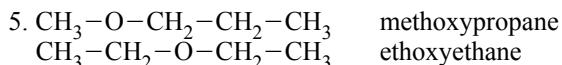
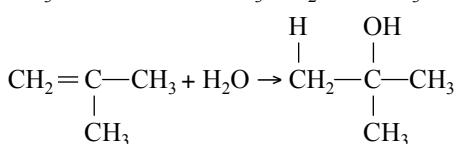
2. Propane is a hydrocarbon, nonpolar, with weak intermolecular forces; thus, it has a low boiling point and is a gas at room temperature. 2-propanol is an alcohol, with a polar hydroxyl group, with strong intermolecular hydrogen bonds; thus, it has a higher boiling point than propane and is a liquid at room temperature.

3. $\text{CH}_2=\text{CH—CH}_2\text{—CH}_2\text{—CH}_2\text{—CH}_3$ 1-hexene
 $\text{CH}_3\text{—CH=CH—CH}_2\text{—CH}_2\text{—CH}_3$ 2-hexene

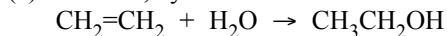
4. (a)



(b)



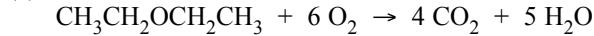
6. (a) addition, hydration



(b) elimination, dehydration



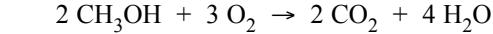
(c) combustion



(d) addition



(e) combustion



7. (a) glycerol: Glycerol has three hydroxyl groups per molecule, ethylene glycol has two. Glycerol can form more hydrogen bonds and has a higher boiling point.
 (b) water: Water has hydroxyl groups which can hydrogen bond; methoxymethane has no hydroxyl groups. Water has a higher boiling point.
 (c) propanol: Both alcohols have hydroxyl groups but propanol has a longer carbon chain and thus has greater van der Waals intermolecular forces.
 (d) propanol: Propanol has hydroxyl groups capable of hydrogen bonding while methoxyethane does not. Propanol has a higher boiling point.

Applying Inquiry Skills

8. Experimental Design

Diethylene glycol has a boiling point (244°C) higher than that of ethanol (78°C) and water (100°C). Use condensation equipment to separate fractions, removing the fraction corresponding to the boiling point of ethylene glycol.

Procedure

- Set up condensation equipment (e.g., round-bottomed flask with thermometer, retort equipment, water-cooled condenser, collection flask).
- Gently heat wine until alcohol and water evaporate and collect condensed fractions.
- When temperature approaches 244°C, change collection flask and collect fraction above 244°C (ethylene glycol) and discard.

Safety Precautions

Do not use open flame. Work in a well-ventilated area. Wear eye and face protection and an apron.

Making Connections

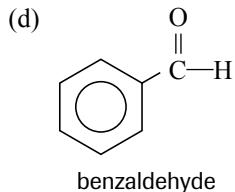
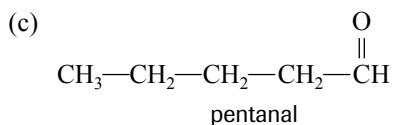
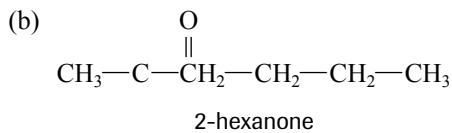
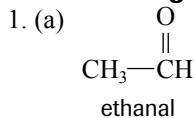
9. (a) $2 \text{ CH}_3\text{OH} + 3 \text{ O}_2 \rightarrow 2 \text{ CO}_2 + 4 \text{ H}_2\text{O}$
 $\text{CH}_3\text{CH}_2\text{OH} + 3 \text{ O}_2 \rightarrow 2 \text{ CO}_2 + 3 \text{ H}_2\text{O}$
- (b) Ethanol has a longer nonpolar carbon chain which makes it a better solvent for the nonpolar hydrocarbons in gasoline.
- (c) Environmental benefits to burning alcohols as fuel: clean burning (lower carbon monoxide emissions than regular gasoline); low in reactivity and high in oxygen content, making it an effective tool in reducing ozone pollution; safe replacement for toxic octane enhancers in gasoline such as benzene, toluene, and xylene.
- (d) Methanol and ethanol, having both polar hydroxyl groups and nonpolar carbon chains, are soluble in both water and in gasoline; thus, water droplets are dissolved in the alcohol and do not form ice, which blocks gasoline flow.

1.6 ALDEHYDES AND KETONES

PRACTICE

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Understanding Concepts



2. (a) 2-heptanone, 3-heptanone, 4-heptanone
(b) heptanal
3. (a) pentanal
(b) 3-hexanone
(c) methanal

PRACTICE

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Understanding Concepts

4. (a) propanone
(b) methanal
(c) ethanal

5. In order of increasing boiling points: propane (b); 1-propanone (a); 1-propanol (c). This order is predicted because (a) contains a carbonyl group (with a polar double bond), making it more polar than (b), which gives 1-propanone a higher boiling point than propane. 1-propanol contains a hydroxyl group, which can hydrogen bond with other molecules, giving (c) a higher boiling point than (a) or (b).

Try This Activity: How Many Can You Build?

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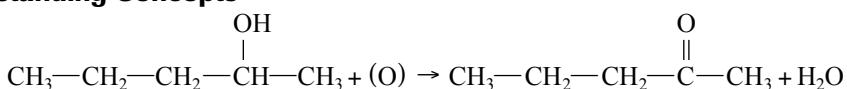
- (a) ethanol (hydroxyl group), methoxymethane (oxygen atom bonded to two alkyl groups, an ether)
(b) 1-hydroxy-1-propene, 3-hydroxy-1-propene, propanal, propanone
(c) The two compounds in (a) are structural isomers; the four compounds in (b) are structural isomers; 1-hydroxy-1-propene has *cis*- and *trans*- isomers.

PRACTICE

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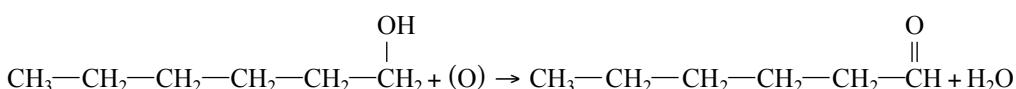
Understanding Concepts

6. (a)



2-pentanol + (controlled oxidation) \rightarrow 2-pentanone + water

(b)



1-hexanol + (controlled oxidation) \rightarrow hexanal + water

7. In increasing order of solubility: butane (c), 2-butanone (a), 1-butanol (b). Butane is a nonpolar hydrocarbon and is less soluble in water than the ketone (a) and the alcohol (b). The ketone (a) has a polar carbonyl group, making it more soluble in water than (c), but it is less soluble than the alcohol (b), which has a hydroxyl group that allows it to hydrogen bond.

8. Generally, the term “oxidation” means a reaction in which a substance gains oxygen atoms or loses hydrogen atoms. Further definitions of oxidation also include reactions that do not involve oxygen or hydrogen atoms.

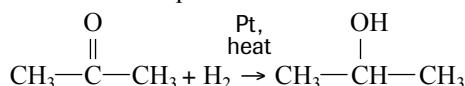
Applying Inquiry Skills

9. Experimental Design

Acetone (propanone) is hydrogenated, at high temperatures and in the presence of a catalyst, to produce 2-propanol.

Procedure

1. Set up equipment for heating acetone and condensing the product.
2. Insert a catalyst (e.g., Pt) where the hot acetone will circulate.
3. Heat the acetone carefully.
4. Condense and collect the product.



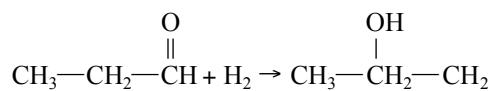
propanone (acetone) + hydrogen \rightarrow 2-propanol (*i*-propyl alcohol)

SECTION 1.6 QUESTIONS

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Understanding Concepts

1. (Sample answer)



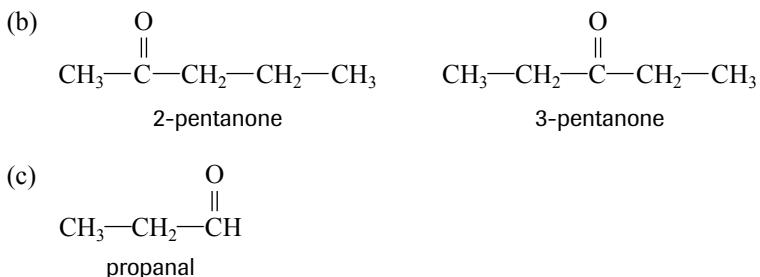
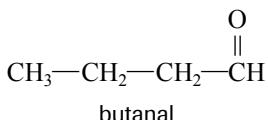
propanal + hydrogen \rightarrow 1-propanol

2. The carbonyl group in butanal must be at the end of the 4-carbon chain; only one structure is possible. The carbonyl group in butanone must be either carbon-2 or carbon-3, not at an end carbon atom; either position results in the same structure.

3. (a) $\text{CH}_3\text{---CH}_2\text{---C(=O)}\text{---H}$

propanal

- (b) O=C=O and H—O—H
carbon dioxide and water
4. (a) The ether ethoxypropane will evaporate at a lower temperature because it is less polar than the pentanal which contains a polar carbonyl group.
 (b) The ether ethoxypropane has higher solubility in nonpolar solvents because it does not contain any carbonyl groups and is less polar than the pentanal.
 (c) The pentanal can undergo an addition reaction with hydrogen at its carbonyl group, but the ether cannot.
5. (a) (Sample answer)



Applying Inquiry Skills

6. Experimental Design

The tertiary alcohol does not undergo controlled oxidation to aldehydes or ketones; each alcohol is allowed to react with sodium dichromate and the alcohol that does not cause a colour change in the dichromate solution is the tertiary alcohol. (Primary alcohols are oxidized to aldehydes, and secondary alcohols are oxidized to ketones.)

Procedure

- Set up three separate test tubes containing each of the alcohols.
- Add the sodium dichromate solution, in the presence of H_2SO_4 .

Safety Precautions:

Do not use open flames. Sulfuric acid is corrosive; avoid contact with skin or clothing. Wear eye protection and a lab apron.

7. Experimental Design

1-butene is hydrolyzed with water, in the presence of acid, to produce 2-butanol. 2-butanol is then made to undergo controlled oxidation (e.g., in KMnO_4) to produce butanone.

Procedure

- Place 1-butene in a container and add sulfuric acid.
- Add $\text{KMnO}_{4(\text{aq})}$ to the mixture.

Safety Precautions:

Do not use open flames. Sulfuric acid is corrosive; avoid contact with skin or clothing. Wear eye protection and a lab apron. Work in a well-ventilated area. Dispose of organic materials in designated containers for collection.

Making Connections

8. Examples include acetone, wood alcohol, rubbing alcohol, formaldehyde, natural gas, barbecue gas, lighter fluid, and glycerin.
9. (a) methanal
 (b) Formaldehyde is a flammable, poisonous, colourless gas with a suffocating odour. It readily polymerizes into paraformaldehyde, a white solid that can be formed into candles and used for fumigating rooms. Formalin, the preservative used in biological materials, is a solution of formaldehyde in water, with a small amount of methanol added.

Other fluids used as preservatives include alcohol (the standard is 70–75% ethanol, or 40–50% 2-propanol); Zenker's fluid (containing mercury(II) chloride, glacial acetic acid, potassium dichromate, and sodium sulfate in water).

10. (a) Acetone contains a carbonyl group that is polar and makes it soluble in aqueous solutions.

(b) $c = 20 \text{ mg}/100 \text{ mL}$

$$c = 200 \text{ mg/L}$$

$$M_{\text{CH}_3\text{C(O)CH}_3} = 58.09 \text{ g/mol}$$

$$n = \frac{200 \text{ mg}}{58.09 \text{ g/mol}}$$

$$n = 0.003 \text{ mol}$$

$$c = 0.003 \text{ mol/L}$$

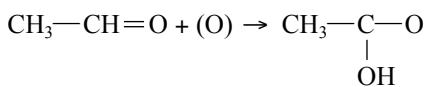
- (c) People who are severely starved or dieting do not have a ready supply of sugars in their bodies and are breaking down fats for energy. The acetone produced in the process is exhaled with the breath.

- (d) Diabetic ketoacidosis (DKA) is a condition that occurs when blood sugar levels get too high. The signs of DKA include nausea and vomiting (which can lead to dehydration), stomach pain, and deep and rapid breathing. Other symptoms include a flushed face, dry skin and mouth, a fruity odour to the breath, a rapid and weak pulse, and low blood pressure. DKA may be avoided by taking the correct amount of insulin, or exercise. In emergency situations, the person must be given fluids and insulin right away, or ketoacidosis can lead to coma and even death.

1.7 CARBOXYLIC ACIDS AND ESTERS

Try This Activity: Making Flavoured Vinegar

(Page 58)



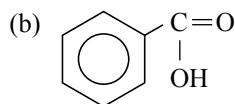
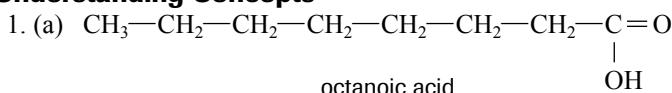
- (b) To test for acid, use pH meter or pH paper; or mix with baking soda and look for bubbles of CO_2 formed.

- (c) Heating the jars of vinegar has the effect of stopping further reaction by the yeast; the high temperature kills the yeast.

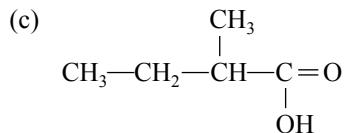
PRACTICE

(Page 60)

Understanding Concepts



benzoic acid



2-methylbutanoic acid

2. (a) methanoic (formic) acid
(b) 3-ethylpentanoic acid
(c) 2,3-diethylhexanoic acid

10. (a) Acetone contains a carbonyl group that is polar and makes it soluble in aqueous solutions.

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$$c = 200 \text{ mg/L}$$

$$M_{\text{CH}_3\text{C(O)CH}_3} = 58.09 \text{ g/mol}$$

$$n = \frac{200 \text{ mg}}{58.09 \text{ g/mol}}$$

$$n = 0.003 \text{ mol}$$

$$c = 0.003 \text{ mol/L}$$

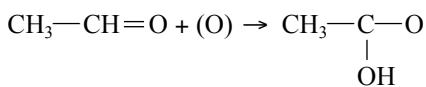
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1.7 CARBOXYLIC ACIDS AND ESTERS

Try This Activity: Making Flavoured Vinegar

(Page 58)



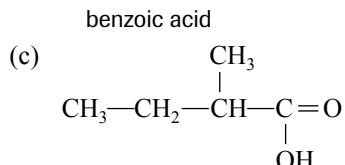
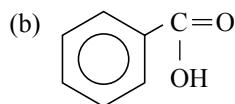
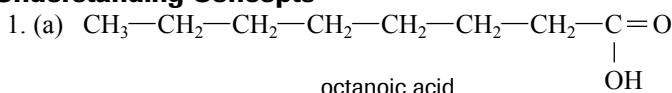
- (b) To test for acid, use pH meter or pH paper; or mix with baking soda and look for bubbles of CO_2 formed.

- (c) Heating the jars of vinegar has the effect of stopping further reaction by the yeast; the high temperature kills the yeast.

PRACTICE

(Page 60)

Understanding Concepts

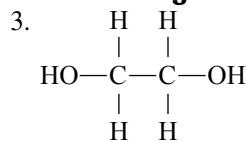


2. (a) methanoic (formic) acid
(b) 3-ethylpentanoic acid
(c) 2,3-diethylhexanoic acid

PRACTICE

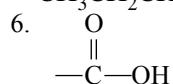
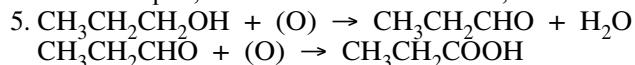
(Page 63)

Understanding Concepts



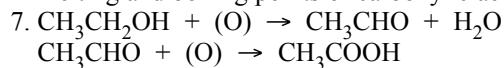
1,2-ethanediol

4. The gas (A) has the lowest boiling point and must be the alkane, the least polar molecule. The liquid (B) has the next highest boiling point and must be the alcohol, which has a hydroxyl group. The solid (C) has a higher melting point than the liquid, and must be the acid which, with its carboxyl group, is the most polar of the three compounds.



carboxyl group

The hydroxyl group in this functional group is polar and can hydrogen bond, making the molecule soluble in water. The carbonyl group is also polar and, with the hydroxyl group, increases intermolecular attractions and thus raises the melting and boiling points of carboxylic acids.

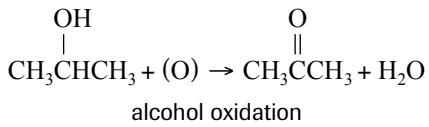


Applying Inquiry Skills

8. Melting and boiling points: the aldehyde and the ketone are more likely liquid at room temperature and the carboxylic acid solid; the carboxyl group in the acid is polar and also can hydrogen bond while the aldehyde and ketone do not contain the hydroxyl group. Litmus and pH test: Carboxylic acids turn litmus red, an acidic pH. Controlled oxidation: The aldehyde can be further oxidized, changing the colour of an oxidizing agent such as sodium dichromate or potassium permanganate, the ketone and the acid will not.

Making Connections

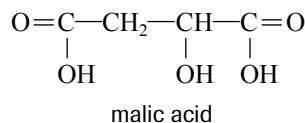
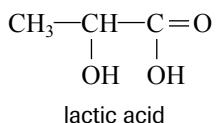
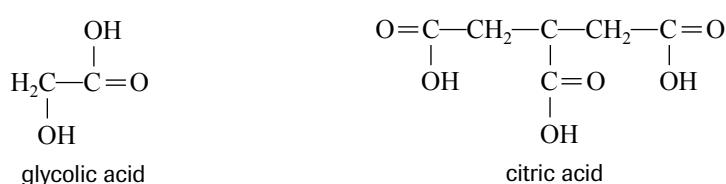
9. Examples: 2-propanol (rubbing alcohol), ethylene glycol (antifreeze). These do not turn sour. For example,



Ketones are not further oxidized by (O).

10. (a) “Alpha hydroxy” is an incomplete name; a parent molecule name is needed, e.g., alpha hydroxy butanoic acid.

(b)



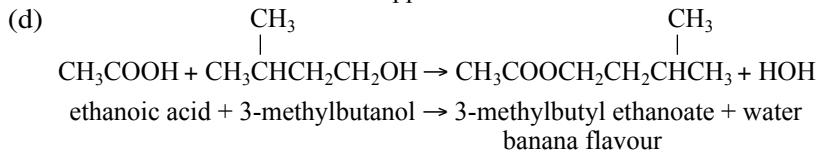
- (c) These acids have the polar carboxyl group and hydroxyl group; they also have a nonpolar hydrocarbon chain.
(d) With the outer layer of the skin removed, the new skin layer is more exposed to the harmful UV rays of the Sun.

PRACTICE

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Understanding Concepts

11. (a) $\text{HCOOH} + \text{CH}_3\text{CH}_2\text{OH} \rightarrow \text{HCOOCH}_2\text{CH}_3 + \text{HOH}$
methanoic acid + ethanol → ethyl methanoate + water
rum flavour
- (b) $\text{C}_6\text{H}_5\text{COOH} + \text{CH}_3\text{CH}_2\text{OH} \rightarrow \text{C}_6\text{H}_5\text{COOCH}_2\text{CH}_3 + \text{HOH}$
benzoic acid + ethanol → ethyl benzoate + water
cherry flavour
- (c) $\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH} + \text{CH}_3\text{OH} \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{COOCH}_3 + \text{HOH}$
butanoic acid + methanol → methyl butanoate + water
apple flavour



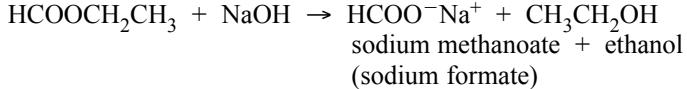
12. (a) ethyl propanoate (from propanoic acid and ethanol)
(b) methyl butanoate (from butanoic acid and methanol)
(c) butyl methanoate (from methanoic acid and 1-butanol)
(d) propyl ethanoate (from ethanoic acid and 1-propanol)

PRACTICE

(Page 67)

Understanding Concepts

13. An ester contains an —OR group in place of the —OH in the carboxylic acid. The OH group is responsible for the acidic properties of carboxylic acids, and also for hydrogen bonding; thus, esters have lower melting and boiling points, are less soluble in water, and are less acidic.
14. The experimental conditions include the presence of an acid or a base, and heat.



Applying Inquiry Skills

15. Experimental Design

Heat ethanol and acetic acid, in the presence of concentrated sulfuric acid.

Procedure

- In a test tube, mix approximately equal amounts of ethanol and acetic acid.
- Under the fume hood, add a few drops of concentrated sulfuric acid. Heat test tube and contents in hot-water bath.

Safety Precautions:

Concentrated sulfuric acid is highly corrosive. Avoid contact with skin and clothing. Wear eye protection and a lab apron. Work under a fume hood and keep test tubes in hot-water bath away from people. Ethanol is flammable, so there should be no open flames in the vicinity. Dispose of materials in designated labelled containers.

Making Connections

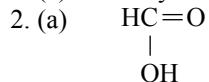
16. $\text{HNO}_3 + \text{NaOH} \rightarrow \text{NaNO}_3 + \text{H}_2\text{O}$
nitric acid + sodium hydroxide → sodium nitrate + water
- $$\text{CH}_3\text{COOH} + \text{CH}_3\text{CH}_2\text{CH}_2\text{OH} \rightarrow \text{CH}_3\text{COOCH}_2\text{CH}_2\text{CH}_3 + \text{H}_2\text{O}$$
- ethanoic acid + propanol → propyl ethanoate + water

SECTION 1.7 QUESTIONS

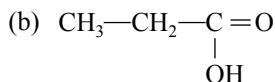
(Page 68)

Understanding Concepts

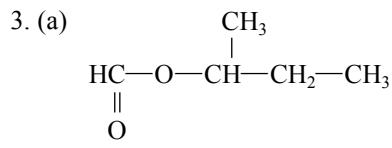
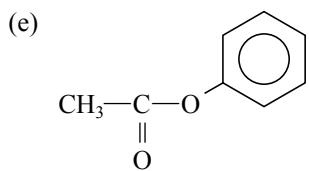
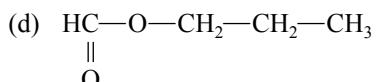
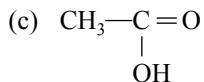
1. (a) propyl propanoate
(b) 2-methylpentyl propanoate
(c) 2-bromopropanoic acid
(d) ethanoic acid
(e) carboxybenzene or phenylmethanoic acid (commonly called benzoic acid)



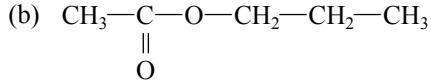
methanoic acid



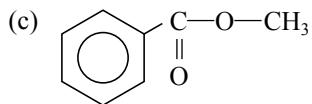
propanoic acid



1-methylpropyl methanoate



propyl ethanoate



methyl benzoate

4. (a) propanoic acid and 1-pentanol
(b) 2-ethylpentanoic acid and propanol
(c) benzoic acid and methanol

Applying Inquiry Skills

5. Heat the ester with a concentrated NaOH solution. The reaction is complete when the insoluble ester changes to soluble products.
6. Esters are less soluble than acids or alcohols in water and can be separated by pouring the reaction mixture into cold water; the ester forms an insoluble layer on top of the water.

Making Connections

7. Examples of controlled oxidation reactions: cellular respiration; rusting of iron; tarnishing of silver; souring of wine.
Controlled oxidations are “preferred” when temperature must be kept low, and rate of oxidation controlled, e.g., molecules of food are “burned” to release energy in the cell, at body temperatures.

Uncontrolled oxidations are ideal when we want energy released quickly, raising the surrounding temperature, e.g., burning of wood as fuel.

8. (Answers may include the following occupations: chemist in perfume industry, wine industry, pharmaceutical industry, or cosmetics industry; nutritionist; forensic scientist. Sample answer)

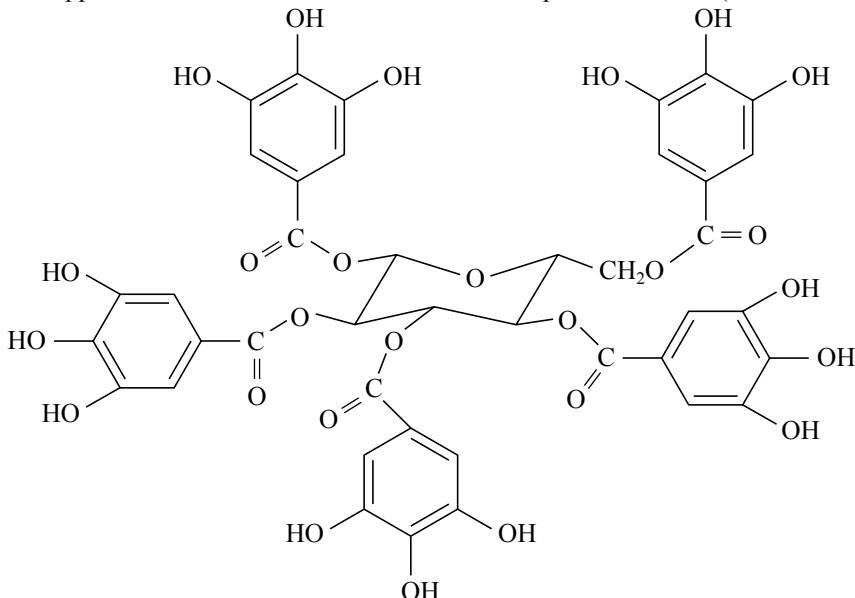
Chemist in wine industry

Strengths and qualities needed – strong scientific background, strong technical analytical skills, research skills, good teamwork skills

Academic training – undergraduate or graduate degree in science, particularly in chemistry, biology, or biochemistry
Degree in Oenology and Viticulture available at Brock University (See weblinks.)

Job opportunities – wineries in Ontario and other parts of Canada (See weblinks.)

9.



Animal hides decompose quickly unless they are cured to remove the water from the skin. The hide is first soaked in water to remove water-soluble substances and hair is removed by soaking in a mixture of lime and water, followed by an enzyme mixture. The hair and any remaining tissue is removed by machine and the hide is washed and treated with tannic acid. The tannic acid displaces water from the spaces between the hide’s protein fibres, allowing the fibres to cement together to form a strong water-resistant leather.

1.8 AMINES AND AMIDES

PRACTICE

(Page 72)

Understanding Concepts

1. putrescine: 1,4-diaminobutane; cadaverine: 1,5-diaminopentane
2. (a) diethylamine, *N*-ethylaminoethane; 2° amine
(b) trimethylamine, *N,N*-diethylaminoethane; 3° amine
(c) *i*-propylamine, 2-aminopropane; 1° amine
(d) *n*-hexylamine, 1-aminohexane; 1° amine
(e) 2-bromo-6-*N*-methylaminohexane; *N*-methyl-*N*-5-bromohexylamine; 2° amine; 2° amine

Making Connections

7. Examples of controlled oxidation reactions: cellular respiration; rusting of iron; tarnishing of silver; souring of wine.
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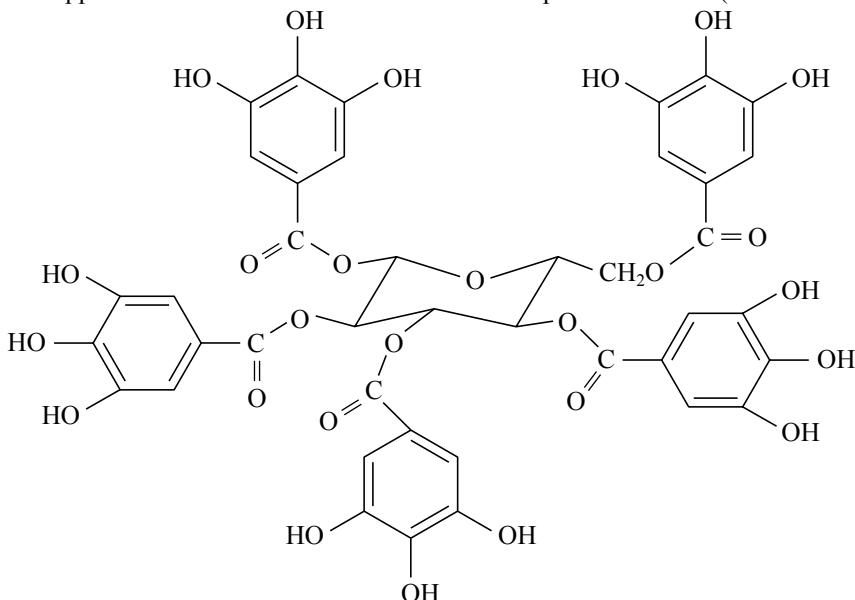
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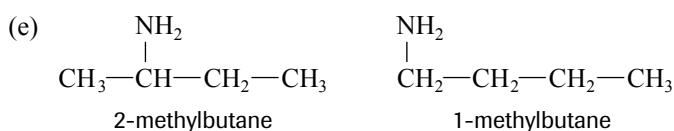
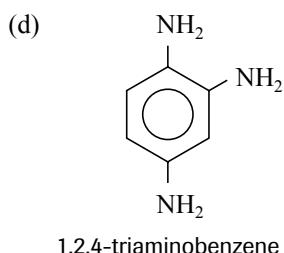
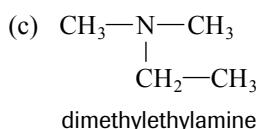
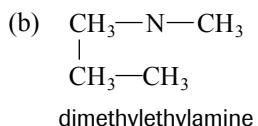
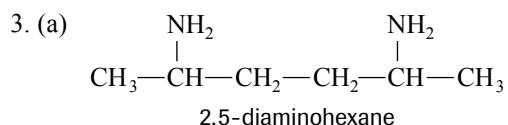
1.8 AMINES AND AMIDES

PRACTICE

(Page 72)

Understanding Concepts

1. putrescine: 1,4-diaminobutane; cadaverine: 1,5-diaminopentane
2. (a) diethylamine, *N*-ethylaminoethane; 2° amine
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(c) *i*-propylamine, 2-aminopropane; 1° amine
(d) *n*-hexylamine, 1-aminohexane; 1° amine
(e) 2-bromo-6-*N*-methylaminohexane; *N*-methyl-*N*-5-bromohexylamine; 2° amine; 2° amine

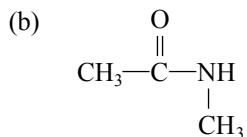
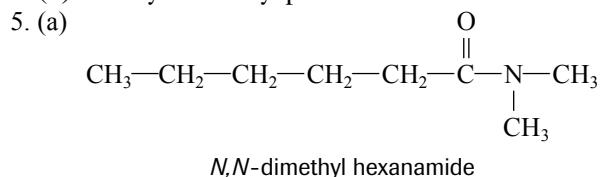


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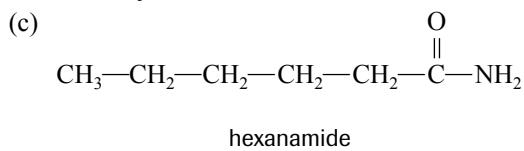
(Page 76)

Understanding Concepts

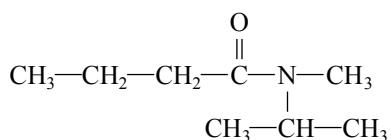
4. (a) *N*-ethyl butanamide
 (b) *N*-methyl propanamide
 (c) *N,N*-dimethyl propanamide
 (d) *N*-ethyl-*N*-methyl pentanamide



N-methyl acetamide



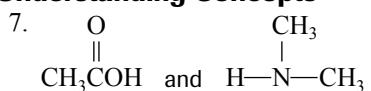
(d)

*N*-isopropyl-*N*-methyl-butanamide

6. (a) amine; propylamine
 (b) amine; ethylmethylamine
 (c) amide; ethanamide

PRACTICE

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Understanding Concepts

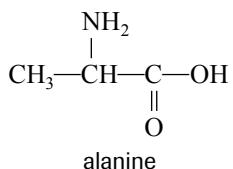
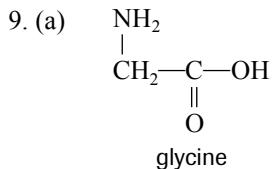
ethanoic acid and dimethylamine

PRACTICE

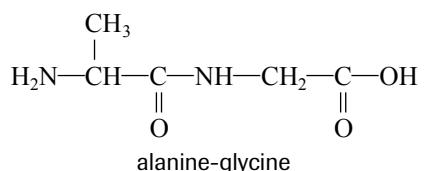
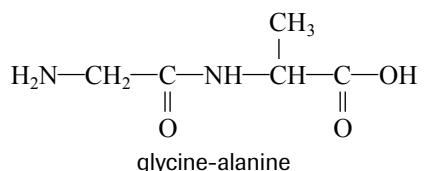
(Page 78)

Understanding Concepts

8. An OH is removed from the carboxylic acid and an H from the amide, to produce a small molecule (H_2O).

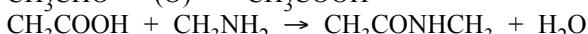
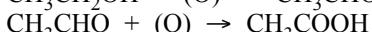
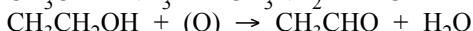
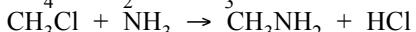
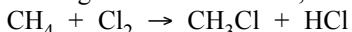


(b)



10. Amines contain —NH groups which are less polar than —OH groups in alcohols, and are less capable of hydrogen bonding than are —OH groups.

11. Starting reactants: methane, chlorine, ammonia, an oxidizing agent



SECTION 1.8 QUESTIONS

(Page 78)

Understanding Concepts

1.



2. (a) alcohol, amine; the OH group in alcohols is more polar than the NH group in amines, making them less soluble in nonpolar solvents than are amines.

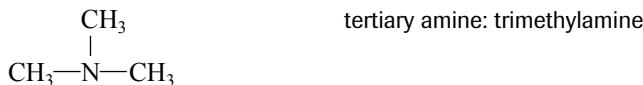
- (b) primary amine, tertiary amine; tertiary amines do not contain the polar NH groups that are present in primary amines. The more polar primary amine is less soluble in nonpolar solvents than is the tertiary amine. However, if the nonpolar group on the primary amine is large, the increased attraction between nonpolar groups may make it more soluble in the nonpolar solvents.

- (c) tertiary amine, hydrocarbon; bonds between N and C are more polar than bonds between H and C, and therefore, tertiary amines are slightly more polar than hydrocarbons, making them less soluble in nonpolar solvents. However, if the nonpolar groups on the tertiary amine are large, the increased attraction between nonpolar groups may make it more soluble in the nonpolar solvents.

- (d) low molecular mass, high molecular mass; both are primary amines with the same number of NH bonds. The higher molecular mass amine has a larger nonpolar hydrocarbon component and is therefore more soluble in nonpolar solvents.

3. $\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{NH}_2$ primary amine: *n*-propylamine

$\text{CH}_3-\text{CH}_2-\text{NH}-\text{CH}_3$ secondary amine: ethylmethylamine

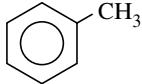


4. (a) $\text{HCOOH} + \text{NH}_3 \rightarrow \text{HCOONH}_2$
(b) $\text{CH}_3\text{CH}_2\text{COOH} + \text{NH}_3 \rightarrow \text{CH}_3\text{CH}_2\text{COONH}_2$

5. (a) propanamide
(b) dimethylpropylamine
(c) *N,N*-diethyl propanamide
(d) 4-amino-2-chloroheptane
(e) 4,6-diamino-1-heptene
(f) 2-aminoethanoic acid

6. (a)

Table 1 Families of Organic Compounds

Family name	General formula	Example	
alkanes	$\begin{array}{c} & \\ — C — & C — \\ & \end{array}$	propane	$\text{CH}_3 — \text{CH}_2 — \text{CH}_3$
alkenes	$\begin{array}{c} & \\ — C & = C — \\ & \end{array}$	propene (propylene)	$\text{CH}_2 = \text{CH} — \text{CH}_3$
alkynes	$— C \equiv C —$	propyne	$\text{CH} \equiv \text{C} — \text{CH}_3$
aromatics		methyl benzene (phenyl methane, toluene)	
organic halides	$\text{R} — \text{X}$	chloropropane	$\text{CH}_3 — \text{CH}_2 — \text{CH}_2 — \text{Cl}$
alcohols	$\text{R} — \text{OH}$	propanol	$\text{CH}_3 — \text{CH}_2 — \text{CH}_2 — \text{OH}$
ethers	$\text{R} — \text{O} — \text{R}'$	methoxyethane (ethyl methyl ether)	$\text{CH}_3 — \text{O} — \text{CH}_2 — \text{CH}_3$
aldehydes	$\begin{array}{c} \text{O} \\ \\ \text{R}[\text{H}] — \text{C} — \text{H} \end{array}$	propanal	$\begin{array}{c} \text{O} \\ \\ \text{CH}_3 — \text{CH}_2 — \text{C} — \text{H} \end{array}$
ketones	$\begin{array}{c} \text{O} \\ \\ \text{R} — \text{C} — \text{R}' \end{array}$	propanone (acetone)	$\begin{array}{c} \text{O} \\ \\ \text{CH}_3 — \text{C} — \text{CH}_3 \end{array}$
carboxylic acids	$\begin{array}{c} \text{O} \\ \\ \text{R}[\text{H}] — \text{C} — \text{OH} \end{array}$	propanoic acid	$\begin{array}{c} \text{O} \\ \\ \text{CH}_3 — \text{CH}_2 — \text{C} — \text{OH} \end{array}$
esters	$\begin{array}{c} \text{O} \\ \\ \text{R}[\text{H}] — \text{C} — \text{O} — \text{R}' \end{array}$	methyl ethanoate (methyl acetate)	$\begin{array}{c} \text{O} \\ \\ \text{CH}_3 — \text{C} — \text{O} — \text{CH}_3 \end{array}$
amines	$\begin{array}{c} \text{R}'[\text{H}] \\ \\ \text{R} — \text{N} — \text{R}''[\text{H}] \end{array}$	propylamine	$\begin{array}{c} \text{H} \\ \\ \text{CH}_3 — \text{CH}_2 — \text{CH}_2 — \text{N} — \text{H} \end{array}$
amides	$\begin{array}{c} \text{O} \quad \text{R}''[\text{H}] \\ \quad \\ \text{R}[\text{H}] — \text{C} — \text{N} — \text{R}'[\text{H}] \end{array}$	propanamide	$\begin{array}{c} \text{O} \quad \text{H} \\ \quad \\ \text{CH}_3 — \text{CH}_2 — \text{C} — \text{N} — \text{H} \end{array}$

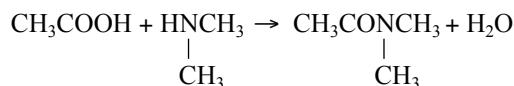
- (b) (No doubt some students will have their own suggestions for simplifying the naming system. Sample answer) The names for esters should reflect the order in which the components are drawn.
7. presence of length of nonpolar hydrocarbon component: $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$
 double or triple bonds: $\text{CH}_2=\text{CH}_2$, $\text{CH}\equiv\text{CCH}_3$
 OH bonds: $\text{CH}_3\text{CH}_2\text{OH}$
 NH bonds: H_2NCH_3
 C=O bonds: CH_3CHO , CH_3COOH

Applying Inquiry Skills

8. The products formed are likely to be a mixture of ethylamine, diethylamine, and triethylamine. These amines have different numbers of NH bonds and different numbers of ethyl groups; thus, they have different intermolecular attractions and different melting points and boiling points. The amines can be separated by fractional distillation.

Making Connections

9. The carboxylic acids such as citric acid in lemons and acetic acid in vinegar react with the amines responsible for the fishy taste in fish to produce amides. For example,



ethanoic acid + dimethylamine $\rightarrow N,N$ -dimethyl ethanamide + water

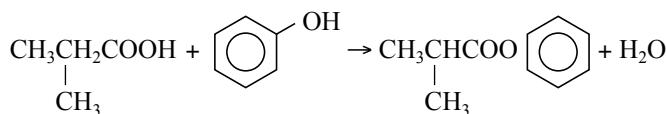
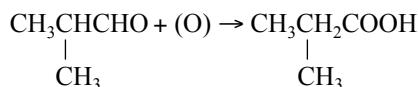
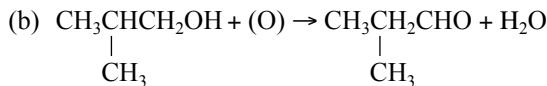
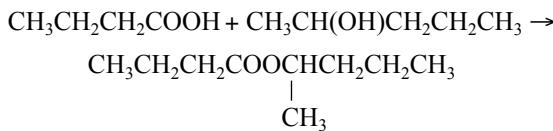
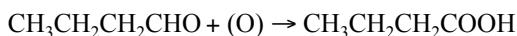
10. (a) Each small unit must contain an amino group and a carboxyl group, so that an amide bond can form between small units.
 (b) With both amino groups and carboxyl groups, amino acids are likely fairly soluble in water; they are capable of forming strong amide bonds.

1.9 SYNTHESIZING ORGANIC COMPOUNDS

PRACTICE

(Page 82)

Understanding Concepts



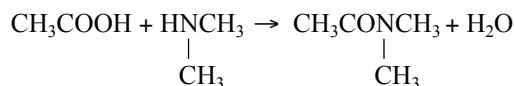
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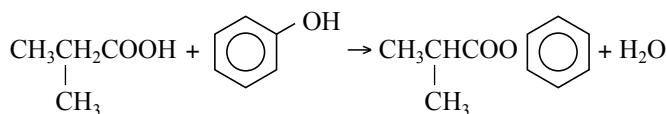
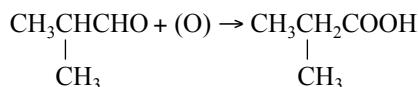
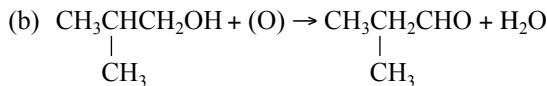
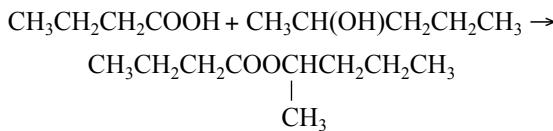
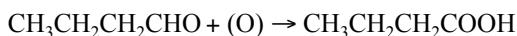
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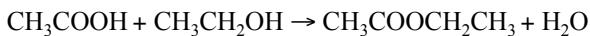
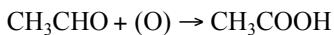
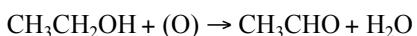
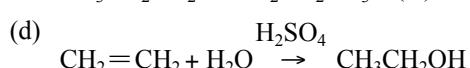
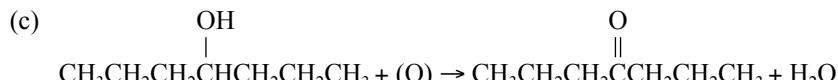
1.9 SYNTHESIZING ORGANIC COMPOUNDS

PRACTICE

(Page 82)

Understanding Concepts



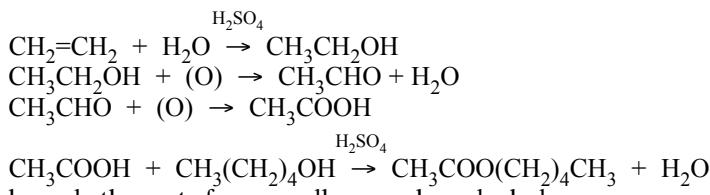


SECTION 1.9 QUESTIONS

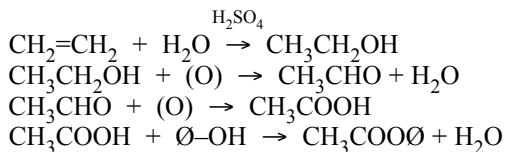
(Page 82)

Understanding Concepts

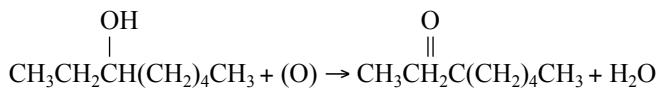
1. (a) pentyl ethanoate from ethene and an alcohol



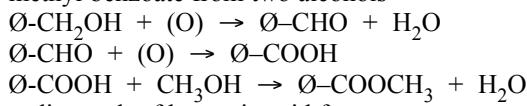
- (b) benzyl ethanoate from an alkene and an alcohol



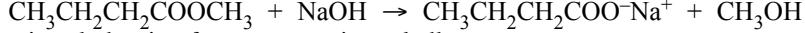
- (c) 3-octanone from a simpler compound



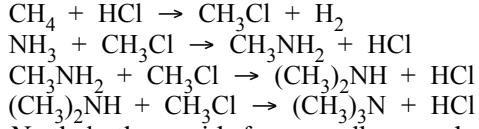
- (d) methyl benzoate from two alcohols



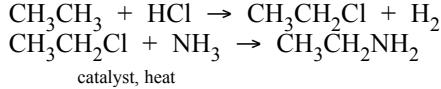
- (e) sodium salt of butanoic acid from an ester



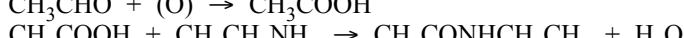
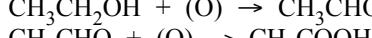
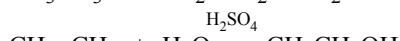
- (f) trimethylamine from ammonia and alkanes



- (g) N-ethyl-ethanamide from an alkane and ammonia

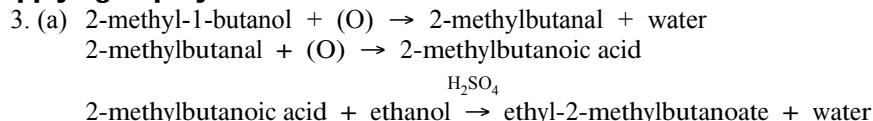


catalyst, heat



2. Controlled oxidation of 1-hexanol, using an oxidizing agent such as $\text{KMnO}_4\text{(aq)}$.

Applying Inquiry Skills



(b) **Procedure**

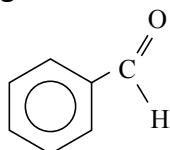
1. Add 2-methyl-1-butanol to an oxidizing agent such as sodium dichromate or potassium permanganate.
2. Add the acid product to an equal amount of ethanol and a few drops of concentrated sulfuric acid.
3. Heat the mixture in a hot-water bath.

Safety Precautions:

Concentrated sulfuric acid is highly corrosive. Avoid contact with skin and clothing. Wear eye protection and a lab apron. 2-methyl-1-butanol is flammable, so there should be no open flames in the vicinity. Dispose of materials in designated labelled containers.

Making Connections

4. (a)



benzaldehyde

- (b) $\text{CH}_3\text{COOCH}_2-\text{O} + \text{NaOH} \rightarrow \text{CH}_3\text{COONa} + \text{O}-\text{CH}_2\text{OH}$
 $\text{O}-\text{CH}_2\text{OH} + (\text{O}) \rightarrow \text{O}-\text{CHO} + \text{H}_2\text{O}$
- (c) Hydrogen cyanide poisoning occurs mainly through inhalation, rapidly leading to death in sufficient concentrations. It is a colourless liquid (boiling point 26°C). In the 1980s it was used as a highly toxic chemical warfare agent by Iraq against Iran and the Kurds.

Benzaldehyde (boiling point 179°C) is used primarily as a flavouring chemical and as an intermediate for dyes. It has the odour of almonds, but inhalation may cause coughing, sore throat, and chest pain; high concentrations have a narcotic effect. Ingestion may cause sore throat, abdominal pain, nausea, central nervous system depression, convulsions, and respiratory failure. Skin contact may cause allergic skin reactions.

Natural products are not always healthier than artificial counterparts; many living organisms produce toxins as a system of defence against pests or predators.

5. (a) Drinking tonic water to treat malaria would not be effective. The required dosage is 1800 mg/d ($6 \times 300 \text{ mg}$); this is equivalent to drinking 90 cans of tonic water per day. (However, there has been some suggestion that the combination of alcohol with the quinine in tonic water enhances the effects!)
- (b) Quinine is water soluble because it contains a hydroxyl group, which allows it to form hydrogen bonds with water molecules.
- (c) Malaria has been recorded since 6000–5500 B.C. Quinine, a toxic plant alkaloid from the bark of the Cinchona tree, was used to treat malaria over 350 years ago. Synthetically produced chloroquine was developed in 1934, sold under the names of Resochin and Sontochin, and was later modified and renamed Chloroquine. In 1950, control of malaria was attempted by spraying with DDT to kill the carrier mosquitoes. By the 1960s, chloroquine-resistant strains of malaria appeared, as a result of over usage and under dosage. Quinine was used, as well as a synthetic analogue called mefloquine. Another antimalarial drug, called Qinghaosu, has been used in China for over two thousand years and is effective in treating all forms of malaria.
6. The new career may be in either the organic chemistry field (e.g., plastics, pharmaceuticals) or organically grown foods (e.g., organic farming, organic produce in supermarkets).
7. (Answers will vary but should include reference to several different products, in a variety of categories. Students should refer to claims made on the labels, and discuss the meanings of these claims. Some personal opinions about the uses of these terms should also be presented.)

CHAPTER 1 LAB ACTIVITIES

LAB EXERCISE 1.3.1 PREPARATION OF ETHYNE

(Page 84)

Prediction

(a) (Sample answer) From the balanced equation,
 $\text{CaC}_{2(\text{s})} + 2 \text{H}_2\text{O}_{(\text{l})} \rightarrow \text{C}_{2\text{H}}_{2(\text{g})} + \text{Ca(OH)}_{2(\text{aq})}$

$$m_{\text{CaC}_2} \text{ reacted} = 6.78 \text{ g}$$

$$M_{\text{CaC}_2} = 64.10$$

$$\text{therefore, } n_{\text{CaC}_2} \text{ reacted} = 6.78 \text{ g} \times \frac{1 \text{ mol}}{64.10 \text{ g}}$$

$$n_{\text{CaC}_2} = 0.106 \text{ mol CaC}_2$$

$$n_{\text{C}_{2\text{H}_2}} = n_{\text{Ca(OH)}_2} = n_{\text{CaC}_2} = 0.106 \text{ mol}$$

$$M_{\text{C}_{2\text{H}_2}} = 26.04$$

$$\text{therefore, } m_{\text{C}_{2\text{H}_2}} = 0.106 \text{ mol} \times 26.04 \text{ g/mol}$$

$$m_{\text{C}_{2\text{H}_2}} = 2.76 \text{ g}$$

$$M_{\text{Ca(OH)}_2} = 74.10$$

$$\text{therefore, } m_{\text{Ca(OH)}_2} = 0.106 \text{ mol} \times 74.10 \text{ g/mol}$$

$$m_{\text{Ca(OH)}_2} = 7.85 \text{ g}$$

The predicted mass of ethyne produced is 2.76 g; the predicted mass of calcium hydroxide produced is 7.85 g.

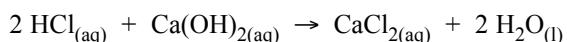
Analysis

(b) $2 \text{HCl}_{(\text{aq})} + \text{Ca(OH)}_{2(\text{aq})} \rightarrow \text{CaCl}_{2(\text{aq})} + 2 \text{H}_2\text{O}_{(\text{l})}$

(c) n_{HCl} in titration = $0.100 \text{ L} \times 1.00 \text{ mol/L HCl}$

$$n_{\text{HCl}} = 0.100 \text{ mol HCl}$$

From the balanced equation,

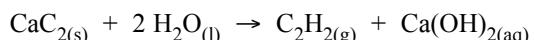


$$n_{\text{Ca(OH)}_2} = 0.100 \text{ mol HCl} \times \frac{1 \text{ mol Ca(OH)}_2}{2 \text{ mol HCl}}$$

$$n_{\text{Ca(OH)}_2} = 0.0500 \text{ mol Ca(OH)}_2$$

Therefore, the amount of Ca(OH)_2 produced is 0.0500 mol.

(d) From the balanced equation,



$$n_{\text{C}_{2\text{H}_2}} = n_{\text{Ca(OH)}_2} = 0.0500 \text{ mol}$$

$$M_{\text{C}_{2\text{H}_2}} = 26.04$$

$$\text{therefore, } m_{\text{C}_{2\text{H}_2}} = 0.0500 \text{ mol} \times 26.04 \text{ g/mol}$$

$$m_{\text{C}_{2\text{H}_2}} = 1.30 \text{ g}$$

The yield of ethyne is 1.30 g.

- (e) As shown in the prediction, answer (a), the theoretical yield of $\text{C}_2\text{H}_2 = 0.106 \text{ mol}$

$$\begin{aligned}\text{percentage yield} &= \frac{\text{actual yield}}{\text{theoretical yield}} \times 100\% \\ &= \frac{1.30 \text{ g}}{2.76 \text{ g}} \times 100\%\end{aligned}$$

$$\text{percentage yield} = 47.2\%$$

Therefore, the CaC_2 is 47.2% pure.

Evaluation

- (f) We assume that the reactants are pure, that $\text{H}_2\text{O}_{(l)}$ is in excess, and that we obtained a 100% yield.

INVESTIGATION 1.5.1 COMPARISON OF THREE ISOMERS OF BUTANOL

(Page 84)

Prediction

- (a) All three alcohols will produce alkyl halides, because they can all undergo substitution reactions where the OH group is substituted by a halogen atom.

The primary alcohol will oxidize to an aldehyde; the secondary alcohol will oxidize to a ketone; and the tertiary alcohol will not readily undergo oxidization.

Evidence

(b)	Alcohol	Reaction with $\text{HCl}_{(aq)}$	Reaction with $\text{KMnO}_{4(aq)}$
	1-butanol	cloudy layer formed after more than 1 min	colour change
	2-butanol	cloudy layer formed in about a minute	colour change
	2-methyl-2-propanol	cloudy layer formed immediately	no reaction

Analysis

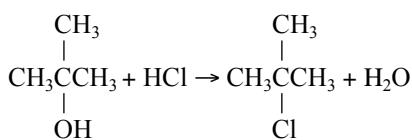
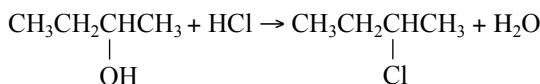
- (c) Each alcohol undergoes halogenation. Only the primary and secondary alcohols undergo controlled oxidation.

Evaluation

- (d) The theory is correct (although the cloudy layer may be difficult to see in the primary alcohol).

Synthesis

- (e) All three alcohols form chlorides. The primary and secondary alcohols undergo controlled oxidation; the tertiary alcohol does not. The chlorides do not contain groups capable of hydrogen bonding and thus are not as soluble as the alcohols in water.



- (e) As shown in the prediction, answer (a), the theoretical yield of $\text{C}_2\text{H}_2 = 0.106 \text{ mol}$

$$\begin{aligned}\text{percentage yield} &= \frac{\text{actual yield}}{\text{theoretical yield}} \times 100\% \\ &= \frac{1.30 \text{ g}}{2.76 \text{ g}} \times 100\%\end{aligned}$$

$$\text{percentage yield} = 47.2\%$$

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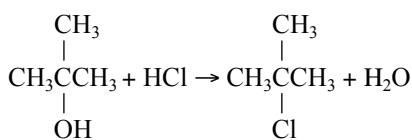
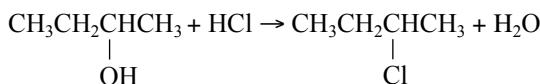
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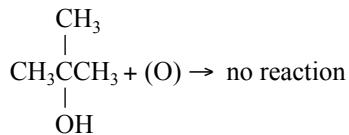
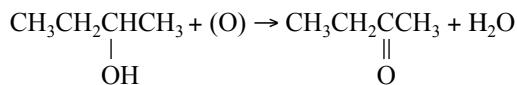
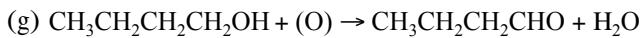
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Synthesis

- (e) All three alcohols form chlorides. The primary and secondary alcohols undergo controlled oxidation; the tertiary alcohol does not. The chlorides do not contain groups capable of hydrogen bonding and thus are not as soluble as the alcohols in water.





(h) 1° , 2° , and 3° alcohols all undergo halogenation reactions, the OH group being substituted with the halogen atom. 1° and 2° alcohols undergo controlled oxidation to aldehydes and ketones respectively, but 3° alcohols do not.

INVESTIGATION 1.5.2 TRENDS IN PROPERTIES OF ALCOHOLS

(Page 86)

Question

(a)–(c)

Name	Structural Formula	b.p. (°C)	m.p. (°C)	Solubility	Diagram
methanol	CH_3OH	65	−94	w, al, eth, ace, bz, chl	$\begin{array}{c} \text{H} \\ \\ \text{H}-\text{C}-\text{H} \\ \\ \text{OH} \end{array}$ methanol
ethanol	$\text{C}_2\text{H}_5\text{OH}$	78	−117	w, al, eth, ace, bz	$\begin{array}{cc} \text{H} & \text{H} \\ & \\ \text{H}-\text{C} & -\text{C}-\text{H} \\ & \\ \text{OH} & \text{H} \end{array}$ ethanol
1-propanol	$\text{C}_3\text{H}_7\text{OH}$	97	−126	w, al, eth, ace, bz	$\begin{array}{ccc} \text{H} & \text{H} & \text{H} \\ & & \\ \text{H}-\text{C} & -\text{C} & -\text{C}-\text{H} \\ & & \\ \text{OH} & \text{H} & \text{H} \end{array}$ 1-propanol
1-butanol	$\text{C}_4\text{H}_9\text{OH}$	117	−89	w, al, eth, ace, bz	$\begin{array}{cccc} \text{H} & \text{H} & \text{H} & \text{H} \\ & & & \\ \text{H}-\text{C} & -\text{C} & -\text{C} & -\text{C}-\text{H} \\ & & & \\ \text{OH} & \text{H} & \text{H} & \text{H} \end{array}$ 1-butanol

KEY:

w: soluble in water;

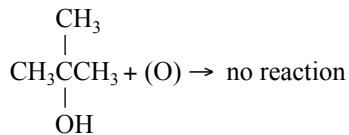
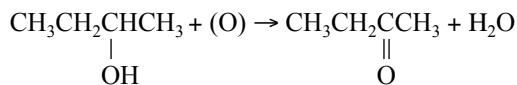
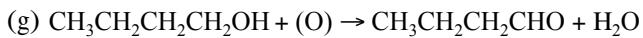
al: soluble in ethanol;

eth: soluble in diethyl ether;

ace: soluble in acetone;

bz: soluble in benzene;

chl: soluble in chloroform



(h) 1° , 2° , and 3° alcohols all undergo halogenation reactions, the OH group being substituted with the halogen atom. 1° and 2° alcohols undergo controlled oxidation to aldehydes and ketones respectively, but 3° alcohols do not.

INVESTIGATION 1.5.2 TRENDS IN PROPERTIES OF ALCOHOLS

(Page 86)

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Name	Structural Formula	b.p. (°C)	m.p. (°C)	Solubility	Diagram
methanol	CH_3OH	65	−94	w, al, eth, ace, bz, chl	$\begin{array}{c} \text{H} \\ \\ \text{H}-\text{C}-\text{H} \\ \\ \text{OH} \end{array}$ methanol
ethanol	$\text{C}_2\text{H}_5\text{OH}$	78	−117	w, al, eth, ace, bz	$\begin{array}{cc} \text{H} & \text{H} \\ & \\ \text{H}-\text{C} & -\text{C}-\text{H} \\ & \\ \text{OH} & \text{H} \end{array}$ ethanol
1-propanol	$\text{C}_3\text{H}_7\text{OH}$	97	−126	w, al, eth, ace, bz	$\begin{array}{ccc} \text{H} & \text{H} & \text{H} \\ & & \\ \text{H}-\text{C} & -\text{C} & -\text{C}-\text{H} \\ & & \\ \text{OH} & \text{H} & \text{H} \end{array}$ 1-propanol
1-butanol	$\text{C}_4\text{H}_9\text{OH}$	117	−89	w, al, eth, ace, bz	$\begin{array}{cccc} \text{H} & \text{H} & \text{H} & \text{H} \\ & & & \\ \text{H}-\text{C} & -\text{C} & -\text{C} & -\text{C}-\text{H} \\ & & & \\ \text{OH} & \text{H} & \text{H} & \text{H} \end{array}$ 1-butanol

KEY:

w: soluble in water;

al: soluble in ethanol;

eth: soluble in diethyl ether;

ace: soluble in acetone;

bz: soluble in benzene;

chl: soluble in chloroform

Analysis

- (d) Boiling points of alcohols increase with increasing length of hydrocarbon chain. Melting points decrease with increasing length of hydrocarbon chain for the first three alcohols. *n*-butanol is less soluble in water than are the first three alcohols.

Synthesis

- (e) The properties of primary alcohols are a combination of the properties of its polar OH group and its nonpolar hydrocarbon component. Molecular models show the increasing length of the nonpolar component and corresponding trends in properties.

INVESTIGATION 1.7.1 PROPERTIES OF CARBOXYLIC ACIDS

(Page 87)

Question

- (a) (Sample answers) How does the length of the hydrocarbon chain in a carboxylic acid affect its melting and boiling points, its solubility, and its reactions with bases and oxidizing agents?

What are the similarities and differences in several properties of two carboxylic acids of different molecular size?

Prediction

- (b) (Sample answer) Stearic acid has a much longer hydrocarbon chain than does acetic acid; thus, stearic acid is more nonpolar than acetic acid and will be less soluble in a polar solvent such as water, and more soluble in a nonpolar solvent such as vegetable oil. Stearic acid will also have a higher melting point because its long hydrocarbon chain allows additional intermolecular forces of attraction (van der Waals). Acetic acid will react readily with the base, but stearic acid will react less readily because it is less soluble in the aqueous solution of the base. Neither acid will react with the potassium permanganate because the carboxyl group does not readily gain oxygen atoms or lose hydrogen atoms.

Evidence

(c) and (d)

Property	Acetic acid	Stearic acid
IUPAC name	ethanoic acid	octadecanoic acid
structural diagram		
molar mass	60.05 g/mol	284.50 g/mol
solubility	soluble in water (also al, ace, bz)	soluble in oil (also eth, ace, chl)
reaction with base	reacts with base	does not readily react
reaction with KMnO ₄	no reaction	no reaction

KEY:

w: soluble in water;

al: soluble in ethanol;

eth: soluble in diethyl ether;

ace: soluble in acetone;

bz: soluble in benzene;

chl: soluble in chloroform

Analysis

- (e) Both acids contain the polar carboxyl group; in addition, stearic acid has a long hydrocarbon group with stronger van der Waals attractions than in the shorter ethanoic acid.

Analysis

(d) Boiling points of alcohols increase with increasing length of hydrocarbon chain. Melting points decrease with increasing length of hydrocarbon chain for the first three alcohols. *n*-butanol is less soluble in water than are the first three alcohols.

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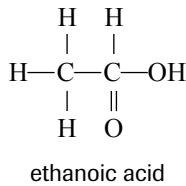
bz: soluble in benzene;

chl: soluble in chloroform

Analysis

(e) Both acids contain the polar carboxyl group; in addition, stearic acid has a long hydrocarbon group with stronger van der Waals attractions than in the shorter ethanoic acid.

- (f) Acetic acid is more soluble in water than is stearic acid, and less soluble in oil; stearic acid, with its long hydrocarbon component, has a longer nonpolar component and is thus more soluble in the nonpolar oil.
- (g) Acetic acid reacts with sodium hydrogen carbonate, as acids do; stearic acid is not soluble in water and does not show a reaction with the aqueous sodium hydrogen carbonate.
- (h) $\text{CH}_3\text{COOH}_{(\text{aq})} + \text{NaHCO}_3_{(\text{aq})} \rightarrow \text{CH}_3\text{COONa}_{(\text{aq})} + \text{CO}_{2(\text{g})} + \text{H}_2\text{O}_{(\text{l})}$
- (i) Carboxylic acids do not undergo controlled oxidation reactions; the C atom to which the OH group is attached is not bonded to an H atom to allow further oxidation of the OH group to a C=O group.



Evaluation

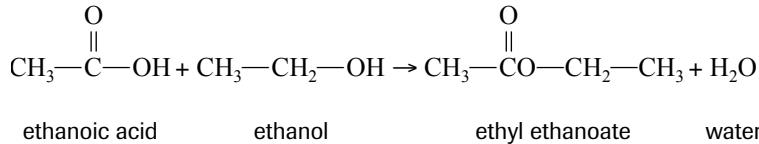
- (j) (Sample answer) Yes, the Experimental Design allowed the collection of appropriate evidence regarding all aspects of this investigation except for the reaction with sodium hydrogen carbonate; since the stearic acid was not highly soluble in water, it is inconclusive whether it reacts with sodium hydrogen carbonate.
- (k) (Sample answer) Answers obtained in the Analysis are in agreement with the Prediction.
- (l) (Sample answer) The theoretical model of carboxylic acids did help in the prediction of the chemical properties of these acids. The effect of the polar and nonpolar components of each acid could be used to predict physical and chemical properties of the compounds.

ACTIVITY 1.7.2 SYNTHESIS OF ESTERS

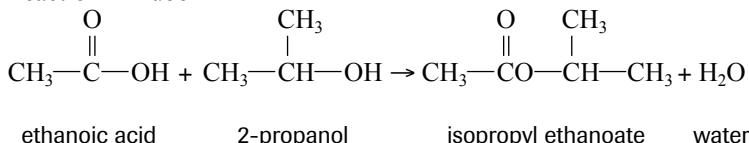
(Page 89)

- (a) Both ethanol and 2-propanol reacted with glacial acetic acid to form products with fruity odours. 1-pentanol reacted with glacial acetic acid to form a product with an odour like bananas.

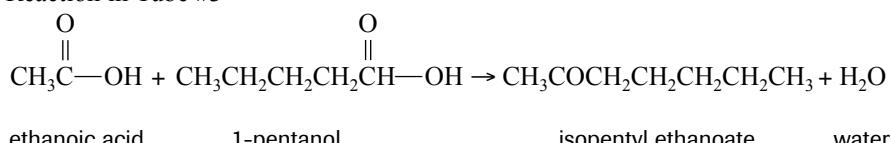
(b) Reaction in Tube #1



Reaction in Tube #2

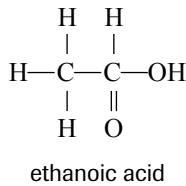


Reaction in Tube #3



- (c) The concentrated sulfuric acid acts as a catalyst.
- (d) The glacial acetic acid mixed with the aqueous sulfuric acid to form a homogeneous mixture; acetic acid is thus soluble in aqueous solution. This is explained by the presence of its polar carboxylic group which can hydrogen bond with water.
- (e) The esters are insoluble in aqueous solution because each one formed a layer on top of the cold water in the evaporating dish. This is explained by the loss of the hydroxyl group from the carboxyl group when the ester bond is formed; thus, the ability to hydrogen bond with water is lost.

- (f) Acetic acid is more soluble in water than is stearic acid, and less soluble in oil; stearic acid, with its long hydrocarbon component, has a longer nonpolar component and is thus more soluble in the nonpolar oil.
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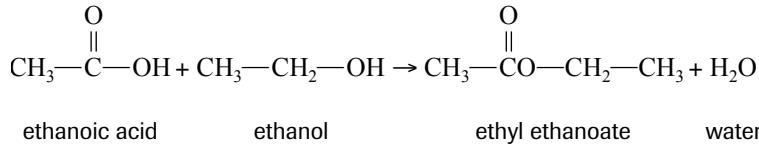
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ACTIVITY 1.7.2 SYNTHESIS OF ESTERS

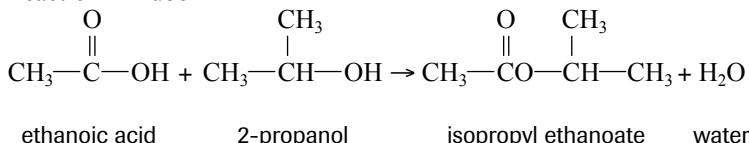
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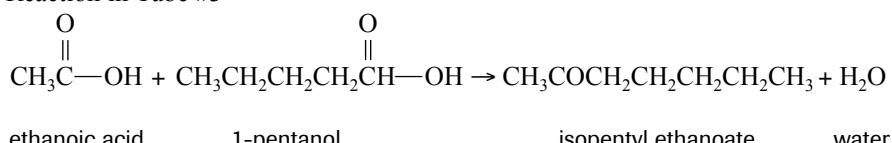
(b) Reaction in Tube #1



Reaction in Tube #2



Reaction in Tube #3

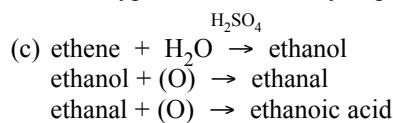


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ACTIVITY 1.9.1 BUILDING MOLECULAR MODELS TO ILLUSTRATE REACTIONS

(Page 90)

- (b) (Answers will vary, depending on the structures created. Reaction #10 would be aromatic; others may be any of the three types, but most likely aliphatic.)

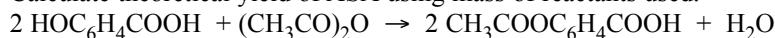


ACTIVITY 1.9.2 PREPARATION OF AN ESTER—ASPIRIN

(Page 90)

- (a) (Answer will depend on actual measurements.)

Calculate theoretical yield of ASA using mass of reactants used.



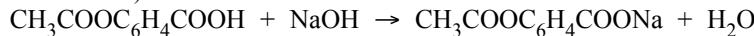
salicylic acid + acetic anhydride → acetylsalicylic acid + water

actual yield = mass of ASA obtained

percentage yield = (actual yield/theoretical yield) × 100%

- (b) The carboxyl group in ASA imparts acidic properties to the compound; one of the properties of an acid is a sour taste.

- (c) The purity of the ASA can be tested by titrating a sample of the ASA with a base (e.g., NaOH, using phenolphthalein as indicator).



Procedure

1. Dissolve a known mass of ASA in methanol in an Erlenmeyer flask.
2. Add a few drops of phenolphthalein.
3. Titrate with a standard solution of $\text{NaOH}_{(\text{aq})}$ delivered from a buret, until the solution just turns pink.
4. Repeat steps 1 to 3 three more times.

Calculations

$$n_{\text{NaOH}} = cV$$

$$n_{\text{ASA}} = n_{\text{NaOH}}$$

$$m_{\text{ASA}} = nM$$

purity of ASA = (m_{ASA} /mass of sample) × 100%

Safety Precautions:

Sodium hydroxide is corrosive. Wear a lab apron and eye protection. If the base comes into contact with skin, wash well with cool water.

Methanol is flammable; keep away from open flames.

CHAPTER 1 SUMMARY

MAKE A SUMMARY

(Page 94)

(Answers will vary.)

CHAPTER 1 SELF-QUIZ

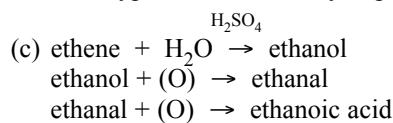
(Page 95)

1. False: An ester is formed when the hydrogen atom from the hydroxyl group of an alcohol and the hydroxyl group of the carboxyl group of an acid are eliminated, and water is condensed.
2. True

ACTIVITY 1.9.1 BUILDING MOLECULAR MODELS TO ILLUSTRATE REACTIONS

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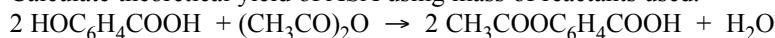


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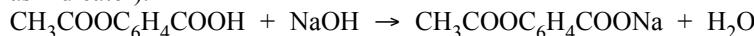
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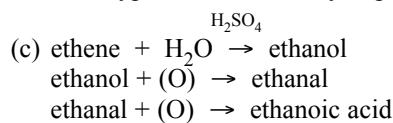
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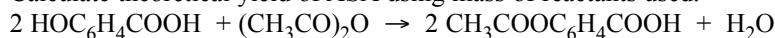


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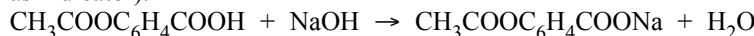
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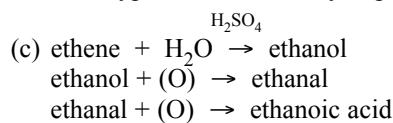
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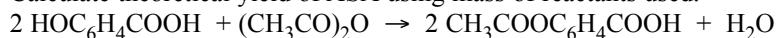


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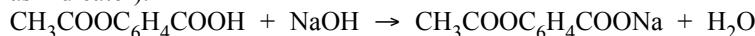
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CHAPTER 1 SUMMARY

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CHAPTER 1 SELF-QUIZ

(Page 95)

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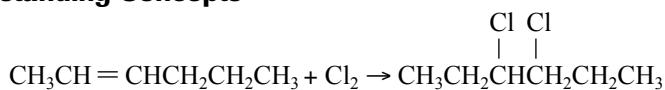
3. True
4. False: In an amide, the nitrogen atom is connected to at least one carbon atom, while in an amine, the nitrogen atom may be connected to 1, 2, or 3 hydrogen atoms.
5. False: When 1-pentanol and 3-pentanol are each oxidized in a controlled way, they produce pentanal and 3-pentanone, respectively.
6. (b)
7. (b)
8. (a)
9. (e)
10. (b)
11. (c)
12. (e)
13. (c)
14. (e)
15. (c)

CHAPTER 1 REVIEW

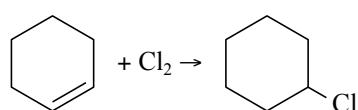
(Page 96)

Understanding Concepts

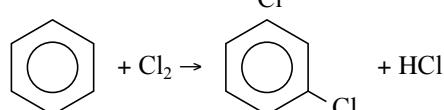
1. (a)



(b)



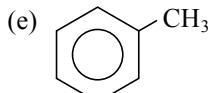
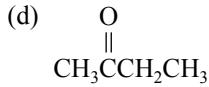
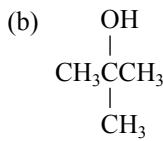
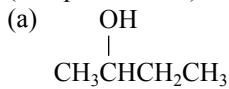
(c)



Reactions in (a) and (b) are addition reactions, and the reaction in (c) is a substitution reaction.

2. C, B, D, A. The reason for this is that more polar compounds have higher boiling points as a result of increased intermolecular forces of attraction. C is an alkane and is nonpolar; B is more polar than C because of its carbonyl group; D is more polar than B because of its OH group, which is capable of hydrogen bonding; A is more polar than D because it has an OH group and a carbonyl group.

3. (Sample answers)



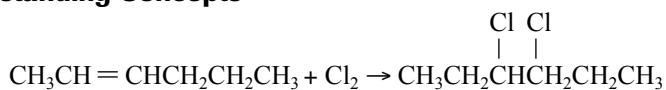
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11. (c)
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13. (c)
14. (e)
15. (c)

CHAPTER 1 REVIEW

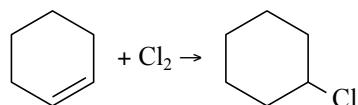
(Page 96)

Understanding Concepts

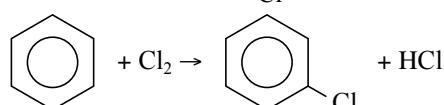
1. (a)



(b)



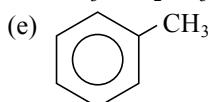
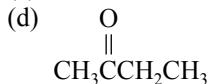
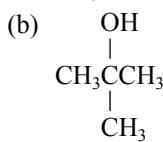
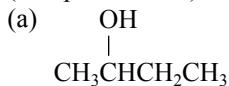
(c)

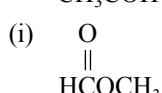
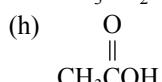
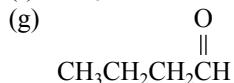


Reactions in (a) and (b) are addition reactions, and the reaction in (c) is a substitution reaction.

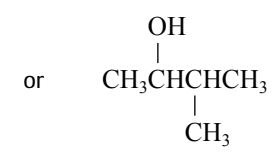
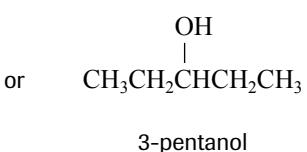
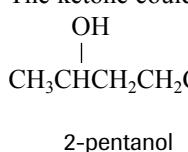
2. C, B, D, A. The reason for this is that more polar compounds have higher boiling points as a result of increased intermolecular forces of attraction. C is an alkane and is nonpolar; B is more polar than C because of its carbonyl group; D is more polar than B because of its OH group, which is capable of hydrogen bonding; A is more polar than D because it has an OH group and a carbonyl group.

3. (Sample answers)





4. The ketone could be



5. (a) alkene: 2-butene

(b) ether: methoxymethane

(c) alcohol: 2-methyl-1-butanol

(d) alkyne: propyne

(e) ester: methyl butanoate

(f) aldehyde: propanal

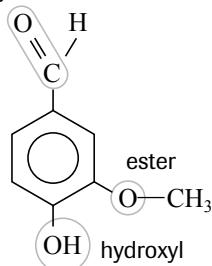
(g) ketone: butanone

(h) amine: 1-aminobutane

(i) alcohol: 3,4-dihydroxy-1-hexene

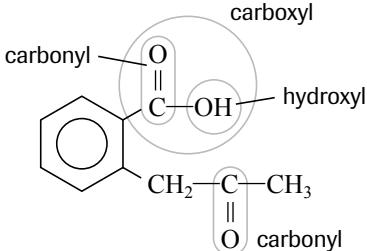
(j) amide: *N*-ethyl butanamide

6. (a) carbonyl



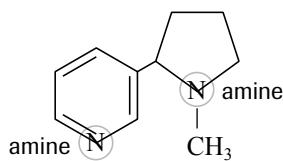
vanillin, used as food flavouring

(b)

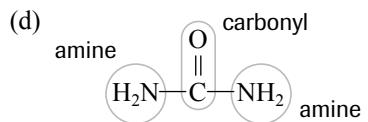


acetylsalicylic acid, used as an analgesic

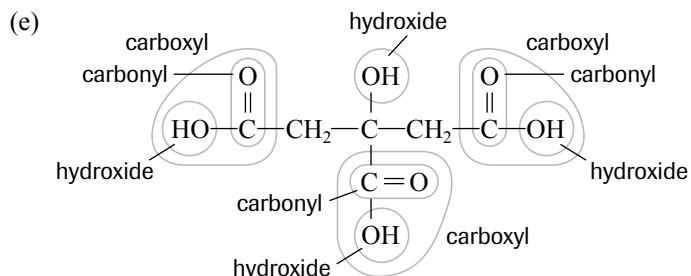
(c)



nicotine, a component of tobacco smoke



urea, synthesized by animals



citric acid, synthesized by some fruits

7. (a) $\text{CH}_3\text{CH}_3 + \text{Br}-\text{Br} \rightarrow \text{CH}_2\text{CH}_3 + \text{HBr}$

Br
|

ethane + bromine → bromoethane + hydrogen bromide
 alkane inorganic alkylhalide inorganic
 substitution reaction

(b) $\text{CH}_2=\text{CHCH}_3 + \text{Cl}-\text{Cl} \rightarrow \begin{array}{c} \text{Cl} & \text{Cl} \\ | & | \\ \text{CH}_2\text{CHCH}_3 \end{array}$

propane + chlorine → 1,2-dichloropropane
 alkane inorganic alkyl halide
 addition reaction

(c) 

$$\text{benzene} + \text{iodine} \rightarrow \text{iodobenzene} + \text{hydrogen iodide}$$

$$\text{aromatic hydrocarbon} \quad \text{inorganic alkyl halide} \quad \text{inorganic}$$

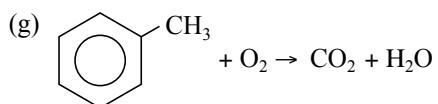
(e) $\text{CH}_3\text{CH}_2\text{CH}_2\overset{\text{O}}{\underset{||}{\text{C}}}\text{OH} + \text{CH}_3\text{OH} \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\overset{\text{O}}{\underset{||}{\text{C}}}\text{OCH}_3 + \text{HOH}$

butanoic acid + methanol → methyl butanoate + water
 carboxylic acid alcohol ester

esterification reaction, condensation reaction

(f) $\begin{array}{c} \text{H} & \text{OH} \\ | & | \\ \text{CH}_2\text{CH}_2 & \rightarrow \text{CH}_2=\text{CH}_2 + \text{HOH} \end{array}$

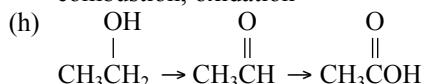
ethanol → ethene + water
 alcohol alkene
 elimination reaction, dehydration reaction



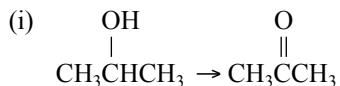
methylbenzene + oxygen → carbon dioxide + water
(phenyl methane)

alkane

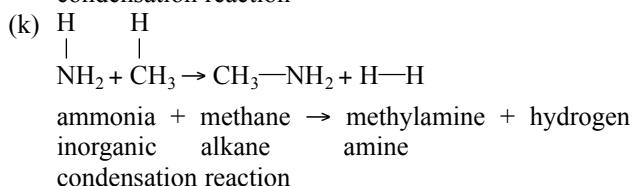
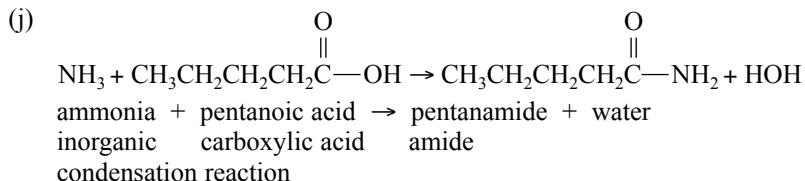
combustion, oxidation



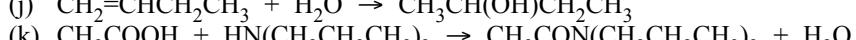
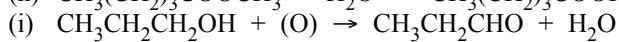
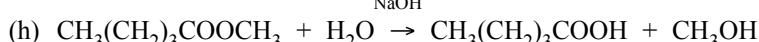
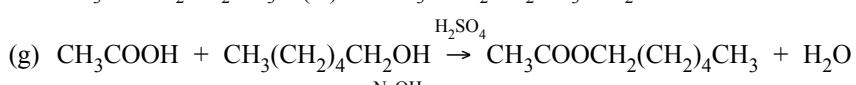
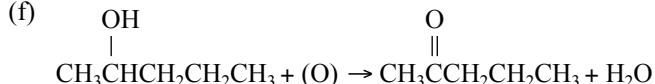
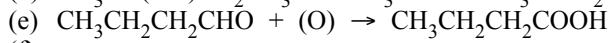
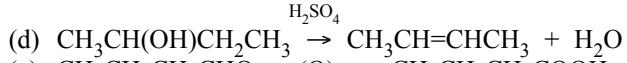
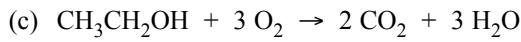
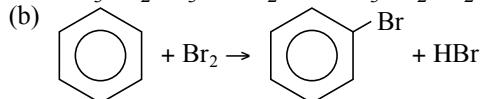
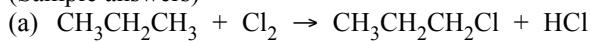
ethanol → ethanal → ethanoic acid
alcohol aldehyde carboxylic acid
controlled oxidation



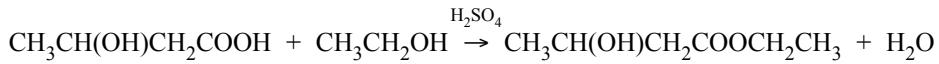
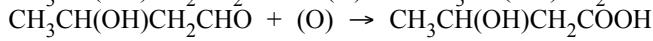
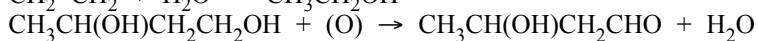
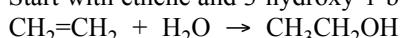
2-propanol → propanone
alcohol ketone
controlled oxidation



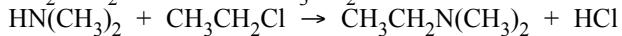
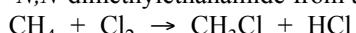
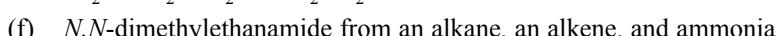
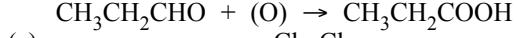
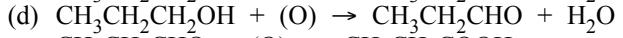
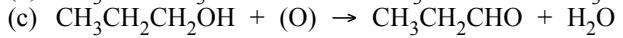
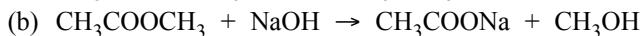
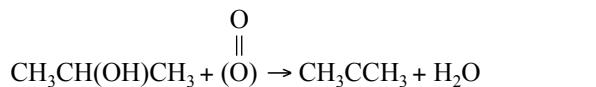
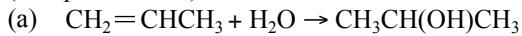
8. (Sample answers)



9. Start with ethene and 3-hydroxy-1-butanol.



- ## 10. (Sample answers)



Applying Inquiry Skills



$$(b) \ n_{C_2H_4} = \frac{m}{M}$$

$$= \frac{2.00 \text{ kg}}{28.06 \text{ g/mol}}$$

$$n_{\text{C}_2\text{H}_4} = 71.3 \text{ mol}$$

$$n_{\text{C}_2\text{H}_4\text{Cl}_2} = n_{\text{C}_2\text{H}_4} = 71.3 \text{ mol}$$

theoretical yield = $m_{C_6H_5Cl}$

$$\equiv nM$$

$$= 71.3 \text{ mol} \times 98.96 \text{ g/mol}$$

theoretical yield = 7.06 kg

actual yield = 6.14 kg

卷之三

$$\text{percentage yield} = \frac{\text{actual yield}}{\text{theoretical yield}} \times 100\%$$

$$= (0.14 \text{ kg} / 1.00 \text{ kg}) \times 100\%$$

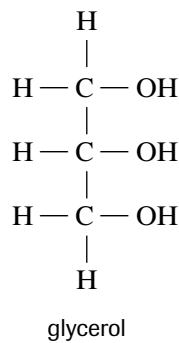
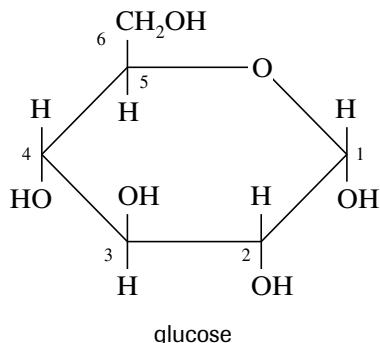
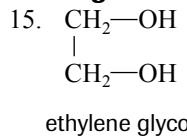
percentage yield = 87.0%

- (c) The actual yield would be less than the theoretical yield if the reactants were impure, if there were some loss of product, or if the reaction were incomplete.

12. The three alcohols have different boiling points that increase in the order: methanol, ethanol, and 1-pentanol. The alcohols can be separated by fractional distillation, using common laboratory equipment. Each alcohol is collected at its boiling point and condensed. All three alcohols have hydroxyl groups capable of hydrogen bonding; the larger alcohols have longer nonpolar hydrocarbon chains that increase the van der Waals attractions.

13. The ester ethyl ethanoate is synthesized from a reaction between ethanol and ethanoic acid, in the presence of concentrated sulfuric acid. Ethanol can be synthesized from hydration of ethene with water, in the presence of sulfuric acid. Ethanoic acid can be synthesized from controlled oxidation of ethanol to ethanal and further to ethanoic acid, using an oxidizing agent such as sodium dichromate or potassium permanganate.

Making Connections



- (a) 2-propanol, ethylene glycol, glycerol, and glucose have, in sequence, increasing numbers of hydroxyl groups, and are thus in increasing order of capability to hydrogen bond, and are in increasing order of relative melting point and boiling point.
 - (b) 2-propanol, ethylene glycol, glycerol, and glucose have, in sequence, increasing numbers of hydroxyl groups, and are thus in increasing order of capability to hydrogen bond, and are in increasing order of their solubility in water.
 - (c) The sweet taste of ethylene glycol attracts animals who ingest it and suffer from its toxic effects.
 - (d) The three compounds all taste sweet and all have hydroxyl groups bonded to carbon chains.
16. (a) $\text{CH}_3\text{COOH} + \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OH} \rightarrow \text{CH}_3\text{COOCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3 + \text{H}_2\text{O}$
- (b) (Answers will vary, but should refer to the raw materials and the method of synthesis.)
- (c) The most commonly used natural source of vanilla flavouring is the vanillin plant, *Vanilla planifolia*, a member of the orchid family. Vanillin, a glucoside, is extracted from ripe vanillin beans, using ethanol and water, under cool temperatures to reduce flavour loss. The extract is then aged from a few days to several years.

Synthetic vanilla flavouring contains a blend of natural vanilla and synthetic chemicals, and cannot be legally labelled "natural." The first synthetic vanilla was made from coniferin, and later from eugenol, found in cloves. More recently, synthetic vanilla is made from ethyl vanillin (made from coal tar), or lignin vanillin, a byproduct of the paper industry. In the 1930s, the Ontario Paper Company solved an environmental problem by turning their industrial waste, a sulfite liquor, into synthetic vanilla.

CHAPTER 2 POLYMERS—PLASTICS, NYLONS, AND FOOD

Reflect on Your Learning

(Page 98)

1. It must be able to join with two other molecules, i.e., it must have two functional groups that will react with other functional groups.
2. Plastics are flexible, strong, mouldable, lightweight, and a large variety exists.
3. Petroleum products are mixtures of hydrocarbons. You would expect to find covalent bonds between C atoms and H atoms, and between C atoms and C atoms within plastic molecules; and van der Waals attractions between long polymer molecules.
4. Strong covalent bonds account for the strength of plastics; weak van der Waals attractions account for their nonrigid structure, mouldability, and relatively low melting points. The large variety of hydrocarbons accounts for the variety of plastics.
5. Carbohydrates (sugars and starches), function: energy and structure; proteins, enzymes, and muscles, function: DNA and RNA, genetic information; fats and oils, function: energy and insulation.

Try This Activity: It's a Plastic World

(Page 99)

(Sample answers)

Product	Function	Properties	Recycling code	Nonplastic alternative	Advantages/disadvantages
toothbrush	cleaning teeth	stiff handle; pliable bristles	none	wood handle; animal-hair bristles	plastic does not promote fungal growth in wet conditions
television or computer casing	hiding and protecting electronics	very rigid; dustproof; nonconducting	none	wood	plastic is lightweight and mouldable
yogurt container	keeping moisture in	lightweight; waterproof;	base:5 lid: 4	glass jar; metal lid	glass is more easily recycled, and reusable but heavier and more easily broken
binders	keeping papers together and protected	colourful; long-lasting	none	cloth, cardboard	plastic is water-resistant

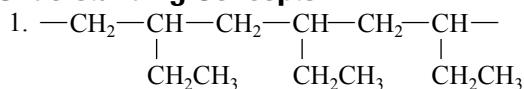
General disadvantage of plastics: petroleum products come from nonrenewable sources, and generally are not biodegradable.

2.1 SYNTHETIC ADDITION POLYMERS

PRACTICE

(Page 102)

Understanding Concepts



CHAPTER 2 POLYMERS—PLASTICS, NYLONS, AND FOOD

Reflect on Your Learning

(Page 98)

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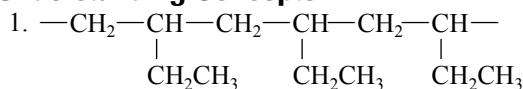
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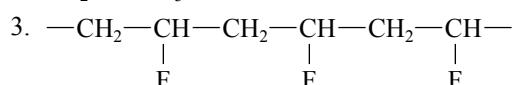
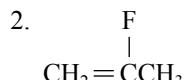
2.1 SYNTHETIC ADDITION POLYMERS

PRACTICE

(Page 102)

Understanding Concepts





Try This Activity: Models of Monomers

(Page 103)

- (a) polyethene
- (b) polypropene
 - a molecule with more than one double bond; e.g., 1,3-butadiene
- (c) 1,3-butadiene, poly-1,3-butadiene
 - Each molecule must have two functional groups that can undergo condensation reactions, e.g., carboxyl group, hydroxyl group, amino group (e.g., 3-aminopropanoic acid).

Try This Activity: Skewering Balloons

(Page 106)

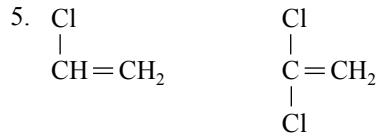
- (a) The intermolecular attractions between polymer chains allow the long molecules to move aside to allow the skewer to push through without breaking, analogous to the noodles moving over each other when needed.

PRACTICE

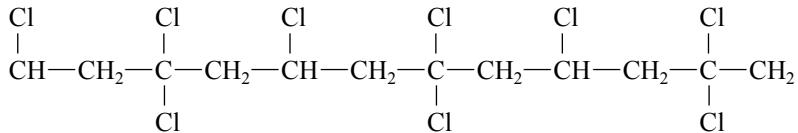
(Page 107)

Understanding Concepts

4. Carbon–carbon double or triple bonds.



vinyl chloride 1,1-dichloroethene

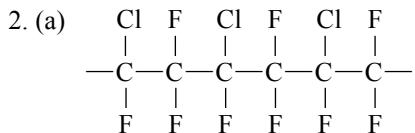


SECTION 2.1 QUESTIONS

(Page 107)

Understanding Concepts

1. (a) Intramolecular forces: covalent bonds; intermolecular forces: van der Waals forces, electrostatic attractions due to any substituted groups present, and, if crosslinking occurs, covalent bonds.
- (b) Properties of the plastics can be designed and controlled by the type of monomer used, and the type of bonding present in the polymer. The polymers are stronger than the monomers, and can be moulded by various processes, depending on the degree of crosslinking.
- (c) The double bonds in the monomers are replaced by single bonds in the polymers, resulting in the polymer having properties similar to the less reactive alkanes than the alkenes of the monomers.



- (b) The presence of the highly electronegative Cl and F atoms makes the polymer more polar, and thus not very soluble in organic solvents. The absence of C—H bonds and the presence of the very strong C—F and C—Cl bonds makes this polymer unreactive. It is also rigid and resistant to heating.
3. (a) 2-butene
 (b) 1-chloro-1,2-difluoropropene
4. (a) The polymer that does not contain an F atom is more soluble. An F atom renders the molecule more polar and less miscible with the organic solvent.
 (b) The polymer that contains a carbonyl group is more soluble. It is more similar to acetone which also contains a carbonyl group.
5. The monomer must have more than one double bond for an addition polymer (e.g., 1,3-pentadiene).
 $\text{CH}_2=\text{CHCH}=\text{CHCH}_3$
6. (a) To be part of a condensed polymer, a molecule must have at least two functional groups that can undergo condensation reactions.
 (b) To be part of an addition polymer, a molecule must have at least one double or triple bond.
7. (a) Typical properties of plastic are flexibility, lightweight, mouldability, and electrically nonconductive. Plastics will also soften when heated.
 (b) Within long polymer molecules you would expect to find intramolecular covalent bonds. Intermolecular bonds would be van der Waals attractions. Electrostatic forces and covalent bonds would exist if crosslinking is present.
 (c) Intramolecular bonding: the prevalence of single, rather than multiple, carbon–carbon bonds makes plastics strong and chemically unreactive. Intermolecular bonding: the intermolecular attractions make the plastic strong, with the degree of crosslinking adding strength or flexibility and mouldability to the plastic.

Applying Inquiry Skills

8. Place the sample in hot water for a few minutes. If the plastic softens, it is not crosslinked and its polymer chains are held by the weak van der Waals attractions. If it does not soften by heat, its polymer chains are linked by strong covalent bonds.

Making Connections

9. (Answers may vary. One sample answer might be:) The following are accepted: code 1 (bottles for carbonated drinks, containers for peanut butter, salad dressings); code 2 (milk, water, juice bottles, grocery bags); code 4 (dry-cleaning and grocery bags, flexible containers and lids); code 5 (ketchup bottles, margarine containers); code 6 (meat trays, plastic knives, spoons, forks). Code 3 is not accepted by municipal recycling services, as they are too large for pickup, or contain medical hazards in medical tubing, etc. However, some construction pipe and siding, window frames, etc., are accepted by a nonprofit environmental program. Students will need to check their local recycling program for specific information.

Table headings: SPI resin code; Type of products; Properties; Accepted by Municipal Recycling Organization; Accepted by Other Recycling Organization.

10. (a) (Sample answer) strong, flexible, chemically unreactive, insoluble in polar and nonpolar solvents, not softened by heat, nonbiodegradable.
 (b) (Sample answer) presence of F or Cl atoms, controlled degree of crosslinking to obtain desired flexibility and strength and resistance to heat.
11. Natural rubber is produced from the sap of the rubber tree, *Hevea brasiliensis*. The sap is collected, exposed to air, and gently heated. Natural rubber is a polymer of 2-methyl-1,3-butadiene (isoprene), $\text{CH}_2=\text{C}(\text{CH}_3)-\text{CH}=\text{CH}_2$. The polymerization reaction is:
- $$n \text{CH}_2=\text{C}(\text{CH}_3)-\text{CH}=\text{CH}_2 \rightarrow -[\text{CH}_2-\text{C}(\text{CH}_3)=\text{CH}-\text{CH}_2]_n-$$
- Charles Goodyear developed the vulcanizing process in which rubber is heated with sulfur; this process produced a more elastic and stable rubber and made it suitable for a wide range of products such as cushions, mattresses, raincoats, and shoes. Rubber is primarily used in car tires, and a filler such as carbon black is added for reinforcement. Synthetic rubber was developed and produced in Germany during World War I, and demand for materials increased research and production of new synthetic rubbers during World War II.

2.2 SYNTHETIC CONDENSATION POLYMERS

PRACTICE

(Page 111)

Understanding Concepts



2. Two functional groups that can undergo condensation reactions, e.g., carboxyl group, hydroxyl group, amino group must be present.
3. Intrachain bonding (within a polyamide chain): covalent bonds; interchain (between adjacent polyamide bonds): van der Waals attractions, electrostatic forces; hydrogen bonding if N—H bonds are present.

Try This Activity: Diaper Dissection

(Page 112)

- (a) The addition of table salt causes some of the water to come out of the gel, as the presence of sodium ions reduces the absorbency of the polymer. The addition of sucrose or calcium chloride does not produce any change as no sodium ions are added.

PRACTICE

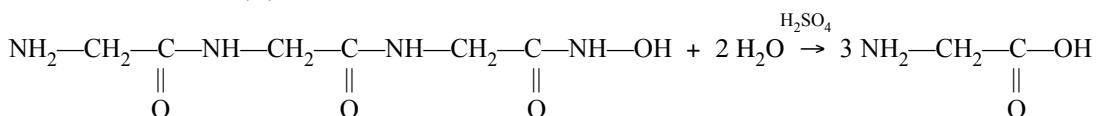
(Page 113)

Applying Inquiry Skills

4. First, obtain two samples of sodium polymethylacrylate of equal mass. Add a known excess volume of distilled water to one sample, and to the other sample, add the same volume of distilled water, into which is dissolved a known mass of NaCl, e.g., to 0.10 mol/L. Allow both samples to sit at the same temperature for the same period of time. Pour off unabsorbed liquid from each sample and find the mass of polymer and absorbed liquid. Calculate and compare the mass of each liquid absorbed per unit time, e.g., mL/min. An example of an approximate decrease in absorption rate would be 10–20%, depending on concentration used.

Making Connections

5. Amides can be hydrolyzed under acidic or basic conditions, similar to hydrolysis of esters. However, the reaction is much slower as the C(O)—NH bond is more stable than the ester bond.



6. Advantages of nylon toothbrushes: controlled degree of rigidity or flexibility, water-resistant and thus dry readily, durable. Drawbacks of nylon toothbrushes: made from nonrenewable resources, nonbiodegradable.

SECTION 2.2 QUESTIONS

(Page 113)

Understanding Concepts

1. A polyester is linked by functional groups that form esters: carboxyl groups and hydroxyl groups (e.g., polymer of a dicarboxylic acid and a diol). A polyamide is linked by functional groups that form amides: carboxyl groups and amines (e.g., polymer of a dicarboxylic acid and a diamine).
 2. $\text{H}_2\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2$ 1,5-diaminopentane
 $\text{HOOCCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{COOH}$ decanedioic acid
 - 3.
- $$\begin{array}{c} \text{O} \quad \text{O} \quad \text{O} \quad \text{O} \\ || \quad || \quad || \quad || \\ —\text{C}—\text{COCH}_2\text{CH}_2\text{OC}—\text{COCH}_2\text{CH}_2\text{OC}—\text{COCH}_2\text{CH}_2\text{O}— \end{array}$$

4. $\text{H}_2\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{COOH}$
6-aminohexanoic acid
[—(H)NCH₂CH₂CH₂CH₂CON(H)CH₂CH₂CH₂CH₂CO—]
5. HOOCCH₂CH₂CH₂CH₂COOH and H₂NCH₂CH₂CH₂CH₂NH₂
hexanedioic acid and 1,6-diaminobutane
6. (a) Covalent bonds: intrachain bonds joining C, H, O, and N atoms.
 (b) Amide bonds: the linkage between the N of the amino group of the amine and the C of the carbonyl group of the acid.
 (c) Hydrogen bonds: interchain attractions between the NH groups and the carbonyl groups.

Applying Inquiry Skills

7. (a) An ideal polymer would be able to do the following: absorb sufficient water to sustain a plant for several weeks, absorb nutrients dissolved in water, would not be harmful to plants, and could be tailored to specific types of application (houseplants, outdoor plants). Also, ideal polymers would degrade after several months into harmless products (e.g., high or low pH), and would be inexpensive.
 (b) Test for absorption: place samples of equal mass of each polymer in equal excess volumes of water and water with dissolved nutrients, and determine mass of liquid absorbed. Test for release of liquid: mix equal swelled mass of each polymer with equal masses of a variety of soil types, measure moisture content over a test period. Examine soil and polymer mixture samples at selected time intervals, and test for pH. Store mixture samples over several months and determine amount of degradation. As a safety precaution, test pH. An appropriate test period would be two weeks.

Sample answer:

A.

polymer; mass of polymer; mass of water added; mass of polymer + absorbed water

polymer A	50.0 g	100.0 g	70.0 g
polymer B	50.0 g	100.0 g	80.0 g

B.

polymer; mass of nutrient solution absorbed; % change in concentration of nutrients in excess solution

polymer A	70.0 g	+ 10%
polymer B	80.0 g	0%

C.

polymer; mass before degradation; mass after degradation (8 weeks); pH

polymer A	50.0 g	25.0 g	pH 5.5
polymer B	50.0 g	40.0 g	pH 6.5

Analysis

Polymer A absorbs less fluid than polymer B, and does not absorb nutrients as well as polymer B; polymer A also degrades to produce acidic substances. Polymer B allows all nutrients to be absorbed but does not degrade as quickly as polymer A.

Making Connections

8. (Sample answers) As potting soil additive for moisture; as a filter for removing traces of moisture from gasoline, oil; as time-release drug delivery system; as material for “grow a dinosaur” type toys.
 9. (Sample answers)

The term “natural” is used to describe products made by plants or animals, such as natural fruit juice. Some molecules made by plants are synthesized in laboratories, e.g., acetylsalicylic acid; others are made by plants but are treated chemically, e.g., decaffeinated coffee contains caffeine which is made by a plant, but has been treated in a chemical process. Should they be classified as synthetic?

“Organic” produce in supermarkets indicates that the item is grown without use of “chemical” substances such as fertilizers, antibiotics, etc. In scientific terminology, all plants and animals, and thus most foods, are organic in nature as they contain molecules such as carbohydrates, proteins, and fats, all of which contain carbon atoms.

The terms “organic” and “natural” denote substances that are not grown using synthetic materials. However, they may require synthetic materials in their use, e.g., cloth diapers need synthetic detergents for washing, plastic for packaging.

The term “chemical” denotes ingredients of chemical compounds with chemical formulas. Are there compounds that are not made of chemical elements?

2.3 CASE STUDY: AN EYEFUL OF POLYMERS: CONTACT LENSES

PRACTICE

(Page 114)

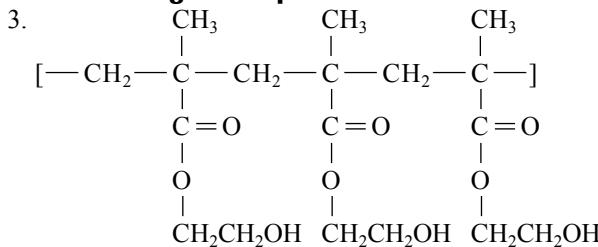
Making Connections

1. (Sample answer) Transparent; refractive properties to enable large corrective factor in a thin lens; sufficiently rigid to keep shape; sufficiently flexible to be comfortable for wearer; permeable to oxygen to nourish eye; chemically unreactive; does not soften and change shape with temperature.
2. (Sample answer) Some polymer molecules such as transparent plastics; some degree of crosslinking to provide rigidity as well as flexibility, and to keep shape with body temperature; selected functional groups to allow interaction with water but not dissolve.

PRACTICE

(Page 115)

Understanding Concepts



4. When a polymer is deformed, its polymer chains are forced out of alignment. Crosslinking pulls the polymer chains back together, returning the lens to its original shape.

Making Connections

5. (Sample answers) Some crosslinking gives the lens elasticity and comfort for the wearer; however, elasticity is at the expense of the lens retaining its shape for correcting vision. A high water content in the lens is needed to provide oxygen to the eye; however, increased water content decreases refractive index of the lens and lowers corrective effect.

PRACTICE

(Page 116)

Understanding Concepts

6. This is a valid statement. Properties of polymers can be changed by altering the type of functional groups and substituted groups on the monomers, and by altering the type of interchain linkages. The possible organic compounds to serve as monomers are almost endless as carbon atoms can form four bonds and can form long carbon chains.

Making Connections

7. (Sample answers) Desirable features include: gas permeable, rigid and easy to maintain, can be worn for long periods of time. Future developments: Design and test polymers with different functional groups and substituted groups, and varying degrees of crosslinking.

SECTION 2.3 QUESTIONS

(Page 116)

Understanding Concepts

1. Hard lenses: Plastic lenses (PMMA) replaced glass lenses for comfort; did not allow sufficient oxygen to reach the eye. Soft lenses: PolyHEMA replaced hard contact lenses, more comfortable and better oxygen permeability; not long-lasting as they were easily deformed. Rigid gas-permeable lenses: New polymer that is gas permeable and retains shape; however, there is an increased risk of protein and lipid deposits on lens. New polymers were developed for rigid

gas-permeable lenses, and research is ongoing to develop new organic compounds with desired properties for use in improving vision and eye care.

Making Connections

2. (Sample answer)

Drug delivery systems, e.g., nicotine patches, estrogen patches.

Problem to be solved: Patients quitting smoking need a bridging program to relieve withdrawal from nicotine; patients requiring estrogen to relieve symptoms due to surgery.

Existing solution: nicotine gum; estrogen capsules. Problems: Patients may forget to take medication. As well, a low but continuous dosage most effective.

Improved solution: Polymers used to provide an adhesive patch on the skin, allowing the nicotine or estrogen to be absorbed through the skin on a continuous basis.

2.4 PROTEINS—NATURAL POLYAMIDES

Try This Activity: Making Chiral Molecules

(Page 117)

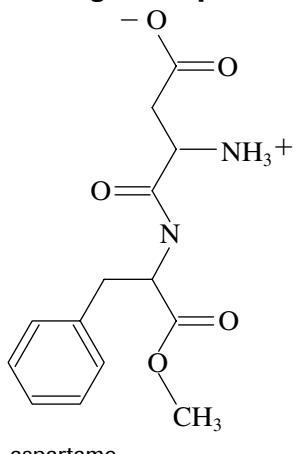
- (a) L-alanine
- (b) D-alanine
- (c) They do not have the same properties because they are structurally different, and are isomers.

PRACTICE

(Page 120)

Understanding Concepts

1. (a)



aspartame

(b) $M_{\text{aspartame}} = 294.34 \text{ g/mol}$

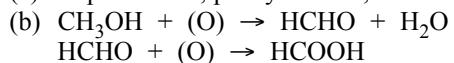
The portion in the aspartame molecule attributable to methanol is CH₃O.

$$m_{\text{CH}_3\text{O}} = 31.04$$

$$\% \text{CH}_3\text{O} = \frac{31.04 \text{ g}}{294.34 \text{ g/mol}} \times 100\%$$

$$\% \text{CH}_3\text{O} = 10.55\%$$

2. (a) Aspartic acid, phenylalanine, methanol (which is further oxidized to formaldehyde and formic acid)



gas-permeable lenses, and research is ongoing to develop new organic compounds with desired properties for use in improving vision and eye care.

Making Connections

2. (Sample answer)

Drug delivery systems, e.g., nicotine patches, estrogen patches.

Problem to be solved: Patients quitting smoking need a bridging program to relieve withdrawal from nicotine; patients requiring estrogen to relieve symptoms due to surgery.

Existing solution: nicotine gum; estrogen capsules. Problems: Patients may forget to take medication. As well, a low but continuous dosage most effective.

Improved solution: Polymers used to provide an adhesive patch on the skin, allowing the nicotine or estrogen to be absorbed through the skin on a continuous basis.

2.4 PROTEINS—NATURAL POLYAMIDES

Try This Activity: Making Chiral Molecules

(Page 117)

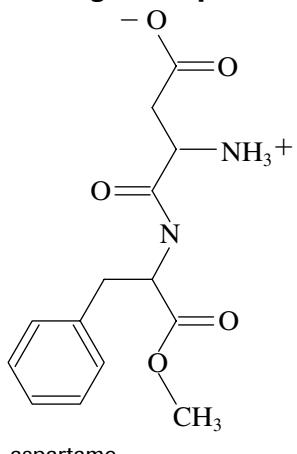
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PRACTICE

(Page 120)

Understanding Concepts

1. (a)



aspartame

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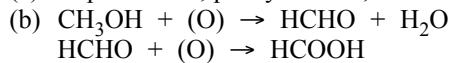
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$$\% \text{CH}_3\text{O} = 10.55\%$$

2. (a) Aspartic acid, phenylalanine, methanol (which is further oxidized to formaldehyde and formic acid)



$$\begin{aligned}
 3. (a) m_{\text{CH}_3\text{OH}} &= 200 \text{ mg} \times \frac{M_{\text{CH}_3\text{OH}}}{M_{\text{aspartame}}} \\
 &= 200 \text{ mg} \times \frac{32.05 \text{ g/mol}}{294.34 \text{ g/mol}} \\
 m_{\text{CH}_3\text{OH}} &= 21.8 \text{ mg} \\
 (b) LD_{50(70 \text{ kg})} &= 0.07 \text{ g/kg} \times 70 \text{ kg} \\
 LD_{50(70 \text{ kg})} &= 4.9 \text{ g} \\
 (c) \text{number of cans of diet pop} &= \frac{4.9 \text{ g}}{21.8 \text{ mg/can}} \\
 &= 220 \text{ cans}
 \end{aligned}$$

Explore an Issue: Take a Stand: Will That Be “Regular” or “Diet”?

(Page 121)

(a) Aspartame:

Reasons for its use: reducing caloric intake, to counter obesity; for sugar-reduced or sugar-free diets, e.g., for diabetic patients; reduce incidence of tooth decay.

Reasons against its use: may have undesirable side effects such as headaches; no nutritive value, may contribute to lower than required intake of minerals and vitamins.

(b) Factors to consider: experimental design, e.g., use of controlled variables; type of system tested, e.g., test done on mice, information transferred to human applications; size of population tested; number of independent research groups reporting findings; funding of the research group, e.g., funded by the manufacturer of the product.

(c) (Sample answer) Risks are still uncertain and debatable; in some cases, benefits outweigh the risks, e.g., sugar-free diets prescribed by doctor; in other cases, should reduce possible risk by keeping daily use of aspartame to a minimum.

Try This Activity: Identifying Fibres by Odour

(Page 123)

(a) Silk and wool fabrics are protein; cotton, linen, and hemp are cellulose; polyester, lycra, and nylon are synthetic.

(b) Matches contain sulfur, which, when burned, confuses the odour of the fabric burning.

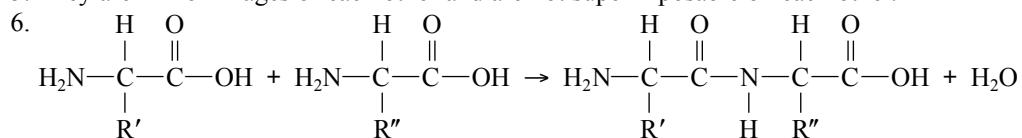
PRACTICE

(Page 124)

Understanding Concepts

4. Proteins are condensation polymers: The carboxyl group of one amino acid reacts with the amino group of another amino acid, forming a peptide bond and eliminating a water molecule.

5. They are mirror images of each other and are not superimposable on each other.



7. Primary structure: the sequence of the amino acids in a polypeptide chain. Secondary structure: the three-dimensional organization of segments of a polypeptide chain; alpha helix or pleated sheet. Tertiary structure: the three-dimensional folding of the alpha-helices and pleated-sheet structures of polypeptide chains. Quaternary structure: several protein subunits may join together. See page 122 in this section for diagrams.

8. Fibrous protein: collagen, function: for structure and strength; structure: long helical chains packed closely together and form crosslinkages. Globular protein: enzymes; function: for mobility throughout the organism; structure: sections of helices and pleated sheets within the same protein attract each other and form a globular shape.

SECTION 2.4 QUESTIONS

(Page 124)

Understanding Concepts

1. The carbon atom in an amino acid has the following attached to it: an amino group, a carboxyl group, a hydrogen, and another substituted group, R. Thus, this carbon atom is attached to four different atoms or groups, making it a chiral molecule. Glycine has two hydrogen atoms attached, and no R group; it is therefore not chiral.
2. Each protein is over hundreds of amino acids in length, arranged in its unique sequence; millions of combinations are possible from 20 amino acids in any sequence.
3. Fibrous proteins are made up of long linear polypeptide chains that can be packed closely together. Interchain attractions such as hydrogen bonding and van der Waals forces are strong and numerous, and, in addition, there may be crosslinkages such as disulfide bonds.
4. A change in primary structure changes the sequence of amino acids, and thus the interactions of amino acids within the same chain. This results in changes in secondary structure, which then changes the tertiary structure.
5. Several protein molecules may join together as a larger unit, e.g., insulin, hemoglobin.
6. (a) covalent bonds: intramolecular linkages; form the peptide bonds. Strong bonds account for the stability of protein molecules.
(b) hydrogen bonds: form between amine groups and carbonyl groups, within different sections of the same protein molecule, or between adjacent molecules. These bonds produce the secondary, tertiary, and quaternary structure of the protein.
(c) van der Waals forces: between sections of the same protein molecule or adjacent molecules. Weaker than the other attractions, but contribute to secondary, tertiary, and quaternary structures.
(d) disulfide bonds: crosslinking between polypeptide chains; gives added strength to the protein.

Applying Inquiry Skills

7. (a) Amount of saccharin fed, percentage of body weight, duration of test, number of rats tested.
(b) Control rats given placebos, researchers are “blind” to identity of test rats, all other conditions identical for test and control rats (food, water, temperature, stress level).
(c) Inconclusive as to health risk to humans: Tests might not have same effects on humans as on rats, as the dosage and body weight of rats and humans not comparable.

Making Connections

8. Enzymes are proteins. When immersed in boiling water, the heat denatures the proteins by disrupting the interchain bonds and altering the secondary, tertiary, and any quaternary structure. Enzyme action and specificity is generally related to protein shape and structure, and a denatured protein loses its enzyme function.
9. Collagen functions as a structural protein, forming tendons and sheets that support soft tissues such as skin and internal organs. The secondary structure of collagen is a triple helix – three chains wound tightly together. Each chain is over 1400 amino acids long, consisting of a primary structure of a repeating sequence – every third amino acid is a glycine that fits perfectly inside the helix.

There are different kinds of collagen molecules, with different tertiary structures. For example, some collagen molecules align side by side to form tough fibrils, like fibres in a rope. These molecules can crisscross cells and serve as pathways for cellular movement during development. Others have a globular head at one end and a tail at the other end; several of these molecules associate at the tails, forming an X-shaped complex. This structure in turn forms an extensive network that suits the function of strong but flexible sheets for supporting internal organs.

10. (Sample answer)
 - (a) Thalidomide was first prescribed as a sedative in 1957, to help combat morning sickness in pregnant women. After the birth of children with deformed limbs and other side effects, the drug was banned. In 1965, a doctor prescribed the drug to a leprosy patient as a sedative, and found surprisingly that it alleviated the swelling. Thalidomide has since been proven effective as an anti-inflammatory drug. The drug also acts to stop the development of blood vessels, thus arresting the development of fetal limbs. This property is tested as a treatment for cancer, AIDS, and other diseases. Other drugs are also being tested as replacements for thalidomide.
 - (b) Thalidomide is a chiral molecule and thus exists as two optical isomers. Laboratory tests showed that one of the isomers was an effective sedative, but the other isomer caused the harmful side effects. It appears that even if only the effective isomer is used, the changes in pH in the body may cause racemizing; that is, the single isomer changes to become a mixture of both isomers. The risk of using thalidomide as a sedative for pregnant women is too high, compared with the cost of developing alternative medications, or with the cost of having no medications available. Proper testing of new medications is essential, at any cost.
 - (c) (Points to include) brief history of use of thalidomide; chemical structure (optical isomers); risks of use; benefits in other treatments; rigour of testing and government control; financial and human cost.

$$\begin{aligned}
 3. (a) m_{\text{CH}_3\text{OH}} &= 200 \text{ mg} \times \frac{M_{\text{CH}_3\text{OH}}}{M_{\text{aspartame}}} \\
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Explore an Issue: Take a Stand: Will That Be “Regular” or “Diet”?

(Page 121)

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(b) Factors to consider: experimental design, e.g., use of controlled variables; type of system tested, e.g., test done on mice, information transferred to human applications; size of population tested; number of independent research groups reporting findings; funding of the research group, e.g., funded by the manufacturer of the product.

(c) (Sample answer) Risks are still uncertain and debatable; in some cases, benefits outweigh the risks, e.g., sugar-free diets prescribed by doctor; in other cases, should reduce possible risk by keeping daily use of aspartame to a minimum.

Try This Activity: Identifying Fibres by Odour

(Page 123)

(a) Silk and wool fabrics are protein; cotton, linen, and hemp are cellulose; polyester, lycra, and nylon are synthetic.

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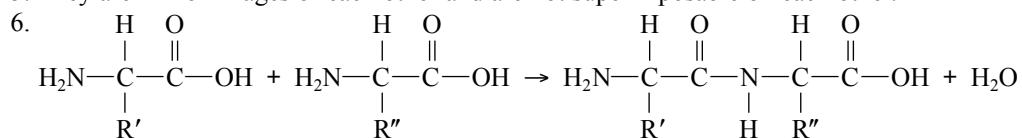
PRACTICE

(Page 124)

Understanding Concepts

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2.5 STARCH AND CELLULOSE—POLYMERS OF SUGARS

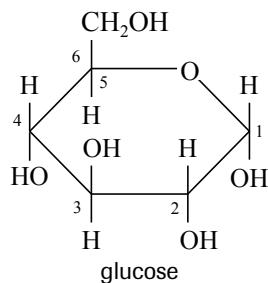
PRACTICE

(Page 128)

Understanding Concepts

1. Both contain carbonyl and hydroxyl groups. In glucose, the carbonyl group forms an aldehyde and in fructose, the carbonyl group forms a ketone.
2. (a) In animals, starch is used for energy and glycogen is used for energy storage. The orientation of the glucose–glucose linkages favours intrachain hydrogen bonds between hydroxyl groups and results in a helical structure. These chains are sufficiently small to make these polysaccharides soluble in water, and easily transported in the organism. Enzymes are present to break down starch and glycogen into glucose.
(b) In plants, starch is used for energy storage and cellulose is used for cell structure and strength in plants. Starch: same answer as (a). The orientation of the glucose–glucose linkages favours interchain hydrogen bonds between hydroxyl groups, which results in a linear structure. These interchain links produce a strong and inflexible structure of layered sheets of cellulose, insoluble in water, ideal for its function.
3. (a) Sugars: monosaccharides or disaccharides, readily soluble in water. Starch: polymers of glucose, soluble in water, requires specific enzymes to be broken down into glucose.
(b) Starch: helical polymer chains of glucose, soluble in water, flexible structure allows ready transport throughout organism. Cellulose: linear polymer chains with interchain hydrogen bonding, rigid and insoluble in water, requires specific enzymes to be broken down into glucose.

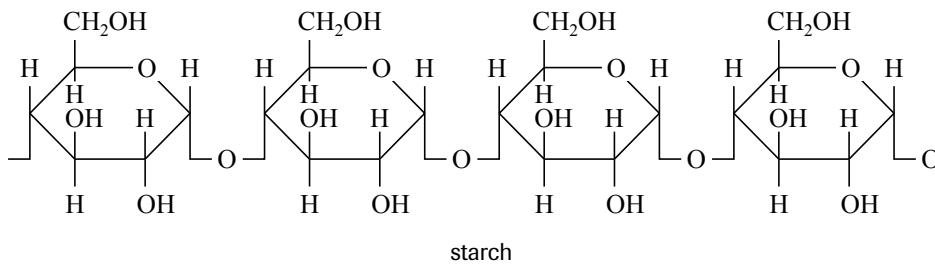
4. (a)



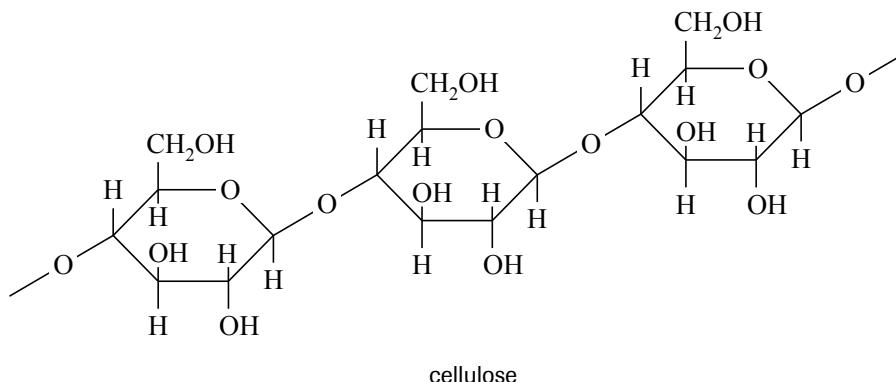
- (b) When the ring structure of a glucose molecule is formed, the OH groups can be fixed either above the ring or below the ring.

5. Molecules of sugars have many hydroxyl groups that are capable of hydrogen bonding with other molecules, resulting in high melting points. The intermolecular attractions in hydrocarbons are mainly the weaker van der Waals forces.

6.



starch



cellulose

The orientation of the attached groups in a glucose ring are fixed, and when glucose molecules form a polymer chain, the monomers added in one orientation produce helical chains (starch), and the monomers added in another orientation produce linear chains (cellulose).

SECTION 2.5 QUESTIONS

(Page 128)

Understanding Concepts

1. (a) glucose
(b) fructose
(c) glucose
(d) sucrose

2. Polysaccharides are condensation polymers. The linkages between monosaccharides in a polysaccharide chain are formed by condensation reactions with the elimination of a water molecule.

3. (a) $C_{12}H_{22}O_{11} + H_2O \rightarrow 2 C_6H_{12}O_6$
(b) $C_{12}H_{22}O_{11} + 12 O_2 \rightarrow 12 CO_2 + 11 H_2O$

4. Glucose has an aldehyde functional group and fructose has a ketone functional group. Since aldehydes can undergo controlled oxidation to acids, and ketones cannot, the glucose is the reducing sugar (because it reduces the oxidizing agent as it itself is oxidized).

5. Propane: hydrocarbon with weak intermolecular attractions (van der Waals forces); low boiling point; gas at room temperature. Rubbing alcohol (2-propanol): an alcohol with some hydrogen bonding between molecules due to presence of a hydroxyl group; higher boiling point than propane; liquid at room temperature. Paint remover (acetone): a ketone with some polar attractions between molecules due to presence of carbonyl group; higher boiling point than propane; volatile liquid at room temperature. Table sugar (sucrose): many hydroxyl groups present, multiple hydrogen bonds between molecules; higher boiling and melting points than propane, 2-propanol, and acetone; solid at room temperature.

6. (a) Potatoes contain starch and our saliva contains an enzyme that is able to break down the starch into its monomers, glucose. The glucose tastes sweet to us.
(b) We do not produce the enzyme required to break down cellulose into glucose, so no glucose is produced in the mouth and grass would not taste sweet to us.
(c) Cows rely on other organisms such as bacteria in their digestive tracts to help digest the cellulose in grass. Cows do not themselves produce the required enzymes in their mouths, and thus the grass would not likely taste sweet when they first chew it.

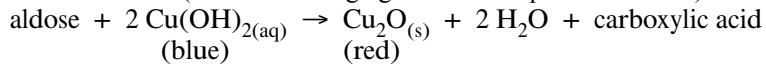
7. Starch and cellulose are both polymers of glucose and, when burned, both produce carbon dioxide and water, with the same amount of energy released. Humans can only break down starch and lack the enzyme to break down cellulose. Thus, cellulose remains unchanged in humans, with no release of energy. Starch can be broken down in humans, with the release of energy.

8. Sugars are small molecules with many hydroxyl groups, making them readily soluble in the aqueous sap. Tree trunks are mainly cellulose, which are long linear polymer chains of glucose, packed tightly together by interchain hydrogen bonds, making them rigid and insoluble in water.

Applying Inquiry Skills

9. Experimental Design

Sugars that contain an aldehyde group can be oxidized by oxidizing agents; ketoses cannot. The sugars can be allowed to react with a weak oxidizing agent (e.g., Cu(OH)₂) and the aldose will cause a change in the oxidizing agent; the ketose will not. (Other oxidizing agents are acceptable answers.)



Materials

An oxidizing agent (commonly Benedict's reagent, solution of Cu(OH)₂), sugars to be tested, test tubes, pipets, hot-water bath.

Procedure

To separate labelled test tubes, add 5 mL Benedict's reagent and 10 drops 1% sugar solution. Place the test tubes in a boiling-water bath and heat for 5 min.

Observations

The aldose sugars such as glucose would produce a red solid with the Benedict's reagent, the ketose sugars such as fructose would not.

Making Connections

10. (Sample answer) Paper or Plastic Bags

Paper:

Advantages—made from renewable resources, e.g., wood fibres; biodegradable and is decomposed in a short time, releasing the atoms and molecules to be recycled; strong; can be reused in many applications, e.g., wrapping parcels, book covers. Disadvantages—can rip easily; becomes soggy when wet; not waterproof.

Plastic:

Advantages—strong and flexible; waterproof; can be reused in many applications, e.g., as garbage bags; less bulky than paper bags when folded for storage; low cost. Disadvantages—made using nonreusable resources; not readily decomposed; takes up landfill sites.

11. (a) The acetylated amino group contains a polar carbonyl group that is capable of forming strong hydrogen bonds with the hydroxyl groups in the polymer. Chitin molecules, being similar to cellulose, are linear and the inter-chain hydrogen bonds pack the polymer chains tightly together, giving the molecule strength and rigidity.

(b) Strong and rigid, insoluble in water (large size) or nonpolar solvents (abundance of polar groups).

(c) Highly suitable as protective covering because of its structural strength and its insolubility in water and nonpolar solvents.

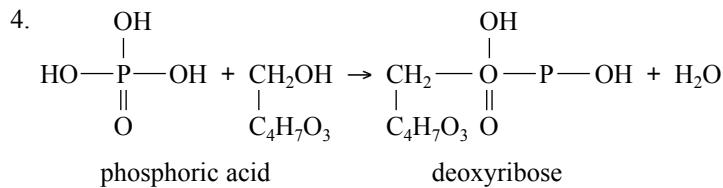
2.6 NUCLEIC ACIDS

PRACTICE

(Page 131)

Understanding Concepts

1. Deoxyribonucleic acid. It carries the genetic information codes for the sequence of amino acids in protein synthesis.
 2. A phosphate group, a five-carbon sugar called ribose, and a nitrogenous base which contains an amino group.
 3. (a) Covalent bonds: formed from condensation reactions between the hydroxyl groups of the phosphate on one nucleotide and the ribose of another nucleotide, forming a ribose–phosphate backbone.
(b) Hydrogen bonds: formed between the NH groups and the C=O groups of the nitrogenous bases from adjacent strands.



5. Its structure allows it to be flexible and coiled into tertiary structures to be stored in the nucleus of the cell. The nucleotides are paired specifically (AT and CG), requiring that one strand in the double helix is an exact opposite copy of the other strand. When each strand is replicated, a new opposite strand identical to its original partner is produced. This mechanism allows the genetic information to be copied and distributed to other cells.

6. (a) Heat, change in pH, and high-energy radiation (e.g., gamma rays, beta rays, X rays, and UV light).
(b) Any change in the DNA sequence causes a change in the sequence of amino acids synthesized in its designated protein. The change in amino sequence results in the synthesis of a different protein or no protein at all; the faulty or absent protein causes a faulty or absent cell function.

SECTION 2.6 QUESTIONS

(Page 132)

Understanding Concepts

1. (a) adenine, guanine, thymine, cytosine
(b) Similarities: They all contain a phosphate group, a ribose, and a nitrogenous base. All four bases are ring structures of carbon and nitrogen, and contain NH groups. They differ in the nitrogenous bases, with A and G having two rings joined together and C and T having a single ring.
 2. RNA is ribonucleic acid. It is similar to DNA and is also involved in protein synthesis. The ribose unit in RNA contains an extra OH group in place of one of the H atoms.

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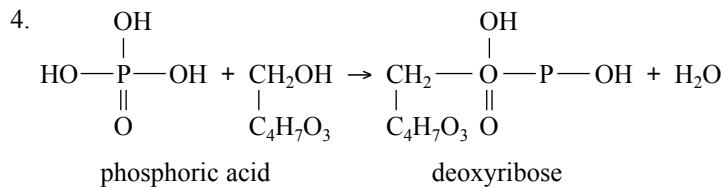
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3. The helical structure allows the DNA molecule more flexibility and the capability of coiling to be stored in a smaller space, the nucleus. This structure also allows the DNA molecule to readily uncoil and be replicated. A linear fibrous structure would give more structural strength, not needed in DNA function, and restrict flexibility.
 4. (a) Hydrogen bonding between groups in different sections of the same DNA strand produces the helical or pleated-sheet secondary structure of a single strand of DNA.
(b) Hydrogen bonding between groups on adjacent strands holds the two strands together, forming a double helix.
 5. Changes in DNA sequence alters its structure, and also alters the sequence of the amino acids in proteins it is coded to synthesize in the cell. This leads to synthesis of incorrect proteins or no proteins; if the missing protein or the faulty section of the protein is essential to cell function, the organism cannot function properly.
 6. Since the number of A = the number of T, and the number of C = the number of G, one might conclude that A and T are always paired, and C and G are always paired.

Applying Inquiry Skills

7. (Sample answers) If each amino acid is coded by 1 nucleotide: 4 nucleotides can code for only 4 amino acids. If each amino acid is coded by 2 nucleotides, we can have AA, AC, AG, AT; CA, CC, CG, CT; GA, GC, GG, GT; TA, TC, TG, TT: total 16 amino acids. Numerically, $4^2 = 16$ combinations, not enough to code for 20 amino acids. If each amino acid is coded by 3 nucleotides, list all combinations beginning with A: AAA, AAC, AAG, AAT; ACA, ACC, ACG, ACT; AGA, AGC, AGG, AGT; ATA, ATC, ATG, ATT; (total 16 combinations). Repeat list combinations beginning with C, then G, then T. Total: $16 \times 4 = 4^3 = 64$ combinations. Therefore, 3 nucleotides assigned per amino acid can code for at least 20 amino acids.

Making Connections

8. (a) Proteins: amino groups and carboxyl groups (carbonyl and hydroxyl groups). Carbohydrates: hydroxyl groups and carbonyl groups. Nucleic acids: hydroxyl groups, amino groups, carbonyl groups.
(b) All form hydrogen bonds between the functional groups listed in (a).
(c) In all the helical structures of these polymers, monomers are linked by strong covalent bonds, giving the polymers stability. Proteins, starch, glycogen, DNA, and RNA are all flexible and mobile in the organism, enabling each polymer to function where needed: proteins such as enzymes where needed, starch and glycogen transported for energy storage or release, and DNA and RNA to replicate or to sites of protein synthesis in the cell.

9. To find out the circuit protected by each fuse, remove the fuses, one at a time, and determine which electrical outlet or electrical appliance no longer functions. (For example, if fuse #1 is removed, and the kitchen outlets and refrigerator are turned off, then fuse #1 must control the circuit for the kitchen and refrigerator.)

10. Minimize time spent in the Sun; wear protective clothing such as hats, long-sleeved shirts, long pants; wear sunscreen; do not use tanning lights.

2.7 FATS AND OILS

PRACTICE

(Page 136)

Understanding Concepts

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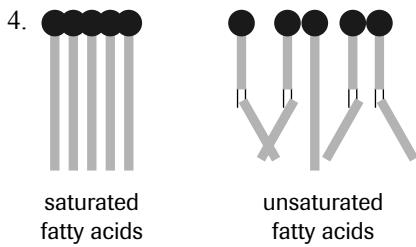
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2.7 FATS AND OILS

PRACTICE

(Page 136)

Understanding Concepts



The presence of double bonds, about which the molecule cannot rotate freely, introduces “bends” into the linear structure. These bends cause the fatty acids to pack less closely together, thus weakening the van der Waals attractions between the fatty acids. The weaker intermolecular attractions account for the lower melting points compared with those of saturated fatty acids.

5. The long hydrocarbon components in fats and oils release large amounts of energy when reacted with oxygen in the cell. The long hydrocarbon chains are bonded as triglycerides, making the melting and boiling points much higher than those of hydrocarbons, and are thus suitable for storage in living systems. The long nonpolar hydrocarbon chains are also insoluble in the aqueous cellular environment, enabling them to be stored undissolved, and mobilized and used as needed.

Applying Inquiry Skills

6. Fats and oils are reacted with a strong base such as NaOH, and heated; the sodium of the fatty acids (soap) and glycerol are produced. Conditions: The fat or oil is heated slowly, with constant stirring, with a concentrated solution of NaOH. The soap formed is precipitated with NaCl and rinsed with a weak acid such as vinegar to remove residual NaOH. Safety precautions include eye protection, a lab apron, no open flames if fat is dissolved in a solvent such as ethanol, and not touching NaOH as it is corrosive to the skin. Take care in handling hot reaction mixture and equipment.

SECTION 2.7 QUESTIONS

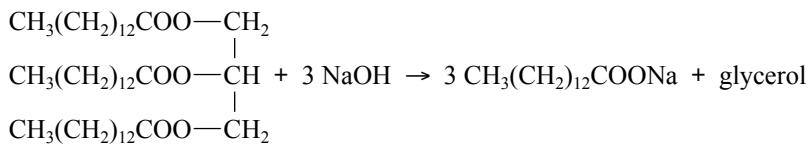
(Page 136)

Understanding Concepts

- Energy storage: e.g., plant oils stored in seeds, animal fat stored under skin. Insulation: animal fat stored under skin serves as insulation for warm-blooded animals such as humans. Solvent: fats and oils act as solvents for fat-soluble vitamins.
- $$3 \text{CH}_3(\text{CH}_2)_{10}\text{COOH} + \text{HOCH}_2\text{CH}_3(\text{CH}_2)_{10}\text{COOCH}_2 + 3 \text{H}_2\text{O}$$

$$\begin{array}{c} | & | \\ \text{HOCH} & \rightarrow \text{CH}_3(\text{CH}_2)_{10}\text{COOCH} \\ | & | \\ \text{HOCH}_2 & \text{CH}_3(\text{CH}_2)_{10}\text{COOCH}_2 \end{array}$$
- (Sample answer) $\text{CH}_3\text{CH}_2\text{CH}=\text{CH}(\text{CH}_2)_{11}\text{COOH}$
- (a) Glycerol is 1,2,3-propanetriol, and triglyceride is the ester formed from the reaction of three fatty acids with glycerol.
(b) Fatty acids are long hydrocarbon chains with a carboxyl group at one end. Fats are triglycerides of fatty acids and glycerol.
(c) Fats are generally solids at room temperature and oils are liquids. Fats generally contain saturated fatty acids and oils contain unsaturated fatty acids.
(d) Lipids include fats, oils, waxes, and steroids.
(e) Esterification is the reaction of an alcohol and a carboxylic acid. Saponification involves the hydrolysis of a fat or oil molecule, forming fatty acids and glycerol. It may be considered the reverse of an esterification reaction.

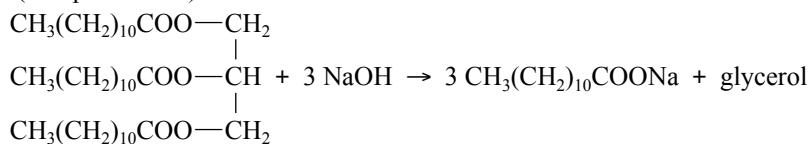
5. (Sample answer)



6. Intramolecular: covalent bonds. Intermolecular: van der Waals attractions between the long hydrocarbon chains in the fatty acids. In oils, the hydrocarbons contain carbon–carbon double bonds, introducing “bends” in the molecule. These “bends” do not allow the fatty acids to pack together as closely as those in unsaturated fatty acids (found in fats). Thus, the more closely packed fats have higher melting points than those of oils, as a result of stronger van der Waals attractions.

7. The polar functional groups in glycerol (hydroxyl groups) and fatty acids (carboxyl groups: carbonyl and hydroxyl groups) are linked together in the esterification reaction. Thus, only a carbonyl group remains in the ester. The long hydrocarbon groups in triglycerides make the molecules insoluble in water.

8. (a) (Sample answer)



(b) Soap molecules have both a polar end (Na) which is soluble in water, and a nonpolar end (the long hydrocarbon chain) which is soluble in fats and oils.

9. (Sample answers)

Polymer	Functional groups	Formation	Function
starch	hydroxyl, carbonyl	condensation reactions	energy storage source
cellulose	hydroxyl, carbonyl	condensation reactions	plant cell structure
proteins	carboxyl, amino	condensation reactions	enzymes, muscle tissue
DNA	amino, hydroxyl, carbonyl	condensation reactions	directs sequence in protein synthesis

Applying Inquiry Skills

10. Experimental Design

Unknown fats or oils are tested for carbon–carbon double bonds using bromine water or potassium permanganate. A change in colour indicates the presence of double bonds.

Materials

eye protection
lab apron
test tubes and racks
potassium permanganate solution

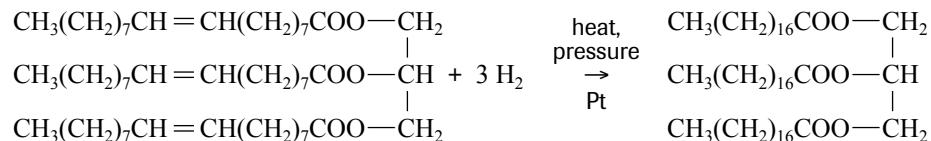
Procedure

- Add 10 drops of an unknown fat or oil into a clean test tube.
- Add 1 drop of the potassium permanganate solution. Shake gently.
- Dispose of materials in labelled containers.

Analysis

A change in colour of the potassium permanganate solution is evidence of an unsaturated fat or oil.

11. A hydrogenation reaction can convert an unsaturated oil into a saturated fat: margarine. Conditions required include high temperature, high pressure, and a catalyst such as powdered platinum.



Making Connections

12. The sodium hydroxide saponifies any fats and oils in the clog, producing the sodium salt of the fatty acids, and glycerol. The sodium salt is soluble in water, and is washed away.
13. (a) Chemical composition of linseed oil: linolenic acid (52–60%); linoleic acid (16–18%); oleic acid (18–20%); stearic acid, leuric acid, and palmitic acid (3%).
- (b) Linseed oil is a yellow to dark amber liquid with a paint-like odour. Its melting point is -19°C , and its boiling point 343°C . It oxidizes very easily, is combustible, and reacts violently with chlorine.

- (c) Linseed oil has several common uses, including as food (as a dietary source of unsaturated fats); as a health supplement (with claims to strengthen the immune system, reverse arteriosclerosis, inhibit tumour formation, and regulate cholesterol levels); and as a solvent for oil-based paints.
 - (d) During processing and storage of linseed oil, avoid excess light and exposure to air; store in dark bottles under constant refrigeration. It is too unstable to be used for frying, or spraying on pans for grilling or basting. Rags soaked in linseed oil may spontaneously combust due to gradual exothermic reaction with oxygen.
 - (e) Linseed oil may be classified as organic (compounds of carbon) as it is made by a plant. It is also natural as it is produced by plants.
14. Olive oil is primarily oleic acid (18 carbons, 1 double bond), which has a melting point of 44.2°C. It is a monosaturated oil, which is the most desirable type of dietary fat, having the effect of lowering LDL cholesterol and total cholesterol levels.

Coconut oil is primarily lauric acid (12 carbons, no double bond), with a melting point of 13.4°C. It is a saturated oil, which is a less desirable type of fat, associated with increased risk of heart disease. It is also thought to increase LDL cholesterol (low-density lipoprotein, or “bad,” cholesterol) and total cholesterol levels, so should make up no more than 7% of total calories in any diet.

Cholesterol has long been thought to have an effect on heart health: LDL is the major cholesterol carrier in the blood. Too much LDL cholesterol in the blood results in a buildup on the artery walls, causing formation of plaque that can clog the arteries. A clot that forms near the plaque can block blood flow to the heart muscle (causing a heart attack) or the brain (causing a stroke).

CAREERS IN CHEMISTRY

PRACTICE

(Page 137)

Making Connections

1. (Answers may vary. Sample answer)

Polymer Chemist

Typical projects for a polymer chemist might include research and development of synthetic polymer for specific consumer needs such as fibres for clothing and carpets, and pharmaceutical work. Attractive features of the job include creativity and innovation, nonroutine and stimulating work, and flexible hours. As well, skills are transferable across industries and locations with chemists working in either academic or industrial settings. Polymer chemists require significant training and education—usually a master’s or doctoral degree in chemistry or a related field. The job might also entail submitting grant proposals for funding research.

CHAPTER 2 LAB ACTIVITIES

INVESTIGATION 2.1.1 IDENTIFICATION OF PLASTICS

(Page 138)

Evidence

- (a) (Sample table)

Sample	Density	Flame colour	Acetone	Melting
1				
2				
3				

Analysis

- (b) Part 1:

In water: Samples that float may be resin codes 2, 4, or 5 (less dense than water, whose density is 1 g/mL); samples that sink may be resin codes 1, 3, or 6.

- (c) Linseed oil has several common uses, including as food (as a dietary source of unsaturated fats); as a health supplement (with claims to strengthen the immune system, reverse arteriosclerosis, inhibit tumour formation, and regulate cholesterol levels); and as a solvent for oil-based paints.
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 - (e) Linseed oil may be classified as organic (compounds of carbon) as it is made by a plant. It is also natural as it is produced by plants.
14. Olive oil is primarily oleic acid (18 carbons, 1 double bond), which has a melting point of 44.2°C. It is a monosaturated oil, which is the most desirable type of dietary fat, having the effect of lowering LDL cholesterol and total cholesterol levels.

Coconut oil is primarily lauric acid (12 carbons, no double bond), with a melting point of 13.4°C. It is a saturated oil, which is a less desirable type of fat, associated with increased risk of heart disease. It is also thought to increase LDL cholesterol (low-density lipoprotein, or “bad,” cholesterol) and total cholesterol levels, so should make up no more than 7% of total calories in any diet.

Cholesterol has long been thought to have an effect on heart health: LDL is the major cholesterol carrier in the blood. Too much LDL cholesterol in the blood results in a buildup on the artery walls, causing formation of plaque that can clog the arteries. A clot that forms near the plaque can block blood flow to the heart muscle (causing a heart attack) or the brain (causing a stroke).

CAREERS IN CHEMISTRY

PRACTICE

(Page 137)

Making Connections

1. (Answers may vary. Sample answer)

Polymer Chemist

Typical projects for a polymer chemist might include research and development of synthetic polymer for specific consumer needs such as fibres for clothing and carpets, and pharmaceutical work. Attractive features of the job include creativity and innovation, nonroutine and stimulating work, and flexible hours. As well, skills are transferable across industries and locations with chemists working in either academic or industrial settings. Polymer chemists require significant training and education—usually a master’s or doctoral degree in chemistry or a related field. The job might also entail submitting grant proposals for funding research.

CHAPTER 2 LAB ACTIVITIES

INVESTIGATION 2.1.1 IDENTIFICATION OF PLASTICS

(Page 138)

Evidence

- (a) (Sample table)

Sample	Density	Flame colour	Acetone	Melting
1				
2				
3				

Analysis

- (b) Part 1:

In water: Samples that float may be resin codes 2, 4, or 5 (less dense than water, whose density is 1 g/mL); samples that sink may be resin codes 1, 3, or 6.

In alcohol solution: Samples that float may be resin codes 4 or 5 (less dense than alcohol solution); samples that sink may be resin code 2.

In oil: Samples that float may be resin code 5 (less dense than resins 4 and 5); samples that sink may be resin code 4.

Part 2:

Flame test: Of possible resin codes 1, 3, or 6, resin code 3 contains chlorine atoms. The sample that produces a green flame is resin code 3.

Part 3:

Acetone test: Of the possible resin codes 1 or 6, resin code 6 softens in acetone. The samples that soften in acetone are resin code 6. The samples that did not soften may be resin code 1.

Part 4:

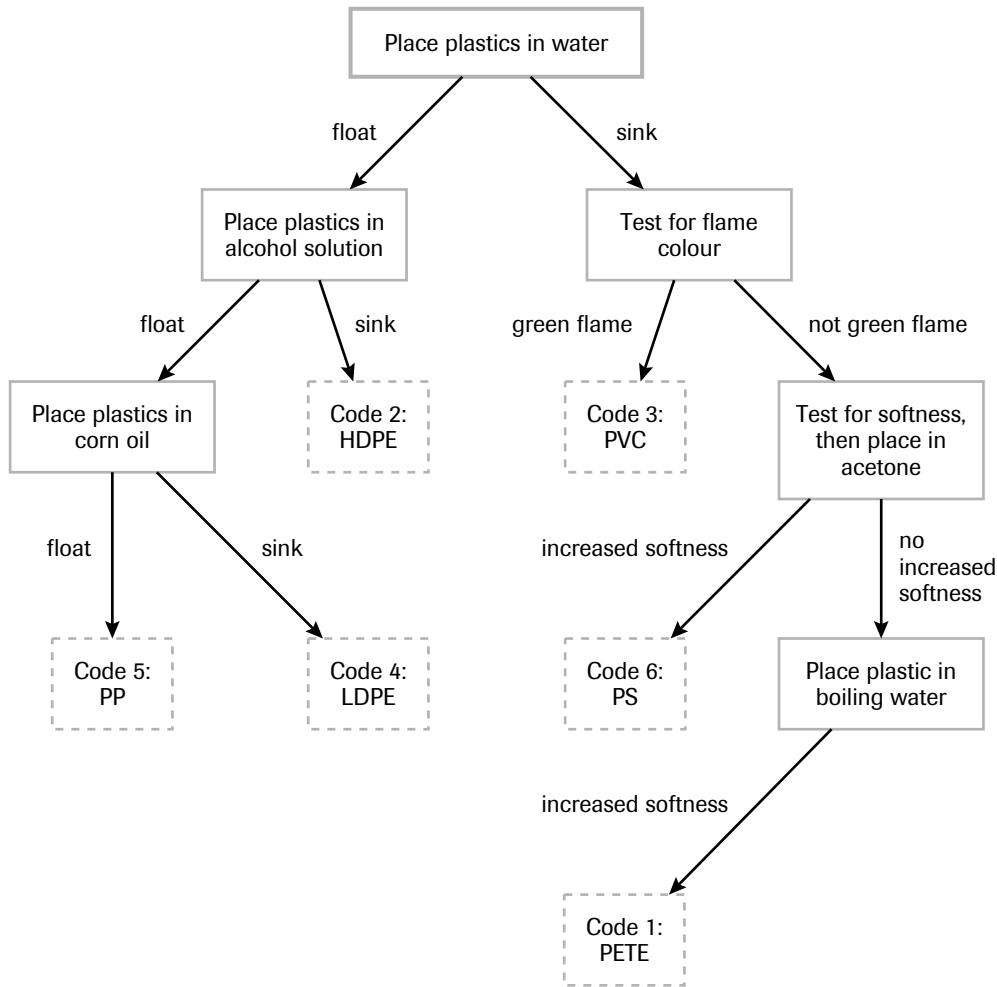
Melting test: possibly resin code 1. If the sample softens in boiling water, this confirms that it is resin code 1.

Evaluation

(c) (Sample answer) Repeat the procedure using known resin samples, codes 1 to 6, to confirm results of tests.

Synthesis

(d)



ACTIVITY 2.1.2 MAKING GUAR GUM SLIME

(Page 140)

- (a) The slime stretches and then returns to its original shape. It is stretchable and flexible.
- (b) The slime breaks.
- (c) The slime breaks with a sharp surface at the break.
- (d) The slime takes on the shape of a long string.
- (e) The slime softens and starts to liquefy.

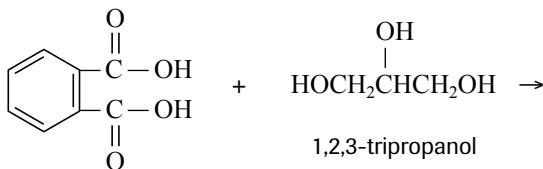
- (f) (a) Crosslinking holds polymer strands together. Any deformation of the slime is restored by the crosslinkages between polymer strands.
 (b) Crosslinking bonds are broken by sharp pulling of the polymer.
 (c) Sharp force on the slime breaks all the crosslinkages along the line of force, leaving the slime broken with a sharp surface.
 (d) As the slime passes gently through the hole of the funnel, some crosslinkages are broken and reformed, leaving the polymer with a new shape.
 (e) The presence of an acid hydrolyzes the interchain crosslinking bonds, resulting in the slime turning into a liquid.

INVESTIGATION 2.2.1 PREPARATION OF POLYESTER—A CONDENSATION POLYMER

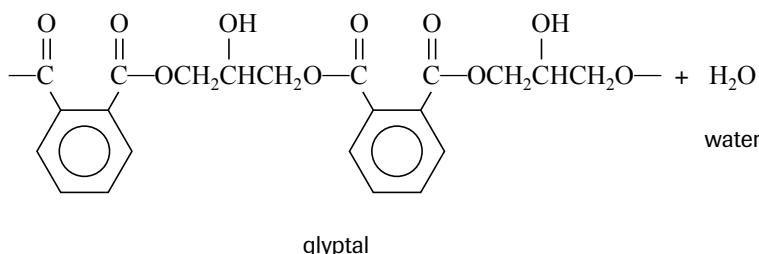
(Page 141)

Prediction

(a)



orthophthalic acid



- (b) The hydroxyl group on carbon 2 in glycerol provides opportunity to form ester bonds with orthophthalic acid, forming strong crosslinkages; therefore, you can predict a hard plastic which does not soften on heating. It will be insoluble in water, but may be soluble in an organic solvent such as acetone.

Analysis

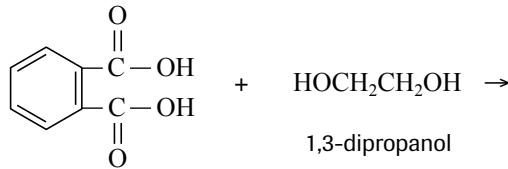
- (c) Sample properties: hard, clear, strong solid; insoluble in water but soluble in acetone (paint thinner or nail polish remover).
 (d) It hardens quickly to form a protective coating that is insoluble in water. It is miscible with organic solvents that may be present in paints.

Evaluation

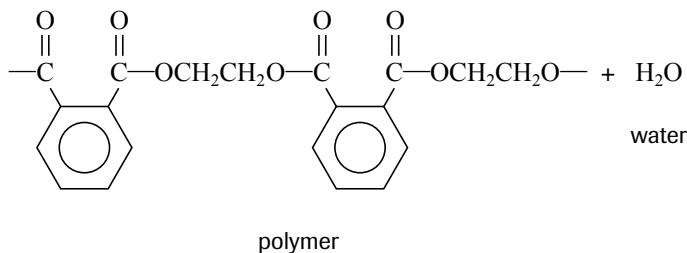
- (e) Heating two component monomers together will produce a polymer with the desired properties.

Synthesis

- (f) 1,2-ethandiol does not contain the extra hydroxyl group that is present on carbon 2 of glycerol. Thus, it is not capable of forming strong covalent bonds as crosslinkages between polymer chains. The prediction should be that this product is not as strong and hard as Glyptal, and softens on heating.



orthophthalic acid

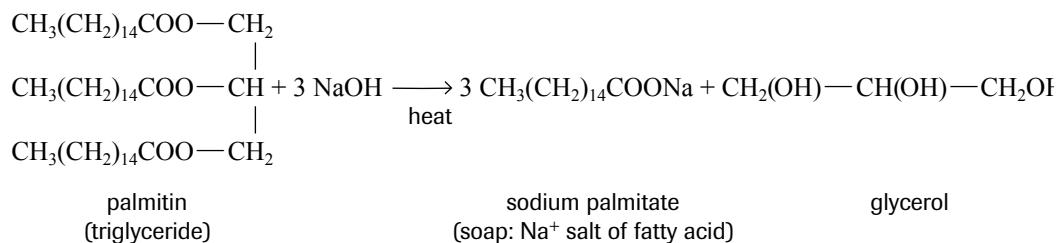


ACTIVITY 2.7.1 MAKING SOAP

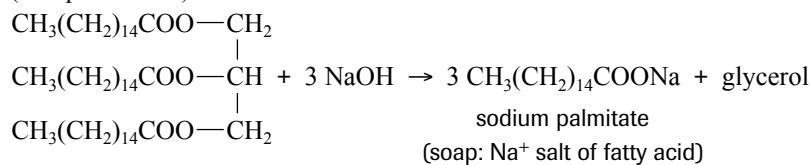
(Page 143)

Analysis

- (a) In saponification, an ester bond is broken and a carboxylic acid (salt) and an alcohol are recovered. In esterification, a carboxylic acid and an alcohol react to form an ester bond.
- (b) If difference exists, it may be explained by differences in saturation of fats and oils and intermolecular forces in saturated and unsaturated hydrocarbon components of fatty acids.
- (c) Soap molecules have a polar end (the ion end) and a nonpolar end (the hydrocarbon end).



- (d) (Sample answer)



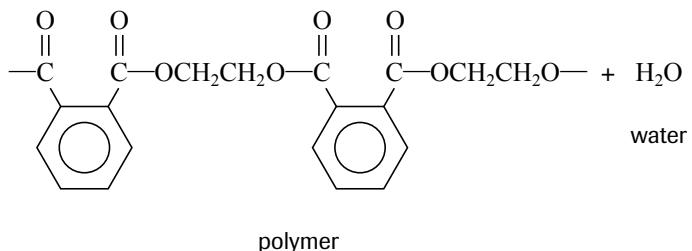
- (e) Filtrate may contain NaCl, NaOH, vinegar, and glycerol.

CHAPTER 2 SUMMARY

Make a Summary

(Page 144)

Polymer	Monomer(s)	Example	Structure	Properties
synthetic polyesters	ester			
synthetic polyamides	amide			
proteins	amino acids			
nucleic acids	sugar, base phosphate			
carbohydrates	monosaccharides			

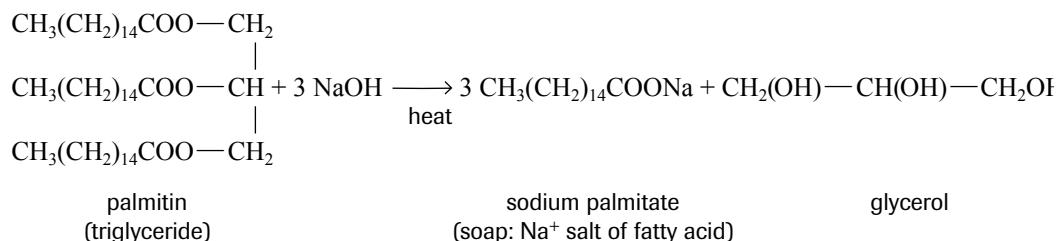


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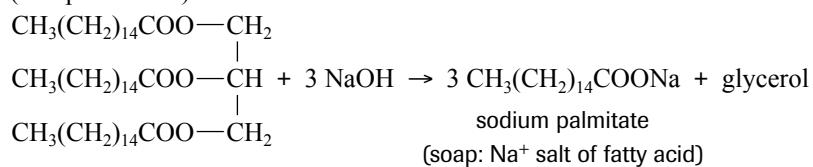
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- (d) (Sample answer)



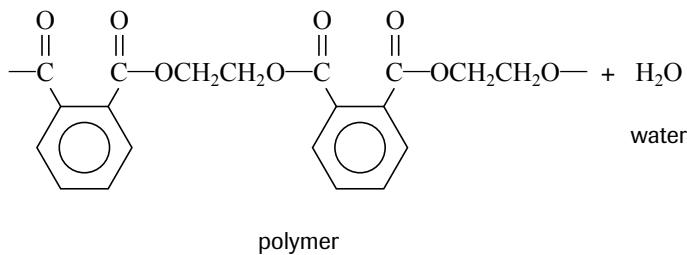
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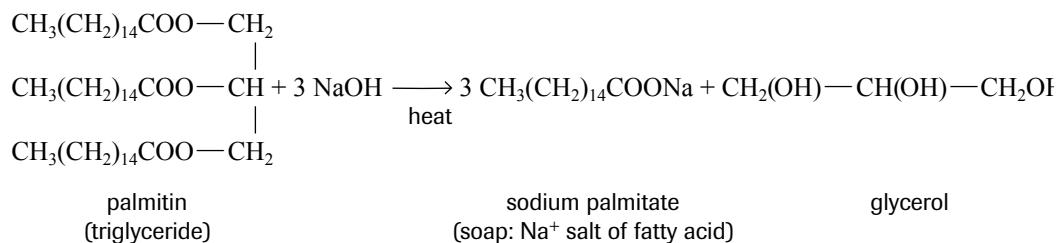


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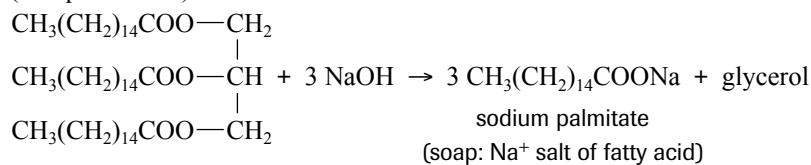
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- (d) (Sample answer)



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synthetic polyamides	amide			
proteins	amino acids			
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carbohydrates	monosaccharides			

CHAPTER 2 SELF-QUIZ

(Page 145)

1. False: Polymers such as nylon are formed from monomer subunits that may be identical or may be different.
2. True
3. True
4. False: Amino acids contain a carbon atom attached to a carboxyl group and an amino group.
5. False: Starch and cellulose are polysaccharides of the monosaccharide glucose; sucrose is a disaccharide of glucose and fructose.
6. (d)
7. (d)
8. (b)
9. (e)
10. (c)
11. (d)
12. (b)
13. (b)
14. (a)
15. (c)

CHAPTER 2 REVIEW

(Page 146)

Understanding Concepts

1. $\text{CH}_2=\text{CH}_2\text{CN}$
2.
$$\begin{array}{c} \text{O} \quad \text{O} \\ || \quad || \\ [-\text{OCHC}-\text{OCHC}-] \\ | \quad | \\ \text{CH}_3 \quad \text{CH}_3 \end{array}$$
3. (a) Crosslinking restores the polymer strands to their original position, after any stretching or other deformation; this makes the polymer elastic.
(b) For crosslinking to occur, a monomer must be able to form bonds other than the bonds forming the polymer chain itself; that is, it must have an additional functional group (e.g., double bond, hydroxyl group, carboxyl group), other than the two involved in the polymer linkages, to link with another polymer chain.
4. (a) There will be hydrogen bonding between the hydroxyl group and the carbonyl group, both intrachain and interchain. The molecule may have a helical structure.
(b) There will be little bonding interaction within the same chain, although the molecules can form crosslinkages between chains from addition reactions of the double bond. The polymer may have a strong elastic structure.
(c) There will be hydrogen bonding between the amino group and the carbonyl group, both intrachain and interchain. The molecule may have a helical structure.
5. (Model-building exercise)
6. (a) (Model-building exercise)
(b) This compound will be a condensation polymer. The carboxyl groups can react in condensation reactions with a monomer with two hydroxyl groups or two amino groups. There are no double bonds to form an addition polymer.

CHAPTER 2 SELF-QUIZ

(Page 145)

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6. (d)
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9. (e)
10. (c)
11. (d)
12. (b)
13. (b)
14. (a)
15. (c)

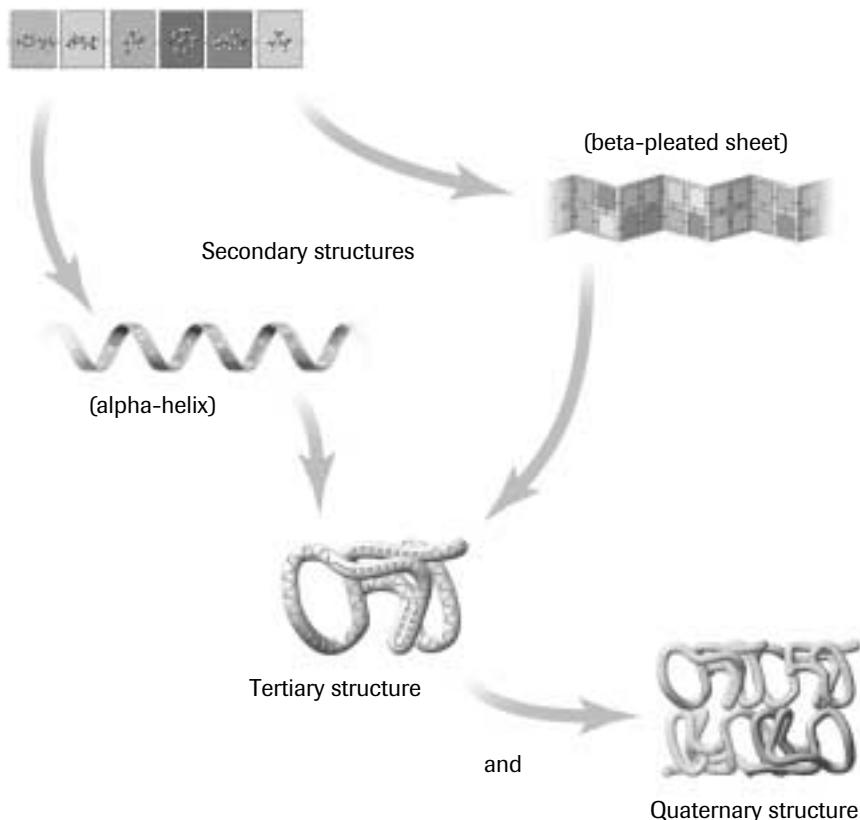
CHAPTER 2 REVIEW

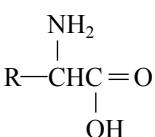
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5. (Model-building exercise)
6. (a) (Model-building exercise)
(b) This compound will be a condensation polymer. The carboxyl groups can react in condensation reactions with a monomer with two hydroxyl groups or two amino groups. There are no double bonds to form an addition polymer.

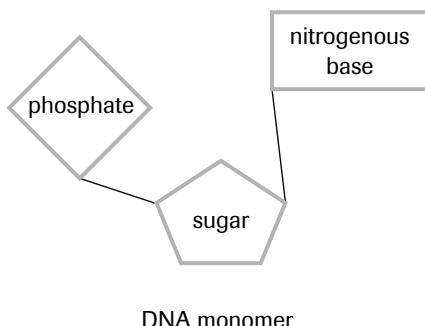
7. (a) Primary structure



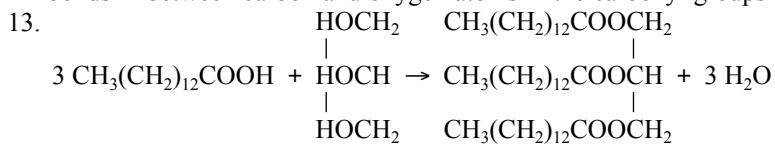


amino acid

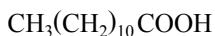
- (b) DNA is made up of nucleotides, each of which contains a phosphate group, a deoxyribose group, and one of four nitrogenous bases.



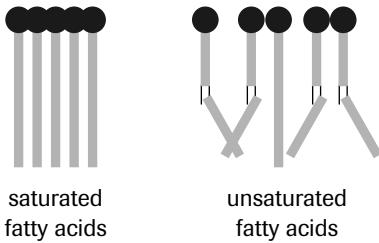
11. (a) hydroxyl groups; condensation reaction
 (b) hydroxyl and carboxyl groups; esterification reaction
12. There are carbon–carbon double bonds in the hydrocarbon portion of the fatty acid chains. There are also double bonds in between carbon and oxygen atoms in the carbonyl groups in the ester linkages.



14. (a) $\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOH}$



- (b) It is likely an oil at ordinary room temperatures because it is unsaturated.



15. (a) The fats in lard contain fatty acids that have a large hydrocarbon component; thus, they burn with amounts of heat released similar to those of burning hydrocarbons. Table sugar is sucrose, which is a carbohydrate and does not release as much heat as hydrocarbons do.
 (b) We do not have the enzymes specific to breaking down the cellulose molecules in paper and thus cannot derive any energy from ingesting paper. When paper is burned, the cellulose molecules are oxidized to carbon dioxide and water, with a release of energy.

Applying Inquiry Skills

16. (a) Softening on heating: If polymer chains are held together by weak van der Waals attractions, the energy from heating weakens the attractions, and the polymer softens. If crosslinking is present, the polymer does not readily soften on heating.
 (b) Softening in acetone: Polymers containing carbonyl groups tend to be softened by acetone as this organic solvent also contains a carbonyl group.
 (c) Strength and rigidity, flame test with copper wire: The strong carbon–halogen bonds make the polymer very strong and chemically unreactive. When a hot copper wire is pressed into the polymer, a green flame indicates the presence of halogen atoms (which forms a halide ion of copper that produces the flame colour).
17. (a) Detergent has a polar end and a nonpolar end, and thus dissolves the fatty molecules as well as itself dissolving in the water molecules.

- (b) Heating the DNA weakens the hydrogen bonds holding each DNA strand in a tightly coiled helix, as well as the hydrogen bonds holding the two strands together in the double helix.
- (c) Cooling solidifies the dissolved fat and protein contaminants, so that they can be removed in the next step. It also stops possible denaturation of the DNA.
- (d) DNA is soluble in water by virtue of its many polar phosphate groups which form its backbone. While ethanol has a hydroxyl group which makes it soluble in water, the presence of its methyl group makes it more nonpolar than water. DNA is thus insoluble in this less polar solvent.

18. (Sample answer)

Experimental Design

Compare the viscosity of the two oils at different temperatures. The less saturated oil likely has weaker intermolecular forces, and thus would be less viscous.

Materials

2 large test tubes with rubber stoppers
marbles of equal size and mass
hot-water bath
timer
thermometer

Procedure

1. Place a marble in each test tube. Fill one labelled test tube with olive oil and the other with coconut oil. Stopper securely.
2. Invert the two test tubes, and record the time taken for the marble to travel to the bottom of the tube.
3. Place the tubes in the hot-water bath and raise the temperature of the test tubes and oils by 5°C.
4. Repeat the procedure for timing the marble. Repeat for several temperature increases.

Analysis

If there is a difference in time taken for the marble to travel down the two different oils, the faster time indicates the less viscous oil, which indicates the more unsaturated oil.

Making Connections

19. (Sample answers)

Synthetic polymer	Use	Monomer	Type of reaction
polyethene	fabrics	ethene	addition reaction
polypropene	rope	propene	addition reaction
polystyrene	foam cups	styrene	addition reaction
nylon	fabrics	dicarboxylic acids and diamines	condensation reaction
Dacron	fabrics	dicarboxylic acids and diamines	condensation reaction

20. (Sample answer) Nylon is a synthetic polymer similar to the natural polymer, silk. Nylon is stable, strong, easy to care for, and affordable. Nylon is made from petroleum products from nonrenewable sources, and is nonbiodegradable.

Cotton was the inspiration for polyester. Polyester is strong, wrinkle-free, and affordable; cotton is more comfortable to wear and is made from renewable materials; polyester is made from petroleum products from nonrenewable sources, and is nonbiodegradable.

Sugar is sweet; so is aspartame. However, sugar is high in calories and linked to tooth decay; aspartame may be linked to health risks, and has an aftertaste. Diabetics cannot ingest sugar but can use aspartame for sweetening foods.

21. (a) Plastic is stronger because it can be designed with strong crosslinkages between the polymer strands. Paper is made of cellulose which are fibrous strands of glucose polymers; the crosslinkages may not be as strong as in plastics.
- (b) Paper may be more quickly decomposed by bacteria which contain enzymes to hydrolyze cellulose. Plastics do not readily break down as this would require the breaking of the covalent bonds holding the monomers together.
- (c) (Sample answer) Paper bags are correctly labelled as organic (as they are made of molecules containing carbon atoms), as natural (as they are made from wood, made by plants), and as chemical (molecules are made of elements). Plastic bags are correctly labelled as organic (made of molecules containing carbon atoms), not as natural (because synthesized in a laboratory or factory), and as chemical (made from chemicals). In general usage, the term “natural” may be applied to paper bags and the term “chemical” to plastic bags.

22. (a) Flour, cork, and jute are plant materials that are mainly cellulose; as these are main ingredients of linoleum, it may be classified as a polymer. All the ingredients are natural; all except the limestone dust are synthesized by living organisms and thus may be classified as organic (carbon-containing compounds). All matter is composed of chemicals, so the linoleum is also chemical.
- (b) The linseed oil, a major ingredient, is a mixture of oils that are esters of fatty acids and alcohols. These ester linkages can be hydrolyzed by strong bases such as high pH cleaning agents, in saponification reactions.
- (c) Advantages: easily decomposed, atoms in materials are recycled when decomposed, does not require nonrenewable resources.
 Disadvantages: the linoleum floor is vulnerable to attack by bacteria or mould, can readily decompose if conditions such as moisture are not controlled, and it is not long-lasting or durable.
- (d) You might want to consider such factors as:
 is it a high-traffic area?
 is it likely to remain damp for extended periods?
 appearance
 availability
 cost
23. (a)
- $$\begin{array}{c} \text{O} & \text{NH}_2 \\ || & | \\ \text{H}_2\text{NCCH}_2\text{CH}_2\text{CHCOONa} \end{array}$$
- (b) Yes. Carbon 2 is attached to 4 different groups or atoms: H, NH₂, COONa, and CH₂CH₂C(O)NH₂. It is, therefore, a chiral molecule.
- (c) There is some evidence that a small portion of the population experiences mild reactions to MSG. These are not classified as allergies, but as a sensitivity or intolerance; they include: effects to the heart, respiratory tract, muscles, eyes, skin, gastrointestinal tract, circulation, and neurological functions. Drinking alcohol or exercising just before or after ingesting MSG may increase the intensity of the adverse reaction.

UNIT 1 PERFORMANCE TASK: CHEMISTRY IN A BATHTUB

(Page 148)

1 Research, Plan, and Synthesize an Ester

Experimental Design

- (a) (Answers may vary. Sample answer) Ethyl butanoate is one ester which could be synthesized. It has a pineapple flavour.
- (b) Butanoic acid + ethanol → ethyl butanoate
 $\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH} + \text{CH}_3\text{CH}_2\text{OH} \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{COOCH}_2\text{CH}_3 + \text{H}_2\text{O}$
 Butanoic acid is heated with ethanol, in the presence of concentrated sulfuric acid as a catalyst, to produce ethyl butanoate. A water molecule is also produced in this condensation reaction, called esterification. As the ester has a low solubility in water, it can be extracted from the reaction mixture by adding the mixture to water and removing the layer of ester floating on the water surface.

Materials

- (c)
- (c) ethanol
 - butanoic acid
 - concentrated sulfuric acid
 - 2 test tubes
 - hot-water bath (large beaker of water over hot plate)
 - hot plate
 - pipette and suction bulb
 - evaporating dish
 - eyedropper

Safety Precautions

Eye protection and a lab apron must be used at all times. Also, conduct experiment in a fume hood.

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- (c) Advantages: easily decomposed, atoms in materials are recycled when decomposed, does not require nonrenewable resources.
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 - 2 test tubes
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 - hot plate
 - pipette and suction bulb
 - evaporating dish
 - eyedropper

Safety Precautions

Eye protection and a lab apron must be used at all times. Also, conduct experiment in a fume hood.

Procedure

(d)

1. Put on the lab apron and eye protection.
2. Prepare a hot-water bath by half-filling a large beaker (500 mL) with water and heating it on a hot plate until a gentle boil is reached.
3. In a test tube, place 2 mL of ethanol and 2 mL of butanoate.
4. Take the test tube to the fume hood, and add 1 mL of concentrated sulfuric acid. Concentrated sulfuric acid is extremely corrosive to the skin and must be handled with care.
5. Take the test tube to the lab bench and carefully place the tube in the hot-water bath, being careful not to point the tube at anyone.
6. Heat for about 5 min; remove the tube from the heat and let cool.
7. Pour the contents of the test tube into an evaporating dish half-filled with cold water.
8. Use an eyeglass dropper to collect the ester floating on the surface of the water; place the ester in a clean test tube.
9. Dispose of remaining reaction mixture and water in the sink and flush with water.

3 Prepare a Product Information Package

(e) (Sample answer) Materials used: an alcohol of choice, a carboxylic acid of choice, citric acid, cornstarch, sodium hydrogen carbonate, vegetable oil of choice, Styrofoam box, silk ribbon. (Other suggestions: cotton bag, nylon string, Styrofoam cup or packing beads, jute rope, Saran wrap, glue, cellophane)

- Chemical names for each compound: ethanol, ethanoic acid (acetic acid, vinegar), 2-hydroxy-1,2,3-propane tricarboxylic acid (citric acid), $\text{HOC}(\text{CH}_2\text{COOH})_2\text{COOH}$, sodium hydrogen carbonate (sodium bicarbonate).
- Each chemical by organic family: ethanol (alcohol), ethanoic acid (carboxylic acid), citric acid (carboxylic acid), cornstarch (carbohydrate, condensation polymer), sodium hydrogen carbonate, vegetable oil of choice (ester), Styrofoam (polystyrene, addition polymer), silk ribbon (protein, condensation polymer).
- Physical properties of each compound: ethanol (soluble in water, alcohol odour, relative high boiling point, liquid at room temperature), ethanoic acid (soluble in water, sour odour, relative high boiling point, less volatile than analogous alcohol, liquid at room temperature), citric acid (soluble in water, sour taste, relatively high melting point and boiling point, solid at room temperature), cornstarch (soluble in water, solid at room temperature), sodium hydrogen carbonate, vegetable oil of choice (insoluble in water, liquid at room temperature), Styrofoam (insoluble in water, lightweight, chemically unreactive), silk ribbon (insoluble in water, shrinks (denatures) when heated).
- (Sample answers)

Nonpolymers:

ethanol (The hydroxyl group renders this compound soluble in water; intermolecular hydrogen bonding accounts for its high boiling point.)

ethanoic acid (The hydroxyl group and carbonyl group on the carboxyl group renders this compound soluble in water; strong intermolecular hydrogen bonding of the two types of polar groups accounts for the high boiling point of this acid.)

citric acid (Each molecule of this acid contains three carboxyl groups and one hydroxyl group; the abundance of polar groups for hydrogen bonding accounts for the very high melting point of this acid, which is a solid at room temperature.)

Natural polymer:

cornstarch (Starch is a helical polymer of glucose monomers; the helical structure allows flexibility and mobility, and renders the starch molecule soluble in water.)

Synthetic polymer:

Styrofoam (Polystyrene is an addition polymer of styrene; long polymer chains, weak interchain attractions account for low rigidity.)

- The citric acid is a solid organic acid which, when dissolved in the bath water, will react with an inorganic base, the sodium hydrogen carbonate, to produce carbon dioxide as one of its products. The carbon dioxide produces the fizzing in the water. Safety concerns: ensure that the ester used is free of contaminants (e.g., concentrated acid) from its synthesis.
- Student choice, justified by definitions of terms.

UNIT 1 SELF-QUIZ

(Page 150)

1. False: Carbonyl groups are present in alcohols, aldehydes, ketones, and esters. They are not present in ethers.
2. True
3. False: The formation of an alcohol when an alkene reacts with water in the presence of an acid is an example of an addition reaction.
4. False: Benzene *does not react* readily with bromine in addition reactions. *Bromine can only be added to a benzene ring by substitution reactions.*
5. False: When methanol and vinegar are allowed to react, *methyl ethanoate* and water are produced from the esterification reaction.
6. True
7. False: 1,2-dibromoethane can be produced from the *addition* reaction of bromine with ethene.
8. False: Polybutene is formed from addition reaction of butene monomers, and the polymer chain consists of carbon atoms single bonded to each other, with ethyl groups attached to *alternate* carbon atoms in the chain.
9. False: Condensation polymers such as *nylon* may have physical properties such as flexibility and strength as a result of the degree of crosslinkages present in the polymer. (*Polystyrene and polypropylene are addition polymers.*)
10. True
11. (d)
12. (e)
13. (b)
14. (e)
15. (d)
16. (c)
17. (c)
18. (d)
19. (d)
20. (a)
21. (c)
22. (d)
23. (c)
24. (b)
25. (e)
26. (e)

UNIT 1 REVIEW

(Page 152)

Understanding Concepts

1. (a) alcohol
(b) carboxylic acid
(c) aldehyde
(d) ether
(e) amine
(f) ketone
(g) ester
(h) amide
(i) ketone
(j) carboxylic acid
2. (a) carbonyl
(b) carbonyl
(c) hydroxyl
(d) carbon–carbon double bond

UNIT 1 SELF-QUIZ

(Page 150)

1. False: Carbonyl groups are present in alcohols, aldehydes, ketones, and esters. They are not present in ethers.
2. True
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11. (d)
12. (e)
13. (b)
14. (e)
15. (d)
16. (c)
17. (c)
18. (d)
19. (d)
20. (a)
21. (c)
22. (d)
23. (c)
24. (b)
25. (e)
26. (e)

UNIT 1 REVIEW

(Page 152)

Understanding Concepts

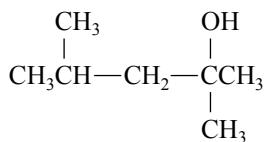
1. (a) alcohol
(b) carboxylic acid
(c) aldehyde
(d) ether
(e) amine
(f) ketone
(g) ester
(h) amide
(i) ketone
(j) carboxylic acid
2. (a) carbonyl
(b) carbonyl
(c) hydroxyl
(d) carbon–carbon double bond

(e) carbonyl (amide linkage)

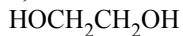
(f) (ether linkage)

(g) carbonyl (ester linkage)

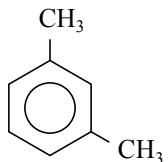
3. (a) 2,4-dimethyl-2-pentanol



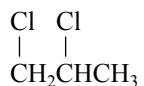
(b) 1,2-ethandiol



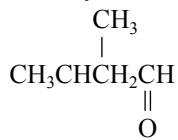
(c) 1,3-dimethylbenzene



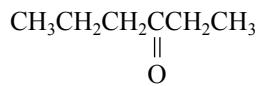
(d) 1,2-dichloropropane



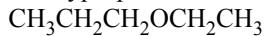
(e) 2-methylbutanal



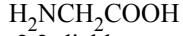
(f) 3-hexanone



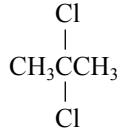
(g) ethoxypropane



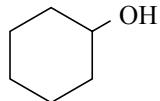
(h) 2-aminoethanoic acid



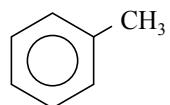
(i) 2,2-dichloropropane



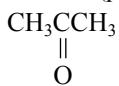
(j) cyclohexanol



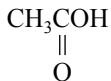
4. (a) toluene (methylbenzene)



(b) acetone (propanone)



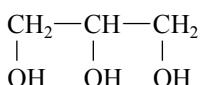
- (c) acetic acid (ethanoic acid)



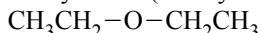
- (d) formaldehyde (methanal)



- (e) glycerol (1,2,3-propanetriol)



- (f) diethyl ether (ethoxyethane)



5. (a) carbonyl group; carbon–carbon double bond; hydroxyl group

- (b) carboxyl group

- (c) amino group

6. (a) ethoxyethane, propanone: The carbonyl group in the ketone makes it more polar and thus it has stronger intermolecular attractions.

- (b) ethanol, ethanoic acid: The acid has an additional hydroxyl group that the aldehyde does not have, making it more polar and capable of hydrogen bonding; thus, the acid has stronger intermolecular attractions.

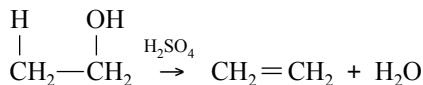
- (c) ethanol, 1-pentanol: Both molecules have a polar hydroxyl group, but the longer hydrocarbon chain in the pentanol increases its intermolecular van der Waals attractions.

7. (a) benzene, benzoic acid: The carboxyl group in benzoic acid makes it more polar and capable of hydrogen bonding with water; thus, the acid is more soluble in water.

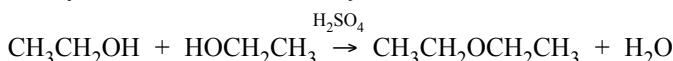
- (b) methyl ethanoate, ethanoic acid: The ester is less soluble in water than is the acid because the acid has a carbonyl group and a hydroxyl group capable of hydrogen bonding with water, but in the ester, the hydroxyl is lost, having been bonded in the ester linkage; thus, the acid is more soluble in water.

- (c) 2-butanone, 2-butanol: The ketone has a carbonyl group, but the alcohol has a hydroxyl group that can hydrogen bond with water and is therefore more soluble in water.

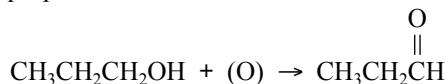
8. (a) ethene from ethanol: dehydration, elimination



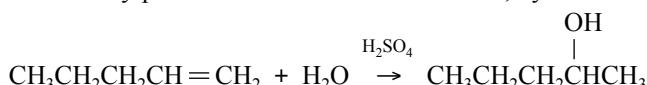
- (b) ethoxyethane from ethanol: dehydration, condensation



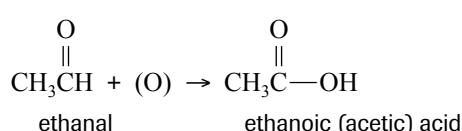
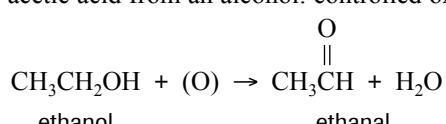
- (c) propanal from an alcohol: controlled oxidation



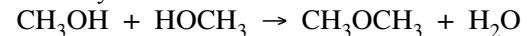
- (d) a secondary pentanol from an alkene: addition, hydration



- (e) acetic acid from an alcohol: controlled oxidation



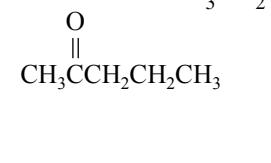
(f) methoxymethane from methanol: condensation



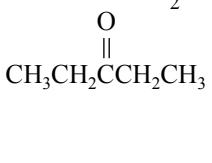
(g) ethyl formate from ethanol and methanoic acid: esterification



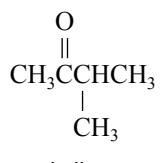
9. (a)



2-pentanone

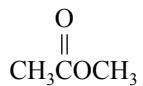


3-pentanone



3-methylbutanone

(b)



methyl ethanoate

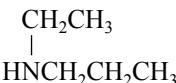


ethyl methanoate

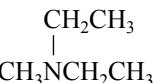
(c)



n-pentylamine
(1-aminopentane)

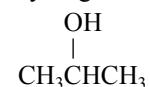


ethylpropylamine
N-ethyl-1-aminopropane

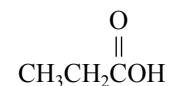


diethylmethylamine
N-ethyl-*N*-methyl-1-aminoethane

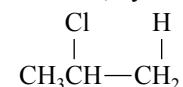
10. (a) hydrogenation



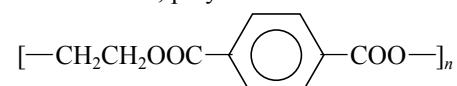
(b) controlled oxidation



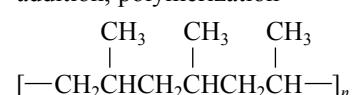
(c) addition, hydrohalogenation



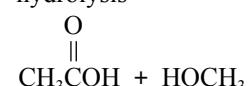
(d) condensation, polymerization



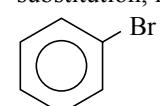
(e) addition, polymerization



(f) hydrolysis

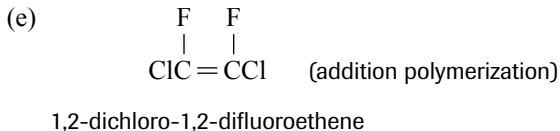
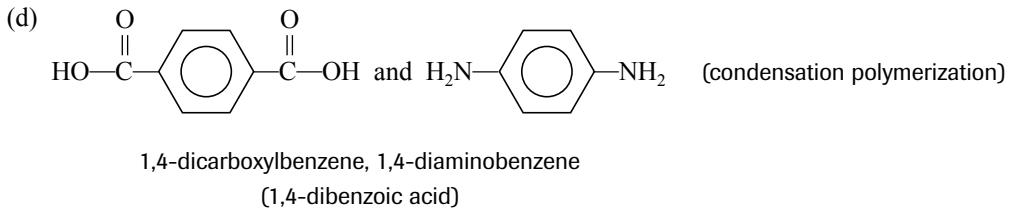
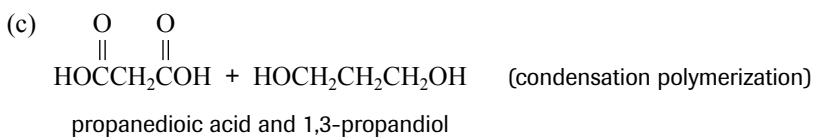


(g) substitution, halogenation

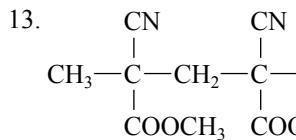
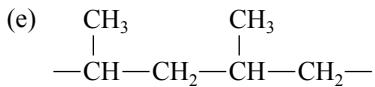
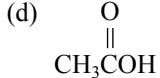
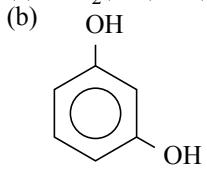
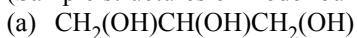


11. (a) HOCH₂CH₂COOH (condensation polymerization)
3-hydroxypropanoic acid

(b) CH₃CH=CH₂ (addition polymerization)
propene



12. (Sample structures of model-building activity)

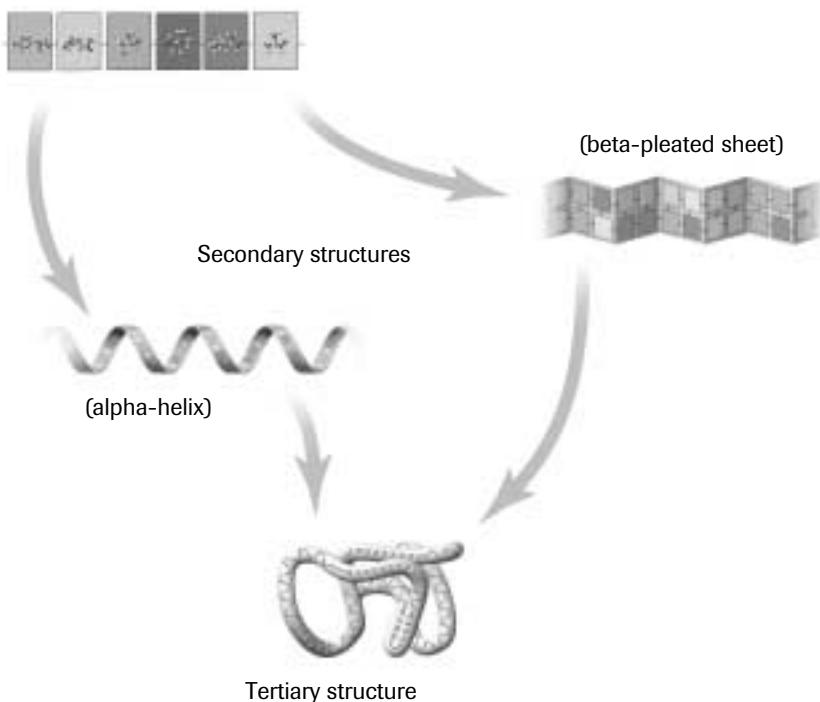


14. In inorganic compounds, the combining ratio of elements is restricted; so a limited number of compounds is possible. In organic compounds, carbon can form four bonds, and bond with other carbon atoms in straight chains, branched chains, or cyclic structures; thus, the possibilities for new compounds are much greater. For example, name specific examples of: new medicines, new synthetic materials for medical procedures, materials for preventing or cleaning up hazardous spills, materials for safety equipment or clothing.

15. (a) Starch is used in plants for energy storage and source. The orientation of the glucose–glucose linkages favours intrachain hydrogen bonds between hydroxyl groups, resulting in a helical structure. These chains are sufficiently small to make these polysaccharides soluble in water, and easily transported in the organism. Enzymes are present to break down starch into glucose.
- (b) Glycogen is used in animals for energy storage and source. The orientation of the glucose–glucose linkages is similar to that in starch, with more branching, and favouring intrachain hydrogen bonds between hydroxyl groups, resulting in a helical structure. Similar to starch, glycogen is also soluble in water, and easily transported in the organism. Enzymes are present in animals to break down glycogen into glucose.

- (c) Cellulose is used for cell structure and strength in plants. The orientation of the glucose–glucose linkages favours interchain hydrogen bonds between hydroxyl groups, resulting in a linear structure. These interchain links produce a strong and inflexible structure of layered sheets of cellulose, insoluble in water, ideal for its function.
16. (Sample answer) Possible arguments: Genetically modified organisms are not natural because altered from natural state; plants are by definition natural and organic, whether the genes were modified or not; “organic” because no synthetic fertilizers and pesticides were used. Corn is composed of organic compounds such as carbohydrates, proteins, and fats and oils; thus, natural products such as corn are not chemical. Cereal is chemical because all matter is made of chemicals.
17. Functional groups: phosphate group, a ribose group (hydroxyl groups), a nitrogenous base (carbonyl groups, amino groups). The monomers are joined by a phosphate–ribose backbone that is formed by condensation reactions.

18. Primary structure



Primary structure, the amino acid sequence, determines the type and position of intrachain interactions, thus determining the secondary structure, coils or pleated sheets. The secondary structure determines the sections of the protein that can fold into globular shapes, or align to form fibrous proteins. These structural features determine the solubility, mobility, and strength of the proteins, and thus their function.

Each amino acid is coded by three nucleotides. The sequence of nucleotides in the DNA determines the sequence of amino acids that will be linked together to form a specific protein.

19. The long hydrocarbon chains in the fatty acids of triglycerides are similar to the hydrocarbons that release large amounts of energy when burned. Thus, fats and oils release more energy when burned than do carbohydrates, which contain more hydroxyl groups.
20. In unsaturated oils, the fatty acid components in the triglycerides contain double bonds. Since a molecule cannot rotate freely about a double bond, the long hydrocarbon component of the fatty acid has “bends” in the molecule. These bends prevent the fatty acid chains from packing as closely together as can saturated fatty acids. The distance between the fatty acid chains weakens the van der Waals attractions between molecules, and thus lowers the melting point. Thus, a more saturated triglyceride would have a higher melting point.

Applying Inquiry Skills

21. Purpose

The purpose of this activity is to determine the identity of three compounds, to match labels for 1-propanol, propanal, and propanoic acid.

Experimental Design

Propanoic acid can be identified by determining the pH of each compound, the lowest value being the acid. The aldehyde and the alcohol can be identified by comparing their boiling points; the aldehyde would have a lower boiling point than the alcohol.

Prediction

The propanoic acid will have the lowest pH. The aldehyde will have a lower boiling point than the alcohol.

Hypothesis

The carboxyl group of the propanoic acid has acidic properties, and carboxylic acids have pH values lower than 7; the other two compounds are not acidic. The aldehyde has a carbonyl group which, although polar, produces weaker intermolecular attractions than the hydroxyl group in the alcohol, because hydroxyl groups can hydrogen bond. Thus, since the hydrocarbon components in the two compounds are comparable, the alcohol will have a higher boiling point than the aldehyde.

Safety Precautions

Wear eye protection and a lab apron. Do not use open flames. When test tubes are being heated, point them away from people. Dispose of the compounds in labelled containers.

22. Experimental Design

propane → propene → propanol → propanone

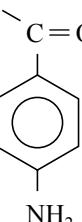
Procedure

The propane is converted to the halide by substitution reaction with chlorine, with heat and UV light. Chloropropane is converted to propene by elimination reaction, in the presence of sodium hydroxide. The propene is converted to propanol by reaction with water, in the presence of sulfuric acid. The 2-propanol is converted to propanone by controlled oxidation with potassium permanganate.

Safety Precautions

Wear eye protection and a lab apron. Do not use open flames. Work in well-ventilated area. Dispose of materials in labelled containers.

Making Connections

23. (a) HO  NH₂

- (b) PABA is benzoic acid with an added NH₂ group, in position 4; thus, it has an additional polar group that is capable of hydrogen bonding. Prediction: solid at room temperature, with boiling point higher than that of benzoic acid. The presence of the carboxyl group and the amino group makes the molecule highly polar and capable of hydrogen bonding, making it soluble in water. The presence of the benzene ring makes it likely soluble in nonpolar solvents such as alcohol and ether as well. With the presence of both a carboxyl group and an amino group, PABA can undergo condensation reactions with other molecules, or undergo condensation polymerization with other PABA molecules.
- (c) (Sample answer) Sunscreens act by providing physical barriers to UV light (as by zinc oxide and titanium dioxide), or chemical barriers. PABA is a chemical sunscreen that acts by absorbing radiation in the wavelengths that are not visible to the human eye; they thus appear transparent and invisible on the skin. PABA is not soluble in water and so must be dissolved in alcohol for use; however, most of the PABA derivatives are water soluble. Sunlight consists of UVA rays (penetrate deep into the base layer of skin) and UVB rays (burning rays); both contribute to skin burning and skin cancer. PABA provides mostly UVB coverage between 260 and 330 nm; consumers should select a sunscreen that screens both UVA and UVB rays – the “broad spectrum” sunscreens.

PABA does pose some possible hazards: Although sunscreens should be used every day to prevent premature aging and skin cancer (80% of the Sun's ultraviolet rays pass through the clouds on a cloudy day), sun exposure

is needed for vitamin D protection; thus, regular users of sunscreen may require vitamin D supplements. The original PABA was sometimes unpopular because it stained clothing; PABA esters such as glycerol PABA, pentyl dimethyl PABA, and octyl dimethyl PABA are now used. Some people are sensitive to PABA and its esters and should choose other sunscreens.

24. (Sample answers)

- (a) Chlorinated hydrocarbons such as tetrachloroethylene, also known as “perchloroethylene” (PERC), are used as cleaning solvents. The effects of PERC on humans include depression of the central nervous system; damage to the liver and kidneys; and impaired memory, confusion, and dizziness. There is also evidence that it may cause cancer in humans. Contamination of ground water from PERC occurs through dumping, spills, or bad practices. PERC does not evaporate and, since it is more dense than water, it is difficult to clean up spills.
- (b) Silicon wafers are used in the semiconductor industry for products such as personal computers, cellular phones, and car engines. An environmental issue arises from the use of large amounts of highly purified water and solvents to rinse and clean a silicon wafer. Scientists are developing new, environmentally friendly ways to manufacture the processors; one such project is the use of a gas-phase process that would replace the use of liquids for chip cleaning. Other research in plastics has resulted in a detergent that would dissolve in liquid CO₂ and has excellent cleaning properties; this project has received a Green Chemistry award.

25. Desired properties of polymers for use in the dental industry include high tensile strength, durable, insoluble in water, nontoxic, does not soften at high temperatures (e.g., hot drinks). Shrinkage of the polymer is a common deficiency.

Dental polymers have three main components: a polymer matrix; fillers of various types, sizes, shapes; and a phase that bonds the other two phases.

Monomers may form branched or linear polymer chains. The linear polymer chains can have a parallel alignment and form crosslinkages between chains; this allows for a crystalline structure, which produces more of the desired properties.

Dental monomers form strong hydrogen bonds, influencing the polymerization process and the network structure formed.

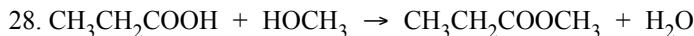
The polymerization process is usually initiated by chemical reduction–oxidation reactions, or by photochemical redox reactions. Dental fillings are generally cured using a curing lamp, a process that results in 2–3% shrinkage; this leads to eventual detachment of the filling from the cavity. Pulse lasers can cause numerous initiations of polymerization at the onset of curing, and may reduce the shrinkage of the fillings.

26. In high-pressure liquid chromatography (HPLC), one solvent — the mobile phase — is continuously applied to the column — the stationary phase. The mobile phase acts as a carrier for the sample solution that is injected into the stationary phase of the chromatography column. The components of the sample solution migrate according to the interactions of the components with the column, the degree of migration and separation of components being determined by the type of mobile phase and column. For example, those samples that have stronger interactions with the stationary phase than with the mobile phase will move more slowly, and thus have a longer retention time. Conversely, components that are highly soluble in the mobile phase will move along with this solvent, travelling further along the column.

Molecules can be separated on the basis of their structure, which includes their size, shape, charge, and hydrophylic/hydrophobic properties. These characteristics determine the type of solvent and gel selected.

27. (Sample answers) paper (natural, polymer); plastic pen (synthetic, polymer); cotton and polyester shirt (natural and synthetic, polymer); running shoes (synthetic, polymer); ketchup (natural, polymer); vinegar (natural, not polymer); butter (natural, not polymer); gasoline (natural, not polymer); television set (synthetic, polymer); CDs (synthetic, polymer)

Extensions



$$n_{\text{methanol}} = \frac{m}{M}$$
$$= \frac{20.0 \text{ g}}{32.05 \text{ g/mol}}$$

$$n_{\text{methanol}} = 0.624 \text{ mol}$$

$$n_{\text{propanoic acid}} = \frac{m}{M}$$
$$= \frac{40.0 \text{ g}}{74.09 \text{ g/mol}}$$

$$n_{\text{propanoic acid}} = 0.540 \text{ mol}$$

The limiting reagent is propanoic acid.

$$\begin{aligned} n_{\text{methyl propanoate}} &= n_{\text{propanoic acid}} \\ &= 0.540 \text{ mol} \end{aligned}$$

Theoretical yield:

$$\begin{aligned} m &= nM \\ &= 0.540 \text{ mol} \times 88.12 \text{ g/mol} \end{aligned}$$

$$m = 47.6 \text{ g}$$

Actual yield: 35.2 g

$$\begin{aligned} \% \text{ yield} &= \frac{35.2 \text{ g}}{47.6 \text{ g}} \times 100\% \\ \% \text{ yield} &= 73.9\% \end{aligned}$$

The theoretical yield of methyl propanoate was 47.6 g, and the percent yield was 73.9%.

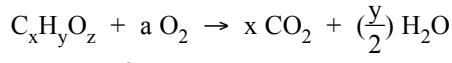
29. (a) Calculate the amount of compound in sample:

$$\begin{aligned} PV &= nRT \\ n &= \frac{PV}{RT} \\ &= \frac{100.0 \text{ kPa} \times 1.29 \text{ L}}{8.31 \frac{\text{kPa} \cdot \text{L}}{\text{mol} \cdot \text{K}}} \times 373 \text{ K} \\ n &= 0.0416 \text{ mol} \end{aligned}$$

Calculate molar mass of compound:

$$\begin{aligned} M &= \frac{m}{n} \\ &= \frac{3.00 \text{ g}}{0.0416 \text{ mol}} \\ M &= 72.12 \text{ g/mol} \end{aligned}$$

Calculate amount of carbon dioxide and water produced in combustion:



$$m_{\text{CO}_2} = 7.35 \text{ g}$$

$$\begin{aligned} n_{\text{CO}_2} &= \frac{m}{M} \\ &= \frac{7.35 \text{ g}}{44.01 \text{ g/mol}} \end{aligned}$$

$$n_{\text{CO}_2} = 0.167 \text{ mol}$$

$$m_{\text{H}_2\text{O}} = 3.01 \text{ g}$$

$$\begin{aligned} n_{\text{H}_2\text{O}} &= \frac{m}{M} \\ &= \frac{3.01 \text{ g}}{18.02 \text{ g/mol}} \end{aligned}$$

$$n_{\text{H}_2\text{O}} = 0.167 \text{ mol}$$

Since 0.0416 mol of the compound produced 0.167 mol of CO₂,

$$\text{number of C atoms in one molecule of compound} = \frac{0.167 \text{ mol}}{0.0416 \text{ mol}} = 4.01 \text{ atoms.}$$

Therefore, the compound must be C₄H_yO.

Since 0.0416 mol of the compound produced 0.167 mol of H₂O,
 number of H atoms in compound = $2 \times \frac{0.167 \text{ mol}}{0.0416 \text{ mol}} = 8.02 \text{ atoms}$.
 (Note that there are two atoms of H in each molecule of H₂O.)

Therefore, the compound must be C₄H₈O_z.

Calculate the number of atoms of O in the formula:

$$M_{\text{compound}} = 72.12 \text{ g/mol} \text{ (calculated above)}$$

The formula contains 4 C atoms and 8 H atoms, totalling 56.12 g/mol.

The remainder is accounted for by oxygen atoms: (72.12 – 56.12) g/mol
 = 16.00 g/mol

Therefore, the molecule must contain just one O atom.

The formula of the compound is therefore C₄H₈O.

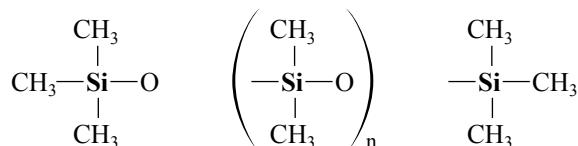
(b) Possible structural formulas for C₄H₈O:



(c) The compound is likely to be a saturated aldehyde or ketone. Evidence: not a hydrocarbon since it contains oxygen. Some polar groups are liquid at ordinary room temperatures, indicating intermolecular forces stronger than van der Waals attractions. Also, they are soluble in alcohols. May also be aldehydes or ketones, or esters: sweet minty odour; soluble in nonpolar solvents such as acetone. Saturated compound: does not undergo addition reaction with aqueous bromine.

Exploring

30. A silicone is a polymer of silicon, oxygen, and organic groups, generally called an organo-silicon polymer (polydimethylsiloxane).



The properties of the polymer can vary widely, so silicone has many uses.

- Low-viscosity fluids: high compressibility, low temperature service and heat transfer properties; soluble in a great variety of solvents including petroleum oils; used as antifoam, flow-control aids in coating applications; has electronic cooling applications in magnetrons.
- Intermediate-viscosity fluids: provide safe, low volatility heat transfer media; used as mould releases for rubber, plastic, and glass parts; in delicate timing and photographic devices; as hydraulic fluids; in protective hand creams; as toners in photocopiers; in brake fluids.
- High-viscosity fluids: as internal lubricants; as liquid springs in shock absorbers; as an additive in paint; as stationary phases in gas chromatography.
- Breast implants: benefits – post-surgery breast replacement, cosmetic appeal; drawbacks – claims that rupture of implants linked to health problems, e.g., autoimmune disease, cancer, silicone infiltration of lymph nodes. Relationship of silicone to diseases is not definitive.

Unit 2 Structure and Properties

ARE YOU READY?

(Page 158)

Safety and Technical Skills

1. Before using an electrical device, check that your hands are dry and that there are no water sources or wet areas nearby; and that the equipment is in good condition, with no frayed cords or damaged plugs.
2. To handle a hazardous chemical safely:
 - (a) wear safety glasses/goggles and a lab apron.
 - (b) wash with water immediately when your skin comes in contact with the chemical.
 - (c) always dispose of a chemical according to correct procedures/instructions as specified in the lab instructions or in the MSD sheets.

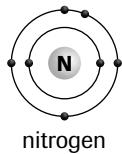
Knowledge and Understanding

3. (a) Statements i and iv apply only to elements.
(b) Statements ii and iii apply only to compounds.
(c) Statements i and iii are empirical—based on observation.
(d) Statements ii and iv are theoretical—based on ideas/concepts.
4. (a) J. J. Thomson described an atom as a sphere of matter with a uniform positive charge, in which smaller negative particles were embedded—the classic “raisin bun” analogy.
(b) Ernest Rutherford described an atom as a sphere that had virtually all of the mass and positive charge in a very tiny part of the volume (the nucleus), with the negative charges somehow occupying nearly all of the volume by moving around the nucleus.
(c) John Dalton described an atom that was a solid, neutral, indivisible sphere, with all atoms of an element identical, and different atoms for each element.
5. (a) electron orbits (b) nucleus (c) electron, e^- (d) proton, p^+ (e) neutron, n
- 6.

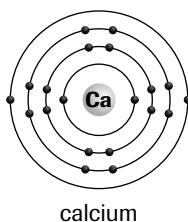
Table 1 Components of Atoms and Ions

Atom/Ion	Number of protons	Number of electrons	Net charge
hydrogen atom	1	1	0
sodium atom	11	11	0
chlorine atom	17	17	0
hydrogen ion	1	0	1+
sodium ion	11	10	1+
chloride ion	17	18	1-

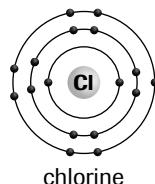
7. (a)



(b)



(c)



8.

Table 2 Properties of Ionic and Molecular Compounds

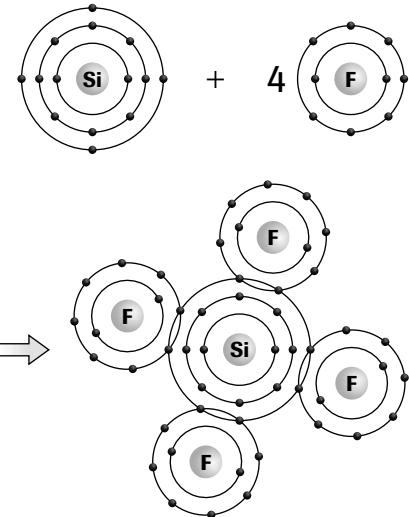
Class of compound	Classes of elements involved	Properties		
		Melting point (high/low)	State at SATP (s, l, g)	Electrolytes (yes/no)
ionic	metals and nonmetals	high	s	yes
molecular	nonmetals	low	s, l, or g	no

9. (a) ionic

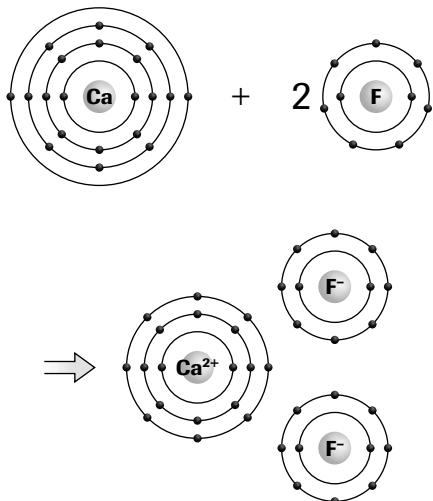
(b) either

(c) molecular

10. (a)



(b)



- (c) In (a), the rearrangement involves “sharing” of electrons by different atoms. In (b), the rearrangement involves loss of electrons by one atom, and gain of electrons by another.
- (d) All atoms attract electrons, but with very different strengths—depending on the atom’s structure. When the attraction (electronegativity) of two different atoms for electrons is very different in strength, electrons may be pulled completely away from one atom and held by another, creating positive and negative ions.

Inquiry and Communication

- 11. A scientific law is empirical, based on observable “facts.” A scientific theory is theoretical, based on unobservable concepts.
- 12. Scientific laws usually precede scientific theories.

CHAPTER 3 ATOMIC THEORIES

Reflect on Your Learning

(Page 160)

1. (a) In the 20th century, we have moved from Dalton's solid indivisible atom model, to the Thomson model which includes electrons embedded in a positively charged sphere, to the Rutherford nuclear atom model, to the Bohr model of electron orbits, and finally, to the quantum mechanical atom model based on electron "clouds." (A more complete answer might include the distinction between orbits and orbitals.)
(b) The current quantum mechanical model differs from all previous atomic models in its complexity, lack of a clear analogy or physical model, and in the way electrons are represented.
(A more complete answer would include the concept of electron waves and probability distribution of electrons in specific energy states.)
2. Scientific concepts are revised and/or replaced when new evidence is discovered that conflicts with or contradicts the current concept.
(A more complete answer would also include the requirement for the new evidence to be replicated by independent scientists and the development of a new or revised concept that is acceptable to the scientific community.)
3. (a) Quantum mechanics has changed the way we describe electrons in atoms from small particles travelling in specific paths or orbits to electrons occupying regions of space called orbitals.
(A more complete answer would include the treatment of electrons as waves and the description of orbitals in terms of probability distributions.)
(b) Our understanding of the periodic table is much greater because of quantum mechanics.
(Initial answers will be nebulous but eventually, students should be able to describe the importance of electron configurations, especially of d-block atoms, in greatly extending the explanation of the periodic table.)
4. (a) (Answers will vary. A typical answer might be the following.) Plastics technologies are based on bonding nonmetal atoms in extremely long carbon-based chains to make very large molecules. Specialized wafers of semiconductor atoms are used to produce microchips with high processing speeds for all types of computer applications.
(A more complete answer might include an explanation of semiconductors or the operation of a laser related to electron energy levels.)
(b) Technological products and processes, like anything else, have risks associated with the benefits they provide. Computer technology provides many benefits but is also used in so-called "smart bombs." Advances in molecular biology make it possible to cure some diseases, but genetic engineering may be used for questionable purposes such as human cloning.

Try This Activity: Molecules and Light

(Page 161)

- (a) The fluorescein solution transmits orange light, but reflects green.
- (b) If the fluorescein solution did not emit light when illuminated, it would appear orange by reflected light, the same colour as when viewed by transmitted light.
- (c) The glow stick is a slow chemical reaction that begins when an inside container is broken, allowing the chemicals to mix. The reaction continues, and emits light energy, for a considerable time. Since the label says the light will be brighter when the stick is warmer, heating speeds this chemical reaction, as we would expect.
- (d) Fluorescence and chemiluminescence both involve the emission of light; but fluorescence is not a chemical reaction—it requires light input to the substance before light can be emitted, and the substance doesn't change. Chemiluminescence is a reaction producing new products, with light produced only while the reaction is occurring.
- (e) Molecular structure changes in chemiluminescence, because new substances (molecules) are formed. Fluorescence must depend on the ability of a molecule to store energy temporarily, somehow without changing its structure.

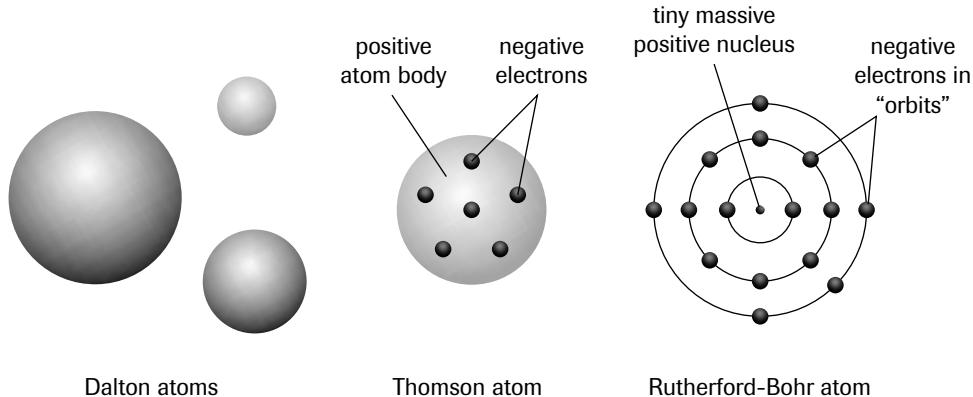
3.1 EARLY HISTORY OF ATOMIC THEORIES

SECTION 3.1 QUESTIONS

(Page 166)

Understanding Concepts

- Dalton's atom concept was a neutral ball of matter. Thomson's was a ball of positive matter with negative particles embedded in it, and Rutherford's was a tiny, massive, positive nucleus surrounded by "orbiting" electrons.



- The experimental evidence that led to the Rutherford model was the results of bombarding a thin metal foil with an alpha particle beam. The beam was mostly undeflected, as expected; however, a small but significant number of alpha particles were deflected—some, through very large angles.
- (a) Rutherford inferred that the nucleus was very small (compared to the size of the atom) because very few alpha particles were deflected at all—so the vast majority had to be completely missing whatever in the atom was "solid."
(b) Rutherford inferred that the nucleus was positively charged because the mathematics of the angles of deflection of the alpha particles was consistent with Coulomb's Law of repulsion of similar charges—and alpha particles were known to be positively charged.
- (a) The experimental evidence used in the discovery of the proton was the study of the behaviour of positive rays in a modified cathode ray tube.
(b) A proton with an electric charge of $1+$ is a small massive subatomic particle found in the atomic nucleus.
- (a) The experimental evidence used in the discovery of the neutron was the effects of alpha bombardment of materials—and the fact that protons and electrons could not account for all of the observed mass of atoms.
(b) A neutron is a small massive subatomic particle found in the atomic nucleus and has no electric charge.

Applying Inquiry Skills

- A "black box" is a system that cannot be directly observed and that must be understood by indirect interpretation of evidence. Atomic structure is an example of a concept built from indirect evidence.
- In ordinary conversation, the word *theory* often means a hypothetical claim, speculation, or guess. In science, the word refers to a comprehensive set of ideas based on general principles that explains a large number of observations.
- The ultimate authority in scientific work is reproducible evidence from experimentation.

Making Connections

- News media stories ordinarily refer to atoms only in terms of uses for atomic energy or isotope radioactivity, or publication of new research evidence related to atomic structure theory.
- (There are many examples students may use. Rutherford did much of his work at McGill University, for instance. Gillespie, LeRoy and Bader, all working in Canada, have each made significant contributions to molecular theory. A typical answer about a Canadian scientist would be something like the following.)
Gerhard Herzberg used advanced spectroscopy to study the geometry and internal energy states of small molecules and free radicals. In the 1950s and 60s, he was Director of Pure Physics at Canada's National Research Council in Ottawa, Ontario. His work, especially the discovery of the spectrum of the CH_2 free radical, led to the 1971 Nobel Prize in Chemistry.

Extensions

11. The phrase “empty space” is misleading. Rutherford stated that almost all of an atom’s volume is empty—in the sense that it contains negligible “solid” matter (material with mass and volume). The 99.999999 % of the atom’s volume that is free of anything with significant mass is nonetheless “full” of energy—the electric field of the electrons present. Another atom cannot occupy this space because the electrons surrounding the two atoms’ nuclei, repel each other. “Solid,” at an atomic level, means full of negative charge.
12. The composition of a proton, according to the current “standard model” theory, is a triplet—made up of two “up” quarks and one “down” quark. The Canadian scientist who received a share of the Nobel Prize (in 1990) for his empirical work in verifying this hypothesis is Dr. Richard Taylor. Dr. Taylor did his work at Stanford University, using the huge particle accelerator there.

3.2 CASE STUDY: A CANADIAN NUCLEAR SCIENTIST

(Page 168)

1. (There are many possible answers like the Harriet Brooks example given in this section. See Teachers’ Resource—Section 3.2 for sources of information and teaching suggestions.)

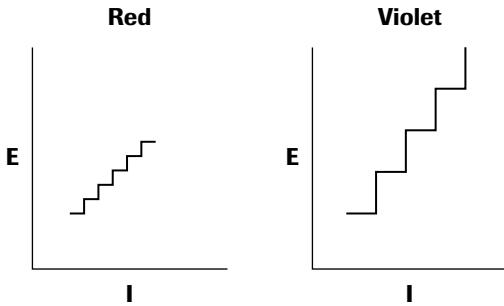
3.3 ORIGINS OF QUANTUM THEORY

PRACTICE

(Page 170)

Understanding Concepts

1. The initial colour of the flame with the air inlet closed is a bright luminous yellow. The final colour—with sufficient air mixed with the gas—is a much less visible blue. The blue flame has a much higher temperature.
2. The colour of the light from a star is directly connected to the temperature of the surface. Bluish stars like Sirius have the highest surface temperatures; and reddish stars like Betelgeuse, the lowest. Our star is yellowish, with an intermediate surface temperature.
- 3.



4. When heated strongly enough, gases produce a light that is observed (when spread out into a spectrum) to be made up of separate bright lines, of specific colours (wavelengths/frequencies).

SECTION 3.3 QUESTIONS

(Page 173)

Understanding Concepts

1. The two most important experimental observations leading to the quantum theory of light were: Max Planck’s observation that electromagnetic radiation emission could only be explained by hypothesizing that such energy release must occur in discrete amounts, or quanta; and Albert Einstein’s observation that the photoelectric effect could be explained by assuming that light energy travels in discrete packages of given energy, which he called “photons.”

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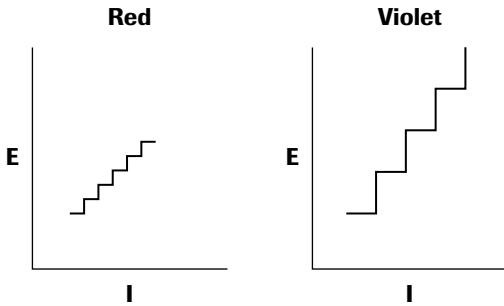
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SECTION 3.3 QUESTIONS

(Page 173)

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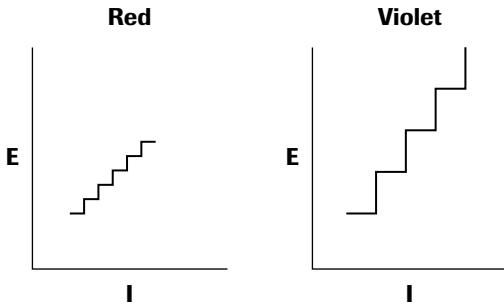
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PRACTICE

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SECTION 3.3 QUESTIONS

(Page 173)

Understanding Concepts

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- Max Planck may be considered the father of quantum theory because he was the first to advance the concept that energy like matter, is quantized, and not continuous.
- The photoelectric effect is the emission of electrons from the surface of a substance when electromagnetic (light) energy strikes the surface. The experiment requires a light source that can be varied in intensity (brightness) and also in frequency (wavelength/colour); and equipment to measure the (photo)electron flow rate (current) and relative electron energy (voltage).
- Quantum is Planck's term for a small, discrete, indivisible quantity. Photon is Einstein's term for a discrete quantity, or quantum, of light.

Applying Inquiry Skills

5. Experimental Design

- (a) Using a photoelectric effect apparatus, light of a constant intensity is varied in colour (frequency/wavelength) and electric current is measured. The light colour is the independent variable; the current is the dependent variable; and the light intensity and type of metal surface are the controlled variables.

Prediction/Hypothesis

- (b) According to Einstein's photon theory, a photon has an energy determined by its colour or frequency, and a certain minimum quantity of energy is required to release an electron from a specific type of atom. If the photon energy is steadily decreased, at some point it will be too low to release electrons from a sodium metal surface. Therefore, at some colour or frequency of light, no photoelectric effect will occur.

Extensions

6. (a) $h = 6.6 \times 10^{-34} \text{ J/Hz}$
 $f = 5.5 \times 10^{14} \text{ Hz}$

$$E = hf$$

$$E = 6.6 \times 10^{-34} \frac{\text{J}}{\text{Hz}} \times 5.5 \times 10^{14} \cancel{\text{Hz}}$$

$$E = 3.6 \times 10^{-19} \text{ J}$$

The minimum photon energy required is $3.6 \times 10^{-19} \text{ J}$.

- (b) The energy absorbed (gained) by a photoelectron is the same as the energy supplied (lost) by the photon that "hits" it, so the minimum photoelectron energy increase is also $3.6 \times 10^{-19} \text{ J}$.

7. (a) $h = 6.6 \times 10^{-34} \text{ J/Hz}$
 $f_{\text{UV}} = 1.5 \times 10^{15} \text{ Hz}$

$$f_{\text{IR}} = 3.3 \times 10^{14} \text{ Hz}$$

$$E = hf$$

$$E = 6.6 \times 10^{-34} \frac{\text{J}}{\text{Hz}} \times 1.5 \times 10^{15} \cancel{\text{Hz}}$$

$$E = 9.9 \times 10^{-19} \text{ J}$$

The ultraviolet photon energy is $9.9 \times 10^{-19} \text{ J}$.

$$E = 6.6 \times 10^{-34} \frac{\text{J}}{\text{Hz}} \times 3.3 \times 10^{14} \cancel{\text{Hz}}$$

$$E = 2.2 \times 10^{-19} \text{ J}$$

The infrared photon energy is $2.2 \times 10^{-19} \text{ J}$.

(b) $\frac{9.9 \times 10^{-19} \text{ J}}{2.2 \times 10^{-19} \text{ J}} = \frac{4.5}{1}$

The UV photon is about 4.5 times as energetic as the IR photon.

- (c) In order of increasing energy of photons, the sequence is infrared, visible, ultraviolet, and X-ray.

3.4 THE BOHR ATOMIC THEORY

PRACTICE

(Page 178)

1. (a)

3 e⁻
2 e⁻
5 p⁺
B
boron atom

(b)

3 e⁻
8 e⁻
2 e⁻
13 p⁺
Al
aluminum atom

(c)

2 e⁻
2 p⁺
He
helium atom

SECTION 3.4 QUESTIONS

(Page 180)

Understanding Concepts

- The main achievement of the Rutherford model was the advancement of atomic theory to include the nucleus. The main problem was explaining the region occupied by the electrons. According to existing theory, electrons should spiral into the nucleus as they lose energy by emitting electromagnetic radiation.
- Bohr's solution to the problem with the Rutherford model was to assume that classical ideas of energy did not hold inside the atom, and that electron energies were quantized in special energy states called stationary states.
- The important new idea used by Bohr was the quantum theory of light, together with the experimental evidence of line spectra.
- (a) Emission spectra consist of light emitted by a sample of a substance. Absorption spectra consist of the missing frequencies (colours) of light after the source light passes through a sample of a substance.
(b) Bohr explained emission spectra as light emitted by an atom when its electrons drop from higher to lower energy states. The dark lines in absorption spectra correspond to the light absorbed by electrons jumping from lower to higher energy states.
- Niels Bohr and Ernest Rutherford both made major contributions, at approximately the same time, to our understanding of the structure of the atom. Rutherford's work described the nucleus, and Bohr's work described the extranuclear region of the atom.

6. (a)

7e⁻
2e⁻
9p⁺
F
fluorine atom

(b)

8e⁻
2e⁻
10p⁺
Ne
neon atom

(c)

1e⁻
8e⁻
2e⁻
11p⁺
Na
sodium atom

- Atomic numbers give the number of protons, and for neutral atoms, the number of electrons as well. The period number shows how many levels of electron energy there are, and the last digit of the group number shows how many electrons are in the valence (highest) energy level.
- Bohr's theory was considered a success because it explained the known emission spectral lines for hydrogen, and predicted successfully some lines in the infrared light spectrum. Bohr's theory also provided a better understanding of the arrangement of elements in the periodic table.
- One significant problem with the Bohr theory was that it did not predict correctly the spectral lines for atoms with more electrons than hydrogen. (It also could not explain some simple observations such as some emission lines were brighter than others.)

Applying Inquiry Skills

- Element 118, based on the periodic law and the Bohr theory of the atom, should be in group 18, making it a noble gas (unreactive chemically) with a full valence electron level (18 electrons in the seventh level), with a very high density for a gas, around 14 ± 3 g/L, and melting and boiling points of around $-20 \pm 20^\circ\text{C}$.

Making Connections

- (Some of the content that students could recognize include references to spectra of elements, arrangement of electrons in shells (2, 8, 18, 32), stationary states, and transitions between states. Much of the discussion about this content, and

- other topics, will be somewhat obscure. At best, probably about three-quarters of the total discussion is beyond students' current understanding. This is a good illustration of how content, even of an apparently "simple" theory like Bohr's, is considerably simplified and restricted at the high school level.)
12. To determine if a sample of table salt, $\text{NaCl}_{(s)}$, contains some potassium chloride, a flame test can be done and the characteristic violet flame will indicate if potassium is present. (The violet colour of potassium is normally overwhelmed by the yellow of sodium; but the colours can be separated by using a spectroscope to view the light, or by viewing the light through deep-blue cobalt glass which absorbs the yellow sodium wavelengths but not the violet potassium wavelengths.)

Extensions

$$13. \text{ (a)} \quad \frac{1}{\lambda} = R_{\text{H}} \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right)$$

$$n_f = 2 \quad n_i = 4$$

$$R_{\text{H}} = 1.10 \times 10^7 \text{ /m}$$

$$\frac{1}{\lambda} = \frac{1.10 \times 10^7}{1 \text{ m}} \left(\frac{1}{2^2} - \frac{1}{4^2} \right)$$

$$\lambda = \frac{1 \text{ m}}{2.06 \times 10^6}$$

$$\lambda = 4.85 \times 10^{-7} \text{ m} = 485 \text{ nm}$$

The wavelength of light emitted is 485 nm.

$$(b) \quad \lambda = \frac{c}{f}$$

$$c = 3.00 \times 10^8 \text{ m/s}$$

$$f = \frac{c}{\lambda} = \frac{3.00 \times 10^8 \text{ m}}{4.85 \times 10^{-7} \text{ m}}$$

$$f = \frac{6.18 \times 10^{14}}{1 \text{ s}} = 6.18 \times 10^{14} \text{ s}^{-1}$$

The frequency of the light emitted is $6.18 \times 10^{14} \text{ s}^{-1}$.

$$(c) \quad E = hf$$

$$h = 6.63 \times 10^{-34} \text{ J/Hz}$$

$$E = \frac{6.63 \times 10^{-34} \text{ J}}{1 \text{ Hz}} \times 6.19 \times 10^{14} \text{ Hz}$$

$$E = 4.1 \times 10^{-19} \text{ J}$$

The electron's energy difference between the second and fourth levels is $4.1 \times 10^{-19} \text{ J}$.

$$(d) \quad \frac{1}{\lambda} = R_{\text{H}} \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right)$$

$$R_{\text{H}} = 1.10 \times 10^7 \text{ /m}$$

$$n_f = 2 \quad n_i = 3$$

$$\frac{1}{\lambda} = \frac{1.10 \times 10^7}{1 \text{ m}} \left(\frac{1}{2^2} - \frac{1}{3^2} \right)$$

$$\lambda = 6.54 \times 10^{-7} \text{ m} = 654 \text{ nm}$$

The wavelength of light emitted is 654 nm.

$$\lambda = \frac{c}{f}$$

$$c = 3.00 \times 10^8 \text{ m/s}$$

$$f = \frac{c}{\lambda}$$
$$= \frac{3.00 \times 10^8 \text{ m}}{1 \text{ s}}$$
$$= \frac{3.00 \times 10^8 \text{ m}}{6.54 \times 10^{-7} \text{ m}}$$

$$f = \frac{4.59 \times 10^{14}}{1 \text{ s}} = 4.59 \times 10^{14} \text{ Hz}$$

The frequency of the light emitted is 4.59×10^{14} Hz.

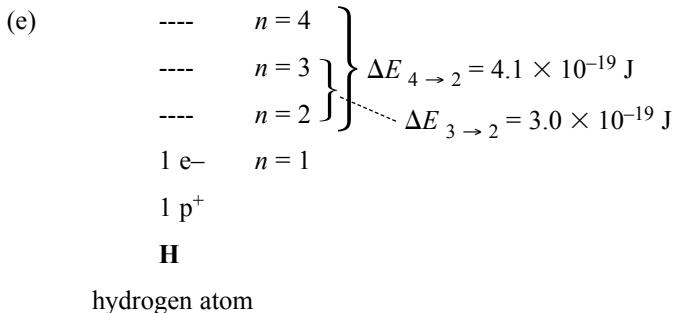
$$E = hf$$

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$$E = \frac{6.63 \times 10^{-34} \text{ J}}{1 \text{ Hz}} \times 4.59 \times 10^{14} \text{ Hz}$$

$$E = 3.0 \times 10^{-19} \text{ J}$$

The electron's energy difference between the second and third levels is 3.0×10^{-19} J.



$$(4.1 \times 10^{-19} \text{ J}) - (3.0 \times 10^{-19} \text{ J}) = 1.1 \times 10^{-19} \text{ J}$$

The energy difference between hydrogen atom electron energy levels $n = 4$ and $n = 3$ will be 1.1×10^{-19} J.

14. The most likely assumption would seem to be that theories would be advanced that would try to describe electron arrangements and energies for atoms more complex than hydrogen.

3.5 QUANTUM NUMBERS

PRACTICE

(Page 182)

Understanding Concepts

1. Bohr and Sommerfeld both used observations of line spectra.
2. Bohr proposed circular electron orbits for hydrogen, while Sommerfeld proposed several elliptical orbits.

The wavelength of light emitted is 654 nm.

$$\lambda = \frac{c}{f}$$

$$c = 3.00 \times 10^8 \text{ m/s}$$

$$f = \frac{c}{\lambda}$$
$$= \frac{3.00 \times 10^8 \text{ m}}{1 \text{ s}}$$
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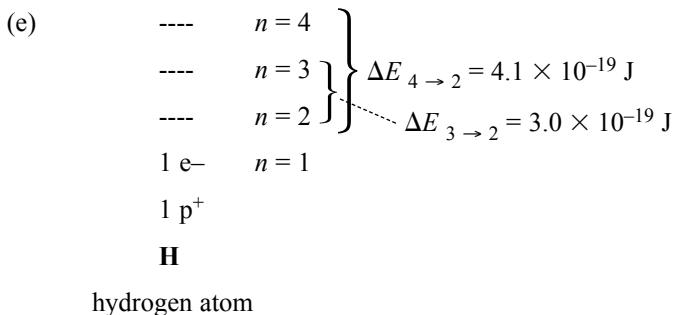
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3.5 QUANTUM NUMBERS

PRACTICE

(Page 182)

Understanding Concepts

1. Bohr and Sommerfeld both used observations of line spectra.
2. Bohr proposed circular electron orbits for hydrogen, while Sommerfeld proposed several elliptical orbits.

3.

Table 3 Sommerfeld's Electron Energy Sublevels

Primary energy level	Principal quantum number, n	Possible secondary quantum numbers, l	Number of sublevels per primary level
1	1	0	1
2	2	0,1	4
3	3	0,1,2	9
4	4	0,1,2,3	16

4. For any principal quantum number, n , the highest possible value of l is $n-1$.

5. For any principal quantum number, n , the possible values of l include all of the integers from 0 to $n-1$.

SECTION 3.5 QUESTIONS

(Page 184)

Understanding Concepts

- The main kind of evidence used comes from atomic line spectra, particularly the splitting of lines.
- The first quantum number describes the main energy level; the second quantum number describes small energy level steps within the main energy level corresponding to different shapes of “orbits”; the third quantum number describes the orientation in space of the electron “orbits”; and the fourth quantum number describes the “spin” of electrons.
- (a) For $l = 0, 1, 2, and }3, there are }0, 3, 5, and 7 possible values of } m_l , respectively.
 (b) Each number is the next greater odd integer (or $2l + 1$ for all } $l \neq 0$).
 (c) From the answer to (b), the number of possible values for } m_l for } $l = 4$ must be 9 (the next odd integer).$
- The fourth quantum number is } m_s , and it is necessary to explain magnetic properties of atoms.
-

5.

Table 4 Summary of Quantum Numbers

(n)	(0 to $n - 1$)	(- l to + l)	(+1/2 or -1/2)
4	0	0	+1/2, -1/2
	1	-1, 0, +1	+1/2, -1/2
	2	-2, -1, 0, +1, +2	+1/2, -1/2
	3	-3, -2, -1, 0, +1, +2, +3	+1/2, -1/2

- It takes four quantum numbers to describe fully an electron in an atom. An example listing labels and values of each quantum number might be $n = 2$, $l = 1$, $m_l = -1$, and $m_s = +1/2$. This might describe an electron in a hydrogen atom in an “excited” state.
- For each principal quantum number from $n = 1$ to $n = 3$ (see Table 4), there can be 2, 8, and 18 different electron descriptions.
- In the development of scientific knowledge, empirical knowledge usually comes first. Examples from this section are the investigation of bright line spectra and of magnetic effects upon these spectra—both of which preceded the theory that attempts to explain them in terms of atomic structure.

3.6 ATOMIC STRUCTURE AND THE PERIODIC TABLE

PRACTICE

(Page 191)

Understanding Concepts

- The aufbau principle states that electrons occupy lowest energy orbitals first. The Pauli exclusion principle states that no more than two electrons (of opposite spin) may occupy the same orbital, and Hund’s rule states that electrons are not paired within sublevel orbitals until each sublevel orbital has at least one electron.

3.

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(Page 184)

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	3	-3, -2, -1, 0, +1, +2, +3	+1/2, -1/2

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3.6 ATOMIC STRUCTURE AND THE PERIODIC TABLE

PRACTICE

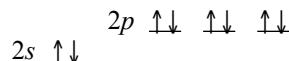
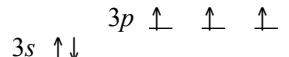
(Page 191)

Understanding Concepts

- The aufbau principle states that electrons occupy lowest energy orbitals first. The Pauli exclusion principle states that no more than two electrons (of opposite spin) may occupy the same orbital, and Hund’s rule states that electrons are not paired within sublevel orbitals until each sublevel orbital has at least one electron.

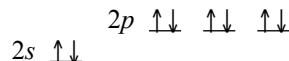
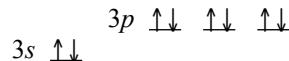
2. A periodic table can be used to help complete energy level diagrams because it is arranged according to electron energy levels, sublevels, and orbitals.

3. (a)



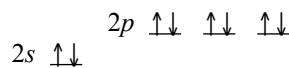
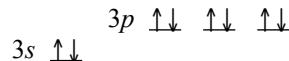
$1s \uparrow\downarrow$
phosphorus atom, P

(b)



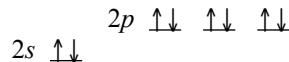
$1s \uparrow\downarrow$
potassium atom, K

(c)



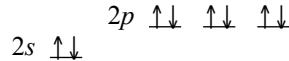
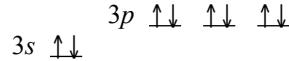
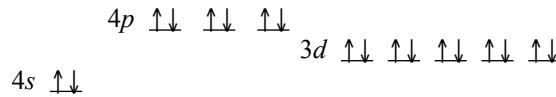
$1s \uparrow\downarrow$
manganese atom, Mn

(d)

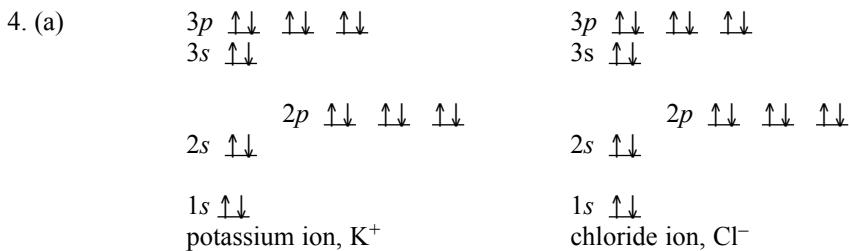
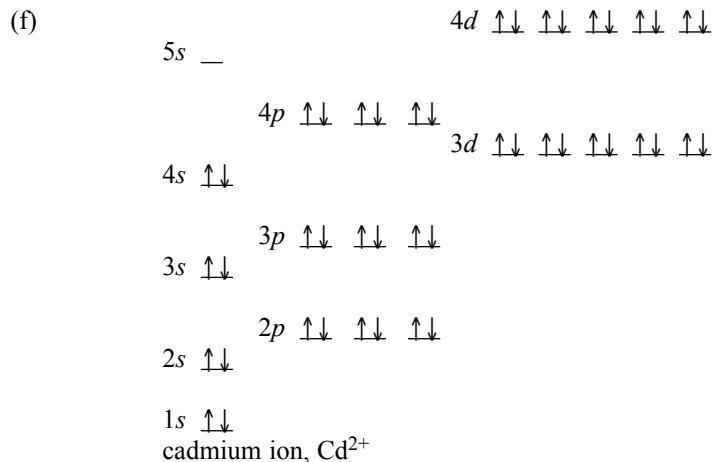


$1s \uparrow\downarrow$
nitride ion, N^{3-}

(e)



$1s \uparrow\downarrow$
bromide ion, Br^-



(b) An atom of the noble gas argon, Ar, has the same electron orbital energy level diagram as do these two ions.

Extension

5. 1s would be $n = 1, l = 0$
 2s would be $n = 2, l = 0$
 2p would be $n = 2, l = 1$
 3d would be $n = 3, l = 2$

PRACTICE

(Page 194)

Understanding Concepts

6. (a) beryllium
 (b) fluorine
 (c) sodium
 (d) sulfur
7. sodium $1s^2 2s^2 2p^6 3s^1$
 magnesium $1s^2 2s^2 2p^6 3s^2$
 aluminum $1s^2 2s^2 2p^6 3s^2 3p^1$
 silicon $1s^2 2s^2 2p^6 3s^2 3p^2$
 phosphorus $1s^2 2s^2 2p^6 3s^2 3p^3$
 sulfur $1s^2 2s^2 2p^6 3s^2 3p^4$
 chlorine $1s^2 2s^2 2p^6 3s^2 3p^5$
 argon $1s^2 2s^2 2p^6 3s^2 3p^6$
8. fluorine [He] $2s^2 2p^5$
 chlorine [Ne] $3s^2 3p^5$
 bromine [Ar] $4s^2 4p^5$
 iodine [Kr] $5s^2 5p^5$
 astatine [Xe] $6s 6p^5$

Each halogen configuration ends with two s and three p orbitals.

Other chemical families, such as the alkali metals, also have similar valence orbital configurations.

9. fluoride ion $1s^2 2s^2 2p^6$
sodium ion $1s^2 2s^2 2p^6$

10. Isoelectronic means having the same number of electrons.

11. zinc ion [Ar] $3d^{10}$
cadmium ion [Kr] $4d^{10}$
mercury(II) ion [Xe] $4f^{14} 5d^8$

SECTION 3.6 QUESTIONS

(Page 197)

Understanding Concepts

1. Maximum number of electrons: (a) $2e^-$ (b) $8e^-$ (c) $18e^-$ (d) $32e^-$

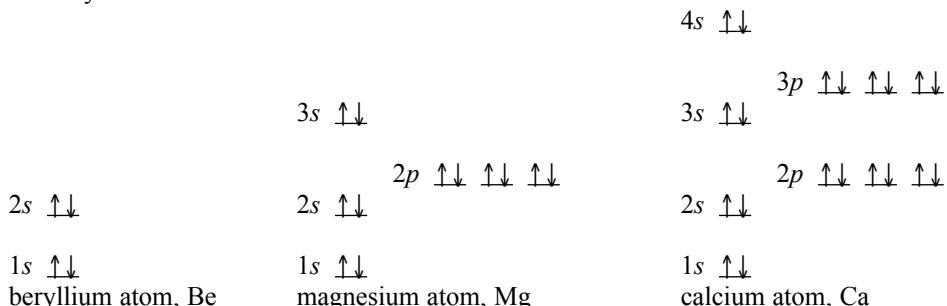
2.

Orbitals and Electrons in s, p, d, and f Sublevels				
Sublevel	Symbol	Value of l	Number of orbitals	Max # of electrons
(a)	s	0	1	2
(b)	p	1	4	8
(c)	d	2	9	18
(d)	f	3	16	32

3. The aufbau principle states that electrons occupy lower energy orbitals first. Either a diagonal orbital diagram or the periodic table can be used to determine this order of occupancy.

4. If four electrons are to be placed into a p subshell, the aufbau principle states that all lower energy levels must already be full, and Hund's rule states that each of the three p orbitals must already have one occupying electron before the fourth is placed in any one of the orbitals.

5. (a)



(b) These diagrams all show two s electrons in the highest energy orbital.

6. (a) s
(b) d
(c) p
(d) f

7. (a) The halide ions have a charge of negative one, -1 .

(b) The electron configuration of each halogen shows one less electron than a full p orbital energy level; for example, fluorine is $1s^2 2s^2 2p^5$, chlorine is $1s^2 2s^2 2p^6 3s^2 3p^5$, bromine is $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^5$, and so on. We explain the ion charge by assuming that halogens strongly attract one extra electron to occupy the unfilled p orbital in the highest orbital energy level.

8. (a) A sodium ion, Na^+ , has a configuration of $1s^2 2s^2 2p^6$, the same as that of a neon atom, Ne.
(b) These two chemical entities are both chemically very stable, and have the same electron configuration; but sodium ions are positively charged and strongly attract negative ions to form ionic solid compounds, while neutral neon atoms have extremely weak attractive forces, and form a noble gas at room conditions.
9. The electron configuration for Sb^{3+} is [Kr] $5s^2 4d^{10}$. The electron configuration for Sb^{5+} is [Kr] $4d^{10}$.
10. The electron configuration for a gallium atom, Ga, is [Ar] $4s^2 3d^{10} 4p^1$. The Ga^{3+} ion has most probably lost three electrons from the fourth shell, and so should have a configuration of [Ar] $3d^{10}$.
11. Copper has an electron configuration of [Ar] $4s^1 3d^{10}$ and therefore has an unpaired electron ($4s^1$). Zinc has an electron configuration of [Ar] $4s^2 3d^{10}$ and has no unpaired electrons.

12. A gold atom should have an electron configuration of [Xe] $6s^2 4f^{14} 5d^9$, if we use the aufbau principle. However, a filled d suborbital creates extra stability, especially in large atoms, so [Xe] $6s^1 4f^{14} 5d^{10}$ is the normal configuration.
13. (a) Sc^{3+} has a probable configuration of $1s^2 2s^2 2p^6 3s^2 3p^6$, or [Ar].
 (b) Ag^+ has a probable configuration of [Kr] $4d^{10}$.
 (c) Fe^{3+} has a probable configuration of [Ar] $3d^5$.
 Fe^{2+} has a probable configuration of [Ar] $4s^1 3d^5$.
 (d) Th^+ has a probable configuration of [Rn] $7s^2 5f^1$.
 Th^{3+} has a probable configuration of [Rn] $5f^1$.
14. Carbon, silicon, and germanium atoms have (respectively) electron configurations of $1s^2 2s^2 2p^2$, $1s^2 2s^2 2p^6 3s^2 3p^2$, and $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^2$. Each of these atoms has four electrons in the highest numbered shell of orbitals, and likely use these four electrons for bonding.

Applying Inquiry Skills

15. (a) The result predicted by classical theory is that the atoms should hit a target to form a solid pattern because the atoms should hit the photographic plate randomly within the beam. The result predicted by quantum theory is that the pattern should be two distinct lines.
 (b) Silver has an electron configuration of [Kr] $5s^1 4d^{10}$, with a single unpaired s valence electron. If all silver atoms were identical, any magnetic moment caused by the external field should move the atoms in random directions, since it could be oriented in any direction as the atoms enter the field. The two distinct lines indicate that a silver atom must have one of two distinct and opposite magnetic moments. This was later interpreted to be due to the valence (unpaired) electron having one of only two possible (and opposite) “spins.”

Making Connections

16. (a) Dimes were shipped out of the country because it is illegal to deface or alter Canadian currency in Canada.
 (b) These metals have very different magnetic properties, which could be used to separate them.
 (c) A magnet should separate these coins easily, because nickel is ferromagnetic (strongly magnetic) and silver is not.
17. ESR spectroscopy places samples of paramagnetic material in a high uniform magnetic field to split the energy levels of the ground state. The results can be used to help determine molecular structures and properties, such as the degree of movement (rotation) of side groups on structures. Another area deals with finding probable redox activation sites on protein molecules. The dynamics (movements) of molecules in liquid and solid phases can be examined to determine properties of new materials.
18. MRI uses alterations to the spin of a proton—which has two quantum states like that of an electron—to cause signals to be emitted from materials such as human tissue that can be used to scan the interior of the material in great detail, without harmful invasion of the material by physical objects or high-energy electromagnetic radiation. Like ESR, MRI uses a very powerful magnetic field to align subatomic particles.

MRI has its major use in medicine, where it provides excellent detailed scans of soft tissue, allowing doctors to diagnose illness and abnormalities much more effectively than with X rays.

The political issue associated with MRI use is the cost of health care. MRI machines are very valuable to doctors, but the machines (and the technicians to run them) are in short supply, highly technical, and very expensive.

3.7 WAVE MECHANICS AND ORBITALS

SECTION 3.7 QUESTIONS

(Page 202)

Understanding Concepts

1. (a) Louis Victor, 7th Duc de Broglie, believed that particles could have properties and characteristics of waves, and that this effect would be significant for tiny, fast-moving particles like electrons.
 (b) Erwin Schrödinger imagined electron behaviour within the atom structure as a wave phenomenon, described by a wave mechanical equation.
 (c) Werner Heisenberg thought that electron behaviour cannot ever be exactly described, but only discussed as a probability system, within limits imposed by his “uncertainty principle.”
2. An electron orbital describes the three-dimensional region of space occupied by an electron, that is, in which we calculate a high probability (usually > 90%) of detecting an electron of a specific energy.

An orbit is a simplified (incorrect, but useful) idea describing electrons as orbiting nuclei in circular or elliptical paths.

12. A gold atom should have an electron configuration of [Xe] $6s^2 4f^{14} 5d^9$, if we use the aufbau principle. However, a filled d suborbital creates extra stability, especially in large atoms, so [Xe] $6s^1 4f^{14} 5d^{10}$ is the normal configuration.
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 (d) Th^+ has a probable configuration of [Rn] $7s^2 5f^1$.
 Th^{3+} has a probable configuration of [Rn] $5f^1$.
14. Carbon, silicon, and germanium atoms have (respectively) electron configurations of $1s^2 2s^2 2p^2$, $1s^2 2s^2 2p^6 3s^2 3p^2$, and $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^2$. Each of these atoms has four electrons in the highest numbered shell of orbitals, and likely use these four electrons for bonding.

Applying Inquiry Skills

15. (a) The result predicted by classical theory is that the atoms should hit a target to form a solid pattern because the atoms should hit the photographic plate randomly within the beam. The result predicted by quantum theory is that the pattern should be two distinct lines.
 (b) Silver has an electron configuration of [Kr] $5s^1 4d^{10}$, with a single unpaired s valence electron. If all silver atoms were identical, any magnetic moment caused by the external field should move the atoms in random directions, since it could be oriented in any direction as the atoms enter the field. The two distinct lines indicate that a silver atom must have one of two distinct and opposite magnetic moments. This was later interpreted to be due to the valence (unpaired) electron having one of only two possible (and opposite) “spins.”

Making Connections

16. (a) Dimes were shipped out of the country because it is illegal to deface or alter Canadian currency in Canada.
 (b) These metals have very different magnetic properties, which could be used to separate them.
 (c) A magnet should separate these coins easily, because nickel is ferromagnetic (strongly magnetic) and silver is not.
17. ESR spectroscopy places samples of paramagnetic material in a high uniform magnetic field to split the energy levels of the ground state. The results can be used to help determine molecular structures and properties, such as the degree of movement (rotation) of side groups on structures. Another area deals with finding probable redox activation sites on protein molecules. The dynamics (movements) of molecules in liquid and solid phases can be examined to determine properties of new materials.
18. MRI uses alterations to the spin of a proton—which has two quantum states like that of an electron—to cause signals to be emitted from materials such as human tissue that can be used to scan the interior of the material in great detail, without harmful invasion of the material by physical objects or high-energy electromagnetic radiation. Like ESR, MRI uses a very powerful magnetic field to align subatomic particles.

MRI has its major use in medicine, where it provides excellent detailed scans of soft tissue, allowing doctors to diagnose illness and abnormalities much more effectively than with X rays.

The political issue associated with MRI use is the cost of health care. MRI machines are very valuable to doctors, but the machines (and the technicians to run them) are in short supply, highly technical, and very expensive.

3.7 WAVE MECHANICS AND ORBITALS

SECTION 3.7 QUESTIONS

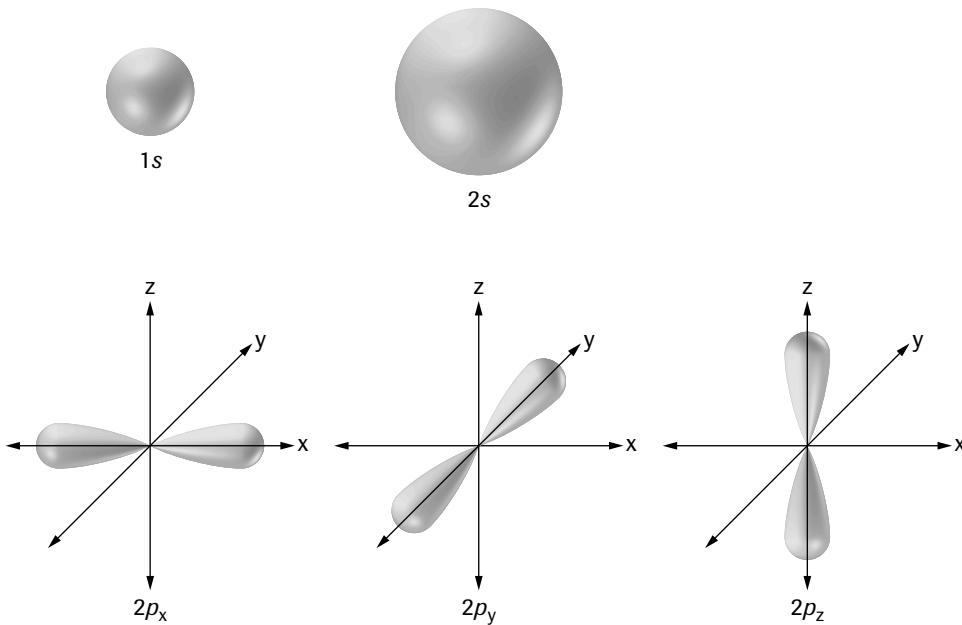
(Page 202)

Understanding Concepts

1. (a) Louis Victor, 7th Duc de Broglie, believed that particles could have properties and characteristics of waves, and that this effect would be significant for tiny, fast-moving particles like electrons.
 (b) Erwin Schrödinger imagined electron behaviour within the atom structure as a wave phenomenon, described by a wave mechanical equation.
 (c) Werner Heisenberg thought that electron behaviour cannot ever be exactly described, but only discussed as a probability system, within limits imposed by his “uncertainty principle.”
2. An electron orbital describes the three-dimensional region of space occupied by an electron, that is, in which we calculate a high probability (usually > 90%) of detecting an electron of a specific energy.

An orbit is a simplified (incorrect, but useful) idea describing electrons as orbiting nuclei in circular or elliptical paths.

- Quantum mechanics provides both the general shape (volume of space), and the electron probability density, within an orbital.
- Quantum mechanics theory says nothing about either the position or about the motion of an electron within an orbital.
- The 1s and 2s orbitals are spherical in shape, with the 2s orbital considerably larger and having two concentric regions of high probability density. A 2p orbital is shaped like a dumbbell, with two areas of high probable density, one on each side of the nucleus.



Making Connections

- Statistics are used to predict situations such as the number of megajoules of electricity that will be used in a city in a given winter month, or the number of students that will achieve honours on a national examination, or the number of cases of influenza that will occur over the winter in a country. All statistical prediction is based on probability, meaning it always includes some uncertainty, and predicts better for larger samples and longer times—as does quantum mechanics.
- Heisenberg would argue that the measured speed included uncertainty; but the amount of this uncertainty is infinitesimal for an object such as a car, certainly many orders of magnitude less than the precision of the “radar” gun.
- Dr. Richard Bader researches the nature of atoms and bonds within molecular structures, attempting to achieve a level of understanding that will allow predictions of the properties of materials to be made by theory using computer calculations. His theory of molecular topologies is directly related to the quantum mechanics of atoms—the constituents of the structures with which he deals.
- Areas where superconductivity is presently used include creating the very strong magnetic fields for MRI scanning (superconducting electromagnets), for magnetic shielding devices, infrared sensors, microwave signal devices, and quantum interference devices. Some projected uses are for “maglev” high-speed trains and ships, power generation and transmission, energy storage systems, high-speed particle accelerators, and precision magnetic separation devices.
- The highest temperature at which superconductivity has been achieved is > 130 K. The substance used is a metal oxide composite (a material that has properties of a ceramic), one of a general class called *peroskovites*. These substances have formulas such as $\text{YBa}_2\text{Cu}_3\text{O}_{7(\text{s})}$, the famous 1-2-3 oxide of yttrium, barium, and copper, which was the first material to superconduct at a temperature higher than that of boiling liquid nitrogen (-196 °C or 77 K).

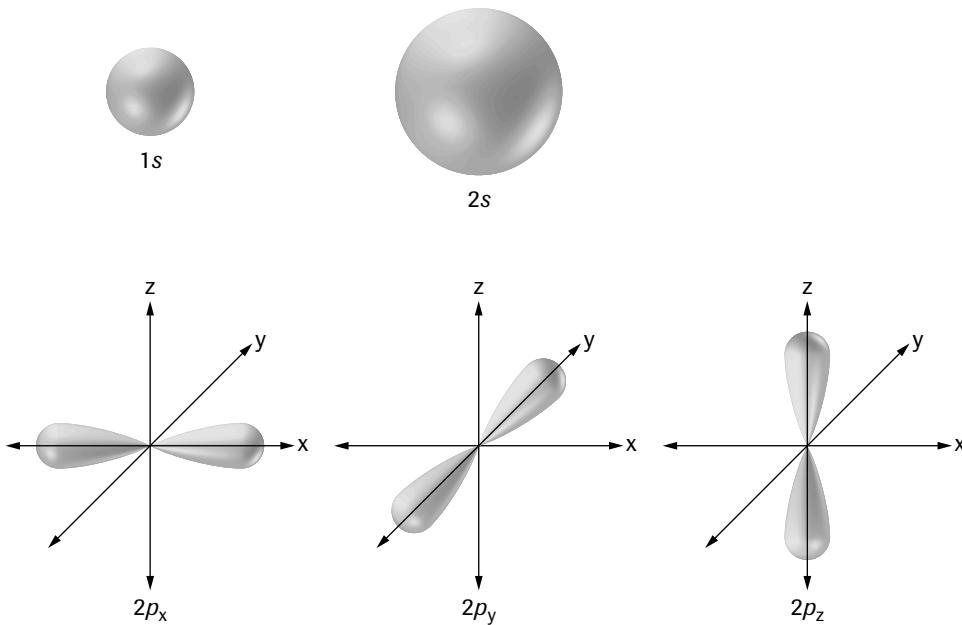
3.8 APPLICATIONS OF QUANTUM MECHANICS

Try This Activity: Bar Code Scanners

(Page 205)

- Red or white areas reflect red laser light strongly; black, dark blue, and green areas least strongly.

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- (b) Bar code scanners read the bright-to-dark-to-bright light level changes, and how long they last (which depends on the code line width) as an information signal.

SECTION 3.8 QUESTIONS

(Page 206)

Understanding Concepts

1. Laser light is *monochromatic* (one colour/wavelength/frequency), *coherent* (acts like one long continuous wave), and *collimated* (rays are quite precisely parallel).
2. Lasers work on a principle of raising many electrons to a higher energy level, and then stimulating them to drop to a lower level all at once, producing an output of a very large number of photons.
3. Applications of the principles of quantum mechanics in medical diagnosis include the use of infrared spectrometers to detect traces of substances in body tissues and fluids; and the use of MRI machines to scan the inside of the body by causing tissues to emit microwave radiation.

Making Connections

4. (Student reports will vary, but should include a basic description and diagrams of X-ray diffraction due to interference of the very short electromagnetic wavelengths with the similarly sized spacings between entities in solid crystals—which provides information about the sizes, shapes, charges, and arrangements of these entities in condensed phases. A simple parallel phenomenon is the diffraction pattern created when a pocket laser pointer beam is reflected from the surface of a CD. The angular displacement of the secondary images is proportional to the line spacing on the CD. Students with physics background in calculations of the diffraction of light from diffraction gratings can easily calculate the CD line spacing using the same technique.)

CAREERS IN CHEMISTRY

PRACTICE

(Page 207)

Making Connections

1. (A typical report would include information such as:)

In the field of Biochemistry, a gene medicine scientist may do precise mass determinations of purified peptides, proteins, and oligosaccharides, using MALDI (Matrix Assisted Laser Desorption/Ionization time of flight) mass spectroscopic analysis. A scientist in charge of this area for a company would also prepare complex biological samples and determine atomic sequencing in organic molecules, in order to identify and develop new therapeutic materials. Such a position would require a Ph.D. in biochemistry or chemistry, preferably with a few years postdoctoral experience, or an M.Sc. in biochemistry with 10+ years of related experience. People in this area are in demand worldwide, and annual salaries on the order of \$100 000 are not uncommon in industrial areas.

CHAPTER 3 LAB ACTIVITIES

INVESTIGATION 3.1.1 THE NATURE OF CATHODE RAYS

(Page 209)

Evidence/Analysis

(a)

Observations of a Cathode Ray and Laser Light		
	Cathode ray	Laser light
Effect of bar magnet	ray moves perpendicular to the long axis of bar magnet	no effect
Effect of charged plates	ray moves toward positive plate and away from negative plate	no effect

- (b) Bar code scanners read the bright-to-dark-to-bright light level changes, and how long they last (which depends on the code line width) as an information signal.

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- (b) According to the evidence collected, both electric charges and magnets change the direction of cathode rays but not laser light. Therefore, cathode rays are different in nature from electromagnetic radiation like visible light.

Evaluation

- (c) There are no obvious flaws in the design. The materials and procedure could be improved by including several different sources of cathode rays and different types of light. This would produce more evidence to make the answer to the question more certain.
(Other effects could also be tested.)
- (d) The hypothesis that cathode rays are a form of electromagnetic radiation has been shown to be false because the evidence clearly shows significant differences between cathode rays and light.

Synthesis

- (e) The bending of cathode rays when passing near electrically charged plates suggests that cathode rays contain charged particles.
- (f) Opposite electric charges attract each other and like charges repel. The evidence that cathode rays are attracted to the positively charged plate and repelled from the negative plate suggests that cathode rays contain negatively charged particles.

ACTIVITY 3.1.1 RUTHERFORD'S GOLD FOIL EXPERIMENT

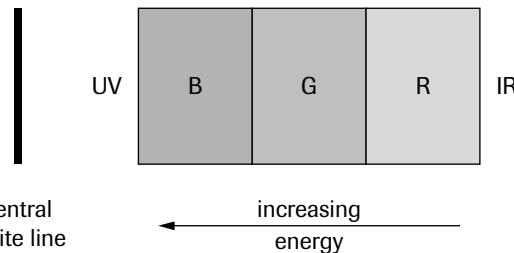
(Page 210)

- animation mode; activity of source = average; scintillations set to remain; time = 5 min
 - Most alpha particles are deflected within 20° of the straight-line path; a few alpha particles are deflected up to 40°, occasionally up to 60°, and very rarely beyond 90° (only 2 in this simulation).
- (a) According to the Thomson atom model, a stream of alpha particles should pass more or less straight through a gold foil, perhaps deflecting a little.
- (b) Rutherford's results showed that the majority of alpha particles deflected little but some alpha particles deflected significantly and few appeared to "bounce back."
- (c) Almost all of the alpha particles were relatively undeflected, suggesting that the nucleus is very much smaller than the atom, because most alpha particles miss it completely.
- (d) The evidence conflicts strongly with the Thomson model, which therefore must be replaced with a new model.
- (e) The general pattern of the results with aluminum foil should be similar to that with the gold foil. With aluminum foil, fewer alpha particles should deflect through significant angles because an aluminum nucleus (13 p^+) is not as positive as a gold nucleus (79 p^+).

ACTIVITY 3.3.1 HOT SOLIDS

(Page 210)

- (a) The filament starts with a dim, orange-red colour that becomes brighter and more orange, and then brighter and more yellow, and then brighter still and white.
- (b) "White hot" objects are much hotter than "red hot" ones.
- (c) Objects in a home that may be red hot at certain times include electric stove elements and wires in electric toasters.
- (d)



The main colours in the visible spectrum to the right of the central white line are blue, green, and red.

- (e) The region beyond the blue is called ultraviolet; and the region beyond the red is called infrared.

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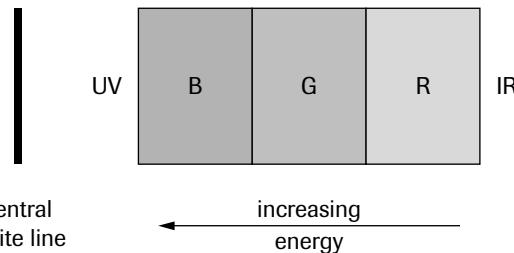
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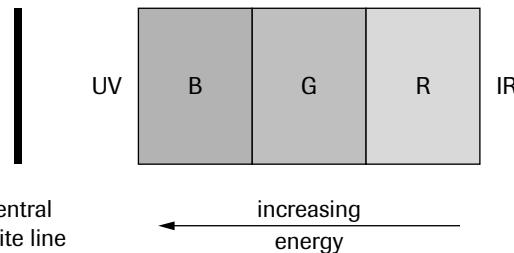
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The main colours in the visible spectrum to the right of the central white line are blue, green, and red.

- (e) The region beyond the blue is called ultraviolet; and the region beyond the red is called infrared.

- (f) A fluorescence indicates the presence of invisible ultraviolet light. (Note that this is not likely visible if the light passes through the lenses of an overhead projector. Evidence for UV is more easily obtained using a diffraction grating and a simple screen without a projector.)
- (g) Being exposed to a red lamp is much more dangerous, because UV photons have much more energy than red photons.
- (h) (on diagram)

INVESTIGATION 3.3.1 THE PHOTOELECTRIC EFFECT

(Page 211)

Evidence

- (a) • When charged, the vane of the electroscope moved to about 45° from the vertical.
- When the charged electroscope was touched, the vane returned to the vertical position.
- The 100-W light bulb did not produce any noticeable change in the angle of the vane of the charged electroscope.
- The UV light source caused the vane of the charged electroscope to immediately return to its vertical position. This was a permanent change because the vane did not return to its charged position when the light was removed.

Analysis

- (b) The bright white light shining on the charged electroscope did not produce any effect, just like the control test. There was no difference if the bright light was near or not.
- (c) Compared to the control, the UV light had the immediate and obvious effect of neutralizing the charged electroscope.
- (d) If the intensity of the light was a factor, the 100-W bulb should have produced the more noticeable effect. The 100-W light bulb is much brighter than the UV light. The results seem quite certain because the white light did not produce any effect and the effect of the UV light was immediate.
- (e) The zinc plate was initially neutral with equal numbers of protons and electrons. When the negatively charged vinyl strip contacts the zinc on the electroscope, some electrons are transferred from the vinyl strip to the zinc and electroscope. The zinc and electroscope now have an excess of electrons compared with protons and hence a negative charge.
- (f) The electroscope became less charged based on the evidence that the vane returned toward its electrically neutral vertical position.
- (g) The evidence suggests that most of the excess electrons on the zinc plate were removed as a result of the action of the UV light. Because the vane of the electroscope did not return to its charged position after the UV light was removed, the electrons must have escaped from the electroscope.

Evaluation

- (h) Another neutral electroscope or some other device with a meter could be placed near the zinc plate to see if any escaping electrons could be detected.
- (i) The vane or leaf electroscope could be replaced by a electrostatic meter attached to the zinc plate. The meter could give a measurement of the charge before, during, and after shining light onto the zinc plate.
- (j) I am not very certain because it is not possible to see or directly detect the electrons leaving the electroscope. It seems logical that electrons are leaving but where are they going?

Synthesis

- (k) If a glass plate is placed between the UV light and the zinc plate, the electroscope should not lose its negative charge and the vane should remain at the original angle.
- (l) Only if the window is open and the sunlight shines directly onto the electroscope should it discharge. Otherwise, the glass in the window would absorb the UV part of the sunlight.

ACTIVITY 3.4.1 LINE SPECTRA

(Page 212)

- (a) Neither glass nor water change the colours in the visible spectrum, so these substances do not absorb visible light.
- (b) The aqueous potassium permanganate absorbs the green light from the visible spectrum. The region of the spectrum that initially showed green is now black, flanked on either side by the blue and red bands.
- (c) The spectrum after passing through the iodine vapour showed the original blue and red but the green region was quite a bit darker with most of the green colour removed. The effect was about the same as the potassium permanganate but not as complete. Based on the disappearance of most of the green, gases such as iodine vapour can also absorb electromagnetic radiation.

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ACTIVITY 3.4.1 LINE SPECTRA

(Page 212)

- (a) Neither glass nor water change the colours in the visible spectrum, so these substances do not absorb visible light.
- (b) The aqueous potassium permanganate absorbs the green light from the visible spectrum. The region of the spectrum that initially showed green is now black, flanked on either side by the blue and red bands.
- (c) The spectrum after passing through the iodine vapour showed the original blue and red but the green region was quite a bit darker with most of the green colour removed. The effect was about the same as the potassium permanganate but not as complete. Based on the disappearance of most of the green, gases such as iodine vapour can also absorb electromagnetic radiation.

- (f) A fluorescence indicates the presence of invisible ultraviolet light. (Note that this is not likely visible if the light passes through the lenses of an overhead projector. Evidence for UV is more easily obtained using a diffraction grating and a simple screen without a projector.)
- (g) Being exposed to a red lamp is much more dangerous, because UV photons have much more energy than red photons.
- (h) (on diagram)

INVESTIGATION 3.3.1 THE PHOTOELECTRIC EFFECT

(Page 211)

Evidence

- (a) • When charged, the vane of the electroscope moved to about 45° from the vertical.
- When the charged electroscope was touched, the vane returned to the vertical position.
- The 100-W light bulb did not produce any noticeable change in the angle of the vane of the charged electroscope.
- The UV light source caused the vane of the charged electroscope to immediately return to its vertical position. This was a permanent change because the vane did not return to its charged position when the light was removed.

Analysis

- (b) The bright white light shining on the charged electroscope did not produce any effect, just like the control test. There was no difference if the bright light was near or not.
- (c) Compared to the control, the UV light had the immediate and obvious effect of neutralizing the charged electroscope.
- (d) If the intensity of the light was a factor, the 100-W bulb should have produced the more noticeable effect. The 100-W light bulb is much brighter than the UV light. The results seem quite certain because the white light did not produce any effect and the effect of the UV light was immediate.
- (e) The zinc plate was initially neutral with equal numbers of protons and electrons. When the negatively charged vinyl strip contacts the zinc on the electroscope, some electrons are transferred from the vinyl strip to the zinc and electroscope. The zinc and electroscope now have an excess of electrons compared with protons and hence a negative charge.
- (f) The electroscope became less charged based on the evidence that the vane returned toward its electrically neutral vertical position.
- (g) The evidence suggests that most of the excess electrons on the zinc plate were removed as a result of the action of the UV light. Because the vane of the electroscope did not return to its charged position after the UV light was removed, the electrons must have escaped from the electroscope.

Evaluation

- (h) Another neutral electroscope or some other device with a meter could be placed near the zinc plate to see if any escaping electrons could be detected.
- (i) The vane or leaf electroscope could be replaced by a electrostatic meter attached to the zinc plate. The meter could give a measurement of the charge before, during, and after shining light onto the zinc plate.
- (j) I am not very certain because it is not possible to see or directly detect the electrons leaving the electroscope. It seems logical that electrons are leaving but where are they going?

Synthesis

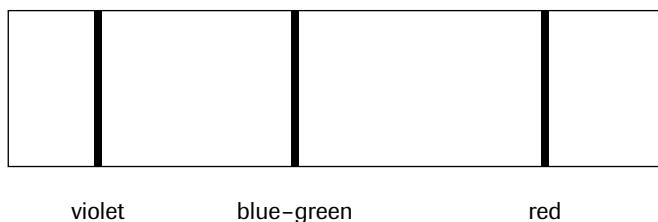
- (k) If a glass plate is placed between the UV light and the zinc plate, the electroscope should not lose its negative charge and the vane should remain at the original angle.
- (l) Only if the window is open and the sunlight shines directly onto the electroscope should it discharge. Otherwise, the glass in the window would absorb the UV part of the sunlight.

ACTIVITY 3.4.1 LINE SPECTRA

(Page 212)

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- (d) The evidence that some light is being absorbed is the dark lines across the spectrum. Possible gases that might be responsible would include the hydrogen and helium in the Sun and gases such as oxygen in Earth's atmosphere. (Almost all the dark lines in the visible region originate from elements in the Sun.)



- (e) Gases produce visible light when they are very hot (or when electricity is passed through them).
 (f) In this case (hot gases), the spectrum produced is a bright-line spectrum.
 (g) Line spectra are used in chemical analysis to identify substances by the colours (wavelengths or frequencies) of light that they emit or absorb.

ACTIVITY 3.4.2 THE HYDROGEN LINE SPECTRUM AND THE BOHR THEORY

(Page 213)

- (a) The wavelengths (shortest to longest) are about 410 nm, 434 nm, 486 nm, and 655 nm.
 (b) The wavelength is 656 nm.
 (c) A photon is released in this transition.
 (d) This transition ($3 \rightarrow 2$) corresponds to the first line in the Balmer series.
- For hydrogen energy-level transition: $n_i = 4, n_f = 2$:
 The wavelength is 486 nm.
 A photon is released.
 This transition corresponds to the blue-green line in the spectrum.
 - For hydrogen energy-level transition: $n_i = 5, n_f = 2$:
 The wavelength is 434 nm.
 A photon is released.
 This transition corresponds to the blue line in the spectrum.
 - For hydrogen energy-level transition: $n_i = 6, n_f = 2$:
 The wavelength is 410 nm.
 A photon is released.
 This transition corresponds to the violet (very deep blue) line in the spectrum.

- (e) Answers from Figure 3 are essentially the same as those from the computer simulation. It seems logical to assume the simulation would be programmed with the correct (accepted) values for these wavelengths.
 (f) An electron that absorbs a photon jumps to a higher energy level.
 (g) The wavelength of light emitted corresponding to the transition from $n_i = 3$ to $n_f = 2$ is identical to that for the light absorbed in the transition from $n_i = 2$ to $n_f = 3$. The Bohr theory requires that the energy of the levels be fixed, so the energy change, and hence the wavelength of the photons of light involved, must be fixed.
 (h) In the Bohr theory, only certain fixed orbits and energies are allowed. These orbits are numbered 1, 2, 3, etc. There are no other orbits in between.

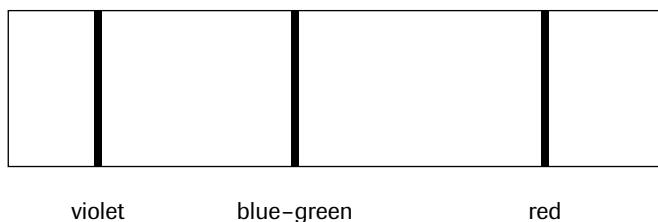
INVESTIGATION 3.5.1 PARAMAGNETISM

(Page 214)

Experimental Design

- (a) The independent variable is the metal ion in the compound. The dependent variable is the effect of the strong magnet. A controlled variable is the sulfate anion in each compound.

- (d) The evidence that some light is being absorbed is the dark lines across the spectrum. Possible gases that might be responsible would include the hydrogen and helium in the Sun and gases such as oxygen in Earth's atmosphere. (Almost all the dark lines in the visible region originate from elements in the Sun.)



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Experimental Design

- (a) The independent variable is the metal ion in the compound. The dependent variable is the effect of the strong magnet. A controlled variable is the sulfate anion in each compound.

Procedure

(b)

1. Place about 1 cm of each solid, packed with a stirring rod, into a clean, dry test tube.
2. Tie the end of about 15–20 cm of thread to the top of each test tube.
3. Set up the lab stand with a horizontal bar.
4. Attach the other end of the threads to the horizontal bar for each test tube. (Tie all four test tubes to the bar if possible, or one at a time.)
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7. Dispose of the solids or return the solids (as directed by your teacher).

Evidence

(c)

Paramagnetism of Metal Salts	
Substance	Effect of magnet
$\text{CaSO}_4\text{(s)}$	no noticeable effect
$\text{ZnSO}_4 \cdot 7\text{H}_2\text{O(s)}$	no noticeable effect
$\text{CuSO}_4 \cdot 5\text{H}_2\text{O(s)}$	a very slight attraction
$\text{MnSO}_4 \cdot \text{H}_2\text{O(s)}$	clearly attracted

Analysis

- (d) Based on the evidence, manganese(II) ions are obviously paramagnetic and copper(II) ions are likely weakly paramagnetic.

Evaluation

- (e) The experimental design should control the amount of the substances used and be more specific about the testing with the magnet, which seems a little vague. Perhaps the metal ions should be tested in solution form.
- (f) More substances should be tested and a much stronger magnet should be available. The procedure should include testing the aqueous solution of each substance. Testing with a magnet should be done inside a box so that air currents are not a factor.
- (g) The evidence for the manganese(II) compound appears quite certain but the others are less certain. Because the observations were not very precise, it is possible that some substances that had no effect might be weakly affected. Some sources of error or uncertainty are the qualitative judgment of any effect, possible air currents, quantity of the substances used, and the strength of the magnet.

LAB EXERCISE 3.6.1 QUANTITATIVE PARAMAGNETISM

(Page 215)

Prediction/Hypothesis

- (a) Based on the hypothesis that unpaired electrons of atoms or ions in a substance are responsible for the paramagnetism of a substance, the greater the number of unpaired electrons per atom, the greater the strength of the paramagnetism.

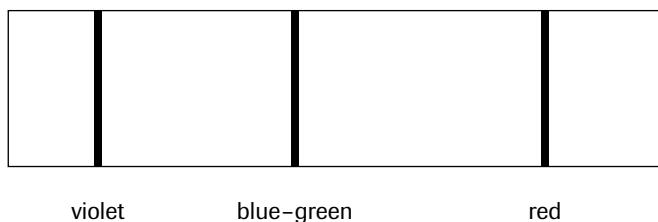
Experimental Design

- (b) The independent variable is the metal ion in the ionic compound tested. The dependent variable is the apparent change in mass as registered on the balance. Some controlled variables are the distance between the test tube and the magnet and the mass of the compound used.

Analysis

- (c) A zero mass reading indicates that the substance in the test tube is not paramagnetic because it does not affect the magnet. A negative mass reading on the balance indicates that a paramagnetic substance is attracting the magnet, lifting it slightly from the balance pan.

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Experimental Design

- (b) The independent variable is the metal ion in the ionic compound tested. The dependent variable is the apparent change in mass as registered on the balance. Some controlled variables are the distance between the test tube and the magnet and the mass of the compound used.

Analysis

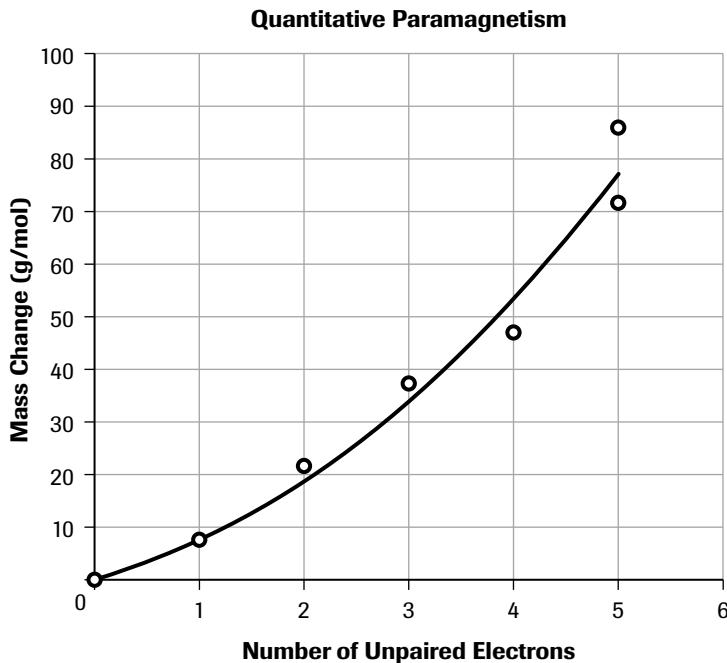
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(d) The greater the change in mass, the stronger the paramagnetism of the substance.

(e)

Quantitative Paramagnetism			
Metal ion	Electron configuration	Number of unpaired electrons	Mass decrease per mole (g/mol)
Ca ²⁺	[Ar]	0	0
Al ³⁺	[Ne]	0	0
Cu ⁺	[Ar]3d ¹⁰	0	0
Cu ²⁺	[Ar]3d ⁹	1	7
Ni ²⁺	[Ar]3d ⁸	2	21
Co ²⁺	[Ar]3d ⁷	3	37
Fe ²⁺	[Ar]3d ⁶	4	47
Mn ²⁺	[Ar]3d ⁵	5	71
Fe ³⁺	[Ar]3d ⁵	5	86

(f)



(g) According to the evidence collected and the graph, as the number of unpaired electrons in an ion increases, the strength of the paramagnetism increases.

Evaluation

(h) There are no obvious flaws in the design of this experiment. It may be better to control the anion present with the metal ion instead of using some chlorides and sulfates. Another improvement might be to specify more precisely the distance when the mass reading is taken. Instead of "just before" contact, a small but specific distance could be used.

- (i) Many more samples repeating the same number of unpaired electrons should be tested. This would make the pattern on the graph and a specific relationship more certain.
- (j) I am relatively confident in the answer because the trend on the graph seems clear.
- (k) The prediction was verified because the experimental answer agrees in principle with the predicted answer.
- (l) The hypothesis that the number of unpaired electrons determines the strength of the paramagnetism appears to be acceptable. The relationship is not a simple, direct one but the strength of the paramagnetism clearly increases with an increasing number of unpaired electrons per ion in the sample.

ACTIVITY 3.7.1 MODELLING STANDING ELECTRON WAVES

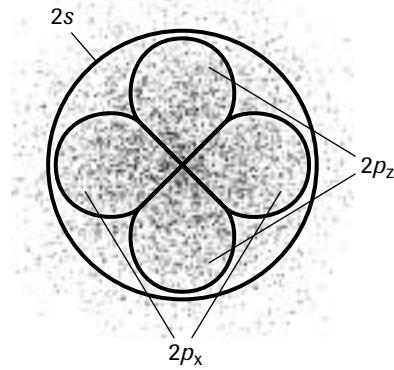
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- (a) Nodes are points along the wire that do not move, while antinodes are regions along the wire that move back and forth more than anywhere else. The antinodes appear like a blur because the wire is moving very quickly back and forth.
- (b) Only certain frequencies produce standing wave patterns. The patterns can form for only specific numbers of wavelengths “contained” around the wire.
- (c) The number of antinodes ranges from as few as one, to as many as about twelve (depending on the size of the loop).
- (d) The wave mechanics model of the atom is thought to be similar, in that electrons act like standing waves within an atom, with only certain allowable vibration energies based on electron wavelength. Some limitations of this comparison are that this activity is restricted to very simple finite patterns restricted to a circular path, whereas electron “standing waves” are three-dimensional probability structures, and sometimes very complex in nature.

ACTIVITY 3.7.2 SIMULATION OF ELECTRON ORBITALS

(Page 217)

- (a) Quantum mechanics theory describes a region in space (an orbital) where an electron is likely to be found at many instances of time. The Bohr theory shows an electron as a tiny particle in a specific orbit or path.
- (b) The 1s orbital shows a probability density that is circular (in 2-D) and decreases in density from the centre. The 2s orbital also has a circular probability density but it is not uniform. There is a high-density region near the centre, then a zero density shell, and then an outer high-density shell.
- (c) A 2s orbital is much larger, and has a much higher energy than a 1s orbital.
- (d) The 2s orbital has a circular electron probability density, whereas the 2p orbital has two lobes (∞). The $2p_x$ and $2p_y$ are identical in distribution but oriented at right angles to each other.
- (e) The $2p_z$ orbital is missing. This orbital is identical in shape to the $2p_x$ and $2p_y$ orbitals except for orientation. It is oriented with its long axis at 90° to the other two p orbitals—into and out of the plane of the screen.
- (f) With 6 electrons, the atom represented would be carbon, C.
- (g) The combined electron probability distribution would be spherical.
- (h)



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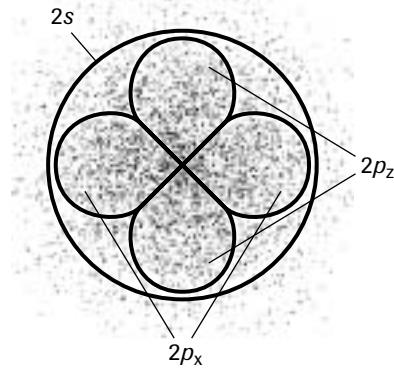
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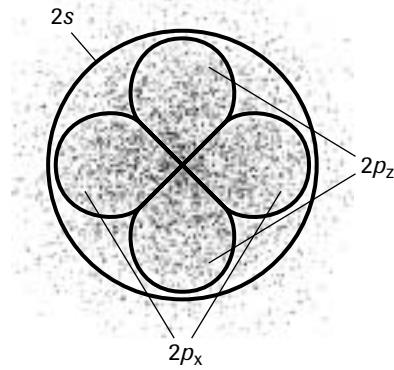
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(Page 217)

- (a) Quantum mechanics theory describes a region in space (an orbital) where an electron is likely to be found at many instances of time. The Bohr theory shows an electron as a tiny particle in a specific orbit or path.
- (b) The 1s orbital shows a probability density that is circular (in 2-D) and decreases in density from the centre. The 2s orbital also has a circular probability density but it is not uniform. There is a high-density region near the centre, then a zero density shell, and then an outer high-density shell.
- (c) A 2s orbital is much larger, and has a much higher energy than a 1s orbital.
- (d) The 2s orbital has a circular electron probability density, whereas the 2p orbital has two lobes (∞). The $2p_x$ and $2p_y$ are identical in distribution but oriented at right angles to each other.
- (e) The $2p_z$ orbital is missing. This orbital is identical in shape to the $2p_x$ and $2p_y$ orbitals except for orientation. It is oriented with its long axis at 90° to the other two p orbitals—into and out of the plane of the screen.
- (f) With 6 electrons, the atom represented would be carbon, C.
- (g) The combined electron probability distribution would be spherical.
- (h)



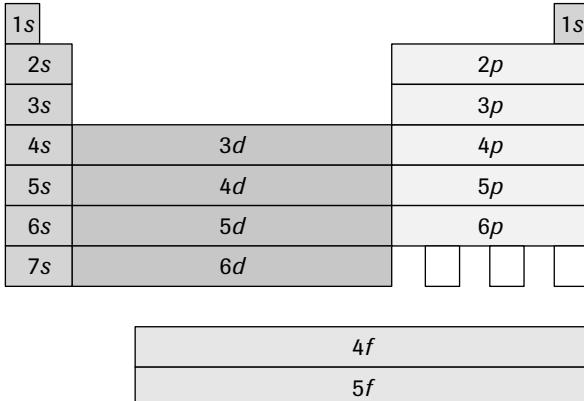
CHAPTER 3 SUMMARY

(Page 218)

Evolution of Atomic Theories		
Atomic theory	Key experimental work	Contribution to theory
Rutherford	-alpha particle scattering through gold foil	-nucleus
Bohr	-hydrogen spectral lines	-quantized energy levels (principal quantum number)
Quantum Mechanics	-hydrogen spectral lines made up of closely spaced lines	-secondary quantum number
	-splitting of spectral lines caused by a magnetic field	-magnetic quantum number
	-magnetism	-spin quantum number
	-wave and particle properties of light and electrons	-wave nature of electrons -wave mechanics

- Planck: first suggestion of a quantum of energy
- Bohr: first use of quantum idea in an atomic model
- Sommerfeld: idea of subshells or sublevels leading to shapes of orbitals
- de Broglie: idea of wave nature of electrons
- Einstein: photon theory to explain photoelectric effect using quantum idea; integral to the development of the Bohr theory
- Schrödinger: extended de Broglie's idea to develop a mathematical model of an atom based on wave mechanics
- Heisenberg: developed probability interpretation of quantum mechanics

- (a)



- (b) Most of the empirical justification comes from the study of atomic spectra but other evidence also comes from physical and chemical properties of elements.
- (c) Quantum mechanics theory of electron energies in orbitals.

CHAPTER 3 SELF-QUIZ

(Page 219)

1. False: The region in space where an electron is most likely to be found is called an orbital.
2. False: Electron configurations are often condensed by writing them using the previous noble-gas core as a starting point. In this system, [Ar] $3d^34s^2$ would represent vanadium.
3. False: The f sublevel is thought to have seven orbitals.
4. True
5. True
6. False: Rutherford knew the nucleus had to be very small because very few alpha particles were deflected when fired through a layer of gold atoms.
7. False: Electrons shifting to lower levels, according to Bohr, would account for emission spectra.
8. True
9. True
10. True
11. False: The Pauli exclusion principle states that no more than two electrons may occupy the same orbital, and that they must have opposite spins.
12. (b)
13. (d)
14. (a)
15. (c)
16. (c)
17. (b)
18. (b)
19. (d)

CHAPTER 3 REVIEW

(Page 220)

Understanding Concepts

1. (a) Rutherford interpreted the deflection of alpha particles travelling through a thin foil to mean that atoms had tiny, massive nuclei.
(b) Bohr interpreted the bright-line spectrum of hydrogen to mean that electrons exist only at specific energy levels.
2. The Rutherford model explained nothing about the nature of electrons. The Bohr model did not make acceptable predictions for atoms larger than hydrogen.
3. Orbit and orbital are terms that both refer to electrons within atoms. An orbit is a simplistic representation of a small particle in a circular path, used in the Bohr–Rutherford model. An orbital is a probability density for a wave function that “occupies” a volume of space, used in the visualizing of the quantum mechanical model.
4. The main kind of experimental work used to develop the concepts of quantum mechanics was spectroscopy, specifically the analysis of bright-line spectra.
5. (a) Quantum is a term referring to a smallest unit or part of something.
(b) Orbital is a term describing a volume of space that is “occupied” by an electron.
(c) Electron probability density describes the calculated likelihood of locating an electron at any point within a given volume of space.
(d) Photon is a quantum of electromagnetic energy—a smallest “piece” or “package” of light.
6.

$2p \uparrow\downarrow \uparrow \uparrow$	(a) the main/principal energy level is the first number: 1, 2, ...
$2s \uparrow\downarrow$	(b) the energy sublevel (subshell) is the letter following: s, p, \dots
$1s \uparrow\downarrow$	(c) the orbital orientation (x, y , or z axis) is the respective <u> </u> line
oxygen atom, O	(d) the spin of the electron (up or down) is the arrow: \uparrow or \downarrow
7. The idea of electron spin comes from observations of line spectra influenced by a magnetic field as well as evidence from different kinds of magnetism.

CHAPTER 3 SELF-QUIZ

(Page 219)

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(Page 220)

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6.

$2p$	$\uparrow\downarrow$	\uparrow	\uparrow
$2s$	$\uparrow\downarrow$		
$1s$	$\uparrow\downarrow$		

(a) the main/principal energy level is the first number: 1, 2, ...
(b) the energy sublevel (subshell) is the letter following: s , p , ...
(c) the orbital orientation (x , y , or z axis) is the respective line
(d) the spin of the electron (up or down) is the arrow: \uparrow or \downarrow

oxygen atom, O
7. The idea of electron spin comes from observations of line spectra influenced by a magnetic field as well as evidence from different kinds of magnetism.

8.	1s		
	2s		2p
	3s		3p
	4s	3d	4p
	5s	4d	5p
	6s	5d	6p
	7s	6d	
		4f	
		5f	

9. According to quantum mechanics, an element's properties relate to its position in the periodic table because its position is directly related to the orbital configuration of its atoms.

- | | | |
|-----|--|--|
| 10. | $3s$ $\uparrow\downarrow$
$3p$ $\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$ | $3s$ $\uparrow\downarrow$
$3p$ $\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$ |
| | $2s$ $\uparrow\downarrow$
$2p$ $\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$ | $2s$ $\uparrow\downarrow$
$2p$ $\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$ |
| | $1s$ $\uparrow\downarrow$
potassium ion, K^+ | $1s$ $\uparrow\downarrow$
sulfide ion, S^{2-} |

An atom of the noble-gas argon, Ar, has the same electron orbital energy-level diagram as do these two ions.

11. (a) All of the alkali metals are soft, metallic solids with low melting and boiling points. They have high chemical reactivity, readily forming +1 ions.
(b) We explain properties, using their electron configurations. All have a single *s* electron in the highest energy orbital, which is easily removed by the attraction of other atoms. The nearly empty valence shell creates the metallic properties—conductivity, shininess, and so on.

12. (a) $1s^2 2s^2 2p^6 3s^2$
(b) $1s^2 2s^2 2p^6 3s^2 3p^6$
(c) $1s^2 2s^2 2p^6 3s^2 3p^6$
(d) $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^1$
(e) $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^1 4f^{14} 5d^{10}$

13. (a) $[\text{Kr}] 5s^2 4d^1$
(b) $[\text{Kr}] 5s^2 4d^{10} 5p^3$
(c) $[\text{Xe}] \text{Ba}^{2+}$

14. Aluminum and titanium should be paramagnetic because these two atoms have unpaired electrons. Beryllium and mercury have atoms with filled orbitals.

15. (a) arsenic atom, As
(b) rubidium ion, Rb^+
(c) iodide ion, I^-
(d) holmium atom, Ho

16. (a) 2e^-
(b) 8e^-
(c) 18e^-
(d) 32e^-

17. A $2p_x$ orbital is identical to the $2p_y$ and $2p_z$ orbitals, except for orientation. It lies at 90° to the other two.

18. (a) Max Planck explained that electromagnetic energy could be released only in smallest given amounts, which he called “quanta,” with the amount determined by the frequency of the radiation.
(b) Louis de Broglie suggested that particles could have properties and characteristics of waves, and that this effect would be significant for tiny, fast-moving particles like electrons.

- (c) Albert Einstein proposed that light (electromagnetic energy) actually travels as quanta, which he called “photons,” and he used this concept to explain the evidence of the phenomenon called the photoelectric effect.
 - (d) Werner Heisenberg hypothesized that electron behaviour cannot ever be exactly described, but only discussed as a probability system, within limits imposed by his “uncertainty principle.”
 - (e) Erwin Schrödinger explained electron behaviour within the atom structure as a wave phenomenon, described by a wave mechanical equation.
19. (a) Both sodium and chlorine atoms have unfilled electron energy levels. When an electron transfers from a sodium atom to a chlorine atom, both attain the same electron configuration as a noble-gas atom. The noble gases are quite unreactive, which is thought to be due to their completely filled electron energy levels.
- (b) The occupied and empty energy levels for lithium and sodium are quite different. Therefore, electron transitions would be different, producing different colours. (It is not possible to explain or predict the specific colours in this course.)
- (c) Both sodium and silver atoms can obtain a more stable electron arrangement of filled electron orbitals if one electron is removed from an atom and it forms a $1+$ ion. A sodium ion becomes [Ne] and a silver ion becomes [Kr] $4d^{10}$. Combined with a chloride ion ($1-$), the formulas are therefore similar.
- (d) A tin atom has the electron configuration [Kr] $5s^2 4d^{10} 5p^2$. This atom could lose its $5p^2$ electrons to form a $2+$ ion or lose both the $5s^2$ electrons and the $5p^2$ electrons to form a $4+$ ion.

Applying Inquiry Skills

20. Evidence is the basis of the scientific process. Careful evaluation of evidence is crucial, since poor evidence may lead to incorrect support of a theory, law, or generalization. Good-quality evidence can also show an existing concept to be false.
21. Useful techniques would likely include spectroscopy—possibly visible, ultraviolet, and/or infrared.
22. (a) The design is basically good but you cannot visually observe the infrared spectrum using a hand-held spectroscope. It is also questionable whether the quality of a hand-held spectroscope will be adequate. The spectrum should be photographed with a good-quality spectroscope and suitable photographic film.
- (b) This design is inadequate to identify the components of a mixture. A flame test could suggest some components, particularly certain metal ions. A qualitative analysis scheme would be necessary to identify other components.
- (c) A better design would be to crush the cereal and insert the magnet directly into the cereal. This would be more likely to attract any small bits of iron present.
- (d) The calcium in calcium sulfate is in the form of calcium ions, not calcium metal. The test with a strong magnet should be done on calcium metal.
23. (a) The analogy is good in the sense that there are certain, fixed steps like quantized energy levels. However, the analogy fails in two ways. Electron energy levels are not evenly spaced and quantum mechanics has no picture of a particle such as an electron physically moving from one location to another.
- (b) The computer simulation can be useful to illustrate some characteristics suggested by the quantum mechanics if using a probability interpretation, not a wave model. Nevertheless, the computer program that is based on some simplified view of quantum mechanics cannot be used to test the theory. Only experimental evidence can provide this kind of a test.

Making Connections

24. (a) Some examples of benefits to medical diagnosis might include light spectroscopy, which is used to identify substances present in the body; MRI scanning, which allows examination of the interior of the body; and lasers, which allow illumination and examination of the body interior through fibre-optic devices.
- (b) Some possible answers and perspectives might include:
Economically, government funding of “pure” research is expensive; and the area does not include a profit or “payback” component.
Socially, the benefits to society from increased knowledge inevitably advance our standard of living in our understanding of the atom.
Scientifically, the entire scientific community constantly lobbies for funding for research to satisfy the *desire to know*.
25. (a) Rutherford won the Nobel Prize for Chemistry in 1908, for the concept of the nuclear atom, for the theory of radioactive disintegration, and for determining the nature of the alpha particle. Soddy won the Nobel Prize for Chemistry in 1921, for the discovery of (explaining the nature of) isotopes of elements.
- (b) Every aspect of modern technological society that has to do with radioactivity or nuclear energy in any form is to some extent directly dependent on work done by Rutherford and Soddy. This includes nuclear power generators, radioisotope uses in industry, research, analysis, and medicine, and our understanding of geologic processes, among many others.

CHAPTER 4 CHEMICAL BONDING

Reflect on Your Learning

(Page 222)

1. *[likely initial answer]* When elements react, the product will be a molecular compound if the reactants are both nonmetals, like chlorine and phosphorus; and the product will be an ionic compound if the reactants are a nonmetal and a metal, like chlorine and potassium.

[a more complete answer] When two nonmetals such as chlorine and phosphorus react, the relatively small difference in electronegativities results in a sharing of valence electrons to produce a covalently bonded molecule. Molecular substances may be solids, liquids, or gases, depending on the intermolecular forces present, and are nonconductors of electricity in any state, including aqueous. When a nonmetal and a metal such as chlorine and potassium react, the relatively large difference in electronegativities results in a transfer of one or more valence electrons from the metal to the nonmetal, producing positive and negative ions. Ionic substances are always solids at ambient temperatures, generally hard with high melting points, and conduct electricity in their molten and aqueous states.

2. *[likely initial answer]* We can explain and predict the bonding of some small, simple molecules with Lewis diagrams, using the octet rule.

[a more complete answer] We can explain and predict the bonding of some small, simple molecules by considering the valence orbitals in an electron configuration. A half-filled valence orbital on one atom can overlap with another half-filled valence orbital on a second atom to form a combined orbital with a pair of electrons of opposite spin. Considering either the shape of these valence orbitals or simply the number of groups of bonded electrons around a central atom, we can explain or predict the shape of a small molecule.

3. *[likely initial answer]* A structural diagram can be drawn for the molecular compounds: $C_5H_{12(l)}$, $CH_3OH_{(l)}$, and $CO_{2(s)}$. These substances will all be nonconductors of electricity in any state. Sodium, $Na_{(s)}$, is made up of sodium atoms and is a shiny, silvery solid that conducts electricity very well. Sodium chloride, $NaCl_{(s)}$, is an ionic compound made up of sodium and chloride ions. Sodium chloride is soluble in water and the solution conducts electricity. Diamond, $C_{(s)}$, is made up of carbon atoms and is a clear, colourless, very hard solid.

[a more complete answer]

$C_5H_{12(l)}$ is a molecular compound whose molecules contain five carbon atoms each with a tetrahedral arrangement of four single covalent bonds. This substance is nonpolar with a low melting and boiling point due to weak intermolecular attractive forces; and is probably not soluble in water.

$CH_3OH_{(l)}$ is a molecular compound whose molecules contain a carbon atom with a tetrahedral arrangement of four single covalent bonds and an oxygen atom with a V-shaped arrangement of two single covalent bonds. This polar compound has a somewhat higher melting and boiling point, compared to similar-sized nonpolar molecules, due to hydrogen bonding intermolecular attractive forces; and is probably soluble in water.

$Na_{(s)}$ is a metallic element with sodium cations in a sea of mobile valence electrons which produces a non-directional bonding. This explains its mechanical properties and electrical conductivity. The low electronegativity of a sodium atom partly explains its reactivity and tendency to form ionic compounds.

$NaCl_{(s)}$ is an ionic compound, with strong ionic bonding between its cations and anions. The ions are arranged in a lattice structure with a regular repeating pattern of alternating positive and negative ions. The structure explains its crystalline nature, hardness, and relatively high melting and boiling point.

$CO_{2(s)}$ is a molecular compound with linear molecules containing double covalent bonds between the carbon and the oxygen atoms. The bond dipoles cancel to produce a nonpolar molecule. Because the molecules are relatively small and only London forces exist between them, the melting and boiling point should be relatively low.

$C_{(s)}$ (diamond) is a nonmetallic element with a continuous network of carbon atoms connected to each other in a tetrahedral bonding arrangement. A diamond is like a single macromolecule. The 3-D arrangement of relatively strong covalent bonds explains its great hardness and very high melting and boiling point.

Try This Activity: Properties and Forces

(Page 223)

- The glass and the plate do not slide over each other easily when pressed together.
- Dishwashing liquid does not make the surface between the glass and plate slippery when they are pressed together.
- The gear oil does make the contact surface between the glass and plate slippery, even when they are pressed together.
- Dishwashing liquid seems to be a more effective adhesive.

- (e) Dishwashing liquid molecules must attract water molecules better than they attract each other because water dissolves the substance and washes it away. Gear oil molecules must attract each other better than they attract water molecules—because water doesn't dissolve the oil or wash it away.
- (f) We observe that the dishwashing liquid will mix with (dissolve) the oil, and the mixture (solution) of the two will dissolve in water, and be washed away. It seems that dishwashing liquid molecules are somehow able to attract both water molecules and oil molecules.
- (g) Dishwasher detergent is thick and viscous, so its molecules are quite cohesive, and seem to be adhesive to glass and water and oil. Gear oil molecules are less cohesive, and not very adhesive to glass or water—only to the dishwashing liquid. This seems logical, since dishwashing liquids are designed to attract and dissolve all kinds of food materials; and gear oil is designed to make metal surfaces slide against each other without wearing down.

4.1 LEWIS THEORY OF BONDING

PRACTICE

(Page 227)

Understanding Concepts

1. (a) Mg - 2, Cl - 1

(b) C - 4, H - 1

(c) H - 1, O - 2

(d) H - 2, S - 2

(e) N - 3, H - 1

2. In the order that they were created by chemists, we have the (c) Dalton atom, (b) empirical formulas, (d) Kekulé structures, (a) Lewis structures, and (e) Schrödinger quantum mechanics.

3. (a) $1s^2 2s^2 2p^6 3s^2 3p^1$ $\cdot\text{Al}\cdot$

(b) $1s^2 2s^2 2p^6 3s^2 3p^5$ $:\ddot{\text{Cl}}:$

(c) $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$ $\cdot\text{Ca}\cdot$

(d) $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^2$ $\cdot\dot{\text{Ge}}\cdot$

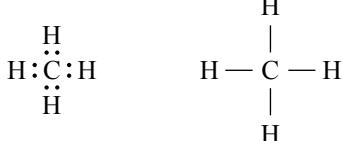
4. (a) $:\ddot{\text{O}}:$

(b) $\cdot\ddot{\text{P}}\cdot$

(c) $:\ddot{\text{Br}}:$

(d) $\text{Rb}\cdot$

5. (a)



- (e) Dishwashing liquid molecules must attract water molecules better than they attract each other because water dissolves the substance and washes it away. Gear oil molecules must attract each other better than they attract water molecules—because water doesn't dissolve the oil or wash it away.
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PRACTICE

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(b) $1s^2 2s^2 2p^6 3s^2 3p^5$ $:\ddot{\text{Cl}}:$

(c) $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$ $\cdot\text{Ca}\cdot$

(d) $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^2$ $\cdot\dot{\text{Ge}}\cdot$

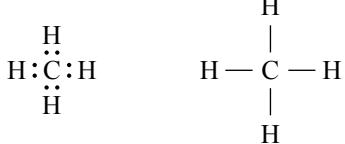
4. (a) $:\ddot{\text{O}}:$

(b) $\cdot\ddot{\text{P}}\cdot$

(c) $:\ddot{\text{Br}}:$

(d) $\text{Rb}\cdot$

5. (a)





Applying Inquiry Skills

6. A new scientific concept must explain existing evidence, and should predict new observations successfully, before it is generally accepted by the scientific community.
7. Decompose a known mass of a pure compound. Identify and measure the masses of the products produced.

Extension

8. Kekulé structures simply showed which atoms were bonded to which, while Lewis structures explain the bonding in terms of electron arrangement.
9. Were Lewis structures derived from quantum theory? Lewis himself said no, and has a body of notes to support this. Others say the parallels with Sommerfeld's work on electron energy sublevels are too great to be due to coincidence. The truth probably lies between, since this was long past any time where scientists worked isolated from knowledge of the work of others.

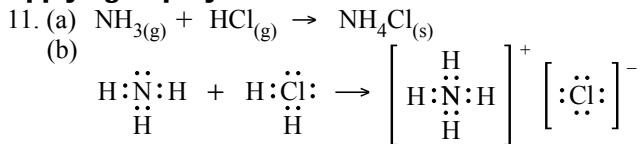
PRACTICE

(Page 229)

Understanding Concepts

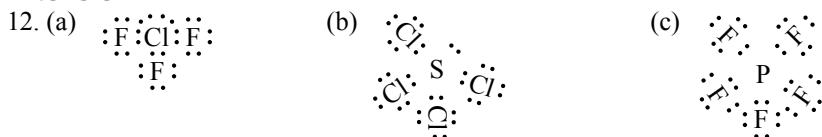
10. (a) $\left[\begin{array}{c} \ddot{\text{O}} \\ | \\ \text{O} \\ | \\ \ddot{\text{O}} \end{array} \text{:Cl} \text{:} \begin{array}{c} \ddot{\text{O}} \\ | \\ \text{O} \\ | \\ \ddot{\text{O}} \end{array} \right]^-$ 32 e⁻ total (b) $\left[\begin{array}{c} \ddot{\text{O}} \\ | \\ \text{O} \\ | \\ \text{C} \\ | \\ \ddot{\text{O}} \end{array} \text{:} \begin{array}{c} \ddot{\text{O}} \\ | \\ \text{O} \\ | \\ \ddot{\text{O}} \end{array} \right]^{2-}$ 24 e⁻ total (c) $[\text{:C} \text{:}\ddot{\text{N}}:]^-$ 10 e⁻ total
- (d) $\left[\begin{array}{c} \text{H} \\ | \\ \ddot{\text{O}} \\ | \\ \text{H} \end{array} \text{:H} \right]^+$ 8 e⁻ total (e) $\left[\begin{array}{c} \ddot{\text{O}} \\ | \\ \text{C} \\ | \\ \ddot{\text{O}} \end{array} \text{:} \begin{array}{c} \ddot{\text{O}} \\ | \\ \text{H} \end{array} \right]^-$ 24 e⁻ total (f) $\left[\begin{array}{c} \ddot{\text{O}} \\ | \\ \text{N} \\ | \\ \ddot{\text{O}} \end{array} \text{:H} \right]^-$ 24 e⁻ total
- (g) $[\text{:N} \text{:}\ddot{\text{O}}:]^+$ 10 e⁻ total

Applying Inquiry Skills



(c) Test the solubility of the product in water. Measure the electrical conductivity of the aqueous solution and add a few crystals of silver nitrate to test for the presence of chloride ions by precipitating silver chloride.

Extension

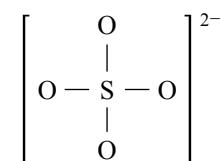
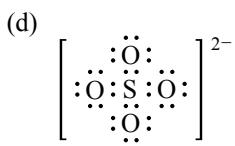
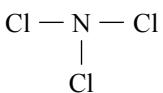
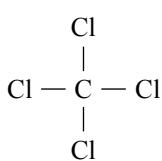
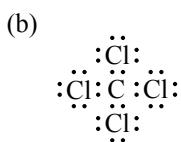
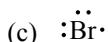
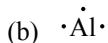
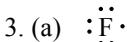
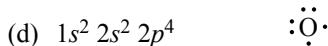
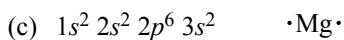
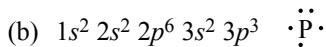


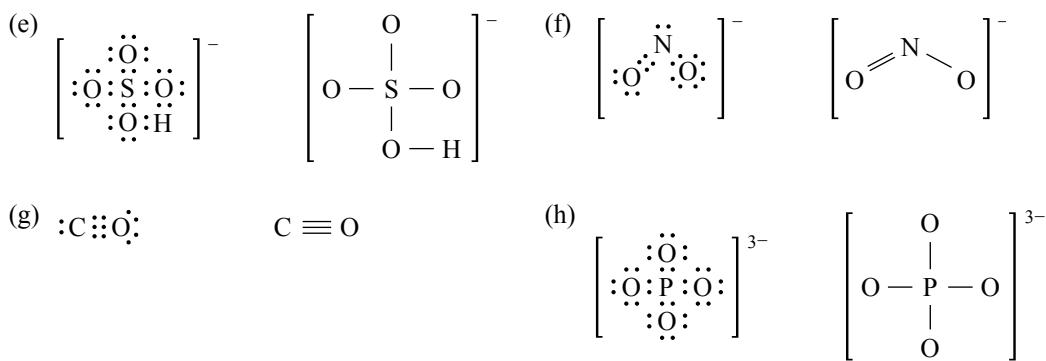
SECTION 4.1 QUESTIONS

(Page 230)

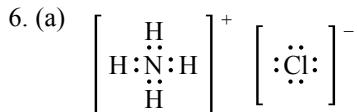
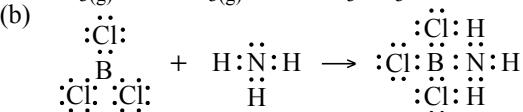
Understanding Concepts

1. The Dalton atom concept made it possible to express chemical composition of compounds as empirical formulas. The later development of electron energy levels in the Bohr atom concept made it possible for Lewis diagrams to show how valence electron rearrangement is involved in reactions.





Extensions



(b) The compound is easy to represent with Lewis structures once you accept the idea of ammonium as a polyatomic positive ion, with nitrogen able to bond four times to hydrogen if an electron is removed.

4.2 THE NATURE OF THE CHEMICAL BOND

PRACTICE

(Page 232)

Understanding Concepts

- A helium atom has a single orbital containing a pair of electrons. Generally, two half-filled orbitals overlap to form a bond.
- An orbital formed from overlap of two atomic orbitals is like an individual atomic orbital in that it is full when two paired electrons occupy it.
- This overlap is not possible because it would include three electrons occupying one shared orbital.

4. (a)

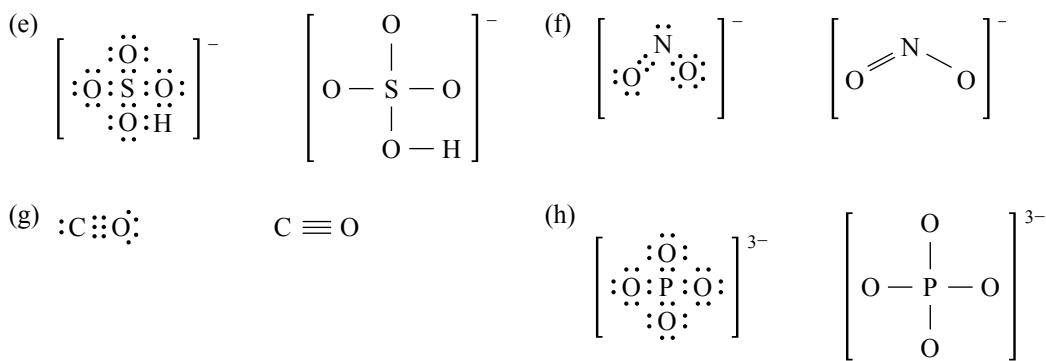


1s and 2p orbitals

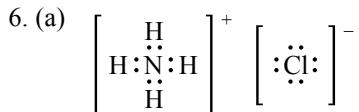
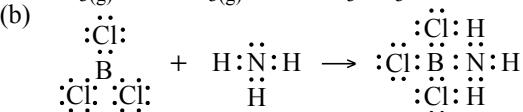
(b)



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Extensions



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PRACTICE

(Page 232)

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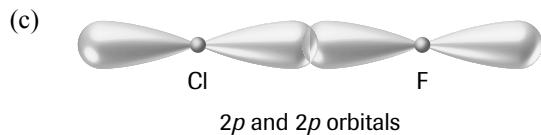


1s and 2p orbitals

(b)

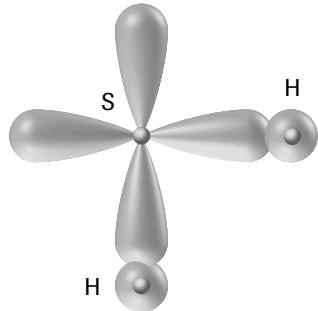


2p and 2p orbitals



Applying Inquiry Skills

5. (a)



two 1s and two 2p orbitals

- (b) The angle for the H—S—H bonds is predicted to be 90° , since that is the angle between the two *p* orbitals of the sulfur that are involved in the bonding.
- (c) The prediction is close to the measured angle and therefore inconclusive. The experimental uncertainty of the measured 92° is required to see if the small difference can be explained by the quality of the measurements. If not, then the valence bond theory may require a revision or adjustment.

Making Connections

6. An understanding of covalent bonding allows us to better understand the relationships between properties of substances and their molecular structure. This allows analyses of substances, which is critical in medicine and industry for diagnosing problems, and also allows the prediction and fabrication of new substances with desired properties, like plastics, pharmaceuticals, and alloys.

Extension

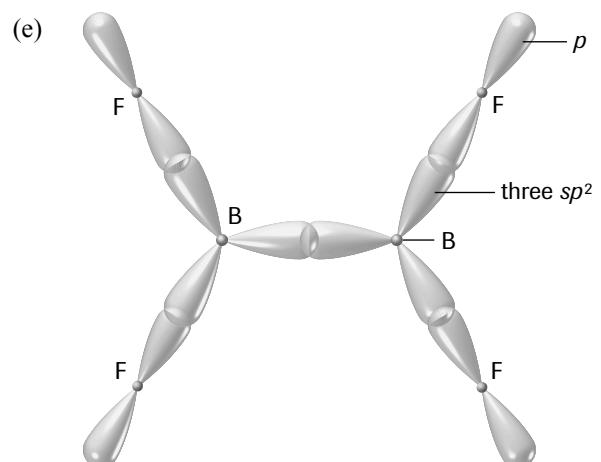
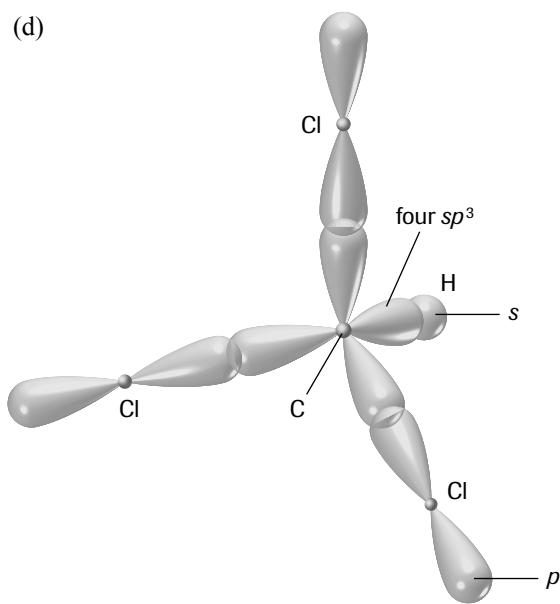
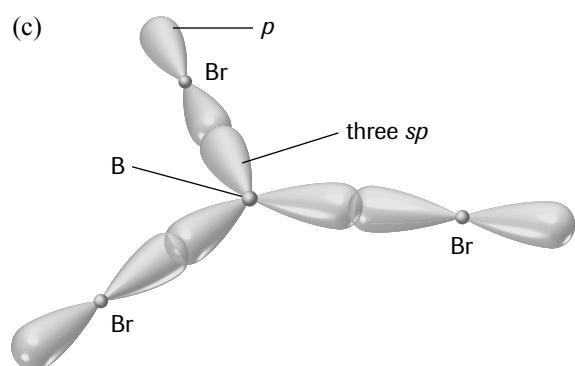
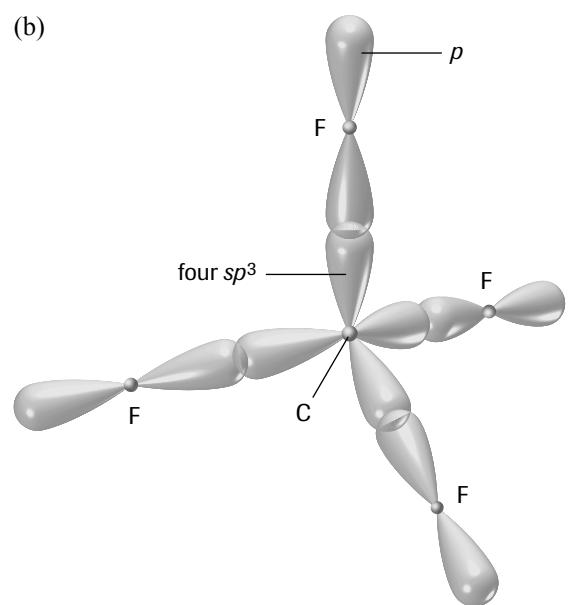
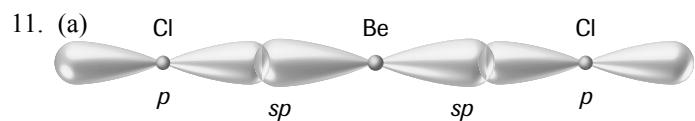
7. Molecular orbital theory is an alternative to the valence bond theory for the theoretical description of the bonding in molecules. Both theories use the concept of an orbital and the same rules for filling orbitals with electrons. However, molecular orbital theory constructs orbitals that encompass all of the nuclei in the molecule. (Valence bond theory uses atomic orbitals, such as *s* and *p*, to construct a bonding orbital by an overlap of atomic orbitals.)

PRACTICE

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Understanding Concepts

8. (a) one 1s orbital
 (b) one 2*p* orbital
 (c) two 3*p* orbitals
 (d) one 4*p* orbital
9. Two electrons are present in an orbital formed from overlap.
10. (a) ground state— $1s^2 2s^2 2p^2$ promoted state— $1s^2 2s^1 2p^3$ sp^3 hybridization
 (b) ground state— $1s^2 2s^2 2p^1$ promoted state— $1s^2 2s^1 2p^2$ sp^2 hybridization
 (c) ground state— $1s^2 2s^2$ promoted state— $1s^2 2s^1 2p^1$ sp hybridization



12. Promoting electrons to higher energy levels uses less energy than is gained by allowing more bonds to form.
13. Hybridized orbitals are formed only during bonding—they do not exist in isolated atoms.
14. The hybridized orbital concept was necessary to explain the similarity of bonds and the observed bond angles in structures like CH_4 , and to explain the formation of double and triple bonds.

Applying Inquiry Skills

15. Two typical examples: Knowledge of empirical formulas preceded and led to the Lewis structure theory, and empirical knowledge of the equivalence of bonding orbitals in carbon preceded and led to the theory of hybridization.
16. To determine the hybridization of atomic orbitals in a molecule, we require experimental evidence for the molecular formula, and experimental evidence for the bond angles.

Extension

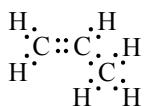
17. (a) PCl_5 requires five hybrid orbitals, and SF_6 requires six, using their valence, from the given formulas for their compounds. Using promotion of electrons in orbital configurations, we obtain the same answer.
(b) Using promotion of electrons in orbital configurations:
P atom: $1s^2 2s^2 2p^6 3s^2 3p^3$ to $1s^2 2s^2 2p^6 3s^1 3p^3 4d^1$
S atom: $1s^2 2s^2 2p^6 3s^2 3p^4$ to $1s^2 2s^2 2p^6 3s^1 3p^3 4d^2$
(c) Scientists know the directions of hybrid orbitals from the molecular shape, which can be determined by spectroscopy and X-ray diffraction.

PRACTICE

(Page 238)

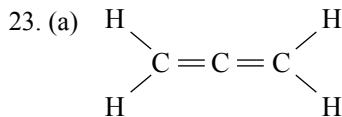
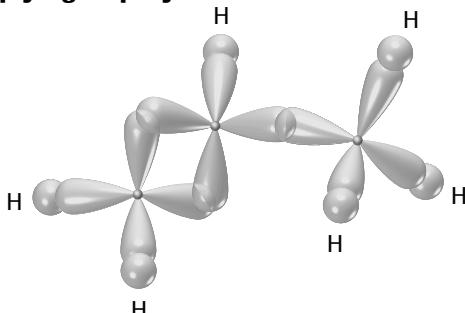
Understanding Concepts

18. Pi bonds are formed by the side-to-side overlap of p orbitals of adjacent atoms.
19. The concept of the pi bond was created to explain double and triple bonding between atoms.
20. (a) $\text{C}_2\text{Cl}_{4(l)}$ molecules have a double bond between the two carbons. Each carbon is sp^2 hybridized, which gives three bonding orbitals in a trigonal planar shape. Two of these sp^2 orbitals form σ bonds with hydrogens, and one with the other carbon. Each carbon also has one more bonding (p) orbital which forms the π bond with the other carbon atom.
(b) $\text{H}_2\text{CO}_{(g)}$ molecules have a double bond between the carbon and the oxygen. The carbon is sp^2 hybridized, which gives three bonding orbitals in a trigonal planar shape. Two of these sp^2 orbitals form σ bonds with hydrogens, and one with the oxygen. The carbon and the oxygen also each have one more bonding (p) orbital which overlaps side to side to form the π bond.
(c) $\text{CO}_{2(g)}$ molecules have double bonds between the carbon and each oxygen. Each carbon is sp hybridized, which gives two bonding orbitals in a linear shape. These two sp orbitals each form σ bonds with an oxygen. The carbon has two more bonding (p) orbitals, and each oxygen has one more bonding (p) orbital; and on each side of the carbon these p orbitals overlap side to side to form the π bond with each oxygen.
21. Propene, $\text{C}_3\text{H}_{6(g)}$, has three central carbon atoms bonded in a chain, with a double bond between the first two carbons. Each of these first two carbons is sp^2 hybridized, which gives three bonding orbitals in a trigonal planar shape. On the first carbon, two of these sp^2 orbitals form (σ) bonds with hydrogens, and one (σ) bond with the other carbon. Each of these first two carbons also has one more bonding (p) orbital. These overlap side to side to form the second (π) bond between the carbons. The third carbon is sp^3 hybridized, creating four bonding orbitals in a tetrahedral shape. One of these forms a (σ) bond with the second carbon, and the other three form (σ) bonds with hydrogens.



Applying Inquiry Skills

22.



- (b) Propadiene, $\text{C}_3\text{H}_{4(g)}$, has three central carbon atoms bonded in a chain, with double bonds between the carbons. Each of the end two carbons is sp^2 hybridized, which gives three bonding orbitals in a trigonal planar shape. On each end carbon, two of these sp^2 orbitals form (σ) bonds with hydrogens, and one (σ) bond with the middle carbon. Each of these first two carbons also has one more bonding (p) orbital. The middle carbon is sp hybridized, creating two bonding orbitals in a linear shape, which form the (σ) bond with the end carbons. This middle carbon also has two more (p) bonding orbitals. These (p) orbitals overlap side to side to form the second (π) bond between the middle and (each) end carbon.
- (c) The shape around the end carbon atoms is trigonal planar.

Extension

24. (a) Each carbon atom is joined (bonded) to three others.
- (b) Three bonds for each carbon atom suggest that each carbon is sp^2 hybridized, forming sigma bonds with the three closest other carbons and a pi bond between two of these carbon atoms.
- (c) Even if we ignore any differences in bond angles between the pentagons and hexagons, the explanation in (b) still cannot be correct. A carbon with sp^2 hybridization would have two single bonds and one double bond. These bonds would not be the same. Therefore, the explanation in (b) is not acceptable.
(The bonds are neither single nor double, if they must all be identical. The electrons in the p orbital (that would form a pi bond) are delocalized, meaning all of them are equally shared among all the carbon atoms in each ring. This is similar in concept to the bonding in a benzene ring.)

PRACTICE

(Page 239)

Understanding Concepts

25. The concept of triple bonding was created to explain the properties of compounds like $\text{C}_2\text{H}_{2(g)}$.
26. (a) $\text{C}_2\text{F}_{2(g)}$ has molecules that have triple bonds between carbon atoms that have sp hybridization, which forms two orbitals on opposite sides of the nucleus, giving a linear shape. Each carbon forms a sigma bond with a fluorine, and a sigma bond and two pi bonds with the other carbon.
- (b) $\text{HCN}_{(g)}$ has molecules that have triple bonds between the carbon and the nitrogen. The carbon atom has sp hybridization, which forms two orbitals on opposite sides of the nucleus, giving a linear shape. The carbon forms a sigma bond with the hydrogen, and a sigma bond and two pi bonds with the nitrogen.
27. Propyne has three central carbon atoms bonded in a chain, with a triple bond between the first two carbons. Each of the first two carbons is sp hybridized, which gives two bonding orbitals in a linear shape. On the first carbon, one of these sp orbitals forms a sigma bond with a hydrogen, and one sigma bond with the middle carbon. Each of these first two carbons also has two more bonding (p) orbitals. These p orbitals overlap side to side to form the two pi bonds. The third carbon is sp^3 hybridized, creating four bonding orbitals in a tetrahedral shape, which form sigma bonds with the second carbon and three hydrogens.
28. Quadruple bonds are not likely for a carbon atom because sp^3 hybridization would only allow three orbitals to overlap — the other orbital would be on the opposite sides of the atoms. As well, with sp^2 hybridization, at least one of the sp^2 orbitals would be on the opposite sides of the atoms, and with sp hybridization, one of the sp orbitals would have to be on the opposite sides of the atoms. If we assume no hybridization, the s orbitals could not likely get close enough to overlap because there would be a p orbital in the same direction, extending much farther out.

Applying Inquiry Skills

29. Hypothesis

- (a) One might logically hypothesize that double bonds should be longer and stronger than single bonds, and triple bonds longer and stronger yet, because more electron orbital density is between the nuclei. More electron density might make the bonds longer with more space required for more electrons but make the bond stronger because there is more electrostatic attraction of electrons and nuclei.

Analysis

- (b) According to the evidence provided, the order of bond length, from shortest to longest is triple, double, and then single bonds. The order of bond strength, from weakest to strongest is single, double, and then triple bonds. Single bonds are the longest but the weakest, and triple bonds are the shortest but the strongest.

Evaluation

- (c) The hypothesis is verified for bond strength, but not for bond length. The reasoning based on electron density appears acceptable for bond strength but does not appear correct for bond lengths. (Note that the reasoning did not take into account the shapes and directions of the p orbitals forming the pi bonds.)

Making Connections

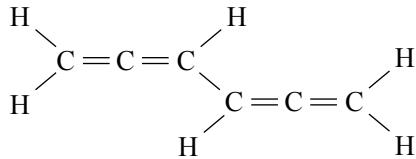
30. (Student reports should contain the following information.)

- (a) Infrared spectroscopy is based on the frequencies absorbed by the internal vibrations of molecules—that is, the vibration of atoms on either side of a bond.
- (b) Each type of bond has a specific vibrational frequency which varies slightly depending on the other atoms in the molecule. Therefore, a unique compound has a unique set of frequencies that it will absorb which allow it to be uniquely identified.
- (c) This technique is used in analysis in medical, pharmaceutical, sports, and industrial chemical laboratories, to name a few.

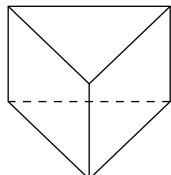
CASE STUDY: THE STRANGE CASE OF BENZENE

(Page 241)

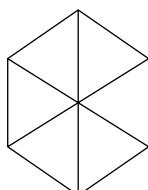
- (d) Benzene is found in coal tar and also in the combustion products of natural materials. Technologically, benzene is produced by the catalytic re-forming of petroleum and is also made from toluene ($C_6H_5CH_3$, or methylbenzene).
- (e) More than half of all benzene is used to produce styrene (phenylethene or vinyl benzene) which is the monomer for the plastic polystyrene. Benzene is also used to make detergents, pharmaceuticals, pesticides, and explosives.
- (f) • Couper and Loschmidt proposed the following non-cyclic structure but could not provide any empirical support.



- Ladenburg tried to explain the chemical reactivity of benzene by proposing a prism-type structure.



- Clause also tried to explain the properties of benzene using a hexagon of carbon atoms with diagonal bonds between opposite carbon atoms.



Applying Inquiry Skills

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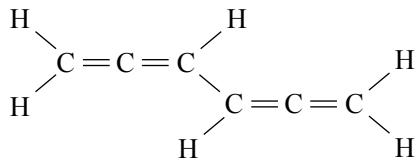
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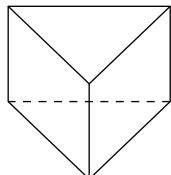
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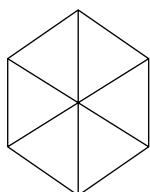
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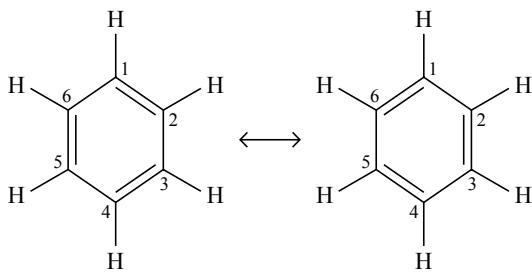
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- Kekulé initially proposed that a benzene molecule is a ring of six carbon atoms with alternating single and double covalent bonds. However, he later realized that the chemical reactivity of benzene could be better explained as two possible structures with their double bonds in different locations. Kekulé suggested that these two structures are in a very rapid equilibrium so that there is no fixed location for a particular double bond.



- (g) According to modern theory, each carbon atom in benzene is bonded to two adjacent carbons (in the ring) and one hydrogen using the three sp^2 hybrid orbitals to form sigma bonds. Each of the six carbon atoms has a half-filled p orbital (perpendicular to the plane of the ring) which overlaps with adjacent p orbitals. The six p orbitals overlap above and below the plane of the carbon atoms. In modern terms, the p electrons are delocalized around the ring. This is a particularly stable arrangement. (This description actually describes only one of three molecular orbitals for benzene, each containing two paired electrons.)

4.3 VSEPR THEORY

Try This Activity: Electrostatic Repulsion Model

(Page 242)

- Two balloons are at about 180° to each other (a linear arrangement).
- Three balloons are at about 120° to each other and all in one plane (a trigonal planar arrangement).
- Four balloons are at about 109° to each other with each one pointing to one corner of a tetrahedron (a tetrahedral arrangement).
- Balloons let you visualize electron orbitals and how they might be arranged. The electrostatic repulsion is modelled by the balloons pushing equally against each other. A disadvantage of the balloon model is that electron orbitals are not physical objects of a fixed size. A balloon only contacts or “repels” where it touches another balloon. Electrostatic repulsion occurs to varying extents between all electrons in the two nearby orbitals. In other words, the repulsion is much more complicated than implied by the two touching balloons.

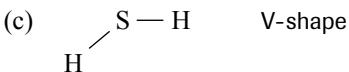
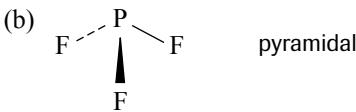
PRACTICE

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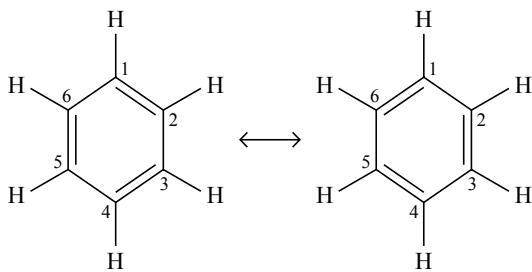
Understanding Concepts

- VSEPR is an acronym for valence shell electron pair repulsion — a theory that predicts molecular shape by assuming that repulsion between all pairs of electrons in the valence shell of an atom controls the direction of those pairs formed by bonding, and thus determines the shapes of molecules.

2. (a) I — Be — I linear



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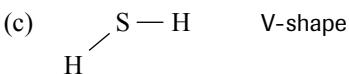
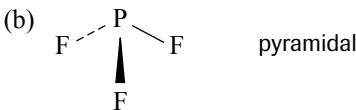
PRACTICE

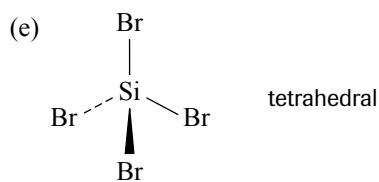
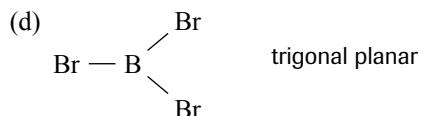
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Understanding Concepts

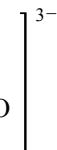
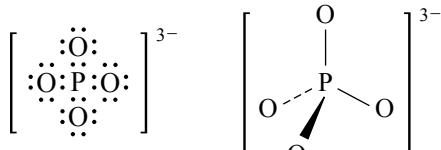
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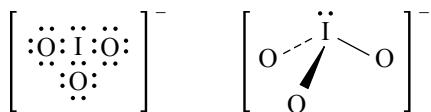




3. (a) PO_4^{3-} will be tetrahedral in shape because it has four bond pairs around the P atom.



(b) IO_3^- will be pyramidal in shape, having three bond pairs and one lone pair around the I atom.



4. (a) According to VSEPR theory, the shape around each carbon atom in cubane should be tetrahedral, since there are four bond pairs around each.

(b) If we assume an ideal cubic shape, three of the bond angles around each carbon have to be 90° .

(c) The normal tetrahedral angle is about 109° . To make these bonding orbitals bend to about 90° would greatly increase the repulsion of the electron pairs. This stress likely makes this molecule very unstable.

Applying Inquiry Skills

5. VSEPR theory was created to explain known molecular shapes. It provided a simpler way to explain shapes and also to predict molecular shapes.

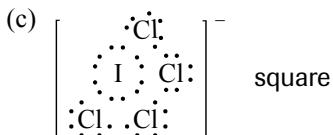
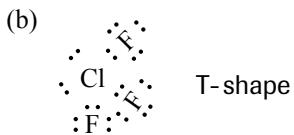
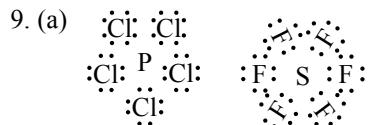
6. (Student reports may use a variety of criteria to evaluate sites. Typical criteria would involve the completeness of information, the opportunity for interaction, and the clarity and conciseness of information provided.)

Making Connections

7. Enzymes catalyze reactions. Their shape is critical, because they fit into precise spaces on the surface of other molecules to alter bond strengths—like a key fits precisely into a lock to allow it to operate.

8. Optical isomers are molecular structures that are identical except for their 3-D orientation. They are so named because the two isomeric structures of such a substance will rotate the plane of polarized light in opposite directions—called levorotatory (counterclockwise), and dextrorotatory (clockwise). Any central atom (such as carbon) to which are bonded four different atoms (or side groups) always has a “left-handed” and a “right-handed” orientation, which are mirror images of each other. That terminology, of course, comes from describing the human hand—which has a front, back, thumb side, and little finger side that can be arranged in space in two ways that are mirror images.

Extension



PRACTICE

(Page 249)

Understanding Concepts

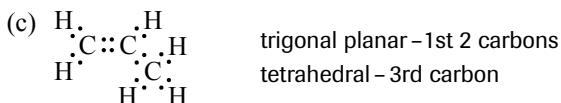
10. To make the rules of VSEPR theory work, multiple bonds must be treated just like single bonds—that is, they are considered to be one bond, which involves 4 or 6 electrons.



linear

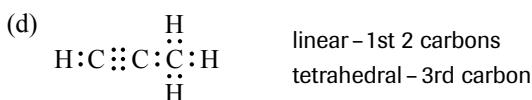


linear



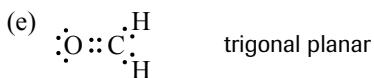
trigonal planar – 1st 2 carbons

tetrahedral – 3rd carbon

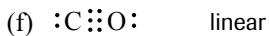


linear – 1st 2 carbons

tetrahedral – 3rd carbon



trigonal planar

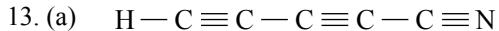


linear

Applying Inquiry Skills

12. VSEPR is a very successful scientific theory. It successfully predicts the shapes of most molecular structures with a minimum of complexity—both being criteria for a “good” theory.

Making Connections



linear shape

- (b) Astronomers detect molecules in space by spectroscopic analysis of electromagnetic radiation (light) absorbed and emitted by regions of space.

Explore an Issue: Take a Stand: Linus Pauling and the Vitamin C Controversy

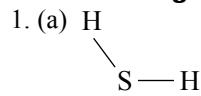
(Page 250)

- (a) It is claimed that large doses of vitamin C:
- reduce occurrence and severity of common cold,
 - lower the risk of heart disease and stroke,
 - reduce risk for most common types of cancer,
 - increase survival time and improve quality of life in terminal cancer patients,
 - improve blood vessel dilation, and
 - lower blood lead (Pb) levels.
- (b) The main criticism of Pauling's claims for the benefits of large doses of vitamin C are:
- The results of Pauling's studies using vitamin C to prevent the common cold are not reproducible. Numerous well-designed studies have shown that vitamin C does not prevent common colds; at best, vitamin C may slightly reduce cold symptoms.
 - Pauling's analyses of vitamin C therapy for the prevention and treatment of cancer is flawed. Independent analyses of the same studies show no significant effect.
 - The Linus Pauling Institute of Medicine is largely funded by the pharmaceutical company that produces most of the world's supply of vitamin C.
 - Pauling has lost scientific credibility by his association with the health food industry, which is notorious for making unsubstantiated claims.
- (c) To be scientifically valid, a claim must be experimentally testable. Then there must exist empirical evidence from well-designed experiments that have suitable controls and controlled variables. Finally, the evidence must be reproducible by independent investigators.
- (d) Pauling's fame was very likely a large factor in influencing public and scientific opinion about the benefits of vitamin C. Pauling's two Nobel Prizes represented significant achievements, and both involved contradicting conventional thinking of the time. It seemed plausible that once again Pauling knew more than his contemporaries.
- A person unknown to the public and with no scientific training would not be taken seriously if he/she made the same claims about vitamin C, because the public would have no basis to believe the claims.
- Reproducible evidence from well-designed studies provides the most reliable basis for deciding which claims to believe. When the empirical evidence is unclear or contradictory, the claim is inconclusive or shown to be false.
- (e) A scientist who goes against the rest of the scientific community risks his career and reputation, if independent research proves his claim to be wrong. On the other hand, if independent research supports his claim, he may enhance his career and receive much recognition.
- The practice and work of science is not always completely objective, especially when new theories are proposed that contradict accepted knowledge. However, if continuing research consistently shows that the new theory is better than the old theory at explaining and predicting experimental evidence, the new theory will eventually be accepted (although this may occasionally take a long time).

SECTION 4.3 QUESTIONS

(Page 250)

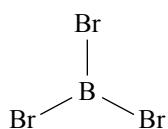
Understanding Concepts



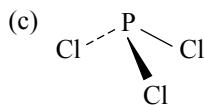
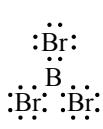
V-shape



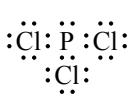
(b)



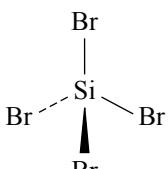
trigonal planar



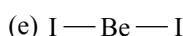
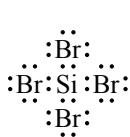
pyramidal



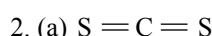
(d)



tetrahedral



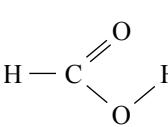
linear



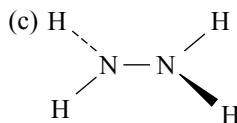
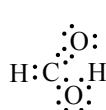
linear



(b)



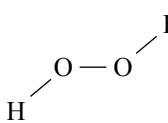
linear (C)
V-shape (O)



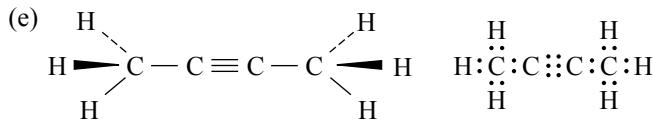
pyramidal
(both Ns)



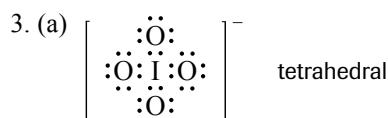
(d)



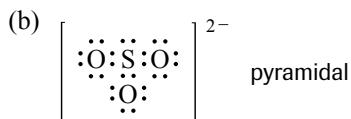
V-shape
(both Os)



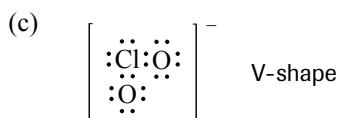
linear (central Cs)
tetrahedral (end Cs)



tetrahedral



pyramidal



V-shape

Making Connections

4. Dr. Bader's work has added to our understanding of molecules by applying quantum mechanics to the overall structure of a molecule. This gives a more comprehensive understanding of the structure and bonding, thus allowing for better predictions of molecular structures and ultimately, new substance properties.

5. Dr. Ronald Gillespie, the co-creator of VSEPR theory, is currently Professor Emeritus at McMaster University. He holds B.Sc. and Ph.D. degrees in science, and a D.Sc. from London University. He has won many significant awards, including the Chemical Institute of Canada Medal, the Henry Marshall Tory Medal of the Royal Society of Canada, and the Izaak Walter Killam Memorial Prize of the Canada Council for Pure Science, to name just a few. He is a visiting professor at nine international universities in Europe, Australia, and Asia, and has been awarded four honorary doctorates. His major topic of research, in cooperation with Dr. Richard Bader, is using calculated electron probability distributions to better understand the VSEPR model.
6. The sense of taste seems to be essentially built around the ability of taste receptors to form hydrogen bonds at specific locations with certain molecules. Thus, artificial sweeteners like saccharin and cyclamate and acesulfame-K are non-nutritive molecules with structural similarities to natural sugars. The molecular structure for sweetness involves part of the molecule being a small pentagon or hexagon of atom with the ability to hydrogen bond at a specific spot on the ring. Similarly, artificial compounds like Bitrex®—added as a safety precaution to many medications to make the taste extremely bitter—are structured to a shape that triggers human taste receptors for bitterness to react strongly.

4.4 POLAR MOLECULES

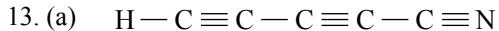
PRACTICE

(Page 253)

Understanding Concepts

1. (a) δ^+ δ^-
 $\text{H} - \text{Cl}$ polar covalent
 2.1 3.0
- (b) δ^- δ^+
 $\text{C} - \text{H}$ polar covalent
 2.5 2.1
- (c) δ^+ δ^-
 $\text{N} - \text{O}$ polar covalent
 3.0 3.5
- (d) δ^+ δ^-
 $\text{I} - \text{Br}$ polar covalent
 2.5 2.8
- (e) + -
 $\text{Mg} - \text{S}$ ionic
 1.2 2.5
- (f) P — H nonpolar covalent
 2.1 2.1
2. (a) polar covalent
 (b) ionic
 (c) nonpolar covalent
3. The list of the bonds in order of increasing bond polarity is assumed to be the same as the order of increasing difference in electronegativity of the bonded atoms. Thus, the orders are as follows:
 (a) H—H, C—H, Be—H, N—H, Li—H, O—H, F—H
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Making Connections



linear shape

- (b) Astronomers detect molecules in space by spectroscopic analysis of electromagnetic radiation (light) absorbed and emitted by regions of space.

Explore an Issue: Take a Stand: Linus Pauling and the Vitamin C Controversy

(Page 250)

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4.4 POLAR MOLECULES

PRACTICE

(Page 253)

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 (c) C—H, C—O, O—H
 (d) C—H, C—Cl, C—F

Applying Inquiry Skills

4. Empirical (measured, observed) values change as new and better methods of determining values are found. As well, the electronegativity of an atom is not an exact concept. It also varies somewhat, depending on the bonded atoms. The new values could be described as more accurate values, but the word “true” cannot properly be applied to relative numerical values of this sort.

Extension

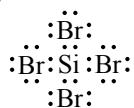
5. Pauling's electronegativity scale is derived from measurements of bond energies; the Mulliken-Jaffé scale is derived from the electron affinity and ionization potentials; and the Allred-Rochow scale is derived from the covalent radius and the effective charge on the electron (allowing for nuclear shielding). The relative values for electronegativity of the elements, and predictions made from these values, naturally vary slightly depending on which scale is used.

PRACTICE

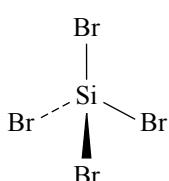
(Page 255)

Understanding Concepts

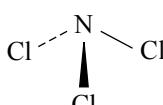
6. (a)



tetrahedral



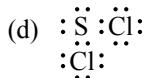
pyramidal



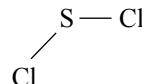
(c)



linear



V-shape

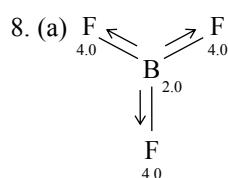


7. (a) $C \equiv N$
 $\delta^+ \rightarrow \delta^-$

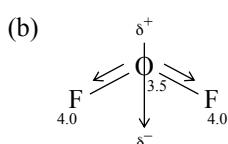
(b) $N = O$
 $\delta^+ \rightarrow \delta^-$

(c) $P - S$
 $\delta^+ \rightarrow \delta^-$

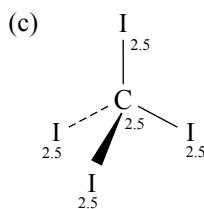
(d) $C - C$
no dipole



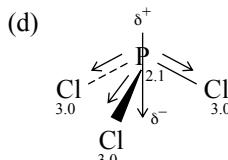
zero resultant



resultant dipole toward F side of molecule



no bond dipoles



resultant dipole toward Cl side of molecule

9. An octane, $C_8H_{18(l)}$, molecule should be nonpolar using the generalization that any molecule composed of carbons and only one other kind of atom is a nonpolar molecule.

10. For $N_2H_{4(l)}$, the molecular structure is symmetrical; thus, the molecule is nonpolar.

Applying Inquiry Skills

11. Hydrogen sulfide, $H_2S(g)$, has a V-shaped molecule, with bond dipoles directed toward the sulfur. Thus, the molecular dipole should be slightly negative on the sulfur side, and slightly positive on the hydrogen side.

The hydrogen sulfide will be cooled to the liquid state, and a thin stream of the liquid allowed to flow downward past a strong electric charge. Molecular polarity should cause deflection of the liquid stream.

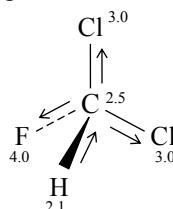
SECTION 4.4 QUESTIONS

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Understanding Concepts

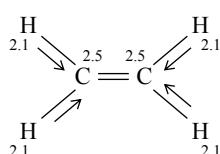
- Beryllium bromide is nonpolar because it is symmetrical. Therefore, the bond dipoles add up to zero for the whole molecule.
- Nitrogen trifluoride is polar because it has polar bonds and is not symmetrical. The sum of all of the bond dipoles produces a non-zero dipole for the whole molecule.
- Methanol is polar because it has polar bonds and is not symmetrical. The sum of all of the bond dipoles produces a non-zero dipole for the whole molecule.
- Hydrogen peroxide is nonpolar because it has polar bonds and is assumed to be symmetrical. The sum of all of the bond dipoles produces a zero dipole for the whole molecule. (Note that this answer ignores any rotation about the O-O bond and considers only the most stable arrangement.)
- Ethylene glycol is nonpolar because it has polar bonds and is symmetrical. The bond dipoles have a zero resultant. (Again, this assumes the most stable arrangement.)

2. (a)



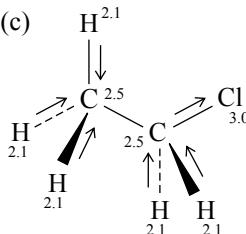
polar nonsymmetric

(b)



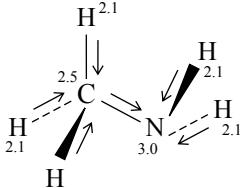
nonpolar
symmetric

(c)



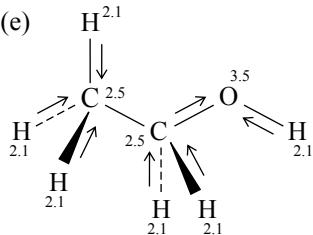
polar
nonsymmetric

(d)



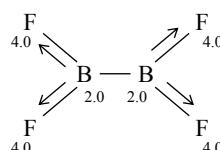
polar
nonsymmetric

(e)



polar
nonsymmetric

(f)



nonpolar
symmetric

3. (a)

Based upon polarity, water is a candidate for use in a capacitor, because it is a V-shaped (nonsymmetrical) molecule with high molecular polarity.

(b)

Other considerations for choosing a liquid inside a capacitor might be toxicity, corrosiveness, cost, ease of fabrication, and effectiveness as a storage material.

Applying Inquiry Skills

4. Cis-1,2-dichloroethene is a nonsymmetrical molecule that should have a resultant molecular dipole; thus, the substance should be polar. The other stereoisomer, trans-1,2-dichloroethene, is symmetrical, and should not be a polar substance. Thin streams of each liquid are allowed to flow downward past a strong electric charge. Any stream deflection is noted. (The polar substance should deflect.)

Making Connections

5. The entire field of cleaning and stain removal is based on a knowledge of polar and nonpolar substances. Stains may be polar or nonpolar substances. Nonpolar substances pose particular problems because the common liquid for washing is water, which is very polar. Soaps and detergents are molecules selected or designed to have both polar and nonpolar regions so that they can dissolve oily or greasy dirt from a stain, and also dissolve in water to carry the material away.

4.5 INTERMOLECULAR FORCES

PRACTICE

(Page 260)

Understanding Concepts

1. (a) dipole–dipole forces and London forces
(b) London forces
(c) London forces
(d) dipole–dipole forces and London forces
(e) dipole–dipole forces and London forces
(f) London forces
2. (a) hydrogen fluoride; the H-F bond is more polar (electronegativity difference is greater)
(b) chloromethane; the C-Cl bond is more polar (electronegativity difference is greater)
(c) nitrogen tribromide; the N-Br bonds are more polar (electronegativity difference is greater)
(d) water; the O-H bonds are more polar (electronegativity difference is greater)
3. (a) ethane; because it has 8 more electrons (and protons) than methane
(b) oxygen; because it has 2 more electrons (and protons) than nitrogen
(c) sulfur dioxide; because it has 18 more electrons (and protons) than nitrogen dioxide
(d) Methane and ammonia are isoelectronic, with 10 electrons each. They should have equal-strength London forces.
4. (a) oxygen difluoride; beryllium difluoride is nonpolar (no dipole–dipole forces) and also has fewer electrons (weaker London forces).
(b) chloromethane; ethane is nonpolar (no dipole–dipole forces) and also has fewer electrons (weaker London forces).
5. Chlorine monoxide bonds are less polar than bonds in nitrogen trifluoride (possibly weaker dipole–dipole forces), and there are fewer bonds per molecule, but nitrogen trifluoride has fewer electrons than chlorine monoxide (weaker London forces). Therefore, no simple prediction is possible in this case.

Applying Inquiry Skills

6. Some patterns found in Table 4 include:
 - In the homologous series for the alkanes, alkenes, and alkynes, the boiling point increases proportionally to the number of electrons per molecule. Because these are all nonpolar molecules, the pattern can be explained as an increase in the strength of the London force.
 - In the comparison of alkanes with their corresponding alkenes (same number of carbons), we find the boiling point of the alkene is slightly lower. This is what we might expect because the molecules are nonpolar and the London force should decrease when the number of electrons is reduced by two.
 - Interestingly, the alkynes have higher boiling points than corresponding alkenes, even though they have fewer electrons. Since polarity is not a factor, there is obviously some other factor involved that has not yet been studied. (Note that the effect of molecular shape on the strength of intermolecular forces has not been considered.)
7. Look up in a reference, or determine experimentally, the melting points of the hydrocarbons listed in Table 4. Possible complications of this proposed experiment include the equipment needed if it is necessary to determine the melting points of substances that have freezing points well below 0°C. The interpretation of the results may also be complicated by the fact that the bonding changes between solid and liquid forms are not as clear as the change between liquid and gas states. With boiling points, we usually assume that no intermolecular bonding forces exist between molecules in a gas.

Applying Inquiry Skills

4. Cis-1,2-dichloroethene is a nonsymmetrical molecule that should have a resultant molecular dipole; thus, the substance should be polar. The other stereoisomer, trans-1,2-dichloroethene, is symmetrical, and should not be a polar substance. Thin streams of each liquid are allowed to flow downward past a strong electric charge. Any stream deflection is noted. (The polar substance should deflect.)

Making Connections

5. The entire field of cleaning and stain removal is based on a knowledge of polar and nonpolar substances. Stains may be polar or nonpolar substances. Nonpolar substances pose particular problems because the common liquid for washing is water, which is very polar. Soaps and detergents are molecules selected or designed to have both polar and nonpolar regions so that they can dissolve oily or greasy dirt from a stain, and also dissolve in water to carry the material away.

4.5 INTERMOLECULAR FORCES

PRACTICE

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Understanding Concepts

1. (a) dipole–dipole forces and London forces
(b) London forces
(c) London forces
(d) dipole–dipole forces and London forces
(e) dipole–dipole forces and London forces
(f) London forces
2. (a) hydrogen fluoride; the H-F bond is more polar (electronegativity difference is greater)
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Extension

8. • OF ₂	b.p. -145°C	BeF ₂	sublimes 800°C
• CH ₃ Cl	b.p. -24°C	C ₂ H ₆	b.p. -89°C
• NF ₃	b.p. -129°C	Cl ₂ O	b.p. 2°C

This prediction was falsified.

This prediction was verified.

No prediction was made.

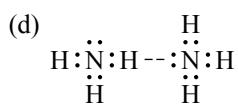
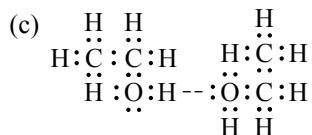
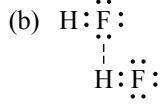
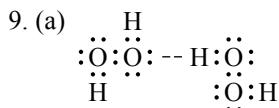
Try This Activity: Floating Pins

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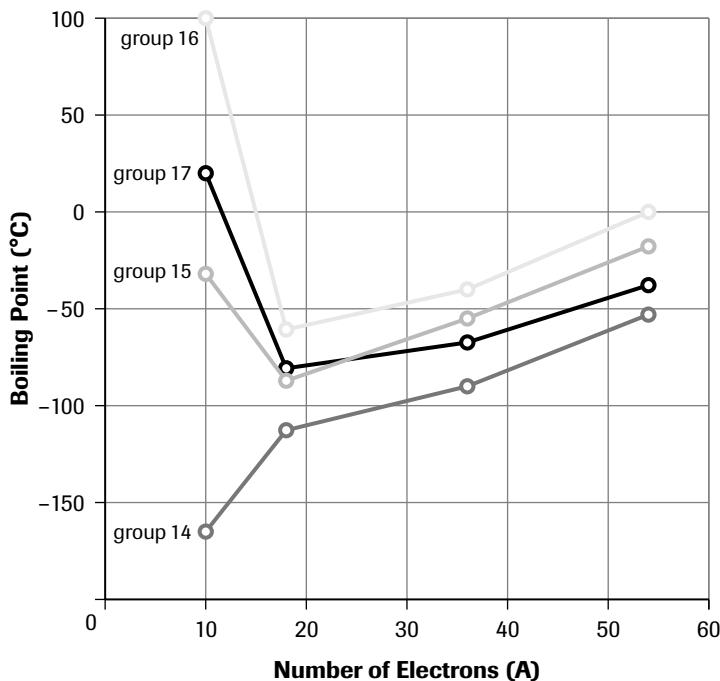
- (a) The pin sits on the surface of the water but not on the surfaces of propanol or hexane. The evidence suggests that the intermolecular forces between water molecules are much greater than those between the molecules of either propanol or hexane. If the intermolecular forces are strong enough, the molecules at the surface act like a skin on the surface.
- (b) The pin drops immediately into the water no matter which end is first. In this case, the entire weight of the pin is concentrated in a very small area. The surface tension is no longer able to support the pressure (force per unit area) exerted by the pin. When the pin is horizontal, the weight of the pin is spread out over a much larger area.
- (c) The pin immediately falls through the water. The detergent must reduce the surface tension of the water perhaps by the detergent molecules coming between or separating the water molecules.

PRACTICE

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Understanding Concepts

10. (a)

Boiling Points of the Hydrogen Compounds of Elements

- (b) The actual boiling points for water and ammonia (compared to an estimate from the graph) are about 170°C and 70°C higher, respectively.
 - (c) The actual boiling points are much higher for both water and ammonia because of hydrogen bonding between molecules in these substances.
 - (d) Likely, the difference is much greater for water (than for ammonia) because oxygen is a more electronegative central atom than nitrogen; and possibly also because of differences in molecular shape. Water molecules have more free lone pairs available for hydrogen bonding; and in ammonia, the third bond dipole acts to partially cancel the other two bond dipoles.
11. Water beading on a surface means that the surface material must have very low intermolecular attraction for water molecules. This would mean no polar areas on the surface molecules, and certainly no hydrogen bonding locations.
12. The two liquids must be something like water and oil—one polar and one nonpolar—so they will have no tendency to mix. The polar molecules attract each other more strongly and exclude the nonpolar molecules. The heat supply at the bottom makes the liquid there rise, so it must be just slightly denser than the other liquid. Thus, heating expansion causes the bottom liquid to become temporarily less dense than the other, and to rise until it cools, and falls again.

Applying Inquiry Skills

13. To investigate hydrogen bonding, you should control the other intermolecular forces, London and dipole–dipole forces, by controlling the number of electrons per molecule and the polarity. You should probably control the shapes of the molecules as well.
14. (a) Equal volumes of various liquids will be exposed to the atmosphere in a fume hood at constant temperature. The remaining volume of liquid will be measured at set time intervals. The independent variable is the substance; the dependent variable is the volume remaining; and the controlled variables include the time intervals, the temperature, the initial volume, the surface area, and the air movement (draft).
- (b) Some liquids to be used might include ethanol, acetic acid (ethanoic acid), and ethylene glycol (1,2-ethanediol). Assuming the hydrogen bonding from OH groups is the most significant intermolecular force, we would predict the acetic acid to be less volatile than the ethanol, because acetic acid molecules have more lone pairs available to form H-bonds, and are also more polar. The ethylene glycol should be least volatile of all, because it has two OH groups and thus overall stronger hydrogen bonding. (A variety of liquids, including polar and nonpolar, could be used.)

15. Prediction/Hypothesis

- (a) According to the concepts and rules of intermolecular bonding, ammonia should have a high solubility in water. Both ammonia and water are polar and have multiple hydrogen bonding sites. This means that the two kinds of molecules should easily attract each other.

Analysis

- (b) Based upon the evidence, ammonia is very soluble in water because water is drawn very rapidly into the flask to replace the dissolved ammonia. (Note that when ammonia dissolves, the internal pressure is greatly reduced and water is forced into the flask by the greater atmospheric pressure on the outside.)

Evaluation

- (c) The prediction is verified, so the reasoning used to make the prediction appears acceptable.

Making Connections

16. Wetting agents are substances that act to change the surface energy of a material to allow a liquid (normally, water) to spread easily over the surface. This can help detergent molecules attract dirt particles to water, or allow fertilizer to penetrate more readily and deeply into soil, for example. The principle is always based on molecular structure and enhanced intermolecular bonding between the agent and the surface material.
17. Polywater was believed to form inside quartz capillary tubes. It purportedly had a higher boiling point, lower freezing point, higher density, and higher surface tension than ordinary water. Theories were developed to explain this in terms of especially strong hydrogen bonding. After finding that experiments with polywater were not reproducible, continued study with better technology established that, in fact, polywater was just ordinary water containing a variety of impurities—mostly absorbed from the capillary tubes used. Yet, for many years, the desire for discovery caused many reputable scientists to pay too little attention to experimental and procedural controls, and to report results without determining that they could be duplicated. The story of polywater is a “cautionary tale” for the scientific community.

SECTION 4.5 QUESTIONS

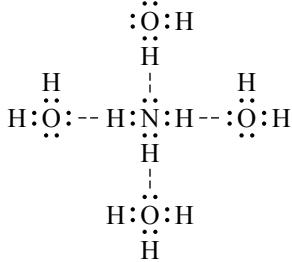
(Page 266)

Understanding Concepts

1. (a) London forces
- (b) hydrogen bonding, dipole–dipole and London forces

- (c) dipole–dipole and London forces
- (d) hydrogen bonding, dipole–dipole and London forces
- (e) dipole–dipole and London forces
- (f) hydrogen bonding, dipole–dipole and London forces
- (g) hydrogen bonding, dipole–dipole and London forces
- (h) dipole–dipole and London forces
- (i) dipole–dipole and London forces

2.



The very high solubility of ammonia in water is due to the high number of hydrogen bonding sites (see diagram). Every ammonia molecule can hydrogen bond at least four times, as can every water molecule in the solution.

- 3. (a) 2-chloropropane should have low or medium solubility, because it is polar and water is also polar.
- (b) 1-propanol should have high solubility, because it is not only polar but can hydrogen bond with water molecules.
- (c) Propanone should have medium solubility, because it is quite polar, and so is water.
- (d) Propane should have low solubility, because it is a nonpolar substance and water is polar.
- 4. (a) Bromine should have stronger intermolecular attractions. Both molecules are nonpolar but bromine has larger molecules with a greater number of electrons, so it should have the stronger London force.
- (b) Hydrogen chloride should have stronger intermolecular attractions. Hydrogen chloride and fluorine are isoelectronic which means the London force should be the same. However, HCl has polar molecules so it should have additional dipole–dipole force.
- (c) Ammonia should have stronger intermolecular attractions. Ammonia and methane are isoelectronic so the London force should be the same. Unlike methane, ammonia is polar and has hydrogen bonding. Ammonia therefore has additional attractions, dipole–dipole force, and hydrogen bonds.
- (d) Water should have stronger intermolecular attractions. Both molecules are polar but hydrogen sulfide is less polar. Although hydrogen sulfide has a greater number of electrons and stronger London forces, water has hydrogen bonding. This is likely much more significant than the difference in London forces.
- (e) Silicon tetrahydride should have stronger intermolecular attractions. Both substances are nonpolar and silicon tetrahydride has more electrons per molecule, so it should have more London force.
- (f) Ethanol should have stronger intermolecular attractions. The two substances are isoelectronic which means the London force should be the same. Both are polar but ethanol has hydrogen bonding and chloromethane does not.
- 5. Ethanol should have the greater surface tension because it has the stronger intermolecular attractions. Propane and ethanol molecules are isoelectronic so the London force is the same for both. There are no other intermolecular attractions between propane molecules because they are nonpolar. However, ethanol has additional dipole–dipole and hydrogen bonds between its molecules.
- 6. When water freezes it expands, unlike most substances. This occurs because hydrogen bonding causes the molecules to arrange in a specific three-dimensional pattern (lattice). Water left to freeze in a pipe may break the pipe open.
- 7. The property that creates a meniscus curve is commonly called “surface tension,” (but is more correctly termed “surface energy”). This results because the molecules on a surface are attracted both sideways and downward, but not upward, by other molecules. This unbalanced attraction causes the surface to act as though it has a “skin” and can contain slightly more water than the level of the top of the glass.
- 8. A LeRoy radius for a molecule represents a theoretical boundary first calculated and used by Dr. R. J. LeRoy of Waterloo University. Within this boundary, the energies of molecular changes are primarily quantum mechanical and chemical (involving electron exchange energies) and beyond it, the energies of molecular changes are classic intermolecular (involving van der Waals forces). This theoretical boundary proved so useful to the scientific community that the term “LeRoy Radius” was coined to describe it.

Applying Inquiry Skills

9. Two liquids such as diethyl ether, $\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3(\text{l})$, and butanol, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}(\text{l})$, are placed in a beaker and a thin wire (or pin) is placed horizontally on the surface of each liquid. The independent variable is the substance;

the dependent variable is the action of the wire; and controlled variables include the molecular size, polarity, and temperature of the substance, and mass and size of the wire or pin.

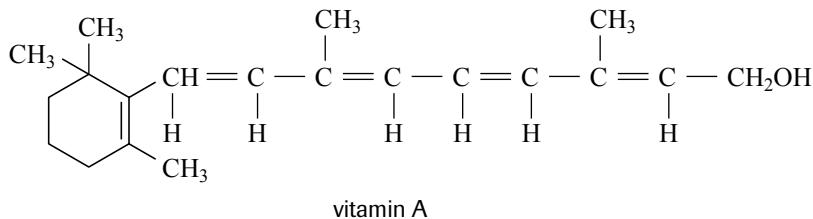
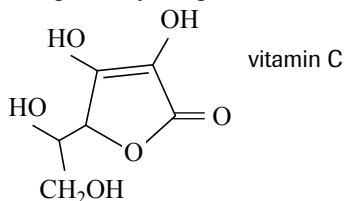
(Some variations include: other combinations of liquids with isoelectronic molecules, several different densities of wires of the same length to determine the mass supported by the liquid surface, measure the force required to lift a specific wire or disk from the surface.)

10. This experiment design is judged unacceptable because it does not stipulate or make clear that comparisons must be done for different liquids using the same kind of capillary tubes of equal diameters. As well, the design does not identify the variables for the experiment.

Making Connections

11. (a) Molecules of water-soluble vitamins probably have hydrogen bonding, and are likely quite polar. Molecules of fat-soluble vitamins are probably nonpolar.

(b)



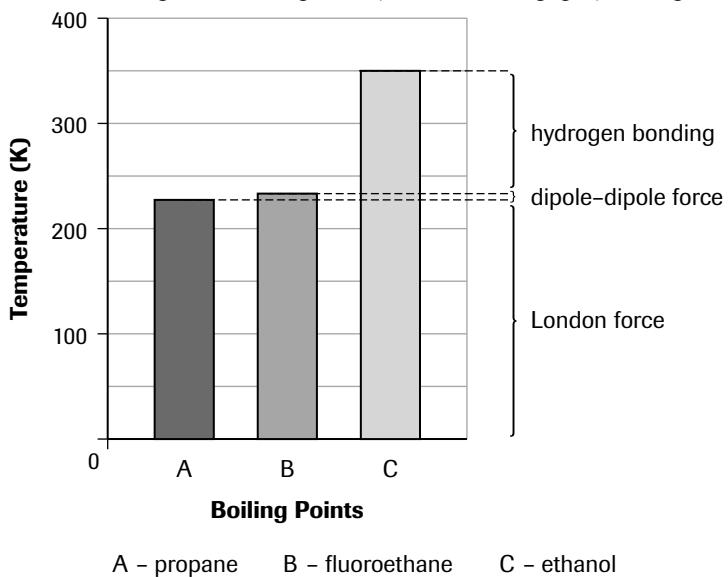
- (c) Vitamins are complex substances that react in very complicated ways with many other chemical substances in the body. A balanced diet is essential to ensure that taking vitamins can be of any benefit to an individual. Using vitamins to replace any elements of a normal diet is often ineffective, and may be very dangerous.
- (d) Vitamin C is water soluble, so it is easily excreted from the body and does not accumulate in humans. Humans are naturally adapted to handle fairly large amounts of this vitamin. Omnivores often ingest significant amounts of it from fruits and vegetables in their diets. Vitamin E is quite another matter. It is not water soluble and cannot be excreted readily. It tends to accumulate quickly to dangerous (toxic) levels if there is too much in the diet. (Large carnivores like polar bears and lions can have so much vitamin E stored in their livers that eating the organ can be fatal to humans.)
12. The structure of a “fuzzyball,” $C_{60}F_{60(s)}$, molecule is essentially a “buckyball” (see p. 238) with a fluorine bonded (on the exterior of the sphere) to each carbon. It is hypothesized that a material made of such molecules would be the slipperiest possible substance—an ideal nonreactive lubricant. As in the polymer Teflon®, the fluorine atoms would bond to the carbons very strongly, preventing any other atom from reacting at that site. The only attractions between fuzzyball molecules and any other matter would be relatively weak London forces.
13. Hard lens polymers do not absorb or attract water. Oxygen moves through holes in the polymer to the eye surface. Soft lenses are made of hydrogel polymers that absorb and attract water. In these lenses, oxygen is carried through by water flow. The polymers in soft lenses must have many surface locations that are very polar and/or allow hydrogen bonding, whereas hard lens polymer surfaces will be nonpolar.
14. Plastic cling wrap is made with a significant amount of a softening material, called a plasticizer, added to the polyvinyl chloride polymer. This causes the film to be very soft and flexible; consequently, it moulds well to any smooth surface (including itself), and the closeness of contact combined with large surface area makes the London force quite significant—the plastic wrap is “clingy.” (It is also likely that this plastic easily acquires an electrostatic charge that helps it cling to itself and nonmetallic objects.)
- Some plasticizers, particularly di-(2-ethylhexyl) adipate (DEHA), have come under fire because of suspicions that they may act as endocrine disruptors, with possible long-term harmful effects on the body. These compounds can be dissolved out of the wrap if the wrapped food contains fats (cheese is a prime example).

The plasticizer molecules are liquid and nonpolar, so London forces will make them soluble in nonpolar fats.

Extensions

15. The London force is affected by the shape and structure of adjacent molecules. The key variables are the distance between charge points, and the number of charge points that can approach closely. Molecules that have a shape that allows them to pack closely together have attractions that are stronger because the distances separating charges are less. Molecules with shapes closer to planar (like a sheet of paper) than spherical (like a ball) will attract more strongly.

16. (a)



- (b) Based on the boiling point graph for these isoelectronic liquids, London force contributes most to intermolecular attraction, hydrogen bonding is usually less significant (about one-half in this example), and dipole–dipole force is almost insignificant.

4.6 THE STRUCTURE AND PROPERTIES OF SOLIDS

PRACTICE

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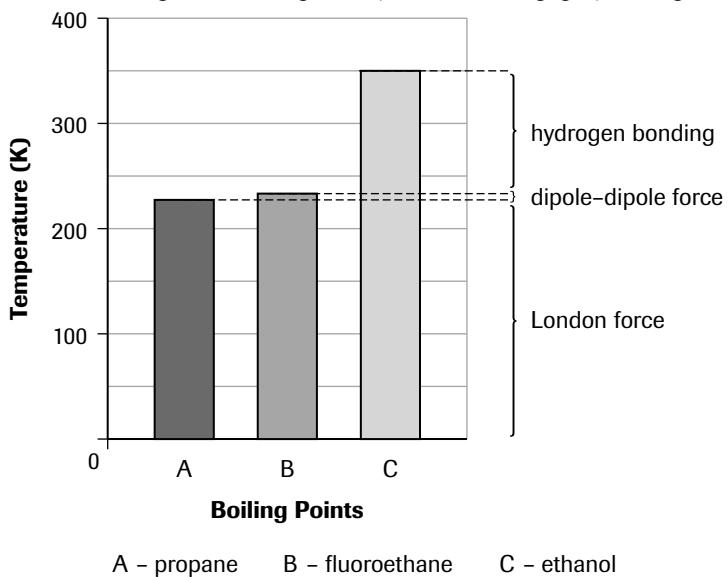
Understanding Concepts

- The main factors that determine the hardness of a solid are the strength and direction of bonds between its entities.
- (a) covalent bonding covalent network crystal
(b) ionic bonding ionic crystal
(c) covalent bonding molecular crystal
(d) covalent bonding covalent network crystal
(e) metallic bonding metallic crystal
(f) ionic bonding ionic crystal
- The melting point of a solid is proportional to the attractive forces between the entities of the solid. Strong bonds like covalent bonds will result in very high melting points, while much weaker bonds like London forces will result in lower melting points.
- Metals are generally malleable, ductile, and flexible because the bonding between atoms in metals is nondirectional—so changing the position of the atoms (shape of the solid) does not “break” the bonding.
- (a) Aluminum is a light, soft, flexible, silvery metal solid, with a fairly low melting point for metals. Aluminum oxide is a very hard network crystalline solid with an extremely high melting point. In aluminum, the bonding is metallic bonds of a lower-than-average strength for metals. In aluminum oxide, very strong ionic bonds lock the aluminum and oxygen ions in a rigid three-dimensional network.
(b) Carbon dioxide is a soft molecular solid with a very low boiling point. Silicon carbide is a very hard network crystal solid with an extremely high boiling point. In carbon dioxide, the molecules are held together by relatively weak nondirectional London forces only. In silicon carbide, the silicon and carbon atoms are locked in a three-dimensional network by very strong covalent bonds.

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4.6 THE STRUCTURE AND PROPERTIES OF SOLIDS

PRACTICE

(Page 273)

Understanding Concepts

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6. (a) The blade must be oriented in the same direction as the plane of the atoms (or ions) in the crystal because the crystal can only break along these “cleavage” planes.
 (b) To cleave a sodium chloride crystal, the knife blade should be perpendicular to a crystal face because the crystal is a cube and planes of ions are at 90° to each other.
 (c) The crystal will shatter into small pieces if struck incorrectly.
 (d) Diamonds and other precious stones are cut into smaller gemstones by this technique before they are polished.
7. (a) high melting point, conducts electricity vanadium, V_(s)
 (b) low melting point, soft phosphorus pentoxide, P₂O_{5(s)}
 (c) high melting point, soluble in water sodium bromide, NaBr_(s)
 (d) very high melting point, non-conductor silicon dioxide, SiO_{2(s)}

Applying Inquiry Skills

8. (a) It seems logical to assume that conductivity of electric current and of heat are related.
 (b) Thick wires of equal diameter and length, made of several common metals, are tested for electrical conductivity with an electrical multimeter. The same wires are tested for heat conduction by heating one end and recording the time for the other end to reach a specified temperature. The independent variable is the type of metal; the dependent variables are the electrical conductivity and time to heat; and the controlled variables are length, diameter, initial temperature, final temperature, and heat source.
 (A common laboratory device has spokes of different metals with a concave end to attach a blob of wax. The relative heat conductivity can be determined by noting the order or time for the wax to fall off each metal.)

Making Connections

9. Graphite may be better than oil in lubricating moving parts of a machine because it is a powdered solid—a dry lubricant that will not stick to dirt, or cake or build up on moving parts. Graphite may also be more stable at higher temperatures than an oil.
10. Nitinol is a nickel-titanium mixture in about a 55%–45% proportion by mass. It has two distinct crystalline structures, called martensitic and austenitic after crystal structure first observed in steels. It exhibits unique properties of “shape memory” and “superelasticity.” It can be deformed easily in the martensitic form, and will return to its original shape upon heating. In its austenitic form, it is extremely elastic, allowing it to be bent severely without breaking or changing the shape to which it returns. Superelasticity is used in making eyeglass frames, cell phone antennas, orthodontic wires and surgical probes that are far more flexible than if made with other metals. Thermal “memory” has a host of medical applications for devices that take final shape only after they are inserted in the body, like vertebral spacers, and heart valve instruments that can be shaped to a patient for an operation, and then returned to original shape later for reuse.
11. (a) Moissanite has a refractive index of 2.67 ± 2 , dispersion of 0.104, hardness of 9.25, and specific gravity of 3.21. Diamond has a refractive index of 2.42, dispersion of 0.044, hardness of 10, and specific gravity of 3.52.
 (b) In theory, any of these properties could distinguish the two materials, given precise measuring equipment and time. Finding specific gravity, for example, requires very precise measure of mass and volume for very small objects.
 (c) Jewellers normally distinguish diamonds from other stones by thermal conductivity, but this doesn’t work with moissanite. The only device that can currently distinguish diamond from moissanite uses absorption of UV light as its operating principle. The stone is first tested for thermal conduction to ensure that it is either diamond or moissanite, and then is tested with the UV sensor device. Diamond transmits certain UV frequencies which moissanite absorbs.

Extension

12. If graphite did not conduct electricity, one might assume that it was composed of double sheets of carbons bonded together, explaining why there are no free electrons. The double sheets should slide over each other still, because they would not be bonded except by London forces.

CAREERS IN CHEMISTRY

PRACTICE

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Making Connections

1. (Reports will vary, but almost all universities provide excellent web site biographical information on faculty members. In Ontario, Dr. LeRoy (Waterloo) and Drs. Gillespie and Bader (McMaster) are examples already used in this course.)

SECTION 4.6 QUESTIONS

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Understanding Concepts

- Ionic substances do not conduct while solid because all ions are locked in position. Upon melting, the ions are free to move and the substance conducts freely. In aqueous solution, the ions are also free to move and the solution will conduct more or less well, depending on concentration.
- A substance conducts electricity when its particles have a charge and are free to move, meaning the particles must be held only by weak forces.
- In calcium oxide, the ions have double the charge that the ions in sodium chloride have, creating a significantly greater interionic attraction.
- In solid carbon dioxide, the bonding consists of London forces between molecules. These relatively weak forces result in very low melting and boiling points, and make the solid a soft substance. By contrast, in silicon dioxide, the bonding consists of a continuous network of covalent bonds between atoms. These very strong forces result in very high melting and boiling points, and make the solid a very hard, brittle substance.
- Most metals have a relatively high density because their atoms are closely packed together in solid form, held together strongly by mobile valence electrons that are dispersed throughout a structure of positive ions.
- Covalent network structures have the highest hardnesses and also the highest melting and boiling points, indicating that covalent bonds are the strongest. Molecular structures have the lowest values for these properties, indicating that intermolecular bonding forces are the weakest. Metals and ionic compound properties fall between these first two, but the values for both metals and ionic compounds vary widely, depending on the specific substance.
- Rubbing your zipper with your pencil will coat it with graphite which will act as a lubricant. Graphite crystals form in layers one atom thick held to each other only by very weak London force, so they slide very easily over each other.
- Diamond is composed of carbon atoms bonded four times each in a three-dimensional covalent network. It is a colourless solid, extremely hard, and a nonconductor. Its main use is as an abrasive; pure crystals are used as gemstones.

Graphite is composed of carbon atoms bonded three times each in a two-dimensional covalent network resulting in layers one atom thick which are held to each other by London force. It is a grey-black solid, very soft and slippery, and a good electrical conductor because of the mobility of the delocalized, unbonded fourth electron of each carbon atom. It has a myriad of uses in industry, most of which have to do with its high melting point and lubricant properties.

Applying Inquiry Skills

9. XCl_a must be an ionic compound. The high melting point suggests that it has very strong bonding holding the entities together, but is water soluble, so it is not likely a covalent network crystal.

YCl_b must be a molecular compound. The melting and boiling points are low, indicating London forces holding the entities together. The solubility argues that the molecules are nonpolar.

Making Connections

10. (Note: Many answers are possible.)

Molecular research in the medical and pharmaceutical fields has produced materials such as human insulin for diabetics, and diagnostic devices such as MRI scans. The plastics industry has produced new contact lens materials and many new fabrics and containers and construction materials. The electronics industry has created new products like rechargeable NiMH batteries, fuel cells, and LEDs for traffic lights.

11. Clay is a term that refers to a general class of minerals produced by long-term weathering of igneous rock into very tiny particles—usually less than a few micrometres in size. The predominant compound present (of a very complex mixture)—in the clays that can be heated to produce pottery—is normally kaolinite, $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_{4(s)}$. In general, all clays may be thought of as hydrated aluminum silicates with varying amounts of other atoms, such as K, Mg, Fe, and Ca included in the mineral's crystal structure. All clays contain at least some tiny particles of SiO_2 and Al_2O_3 .

Ceramic is a term that refers to any manufactured materials that have essentially a network crystalline structure. This includes abrasives, porcelain, china, refractories (heat-shielding materials), structural clay products (brick and pottery), electrical ceramics (for electronics), and glasses. Glasses account for nearly half of all ceramic production.

Clay, when wet, is a soft, slippery plastic material. It is easily moulded into shapes, because the tiny particles are attracted to each other by low-strength London forces and hydrogen bonds. By heating these siliceous minerals at very high temperatures, new bonds form to change the material into a very hard, brittle network solid. The networks are mostly covalent—but also somewhat ionic—in crystalline character. The bonding structure is extremely complex, but may be thought of as a tetrahedral silicon-oxygen network modified with many substituted atoms and ions, all held together within an overall glass structure. All glasses have a crystal structure that is unique—the arrangement of atoms in glasses is like the arrangement in liquids—because there is no regular repetitive pattern to the structure.

12. Boron nitride, BN_(s), is a network covalent compound with unique properties. It has very high melting and boiling points, conducts heat well, is a soft slippery solid like graphite, but unlike graphite, is a nonconductor of electricity. It is used as an additive to plastics, ceramic mixes, and lubricants, where it adds lubricating and thermal transmission properties and, to ceramics, increased strength. It can be used as a dry lubricant in powdered form. The network structure is planar hexagonal sheets, much like graphite, except that the hexagon corners are alternating B and N atoms. As in graphite, the atoms within a single crystal sheet of boron nitride are strongly bonded with covalent bonds, while each sheet is attracted to the next only by London force.
13. Biological computers have been a scientific dream for years. The progressive technology of miniaturization is driven by the fact that the more transistors one can place on a microchip, the faster and more powerful the processor will be. The logical limit to miniaturization is at the level where individual switches would be molecular (or even atomic) in size. Current mechanical computers depend on a huge number of possible circuits through microscopic transistor "switches" engraved photographically on silicon-based semiconducting microchips.

Recently, Dr. Ehud Shapiro, working at the Weismann Institute in Israel, constructed a different kind of mechanical computer that is designed along the theoretical lines of proposed biological computers. The key point here is that such a computer operates as a continuous ribbon of individual information "cells." These cells are scanned by a read/write head that moves along the ribbon from cell to cell, reading symbols, writing symbols, and changing its control state as it goes. Alan Turing created such a concept on paper in 1936, and the system has been called a Turing Machine ever since. Biologists believe that ribosomes operate in a somewhat similar fashion—they may be thought of as biological computers preprogrammed by messenger RNA to assemble proteins.

Scientists theorize that someday the ability to build such computers from biological components might result, for example, in microscopic devices that could be programmed to adjust any desired chemical levels within the body. Perhaps they might also produce needed proteins on demand, and replace many or most medical treatments now in existence. The possibilities seem endless, and will certainly include applications not yet dreamed of.

CHAPTER 4 LAB ACTIVITIES

ACTIVITY 4.3.1 SHAPES OF MOLECULES

(Page 277)

Prediction

(a) According to the VSEPR theory,

CCl₄ should be tetrahedral, with 4 bond pairs around the carbon atom.

C₂Cl₄ should be trigonal planar at each end, with three groups of electrons (one double bond and two single bonds) around each carbon atom. The overall molecule should be flat (i.e., in one plane).

C₂F₂ should be linear around each carbon atom, with two groups of electrons (a triple bond and a single bond) around each carbon atom. The overall shape of the molecule should also be linear.

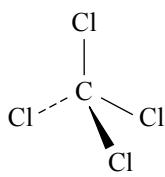
NCl₃ should be pyramidal, with 3 bond pairs and 1 lone pair around the nitrogen atom.

OF₂ should be V-shaped, with 2 bond pairs and 2 lone pairs around the oxygen atom.

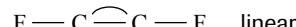
NH₂OH should be pyramidal around the nitrogen, with 3 bond pairs and 1 lone pair around the nitrogen atom; and V-shaped around the oxygen, with 2 bond pairs and 2 lone pairs around the oxygen atom. There is no simple description of the overall shape of the whole molecule.

Evidence/Analysis

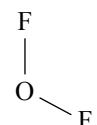
(b)



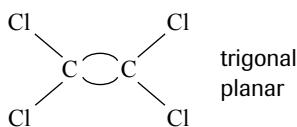
tetrahedral



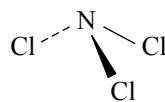
linear



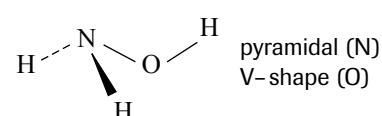
V-shape



trigonal
planar



pyramidal



pyramidal (N)
V-shape (O)

12. Boron nitride, $\text{BN}_{(s)}$, is a network covalent compound with unique properties. It has very high melting and boiling points, conducts heat well, is a soft slippery solid like graphite, but unlike graphite, is a nonconductor of electricity. It is used as an additive to plastics, ceramic mixes, and lubricants, where it adds lubricating and thermal transmission properties and, to ceramics, increased strength. It can be used as a dry lubricant in powdered form. The network structure is planar hexagonal sheets, much like graphite, except that the hexagon corners are alternating B and N atoms. As in graphite, the atoms within a single crystal sheet of boron nitride are strongly bonded with covalent bonds, while each sheet is attracted to the next only by London force.
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CHAPTER 4 LAB ACTIVITIES

ACTIVITY 4.3.1 SHAPES OF MOLECULES

(Page 277)

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(a) According to the VSEPR theory,

CCl_4 should be tetrahedral, with 4 bond pairs around the carbon atom.

C_2Cl_4 should be trigonal planar at each end, with three groups of electrons (one double bond and two single bonds) around each carbon atom. The overall molecule should be flat (i.e., in one plane).

C_2F_2 should be linear around each carbon atom, with two groups of electrons (a triple bond and a single bond) around each carbon atom. The overall shape of the molecule should also be linear.

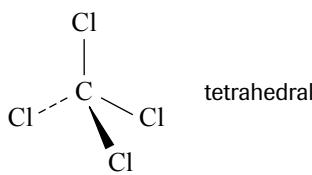
NCl_3 should be pyramidal, with 3 bond pairs and 1 lone pair around the nitrogen atom.

OF_2 should be V-shaped, with 2 bond pairs and 2 lone pairs around the oxygen atom.

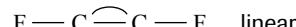
NH_2OH should be pyramidal around the nitrogen, with 3 bond pairs and 1 lone pair around the nitrogen atom; and V-shaped around the oxygen, with 2 bond pairs and 2 lone pairs around the oxygen atom. There is no simple description of the overall shape of the whole molecule.

Evidence/Analysis

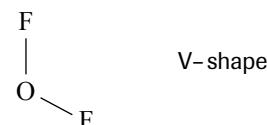
(b)



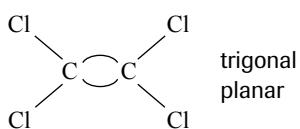
tetrahedral



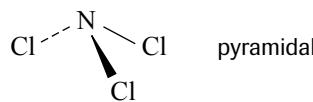
linear



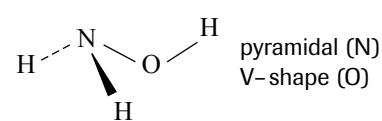
V-shape



trigonal
planar



pyramidal



pyramidal (N)
V-shape (O)

Evaluation

- (c) The evidence from the molecular models agrees with the predictions for each central atom. In all cases, except NH_2OH , the shape of the whole molecule was predicted. NH_2OH does not seem to have an overall shape because the ends of the molecule can rotate. Therefore, the predictions are generally verified, indicating an adequate understanding of VSEPR theory as it applies to the structure of small molecules. Additional information may be needed to know if there is a preferred orientation of molecules with two or more central atoms which can rotate about a bond axis.

INVESTIGATION 4.4.1 TESTING FOR POLAR MOLECULES

(Page 277)

Prediction

- (a) According to the empirical rules in Table 1, water, ethanol, 1,2-ethanediol, and acetone all have polar molecules because they fall into the category of oxygen and other atoms, or carbon and two other kinds of atoms. Pentane and hexane have nonpolar molecules because they fall into the category of carbon and only one other kind of atom.

Evidence

(b)

Testing Liquids with Charged Strips			
Substance	Chemical formula	Effect of charged strip	
		Acetate	Vinyl
acetone	$(\text{CH}_3)_2\text{CO}_{(l)}$	attracted	attracted
1,2-ethanediol	$\text{C}_2\text{H}_4(\text{OH})_{2(l)}$	attracted	attracted
ethanol	$\text{C}_2\text{H}_5\text{OH}_{(l)}$	attracted	attracted
hexane	$\text{C}_6\text{H}_{14(l)}$	no effect	no effect
pentane	$\text{C}_5\text{H}_{12(l)}$	no effect	no effect
water	$\text{H}_2\text{O}_{(l)}$	attracted	attracted

Analysis

- (c) According to the evidence collected, acetone, 1,2-ethanediol, ethanol, and water all have polar molecules because they were all attracted to the charged strips. Hexane and pentane were not attracted. Therefore, they do not have polar molecules.

Evaluation

- (d) The experimental design seems very simple with no obvious flaws. The question was clearly answered. An improvement might be to specify more specifically where the charged strip should be placed. It is also not clear if the strips were charged the same each time. This could be somewhat controlled by rubbing the strip the same number of times each time it is charged. Neither of these should substantially affect the results. If quantitative results are desired, more sophisticated equipment and procedure would be required. Overall, I am reasonably confident with the evidence.
- (e) The results clearly agree with the prediction. Therefore, the prediction has been verified and the empirical rules appear acceptable.

LAB EXERCISE 4.5.1 BOILING POINTS AND INTERMOLECULAR FORCES

(Page 278)

Prediction

- (a) Molecules of the hydrogen compounds of one group will all be similar in shape and polarity (polar versus nonpolar). Therefore, the dipole–dipole forces between molecules for members of the same group should be similar. For example, the Group 14 hydrogen compounds all have symmetrical tetrahedral molecules and therefore should be nonpolar. The other groups have molecules that are all nonsymmetrical and therefore will be somewhat polar, producing some dipole–dipole effects. The only significant difference within a group of hydrogen compounds will be the increasing number of electrons per molecule as you go down the group. Therefore, based on the rule for London forces, the strength of these forces should increase down the group and the boiling points should increase accordingly. This tendency should produce a graph that has the following general trend for each group of hydrogen compounds.

Evaluation

- (c) The evidence from the molecular models agrees with the predictions for each central atom. In all cases, except NH_2OH , the shape of the whole molecule was predicted. NH_2OH does not seem to have an overall shape because the ends of the molecule can rotate. Therefore, the predictions are generally verified, indicating an adequate understanding of VSEPR theory as it applies to the structure of small molecules. Additional information may be needed to know if there is a preferred orientation of molecules with two or more central atoms which can rotate about a bond axis.

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INVESTIGATION 4.4.1 TESTING FOR POLAR MOLECULES

(Page 277)

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Analysis

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Evaluation

- (d) The experimental design seems very simple with no obvious flaws. The question was clearly answered. An improvement might be to specify more specifically where the charged strip should be placed. It is also not clear if the strips were charged the same each time. This could be somewhat controlled by rubbing the strip the same number of times each time it is charged. Neither of these should substantially affect the results. If quantitative results are desired, more sophisticated equipment and procedure would be required. Overall, I am reasonably confident with the evidence.
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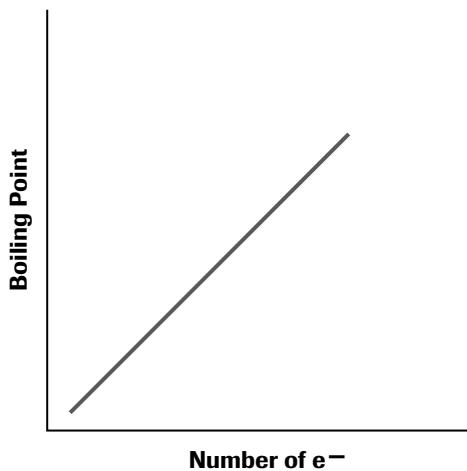
LAB EXERCISE 4.5.1 BOILING POINTS AND INTERMOLECULAR FORCES

(Page 278)

Prediction

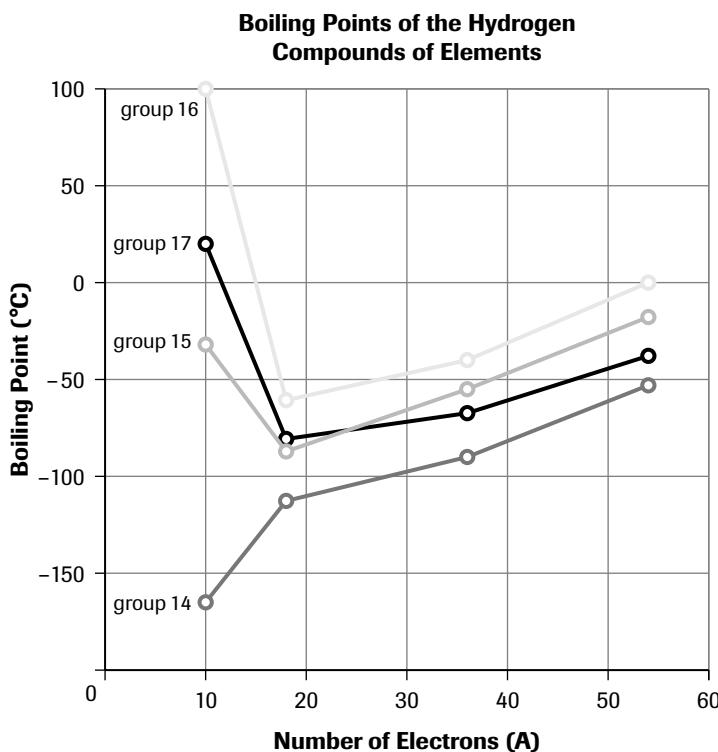
- (a) Molecules of the hydrogen compounds of one group will all be similar in shape and polarity (polar versus nonpolar). Therefore, the dipole–dipole forces between molecules for members of the same group should be similar. For example, the Group 14 hydrogen compounds all have symmetrical tetrahedral molecules and therefore should be nonpolar. The other groups have molecules that are all nonsymmetrical and therefore will be somewhat polar, producing some dipole–dipole effects. The only significant difference within a group of hydrogen compounds will be the increasing number of electrons per molecule as you go down the group. Therefore, based on the rule for London forces, the strength of these forces should increase down the group and the boiling points should increase accordingly. This tendency should produce a graph that has the following general trend for each group of hydrogen compounds.

Boiling Point Trend for Hydrogen Compounds



Analysis

(b)



- (c) According to the evidence, the boiling point generally increases with increasing number of electrons, with some obvious exceptions such as NH_3 , H_2O , and HF .

Evaluation

- (d) Three out of the sixteen compounds tested (about 19%) differed substantially from the prediction. For this reason, the prediction is judged to be inconclusive. The rules for intermolecular forces, in particular London forces, remain acceptable, but further tests need to be done to increase the certainty of this evaluation. More families of compounds of Groups 14 to 17 elements need to be investigated, especially compounds of nitrogen, oxygen, and fluorine.
- (e) The evidence for NH_3 , H_2O , and HF was an anomaly. It may be that hydrogen compounds of these same elements are exceptions and the London force theory has to be restricted or revised depending on the results of further tests. There may be other forces at work, or perhaps some dipole–dipole forces in the selected compounds are exceptionally strong.

INVESTIGATION 4.5.2 HYDROGEN BONDING

(Page 279)

Prediction

- (a) According to the theory of energy changes associated with changes in bonding, the temperature change for the mixture of glycerol and water should be greater than the temperature change for ethanol and water. In both cases, additional hydrogen bonds would be formed between the solute molecules and water molecules. However, a glycerol molecule, $C_3H_5(OH)_3(l)$, has three hydroxyl groups that can form hydrogen bonds with water molecules. An ethanol molecule, $C_2H_5OH(l)$, has only one hydroxyl group that can form hydrogen bonds with water molecules. Because energy is released when bonds are formed, more hydrogen bonds should mean more energy released and a larger temperature change for glycerol and water.

Experimental Design

- (b) The independent variable is the number of hydroxyl groups per alcohol molecule. The dependent variable is the temperature change produced when the alcohol and water are mixed. Some important controlled variables are the volumes of liquids mixed, the particular calorimeter used, and the purity of the alcohol used.

Procedure

(c)

1. Using a 10-mL graduated cylinder, measure 10.0 mL of ethanol and place it into clean, dry, nested polystyrene cups (calorimeter).
2. Place a thermometer into the ethanol and measure its temperature to one decimal place.
3. Using a different 10-mL graduated cylinder, measure 10.0 mL of pure water.
4. Measure the temperature of the water in the graduated cylinder.
5. Quickly pour all of the water into the ethanol and place the lid on the cups.
6. Swirl the mixture and measure the highest temperature reached by the mixture.
7. Dispose of the mixture into the sink, and rinse and dry the calorimeter.
8. Repeat Steps 1 to 7 two more times.
9. Repeat Steps 1 to 8 using glycerol instead of ethanol.

Evidence/Analysis

Ethanol and Water Mixture			
Trials	Initial temperature (°C)	Final temperature (°C)	Temperature change (°C)
ethanol water	22.2 22.0	29.2	7.1
ethanol water	22.0 22.0	29.2	7.2
ethanol water	22.2 22.2	29.2	7.0

Glycerol and Water Mixture			
Trials	Initial temperature (°C)	Final temperature (°C)	Temperature change (°C)
glycerol water	23.4 22.2	28.5	5.7
glycerol water	23.5 22.4	28.4	5.5
glycerol water	23.4 22.4	28.2	5.3

- Glycerol was very viscous and flowed very slowly out of the graduated cylinder. It was hard to tell how long to wait for this liquid to flow out.
 - The initial temperatures were averaged together before subtracting them from the final temperature.
- (d) According to the evidence collected, the average temperature change of the ethanol-water mixture was noticeably higher than the glycerol-water mixture.

Evaluation

- (e) The evidence is questionable because the design did not take into account the fact that the same volume of two different liquids would contain different numbers of molecules. This is a flaw in the design that needs to be corrected. The materials were of suitable quality to provide reasonable evidence. The procedure appears to be adequate because the steps were sufficiently clear and included multiple trials to increase the reliability of the evidence. The difficulty experienced with pouring the viscous glycerol could be eliminated by measuring the mass used instead of the volume. This change would also make it easier to compare or control the number of molecules of the alcohol used.
- (f) I am not very certain about the evidence because of the flaw identified in the design. Measurements of the temperature and volume also provide some experimental error but this is not expected to be a major factor.
- (g) The evidence is sufficiently uncertain to make a judgment of the prediction quite unreliable. It is hard to tell if the disagreement of the evidence with the prediction is due to the flaw identified or other factors related to the mixing and bonds breaking and forming. The experiment needs to be redesigned and redone.

INVESTIGATION 4.6.1 CLASSIFYING MYSTERY SOLIDS

(Page 279)

Experimental Design

- (a) The class of each solid is identified by observing the appearance, electrical conductivity, solubility in water, electrical conductivity in water, and effect of heating (relative melting point).

Materials

- (b) tweezers
stirring rod
conductivity tester
4 small beakers
distilled water
hot plate
vials with mystery solids

Procedure

- (c)
1. Observe the appearance of each solid.
 2. Test a crystal of each solid for electrical conductivity.
 3. Place a crystal of each solid on a hot plate at a low heat setting. Observe the solids as the heat is slowly increased.
 4. Test the electrical conductivity of pure water in a clean, dry beaker.
 5. Place a few crystals of each solid in separate beakers and add about 10 mL of water to each. Stir to dissolve as much as possible.
 6. Test the electrical conductivity of each mixture.
 7. Dispose of solids into the waste basket and liquids in the sink.

Evidence

Properties of the Mystery Solids				
Solids	1	2	3	4
Appearance	clear, colourless	clear, colourless, some white patches	silvery grey	clear, colourless
Conductivity of solid	none	none	good	none
Effect of heating	no change	no change	none	melts quickly and turns black
Solubility in water	did not dissolve	dissolved	did not dissolve	dissolved
Conductivity in water	none	good	none	none

Evaluation

- (e) The evidence is questionable because the design did not take into account the fact that the same volume of two different liquids would contain different numbers of molecules. This is a flaw in the design that needs to be corrected. The materials were of suitable quality to provide reasonable evidence. The procedure appears to be adequate because the steps were sufficiently clear and included multiple trials to increase the reliability of the evidence. The difficulty experienced with pouring the viscous glycerol could be eliminated by measuring the mass used instead of the volume. This change would also make it easier to compare or control the number of molecules of the alcohol used.
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 5. Place a few crystals of each solid in separate beakers and add about 10 mL of water to each. Stir to dissolve as much as possible.
 6. Test the electrical conductivity of each mixture.
 7. Dispose of solids into the waste basket and liquids in the sink.

Evidence

Properties of the Mystery Solids				
Solids	1	2	3	4
Appearance	clear, colourless	clear, colourless, some white patches	silvery grey	clear, colourless
Conductivity of solid	none	none	good	none
Effect of heating	no change	no change	none	melts quickly and turns black
Solubility in water	did not dissolve	dissolved	did not dissolve	dissolved
Conductivity in water	none	good	none	none

Analysis

(d) According to the evidence collected, solid 1 is network covalent, 2 is ionic, 3 is metallic, and 4 is molecular.

Evaluation

(e) Most of the evidence was sufficient to classify the majority of the solids. The classification of the network covalent solid fits with the properties of network covalent solids but was done mainly by elimination once the others were classified. This classification is very uncertain and it is possible that solid 1 may be a low-solubility ionic solid. The classification of solids 2, 3, and 4 seems relatively certain.

Other properties such as hardness and melting points would help to make the classification more certain.

CHAPTER 4 SUMMARY

(Page 280)

Force or bond	Central particle	Surrounding particles
covalent	electron pair	nuclei
covalent network	electron pair	nuclei
dipole–dipole	charge site	opposite charge sites
hydrogen	proton	electron pairs
ionic	ion	oppositely charged ions
London	nuclei	nearby valence electrons
metallic	nuclei	mobile valence electrons (electron sea)

Substance	Hardness	Melting point	Electrical conductivity		
			Solid	Liquid	Solution
molecular	low	low	negligible	negligible	negligible
ionic	medium to high	high	negligible	high	high
covalent network	high	very high	negligible	negligible	n/a
metallic	medium	medium to high	high	high	n/a

CHAPTER 4 SELF-QUIZ

(Page 281)

1. False: The shape of molecules of the rocket fuel hydrazine, $\text{N}_2\text{H}_{4(\text{l})}$, is predicted by VSEPR theory to be pyramidal around each nitrogen.
2. True
3. False: A central atom with two bonded atoms and two unshared electron pairs has a V-shaped arrangement of its electron pairs.
4. False: Ionic substances are ionic solids, with ionic bonding.
5. False: Hydrogen bonding is possible whenever the molecule contains hydrogen atoms bonded to N, O, or F atoms.
6. False: A molecule with a pyramidal shape and polar bonds will be polar.
7. True
8. True
9. False: The end of a soap molecule that attracts and dissolves oily dirt must be nonpolar.
10. True
11. (b)
12. (b)

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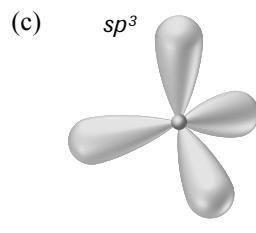
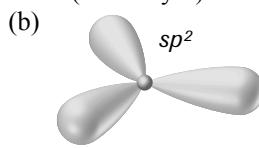
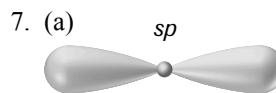
13. (d)
14. (a)
15. (c)
16. (c)
17. (c)
18. (a)
19. (b)
20. (d)

CHAPTER 4 REVIEW

(Page 282)

Understanding Concepts

1. (a) $\cdot\text{Ca}\cdot$ (2) (b) $:\ddot{\text{Cl}}\cdot$ (1) (c) $.\ddot{\text{P}}\cdot$ (3) (d) $.\ddot{\text{Si}}\cdot$ (4) (e) $:\ddot{\text{S}}\cdot$ (2)
2. For a covalent bond to form between two approaching atoms, both atoms must have a valence orbital occupied by a single electron (or one atom must have a vacant valence orbital and the other must have a lone pair of electrons) and the orbitals must be able to overlap in space.
3. (a) three lone pairs
 (b) one lone pair
 (c) two lone pairs
 (d) no lone pairs
 (e) one lone pair
4. (a) $:\ddot{\text{F}}\cdot$ (b) $:\ddot{\text{P}}\cdot$ (c) $\text{K}\cdot$ (d) $:\ddot{\text{Se}}\cdot$ (e) $\cdot\text{Sr}\cdot$
5. The electron configuration that gives an atom maximum stability is one with eight electrons in the shell with the highest principal quantum number (the “valence” shell).
6. (a) $1s^2 2s^2 2p^6$
 (b) A carbide-12 ion has 6 protons and 6 neutrons in the nucleus, with 2 electrons in the first shell (inner layer), and 8 more electrons in the second shell (outer layer).



8. (a) sp^3
 (b) sp^2
 (c) sp
 (d) sp^3

9. A sigma bond involves overlap of orbitals directly, or end to end, between the atomic nuclei.
 A pi bond involves side-by-side overlap of the two lobes of p orbitals above and below a line between the atomic nuclei.
10. (a) 2 sigma bonds
 (b) 3 sigma bonds and 2 pi bonds
 (c) 5 sigma bonds and 1 pi bond
 (d) 7 sigma bonds
11. The B atom has sp^2 hybridization initially, and the N atom has sp^3 hybridization (with an unshared pair of electrons in the fourth hybrid orbital). After reaction, both central atoms must be sp^3 hybridized (they are each bonded to four other atoms). This occurs because the N supplies both electrons for the B-N sigma bond.

13. (d)
14. (a)
15. (c)
16. (c)
17. (c)
18. (a)
19. (b)
20. (d)

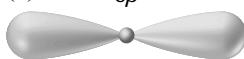
CHAPTER 4 REVIEW

(Page 282)

Understanding Concepts

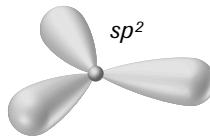
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7. (a)



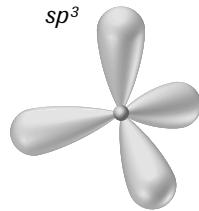
linear

(b)



trigonal planar

(c)



tetrahedral

8. (a) sp^3
 (b) sp^2
 (c) sp
 (d) sp^3

9. A sigma bond involves overlap of orbitals directly, or end to end, between the atomic nuclei.

A pi bond involves side-by-side overlap of the two lobes of p orbitals above and below a line between the atomic nuclei.

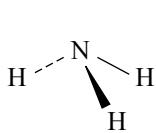
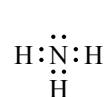
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12. (a) Valence shell refers to the energy level of electrons with the highest principal quantum number.
 (b) Bonding pair refers to a pair of electrons shared between atoms in a valence orbital.
 (c) Lone pair refers to a pair of electrons in a valence orbital that are not shared with another atom.
 (d) Electron pair repulsion assumes that valence orbitals occupied by a pair of electrons are “full” and will repel any other full valence orbital.

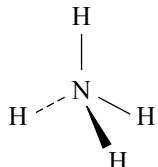
13. To predict the shape of a molecule using the VSEPR model, you first, draw a Lewis diagram for the molecule, and second, count the lone pairs and bond pairs around the central atom(s), and finally, predict the shape around the central atom(s) from the electron pair numbers.

14. (a) linear
 (b) trigonal planar
 (c) tetrahedral
 (d) tetrahedral
 (e) linear
 (f) V-shaped
 (g) tetrahedral
 (h) V-shaped (around each O)

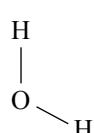
15. (a)



pyramidal



tetrahedral



V-shape

- (b) In methane, the bond angles are the normal tetrahedral angle. In ammonia, repulsion from the lone pair compresses the bond angles a bit, and in water, stronger repulsion from two lone pairs compresses the bond angle even more.

16. (a) $\ddot{\text{O}} \cdot \text{C} \cdot \ddot{\text{O}}$:

- (b) A carbon dioxide molecule is linear, with a bond angle of 180° .

- (c) Carbon dioxide has two double bonds, each of which is strongly polar. The two bond polarities are exactly opposite and so the resultant is zero, and the molecule is nonpolar.

17. (a) An N–Cl bond is not noticeably polar, with an electronegativity difference of 0.0; whereas a C–Cl bond is polar, with an electronegativity difference of 0.5.

- (b) A molecule of $\text{NCl}_{3(l)}$ should be nonpolar because the bonds are nonpolar. A molecule of $\text{CCl}_{4(l)}$ should be nonpolar because it is symmetrical, so the bond dipoles balance, cancelling any molecular polarity.

18. (a) BeH_2 is a nonpolar molecule because it is linear and symmetrical, so its bond dipoles balance each other. H_2S is a polar molecule because it is V-shaped and not symmetrical, so its bond dipoles combine to produce a nonzero resultant dipole.

- (b) BH_3 is trigonal planar, while NH_3 is pyramidal in shape, because NH_3 has a lone pair of electrons repelling the three bond pairs.

- (c) LiH has a melting point of 688°C because solid LiH has an ionic crystal structure, with ions held together by relatively strong ionic bonding. HF has a melting point of -83°C because solid HF has a molecular crystal structure, with molecules held together by much weaker intermolecular forces.

19. The larger molecules have stronger London force intermolecular bonding because the molecules have a greater number of electrons per molecule. Therefore, the larger the molecule in this series, the higher the boiling point.

20. $\text{CH}_{4(g)}$ (-164°C), has London force; $\text{NH}_{3(g)}$ (-33°C), has London force, dipole–dipole force, and hydrogen bonding; and $\text{BF}_{3(g)}$ (-100°C), has London force. Ammonia has the strongest intermolecular bonds because of the hydrogen bonding; boron trifluoride has London force from a 32-electron molecule; and methane has weaker London force from a 10-electron molecule.

21. (a) Nickel has a much higher melting point than sodium chloride because the metallic bonding holding nickel atoms together is stronger than the ionic bonding holding sodium and chloride ions together.
- (b) Solid nickel will conduct well, because the atoms' valence electrons are free to move. Solid sodium chloride will not conduct because the charges (ions) are not free to move.
- (c) Solid nickel will not dissolve, because the atoms attract each other much more than water molecules can attract them. Solid sodium chloride will dissolve because the charges (ions) are strongly attracted by polar water molecules.
22. (a) Hexane has London force.
- (b) 1-butanol has London force, dipole–dipole force, and hydrogen bonding.
- (c) Ethylamine has London force, dipole–dipole force, and hydrogen bonding.
- (d) Chloroethane has London force and dipole–dipole force.
- (e) Calcium carbonate has ionic bonds.
- (f) Diamond has covalent bonds.

Applying Inquiry Skills

23. (a) Prediction

According to intermolecular forces concepts, the order from lowest to highest solubility in water is pentane, diethyl ether, 1-butanol, and butanoic acid. Pentane, $C_5H_{12(l)}$, has symmetrical, nonpolar molecules and therefore should have little solubility in water. Diethyl ether, $(C_2H_5)_2O(l)$, has polar molecules and should have some solubility in water. 1-butanol, $C_4H_9OH(l)$, has polar molecules as well as the possibility for hydrogen bonding with water molecules. The solubility of 1-butanol should be high. Butanoic acid, $C_3H_7COOH(l)$, is like 1-butanol but has more hydrogen bonding sites available. The solubility of butanoic acid should be very high, perhaps miscible with water.

(b) Experimental Design

Slowly add each of the liquids to a small quantity of distilled water until no more dissolves and two layers form. The independent variable is the substance added to the water, the dependent variable is the volume of the substance that dissolves, and the controlled variables are the volume of water and the temperature.

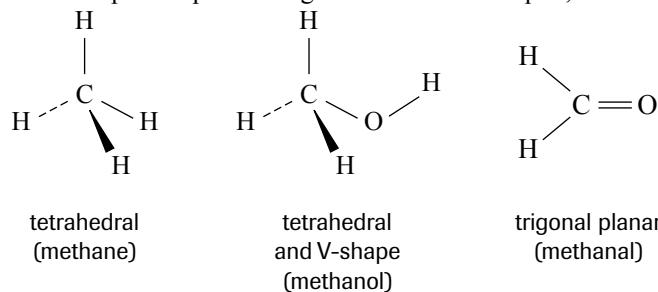
(c) Materials

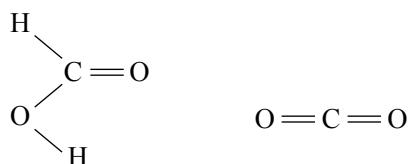
- lab apron
- eye protection
- medium-sized test tube with stopper
- 5 10-mL graduated cylinders
- 5 droppers or disposable pipets
- waste container for organic mixtures
- bottle of distilled water
- samples of pentane, 1-butanol, diethyl ether, butanoic acid

(d) Procedure

1. Measure 10.0 mL of water with a graduated cylinder and place it into the test tube.
2. Measure 10.0 mL of pentane in another graduated cylinder.
3. Start adding a little of the pentane to the water, and stopper and invert between each addition.
4. Stop adding pentane when a second layer is noticed in the test tube. Note the volume of pentane added.
5. Dispose of mixture into the labelled waste container.
6. Clean and dry the test tube.
7. Repeat steps 1 through 6 with the next liquid, until all liquids have been tested.

24.



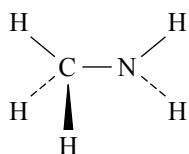
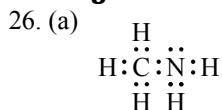


trigonal planar
and V-shape
(methanoic acid)

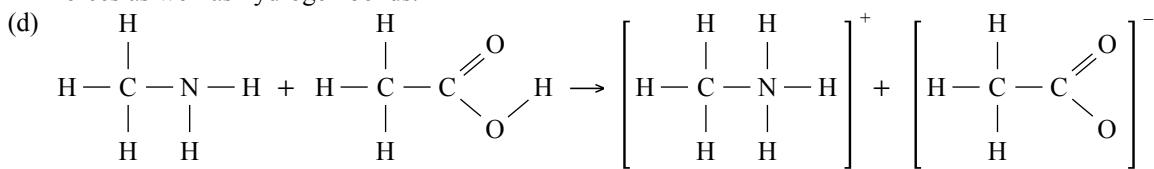
linear
(carbon dioxide)

25. (a) Metallic solids are composed of atoms with mobile valence electrons—they may be thought of as an arrangement of close-packed positive ions held together by strong mutual attraction for electrons that permeate the structure.
Network solids are composed of atoms held together by very strong (directional) covalent bonds.
- (b) Network solids are composed of atoms held together by very strong (directional) covalent bonds. Molecular solids are composed of molecules held together by relatively weak intermolecular forces.
- (c) Molecular solids are composed of molecules held together by relatively weak intermolecular forces. Ionic solids are composed of positive and negative ions held together by relatively strong (nondirectional) ionic bonds.

Making Connections



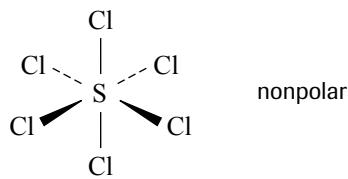
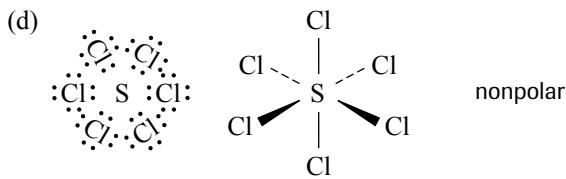
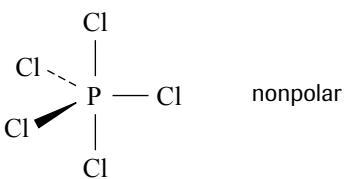
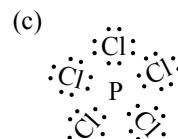
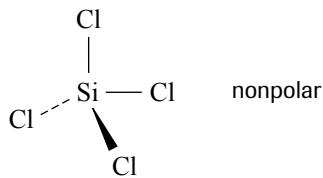
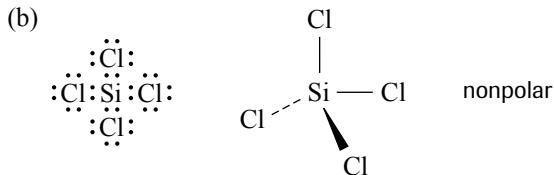
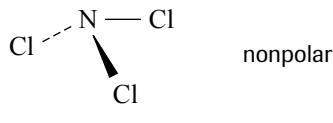
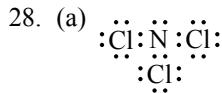
- (b) The shape around the carbon atom is tetrahedral, and the shape around the nitrogen atom is pyramidal.
(c) Methylamine has a much higher boiling point because methylamine molecules have additional dipole–dipole forces as well as hydrogen bonds.



- (e) Vinegar and lemon juice reduce the odour of fish because they are acidic, and react to neutralize the basic amines that cause “fishy” odours.

27. The material used for the skin of stealth aircraft is a carbon fibre composite material. It has fibres of carbon embedded in a matrix—the same basic type of structure as fibreglass composites, but very much stronger. The material can also be structured as a “honeycomb” to give a very high strength-to-weight ratio for solid pieces. The material is suited for radar “stealthing” because it can be made to absorb microwaves, greatly reducing any detectable reflection.

Extension



UNIT 2 PERFORMANCE TASK: A STUDY OF AN ELEMENT

(Page 284)

A STUDY OF ARGON

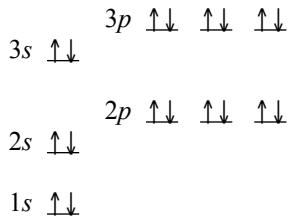
History

The English scientist, Henry Cavendish, was shy and reclusive to the point of phobia, and, consequently, never took examinations for his degree at Cambridge, which would have involved personal contact with the examiners. Nonetheless, his contributions to science guarantee his place in history. He is most famous for the physics experiment in which he determined the value of G, the universal gravitational constant; but in 1785, he performed chemical experiments with air which eventually led to the discovery of argon. When he chemically combined all of the oxygen and nitrogen in a sample of dry air, he found that a small bubble of gas, about 1% of the total volume, remained no matter what he did to get it to react. He speculated at the time that air contains an unknown gas that is resistant to chemical reaction. This was correct—he had discovered a new element.

The Cavendish experiment was ignored for more than a century until it was repeated by Sir William Ramsay in 1892 in an attempt to solve a problem publicized by Lord Rayleigh. Rayleigh had found that nitrogen obtained from air had a slightly higher density than did nitrogen obtained from its compounds. Ramsay and Rayleigh used a spectroscope to analyze the bright-line spectrum emitted by the unreacted gas from an air sample, and found it to be an unknown element. They named the new element argon, from the Greek word for “inert.” Discovery of the other inert gases followed quickly from this research. In 1904, Ramsay won the Nobel Prize for Chemistry and Rayleigh the Nobel Prize for Physics, for their discovery and determination of the properties of argon.

Structure and Bonding

An atom of argon is theoretically described as having atomic number 18, meaning a nuclear structure made up of 18 protons, and, most commonly, 22 neutrons. About 0.34% of argon atom nuclei have 20 neutrons, and about 0.07% have 18 neutrons. There are at least 12 other unstable (radioactive) isotopes of argon known to exist. The atomic volume is occupied by 18 electrons, described by a quantum mechanical configuration of $1s^2 2s^2 2p^6 3s^2 3p^6$. (See diagram below.)



Ground-state electron configuration for an argon atom, Ar

The octet of electrons of the highest energy level results in a particularly stable (low) energy configuration. Notice that all orbitals contain a pair of electrons and that there are no half-filled orbitals. Theoretically then, argon should exist as a monatomic element with very low melting and boiling points because the attraction between atoms is limited to London forces. These forces should not be very strong because the total number of electrons per atom is low. By the same argument, argon should be extremely unlikely to combine chemically with other atoms because there are no half-filled orbitals to overlap with half-filled orbitals of other atoms to form a covalent bond or to transfer electrons to achieve a more stable configuration.

Physical Properties

Argon is a colourless, odourless gas at SATP and has a molar mass of 39.95 g/mol. The gas condenses to a colourless, odourless liquid at -186°C , and freezes to a solid at -189°C (both values measured at 1 atm pressure). The density of argon gas is 1.78 g/L at STP, and the solubility in water at 0°C is 56 mL/L, slightly more than oxygen. In rare instances, argon is found to be combined with other substances in a fixed-mass ratio. Argon forms a hydrate with water under very high pressure and low temperature, and a clathrate with β -hydroquinone, but in these cases the scientific community assumes that the argon atoms are trapped within the crystals and held in place by van der Waals forces, and not by chemical bonds.

Chemical Properties

Argon has no known chemical compounds, which agrees very well with the prediction from the theoretical atomic structure. This evidence strongly supports the quantum mechanical and bonding theories. I am not sure why one or more valence elec-

trons of an argon atom could not be promoted to the $3d$ level to perhaps form some covalently bonded compounds. These compounds are obviously unstable since no one has found any but maybe some could be formed at very low temperatures.

Technological Applications

Most of the technological uses of argon in society are based on three factors. It is readily available since it makes up nearly 1% of the atmosphere of the Earth. It is inexpensive because it is easily extracted in high purity from air. And finally, it is chemically inert. There are many situations where technology requires that chemical reaction not take place, and in these situations argon finds its primary uses. Some common examples include the following:

- Argon is placed in incandescent and fluorescent light bulbs at about 400 Pa pressure, which inhibits the tendency of metal atoms to boil off the surface of very hot filaments, thus prolonging filament life. Other gases would react with the hot metals themselves, but argon does not.
- Argon is widely used in welding and torch-cutting systems to create an inert blanketing atmosphere around the high-temperature area. This gaseous blanket prevents the metal from oxidizing while it is very hot.
- Argon is used as the atmosphere in metallurgy vessels where reactive elements, such as titanium, are produced. An argon atmosphere keeps them from reacting the instant they are formed.
- Silicon and germanium crystals—which are critical for production of semiconductors and microchip circuits—may be grown in an argon atmosphere to ensure high purity and evenness of atomic arrangement in such crystals.

Argon produces a bluish light when present at low pressure in a glass tube connected to a high potential difference (voltage). This has been used for decades as a way to produce a blue colour in commercial display signs, just as neon is used to produce a red-orange colour. Modern technology has developed many new uses for the light emitted by argon.

The emission of light by excited argon atoms is presumed to be due to electron energy-level shifts—consistent with atomic structure theory from Bohr through to quantum mechanics. The argon atoms' electrons are raised to various excited states, and then emit several characteristic frequencies (wavelengths) of monochromatic light as they drop back to a ground state. An examination of argon's spectrum for light emitted by a low-pressure, high-voltage tube shows it to be a typical “bright-line” spectrum. An application of quantum mechanical technology allows lasers to be created that operate using argon as one of the gases producing the desired monochromatic light. Following are two special examples of this technology:

- Laser eye surgery commonly uses argon-fluorine “excimer” lasers to produce a coherent beam at 193 nm wavelength to vaporize corneal tissue, allowing reshaping of the eye surface to improve vision acuity.
- Laser “light show” systems are becoming common in the world of entertainment. Argon lasers produce bright blue and green colour wavelengths, and krypton lasers produce vivid red colour, so a laser using a mixture of these two gases can be constructed to produce all three primary colours. This means that, just as on a television screen, these three colours can be combined to produce all apparent colours of the visible spectrum. The very bright laser beams can be projected separately onto a screen, and moved at high speed to produce stunning visual effects.

Careers Involving Argon

Some careers directly involving argon include:

- Gas Plant (Liquid Air) Operator/Technician

Individuals working in plant operations involving the extraction of argon from the atmosphere; usually operating compression and fractionation equipment and control systems.

- Inert Gas Welder

Individuals using modern technology and equipment to perform inert gas welding and cutting operations on metals.

- Light Bulb Manufacturing Plant Operator/Technician

Individuals working in plant operations involving the placement of argon into light sources using specialized equipment and control systems.

- Semiconductor Production Plant Operator/Technician

Individuals working in plant operations involving the growing and doping of crystals in special argon atmospheres, and associated technology and quality control.

- Laser Eye Surgeon

Medical doctors specially trained to use excimer lasers to perform corrective eye-surface restructuring.

- Surgical Optical Laser Technician

Individuals specially trained to service and adjust precise tolerance lasers for eye surgeries.

- Light Show Operators/Technicians
Individuals specially trained to operate, program, service, and adjust light show lasers.

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Web Sites

http://lasereye.net/laser_eye_surgery_hawaii_kw.htm#Laser%20Types

http://www.laserist.org/Laserist/showbasics_laser.html

UNIT 2 SELF-QUIZ

(Page 286)

1. False: The term orbital refers to the volume of space an electron occupies near a nucleus.
2. True
3. True
4. True
5. False: The ground state electron configuration for all alkali metals shows that the highest energy electrons are in an *s* sublevel.
6. False: There are thought to be five *d* energy sublevels.
7. True
8. False: Schrödinger became famous by developing wave equation mathematics to describe electrons as wave functions.
9. True
10. True
11. False: VSEPR theory predicts that a central atom with three bonded atoms and one lone pair of electrons should have a pyramidal shape.
12. True
13. True
14. False: VSEPR and Lewis theories are complete enough to explain the structure and shape of the molecules in gaseous silane, SiH_{4(g)}, which is used as a doping agent in the manufacture of semiconductors for solid-state devices.
15. True
16. True
17. True
18. False: Ionic bonding involves three-dimensional structures with positive and negative ions attracting each other.
19. True
20. (a)
21. (b)
22. (c)
23. (a)
24. (a)
25. (a)
26. (c)
27. (d)
28. (b)
29. (d)
30. (b)

- Light Show Operators/Technicians
Individuals specially trained to operate, program, service, and adjust light show lasers.

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25. (a)
26. (c)
27. (d)
28. (b)
29. (d)
30. (b)

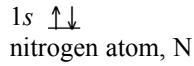
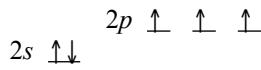
31. (b)
 32. (a)
 33. (b)
 34. (c)
 35. (a)
 36. (c)
 37. (b)
 38. (c)
 39. (a)
 40. (d)

UNIT 2 REVIEW

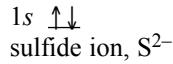
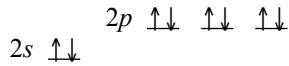
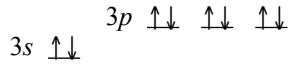
(Page 288)

Understanding Concepts

- When most alpha particles pass through the thin foil essentially unaffected, it indicates that somehow they are meeting negligible resistance; so most of the structure of the atoms they are hitting seems to be essentially empty space. When a very few alpha particles are very significantly deflected, it indicates that a tiny part of the structure of the target atoms must be relatively massive and positively charged.
- (a) The electron was discovered as a result of the qualitative studies of cathode rays by Crookes and, in particular, by the quantitative studies of cathode rays by Thomson.
 (b) The proton was discovered as a result of the alpha particle scattering experiments by Rutherford and, in particular, by the studies of positive rays (hydrogen ions) in a cathode ray tube by Rutherford and Thomson.
 (c) The neutron was discovered as a result of radioactive decay studies by Soddy, mass spectrometer work by Aston, and, in particular, by bombarding elements with alpha particles by Chadwick.
- (a) Atoms of an element may have different numbers of neutrons in their nuclei. These different nuclei therefore differ in mass; and, if a nucleus containing a given number of neutrons is unstable, that nucleus will be radioactive.
 (b) The term applied to such atoms is *isotope*.
- Max Planck suggested that energy radiated from heat sources was quantized, meaning that it could not be any frequency at all, but must be a multiple of some smallest value. He could not form an equation to correctly predict the frequencies radiated without this supposition, even though it seemed completely illogical at the time.
- Rutherford knew that a stationary electron would be attracted by, and pulled into, the positive nucleus of an atom. He thought the electrons would be orbiting just like the planets around the Sun.
- Bohr knew that if electrons were travelling in orbits, they would be accelerating and therefore radiating electromagnetic energy constantly. This would mean that all atoms would collapse and this is not observed.
- Bohr's First Postulate states (assumes) that electrons do not radiate energy as they orbit the nucleus because each orbit corresponds to a state of constant energy, called a stationary state.
- Bohr's Second Postulate assumes that electrons may increase or decrease in energy only by undergoing a transition (jump) from one stationary state to another.
- (a)



(b)



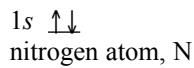
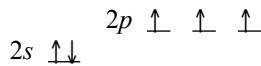
31. (b)
 32. (a)
 33. (b)
 34. (c)
 35. (a)
 36. (c)
 37. (b)
 38. (c)
 39. (a)
 40. (d)

UNIT 2 REVIEW

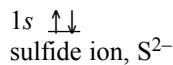
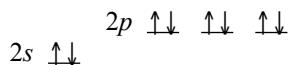
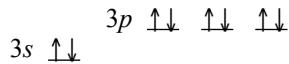
(Page 288)

Understanding Concepts

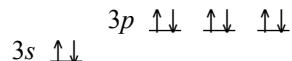
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- (a)



(b)



(c)



$$2s \uparrow\downarrow \quad 2p \uparrow\downarrow \quad \uparrow\downarrow \quad \uparrow\downarrow$$

$1s \uparrow\downarrow$
potassium ion, K^+

(d)

$2s$ 

$1s \uparrow\downarrow$
beryllium atom, Be

(e)

$$4p \uparrow\downarrow \quad \uparrow\downarrow \quad \uparrow\downarrow$$

$$3d \uparrow\downarrow \quad \uparrow\downarrow \quad \uparrow\downarrow \quad \uparrow\downarrow \quad \uparrow\downarrow \quad \uparrow\downarrow$$

$$3s \quad \uparrow \downarrow \quad 3p \quad \begin{array}{c} \uparrow \downarrow \\ \uparrow \downarrow \\ \uparrow \downarrow \end{array}$$

$$2s \quad \uparrow \downarrow \quad 2p \quad \begin{array}{c} \uparrow \\ \downarrow \end{array} \quad \begin{array}{c} \uparrow \\ \downarrow \end{array} \quad \begin{array}{c} \uparrow \\ \downarrow \end{array}$$

$1s$ $\uparrow\downarrow$
zirconium atom, Zr

10. Technetium metal has an electron configuration of [Kr] $5s^2 4d^5$. This means that it has five unpaired electrons in d orbitals. Unpaired electrons usually indicates that the substance will be at least paramagnetic and attracted by a magnet.

11. The bottom of the glass filling first is similar to the aufbau principle; lower energy levels are filled first. The level surface is similar to Hund's Rule. There should be an electron in each orbital of a level before any orbital is assigned a second electron.

12. Once you get to the fourth period in the table, the energies of the s and d orbitals of different principal quantum numbers start to cross. This means that transition metal atoms are filling the s orbital of a higher level while filling the d orbital of a lower level. In addition, some rearrangement of the distribution of electrons in s and d orbitals occurs to utilize the extra stability of a half-filled or filled d orbital.

13. (a) Ti $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^2$
(b) Tc $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^5$
(c) Fe^{3+} $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5$
(d) Br^- $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6$
(e) Se^{2-} $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6$

14. (a) Zr [Kr] $5s^2 4d^2$
(b) Hg [Xe] $6s^2 4f^{14} 5d^{10}$
(c) Ra [Rn] $7s^2$
(d) I^- [Kr] $5s^2 4d^{10} 5p^6$ or [Xe]
(e) U^{6+} [Rn]

15. An f sublevel consists of 7 possible orbitals which can be occupied by a maximum of 14 electrons.

16. (a) Br atom
(b) Ag^+ silver ion
(c) Hf^{4+} hafnium(IV) ion
(d) In indium atom
(e) S^{2-} sulfide ion

17. For an ionic bond to form between two approaching neutral atoms, one must have valence orbitals nearly full of electrons, and the other must have several valence orbitals that are vacant (contain no electrons) or contain very few valence electrons.
18. The primary factor in the packing of ions is the electric charge on the ions. Another factor is the size of the ions.
19. For a hydrogen bond to form between two molecules, one must have at least one nitrogen or oxygen atom in its structure, and the other must have at least one hydrogen atom bonded to a nitrogen or oxygen in its structure.

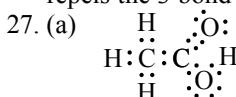
20. (a) : $\ddot{\text{Se}}$. (b) · $\dot{\text{Sn}}$ · (c) · Ca · (d) · $\dot{\text{In}}$ · (e) · Ba ·

21. Elements with electron configurations ending in s^1 are members of the alkali metal family. They are soft shiny metals with high conductivity of heat and electric current, and they are very reactive chemically, forming 1^+ ions.
22. Elements with electron configurations ending in p^6 are members of the noble-gas family. They are all colourless gases that are extremely unreactive chemically.
23. Elements with electron configurations ending in p^5 are members of the halogen family. They are all reactive chemically, forming 1^- ions. Their physical properties at SATP vary markedly with the size of the diatomic molecule formed, so that the two smallest atoms form gaseous elements, the next is liquid, and the larger ones are solid.

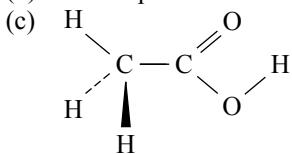
24. VSEPR is an acronym for Valence Shell Electron Pair Repulsion.

25. (a) V-shaped
 (b) tetrahedral
 (c) pyramidal
 (d) V-shaped
 (e) linear

26. NF_3 should have smaller bond angles than SiF_4 because, according to VSEPR theory, in NF_3 the lone pair of electrons repels the 3 bond pairs more than a fourth bond pair would.



(b) The shapes are: first C—tetrahedral; second C—trigonal planar; and the O—V-shaped.



- (d) The C-H bonds are polar, the C-C bond is nonpolar, the C=O double bond is polar, the C-O single bond is polar, and the O-H bond is very polar (forms a hydrogen bond). The bond polarities do not balance each other, so the overall molecule is polar.
- (e) The predominant type of intermolecular bonding between acetic acid molecules is probably hydrogen bonding.
28. Isoelectronic means having the same total number of electrons. London force may be predicted (approximately) for isoelectronic substances, because it is roughly proportional to number of electrons.
29. $\text{H}_2\text{S}_{(g)}$ should have a higher boiling point than $\text{F}_{2(g)}$ because hydrogen sulfide is a polar molecule with dipole–dipole attractions as well as London force between molecules. Fluorine is a nonpolar molecule, with only London force for intermolecular attraction. Because these two molecules are isoelectronic, we assume they have approximately equal London force. VSEPR theory allows prediction of their molecular shape, and electronegativity tables allow prediction of their bond polarities to allow prediction of their molecular polarities.

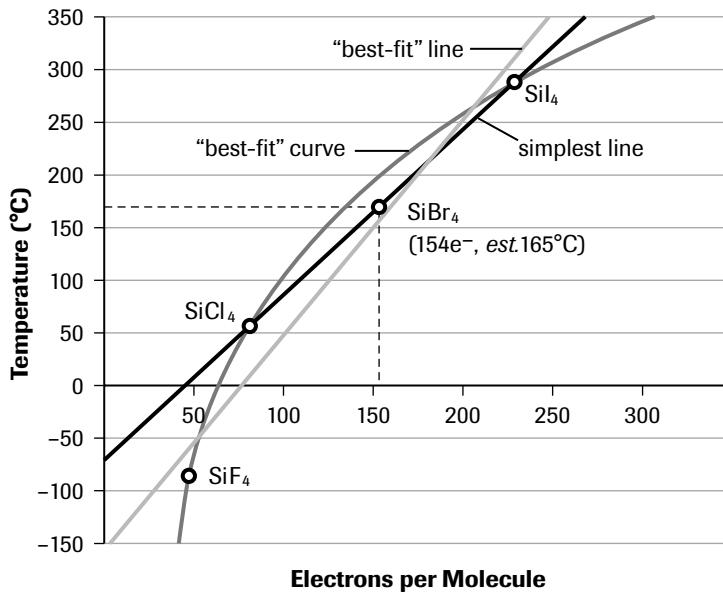
Applying Inquiry Skills

30. (a) Helium and neon can be distinguished by determining their boiling points. Both atoms have only London forces between their molecules. Neon has a significantly greater number of electrons per molecule which means stronger London forces and a higher boiling point.
 (Alternatively, helium and neon can be distinguished by their emission spectra. Neon has more electrons and therefore, many more possible transitions to produce lines in the emission spectrum. The colour of a neon light is also well known (red) and this can be used to distinguish the gases.)
- (b) $\text{MnCl}_{2(s)}$ and $\text{ZnCl}_{2(s)}$ can be distinguished by testing a sample of each solid with a strong magnet. $\text{MnCl}_{2(s)}$ is paramagnetic because the Mn^{2+} ion has 5 unpaired $3d$ electrons. $\text{ZnCl}_{2(s)}$ is not paramagnetic because the Zn^{2+} ion has a $3d^{10}$ outer electron configuration with all electrons paired.
- (c) Zinc and iodine can be distinguished (other than by their appearance) by their electrical conductivity. Zinc is a metal with empty valence orbitals and with some mobile valence electrons. This makes zinc a good electrical

conductor. On the other hand, iodine is molecular with filled valence and bonding orbitals. The electrons are restricted to the atoms or shared between the atoms, and none are free to move between molecules. This makes iodine a nonconductor.

- (d) Calcium carbonate and silicon dioxide may be able to be distinguished based on their melting points. Calcium carbonate is an ionic compound and likely has a relatively high melting point because of the strong attractions of positive and negative ions. However, silicon dioxide is a network covalent crystal whose melting point should be very high because of its network of strong covalent bonds. Once melted, calcium carbonate liquid should conduct electricity because the ions will now be free to move. Molten silicon dioxide will be a molecular liquid with no charged particles to conduct the charge.
31. Standing waves maintain steady characteristics within a moving system, explaining stationary states. Also, standing waves can only exist for whole-number multiples of the wavelength, explaining discrete but different energy states.
32. In de Broglie's theory, the electron is treated as a wave and not a particle. The release of electromagnetic radiation only applies to accelerating electric charges and not to standing or stationary waves.
33. (a) The independent variable is the solid used and the dependent variable is the appearance of a scratch mark on the surface. Some controlled variables are: the nature of the surface (smoothness, cleanliness, flaws, etc.), force applied by one solid on the other, and the angle between the two surfaces.
- (b) Hardness is the property being tested.
- (c) To make a scratch on a surface, some particles must be dislodged from the surface. The nature of the particles determines the type of bonding force(s) present, and the type of force determines how easily particles can be separated from each other.
- (d) A network covalent crystal, like a diamond, would likely not be able to be scratched by any other types of solids.

34. (a) **Analysis**



According to the graph, the value predicted is about 165°C.

(Note: The data points are not in a straight line, and there are only three points. Student predictions will vary depending on how the students choose to interpret the scanty data. If they make the simplest choice and draw a straight line between the SiI₄ and SiCl₄ points, they will get a value close to 165°C. If they try a "best-fit" straight line, their value will be lower than this (and more accurate); and if they try to draw a "best-fit" curve, the value will be higher than this (and less accurate). This provides an excellent specific example of the predicting power of an assumption—that London force is proportional to electron count. It is obviously a good approximation, but only an approximation.)

(b) **Evaluation**

An accepted reference value for the boiling point of SiBr₄ is 153°C. The difference in the predicted and referenced values is (165 – 153)°C = 12°C

$$\% \text{ difference} = \frac{|\text{difference}|}{\text{accepted value}} \times 100\%$$

$$\% \text{ difference} = \frac{12^\circ\text{C}}{153^\circ\text{C}} \times 100\%$$

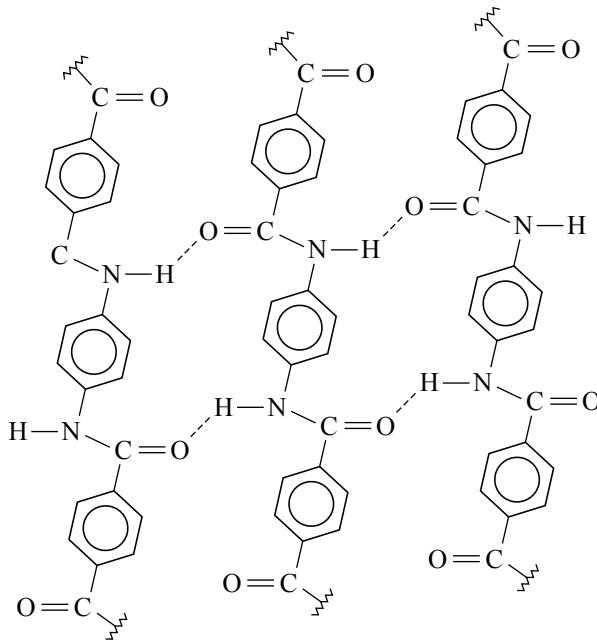
$$\% \text{ difference} = 7.8\%$$

The percentage difference of the prediction from the referenced value is 7.8%, which is fairly, but not highly, accurate. The molecular count method used here gives a fairly good approximate answer.

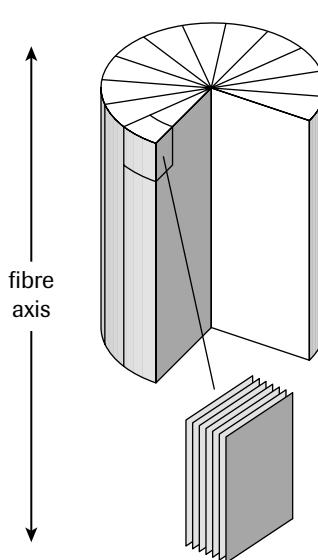
Making Connections

35. An optical pyrometer is also called a wire pyrometer. It has an optical tube, like a telescope, through which the hot steel is viewed. A wire in the field of view appears as a dark line across a bright background. Turning a dial causes a current to flow in the wire which heats and glows proportionally to its temperature. The wire brightness is adjusted to match the background steel, at which point the wire seems to disappear. The dial on the pyrometer is calibrated in temperature units, allowing the temperature of the observed steel to be read directly. Planck's theory holds that the wavelengths of light emitted by hot metals are proportional to the average energy (temperature) of its particles, making this kind of comparison measurement possible.
36. The nitrogen bases bonded to form the DNA double helix structure are: thymine to adenine, which form two hydrogen bonds with each other; and guanine to cytosine, which form three hydrogen bonds with each other.
37. A carbon nanotube may be thought of as a graphite structure (carbon atoms in hexagons) tube with hemispherical ends composed of carbon atoms in pentagons. The tubes have been made up to a millimetre long, and they can theoretically be of any length. The diameter of a nanotube is on the order of 1/50 000 that of a human hair. Most properties of such a structure are unique. Perhaps the property most likely to soon be useful is that the tubes have the strength of diamond along their length. If they can be made long enough, they can be used to make composite material layers much stronger than anything in existence now. They are chemically inert, conduct heat very well, and, depending on their structure, can act as conductors or semiconductors. Samsung uses nanotubes to fire electrons at a flat panel display screen. A nanotube "pen" has been made that deposits atoms the way a pen deposits ink. Nanotubes can be opened and filled with other substances, like tiny test tubes—a property of great interest to biologists. In August 2001, IBM physicists built the world's smallest logic circuit out of a single nanotube. It has been suggested that nanotubes could be used for hydrogen storage for fuel cell power supplies, and that they might form the basic structure of artificial muscles. The field is only a decade old, and it seems likely that applications for nanotubes will multiply with research and improvements in technology the way laser applications did following that discovery.
38. Kevlar is a brand name for a liquid crystal polymer developed by DuPont and originally intended as a superior material to nylon or rayon for fabric plies in automotive tires. In Kevlar, the polymer chain is poly(p-phenylene terephthalamide). (A diagram is shown below.) In Kevlar, the basic chain structure is made up of rigid aromatic rings, rather than a flexible hydrocarbon chain, so a molecule cannot stretch when it is pulled, and cannot be broken by pulling unless the pull is hard enough to break all the bonds at once. This causes Kevlar to have enormous tensile strength when formed into fibres. Cloth made from cross-woven Kevlar fibres is flexible, but cannot be stretched in any direction except by very strong forces. Kevlar is used in "bulletproof" vests, sails, parachutes, climbers' ropes, and as reinforcing layers in high-strength composite materials for a myriad of applications.

Hydrogen-Bonded Sheet



Sheets Stack Together



39. Diamond is shaped and polished with abrasive wheels impregnated with diamond dust. The only material hard enough to shape diamond by grinding is diamond itself. Large diamonds can be “cut” by skilled technicians who actually break the crystal structure by applying a sharp hard force in precisely the right spot. This is also called cleaving the structure, along a surface called a cleavage plane—usually established by the presence of impurities in the crystal which make it slightly weaker in specific places and along specific directions.

Extensions

40. In a thermocouple, two different metals have surfaces in contact in two places. This design may be as simple as two different metal wires of equal length, joined only at their ends. When one of the contact surfaces (ends) is heated, the attraction of the metal atoms for electrons is changed, but not by the same amount for each metal. This difference is partly due to the difference in energy levels for “excited” states of the different atoms. The net effect is that electrons will tend to flow from one metal to the other across the hot junction, continuing around the circuit to create an electric current. This current is proportional to the temperature difference between the two junctions. Measuring the current allows the temperature to be determined, and if metals with very high melting points are used, very high temperatures may be accurately measured in this way.
41. Light-emitting diodes are *p-n* semiconductor junctions where a potential difference causes electrons to move from the *n*-type semiconductor to the *p*-type semiconductor. Electron energies are raised in the *n*-type substance until the excited electrons become “free” and are able to jump to the *p*-type substance where they fall to a valence (ground-state) level of an atom. This drop in energy is evident as an emitted photon of light, and since the energy-level drop is fixed, so is the wavelength of light emitted. The shorter the wavelength, the greater the voltage drop required — an LED producing green light must operate at a higher voltage than one producing red light. Blue light (the shortest wavelengths visible) is very difficult to produce this way, because the high energy drop means the materials have to be nearly perfect insulators. Production of white light for displays requires the mixing of red, green, and blue light. Therefore, blue LED research is an area of serious interest.
42. Gold films are typically gold in colour by reflected light, even when extremely thin. Gold reflects infrared, ultraviolet, and visible light very well, but reflects especially well in the middle of the visible spectrum. This gives the characteristic golden hue. Gold can be made into extraordinarily thin sheets (in this form, it is usually called gold “leaf”) which will adhere to other materials (a process called “gilding”) causing the surface to appear golden. Gold leaf can be made so thin that 1 troy ounce (about 31 g) will cover 2 m² at a thickness of 2.5 µm. If the gold layer is formed by condensing gold vapour in a very thin layer on a cool transparent surface like glass, a significant amount of light will be transmitted. The amount of light transmitted is proportional to the thickness of the metal layer created. The transmitted light will normally appear dark green because of the subtraction of yellow from the visible spectrum. The material coating the sunshield on NASA astronauts’ EVA suits incorporates a thin gold film which is evident in any colour photograph of an astronaut on a “space walk.” Sunglasses with mirror surfaces are now made in many colours by depositing very thin films of various metals on their surfaces.

$$43. c = 3.00 \times 10^8 \text{ m/s}$$

$$\lambda_L = 700 \text{ nm} = 700 \times 10^{-9} \text{ m} \quad (\text{longest visible})$$

$$\lambda_S = 400 \text{ nm} = 400 \times 10^{-9} \text{ m} \quad (\text{shortest visible})$$

$$c = f\lambda$$

$$f = \frac{c}{\lambda}$$

$$f_L = \frac{3.00 \times 10^8 \text{ m}}{\frac{1 \text{ s}}{700 \times 10^{-9} \text{ m}}}$$

$$f_L = \frac{4.29 \times 10^{14}}{1 \text{ s}} = 4.29 \times 10^{14} \text{ Hz}$$

$$f_S = \frac{\frac{3.00 \times 10^8 \text{ m}}{1 \text{ s}}}{400 \times 10^{-9} \text{ m}}$$

$$f_S = \frac{7.50 \times 10^{14}}{1 \text{ s}} = 7.50 \times 10^{14} \text{ Hz}$$

The frequency of the longest visible wavelength of light is 4.29×10^{14} Hz, and of the shortest visible wavelength of light is 7.50×10^{14} Hz.

44. $h = 6.63 \times 10^{-34} \text{ J} \cdot \text{s}$

$$f_H = \frac{7.50 \times 10^{14}}{1 \text{ s}} = 7.50 \times 10^{14} \text{ Hz} \quad (\text{highest visible})$$

$$f_L = \frac{4.29 \times 10^{14}}{1 \text{ s}} = 4.29 \times 10^{14} \text{ Hz} \quad (\text{lowest visible})$$

$$\Delta E = hf$$

$$\Delta E_H = \frac{6.63 \times 10^{-34} \text{ J}}{1 \text{ Hz}} \times 7.50 \times 10^{14} \text{ Hz}$$

$$\Delta E_H = 4.97 \times 10^{-19} \text{ J}$$

$$\Delta E_L = \frac{6.63 \times 10^{-34} \text{ J}}{1 \text{ Hz}} \times 4.29 \times 10^{14} \text{ Hz}$$

$$\Delta E_L = 2.84 \times 10^{-19} \text{ J}$$

The energy of the highest-frequency visible photon is $4.97 \times 10^{-19} \text{ J}$ and the energy of the lowest-frequency visible photon is $2.84 \times 10^{-19} \text{ J}$.

45. The shorter the wavelength, the higher the frequency, and the higher the photon energy, for electromagnetic radiation. Because X rays have very short wavelengths and very high frequency, their photons have very high energies which can penetrate and damage living cells. Radio waves have extremely long wavelengths, and correspondingly extremely low (and harmless) photon energies.

46. $\Delta E = hf$

$$c = f\lambda$$

$$f = \frac{c}{\lambda}$$

$$\Delta E = \frac{hc}{\lambda}$$

$$\Delta E = \frac{6.63 \times 10^{-34} \text{ J} \cdot \text{s} \times 3.00 \times 10^8 \text{ m/s}}{300 \times 10^{-9} \text{ m}}$$

$$\Delta E = 6.63 \times 10^{-19} \text{ J}$$

The energy of a photon of 300 nm light is $6.63 \times 10^{-19} \text{ J}$.

The energy of a photon of 600 nm (orange) light is half the preceding value, since photon energy is inversely proportional to wavelength. Therefore, $6.63 \times 10^{-19} \text{ J} \div 2 = 3.32 \times 10^{-19} \text{ J}$.

The energy of a photon of 600 nm light is $3.32 \times 10^{-19} \text{ J}$.

47. (a) Fluorescein absorbs (and emits) green photons. Red photons are lower in energy and not high enough to be absorbed, so no light should be emitted.

(b) Ultraviolet light photons are very high energy and they should be absorbed. Green photons should be emitted.

(c) Infrared light photons are very low energy and they should not be absorbed. No green photons should be emitted.

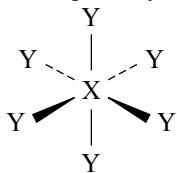
(d) Blue light photons are higher energy than green and they should be absorbed. Green photons should be emitted.

48. According to the stability “subrule,” molybdenum should have a configuration of $[\text{Kr}] 5s^1 4d^5$ to half-fill its d level, and silver should have a configuration of $[\text{Kr}] 5s^1 4d^{10}$ to completely fill its d level.

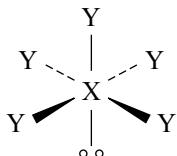
49. In ferromagnetic elements, a quantum effect enables the atoms to align the magnetic dipoles of neighbouring atoms. This creates volumes of very large numbers of atoms with aligned dipoles that scientists call *domains*. Domains form metallic crystals that act like tiny magnets within the solid material, and if these domains are mostly aligned with each other by an external magnetic field, the solid will show the tendencies and properties of a “permanent” magnet. The other two ferromagnetic elements are gadolinium and dysprosium.

Strong heating increases atomic motion and causes domains to become unaligned. This causes their magnetic dipoles to partially cancel, and weakens the overall magnetism of the solid magnet.

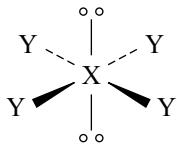
50.



6 bond pairs, 0 lone pairs
octahedral structure



5 bond pairs, 1 lone pair
square pyramid structure



4 bond pairs, 2 lone pairs
square planar structure

Molecules of uranium hexafluoride, $\text{UF}_{6(\text{g})}$, should be octahedral, with six bond pairs and no lone pairs.

Unit 3 Energy Changes and Rates of Reaction

ARE YOU READY?

(Page 294)

Knowledge and Understanding

1. (a) balloon: chemical potential energy
(b) dragster: chemical potential energy
(c) solar panel: solar or light energy
(d) nuclear power station: nuclear potential energy
2. Chemical energy is energy stored in molecules.
3. (a) An exothermic process, such as the burning of wood, releases energy to the surroundings. An endothermic process, such as the melting of ice, absorbs energy from the surroundings. The difference is in the direction of heat transfer.
(b) (i) and (iii) are exothermic; (ii) and (iv) are endothermic.
4. (a) Heat the acid, use more concentrated acid, grind the chalk into finer particles, or add a catalyst.
5. (a) q is heat transferred, m is mass of water, c is the specific heat capacity, and ΔT is temperature change.
(b) Units are joules or calories for q , grams or kilograms for m , joules per gram $^{\circ}\text{C}$ for c , and $^{\circ}\text{C}$ for ΔT .
(c)
$$q = mc\Delta T \\ = (200.0 \text{ g})(4.18 \text{ J/g}^{\circ}\text{C})(45 - 30^{\circ}\text{C}) \\ q = 12\,540 \text{ J or } 12 \text{ kJ}$$

Inquiry and Communication

6.
$$\begin{aligned} \text{CH}_{4(\text{g})} + 2 \text{O}_{2(\text{g})} &\rightarrow \text{CO}_{2(\text{g})} + 2 \text{H}_{2\text{O}(\text{g})} + 890 \text{ kJ} \\ 2 \text{C}_{2\text{H}_{6(\text{g})}} + 7 \text{O}_{2(\text{g})} &\rightarrow 4 \text{CO}_{2(\text{g})} + 6 \text{H}_{2\text{O}(\text{g})} + 3120 \text{ kJ} \\ \text{C}_3\text{H}_{8(\text{g})} + 5 \text{O}_{2(\text{g})} &\rightarrow 3 \text{CO}_{2(\text{g})} + 4 \text{H}_{2\text{O}(\text{g})} + 2220 \text{ kJ} \\ 2 \text{C}_4\text{H}_{10(\text{g})} + 13 \text{O}_{2(\text{g})} &\rightarrow 8 \text{CO}_{2(\text{g})} + 10 \text{H}_{2\text{O}(\text{g})} + 5716 \text{ kJ} \end{aligned}$$

(Note that the heats of combustion are expressed as absolute values, and that the heat of reaction is doubled if 2 mol of fuel are burned.)

7.
$$\begin{aligned} \text{CH}_{4(\text{g})} + 2 \text{O}_{2(\text{g})} &\rightarrow \text{CO}_{2(\text{g})} + 2 \text{H}_{2\text{O}(\text{g})} + 890 \text{ kJ} \\ \text{C}_2\text{H}_{6(\text{g})} + 7/2 \text{O}_{2(\text{g})} &\rightarrow 2 \text{CO}_{2(\text{g})} + 3 \text{H}_{2\text{O}(\text{g})} + 1560 \text{ kJ} \\ \text{C}_3\text{H}_{8(\text{g})} + 5 \text{O}_{2(\text{g})} &\rightarrow 3 \text{CO}_{2(\text{g})} + 4 \text{H}_{2\text{O}(\text{g})} + 2220 \text{ kJ} \\ \text{C}_4\text{H}_{10(\text{g})} + 13/2 \text{O}_{2(\text{g})} &\rightarrow 4 \text{CO}_{2(\text{g})} + 5 \text{H}_{2\text{O}(\text{g})} + 2858 \text{ kJ} \end{aligned}$$

Mathematical Skills

8. (a) $2 \text{NaHCO}_{3(\text{s})} + \text{H}_2\text{SO}_{4(\text{aq})} \rightarrow \text{Na}_2\text{SO}_{4(\text{aq})} + 2 \text{H}_2\text{O}_{(\text{l})} + 2 \text{CO}_{2(\text{g})}$
- (b) rate, $r = \frac{\Delta n_{\text{NaHCO}_3}}{\Delta T}$
$$= 10 \text{ mol}/4 \text{ min}$$

$$r = 2.5 \text{ mol NaHCO}_3/\text{min}$$
- (c) 10 mol
- (d) rate = 2.5 mol CO₂/min

Technical Skills and Safety

9. Possible answers include the following:

- Know the location of the fire extinguisher, fire blanket, and emergency gas shut-off valve.
- Tie back long hair.
- Remove or secure loose clothing.
- Know about the “drop and roll” technique if clothing catches fire.

Making Connections

10. Use smaller pieces of wood; shield the fire from wind to keep the temperature high at the beginning; blow on the fire to increase concentration of oxygen; use dry wood or bark that burns more easily.

CHAPTER 5 THERMOCHEMISTRY

Reflect on Your Learning

(Page 296)

1. Absorbing energy: ice melting, water evaporating, photosynthesis.
Releasing energy: water vapour condensing, respiration, combustion of gasoline.
2. Nuclear power plants, fossil fuel-burning power plants, hydroelectric power (largely from Niagara), solar power.
3. Both technologies drive turbines to generate electricity, but one uses falling water to drive the turbine and the other uses nuclear energy to create pressurized steam to drive the turbine.

Try This Activity: Burning Food

(Page 297)

- (a) Use $q = mc\Delta T$ with student data.
- (b) The heat released equalled the difference in potential energy of the reactants and products.
- (c) Divide the heat by the mass of the nut.
- (d) The reactants would be the same but the nut might not be completely digested, so there would be products other than carbon dioxide and water. The energy might be stored rather than released to the surroundings as heat. The process would be more efficient in terms of production of energy in useful forms, rather than heat.
- (e) Much heat is lost to the surroundings, apart from the water in the can. Insulating the apparatus would improve results.

5.1 CHANGES IN MATTER AND ENERGY

PRACTICE

(Page 300)

Understanding Concepts

1. (a) chemical (new products: water and carbon dioxide)
(b) physical (no new products)
(c) chemical (new products: water and carbon dioxide)
(d) physical (no new products)
(e) chemical (new products: hydrogen gas and zinc chloride)
(f) physical (no new products)

2.

System	Surroundings
(a) gas and oxygen	air and metal parts
(b) ice	hand
(c) gas and oxygen	air and metal parts
(d) wax	stove
(e) zinc and acid	beaker and water solvent
(f) ice	body part

3. All of these systems may be regarded as open because energy and/or matter may escape from the system, often in the form of gases. However, (a) may be considered a closed system for the instant at which the air-fuel mixture ignites.
4. The thimbleful has greater average thermal energy per molecule, but the pool has greater total thermal energy.
5. (a) exothermic
(b) exothermic
(c) endothermic

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3. All of these systems may be regarded as open because energy and/or matter may escape from the system, often in the form of gases. However, (a) may be considered a closed system for the instant at which the air-fuel mixture ignites.
4. The thimbleful has greater average thermal energy per molecule, but the pool has greater total thermal energy.
5. (a) exothermic
(b) exothermic
(c) endothermic

Making Connections

6. (a) Answers could include biological examples such as:
- cellular respiration (chemical, exothermic, open);
 - combustion of fuel examples such as burning gasoline (chemical, exothermic, open);
 - change of state examples such as boiling water (physical, endothermic, open) or condensation (physical, exothermic, open);
 - household processes such as the use of drain cleaner (physical, exothermic, open).
- (b) Exothermic reactions are more common.
7. (a) 1 calorie = 4.18 J; 1 Calorie = 1000 calories = 4.18 kJ.
(b) The reaction is controlled oxidation of food: a “slow burn” that releases energy.
(c) Bomb calorimetry is used.

PRACTICE

(Page 302)

Understanding Concepts

8. Aluminum has the lowest specific heat capacity, which implies that it requires the least amount of heat to change temperature, and will undergo the greatest temperature change.

9. $q = mc\Delta T$

$$= 1.50 \text{ kg} \times 4.18 \text{ kJ/(kg}\cdot^\circ\text{C)} \times (98.7 - 18.0)^\circ\text{C}$$

$$q = 506 \text{ kJ}$$

10. $m = \frac{q}{(c\Delta T)}$

$$= 80\,000 \text{ J}/(4.18 \text{ kJ/(kg}\cdot^\circ\text{C)} \times 50^\circ\text{C})$$

$$m = 383 \text{ g}$$

11. $\Delta T = \frac{q}{(mc)}$

$$= 250\,000 \text{ J}/(4000 \text{ g} \times 3.5 \text{ J/(g}\cdot^\circ\text{C)})$$

$$\Delta T = 18^\circ\text{C}$$

12. (a) $q = mc\Delta T$

$$= 100 \text{ kg} \times 4.18 \text{ kJ/(kg}\cdot^\circ\text{C)} \times (45 - 10)^\circ\text{C}$$

$$q = 1.5 \times 10^4 \text{ kJ, or } 15 \text{ MJ}$$

(b) money saved = $14.6 \text{ MJ} \times 0.351\text{¢}/\text{MJ} \times 1500$

$$= 7.7 \times 10^3\text{¢, or } \$77$$

13. (a) $q = mc\Delta T$

$$= 100 \text{ kg} \times 4.18 \text{ kJ/(kg}\cdot^\circ\text{C)} \times (75 - 45)^\circ\text{C}$$

$$q = 1.0 \times 10^4 \text{ kJ, or } 10 \text{ MJ}$$

(b) money saved = $10 \text{ MJ} \times 0.351\text{¢}/\text{MJ} \times 1500$

$$= 5.5 \times 10^3\text{¢, or } \$55$$

PRACTICE

(Page 304)

Understanding Concepts

14. When a change occurs in a system, the potential energy change (ΔH) of the system is numerically equal to the change in thermal kinetic energy (q) of the surroundings.
15. Chemical changes have generally greater enthalpy changes than physical changes; nuclear changes have much greater enthalpy changes than chemical changes.

Applying Inquiry Skills

16. Experimental Design

- A measured mass of the metal is added to a measured mass of dilute acid, and the temperature change in the solution is determined.
- The heat gained by the solution is calculated using $q = mc\Delta T$.
- The heat released per gram is calculated by dividing the heat by the mass of metal, and the result is compared to the three accepted values.

SECTION 5.1 QUESTIONS

(Page 305)

Understanding Concepts

- Changes of state from solid to liquid, liquid to gas, and solid to gas are endothermic; changes of state from gas to liquid, liquid to solid, and gas to solid are exothermic.
- mass, temperature change, specific heat capacity
- (a) chemical (new products; rearrangement of atoms to new molecules)
(b) physical (no new product; same molecules)
(c) nuclear (uranium decays to form new atoms)
-
- (a) open
(b) open (because there is no container keeping the water vapour in contact with the liquid water)
(c) isolated (although open if one considers the waste heat produced)
- Energies per mol for physical, chemical, and nuclear changes are on the order of 101, 103, and 1011 kJ/mol, respectively.

Making Connections

- See the Nelson *Chemistry 12* web site for possible useful sources of information. Bomb calorimeters are used to determine the energy content of foods, fuels, and even organisms in ecological food chains.
- See the Nelson *Chemistry 12* web site for possible useful sources of information. Cold packs typically contain ammonium salts which, when mixed with water, absorb energy. Some hot packs contain iron filings which slowly oxidize in air and produce heat.

5.2 MOLAR ENTHALPIES

PRACTICE

(Page 308)

Understanding Concepts

$$1. \text{ amount of water, } n = 100.0 \text{ g} \times \frac{1 \text{ mol}}{18.0 \text{ g}}$$
$$n = 5.56 \text{ mol}$$

$$\Delta H = n\Delta H_{\text{vap}}$$
$$= 5.56 \text{ mol} \times \frac{40.8 \text{ kJ}}{1 \text{ mol}}$$
$$\Delta H = 227 \text{ kJ}$$

Applying Inquiry Skills

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- A measured mass of the metal is added to a measured mass of dilute acid, and the temperature change in the solution is determined.
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2. molar mass of Freon, $M = 120.9 \text{ g/mol}$

$$n_{\text{Freon}} = 500 \text{ g} \times \frac{1 \text{ mol}}{120.9 \text{ g}}$$

$$n_{\text{Freon}} = 4.14 \text{ mol}$$

$$\begin{aligned}\Delta H &= n\Delta H_{\text{vap}} \\ &= 4.14 \text{ mol} \times 34.99 \text{ kJ/mol}\end{aligned}$$

$$\Delta H = 145 \text{ kJ}$$

3. amount of water, $n = 1.00 \times 10^6 \text{ g} \times \frac{1 \text{ mol}}{18.0 \text{ g}}$

$$n = 5.56 \times 10^4 \text{ mol}$$

$$\begin{aligned}\Delta H &= n\Delta H_{\text{vap}} \\ &= 5.56 \times 10^4 \text{ mol} \times 6.03 \text{ kJ/mol} \\ \Delta H &= 3.35 \times 10^5 \text{ kJ}\end{aligned}$$

PRACTICE

(Page 310)

Understanding Concepts

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

$$= 150 \text{ g} \times 4.18 \text{ J/g}^\circ\text{C} \times (20.4 - 16.7)^\circ\text{C}$$

$$q_{\text{water}} = 2320 \text{ J, or } 2.32 \text{ kJ}$$

molar mass of urea, $M = 60.0 \text{ g/mol}$

$$n_{\text{urea}} = 10.0 \text{ g} \times \frac{1 \text{ mol}}{60 \text{ g}}$$

$$n_{\text{urea}} = 0.167 \text{ mol}$$

$n\Delta H_{\text{solution}} = q_{\text{water}}$

$$\begin{aligned}\Delta H_{\text{solution}} &= \frac{q_{\text{water}}}{n_{\text{urea}}} \\ &= \frac{2.32 \text{ kJ}}{0.167 \text{ mol}}\end{aligned}$$

$$\Delta H_{\text{solution}} = 13.9 \text{ kJ/mol}$$

Because the reaction is endothermic, $\Delta H_{\text{solution}}$ is +13.9 kJ/mol.

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

$$= 50.0 \text{ g} \times 4.18 \text{ J/g}^\circ\text{C} \times (27.8 - 24.0)^\circ\text{C}$$

$$q_{\text{water}} = 794 \text{ J}$$

molar mass of gallium, $M = 69.72 \text{ g/mol}$

$$n_{\text{gallium}} = 10.0 \text{ g} \times 1 \text{ mol} / 69.72 \text{ g}$$

$$n_{\text{gallium}} = 0.143 \text{ mol}$$

$n\Delta H_{\text{solution}} = q_{\text{water}}$

$$\begin{aligned}\Delta H_{\text{solution}} &= \frac{q_{\text{water}}}{n_{\text{gallium}}} \\ &= \frac{794 \text{ J}}{0.143 \text{ mol}}\end{aligned}$$

$$\Delta H_{\text{solution}} = 5.54 \times 10^3 \text{ J/mol or } 5.54 \text{ kJ/mol}$$

Because the reaction is exothermic, $\Delta H_{\text{solution}}$ is -5.54 kJ/mol.

PRACTICE

(Page 311)

Understanding Concepts

6. No heat is transferred to the outside environment; negligible heat is transferred to calorimeter materials; dilute aqueous solutions have the same specific heat capacity as water.

7. (a) $\Delta H_{\text{vaporization}}$

(b) $\Delta H_{\text{sublimation}}$

(c) $\Delta H_{\text{solution}}$

(d) $\Delta H_{\text{combustion}}$

(e) $\Delta H_{\text{neutralization}}$

Applying Inquiry Skills

8. Certainty is limited by the balance used to measure masses of reactants and solutions, graduated cylinders or other containers used to measure volumes of water and solutions, and thermometers used to measure temperature.

9. (a) $q_{\text{water}} = mc\Delta T$

$$= 500 \text{ g} \times 4.18 \text{ J/g}^{\circ}\text{C} \times (21.8 - 19.2)^{\circ}\text{C}$$

$$q_{\text{water}} = 5434 \text{ J, or } 5.43 \text{ kJ}$$

$$\text{amount of HCl}_{(\text{aq})}, n = MV$$

$$= 11.6 \text{ mol/L} \times 0.0431 \text{ L}$$

$$n = 0.500 \text{ mol}$$

$$n\Delta H_{\text{dilution}} = q_{\text{water}}$$

$$\Delta H_{\text{dilution}} = \frac{q_{\text{water}}}{n}$$

$$= \frac{5.43 \text{ kJ}}{0.500 \text{ mol}}$$

$$\Delta H_{\text{dilution}} = 10.9 \text{ kJ/mol}$$

Because the reaction is exothermic, $\Delta H_{\text{dilution}}$ is -10.9 kJ/mol .

(b) The observed temperature increase would be too small, making the calculated ΔH too small.

(c) The large amount of heat can cause the water to boil rapidly and spatter the acid solution about.

10. Analysis

Assume 2.0 L of solution is 2000 g water.

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

$$= 2000 \text{ g} \times 4.18 \text{ J/g}^{\circ}\text{C} \times (29.1 - 26.0)^{\circ}\text{C}$$

$$q_{\text{water}} = 25.9 \text{ kJ}$$

$$\text{amount of Ba(NO}_3)_2{}_{(\text{aq})}, n = 261 \text{ g} \times \frac{1 \text{ mol}}{261.3 \text{ g}}$$

$$n = 1.00 \text{ mol}$$

$$n\Delta H_{\text{reaction}} = q_{\text{water}}$$

$$\Delta H_{\text{reaction}} = \frac{q_{\text{water}}}{n}$$

$$= \frac{25.9 \text{ kJ}}{1.00 \text{ mol}}$$

$$\Delta H_{\text{reaction}} = 25.9 \text{ kJ/mol Ba(NO}_3)_2{}_{(\text{aq})}$$

Because the reaction is exothermic, $\Delta H_{\text{reaction}}$ is -26 kJ/mol .

SECTION 5.2 QUESTIONS

(Page 312)

Understanding Concepts

$$1. (a) q = n\Delta H_{\text{comb}}$$
$$= 5.0 \text{ mol} \times 1.56 \text{ MJ/mol}$$

$$q = 7.8 \text{ MJ}$$

$$(b) \text{ molar mass of ethane, } (\text{C}_2\text{H}_6) = 30.0 \text{ g/mol}$$

$$q = n\Delta H_{\text{comb}}^{\circ}$$
$$= 40.0 \text{ g} \times (1 \text{ mol}/30.0 \text{ g}) \times (1.56 \text{ MJ/mol})$$
$$q = 2.08 \text{ MJ}$$

$$2. q_{\text{water}} = n\Delta H_{\text{solution}}^{\circ}$$
$$= 40.0 \text{ g NH}_4\text{Cl} \times 1 \text{ mol}/53.5 \text{ g} \times 14.8 \text{ kJ/mol}$$

$$q_{\text{water}} = 11.1 \text{ kJ}$$

$$\Delta T = \frac{q}{mc}$$
$$= \frac{11.100}{(200.0 \times 4.18)}$$

$$\Delta T = 13.2^\circ\text{C}$$

Since the dissolving is endothermic, the temperature of the water will fall.

$$T_f = T_i - \Delta T$$
$$= 25 - 13$$

$$T_f = 12^\circ\text{C}$$

$$3. q_{\text{water}} = mc\Delta T$$
$$= 500.0 \text{ g} \times 4.18 \text{ J/g}^\circ\text{C} \times (55.0 - 20.0)^\circ\text{C}$$

$$q_{\text{water}} = 71750 \text{ J} = 0.0718 \text{ MJ}$$

$$\text{molar mass of decane, } M = 142 \text{ g}$$

$$n\Delta H_{\text{combustion}} = q_{\text{water}}$$
$$\text{amount of decane, } n = \frac{q}{\Delta H_{\text{combustion}}}$$
$$= \frac{0.0718 \text{ MJ}}{6.78 \text{ MJ/mol}}$$
$$n = 0.0106 \text{ mol}$$

$$\text{mass decane, } m = 0.0106 \text{ mol} \times 142 \text{ g/mol}$$

$$m = 1.50 \text{ g}$$

$$4. \text{ molar mass of salt, } M = 322.1 \text{ g/mol}$$

$$\text{amount of salt, } n = 1000 \text{ g} \times (1 \text{ mol}/322.1 \text{ g})$$

$$n = 3.10 \text{ mol}$$

$$\Delta H = n\Delta H_{\text{solid}}$$
$$= 3.10 \text{ mol} \times 78.0 \text{ kJ/1 mol}$$

$$\Delta H = 242 \text{ kJ}$$

Applying Inquiry Skills

5. Assume that 200 mL of solution is 200 g water.

$$q_{\text{water}} = mc\Delta T$$
$$= 200 \text{ g} \times 4.18 \text{ J/g}^\circ\text{C} \times (28.1 - 21.0)^\circ\text{C}$$

$$q_{\text{water}} = 5.94 \text{ kJ}$$

amount of KOH = n

$$= 5.2 \text{ g} \times 1 \text{ mol}/56.1 \text{ g}$$

$$n = 0.0927 \text{ mol}$$

$$n\Delta H_{\text{reaction}} = q_{\text{water}}$$

$$\Delta H_{\text{reaction}} = \frac{q_{\text{water}}}{n}$$
$$= \frac{5.94 \text{ kJ}}{0.0927 \text{ mol}}$$

$$\Delta H_{\text{reaction}} = 64 \text{ kJ/mol Ba(NO}_3)_2$$

Because the reaction is exothermic, $\Delta H_{\text{reaction}}$ is -64 kJ/mol .

6. Answers will vary, but the student could use a polystyrene (Styrofoam) coffee cup calorimeter and thermometer to investigate temperature changes that occurred when the dextrose tablets were added to water. A mortar and pestle might be used to simulate the grinding process that occurs in chewing. Ambitious students might even investigate whether there was any effect of amylase (found in saliva) on the process.

Making Connections

7. See the Nelson *Chemistry 12* web site for possible useful sources of information. In general, the propane is used to vaporize and separate the components of an aqueous ammonia mixture. The ammonia gas then goes through cycles of condensation (outside the compartment, releasing heat to the air) and evaporation inside the compartment (absorbing heat from food).

5.3 REPRESENTING ENTHALPY CHANGES

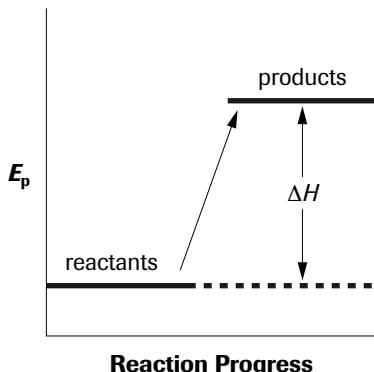
PRACTICE

(Page 319)

Understanding Concepts

1. (a) $2 \text{ C}_{(\text{s})} + \text{H}_{2(\text{g})} + 228 \text{ kJ} \rightarrow \text{C}_2\text{H}_{2(\text{g})}$
- $$2 \text{ C}_{(\text{s})} + \text{H}_{2(\text{g})} \rightarrow \text{C}_2\text{H}_{2(\text{g})} \quad \Delta H = +228 \text{ kJ}$$
- $$\Delta H_f^\circ = +228 \text{ kJ/mol acetylene}$$

Endothermic Reaction



Applying Inquiry Skills

5. Assume that 200 mL of solution is 200 g water.

$$q_{\text{water}} = mc\Delta T$$
$$= 200 \text{ g} \times 4.18 \text{ J/g}^\circ\text{C} \times (28.1 - 21.0)^\circ\text{C}$$

$$q_{\text{water}} = 5.94 \text{ kJ}$$

amount of KOH = n

$$= 5.2 \text{ g} \times 1 \text{ mol}/56.1 \text{ g}$$

$$n = 0.0927 \text{ mol}$$

$$n\Delta H_{\text{reaction}} = q_{\text{water}}$$

$$\Delta H_{\text{reaction}} = \frac{q_{\text{water}}}{n}$$
$$= \frac{5.94 \text{ kJ}}{0.0927 \text{ mol}}$$

$$\Delta H_{\text{reaction}} = 64 \text{ kJ/mol Ba(NO}_3)_2$$

Because the reaction is exothermic, $\Delta H_{\text{reaction}}$ is -64 kJ/mol .

6. Answers will vary, but the student could use a polystyrene (Styrofoam) coffee cup calorimeter and thermometer to investigate temperature changes that occurred when the dextrose tablets were added to water. A mortar and pestle might be used to simulate the grinding process that occurs in chewing. Ambitious students might even investigate whether there was any effect of amylase (found in saliva) on the process.

Making Connections

7. See the Nelson *Chemistry 12* web site for possible useful sources of information. In general, the propane is used to vaporize and separate the components of an aqueous ammonia mixture. The ammonia gas then goes through cycles of condensation (outside the compartment, releasing heat to the air) and evaporation inside the compartment (absorbing heat from food).

5.3 REPRESENTING ENTHALPY CHANGES

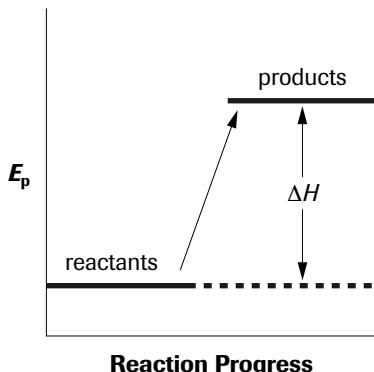
PRACTICE

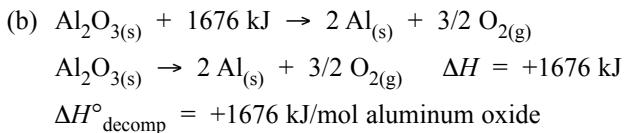
(Page 319)

Understanding Concepts

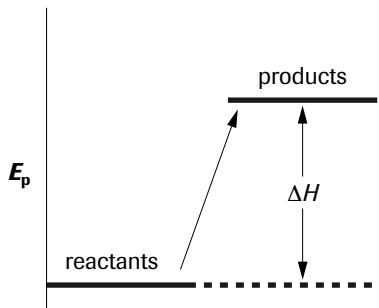
1. (a) $2 \text{ C}_{(\text{s})} + \text{H}_{2(\text{g})} + 228 \text{ kJ} \rightarrow \text{C}_2\text{H}_{2(\text{g})}$
- $$2 \text{ C}_{(\text{s})} + \text{H}_{2(\text{g})} \rightarrow \text{C}_2\text{H}_{2(\text{g})} \quad \Delta H = +228 \text{ kJ}$$
- $$\Delta H_f^\circ = +228 \text{ kJ/mol acetylene}$$

Endothermic Reaction

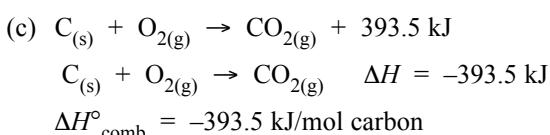




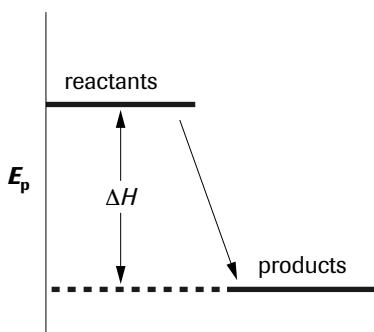
Endothermic Reaction



Reaction Progress



Exothermic Reaction



Reaction Progress

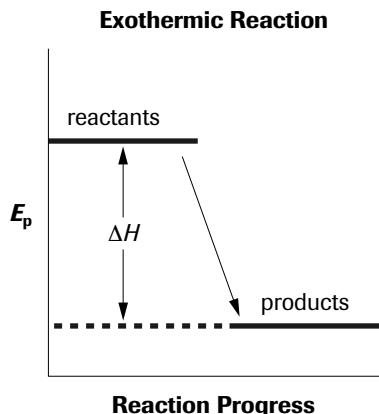
2. (a) $\Delta H_{\text{comb}} = -241.8 \text{ kJ/mol H}_2$
(b) $\Delta H_{\text{comb}} = -283.6 \text{ kJ/mol NH}_3$
(c) $\Delta H_{\text{comb}} = +81.6 \text{ kJ/mol N}_2$
(d) $\Delta H_{\text{comb}} = -372.8 \text{ kJ/mol Fe}$
3. (a) $\Delta H = -114 \text{ kJ}$
(b) $\text{H}_2\text{SO}_{4(\text{aq})} + 2 \text{NaOH}_{(\text{aq})} \rightarrow \text{Na}_2\text{SO}_{4(\text{aq})} + 2 \text{H}_2\text{O}_{(\text{l})} \quad \Delta H = -114 \text{ kJ}$
(c) $\Delta H_{\text{neut}} = -114 \text{ kJ/mol H}_2\text{SO}_4$
(d) $\Delta H_{\text{neut}} = -57 \text{ kJ/mol NaOH}$
4. (a) $\text{H}_{2(\text{g})} + 1/2 \text{O}_{2(\text{g})} \rightarrow \text{H}_2\text{O}_{(\text{g})} \quad \Delta H = -241.8 \text{ kJ}$
 $\text{H}_2\text{O}_{(\text{g})} \rightarrow \text{H}_{2(\text{g})} + 1/2 \text{O}_{2(\text{g})} \quad \Delta H = +241.8 \text{ kJ}$
(b) Such equations have the same enthalpy change with a different sign.
5. (a) The reaction is exothermic because potential energy is converted to heat lost to the surroundings.
(b) The reaction is endothermic because heat absorbed from the surroundings is converted to potential energy.

SECTION 5.3 QUESTIONS

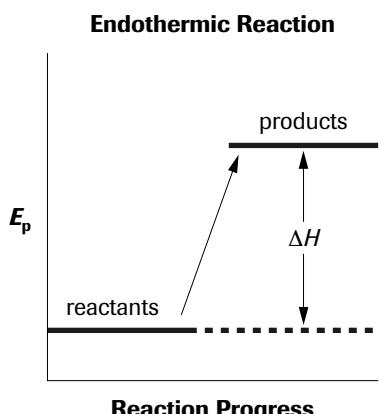
(Page 320)

Understanding Concepts

1. (a) Since the reaction is exothermic, the PE diagram will resemble this. Reactants are octane and oxygen; the products are carbon dioxide and water.



- (b) Since the reaction is endothermic, the PE diagram will resemble this. Reactants are boron and hydrogen; the product is diborane.



2. (a) $\text{Mg}_{(s)} + \text{O}_{2(g)} + \text{H}_{2(g)} \rightarrow \text{Mg(OH)}_{(s)}$ $\Delta H = -925 \text{ kJ}$
(b) $\text{C}_5\text{H}_{12(g)} + 8 \text{O}_{2(g)} \rightarrow 5 \text{CO}_{2(g)} + 6 \text{H}_2\text{O}_{(g)}$ $\Delta H^\circ = -2018 \text{ kJ}$
(c) $\text{NiO}_{(s)} \rightarrow \text{Ni}_{(s)} + 1/2 \text{O}_{2(g)}$ $\Delta H^\circ = 240 \text{ kJ}$
3. (a) $\text{C}_4\text{H}_{10(g)} + 13/2 \text{O}_{2(g)} \rightarrow 4 \text{CO}_{2(g)} + 5 \text{H}_2\text{O}_{(g)} + 2.87 \text{ MJ}$
(b) $\text{C}_{(\text{graphite})} + 2 \text{ kJ} \rightarrow \text{C}_{(\text{diamond})}$
(c) $\text{C}_2\text{H}_6\text{O}_{(l)} + 3 \text{O}_{2(g)} \rightarrow 2 \text{CO}_{2(g)} + 3 \text{H}_2\text{O}_{(g)} + 1.28 \text{ MJ}$

Applying Inquiry Skills

4. Analysis

(a) $q_{\text{water}} = mc\Delta T$
 $= 200.0 \text{ g} \times 4.18 \text{ J/(g}^\circ\text{C)} \times (76.0 - 21.0)^\circ\text{C}$
 $q_{\text{water}} = 45.9(8) \text{ kJ}$ [Digit in parentheses will be lost in rounding.]

$$\begin{aligned}
q_{\text{copper}} &= mc\Delta T \\
&= 50.0 \text{ g} \times 0.385 \text{ J/(g}^\circ\text{C)} \times (76.0 - 21.0)^\circ\text{C} \\
q_{\text{copper}} &= 1.06 \text{ kJ} \\
n\Delta H_{\text{reaction}} &= q_{\text{total}} \\
&= q_{\text{water}} + q_{\text{copper}} \\
n\Delta H_{\text{reaction}} &= 47.0(4) \text{ kJ} \text{ [Digit in parentheses will be lost in rounding.]} \\
m_{\text{eicosane}} &= 8.567 - 7.357 \text{ g} \\
m_{\text{eicosane}} &= 1.21 \text{ g} \\
M_{\text{eicosane (C}_{20}\text{H}_{42})} &= 282 \text{ g/mol} \\
n_{\text{eicosane}} &= 1.21 \text{ g} \times \frac{1 \text{ mol}}{282 \text{ g}} \\
n_{\text{eicosane}} &= 4.29 \times 10^{-3} \text{ mol} \\
\Delta H_{\text{comb}} &= \frac{q_{\text{total}}}{n} \\
&= \frac{47.0(4) \text{ kJ}}{4.29 \times 10^{-3} \text{ mol}} \\
\Delta H_{\text{comb}} &= 1.10 \times 10^4 \text{ kJ/mol C}_{20}\text{H}_{42}
\end{aligned}$$

Because the reaction is exothermic, $\Delta H_{\text{reaction}}$ is -11.0 MJ/mol .

- (b) The reaction was exothermic, because heat was released to the surroundings and the temperature increased.
(c) $\text{C}_{20}\text{H}_{42(s)} + 61/2 \text{ O}_{2(g)} \rightarrow 20 \text{ CO}_{2(g)} + 21 \text{ H}_2\text{O}_{(g)} + 11.0 \text{ MJ}$
 $\text{C}_{20}\text{H}_{42(s)} + 61/2 \text{ O}_{2(g)} \rightarrow 20 \text{ CO}_{2(g)} + 21 \text{ H}_2\text{O}_{(g)} \quad \Delta H = -11.0 \text{ MJ}$

Evaluation

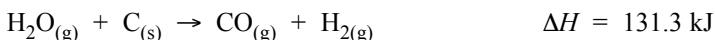
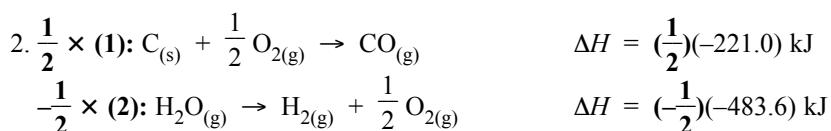
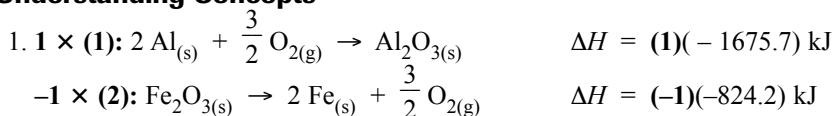
$$\begin{aligned}
(\text{d}) \text{ Percentage error} &= \frac{(13.3 - 11.0)}{13.3} \times 100 \\
&= 17\%
\end{aligned}$$

5.4 HESS'S LAW OF ADDITIVITY OF REACTION ENTHALPIES

PRACTICE

(Page 326)

Understanding Concepts



$$\begin{aligned}
q_{\text{copper}} &= mc\Delta T \\
&= 50.0 \text{ g} \times 0.385 \text{ J/(g}^\circ\text{C)} \times (76.0 - 21.0)^\circ\text{C} \\
q_{\text{copper}} &= 1.06 \text{ kJ} \\
n\Delta H_{\text{reaction}} &= q_{\text{total}} \\
&= q_{\text{water}} + q_{\text{copper}} \\
n\Delta H_{\text{reaction}} &= 47.0(4) \text{ kJ} \text{ [Digit in parentheses will be lost in rounding.]} \\
m_{\text{eicosane}} &= 8.567 - 7.357 \text{ g} \\
m_{\text{eicosane}} &= 1.21 \text{ g} \\
M_{\text{eicosane (C}_{20}\text{H}_{42})} &= 282 \text{ g/mol} \\
n_{\text{eicosane}} &= 1.21 \text{ g} \times \frac{1 \text{ mol}}{282 \text{ g}} \\
n_{\text{eicosane}} &= 4.29 \times 10^{-3} \text{ mol} \\
\Delta H_{\text{comb}} &= \frac{q_{\text{total}}}{n} \\
&= \frac{47.0(4) \text{ kJ}}{4.29 \times 10^{-3} \text{ mol}} \\
\Delta H_{\text{comb}} &= 1.10 \times 10^4 \text{ kJ/mol C}_{20}\text{H}_{42}
\end{aligned}$$

Because the reaction is exothermic, $\Delta H_{\text{reaction}}$ is -11.0 MJ/mol .

- (b) The reaction was exothermic, because heat was released to the surroundings and the temperature increased.
(c) $\text{C}_{20}\text{H}_{42(s)} + 61/2 \text{ O}_{2(g)} \rightarrow 20 \text{ CO}_{2(g)} + 21 \text{ H}_2\text{O}_{(g)} + 11.0 \text{ MJ}$
 $\text{C}_{20}\text{H}_{42(s)} + 61/2 \text{ O}_{2(g)} \rightarrow 20 \text{ CO}_{2(g)} + 21 \text{ H}_2\text{O}_{(g)} \quad \Delta H = -11.0 \text{ MJ}$

Evaluation

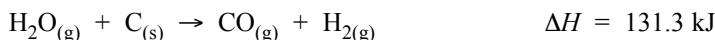
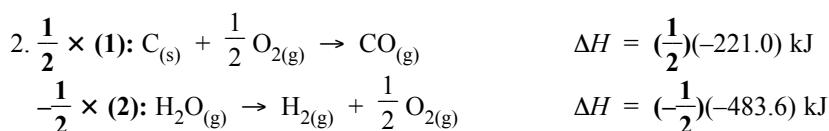
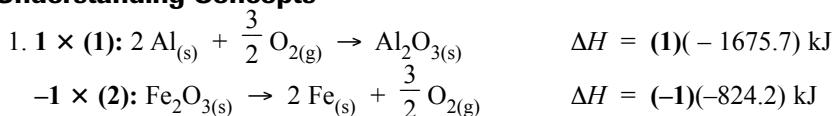
$$\begin{aligned}
(\text{d}) \text{ Percentage error} &= \frac{(13.3 - 11.0)}{13.3} \times 100 \\
&= 17\%
\end{aligned}$$

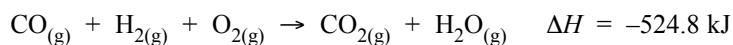
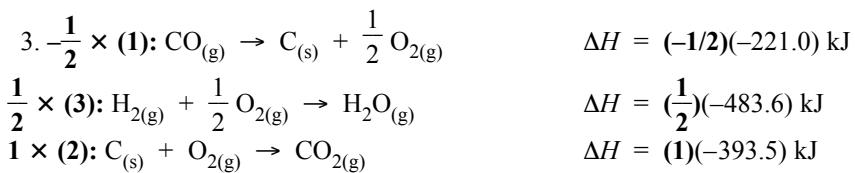
5.4 HESS'S LAW OF ADDITIVITY OF REACTION ENTHALPIES

PRACTICE

(Page 326)

Understanding Concepts

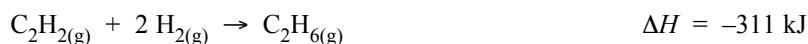
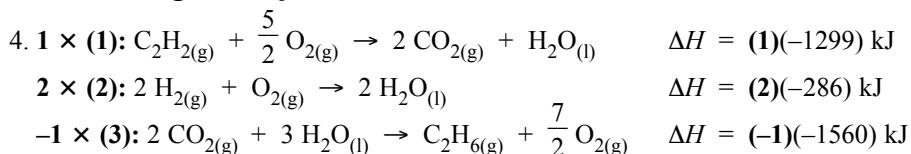




PRACTICE

(Page 329)

Understanding Concepts



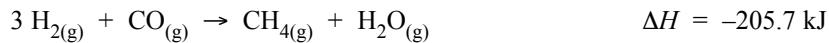
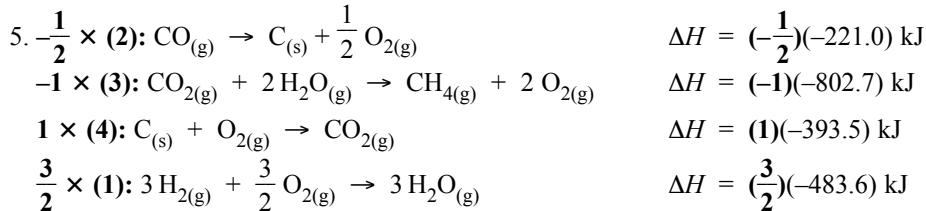
Since the reaction is written for one mole of ethyne, the molar enthalpy of combustion of ethyne, ΔH_{comb} , is -311 kJ/mol .

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

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

$$\begin{aligned}
 \Delta H &= n\Delta H_{\text{comb}} \\
 &= 7.69 \text{ mol} \times (-311 \text{ kJ/mol})
 \end{aligned}$$

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



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

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

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

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

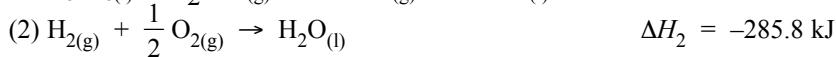
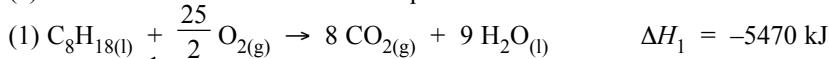
$$\Delta H = -2.20 \times 10^3 \text{ kJ}$$

SECTION 5.4 QUESTIONS

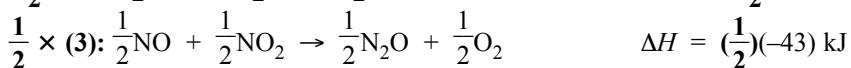
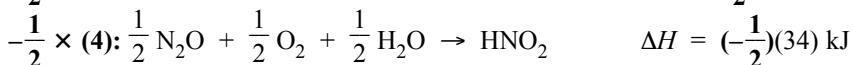
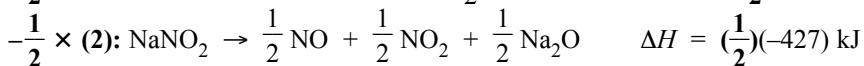
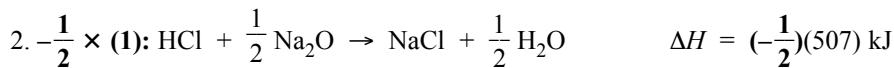
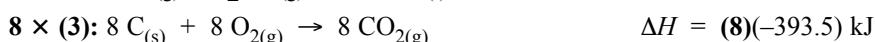
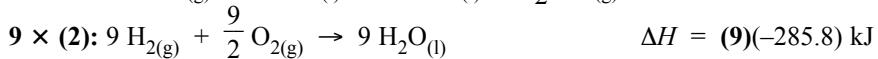
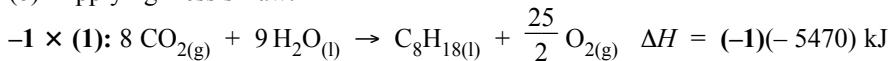
(Page 330)

Understanding Concepts

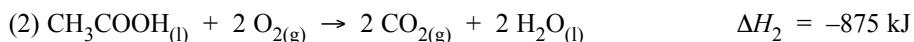
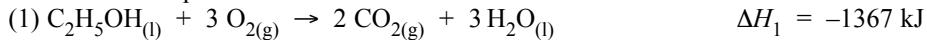
1. (a) The reference thermochemical equations are:



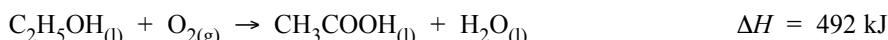
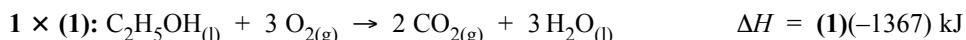
(b) Applying Hess's Law:



3. The reference equations are:



Applying Hess's Law:



Applying Inquiry Skills

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



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

Experiment 1:

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

$$= 200.0 \text{ g} \times 4.18 \text{ J/g}^\circ\text{C} \times (22.5 - 20.0)^\circ\text{C}$$

$$q_{\text{water}} = 2.09 \text{ kJ}$$

$$n\Delta H_1 = q_{\text{water}}$$

$$= 2.09 \text{ kJ}$$

amount of KOH, $n = CV$

$$= 1.00 \text{ mol/L} \times 0.100 \text{ L}$$

$$n = 0.100 \text{ mol}$$

$$\Delta H_1 = \frac{q}{n}$$

$$= \frac{2.09 \text{ kJ}}{0.100 \text{ mol}}$$

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

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

Experiment 2:

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

$$= 200.0 \text{ g} \times 4.18 \text{ J/g}^\circ\text{C} \times (24.1 - 20.0)^\circ\text{C}$$

$$q_{\text{water}} = 3.43 \text{ kJ}$$

$$n\Delta H_2 = q_{\text{water}}$$

$$= 3.43 \text{ kJ}$$

molar mass of KOH, $M = 56.1 \text{ g/mol}$

$$\text{amount of KOH, } n = 5.61 \text{ g} \times \frac{1 \text{ mol}}{56.1 \text{ g}}$$

$$n = 0.100 \text{ mol}$$

$$\Delta H_2 = \frac{q}{n}$$

$$= \frac{3.43 \text{ kJ}}{0.100 \text{ mol}}$$

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

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

Experiment 3:

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

$$= 200.0 \text{ g} \times 4.18 \text{ J/g}^\circ\text{C} \times (26.7 - 20.0)^\circ\text{C}$$

$$q_{\text{water}} = 5.60 \text{ kJ}$$

$$n\Delta H_{\text{reaction}} = q_{\text{water}}$$

$$= 5.60 \text{ kJ}$$

$$\text{amount of KOH, } n = 5.61 \text{ g} \times \frac{1 \text{ mol}}{56.1 \text{ g}}$$

$$n = 0.100 \text{ mol}$$

$$\Delta H_3 = \frac{q}{n}$$

$$= \frac{5.60 \text{ kJ}}{0.100 \text{ mol}}$$

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

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

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

5.5 STANDARD ENTHALPIES OF FORMATION

PRACTICE

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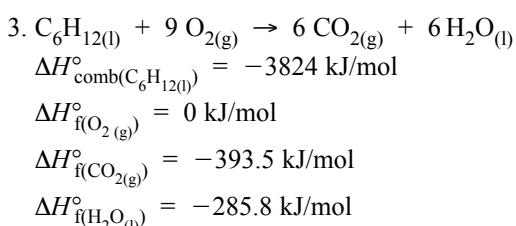
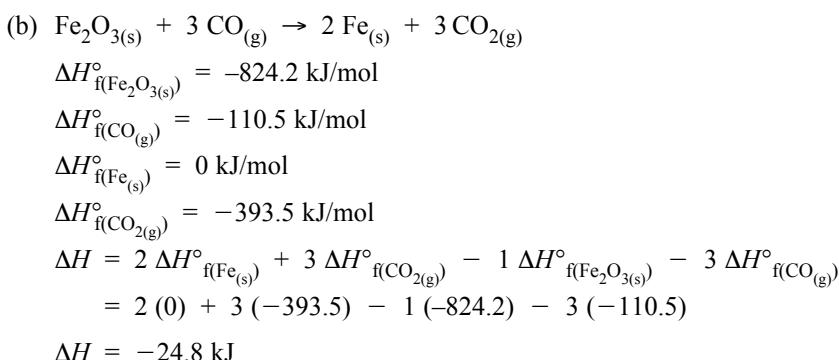
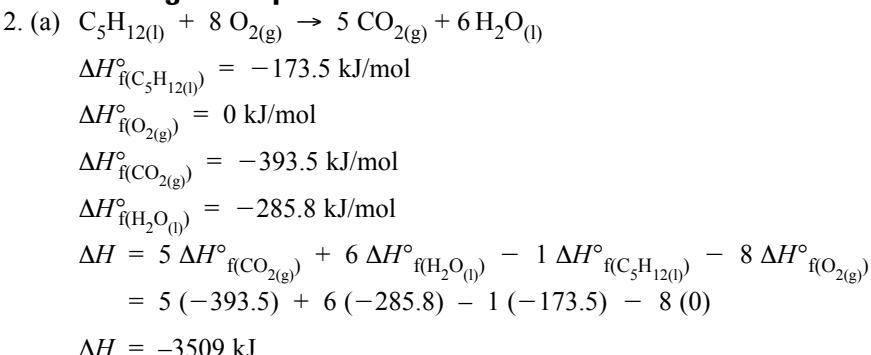
Understanding Concepts

1. (a) $6 \text{C}_{(s)} + 3 \text{H}_{2(g)} \rightarrow \text{C}_6\text{H}_{6(l)}$
- (b) $\text{K}_{(s)} + \frac{1}{2} \text{Br}_{2(l)} + 3/2 \text{O}_{2(g)} \rightarrow \text{KBrO}_{3(s)}$
- (c) $6 \text{C}_{(s)} + 6 \text{H}_{2(g)} + 3 \text{O}_{2(g)} \rightarrow \text{C}_6\text{H}_{12}\text{O}_{6(s)}$
- (d) $\text{Mg}_{(s)} + \text{H}_{2(g)} + \text{O}_{2(g)} \rightarrow \text{Mg(OH)}_{2(s)}$

PRACTICE

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Understanding Concepts



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

5.5 STANDARD ENTHALPIES OF FORMATION

PRACTICE

(Page 332)

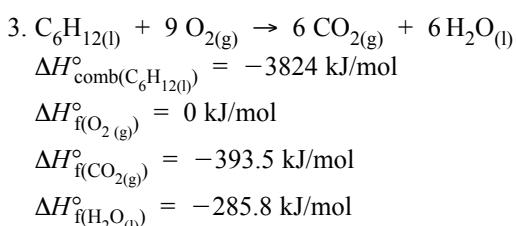
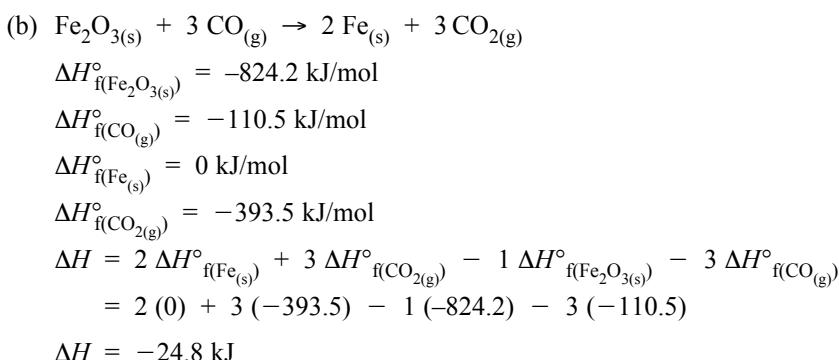
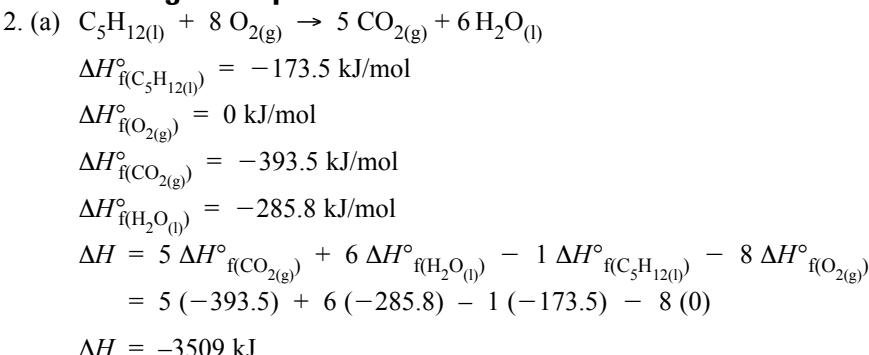
Understanding Concepts

1. (a) $6 \text{C}_{(s)} + 3 \text{H}_{2(g)} \rightarrow \text{C}_6\text{H}_{6(l)}$
- (b) $\text{K}_{(s)} + \frac{1}{2} \text{Br}_{2(l)} + 3/2 \text{O}_{2(g)} \rightarrow \text{KBrO}_{3(s)}$
- (c) $6 \text{C}_{(s)} + 6 \text{H}_{2(g)} + 3 \text{O}_{2(g)} \rightarrow \text{C}_6\text{H}_{12}\text{O}_{6(s)}$
- (d) $\text{Mg}_{(s)} + \text{H}_{2(g)} + \text{O}_{2(g)} \rightarrow \text{Mg(OH)}_{2(s)}$

PRACTICE

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Understanding Concepts



$$\begin{aligned}\Delta H^\circ_{\text{comb}(C_6H_{12(l)})} &= 6 \Delta H^\circ_{f(CO_{2(g)})} + 6 \Delta H^\circ_{f(H_2O_{(l)})} - 1 \Delta H^\circ_{f(C_6H_{12(l)})} - 9 \Delta H^\circ_{f(O_{2(g)})} \\ -3824 &= 6(-393.5) + 6(-285.8) - 1(\Delta H^\circ_{f(C_6H_{12(l)})}) - 9(0) \\ \Delta H^\circ_{f(C_6H_{12(l)})} &= 6(-393.5) + 6(-285.8) - 9(0) + 3824 \text{ kJ} \\ \Delta H^\circ_{f(C_6H_{12(l)})} &= -252 \text{ kJ/mol}\end{aligned}$$

The standard enthalpy of combustion of liquid cyclohexane is -252 kJ/mol .

$$\begin{aligned}4. (a) \quad \Delta H^\circ_{f(CH_{4(g)})} &= -74.4 \text{ kJ/mol} \\ \Delta H^\circ_{f(H_2O_{(l)})} &= -285.8 \text{ kJ/mol} \\ \Delta H^\circ_{f(CO_{(g)})} &= -110.5 \text{ kJ/mol} \\ \Delta H^\circ_{f(H_2(g))} &= 0 \text{ kJ/mol} \\ \Delta H &= 1 \Delta H^\circ_{f(CO_{(g)})} + 3 \Delta H^\circ_{f(H_2(g))} - 1 \Delta H^\circ_{f(CH_{4(g)})} - 1 \Delta H^\circ_{f(H_2O_{(l)})} \\ &= 1(-110.5) + 3(0) - 1(-74.4) - 1(-285.8) \\ \Delta H &= 249.7 \text{ kJ}\end{aligned}$$

ΔH for the reaction is 249.7 kJ .

$$\begin{aligned}(b) \quad \Delta H^\circ_{f(CO_{(g)})} &= -110.5 \text{ kJ/mol} \\ \Delta H^\circ_{f(H_2O_{(l)})} &= -285.8 \text{ kJ/mol} \\ \Delta H^\circ_{f(CO_{2(g)})} &= -393.5 \text{ kJ/mol} \\ \Delta H^\circ_{f(H_2(g))} &= 0 \text{ kJ/mol} \\ \Delta H &= 1 \Delta H^\circ_{f(CO_{2(g)})} + 1 \Delta H^\circ_{f(H_2(g))} - 1 \Delta H^\circ_{f(CO_{(g)})} - 1 \Delta H^\circ_{f(H_2O_{(l)})} \\ &= 1(-393.5) + 1(0) - 1(-110.5) - 1(-285.8)\end{aligned}$$

$$\Delta H = 2.8 \text{ kJ}$$

ΔH for the reaction is 2.8 kJ .

$$\begin{aligned}(c) \quad \Delta H^\circ_{f(N_{2(g)})} &= 0 \text{ kJ/mol} \\ \Delta H^\circ_{f(H_2(g))} &= 0 \text{ kJ/mol} \\ \Delta H^\circ_{f(NH_{3(g)})} &= -45.9 \text{ kJ/mol} \\ \Delta H &= 2 \Delta H^\circ_{f(NH_{3(g)})} - 1 \Delta H^\circ_{f(N_{2(g)})} - 3 \Delta H^\circ_{f(H_2(g))} \\ &= 2(-45.9) - 1(0) - 3(0)\end{aligned}$$

$$\Delta H = -91.8 \text{ kJ}$$

ΔH for the reaction is -91.8 kJ .

$$\begin{aligned}5. (a) \quad \Delta H^\circ_{f(NH_{3(g)})} &= -45.9 \text{ kJ/mol} \\ \Delta H^\circ_{f(O_{2(g)})} &= 0 \text{ kJ/mol} \\ \Delta H^\circ_{f(NO_{(g)})} &= 90.2 \text{ kJ/mol} \\ \Delta H^\circ_{f(H_2O_{(l)})} &= -285.8 \text{ kJ/mol} \\ \Delta H &= 4 \Delta H^\circ_{f(NO_{(g)})} + 6 \Delta H^\circ_{f(H_2O_{(l)})} - 4 \Delta H^\circ_{f(NH_{3(g)})} - 5 \Delta H^\circ_{f(O_{2(g)})} \\ &= 4(+90.2) + 6(-285.8) - 4(-45.9) - 5(0)\end{aligned}$$

$$\Delta H = -1170.4 \text{ kJ}$$

ΔH for the reaction is -1170.4 kJ .

$$\begin{aligned}(b) \quad \Delta H^\circ_{f(NO_{(g)})} &= 90.2 \text{ kJ/mol} \\ \Delta H^\circ_{f(O_{2(g)})} &= 0 \text{ kJ/mol} \\ \Delta H^\circ_{f(NO_{2(g)})} &= 33.2 \text{ kJ/mol}\end{aligned}$$

$$\Delta H = 2 \Delta H^\circ_{f(NO_{2(g})} - 2 \Delta H^\circ_{f(NO_{(g})} - 1 \Delta H^\circ_{f(O_{2(g})}$$

$$= 2(+33.2) - 2(+90.2) - 1(0)$$

$$\Delta H = -114.2 \text{ kJ}$$

ΔH for the reaction is -114.2 kJ .

(c) $\Delta H^\circ_{f(NO_{2(g})} = 33.2 \text{ kJ/mol}$

$$\Delta H^\circ_{f(H_2O_{(l})} = -285.8 \text{ kJ/mol}$$

$$\Delta H^\circ_{f(HNO_{3(l})} = -174.1 \text{ kJ/mol}$$

$$\Delta H^\circ_{f(NO_{(g})} = 90.2 \text{ kJ/mol}$$

$$\Delta H = 2 \Delta H^\circ_{f(HNO_{3(l})} + 1 \Delta H^\circ_{f(NO_{(g})} - 3 \Delta H^\circ_{f(NO_{2(g})} - 1 \Delta H^\circ_{f(H_2O_{(l})}$$

$$= 2(-174.1) + 1(+90.2) - 3(+33.2) - 1(-285.8)$$

$$\Delta H = -71.8 \text{ kJ}$$

ΔH for the reaction is -71.8 kJ .

Making Connections

- raw materials + light energy + fertilizer (chemical energy) \rightarrow plant (chemical energy) \rightarrow prepared food (chemical energy) \rightarrow blood sugars (chemical energy) \rightarrow body tissue (chemical energy), movement (kinetic energy), or heat loss (thermal energy)
- The advantage of using fertilizers to increase crop yield is that, although we input energy to make the fertilizers, the energy we gain back is now in a form that is usable by our bodies. The question of whether or not we should fertilize our crops goes far beyond a consideration of the amount of energy used to produce the fertilizer. It should include a weighing of the risks and benefits of both fertilizing (e.g., possibly polluting the ground water) and not fertilizing (e.g., producing less food).

PRACTICE

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Making Connections

7. (a) $\Delta H^\circ_{f(NH_{3(g})} = -45.9 \text{ kJ/mol}$

$$\Delta H^\circ_{f(HNO_{3(l})} = -174.1 \text{ kJ/mol}$$

$$\Delta H^\circ_{f(NH_4NO_{3(s})} = -365.6 \text{ kJ/mol}$$

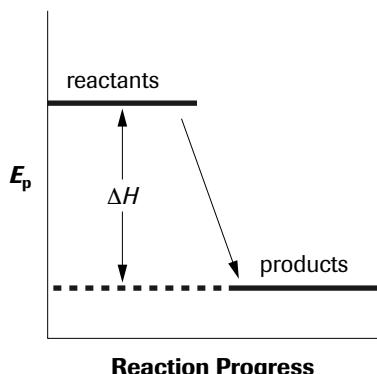
$$\Delta H = 1 \Delta H^\circ_{f(NH_4NO_{3(s})} - 1 \Delta H^\circ_{f(NH_{3(g})} - 1 \Delta H^\circ_{f(HNO_{3(l})}$$

$$= 1(-365.6) - 1(-45.9) - 1(-174.1)$$

$$\Delta H = -145.6 \text{ kJ}$$

ΔH for the reaction is -145.6 kJ .

(b) **Exothermic Reaction**



(c) molar mass of NH_4NO_3 , $M = 80.0 \text{ g/mol}$
amount of NH_4NO_3 , $n = 5.0 \times 10^7 \text{ g} \times \frac{1 \text{ mol}}{80.0 \text{ g}}$
 $n = 6.25 \times 10^5 \text{ mol}$

$$\begin{aligned} q &= \Delta H \\ &= n\Delta H_r^\circ \\ &= 6.25 \times 10^5 \text{ mol} \times 145.6 \text{ kJ} \\ q &= 9.10 \times 10^7 \text{ kJ} \end{aligned}$$

As the reaction is exothermic, $9.10 \times 10^7 \text{ kJ}$ of heat will be lost to the surroundings during the reaction.

8. $\Delta H_{f(\text{coal}_{(s)})}^\circ = -396.4 \text{ kJ/mol}$
 $\Delta H_{f(\text{O}_{2(g)})}^\circ = 0 \text{ kJ/mol}$
 $\Delta H_{f(\text{CO}_{2(g)})}^\circ = -393.5 \text{ kJ/mol}$
 $\Delta H_{f(\text{H}_2\text{O}_{(g)})}^\circ = -241.8 \text{ kJ/mol}$
 $\Delta H = 104 \Delta H_{f(\text{CO}_{2(g)})}^\circ + 16 \Delta H_{f(\text{H}_2\text{O}_{(g)})}^\circ - 2 \Delta H_{f(\text{coal}_{(s)})}^\circ - 111 \Delta H_{f(\text{O}_{2(g)})}^\circ$
 $= 104(-393.5) + 16(-241.8) - 2(-396.4) - 111(0)$

$$\begin{aligned} \Delta H &= -4.40 \times 10^4 \text{ kJ or } -44.0 \text{ MJ} \\ \Delta H_{\text{comb}} &= \frac{\Delta H}{n} \\ &= \frac{-44.0 \text{ MJ}}{2 \text{ mol coal}} \end{aligned}$$

$$\Delta H = -22.0 \text{ MJ/mol coal}$$

molar mass of $\text{C}_{52}\text{H}_{16}\text{O}$, $M = 656 \text{ g/mol}$
amount of $\text{C}_{52}\text{H}_{16}\text{O}$, $n = 1.00 \times 10^5 \text{ g} \times \frac{1 \text{ mol}}{656 \text{ g}}$
 $n = 152 \text{ mol}$

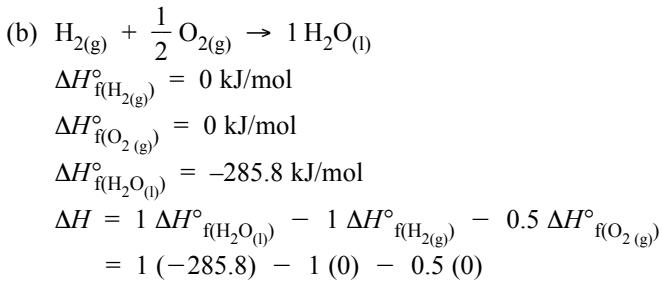
$$\begin{aligned} q &= \Delta H \\ &= n\Delta H_r^\circ \\ &= 152 \text{ mol} \times 22.0 \text{ MJ/mol} \\ q &= 3.34 \times 10^3 \text{ MJ} \end{aligned}$$

Burning 100.0 kg anthracite coal will produce $3.34 \times 10^3 \text{ MJ}$ of thermal energy.

9. (a) $\text{CH}_3\text{OH}_{(l)} + \frac{3}{2} \text{O}_{2(g)} \rightarrow 1 \text{CO}_{2(g)} + 2 \text{H}_2\text{O}_{(l)}$
 $\Delta H_{f(\text{CH}_3\text{OH}_{(l)})}^\circ = -239.1 \text{ kJ/mol}$
 $\Delta H_{f(\text{O}_{2(g)})}^\circ = 0 \text{ kJ/mol}$
 $\Delta H_{f(\text{CO}_{2(g)})}^\circ = -393.5 \text{ kJ/mol}$
 $\Delta H_{f(\text{H}_2\text{O}_{(l)})}^\circ = -285.8 \text{ kJ/mol}$
 $\Delta H = 1 \Delta H_{f(\text{CO}_{2(g)})}^\circ + 2 \Delta H_{f(\text{H}_2\text{O}_{(l)})}^\circ - 1 \Delta H_{f(\text{CH}_3\text{OH}_{(l)})}^\circ - 1.5 \Delta H_{f(\text{O}_{2(g)})}^\circ$
 $= 1(-393.5) + 2(-285.8) - 1(-239.1) - 1.5(0)$

$$\begin{aligned} \Delta H &= -726 \text{ kJ} \\ \text{molar mass of CH}_3\text{OH}, M &= 32.0 \text{ g/mol} \\ \text{amount of CH}_3\text{OH}, n &= 1.00 \times 10^3 \text{ g} \times \frac{1 \text{ mol}}{32.0 \text{ g}} \\ n &= 31.3 \text{ mol} \end{aligned}$$

$$\begin{aligned}
q &= \Delta H \\
&= n\Delta H^\circ_{\text{comb}} \\
&= 31.3 \text{ mol} \times 726 \text{ kJ/mol} \\
q &= 2.27 \times 10^4 \text{ kJ, or } 22.7 \text{ MJ for one mole burned.}
\end{aligned}$$



$$\Delta H = -285.8 \text{ kJ}$$

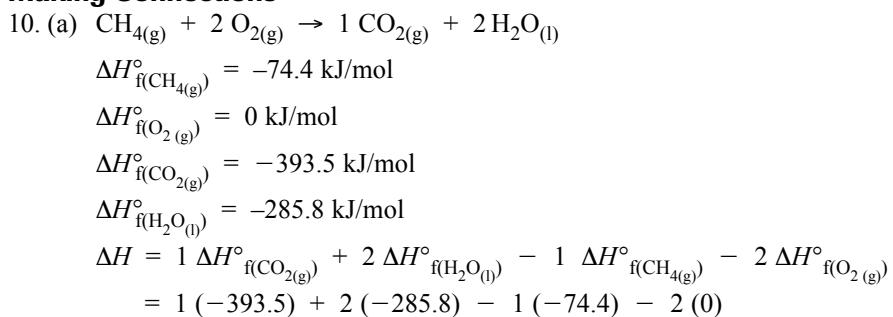
$$\begin{aligned}
\text{molar mass of H}_2, M &= 2.02 \text{ g/mol} \\
\text{amount of H}_2, n &= 1.00 \times 10^3 \text{ g} \times \frac{1 \text{ mol}}{2.02 \text{ g}} \\
n &= 495 \text{ mol}
\end{aligned}$$

$$\begin{aligned}
q &= \Delta H \\
&= n\Delta H^\circ_{\text{comb}} \\
&= 495 \text{ mol} \times 285.8 \text{ kJ/mol}
\end{aligned}$$

$$q = 1.42 \times 10^5 \text{ kJ, or } 142 \text{ MJ for one mole burned.}$$

- (c) Both of these fuels produce less energy per mole than octane.
- (d) Cost of the fuels and availability are two economic factors. Consumer safety concerns are also an issue since hydrogen is viewed as a more explosive gas.

Making Connections



$$\Delta H = -890.7 \text{ kJ/mol methane}$$

$$\text{Thus, } \Delta H^\circ_{\text{comb}} = -890.7 \text{ kJ/mol methane}$$

$$\begin{aligned}
q_{\text{water}} &= mc\Delta T \\
&= 1.00 \times 10^5 \text{ g} \times 4.18 \text{ J/(g}^\circ\text{C)} \times (70 - 5)^\circ\text{C}
\end{aligned}$$

$$q_{\text{water}} = 2.7 \times 10^4 \text{ kJ}$$

$$n\Delta H^\circ_{\text{comb}} = q_{\text{water}}$$

$$\begin{aligned}
n &= \frac{q_{\text{water}}}{\Delta H^\circ_{\text{comb}}} \\
&= \frac{2.7 \times 10^4 \text{ kJ}}{-890.7 \text{ kJ/mol}}
\end{aligned}$$

$$n = 30 \text{ mol}$$

$$\begin{aligned}m &= n \times M \\&= 30 \text{ mol} \times 16.0 \text{ g/mol} \\m &= 480 \text{ g}\end{aligned}$$

480 g of methane will heat 100 kg of water from 5°C to 70°C.

- (b) Insulating water pipes and setting the thermostat at a lower temperature are ways to conserve energy.
- (c) Electricity and propane combustion are commonly used for heating water.

SECTION 5.5 QUESTIONS

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Understanding Concepts

1. (a) $2 \text{C}_{(\text{s})} + \text{H}_{2(\text{g})} \rightarrow \text{C}_{2\text{H}}_{2(\text{g})}$
- (b) $4 \text{C}_{(\text{s})} + 9/2 \text{H}_{2(\text{g})} + 3/2 \text{N}_{2(\text{g})} + \text{O}_{2(\text{g})} \rightarrow \text{C}_{4\text{H}}_{9\text{N}}_{3\text{O}}_{2(\text{s})}$
- (c) $\text{K}_{(\text{s})} + 1/2 \text{I}_{2(\text{s})} \rightarrow \text{KI}_{(\text{s})}$
- (d) $\text{Fe}_{(\text{s})} + \text{S}_{(\text{s})} + 2 \text{O}_{2(\text{g})} \rightarrow \text{FeSO}_{4(\text{s})}$
2. (a) $\text{MgCO}_{3(\text{s})} \rightarrow \text{MgO}_{(\text{s})} + \text{CO}_{2(\text{g})}$

$$\Delta H = 1 \Delta H_{\text{f}}^{\circ}(\text{CO}_{2(\text{g})}) + 1 \Delta H_{\text{f}}^{\circ}(\text{MgO}_{(\text{s})}) - 1 \Delta H_{\text{f}}^{\circ}(\text{MgCO}_{3(\text{s})})$$

 $= 1(-393.5) + 1(-601.6) - 1(-1095.8)$
 $\Delta H = 100.7 \text{ kJ}$
- (b) $\text{C}_{2\text{H}}_{4(\text{g})} + 3 \text{O}_{2(\text{g})} \rightarrow \text{CO}_{2(\text{g})} + 2 \text{H}_2\text{O}_{(\text{l})}$

$$\Delta H = 2 \Delta H_{\text{f}}^{\circ}(\text{CO}_{2(\text{g})}) + 2 \Delta H_{\text{f}}^{\circ}(\text{H}_2\text{O}_{(\text{l})}) - 1 \Delta H_{\text{f}}^{\circ}(\text{C}_{2\text{H}}_{4(\text{g})}) - 3 \Delta H_{\text{f}}^{\circ}(\text{O}_{2(\text{g})})$$

 $= 2(-393.5) + 2(-285.8) - 1(+52.5) - 3(0)$
 $\Delta H = -1411 \text{ kJ}$
- (c) $\text{C}_{12}\text{H}_{22}\text{O}_{11(\text{s})} + 12 \text{O}_{2(\text{g})} \rightarrow 12 \text{CO}_{2(\text{g})} + 11 \text{H}_2\text{O}_{(\text{l})}$

$$\Delta H = 12 \Delta H_{\text{f}}^{\circ}(\text{CO}_{2(\text{g})}) + 11 \Delta H_{\text{f}}^{\circ}(\text{H}_2\text{O}_{(\text{l})}) - 1 \Delta H_{\text{f}}^{\circ}(\text{sucrose}_{(\text{s})}) - 12 \Delta H_{\text{f}}^{\circ}(\text{O}_{2(\text{g})})$$

 $= 12(-393.5) + 11(-285.8) - 1(-2225.5) - 12(0)$
 $\Delta H = -5640 \text{ kJ}$
3. (a) $\text{C}_{8}\text{H}_{18(\text{g})} + 3 \text{H}_{2(\text{g})} \rightarrow \text{CH}_{4(\text{g})} + 2 \text{C}_{2\text{H}}_{6(\text{g})} + \text{C}_{3}\text{H}_{8(\text{g})}$
(b)
$$\Delta H = 1 \Delta H_{\text{f}}^{\circ}(\text{CH}_{4(\text{g})}) + 2 \Delta H_{\text{f}}^{\circ}(\text{C}_{2\text{H}}_{6(\text{g})}) + 1 \Delta H_{\text{f}}^{\circ}(\text{C}_{3}\text{H}_{8(\text{g})}) - 1 \Delta H_{\text{f}}^{\circ}(\text{C}_{8}\text{H}_{18(\text{g})}) - 3 \Delta H_{\text{f}}^{\circ}(\text{H}_{2(\text{g})})$$

 $= 1(-74.4) + 2(-83.8) + 1(-104.7) - 1(-250.1) - 3(0)$
 $\Delta H = -96.6 \text{ kJ}$

Applying Inquiry Skills

4. Prediction

- (a) $\text{C}_3\text{H}_6\text{O}_{(\text{l})} + 4 \text{O}_{2(\text{g})} \rightarrow 3 \text{CO}_{2(\text{g})} + 3 \text{H}_2\text{O}_{(\text{l})}$

$$\Delta H = 3 \Delta H_{\text{f}}^{\circ}(\text{CO}_{2(\text{g})}) + 3 \Delta H_{\text{f}}^{\circ}(\text{H}_2\text{O}_{(\text{l})}) - 1 \Delta H_{\text{f}}^{\circ}(\text{acetone}_{(\text{l})}) - 4 \Delta H_{\text{f}}^{\circ}(\text{O}_{2(\text{g})})$$

 $= 3(-393.5) + 3(-285.8) - 1(248.1) - 4(0)$
 $\Delta H = -1789.8 \text{ kJ}$ or
 $\Delta H_c = -1.79 \text{ MJ/mol acetone}$

Analysis

(b) $q_{\text{water}} = mc\Delta T$
= $100.0 \text{ g} \times 4.18 \text{ J/g}^\circ\text{C} \times (25.0 - 20.0)^\circ\text{C}$
 $q_{\text{water}} = 2.09 \text{ kJ}$
 $q_{\text{aluminum}} = c\Delta T$
= $50.0 \text{ g} \times 0.91 \text{ J/g}^\circ\text{C} \times (25.0 - 20.0)^\circ\text{C}$
 $q_{\text{aluminum}} = 0.23 \text{ kJ}$
 $q_{\text{total}} = q_{\text{water}} + q_{\text{aluminum}}$
 $q_{\text{water}} + q_{\text{aluminum}} = 2.32 \text{ kJ}$
 $n\Delta H_c = q_{\text{total}}$
 $m_{\text{acetone}} = 0.092 \text{ g}$
 $M_{\text{acetone}} = 58.0 \text{ g}$
 $n_{\text{acetone}} = 0.092 \text{ g} \times \frac{1 \text{ mol}}{58.0 \text{ g}}$
 $n_{\text{acetone}} = 0.0016 \text{ mol}$
 $\Delta H_c = \frac{q_{\text{total}}}{n}$
= $\frac{2.32 \text{ kJ}}{0.0016 \text{ mol}}$
 $\Delta H_c = 1.5 \text{ MJ/mol acetone}$

Because the reaction is exothermic, the molar enthalpy of combustion of acetone, ΔH_c , is -1.5 MJ/mol .

Evaluation

(c) Percentage error = $\frac{|(1.5 - 1.79)|}{1.79} \times 100\%$
= 16%

- (d) The percentage error suggests that heat has been lost to the surroundings as part of experimental error.
(e) If heat is lost to the surroundings, then the observed temperature change in the water and calorimeter, the calculated q values, and the experimental ΔH all will be smaller than predicted.

5.6 THE ENERGY DEBATE

PRACTICE

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Understanding Concepts

1. (a) hydroelectric power, nuclear power, burning fossil fuels
(b) All produce power by driving turbines: nuclear and fossil fuels heat water to drive steam turbines, whereas hydroelectric power uses falling water. Hydroelectric and nuclear energy have higher capital costs. Hydroelectric is relatively environmentally benign, fossil fuel burning produces the greatest amount of pollution, and nuclear energy poses the greatest safety risk.

Making Connections

2. (Sample answer) The CANDU system uses a heavy water moderator and ordinary uranium fuel, whereas some other systems use ordinary water as a moderator and enriched uranium fuel.

Analysis

(b) $q_{\text{water}} = mc\Delta T$
 $= 100.0 \text{ g} \times 4.18 \text{ J/g}^\circ\text{C} \times (25.0 - 20.0)^\circ\text{C}$
 $q_{\text{water}} = 2.09 \text{ kJ}$
 $q_{\text{aluminum}} = c\Delta T$
 $= 50.0 \text{ g} \times 0.91 \text{ J/g}^\circ\text{C} \times (25.0 - 20.0)^\circ\text{C}$
 $q_{\text{aluminum}} = 0.23 \text{ kJ}$
 $q_{\text{total}} = q_{\text{water}} + q_{\text{aluminum}}$
 $q_{\text{water}} + q_{\text{aluminum}} = 2.32 \text{ kJ}$
 $n\Delta H_c = q_{\text{total}}$
 $m_{\text{acetone}} = 0.092 \text{ g}$
 $M_{\text{acetone}} = 58.0 \text{ g}$
 $n_{\text{acetone}} = 0.092 \text{ g} \times \frac{1 \text{ mol}}{58.0 \text{ g}}$
 $n_{\text{acetone}} = 0.0016 \text{ mol}$
 $\Delta H_c = \frac{q_{\text{total}}}{n}$
 $= \frac{2.32 \text{ kJ}}{0.0016 \text{ mol}}$
 $\Delta H_c = 1.5 \text{ MJ/mol acetone}$

Because the reaction is exothermic, the molar enthalpy of combustion of acetone, ΔH_c , is -1.5 MJ/mol .

Evaluation

(c) Percentage error = $\frac{|(1.5 - 1.79)|}{1.79} \times 100\%$
= 16%

- (d) The percentage error suggests that heat has been lost to the surroundings as part of experimental error.
(e) If heat is lost to the surroundings, then the observed temperature change in the water and calorimeter, the calculated q values, and the experimental ΔH all will be smaller than predicted.

5.6 THE ENERGY DEBATE

PRACTICE

(Page 344)

Understanding Concepts

1. (a) hydroelectric power, nuclear power, burning fossil fuels
(b) All produce power by driving turbines: nuclear and fossil fuels heat water to drive steam turbines, whereas hydroelectric power uses falling water. Hydroelectric and nuclear energy have higher capital costs. Hydroelectric is relatively environmentally benign, fossil fuel burning produces the greatest amount of pollution, and nuclear energy poses the greatest safety risk.

Making Connections

2. (Sample answer) The CANDU system uses a heavy water moderator and ordinary uranium fuel, whereas some other systems use ordinary water as a moderator and enriched uranium fuel.

Explore an Issue: Take a Stand: Energy Options

(Page 345)

(Answers will vary.)

Advantages	Disadvantages
hydroelectric power; no air pollution	impact on watersheds of major development such as James Bay; high capital cost
fossil fuel power; low capital cost	pollution, including acid rain and greenhouse effect; ready access to fuel gases
nontraditional fuels; no air pollution	limited application due to geography; high capital cost per unit of power produced
soft energy paths; no air pollution	resistance of people unwilling to change lifestyle
no consumption of natural resources	

PRACTICE

(Page 346)

Understanding Concepts

$$3. (a) \Delta H = n\Delta H_{\text{fission}} \\ = 4.26 \text{ mol} \times 1.9 \times 10^{10} \text{ kJ/mol}$$

$$\Delta H = 8.1 \times 10^{10} \text{ kJ}$$

$$(b) n_{\text{He}} = 1000 \text{ g} \times \frac{1 \text{ mol}}{4.00 \text{ g}}$$

$$n_{\text{He}} = 250 \text{ mol}$$

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

$$= 250 \text{ mol} \times 1.7 \times 10^9 \text{ kJ/mol}$$

$$\Delta H = 4.3 \times 10^{11} \text{ kJ}$$

(c) Helium has a much lower molar mass, so 1 kg represents many more moles.

4. (a) Answers will vary, but fusion reactions require temperatures and concentrations of isotopes that are technologically challenging. No safe and efficient nuclear fusion reactors have been developed as of 2002.

SECTION 5.6 QUESTIONS

(Page 346)

Understanding Concepts

1. Fission of uranium produces about 2×10^{10} kJ/mol and fusion of hydrogen produces about 2×10^9 kJ/mol. Thus, uranium produces about 10 times as much energy, per mole, as hydrogen. However, there are many more moles of hydrogen per kilogram, so the energy production per kilogram would be greater from hydrogen fusion than from uranium fission.

Making Connections

2. Answers will vary, but will include: descriptions of the Pickering and Bruce nuclear power stations; recent information on power output; and mention of the “pollution-free” nature of atomic energy balanced against the problems of disposal and large capital cost of facilities.

3. (Answers will vary.) Choices of alternative fossil fuels include natural gas (largely methane), propane, and other petroleum fractions.

Generating Power from Propane

Advantages	Disadvantages
Propane generators are portable.	Their portability makes them easy targets for thieves.
Power can be made available in an emergency.	Generators are very noisy.
Propane is readily available.	Propane is a relatively expensive form of fuel.

4. (Answers will vary.) Geothermal energy is very useful in areas that are geographically suitable, but few such areas exist in Canada. Solar energy is highly useful for small-scale energy production and many homes already use this source for home and water heating. Canada does not get sufficient intense sunshine for large-scale production.
5. (Answers will vary.) Hydrogen fuel has potential in combustion engines, but probably more in fuel cell application as suggested at the Ballard web site provided.
6. (Answers will vary.) The Chernobyl disaster was a significant example of human error leading to catastrophic short- and long-term effects.

CHAPTER 5 LAB ACTIVITIES

INVESTIGATION 5.1.1 MEDICAL COLD PACKS

(Page 347)

Experimental Design

- (a) Add a measured mass of the unknown salt to a measured mass of water and stir to dissolve the solid. Measure the temperature change that occurs in the water, and use calorimetric calculations to determine an experimental enthalpy of solution which may be compared to accepted values.
- (b) mass of water = m_1

$$\text{mass of solid} = m_2$$

$$\text{initial temperature of water} = T_1$$

$$\text{final temperature of water} = T_2$$

$$q = mc\Delta T$$

$$q = m_1(4.18)(T_1 - T_2)$$

$$\text{enthalpy of solution} = \frac{q}{m_2}$$

Procedure

- (c) 1. Measure 100 g of water into a Styrofoam cup.
 2. Measure its initial temperature.
 3. Add a measured mass of the unknown salt to the water.
 4. Stir to dissolve the solid, and measure the minimum final temperature of the solution.

Analysis

- (d) See above. A mass of 10 g of ammonium chloride would absorb about 2800 J of heat, causing a temperature change in 100 g of water of about 6.7°C.

Evaluation

$$(e) \% \text{ difference} = \frac{|\text{accepted value} - \text{experimental value}|}{\text{accepted value}} \times 100\%$$

- (f) We are not completely confident: Errors could occur in measurements of mass or temperatures, or as a consequence of heat loss to the air.
 (g) Since the temperature change in the water would be too small, the calculated heat of solution would be too low.
 (h) Since the temperature change in the water would be too small, the calculated heat of solution would be too low.

Explore an Issue: Take a Stand: Energy Options

(Page 345)

(Answers will vary.)

Advantages	Disadvantages
hydroelectric power; no air pollution	impact on watersheds of major development such as James Bay; high capital cost
fossil fuel power; low capital cost	pollution, including acid rain and greenhouse effect; ready access to fuel gases
nontraditional fuels; no air pollution	limited application due to geography; high capital cost per unit of power produced
soft energy paths; no air pollution	resistance of people unwilling to change lifestyle
no consumption of natural resources	

PRACTICE

(Page 346)

Understanding Concepts

3. (a) $\Delta H = n\Delta H_{\text{fission}}$
= $4.26 \text{ mol} \times 1.9 \times 10^{10} \text{ kJ/mol}$

$$\Delta H = 8.1 \times 10^{10} \text{ kJ}$$

(b) $n_{\text{He}} = 1000 \text{ g} \times \frac{1 \text{ mol}}{4.00 \text{ g}}$

$$n_{\text{He}} = 250 \text{ mol}$$

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

$$= 250 \text{ mol} \times 1.7 \times 10^9 \text{ kJ/mol}$$

$$\Delta H = 4.3 \times 10^{11} \text{ kJ}$$

(c) Helium has a much lower molar mass, so 1 kg represents many more moles.

4. (a) Answers will vary, but fusion reactions require temperatures and concentrations of isotopes that are technologically challenging. No safe and efficient nuclear fusion reactors have been developed as of 2002.

SECTION 5.6 QUESTIONS

(Page 346)

Understanding Concepts

1. Fission of uranium produces about $2 \times 10^{10} \text{ kJ/mol}$ and fusion of hydrogen produces about $2 \times 10^9 \text{ kJ/mol}$. Thus, uranium produces about 10 times as much energy, per mole, as hydrogen. However, there are many more moles of hydrogen per kilogram, so the energy production per kilogram would be greater from hydrogen fusion than from uranium fission.

Making Connections

2. Answers will vary, but will include: descriptions of the Pickering and Bruce nuclear power stations; recent information on power output; and mention of the “pollution-free” nature of atomic energy balanced against the problems of disposal and large capital cost of facilities.

3. (Answers will vary.) Choices of alternative fossil fuels include natural gas (largely methane), propane, and other petroleum fractions.

Generating Power from Propane

Advantages	Disadvantages
Propane generators are portable.	Their portability makes them easy targets for thieves.
Power can be made available in an emergency.	Generators are very noisy.
Propane is readily available.	Propane is a relatively expensive form of fuel.

4. (Answers will vary.) Geothermal energy is very useful in areas that are geographically suitable, but few such areas exist in Canada. Solar energy is highly useful for small-scale energy production and many homes already use this source for home and water heating. Canada does not get sufficient intense sunshine for large-scale production.
5. (Answers will vary.) Hydrogen fuel has potential in combustion engines, but probably more in fuel cell application as suggested at the Ballard web site provided.
6. (Answers will vary.) The Chernobyl disaster was a significant example of human error leading to catastrophic short- and long-term effects.

CHAPTER 5 LAB ACTIVITIES

INVESTIGATION 5.1.1 MEDICAL COLD PACKS

(Page 347)

Experimental Design

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- (b) mass of water = m_1

$$\text{mass of solid} = m_2$$

$$\text{initial temperature of water} = T_1$$

$$\text{final temperature of water} = T_2$$

$$q = mc\Delta T$$

$$q = m_1(4.18)(T_1 - T_2)$$

$$\text{enthalpy of solution} = \frac{q}{m_2}$$

Procedure

- (c) 1. Measure 100 g of water into a Styrofoam cup.
 2. Measure its initial temperature.
 3. Add a measured mass of the unknown salt to the water.
 4. Stir to dissolve the solid, and measure the minimum final temperature of the solution.

Analysis

- (d) See above. A mass of 10 g of ammonium chloride would absorb about 2800 J of heat, causing a temperature change in 100 g of water of about 6.7°C.

Evaluation

$$(e) \% \text{ difference} = \frac{|\text{accepted value} - \text{experimental value}|}{\text{accepted value}} \times 100\%$$

- (f) We are not completely confident: Errors could occur in measurements of mass or temperatures, or as a consequence of heat loss to the air.
- (g) Since the temperature change in the water would be too small, the calculated heat of solution would be too low.
- (h) Since the temperature change in the water would be too small, the calculated heat of solution would be too low.

INVESTIGATION 5.2.1 MOLAR ENTHALPY OF A CHEMICAL CHANGE

(Page 348)

Experimental Design

$$(a) n_{\text{NaOH}} = C_{\text{NaOH}} V_{\text{NaOH}} \\ = 1.0 \text{ mol/L} \times 50 \text{ mL}$$

$n_{\text{NaOH}} = 50 \text{ mmol}$, which would require 25 mmol of acid to be completely consumed

$$n_{\text{H}_2\text{SO}_4} = C_{\text{H}_2\text{SO}_4} V_{\text{H}_2\text{SO}_4} \\ = 1.0 \text{ mol/L} \times 30 \text{ mL}$$

$$n_{\text{H}_2\text{SO}_4} = 30 \text{ mmol}$$

Analysis

$$(b) (i) m_{\text{total}} = m_{\text{NaOH}_{(\text{aq})}} + m_{\text{H}_2\text{SO}_4_{(\text{aq})}} \\ = 30 \text{ g} + 50 \text{ g}$$

$$m_{\text{total}} = 80 \text{ g}$$

(ii) temperature change, ΔT

(Sample answer)

$$\Delta T = 8.0^\circ\text{C}$$

$$(iii) q = 80 (4.18) \Delta T \text{ J}$$

$$= 2675 \text{ kJ}$$

$$q = 2.7 \text{ kJ}$$

$$(iv) n_{\text{NaOH}} = 50 \text{ mmol} \text{ or } 0.050 \text{ mol}$$

$$(v) \Delta H_{\text{neut}} = (2.7 \text{ kJ}) / 0.050 \text{ J/mol} = -54 \text{ kJ/mol}$$

Evaluation

$$(c) \% \text{ difference} = \frac{|\text{accepted value} - \text{experimental value}|}{\text{accepted value}} \times 100\%$$

The accepted value is -57 kJ/mol , which would imply an experimental error of about 5%.

(d) Errors could occur in measurements of mass or temperatures, or as a consequence of heat loss to the air.

Synthesis

- (e) (i) The acid would still be in excess, so that the ΔH would be unchanged.
(ii) The base solution would be less than fully reacted, so that the ΔT and ΔH values would be low.

INVESTIGATION 5.3.1 COMBUSTION OF ALCOHOLS

(Page 349)

Prediction

- (a) (Sample answer) The ΔH_{comb} values would become greater because the reactant molecules are larger.
(The trend is correctly guessed but the rationale is not. In fact, bond breakage in larger molecules requires more energy input but this is more than compensated for by the larger number of bonds formed exothermically in water and carbon dioxide products.)

Analysis

(b) Ethanol:

$$(i) q = (m_{\text{water}}) (4.18 \text{ J/g}^\circ\text{C}) (T) \\ = 100 \text{ g} \times 4.18 \text{ J/g}^\circ\text{C} \times 20.0^\circ\text{C}$$

$$q = 8200 \text{ J, or } 8.2 \text{ kJ}$$

INVESTIGATION 5.2.1 MOLAR ENTHALPY OF A CHEMICAL CHANGE

(Page 348)

Experimental Design

$$(a) n_{\text{NaOH}} = C_{\text{NaOH}} V_{\text{NaOH}} \\ = 1.0 \text{ mol/L} \times 50 \text{ mL}$$

$n_{\text{NaOH}} = 50 \text{ mmol}$, which would require 25 mmol of acid to be completely consumed

$$n_{\text{H}_2\text{SO}_4} = C_{\text{H}_2\text{SO}_4} V_{\text{H}_2\text{SO}_4} \\ = 1.0 \text{ mol/L} \times 30 \text{ mL}$$

$$n_{\text{H}_2\text{SO}_4} = 30 \text{ mmol}$$

Analysis

$$(b) (i) m_{\text{total}} = m_{\text{NaOH}_{(\text{aq})}} + m_{\text{H}_2\text{SO}_4_{(\text{aq})}} \\ = 30 \text{ g} + 50 \text{ g}$$

$$m_{\text{total}} = 80 \text{ g}$$

(ii) temperature change, ΔT

(Sample answer)

$$\Delta T = 8.0^\circ\text{C}$$

$$(iii) q = 80 (4.18) \Delta T \text{ J}$$

$$= 2675 \text{ kJ}$$

$$q = 2.7 \text{ kJ}$$

$$(iv) n_{\text{NaOH}} = 50 \text{ mmol} \text{ or } 0.050 \text{ mol}$$

$$(v) \Delta H_{\text{neut}} = (2.7 \text{ kJ}) / 0.050 \text{ J/mol} = -54 \text{ kJ/mol}$$

Evaluation

$$(c) \% \text{ difference} = \frac{|\text{accepted value} - \text{experimental value}|}{\text{accepted value}} \times 100\%$$

The accepted value is -57 kJ/mol , which would imply an experimental error of about 5%.

(d) Errors could occur in measurements of mass or temperatures, or as a consequence of heat loss to the air.

Synthesis

- (e) (i) The acid would still be in excess, so that the ΔH would be unchanged.
(ii) The base solution would be less than fully reacted, so that the ΔT and ΔH values would be low.

INVESTIGATION 5.3.1 COMBUSTION OF ALCOHOLS

(Page 349)

Prediction

- (a) (Sample answer) The ΔH_{comb} values would become greater because the reactant molecules are larger.
(The trend is correctly guessed but the rationale is not. In fact, bond breakage in larger molecules requires more energy input but this is more than compensated for by the larger number of bonds formed exothermically in water and carbon dioxide products.)

Analysis

(b) Ethanol:

$$(i) q = (m_{\text{water}}) (4.18 \text{ J/g}^\circ\text{C}) (T) \\ = 100 \text{ g} \times 4.18 \text{ J/g}^\circ\text{C} \times 20.0^\circ\text{C}$$

$$q = 8200 \text{ J, or } 8.2 \text{ kJ}$$

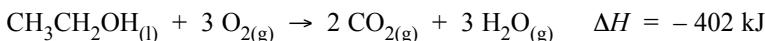
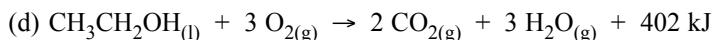
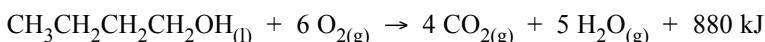
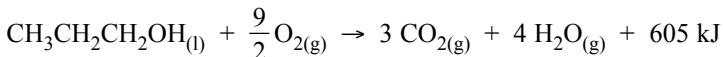
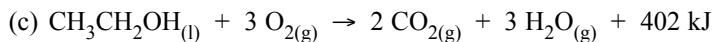
$$\begin{aligned} \text{(ii) heat produced per gram of ethanol} &= \frac{q}{m_{\text{ethanol}}} \\ &= \frac{8.2 \text{ kJ}}{0.94 \text{ g}} \\ &= 8.7 \text{ kJ/g mol} \end{aligned}$$

$$\begin{aligned} \text{(iii) } n_{\text{ethanol}} &= \frac{m_{\text{ethanol}}}{M_{\text{ethanol}}} \\ &= \frac{0.94 \text{ g}}{46.0 \text{ g/mol}} \\ n_{\text{ethanol}} &= 0.0204 \text{ mol} \end{aligned}$$

$$\text{(iv) heat produced per mole of ethanol} = \Delta H_{\text{comb}}$$

$$\begin{aligned} \Delta H_{\text{comb}} &= \frac{q}{n_{\text{ethanol}}} \\ &= \frac{8.2 \text{ kJ}}{0.0204 \text{ mol}} \\ \Delta H_{\text{comb}} &= -402 \text{ kJ/mol} \end{aligned}$$

Similarly, in order to produce a temperature change of 20.0°C, typically 0.83 g of propanol and 0.70 g of butanol need to be burned. All of these values are a fraction of the expected values but the trends in values calculated for these alcohols follow that predicted trend: the larger the alcohol, the larger the heat of combustion (ethanol 402 kJ/mol; propanol 605 kJ/mol; butanol 880 kJ/mol).



$$\Delta H = 2(-402 \text{ kJ})$$

$$\Delta H = -804 \text{ kJ}$$

Since the reaction is exothermic, the PE diagram will resemble Figure 6(a) on p. 318.

(e) (Answers will vary.) The experimental heats of combustion follow the observed trend but are typically about one-third of the accepted values because of the considerable loss of heat to the surroundings.

Evaluation

(f) There is considerable loss of heat to the surroundings.

(g) (Answers will vary.) All of these values are a fraction of the expected values, but the trends in values calculated for these alcohols follow the predicted trend: the larger the alcohol, the larger the heat of combustion (ethanol 402 kJ/mol; propanol 605 kJ/mol; butanol 880 kJ/mol). The Experimental Design was not ideal because of the amount of heat lost to the surroundings. Minimizing heat loss would be an improvement.

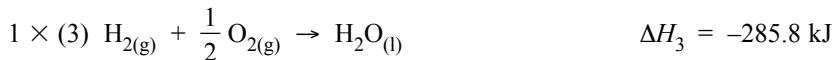
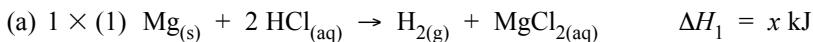
Synthesis

(h) (Answers will vary.) Factors could include heat produced per gram, availability of the fuel, transportation cost and safety, and the extent to which the fuel combusts cleanly.

INVESTIGATION 5.4.1 HESS'S LAW

Prediction

(Page 351)



Analysis

(b) Since the temperature of the solution (surroundings) increased, the changes were exothermic and would have to have negative values if written as ΔH values.

(c) (Answers will vary.) Assume a 11.0°C temperature change for 100 mL of acid and 0.500 g of magnesium used:

$$q = mc\Delta T$$

$$= 0.100 \text{ kg} \times 4.18 \text{ kJ/kg}^{\circ}\text{C} \times 15.0^{\circ}\text{C}$$

$$q = 6.27 \text{ kJ}$$

$$n_{\text{Mg}} = \frac{0.500 \text{ g}}{24.3 \text{ g/mol}}$$

$$n_{\text{Mg}} = 0.0205 \text{ mol}$$

$$\Delta H = \frac{q}{n}$$
$$= \frac{6.27 \text{ kJ}}{0.0205 \text{ mol}}$$

$\Delta H = -306 \text{ kJ/mol Mg}$ (ΔH is given a negative sign because the reaction was exothermic.)



(e) (Answers will vary.) Assume a 5.0°C temperature change for 100 mL of acid and 1.00 g of magnesium oxide used:

$$q = mc\Delta T$$

$$= 0.100 \text{ kg} \times 4.18 \text{ kJ/kg}^{\circ}\text{C} \times 5.0^{\circ}\text{C}$$

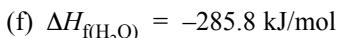
$$q = 2.1 \text{ kJ}$$

$$n_{\text{MgO}} = \frac{1.00 \text{ g}}{40.3 \text{ g/mol}}$$

$$n_{\text{MgO}} = 0.0248 \text{ mol}$$

$$\Delta H = \frac{q}{n}$$
$$= \frac{2.1 \text{ kJ}}{0.0248 \text{ mol}}$$

$\Delta H = -84 \text{ kJ/mol MgO}$ (ΔH is given a negative sign because the reaction was exothermic.)



$$\Delta H_{\text{net}} = \Delta H_1 - \Delta H_2 - \Delta H_3$$

$$= -306 \text{ kJ} - (-84 \text{ kJ}) - 286 \text{ kJ}$$

$$\Delta H_{\text{net}} = -508 \text{ kJ}$$

The molar enthalpy of combustion of magnesium is -508 kJ .

(g) The temperature measurements had the most uncertainty because of thermometer limitations.

Evaluation

- (h) (i) If heat was lost to the surroundings, the ΔT and ΔH values would be low.
(ii) If MgO was on the surface of the magnesium, less Mg would be present and again the ΔT and ΔH values would be low.
- (i) Temperature and mass measurements may be inaccurate, and heat may be lost to the surroundings.
- (j) % difference =
$$\frac{|\text{accepted value} - \text{experimental value}|}{\text{accepted value}} \times 100\%$$
$$= \frac{|2601.6 \text{ kJ/mol} - (-508 \text{ kJ/mol})|}{2601.6 \text{ kJ/mol}} \times 100\%$$
% difference = 15.5%

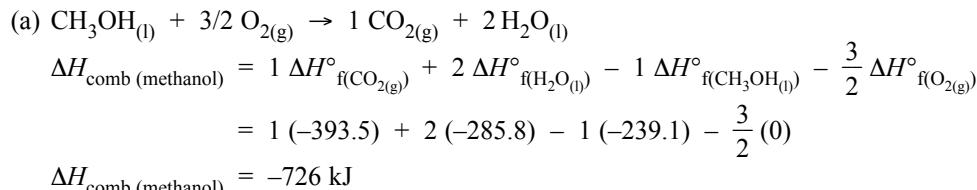
Synthesis

(k) (Answers will vary.) The accuracy of this method depends on the sophistication of the apparatus. If bomb calorimetry had been used, the values would have been more accurate.

LAB EXERCISE 5.5.1 TESTING ENTHALPIES OF FORMATION

(Page 352)

Prediction



The molar enthalpy of combustion of methanol is -726 kJ.

Analysis

(b) $q_{\text{water}} = c \times \Delta T$
 $= 10.9 \text{ kJ}/^\circ\text{C} \times (27.9^\circ\text{C} - 20.4^\circ\text{C})$

$$\begin{aligned}q_{\text{water}} &= 81.7(5) \text{ kJ} \\ n_{\text{methanol}} &= 4.38 \text{ g} \times \frac{1 \text{ mol}}{32.0 \text{ g}} \\ n_{\text{methanol}} &= 0.137 \text{ mol} \\ \Delta H_{\text{comb}}(\text{methanol}) &= \frac{q_{\text{water}}}{n} \\ &= \frac{81.7(5) \text{ kJ}}{0.137 \text{ mol}} \\ \Delta H_{\text{comb}}(\text{methanol}) &= 597 \text{ kJ/mol}\end{aligned}$$

Because the reaction is exothermic, the molar heat of combustion of methanol is -597 kJ/mol.

Evaluation

(c) % difference =
$$\frac{|\text{accepted value} - \text{experimental value}|}{\text{accepted value}} \times 100\%$$
$$= \frac{|726 \text{ kJ/mol} - (-597 \text{ kJ/mol})|}{726 \text{ kJ/mol}} \times 100\%$$

$$\% \text{ difference} = 18\%$$

This is a reasonable result, given relatively simple apparatus.

Evaluation

- (h) (i) If heat was lost to the surroundings, the ΔT and ΔH values would be low.
(ii) If MgO was on the surface of the magnesium, less Mg would be present and again the ΔT and ΔH values would be low.
- (i) Temperature and mass measurements may be inaccurate, and heat may be lost to the surroundings.
- (j) % difference =
$$\frac{|\text{accepted value} - \text{experimental value}|}{\text{accepted value}} \times 100\%$$
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% difference = 15.5%

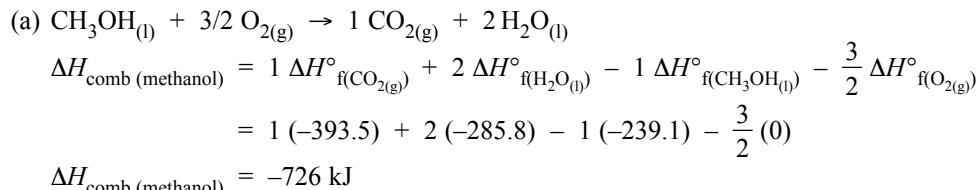
Synthesis

(k) (Answers will vary.) The accuracy of this method depends on the sophistication of the apparatus. If bomb calorimetry had been used, the values would have been more accurate.

LAB EXERCISE 5.5.1 TESTING ENTHALPIES OF FORMATION

(Page 352)

Prediction



The molar enthalpy of combustion of methanol is -726 kJ.

Analysis

(b) $q_{\text{water}} = c \times \Delta T$
 $= 10.9 \text{ kJ}/^\circ\text{C} \times (27.9^\circ\text{C} - 20.4^\circ\text{C})$

$$\begin{aligned}q_{\text{water}} &= 81.7(5) \text{ kJ} \\ n_{\text{methanol}} &= 4.38 \text{ g} \times \frac{1 \text{ mol}}{32.0 \text{ g}} \\ n_{\text{methanol}} &= 0.137 \text{ mol} \\ \Delta H_{\text{comb}}(\text{methanol}) &= \frac{q_{\text{water}}}{n} \\ &= \frac{81.7(5) \text{ kJ}}{0.137 \text{ mol}} \\ \Delta H_{\text{comb}}(\text{methanol}) &= 597 \text{ kJ/mol}\end{aligned}$$

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Evaluation

(c) % difference =
$$\frac{|\text{accepted value} - \text{experimental value}|}{\text{accepted value}} \times 100\%$$
$$= \frac{|726 \text{ kJ/mol} - (-597 \text{ kJ/mol})|}{726 \text{ kJ/mol}} \times 100\%$$

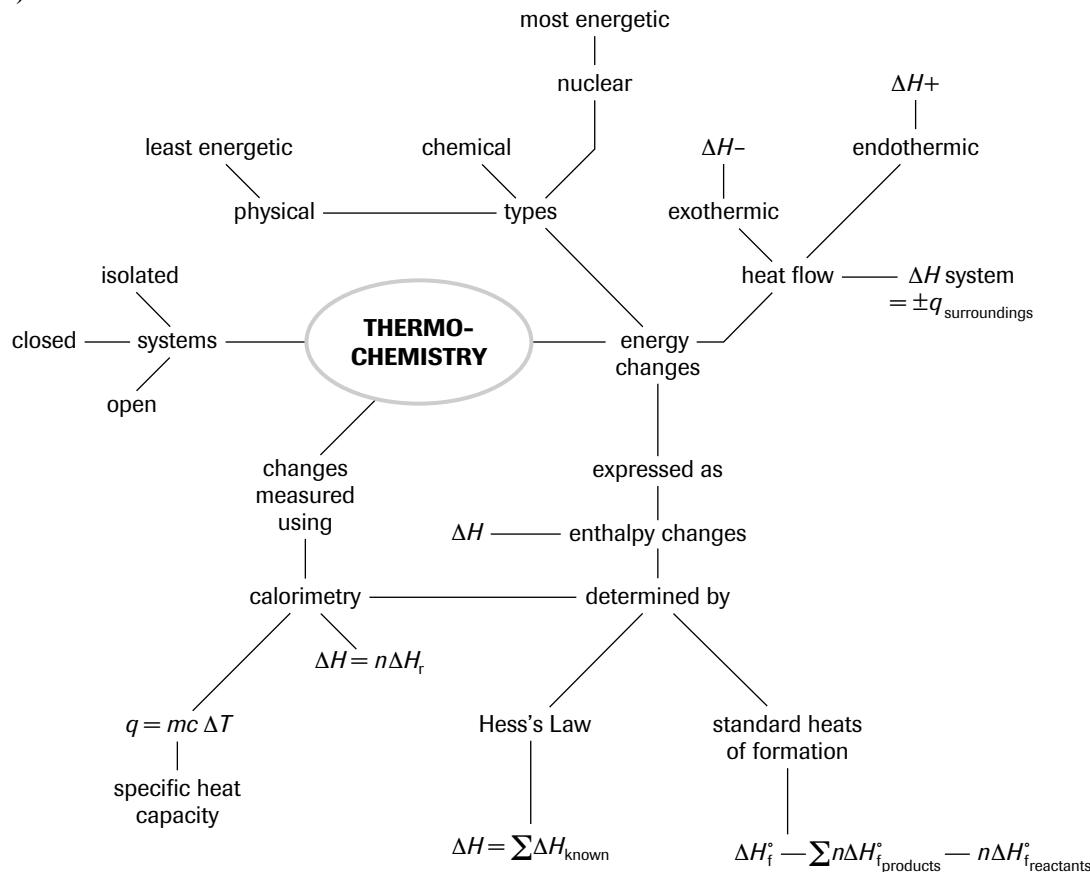
$$\% \text{ difference} = 18\%$$

This is a reasonable result, given relatively simple apparatus.

CHAPTER 5 SUMMARY

MAKE A SUMMARY

(Page 354)



CHAPTER 5 SELF-QUIZ

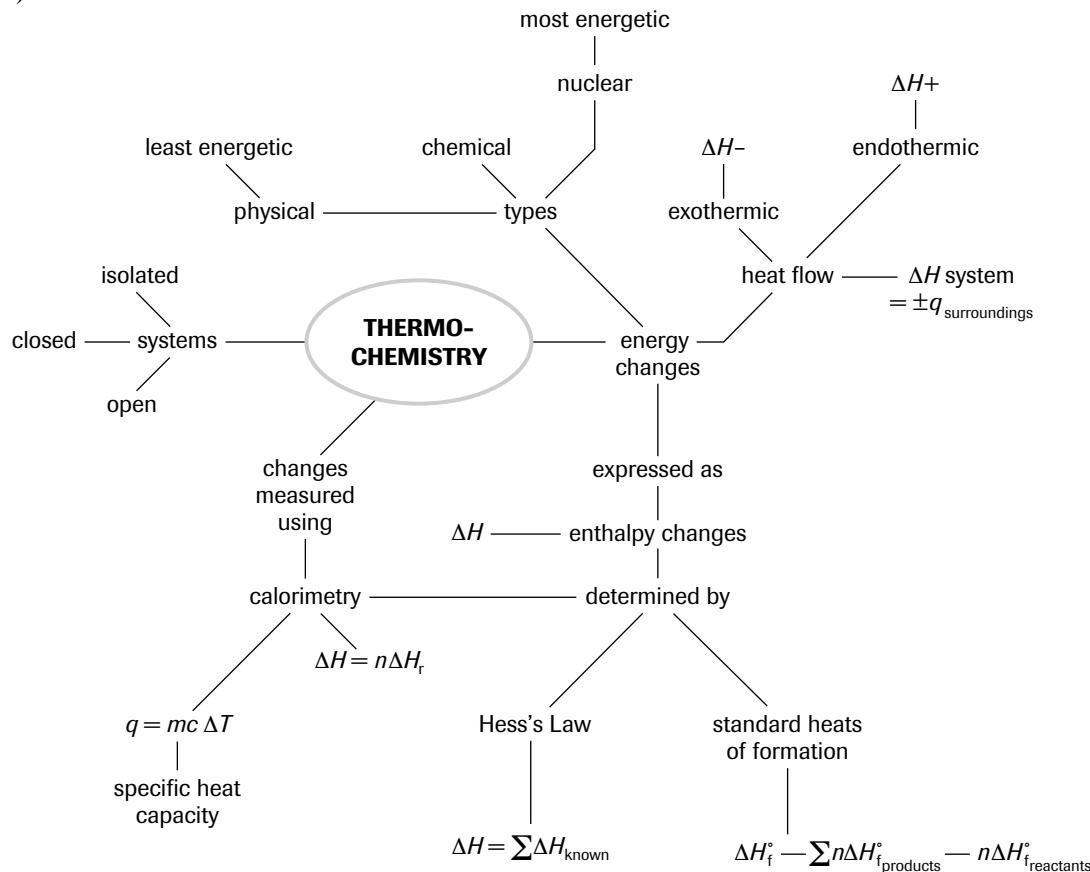
(Page 355)

1. False: Nuclear changes generally *produce* more energy than chemical changes.
2. False: In exothermic reactions, the reactants have more *potential* energy than the products.
3. True
4. False: In endothermic reactions, the heat term is written on the *left* side of the equation.
5. True
6. True
7. False: Burning of gasoline is an example of an *exothermic* physical change.
8. True
9. False: Specific heat capacity is the amount of heat required to change *one gram* through 1°C.
10. True
11. (c)
12. (b)
13. (e)
14. (c)
15. (c)
16. (c)
17. (e)
18. (c)

CHAPTER 5 SUMMARY

MAKE A SUMMARY

(Page 354)



CHAPTER 5 SELF-QUIZ

(Page 355)

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12. (b)
13. (e)
14. (c)
15. (c)
16. (c)
17. (e)
18. (c)

Worked Answers:

$$13. \Delta H_{\text{vap}}(\text{methanol}) = 32.0 \frac{\text{g}}{\text{mol}} \times 1.18 \frac{\text{kJ}}{\text{g}} = 37.8 \text{ kJ/mol (e)}$$

$$16. \frac{120 \text{ g}}{(2 \text{ mol} \times 39.1 \text{ g/mol})} \times 160 \text{ kJ} = 246 \text{ kJ (c)}$$

CHAPTER 5 REVIEW

(Page 356)

Understanding Concepts

1.

Physical	Chemical	Nuclear
(a) change in state or change in arrangement of atoms in molecules	change in arrangement of atoms in molecules	change in arrangement of nuclei
(b) about 10 kJ/mol	about 10^3 kJ/mol	about 10^{11} kJ/mol
(c) freezing water or melting butter	burning gasoline or cooking food	uranium decay or hydrogen fusion in Sun

$$\begin{aligned} 2. c &= \frac{q}{m\Delta T} \\ &= \frac{16\,000 \text{ J}}{938 \text{ g} \times (35.0^\circ\text{C} - 19.5^\circ\text{C})} \\ c &= 1.10 \text{ J/g}^\circ\text{C} \end{aligned}$$

The specific heat capacity of the brick is 1.10 J/g $^\circ$ C.

3. We assume that no heat is lost to the environment, negligible heat is lost to the calorimeter materials unless specific information is given about the container, and dilute aqueous solutions have density and specific heat capacity of water.

$$\begin{aligned} 4. q_{\text{water}} &= mc\Delta T \\ &= 500 \text{ g} \times 4.18 \text{ J/g}^\circ\text{C} \times (80^\circ\text{C} - 20^\circ\text{C}) \\ q_{\text{water}} &= 1.25 \times 10^5 \text{ J} \\ q_{\text{copper}} &= mc\Delta T \\ &= 2000 \text{ g} \times 0.385 \text{ J/g}^\circ\text{C} \times (80^\circ\text{C} - 20^\circ\text{C}) \\ q_{\text{copper}} &= 4.6 \times 10^4 \text{ J} \\ q_{\text{total}} &= q_{\text{water}} + q_{\text{copper}} \\ q_{\text{total}} &= 1.7 \times 10^5 \text{ J, or } 170 \text{ kJ} \\ 170 \text{ kJ of heat is required.} \end{aligned}$$

$$\begin{aligned} 5. m_{\text{water}} &= d \times V \\ &= 1.00 \text{ g/mL} \times 200\,000 \text{ g} \\ m_{\text{water}} &= 2.00 \times 10^5 \text{ g} \\ q_{\text{water}} &= mc\Delta T \\ &= 2.00 \times 10^5 \text{ g} \times 4.18 \text{ J/g}^\circ\text{C} \times (65^\circ\text{C} - 20^\circ\text{C}) \\ q_{\text{water}} &= 3.76 \times 10^4 \text{ kJ} \end{aligned}$$

Worked Answers:

$$13. \Delta H_{\text{vap}}(\text{methanol}) = 32.0 \frac{\text{g}}{\text{mol}} \times 1.18 \frac{\text{kJ}}{\text{g}} = 37.8 \text{ kJ/mol (e)}$$

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CHAPTER 5 REVIEW

(Page 356)

Understanding Concepts

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$$\begin{aligned} 5. m_{\text{water}} &= d \times V \\ &= 1.00 \text{ g/mL} \times 200\,000 \text{ g} \\ m_{\text{water}} &= 2.00 \times 10^5 \text{ g} \\ q_{\text{water}} &= mc\Delta T \\ &= 2.00 \times 10^5 \text{ g} \times 4.18 \text{ J/g}^\circ\text{C} \times (65^\circ\text{C} - 20^\circ\text{C}) \\ q_{\text{water}} &= 3.76 \times 10^4 \text{ kJ} \end{aligned}$$

$$n = \frac{q_{\text{water}}}{\Delta H_{\text{comb}}} \\ = \frac{3.76 \times 10^4 \text{ kJ}}{2200 \text{ kJ/mol}}$$

$$n = 17.1 \text{ mol}$$

$$M_{C_3H_8} = 32.0 \text{ g/mol}$$

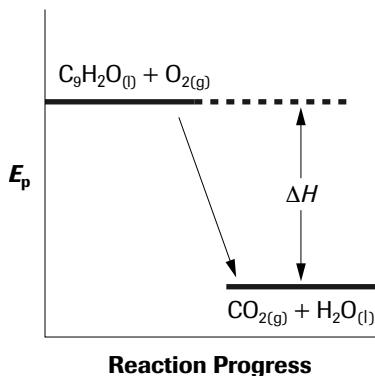
$$m_{C_3H_8} = 17.1 \text{ mol} \times 32.0 \text{ g/mol}$$

$$m_{C_3H_8} = 547 \text{ g propane}$$

You would have to burn 547 g of propane to heat the water.

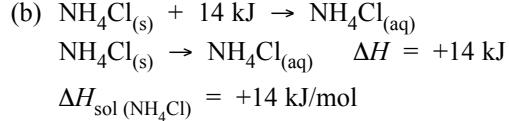
6.

Potential Energy Diagram of the Combustion of Nonane



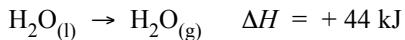
Reaction Progress

7. (a) The enthalpy changes for a reaction may be represented as an energy term in the equation, a ΔH value, the molar enthalpy, or a potential energy diagram.

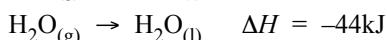


Since the reaction is endothermic, the potential energy diagram will resemble Figure 6(b) on p. 318. Reactant is ammonium chloride solid; product is aqueous ammonium chloride.

8. (a) $H_2O(l) + 44 \text{ kJ} \rightarrow H_2O(g)$ or



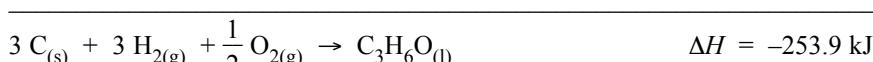
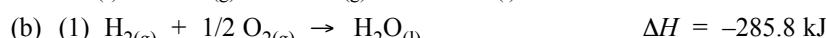
- (b) $H_2O(g) \rightarrow H_2O(l) + 44 \text{ kJ}$ or



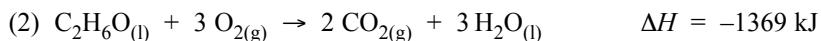
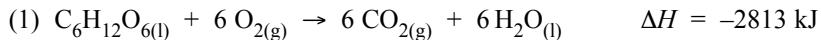
- (c) $2 H_2O(l) + 88 \text{ kJ} \rightarrow 2 H_2O(g)$



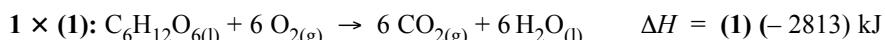
9. (a) $3 C_{(s)} + 3 H_{2(g)} + 1/2 O_{2(g)} \rightarrow C_3H_6O(l)$



10. The known equations are:



The target equation is $\text{C}_6\text{H}_{12}\text{O}_{6(l)} \rightarrow 2 \text{C}_2\text{H}_6\text{O}_{(l)} + 2 \text{CO}_{2(g)}$



or $\Delta H_{\text{comb}} = -74 \text{ kJ/mol}$ glucose

molar mass of glucose, $M = 180 \text{ g/mol}$

$$n_{\text{glucose}} = 500 \text{ g} \times \frac{1 \text{ mol}}{180 \text{ g}}$$

$$n_{\text{glucose}} = 2.78 \text{ mol}$$

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

$$= 2.78 \text{ mol} \times -74 \text{ kJ/mol}$$

$$\Delta H = -206 \text{ kJ}$$

The enthalpy change would be -206 kJ .

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

$$= 3770 \text{ g} \times 4.18 \text{ J/g}^\circ\text{C} \times (98.6 - 16.8)^\circ\text{C}$$

$$q_{\text{water}} = 1.29 \times 10^3 \text{ kJ}$$

$$n\Delta H_{\text{comb}} = q_{\text{water}}$$

$$n = \frac{q_{\text{water}}}{\Delta H_{\text{comb}}}$$

$$= \frac{1.29 \times 10^3 \text{ kJ}}{802 \text{ kJ/mol}}$$

$$n = 1.61 \text{ mol}$$

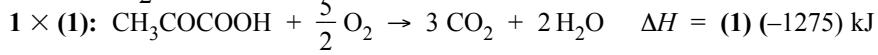
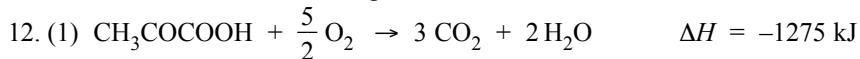
$$M_{\text{CH}_4} = 16.0 \text{ g/mol}$$

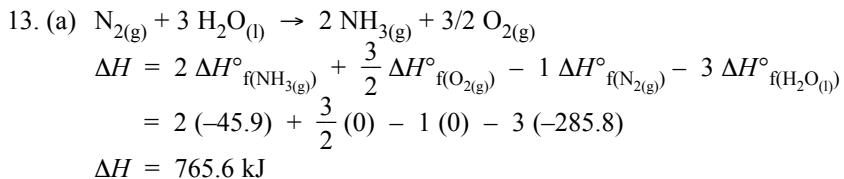
$$m = nM$$

$$= 1.61 \text{ mol} \times 16.0 \text{ g/mol}$$

$$m = 25.7 \text{ g}$$

The minimum mass of natural gas that must be burned to heat 3.77 L of water from 16.8°C to 98.6°C is 25.7 g.





$$\Delta H = 765.6 \text{ kJ}$$

$$\Delta H_r = 765.6 \text{ kJ}/2 \text{ mol } NH_3$$

$$\Delta H_r = 382.8 \text{ kJ/mol } NH_3$$

(b) $n_{\text{ammonia}} = \frac{m}{M}$
 $= \frac{1000 \text{ g}}{17.0 \text{ g/mol}}$

$$n_{\text{ammonia}} = 58.8 \text{ mol}$$

$$\Delta H = n\Delta H_r$$

$$= 58.8 \text{ mol } NH_3 \times 382.8 \text{ kJ/mol } NH_3$$

$$\Delta H = 2.25 \times 10^4 \text{ kJ}$$

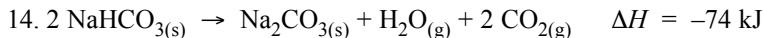
$2.25 \times 10^4 \text{ kJ}$ of solar energy is needed to produce 1.00 kg of ammonia.

(c) area, $a = \frac{2.25 \times 10^4 \text{ kJ}}{(3.60 \times 10^3 \text{ kJ/m}^2)}$

$$a = 6.25 \text{ m}^2$$

An area of 6.25 m^2 would be needed to produce 1.00 kg of ammonia in one day.

- (d) The assumption is made that all of the solar energy will go into the reaction and none will be lost to the surroundings.

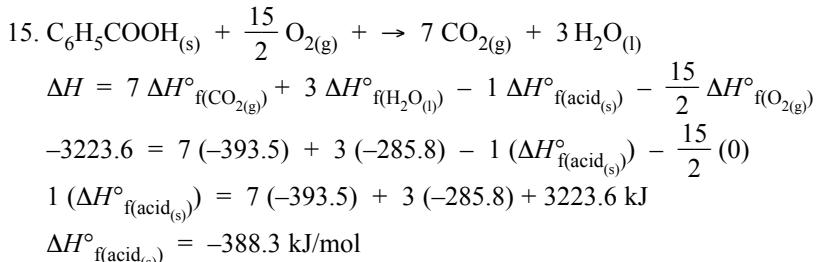


$$\Delta H = 2 \Delta H^\circ_{f(CO_{2(g)})} + 1 \Delta H^\circ_{f(H_{2(l)})} + 1 \Delta H^\circ_{f(Na_2CO_{3(s)})} - 2 \Delta H^\circ_{f(NaHCO_{3(s)})}$$

$$= 2(-393.5) + 1(-241.6) + 1(-1131) - 2(-947.7)$$

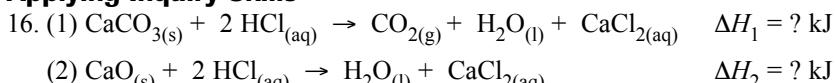
$$\Delta H = -264 \text{ kJ}$$

The enthalpy change for the reaction is -264 kJ .



The molar enthalpy of formation of benzoic acid is -388.3 kJ/mol .

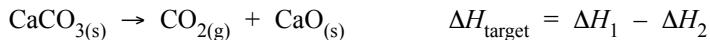
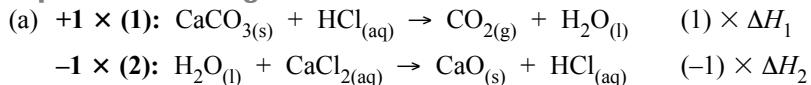
Applying Inquiry Skills



The target equation is



Experimental Design



Procedure

- (b)
- Find the mass of a Styrofoam cup, add about 170 mL of dilute acid, and find the mass of the cup again.
 - Find the mass accurately of about 4 g of CaCO_3 solid.
 - Measure the initial temperature of the acid solution.
 - Add the solid to the acid and stir until a maximum temperature is reached. Record this temperature.
 - Repeat the previous steps for a new cup, sample of acid, and mass of calcium oxide solid.

Analysis

(c) In all three experiments, assume that the acid solution has the same density as water: 1 g/mL.

Experiment 1:

$$\text{mass of acid solution, } m = 173.2 \text{ g} - 3.0 \text{ g}$$

$$m = 170.2 \text{ g}$$

$$q_{\text{water}} = mc\Delta T$$
$$= 170.2 \text{ g} \times 4.18 \text{ J/g}^\circ\text{C} \times (31.0 - 29.0)^\circ\text{C}$$

$$q_{\text{water}} = 1.4(2) \text{ kJ}$$

$$n\Delta H_1 = q_{\text{water}}$$

$$n\Delta H_1 = 1.4(2) \text{ kJ}$$

$$n_{\text{CaCO}_3} = \frac{m}{M}$$
$$= 4.2 \text{ g CaCO}_3 \times \frac{1 \text{ mol}}{100.1 \text{ g CaCO}_3}$$

$$n_{\text{CaCO}_3} = 0.042 \text{ mol}$$

$$\Delta H_1 = \frac{q_{\text{water}}}{n_{\text{CaCO}_3}}$$

$$\Delta H_1 = \frac{1.4(2) \text{ kJ}}{0.042 \text{ mol}}$$

$$\Delta H_1 = 34 \text{ kJ/mol CaCO}_3$$

Because the reaction is exothermic and is written for one mole of CaCO_3 , $\Delta H_1 = -34 \text{ kJ}$.

Experiment 2:

$$\text{mass of acid solution, } m = 158.6 \text{ g} - 3.1 \text{ g}$$

$$m = 155.5 \text{ g}$$

$$q_{\text{water}} = mc\Delta T$$
$$= 155.5 \text{ g} \times 4.18 \text{ J/g}^\circ\text{C} \times (36.0 - 29.0)^\circ\text{C}$$

$$q_{\text{water}} = 4.5(5) \text{ kJ}$$

$$n\Delta H_2 = q_{\text{water}}$$

$$n\Delta H_2 = 4.5(5) \text{ kJ}$$

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

$$= 4.6 \text{ g CaO} \times \frac{1 \text{ mol}}{56.1 \text{ g CaO}}$$

$$n_{\text{CaO}} = 0.0820 \text{ mol}$$

$$\Delta H_2 = \frac{q_{\text{water}}}{n_{\text{CaO}}}$$

$$= \frac{4.5(5) \text{ kJ}}{0.0820 \text{ mol}}$$

$$\Delta H_2 = 55 \text{ kJ/mol CaO}$$

Because the reaction is exothermic and is written for one mole of CaO, $\Delta H_2 = -55 \text{ kJ}$.

$$(d) \Delta H_{\text{target}} = \Delta H_1 - \Delta H_2$$

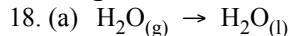
$$= -34 \text{ kJ} - (-55 \text{ kJ})$$

$$\Delta H_{\text{target}} = +19 \text{ kJ}$$

- (e) (i) Less solid would react, so the observed temperature change, calculated q , and ΔH would be smaller than expected.
(ii) Less heat would go into the water, so the observed temperature change, calculated q , and ΔH would be smaller than expected.

17. (a) One possibility is to burn a mass of the alcohol in a bomb calorimeter and determine its heat of combustion, which could be compared to a tabulated value. Another is to dissolve a known mass in water and determine its heat of solution, which could be compared to a tabulated value.
(b) The boiling point of the liquid could be determined. Various diagnostic organic tests could be used to confirm its identity as an alcohol. Derivatives could be made of the alcohol (for example, esters) whose melting and boiling points could be compared to tabulated values.

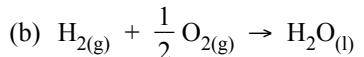
Making Connections



$$\Delta H = \Delta H^\circ_{\text{f}(\text{H}_2\text{O}_{(\text{l})})} - \Delta H^\circ_{\text{f}(\text{H}_2\text{O}_{(\text{g})})}$$

$$= (-285.8) - (-241.8)$$

$$\Delta H = -44 \text{ kJ}$$



$$\Delta H^\circ_{\text{f}(\text{H}_2\text{O}_{(\text{l})})} = -285.5 \text{ kJ/mol}$$

(c) $\Delta H_{\text{fusion}} = -1.7 \times 10^9 \text{ kJ}$

(d) $\Delta H_{\text{condensation}}$ would be about $44/100 \text{ cm}$, or 0.4 cm .

$$\Delta H^\circ_{\text{f}(\text{H}_2\text{O}_{(\text{l})})} \text{ would be about } 285.5/100 \text{ cm}, \text{ or } 3 \text{ cm.}$$

$$\Delta H_{\text{fusion}} \text{ would be about } -1.7 \times 10^9/100 \text{ cm}, \text{ or } 10^8 \text{ cm, or } 1000 \text{ km.}$$

(e) (Answers will vary.) 0.4 g is about the mass of a fingernail; 3 g is about the mass of a teaspoon of sugar; 1000 kg is about the mass of a small car.

19. Answers will vary, but could include the special demands of geography (Canada is a large country requiring transportation over great distances), temperature (Canada is a cool country requiring heating of homes and businesses), and the economy (Canada is an economically strong country with heavy industry that demands power). Furthermore, Canadians enjoy and expect a high standard of living, with many consumer goods.

CHAPTER 6 CHEMICAL KINETICS

Reflect on Your Learning

(Page 358)

1. (a) Some possibilities include increasing temperature, using a higher concentration of reactants, increasing the surface area of the reactants if the system is heterogeneous, or adding a catalyst.
(b) Examples are, respectively: cooking food, using concentrated acid, starting a campfire with twigs, and using industrial catalysts.
2. Answers will vary but the mechanism of the reaction involves collisions of octane and oxygen molecules in which single carbon–carbon and single carbon–hydrogen bonds are broken in succession down the hydrocarbon chain with reformation of bonds to form carbon dioxide and water molecules.
3. Some reactant molecules have complex structures and strong chemical bonds which make reaction more difficult. Other reactions involve simple ions or molecules with weak or unstable chemical bonds in which most collisions result in reaction. Some reactions produce large amounts of heat that accelerate further reaction.

Try This Activity: Slowing the Browning Process

(Page 359)

- (a) Apples react with oxygen from the air.
- (b) The lemon juice is an antioxidant that slows the reaction.
- (c) Temperature is the variable.
- (d) Reducing the concentration of a reactant is investigated.
- (e) Lemon juice, refrigeration, and removal of oxygen should all reduce rate.

6.1 RATE OF REACTION

PRACTICE

(Page 361)

Understanding Concepts

$$\begin{aligned}1. \quad r &= \frac{\Delta c}{\Delta t} \\&= \frac{(0.200 \text{ mol/L})}{40 \text{ s}} \\r &= 0.0050 \text{ mol/(L}\cdot\text{s})\end{aligned}$$

$$\begin{aligned}2. \quad r &= \frac{\Delta c}{\Delta t} \\&= \frac{(0.60 \text{ mol/L})}{5 \text{ min}} \\r &= 0.12 \text{ mol/(L}\cdot\text{min})\end{aligned}$$

PRACTICE

(Page 364)

Understanding Concepts

1. Rate of reaction with respect to $\text{Fe}_{(\text{aq})}^{+2}$ consumption is $2.0 \times 10^{-1} \text{ mol Fe}_{(\text{aq})}^{+2}/(\text{L}\cdot\text{min})$
 $\text{H}_{(\text{aq})}^+$ consumption is $3.2 \times 10^{-1} \text{ mol H}_{(\text{aq})}^+/(\text{L}\cdot\text{min})$

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Reflect on Your Learning

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PRACTICE

(Page 361)

Understanding Concepts

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PRACTICE

(Page 364)

Understanding Concepts

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 $\text{H}_{(\text{aq})}^+$ consumption is $3.2 \times 10^{-1} \text{ mol H}_{(\text{aq})}^+/(\text{L}\cdot\text{min})$

$Mn_{(aq)}^{+2}$ production is $4.0 \times 10^{-2} \text{ mol } Mn_{(aq)}^{+2}/(\text{L}\cdot\text{min})$

$Fe_{(aq)}^{+3}$ production is $2.0 \times 10^{-1} \text{ mol } Fe_{(aq)}^{+3}/(\text{L}\cdot\text{min})$

$H_2O_{(l)}$ production is $1.6 \times 10^{-1} \text{ mol } H_2O_{(l)}/(\text{L}\cdot\text{min})$

2. (a) $\frac{\Delta[O_{2(g)}]}{\Delta t} = \frac{5}{4} \times 2.0 \times 10^{-2} \text{ mol } O_{2(g)}/(\text{L}\cdot\text{s})$

(b) $\frac{\Delta[H_2O_{(g)}]}{\Delta t} = \frac{6}{4} \times 2.0 \times 10^{-2} \text{ mol } H_2O_{(g)}/(\text{L}\cdot\text{s})$

$$= 3.0 \times 10^{-2} \text{ mol } H_2O_{(g)}/(\text{L}\cdot\text{s})$$

3. (a) Rate of production of NO_2 :

$$+\frac{\Delta[NO_2]}{\Delta t} = 4.0 \times 10^{-3} \text{ mol } NO_2/(\text{L}\cdot\text{s})$$

- (b) Rate of consumption of NO :

$$\frac{\Delta[NO]}{\Delta t} = 4.0 \times 10^{-3} \text{ mol } NO/\text{L}\cdot\text{s}$$

Rate of consumption of O_2 :

$$-\Delta\frac{[O_2]}{\Delta t} = 2.0 \times 10^{-3} \text{ mol } O_2/(\text{L}\cdot\text{s})$$



- (a) Rate of consumption of $NaHCO_3$:

$$\frac{\Delta m}{\Delta t} = 3.25 \text{ g } NaHCO_3/20 \text{ s}$$

$$\frac{\Delta m}{\Delta t} = 0.16(3) \text{ g } NaHCO_3/\text{s}$$

(b) $n_{NaHCO_3} = 3.25 \text{ g} \times \frac{1 \text{ mol}}{84.0 \text{ g}}$

$$n_{NaHCO_3} = 0.0387 \text{ mol}$$

$$n_{H_2SO_4} = 0.0387 \text{ mol } NaHCO_3 \times \frac{1 \text{ mol } H_2SO_4}{2 \text{ mol } NaHCO_3}$$

$$n_{H_2SO_4} = 0.0193 \text{ mol } H_2SO_4$$

$$m_{H_2SO_4} = 0.0193 \text{ mol} \times \frac{98.1 \text{ g}}{1 \text{ mol}}$$

$$m_{H_2SO_4} = 1.89 \text{ g } H_2SO_4$$

Rate of consumption of H_2SO_4 :

$$\frac{\Delta m}{\Delta t} = \frac{1.89 \text{ g } H_2SO_4}{20 \text{ s}}$$

$$\frac{\Delta m}{\Delta t} = 0.095 \text{ g } H_2SO_4/\text{s}$$

(c) $\frac{n_{H_2SO_4}}{\Delta t} = \frac{0.0193 \text{ mol } H_2SO_4}{20 \text{ s}}$

$$\frac{n_{H_2SO_4}}{\Delta t} = 9.7 \times 10^{-4} \text{ mol } H_2SO_4/\text{s}$$

(d) $\frac{n_{CO_2}}{\Delta t} = \frac{0.0387 \text{ mol } CO_2}{20 \text{ s}}$

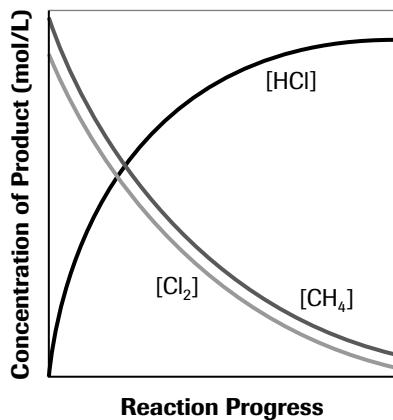
$$\frac{n_{CO_2}}{\Delta t} = 1.9 \times 10^{-3} \text{ mol } CO_2/\text{s}$$

PRACTICE

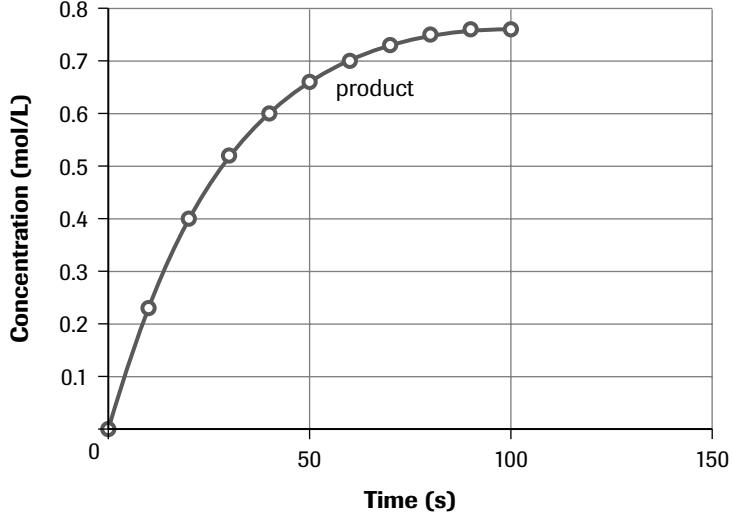
(Page 365)

Understanding Concepts

5. Pressure or volume (of gases), colour, conductivity, or pH (of solutions) could all be used to measure a reaction rate.
6. (a) colour (Permanganate is purple.)
(b) pressure or volume of hydrogen gas
7. Concentrations of reactants are highest at the beginning of a reaction, and rate depends on concentrations.
8. **Change of Concentration Over Time**



9. (a)



$$(b) \frac{\Delta c_{\text{product}}}{\Delta t} = \frac{0.70 \text{ mol/L} - 0 \text{ mol/L}}{60 \text{ s} - 0 \text{ s}}$$

$$\frac{\Delta c_{\text{product}}}{\Delta t} = 0.011(7) \text{ mol/(L}\cdot\text{s)}$$

$$(c) \frac{\Delta c_{\text{product}}}{\Delta t} = \frac{0.70 \text{ mol/L} - 0.40 \text{ mol/L}}{60 \text{ s} - 20 \text{ s}}$$

$$\frac{\Delta c_{\text{product}}}{\Delta t} = 0.0075 \text{ mol/(L}\cdot\text{s)}$$

$$(d) \quad r = \frac{\Delta c_{\text{product}}}{\Delta t}$$

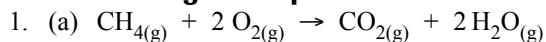
$$= \frac{(0.40 - 0.13) \text{ mol/L}}{(20 - 0) \text{ s}}$$

$$\frac{\Delta c_{\text{product}}}{\Delta t} = 0.014 \text{ mol/(L}\cdot\text{s)}$$

SECTION 6.1 QUESTIONS

(Page 366)

Understanding Concepts



Rate of consumption of methane:

$$\frac{-\Delta[\text{CH}_4]}{\Delta t} = \frac{8.0 \text{ mol}}{2.00 \text{ L} \times 3.2 \text{ s}}$$

$$\frac{-\Delta[\text{CH}_4]}{\Delta t} = 1.2(5) \text{ mol/(L}\cdot\text{s)}$$

(b) Rate of consumption of oxygen:

$$\frac{-\Delta[\text{O}_2]}{\Delta t} = \frac{2}{1} \times 1.2(5) \text{ mol/(L}\cdot\text{s)}$$

$$\frac{-\Delta[\text{O}_2]}{\Delta t} = 2.5 \text{ mol/(L}\cdot\text{s)}$$

(c) Rate of production of carbon dioxide:

$$\frac{+\Delta[\text{CO}_2]}{\Delta t} = \frac{1}{1} \times 1.2(5) \text{ mol/(L}\cdot\text{s)}$$

$$\frac{+\Delta[\text{CO}_2]}{\Delta t} = 1.2(5) \text{ mol/(L}\cdot\text{s)}$$

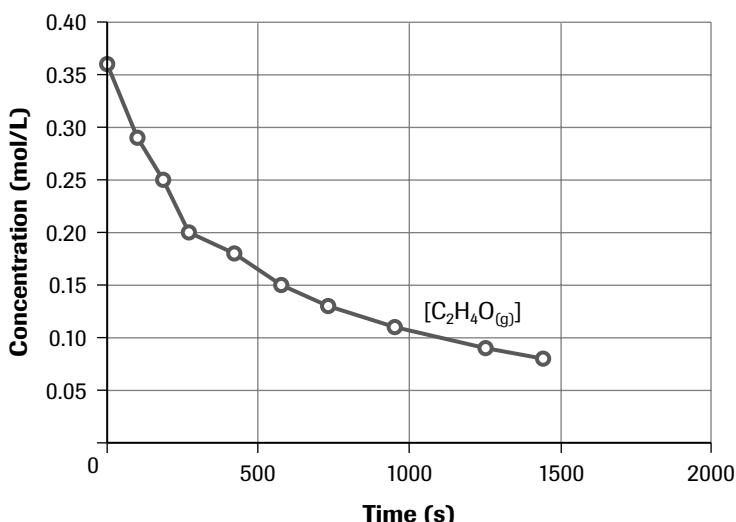
(d) Rate of production of water vapour:

$$\frac{+\Delta[\text{H}_2\text{O}]}{\Delta t} = \frac{2}{1} \times 1.2(5) \text{ mol/(L}\cdot\text{s)}$$

$$\frac{+\Delta[\text{H}_2\text{O}]}{\Delta t} = 2.5 \text{ mol/(L}\cdot\text{s)}$$

2. (a)

Concentration of Ethanal During Thermal Decomposition



$$(b) \text{ rate}_{(t=0 \text{ to } 420 \text{ s})} = \frac{(0.360 - 0.180) \text{ mol/L}}{(420 - 0) \text{ s}} \\ = 4.3 \times 10^{-4} \text{ mol/(L}\cdot\text{s)}$$

$$(c) \text{ rate}_{(t=420 \text{ to } 1250 \text{ s})} = \frac{(0.180 - 0.090) \text{ mol/L}}{(1250 - 420) \text{ s}} \\ = 1.1 \times 10^{-4} \text{ mol/(L}\cdot\text{s)}$$

- (d) Rate falls as the concentration of the reactant(s) falls.
(e) Extrapolation yields a value of about 2000 s.
(f) From slopes of the appropriate tangents, approximate rates are:

$$\text{rate}_{(c=0.20 \text{ mol/L})} = 2.8 \times 10^{-4} \text{ mol/(L}\cdot\text{s)}$$

$$\text{rate}_{(c=0.10 \text{ mol/L})} = 8.3 \times 10^{-5} \text{ mol/(L}\cdot\text{s)}$$

Making Connections

3. (a) (Answers will vary.) Some possibilities include increasing temperature, using a higher concentration of reactants, increasing the surface area of the reactants if the system is heterogeneous, or adding a catalyst.
- (b) Examples are, respectively: baking a cake, using pure oxygen gas in an oxyacetylene torch, dust explosions, and using a catalyst disc in contact lens solution.
- (c) (Answers will vary, depending on individual student responses.)

6.2 FACTORS AFFECTING REACTION RATE

PRACTICE

(Page 371)

Understanding Concepts

1. The five factors are: the chemical nature of reactants (gold vs. sodium in water); temperature (burning wood); surface area (steel wool burning in pure oxygen); concentration (magnesium into dilute or concentrated acid); catalysis (manganese dioxide in hydrogen peroxide).
2. Only one factor — surface area — applies to heterogeneous systems (e.g., grain dust explodes whereas grain smoulders).
3. The rate would double or triple for each increase of 10°C; for a 20°C rise, the rate would increase by a factor of roughly 4 to 10 times.
4. Increased surface area increases reaction rate. The lump of coal has a very small surface area, compared to that of a similar mass of coal dust.
5. Possible leaks of these gases would increase concentrations of reactants, thus increasing the possible rate of combustion of fuels.

Making Connections

6. Enzymes are key catalysts in metabolic reactions. “Poisoning” of these catalysts can seriously upset body chemistry.
7. BHT is an antioxidant or inhibitor (negative catalyst) that decreases the rate of food decay reactions.

SECTION 6.2 QUESTIONS

(Page 371)

Understanding Concepts

1. (a) chemical nature of reactant
(b) temperature
(c) catalysis
(d) surface area
(e) concentration

$$(b) \text{ rate}_{(t=0 \text{ to } 420 \text{ s})} = \frac{(0.360 - 0.180) \text{ mol/L}}{(420 - 0) \text{ s}} \\ = 4.3 \times 10^{-4} \text{ mol/(L}\cdot\text{s)}$$

$$(c) \text{ rate}_{(t=420 \text{ to } 1250 \text{ s})} = \frac{(0.180 - 0.090) \text{ mol/L}}{(1250 - 420) \text{ s}} \\ = 1.1 \times 10^{-4} \text{ mol/(L}\cdot\text{s)}$$

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Making Connections

3. (a) (Answers will vary.) Some possibilities include increasing temperature, using a higher concentration of reactants, increasing the surface area of the reactants if the system is heterogeneous, or adding a catalyst.
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PRACTICE

(Page 371)

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Making Connections

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7. BHT is an antioxidant or inhibitor (negative catalyst) that decreases the rate of food decay reactions.

SECTION 6.2 QUESTIONS

(Page 371)

Understanding Concepts

1. (a) chemical nature of reactant
(b) temperature
(c) catalysis
(d) surface area
(e) concentration

2. Hydrochloric acid has a much higher concentration of reactive hydrogen ions in solution than carbonic acid. Most of the carbonic acid remains in solution undissociated.

Making Connections

3. To be suitable for starting a campfire, fuel should be flammable (chemical nature), and have a high surface area (more subdivided if a solid).
4. Heterogeneous catalysts are easier to separate from the products and reuse. Since many catalysts are very expensive, reuse is very important economically. For example, vanadium(V) oxide is a solid catalyst used in the industrial production of millions of tonnes of sulfuric acid; platinum is used in the manufacture of nitrogen dioxide, and so on.
5. Catalytic converters are used to remove carbon monoxide, VOCs (volatile organic compounds), and NOx (nitrogen oxides) from exhaust. Two separate types of catalysts, reduction and oxidation catalysts, are arranged in a honeycomb pattern. Nitrogen oxides are reduced to nitrogen and oxygen by the reduction catalyst. The oxidation catalyst changes carbon monoxide and unburned hydrocarbons (VOCs) into carbon dioxide and water.

6.3 RATE LAWS AND ORDER OF REACTION

PRACTICE

(Page 377)

Understanding Concepts

1. Order of reaction refers to the rate dependence or exponential index of one species in the rate law, whereas overall order is the sum of all the indices. If a rate law were $r = k[A][B]^2$, the order of reaction with respect to A would be 1, the order of reaction with respect to B would be 2, and the overall order would be 3.
2. This is a first-order reaction, so doubling the initial concentration should double the initial rate.

$$\begin{aligned} 3. \text{ (a)} \quad k &= \frac{r}{([\text{NH}_4^{+}] [\text{NO}_2^{-}])} \\ &= \frac{2.40 \times 10^{-7} \text{ mol/(L}\cdot\text{s})}{(0.200 \text{ mol/L} \times 0.00500 \text{ mol/L})} \\ k &= 2.4 \times 10^{-4} \text{ L/(mol}\cdot\text{s}) \end{aligned}$$

$$\begin{aligned} \text{(b)} \quad r &= k[\text{NH}_4^{+}][\text{NO}_2^{-}] \\ &= 3.20 \times 10^{-4} \text{ L/(mol}\cdot\text{s}) \times 0.100 \text{ mol/L} \times 0.0150 \text{ mol/L} \\ r &= 4.8 \times 10^{-7} \text{ mol/(L}\cdot\text{s}) \end{aligned}$$

4. (a) Rate is second order with respect to A, first order with respect to B, zeroth order with respect to C.
 (b) $r = k[A]^2[B]$
5. (a) The reaction rate constant increases.
 (b) The reaction rate constant is unchanged.
6. (a) When we compare Trials 1 and 2, we see that as [A] is doubled, rate is multiplied by 4; therefore, rate depends on $[A]^2$.
 When we compare Trials 1 and 3, we see that as [B] is tripled, rate is multiplied by 1; therefore, rate depends on $[B]^0$.
 When we compare Trials 2 and 4, we see that as [C] is doubled, rate is multiplied by 2; therefore, rate depends on $[C]^1$.
 (b) $r = k[A]^2[C]^1$

- (c) When we use data from Trial 1,

$$\begin{aligned} k &= \frac{r}{[A]^2[C]} \\ &= \frac{3.0 \times 10^{-4} \text{ mol/(L}\cdot\text{s})}{(0.10 \text{ mol/L})^2 \times 0.10 \text{ mol/L}} \\ k &= 0.30 \text{ L}^2/(\text{mol}^2\cdot\text{s}) \end{aligned}$$

2. Hydrochloric acid has a much higher concentration of reactive hydrogen ions in solution than carbonic acid. Most of the carbonic acid remains in solution undissociated.

Making Connections

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6.3 RATE LAWS AND ORDER OF REACTION

PRACTICE

(Page 377)

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$$\begin{aligned} \text{(b)} \quad r &= k[\text{NH}_4^{+}][\text{NO}_2^{-}] \\ &= 3.20 \times 10^{-4} \text{ L/(mol}\cdot\text{s}) \times 0.100 \text{ mol/L} \times 0.0150 \text{ mol/L} \\ r &= 4.8 \times 10^{-7} \text{ mol/(L}\cdot\text{s}) \end{aligned}$$

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 When we compare Trials 2 and 4, we see that as [C] is doubled, rate is multiplied by 2; therefore, rate depends on $[C]^1$.
 (b) $r = k[A]^2[C]^1$
- (c) When we use data from Trial 1,

$$\begin{aligned} k &= \frac{r}{[A]^2[C]} \\ &= \frac{3.0 \times 10^{-4} \text{ mol/(L}\cdot\text{s})}{(0.10 \text{ mol/L})^2 \times 0.10 \text{ mol/L}} \\ k &= 0.30 \text{ L}^2/(\text{mol}^2\cdot\text{s}) \end{aligned}$$

$$\begin{aligned}
 (d) \quad r &= k[A]^2[C]^1 \\
 &= 0.30 \text{ L}^2/(\text{mol}^2\cdot\text{s}) \times (0.40 \text{ mol/L})^2 \times 0.40 \text{ mol/L} \\
 r &= 1.9 \times 10^{-2} \text{ mol/(L}\cdot\text{s})
 \end{aligned}$$

PRACTICE

(Page 381)

Understanding Concepts

7. (a) 72 a is three half-lives.
 Remaining mass, $m = 0.084 \text{ g} \times \frac{1}{2} \times \frac{1}{2} \times \frac{1}{2}$
 $m = 0.0105 \text{ g}$
- (b) 192 a is eight half-lives.
 Remaining mass, $m = 0.084 \times (\frac{1}{2})^8$
 $= \frac{0.084 \text{ g}}{256}$
 $m = 3.3 \times 10^{-4} \text{ g}$
8. (a) $t_{1/2} = \frac{0.693}{k}$
 $= \frac{0.693}{2.34 \times 10^{-3} \text{ s}^{-1}}$
 $t_{1/2} = 296 \text{ s}$
- (b) 12.5% is $1/8$ or $(1/2)^3$, which suggests three half-lives have passed.
 The time elapsed will be $3 \times 296 \text{ s} = 888 \text{ s}$.

Making Connections

9. Radioisotopes in such patients emit dangerous radioactive particles within the body and to the surroundings, but this emission declines over time. The most appropriate isotopes are those with a short half-life.

SECTION 6.3 QUESTIONS

(Page 381)

Understanding Concepts

1. First-order reaction implies a rate law in which only one species is present, with a rate dependence of one (e.g., $r = k[A]^1$).
 Second-order reaction implies a rate law in which two molecules are present, with a total rate dependence of two (e.g., $r = k[A]^2$ or $r = k[A][B]$).
2. (a) The orders of reaction are: 1 with respect to $\text{Cl}_{2(g)}$, and 2 with respect to $\text{NO}_{(g)}$.
 (b) The rate would double.
 (c) The rate would multiply by 9.
 (d) $k = \frac{r}{[\text{Cl}_2][\text{NO}]^2}$
 $= \frac{0.0242 \text{ mol/(L}\cdot\text{s)}}{0.20 \text{ mol/L} \times (0.20 \text{ mol/L})^2}$
 $k = 3.0 \text{ L/(mol}\cdot\text{s)}$
- (e) $r = k[\text{Cl}_2][\text{NO}]^2$
 $= 3.00 \text{ L/(mol}\cdot\text{s}) \times 0.44 \text{ mol/L} \times (0.025 \text{ mol/L})^2$
 $r = 8.2(5) \times 10^{-4} \text{ mol/(L}\cdot\text{s)}$

3. (a) $r = k [\text{antibiotic}]$

$$\begin{aligned} \text{(b)} \quad t_{1/2} &= 0.693/k \\ &= \frac{0.693}{1.40 \text{ a}^{-1}} \\ t_{1/2} &= 0.495 \text{ a} \end{aligned}$$

(c) 2.0 a is about 4 half-lives.

$$m = 20 \text{ g} \times (1/2)^4$$

$$m = 2.5 \text{ g}$$

4. $1.84 \times 10^6 \text{ a} \text{ is } \frac{1.84 \times 10^6 \text{ a}}{2.3 \times 10^8 \text{ a}} = 8 \text{ half-lives}$

$$m = 10.0 \text{ g} \times \left(\frac{1}{2}\right)^8$$

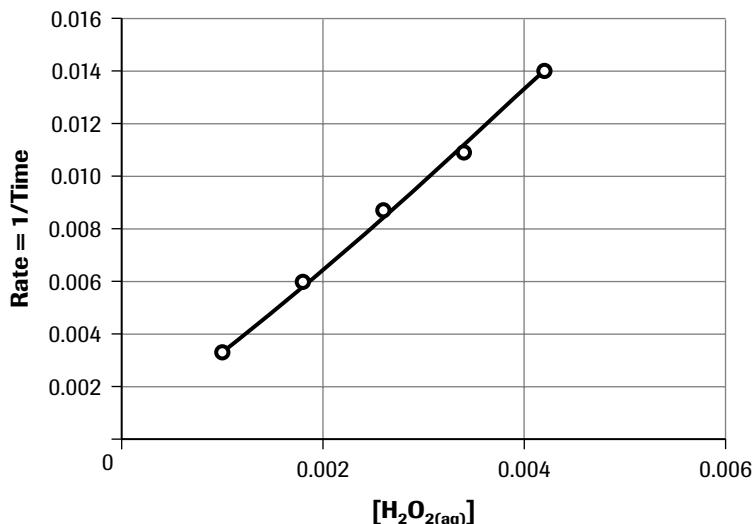
$$m = 0.039 \text{ g}$$

Applying Inquiry Skills

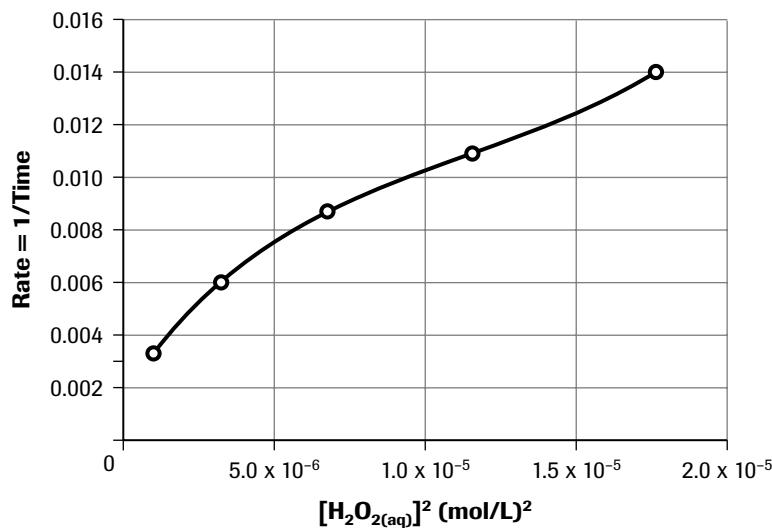
5. Analysis

(a) The order of reaction can be determined by plotting 1/time vs. $[\text{H}_2\text{O}_2]$.

First-Order Plot at Different Concentrations



Second-Order Plot at Different Concentrations



6. Question

What is the effect on rate of reaction on the iodine clock reaction?

Prediction

Predict qualitatively what will happen to the time of reaction as the temperature is increased. What will happen to the rate of reaction?

Experimental Design

A series of solutions will be prepared in which the only variable is the temperature. Equal amounts of starch, sodium bisulfite, and hydrochloric acid will be mixed with each of these solutions, so that the time from mixing to formation of a blue-black product can be recorded. The evidence will be analyzed graphically.

Materials

lab apron

eye protection

0.020 mol/L potassium iodate solution (Solution A)

0.001 00 mol/L sodium bisulfite/hydrochloric acid/starch solution (Solution B)

distilled water

3 plastic micropipets, labelled A, B, and H₂O

3 100-mL beakers, labelled A, B, and H₂O

2 large-well microtrays or spot plates, labelled A and B

stopwatch

hot plate

CAUTION:

There are no major safety concerns with this investigation. Follow general lab safety procedures.

Procedure

1. Place a test tube of Solution A and a test tube of Solution B in each of five water baths at different temperatures.
2. Place the two microtrays on clean sheets of white paper. For microtray A, using the appropriate micropipets, place 10 drops of Solution A (at different temperatures) in Wells 1–5. For microtray B, using the appropriate micropipets, place 10 drops of Solution B (at corresponding temperatures) in Wells 1–5.
3. With stopwatch ready, and using the water pipet, transfer the contents of Plate A Well 1 into Plate B Well 1. In doing so, insert the tip of the pipet below the surface of the liquid in Plate B to ensure that the solutions mix thoroughly and keep stirring. Start timing at the moment the pipet is squeezed and stop when the colour first appears. Record your observations.
4. Repeat this process for the other four temperatures of solutions.
5. Dispose of solutions down the drain with lots of running water.

Making Connections

7. (Answers will vary.) Most carbon on Earth is carbon-12. However, the atmosphere contains a small constant percentage of carbon-14, because there is an equilibrium between the rate of its production and its decay. Living animals and plants also contain a constant level of C-14, but at death the organism becomes isolated from the atmosphere and the C-14 starts to decay at a known rate of about 1.2% every century. The remaining percentage of C-14 in artifacts can be used to determine their age. Other radioisotopes used in dating artifacts and soil samples include U-238, Th-232, and K-40.
8. (a) (Answers will vary.) Types of nuclear wastes produced from electricity generation activities can be categorized as low-level wastes and high-level wastes. Low-level wastes are mostly items related to operations, such as mops, plastic sheeting, protective clothing, and paper products. These make up around 1% of the waste and are easily stored in monitored facilities. High-level waste is the used nuclear fuel removed from the reactors. This fuel is in the form of solid ceramic pellets, which must be stored in shielded facilities.
(b) AECL stores some solid low-level radioactive wastes at its Chalk River Laboratories in Ontario, in above-ground storage buildings. Since used reactor fuel is compact, solid, low in volume, and stable in a water environment, it is initially stored in deep-water pools used for cooling and shielding. After a few years, the used fuel may be moved to above-ground dry storage in concrete canisters.
(c) Proposed methods include storage deep underground in unused mines.
(d) Opposition could be based on environmental concerns. Support could be based on economic benefits to the community.

6.4 COLLISION THEORY AND RATE OF REACTION

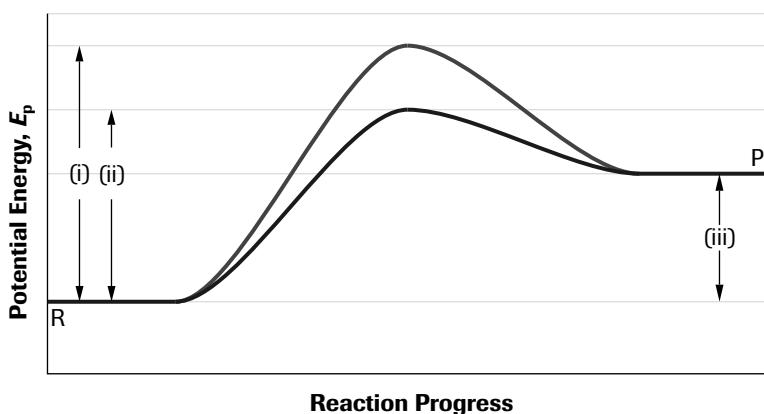
PRACTICE

(Page 387)

Understanding Concepts

1. (a)

Potential Energy Diagram for System R→P



- (b) The lower curve represents a catalyzed reaction; the upper curve represents the uncatalyzed reaction.
- (c) The reaction is endothermic so heat flows from the surroundings into the system.
- (d) (i) is the activation energy for the uncatalyzed reaction; (ii) is the activation energy for the catalyzed reaction; (iii) is the enthalpy change.

PRACTICE

(Page 390)

Understanding Concepts

- 2. (a) When we compare Trials 1 and 2, we see that as $[A_2]$ is doubled, rate is multiplied by 2; therefore, rate depends on $[A_2]^1$.
When we compare Trials 1 and 3, we see that as $[B]$ is doubled, rate is multiplied by 1; therefore, rate depends on $[B]^0$.
Overall, rate, $r = k [A_2]^1$.
- (b) The rate-determining step is $A_2 \rightarrow$ product.
- (c) $A_2 \rightarrow A + A$ (slow step)
 $A + B \rightarrow AB$ (fast step)

SECTION 6.4 QUESTIONS

(Page 391)

Understanding Concepts

- 1. An elementary step involves one, two, or three molecule collisions in a mechanism. The slowest elementary step in a mechanism is the rate-determining step.
- 2. (a) $2 A + B + E \rightarrow F$
(b) The first step involves the most molecules and is probably the slowest, or rate-determining, step.
- 3. (a) 60 kJ (from reactants to highest activated complex)
(b) -35 kJ
(c) $R \rightarrow W$ (biggest individual activation energy)
(d) exothermic overall
(e) V, X, Z
(f) W, Y

Making Connections

4. (a) (Answers will vary.) The mechanism of the reaction involves collisions of octane and oxygen molecules in which single carbon–carbon and single carbon–hydrogen bonds are broken in succession down the hydrocarbon chain with reformation of bonds to form carbon dioxide and water molecules at each step.
(b) (Answers will vary.) Rates can be explained and predicted on the basis of collisions of molecules.
5. (a) (Answers will vary.) Ground-level ozone can damage lung tissue.
(b) Ground-level ozone is produced in the atmosphere by a photochemical smog mechanism, which involves the oxidations of volatile organic compounds in the presence of nitrogen oxides and sunlight.
(c) The reaction is catalyzed by the partially combusted hydrocarbon molecules that are produced in automobile exhausts.
6. (Answers will vary, but should include information about award-winning and more recent research and discoveries.)

6.5 EXPLAINING AND APPLYING CHEMICAL KINETICS

PRACTICE

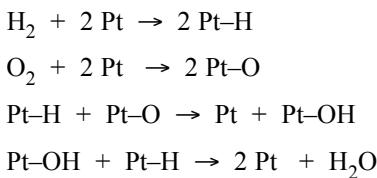
(Page 396)

Understanding Concepts

1. (a) temperature, concentration, surface area
(b) temperature, catalysis, chemical nature of reactants
2. (a) $2 \text{H}_{2(\text{g})} + \text{O}_{2(\text{g})} \rightarrow 2 \text{H}_2\text{O}_{(\text{g})}$

This reaction is unlikely to occur in a single step because it would involve the collision of three molecules simultaneously.

- (b) (Answers will vary.) The actual mechanism appears to be:



(from <http://www.iupac.org/news/prize/2001/michaelides.html>)

3. (a) heterogeneous
(b) homogeneous (all gases)
(c) homogeneous (all aqueous)
(d) heterogeneous
4. (a) Oxalate ions are more complex than ferrous ions, requiring more precise collision geometry and a higher activation energy. The fraction of successful collisions is lower.
(b) Steel wool has a larger surface area than a nail. The collision frequency (i.e., the number of collisions per second among reactant molecules) is higher.
(c) Nitroglycerin tablets have a much lower concentration. The collision frequency (i.e., the number of collisions per second among reactant molecules) is higher.

Making Connections

5. (a) $\text{Cl}_{2(\text{g})} + \text{H}_{2(\text{g})} \rightarrow 2 \text{HCl}_{(\text{g})}$
(b) Cl_(g) and H_(g)
(c) Because a smaller activation energy barrier indicates a faster reaction rate, the collision with atomic chlorine must have a much smaller activation energy than that for molecular chlorine.
6. (Answers will vary, and should include specific reference to industrial applications catalyzed by platinum.) Examples include hydrogenation of ethene to ethane, formation of sulfur trioxide in sulfuric acid production, and even application in setting of dental impression compounds.
7. (Answers might include the following:
 - addition of chemicals like salt or sugar (somewhat like inhibition or negative catalysis)
 - sealing (reducing concentration of oxygen in air))

Making Connections

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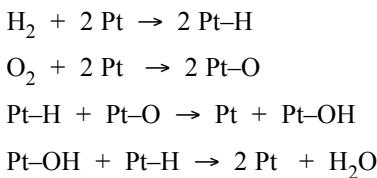
(Page 396)

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(b) temperature, catalysis, chemical nature of reactants
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7. (Answers might include the following:
 - addition of chemicals like salt or sugar (somewhat like inhibition or negative catalysis)
 - sealing (reducing concentration of oxygen in air))

- refrigeration (reduction of temperature)
- preserving large blocks of food (reducing surface area)
- choosing foodstuffs that naturally decay more slowly (chemical nature of reactants)

Explore an Issue: Debate: Food Preservation

(Page 397)

- (Answers will vary, but should include research from several stated sources, organized into relevant categories (e.g., from the manufacturing industry, from health-watch groups, from the medical community), and used to back up the students' arguments.)
- (Answers will vary, but should outline how and possibly why the vote changed.)

PRACTICE

(Page 398)

Making Connections

- (Answers will vary, depending on career chosen and geographical location.)

PRACTICE

(Page 400)

Understanding Concepts

- $k = Ae^{-E_a/RT}$

At $T = 20^\circ\text{C}$,

$$E_a/RT = \frac{2.00 \times 10^5}{8.31 \times 293}$$

$$E_a/RT = 82.1$$

$$k_{20\ 200} = A \times e^{-82.1}$$

$$k_{20\ 200} = A \times 2.2 \times 10^{-36}$$

At $T = 25^\circ\text{C}$,

$$E_a/RT = \frac{2.00 \times 10^5}{8.31 \times 298}$$

$$E_a/RT = 80.8$$

$$k_{25\ 200} = A \times e^{-80.8}$$

$$k_{25\ 200} = A \times 8.1 \times 10^{-36}$$

$$\frac{k_{25\ 200}}{k_{20\ 200}} = \frac{A \times 8.1 \times 10^{-36}}{A \times 2.2 \times 10^{-36}}$$

$$\frac{k_{25\ 200}}{k_{20\ 200}} = 3.7$$

An increase in temperature of 5°C increases the rate almost four times.

- At $E_a = 180 \text{ kJ/mol}$

$$E_a/RT = \frac{1.80 \times 10^5 \text{ J/mol}}{8.31 \times 293}$$

$$E_a/RT = 73.9$$

$$k_{20\ 180} = A \times e^{-73.9}$$

$$k_{20\ 180} = A \times 8.0 \times 10^{-33}$$

$$\frac{k_{20\ 180}}{k_{20\ 200}} = \frac{A \times 8.0 \times 10^{-33}}{A \times 2.2 \times 10^{-36}}$$

$$\frac{k_{20\ 180}}{k_{20\ 200}} = 3636$$

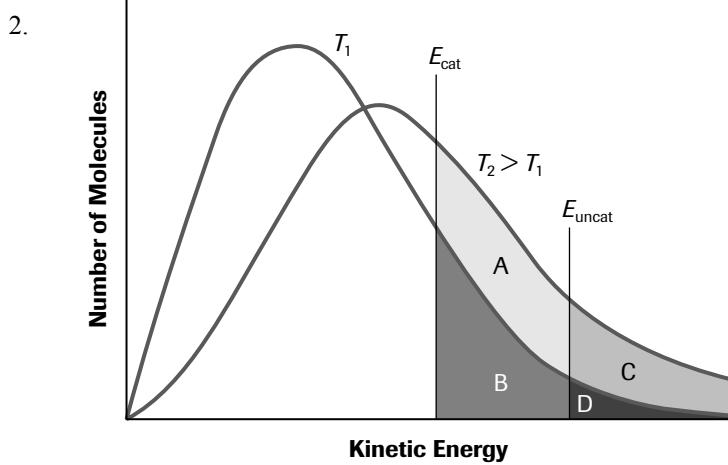
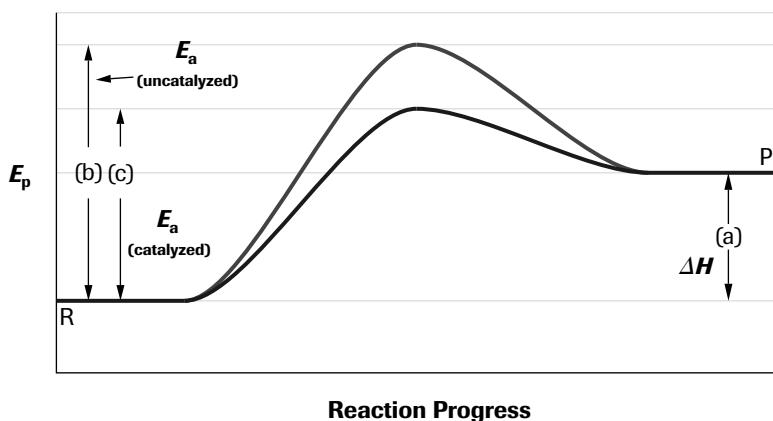
A decrease of activation energy of 10% increases the rate about 3600 times.

SECTION 6.5 QUESTIONS

(Page 400)

Understanding Concepts

1. Potential Energy Diagram of Catalyzed and Uncatalyzed Pathways



Fraction of molecules able to react

- at T_1 uncatalyzed = D
- at T_1 catalyzed = B + D
- at T_2 uncatalyzed = C + D
- at T_2 catalyzed = A + B + C + D

Making Connections

3. (a) Stratospheric ozone blocks harmful solar ultraviolet radiation, which can cause skin cancer.
- (b) Atomic chlorine is a vastly more effective catalyst than nitric oxide because its activation energy is very much lower. Therefore, a much higher fraction of its collisions with ozone leads to successful reaction.

4. (Partial answer)

Fast reactions	Slow reactions
cooking in the stove or microwave (use temperature to increase the kinetic energy of reacting molecules) contact lens cleaning solutions and meat tenderizers (use catalysts: hydrogen peroxide and papain) fireworks burning of fuels in home heating, lighters, and automobiles	decay of food, perfumes, and pharmaceutical products (controlled by lowering temperature) corrosion of garden implements (controlled by painting, which reduces the contact of oxygen with the metal and keeps salt away)

5. (Answers will vary.) Fast reactions could include burning of any hydrocarbon fuel (barbecues, automobiles, home-heating systems, cigarette lighters), rapid cooking of food (frying, broiling), explosive reactions (fireworks, highway building, mining), and use of some household cleansers (bleach, tarnish remover). Slow reactions could include paint drying, decay of food, corrosion (rusting, oxidation of other metals), photochemical degradation of plastics, and slow bleaching of dyes by the Sun.
6. (a) Some reactant molecules have complex structures and strong chemical bonds that make reaction more difficult. In such situations, the chemical nature of the reactants gives them large activation energies. Other reactions involve simple ions or molecules with weak or unstable chemical bonds in which most collisions result in reaction. In these situations, the chemical nature of the reactants gives them small activation energies. Some exothermic reactions produce large amounts of heat which then accelerate further reaction by giving a larger fraction of molecules sufficient energy to exceed the activation energy barrier. A few reactions are autocatalytic: Their products include catalyst molecules which accelerate the reaction by lowering the activation energy barrier.
 (b) (Answers will vary, but the student should have a more sophisticated view of the explanation of chemical reaction rate in terms of activation energy barriers and collision mechanisms.)

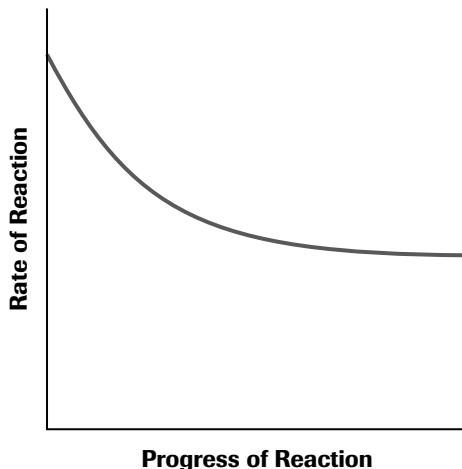
CHAPTER 6 LAB ACTIVITIES

LAB EXERCISE 6.1.1 DETERMINING A RATE OF REACTION

(Page 401)

Prediction

(a) (Sample answer)



- refrigeration (reduction of temperature)
- preserving large blocks of food (reducing surface area)
- choosing foodstuffs that naturally decay more slowly (chemical nature of reactants)

Explore an Issue: Debate: Food Preservation

(Page 397)

- (Answers will vary, but should include research from several stated sources, organized into relevant categories (e.g., from the manufacturing industry, from health-watch groups, from the medical community), and used to back up the students' arguments.)
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PRACTICE

(Page 398)

Making Connections

- (Answers will vary, depending on career chosen and geographical location.)

PRACTICE

(Page 400)

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At $T = 20^\circ\text{C}$,

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$$E_a/RT = 82.1$$

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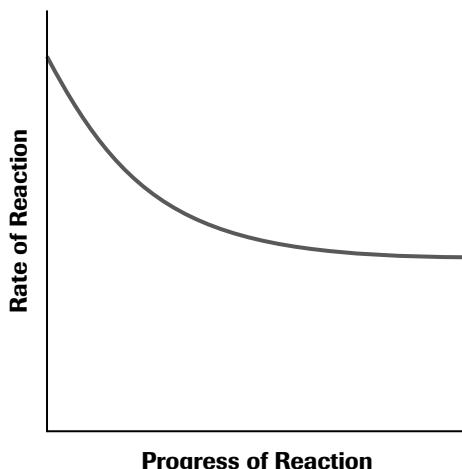
CHAPTER 6 LAB ACTIVITIES

LAB EXERCISE 6.1.1 DETERMINING A RATE OF REACTION

(Page 401)

Prediction

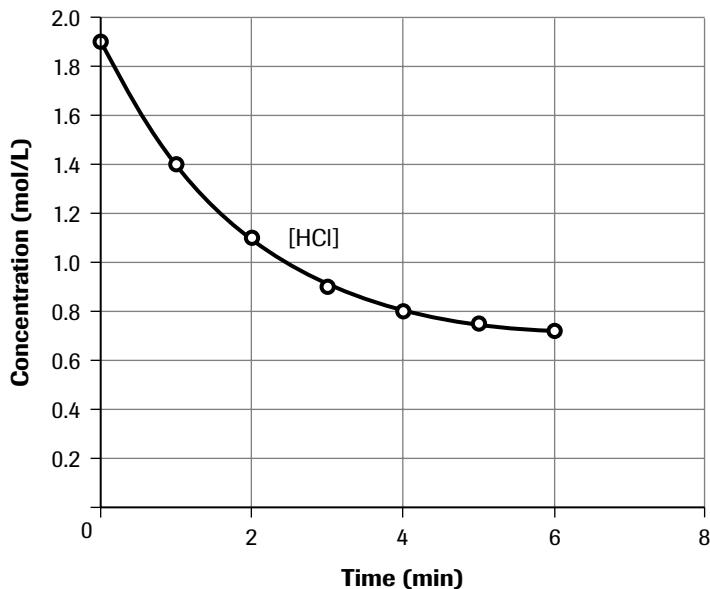
(a) (Sample answer)



Analysis

(b)

Graph of Hydrochloric Acid Concentration Decrease



$$\begin{aligned} \text{(c) (i)} \quad r &= \frac{\Delta c}{\Delta t} \\ &= \frac{1.10 \text{ mol/L} - 1.90 \text{ mol/L}}{2 \text{ min}} \\ r &= 0.4 \text{ mol/(L}\cdot\text{min)} \end{aligned}$$

$$\begin{aligned} \text{(ii)} \quad r &= \frac{\Delta c}{\Delta t} \\ &= \frac{0.75 \text{ mol/L} - 0.9 \text{ mol/L}}{2 \text{ min}} \\ r &= 0.075 \text{ mol/(L}\cdot\text{min)} \end{aligned}$$

(d) When we use slopes of tangents for instantaneous rate, approximate values are

$$\text{(i)} \quad r_{t=1} = 0.41 \text{ mol/(L}\cdot\text{min)}$$

$$\text{(ii)} \quad r_{t=4} = 0.075 \text{ mol/(L}\cdot\text{min)}$$

(e) The reaction rate decreases with time.

Evaluation

(f) In controlled experiments, only one variable changes. In this heterogeneous system, changes are occurring in the calcium carbonate surface area as the reaction proceeds. Therefore, this is not truly a controlled situation.

(g) (Answers will vary, and will depend on the student's original prediction.)

Synthesis

$$\text{(h)} \quad r_{t=1} \text{ for HCl} = \frac{-\Delta[\text{HCl}]}{\Delta t}$$
$$r_{t=1} = 0.41 \text{ mol/(L}\cdot\text{min)}$$

$$\frac{-\Delta[\text{CaCO}_3]}{\Delta t} = 0.21 \text{ mol/(L}\cdot\text{min)} \quad (\text{half as much})$$

$$\frac{+\Delta[\text{CO}_2]}{\Delta t} = 0.21 \text{ mol/(L}\cdot\text{min)} \quad (\text{half as much})$$

- (i) The solution becomes a better conductor as three product ions are produced from two reactant ions; pressure or volume of hydrogen gas also increases over time.

INVESTIGATION 6.2.1 CHEMICAL KINETICS AND FACTORS AFFECTING RATE

(Page 402)

Question

- (a) How do chemical nature of reactants, concentration, temperature, surface area, and catalysis affect rate of reaction?

Prediction

- (b) (Answers will vary, given that catalysts and changes in surface area do not apply to all of the systems that the student may choose. A sample answer is provided.) In reacting a metal like zinc with sulfuric acid, surface area, concentration of acid, temperature, chemical nature of reactants, and catalysts may all be variables. Catalysis will not be a consideration for the bicarbonate system, and surface area will be irrelevant for the decomposition of hydrogen peroxide because the system is homogeneous.

Experimental Design

- (c) (Answers will vary.) For the peroxide system, the control could be a fixed volume of 3% hydrogen peroxide at 20°C to which a lump of pyrolusite rock or a fixed amount of manganese dioxide is added. Other trials would keep all variables constant except one of the following:

- (i) vary temperature by using separate samples at 10, 15, and 25°C,
- (ii) vary catalysis by using gravel pellets or a small rock instead of the catalyst,
- (iii) vary concentration by using separate samples of 2% and 5% hydrogen peroxide, or
- (iv) vary chemical nature of reactant by using the same volume of water instead of hydrogen peroxide.

Materials

- (d) (Sample answer)

lab apron

eye protection

6% hydrogen peroxide

pyrolusite rock or granular manganese dioxide

Erlenmeyer flask

stopper-delivery tube assembly

pneumatic trough

graduated cylinder

retort clamp

retort stand

Procedure

- (e) (Sample answer) Place 30 mL of hydrogen peroxide in a flask, and close with a rubber stopper and delivery tube leading to an inverted graduated cylinder, filled with water and inverted in a pneumatic trough. Add a lump of pyrolusite rock to the solution, quickly stopper the flask, and measure the time required for 20 mL of gas to be produced. Repeat the procedure, changing single variables as described in the experimental design.

Evidence

- (f) (Sample answer) The control will typically take 2 min. Halving the concentration of hydrogen peroxide will double the reaction time to about 4 min. Colder peroxide will take more time. Using water in place of peroxide will produce no gas at all.

Analysis

- (g) (Sample answer) The rate may be expressed in mL of gas produced per min, or converted to mol/min. (Some students may plot rate as a function of concentration of peroxide.)

- (h) Generally, temperature and concentration changes provide the best and most predictable results. Catalytic effects can be dramatic if a catalyst is known.

Evaluation

- (i) More trials with any particular set of conditions will improve results. Experiments involving gas collection are subject to errors caused by leakage of gas.

- (j) (Answers will vary, and will depend on the prediction that the student originally made.)

- (i) The solution becomes a better conductor as three product ions are produced from two reactant ions; pressure or volume of hydrogen gas also increases over time.

INVESTIGATION 6.2.1 CHEMICAL KINETICS AND FACTORS AFFECTING RATE

(Page 402)

Question

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Materials

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lab apron

eye protection

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Procedure

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Analysis

- (g) (Sample answer) The rate may be expressed in mL of gas produced per min, or converted to mol/min. (Some students may plot rate as a function of concentration of peroxide.)

- (h) Generally, temperature and concentration changes provide the best and most predictable results. Catalytic effects can be dramatic if a catalyst is known.

Evaluation

- (i) More trials with any particular set of conditions will improve results. Experiments involving gas collection are subject to errors caused by leakage of gas.
- (j) (Answers will vary, and will depend on the prediction that the student originally made.)

INVESTIGATION 6.3.1 THE IODINE CLOCK REACTION

(Page 403)

Prediction

(a) As concentration increases, time decreases as rate increases.

Experimental Design

(b) Initial iodate concentrations will be 0.002, 0.004, 0.006, 0.008, 0.010, 0.012, 0.014, 0.016, and 0.018 mol/L, based on dilution.

Evidence

Analysis

(c) After Step 3, the initial iodate concentrations will be 0.001, 0.002, 0.003, 0.004, 0.005, 0.006, 0.007, 0.008, and 0.009 mol/L, based on dilution.

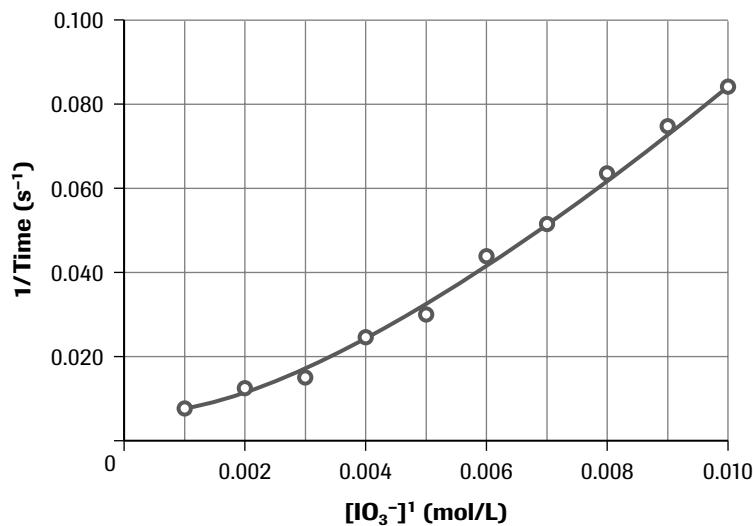
(d) Two clear colourless solutions remained so on mixing until a sudden colour change to clear blue occurred.

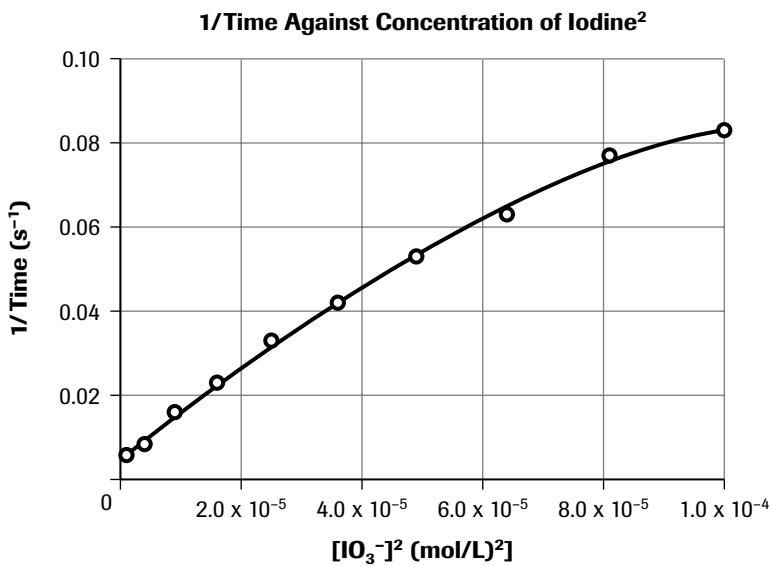
(e) Note: At step 3, the concentration of iodate ions in each well is halved.

Table of Data for Establishing Order of Iodine Reaction

Trial	Initial $[IO_3^-]$ (mol/L)	Time to reaction (s)	1/Time (s^{-1})	Initial $[IO_3^-]^2$ (mol/L) ²
1	0.0010	172	5.8×10^{-3}	1.0×10^{-6}
2	0.0020	119	8.4×10^{-3}	4.0×10^{-6}
3	0.0030	64	1.6×10^{-2}	9.0×10^{-6}
4	0.0040	43	2.3×10^{-2}	1.6×10^{-5}
5	0.0050	30	3.3×10^{-2}	2.5×10^{-5}
6	0.0060	24	4.2×10^{-2}	3.6×10^{-5}
7	0.0070	19	5.3×10^{-2}	4.9×10^{-5}
8	0.0080	16	6.3×10^{-2}	6.4×10^{-5}
9	0.0090	13	7.7×10^{-2}	8.1×10^{-5}
10	0.0010	12	8.3×10^{-2}	1.0×10^{-4}

1/Time Against Concentration of Iodine





The graph of 1/time against $[\text{IO}_3^-]^2$ is more linear than the graph of 1/time against $[\text{IO}_3^-]^1$. This indicates a second-order dependence. (The theoretically expected result is first order.)

- (f) According to the evidence, $r \propto [\text{IO}_3^-]^2$.

Evaluation

- (g) Temperature, starch concentration, and acid concentration were also controlled.
 (h) (Answers will vary.) Repetition of trials and more accurate volume measurements, perhaps with larger quantities, might improve results.
 (i) (Sample answer) The prediction was validated qualitatively, as no particular prediction was made as to whether the reaction was first or second order.

Synthesis

- (j) Keeping the total volume of solution A constant by adding water was necessary so that no changes would occur to the concentrations of bisulfite and acid in solution B.

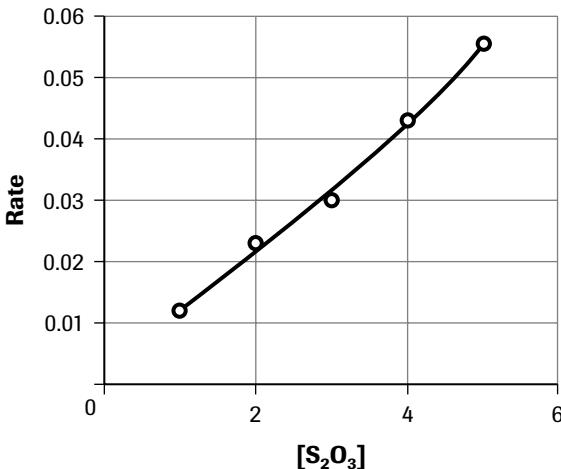
LAB EXERCISE 6.4.1 THE SULFUR CLOCK

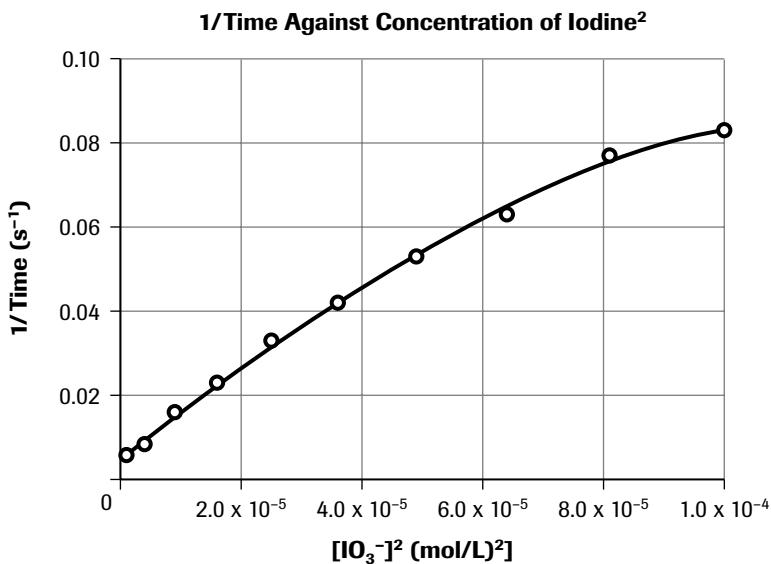
(Page 404)

Analysis

- (a) Colourless solutions on mixing gradually formed a cloudy, pale-yellow mixture which eventually became opaque. As initial $[\text{S}_2\text{O}_3^{2-}]$ increases, the time of reaction decreases or rate increases.
 (b)

First-Order Plot of Rate Against Concentration of S_2O_3





The graph of 1/time against $[\text{IO}_3^-]^2$ is more linear than the graph of 1/time against $[\text{IO}_3^-]^1$. This indicates a second-order dependence. (The theoretically expected result is first order.)

- (f) According to the evidence, $r \propto [\text{IO}_3^-]^2$.

Evaluation

- (g) Temperature, starch concentration, and acid concentration were also controlled.
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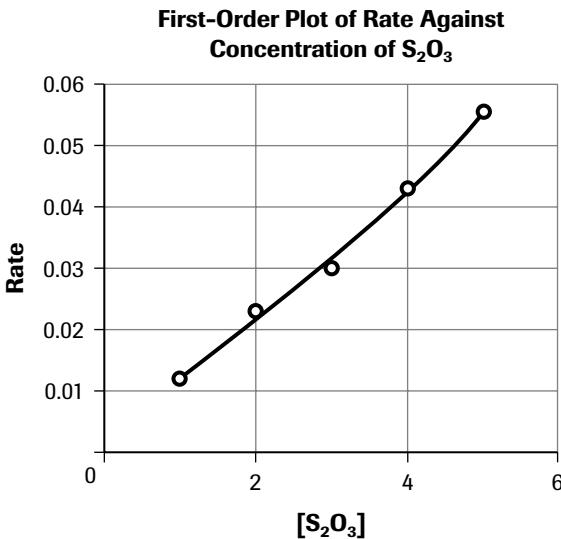
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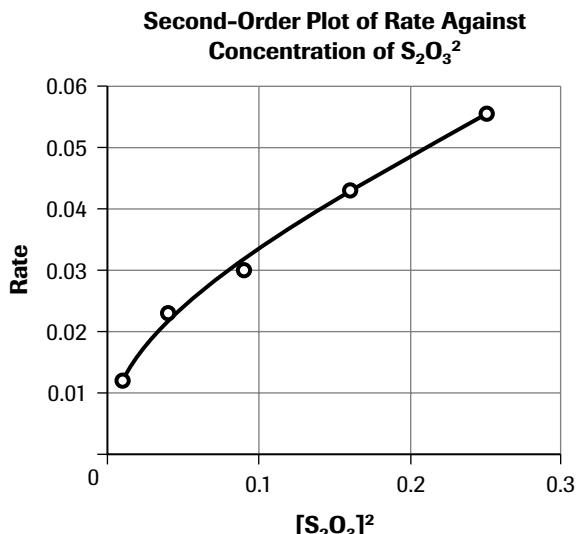
LAB EXERCISE 6.4.1 THE SULFUR CLOCK

(Page 404)

Analysis

- (a) Colourless solutions on mixing gradually formed a cloudy, pale-yellow mixture which eventually became opaque. As initial $[\text{S}_2\text{O}_3^{2-}]$ increases, the time of reaction decreases or rate increases.
 (b)





The first-order plot is most linear, so we would conclude that the reaction is first order overall.

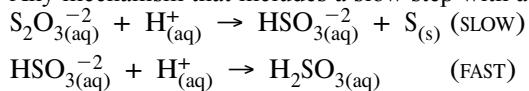
- (c) $r = k [\text{S}_2\text{O}_3^{2-}]^1$
- (d) One thiosulfate ion is involved in the rate-determining step.

Evaluation

- (e) The “X,” which gradually disappears, must be one of the controlled variables.
- (f) Time for the disappearance of the letter can be somewhat subjective.
- (g) (Answers will vary.) More trials at each concentration could be done to improve accuracy. A more quantitative measure of concentration might be achieved by using a colorimeter to measure absorbency.

Synthesis

- (h) Any mechanism that includes a slow step with a single thiosulfate ion will be acceptable.

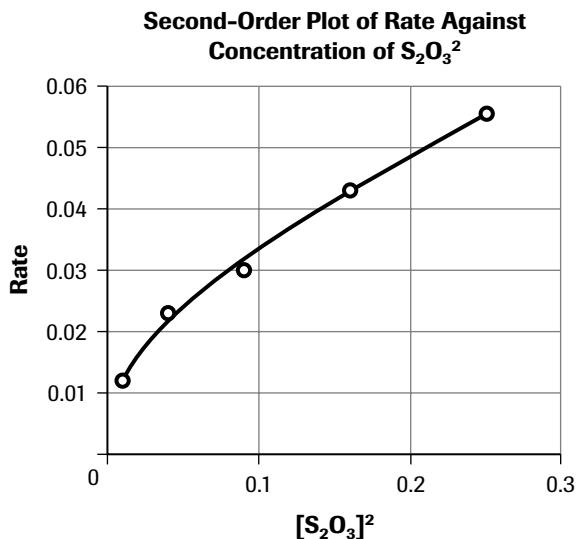


- (i) The experiment would involve varying the acid concentration while keeping all other variables constant.

ACTIVITY 6.5.1 CATALYSTS IN INDUSTRY AND BIOCHEMICAL SYSTEMS

(Page 405)

- (a), (b), and (c) (Answers will vary depending on the catalyst or enzyme chosen. If the student chooses an industrial catalyst such as vanadium(V) oxide, the focus will be on the particular industrial reaction (e.g., sulfuric acid production); the step in the process that it catalyzes (the production of sulfur trioxide); and the economic implications (sulfuric acid production is an indicator of a country’s economic strength). If the student chooses an enzyme (e.g., cytochromases, necessary for respiration), the focus will be on physiological implications (e.g., cyanide is poisonous because it blocks the active sites of these enzymes and asphyxiates the cell). The students may pick enzymes that have direct effects on their own family (e.g., lactase).)



The first-order plot is most linear, so we would conclude that the reaction is first order overall.

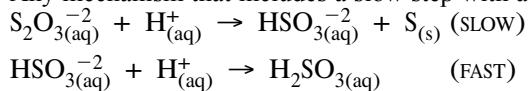
- (c) $r = k [\text{S}_2\text{O}_3]_2^2$
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ACTIVITY 6.5.1 CATALYSTS IN INDUSTRY AND BIOCHEMICAL SYSTEMS

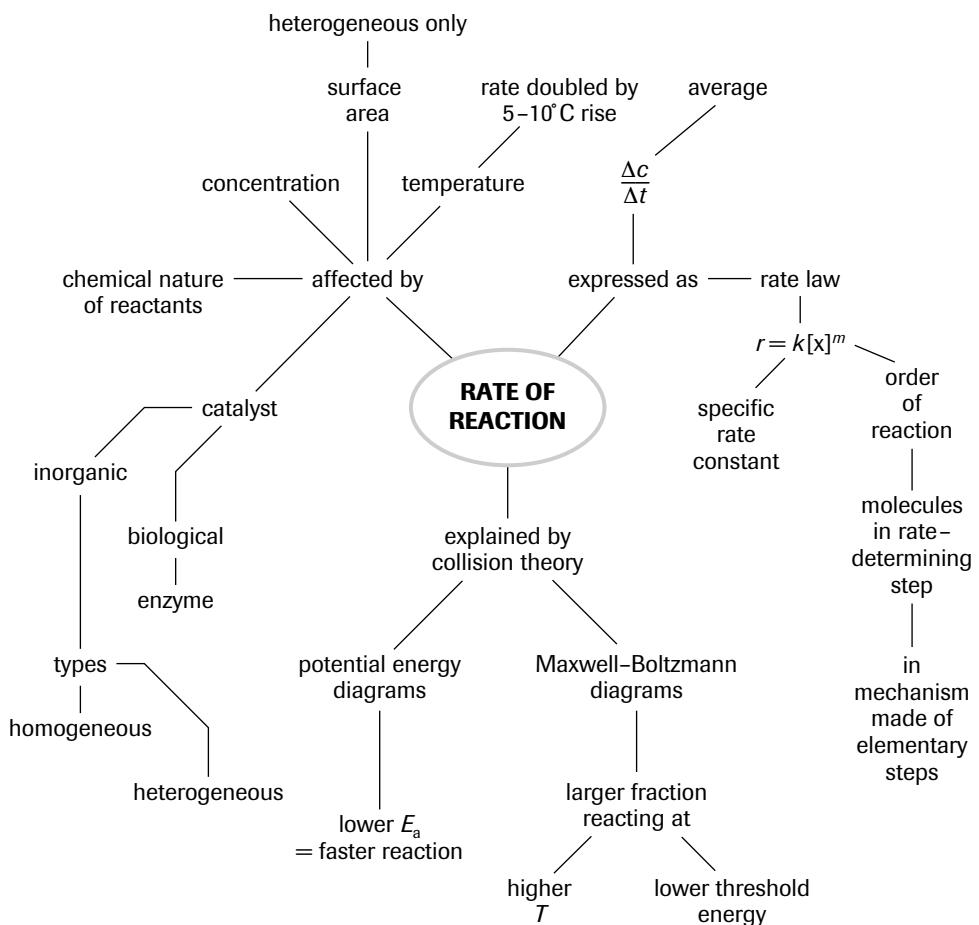
(Page 405)

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CHAPTER 6 SUMMARY

(Page 406)

MAKE A SUMMARY



CHAPTER 6 SELF-QUIZ

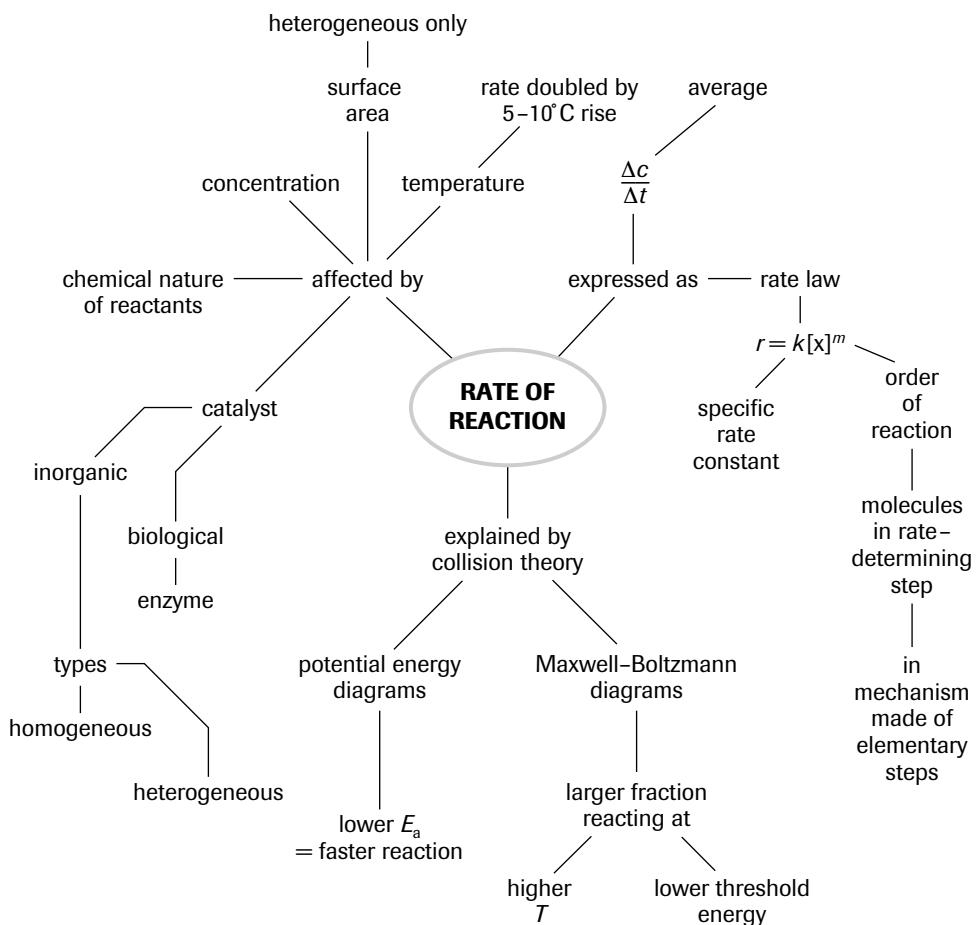
(Page 407)

1. False: The molecular species that exists at a maximum of potential energy is called the *activated complex*.
2. True
3. False: Elementary steps in reaction mechanisms generally involve *one or two* molecule collisions.
4. True
5. True
6. False: The enthalpy change is *the same* for a catalyzed chemical reaction.
7. True
8. True
9. False: The rate-determining step in a mechanism is the *slowest* step.
10. False: A homogeneous catalyst is one in which the catalyst and the reactants are in *the same* phase.
11. (b)
12. (e)
13. (d)

CHAPTER 6 SUMMARY

(Page 406)

MAKE A SUMMARY



CHAPTER 6 SELF-QUIZ

(Page 407)

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11. (b)
12. (e)
13. (d)

14. (c)
15. (a)
16. (b)
17. (d)
18. (b)

CHAPTER 6 REVIEW

(Page 408)

Understanding Concepts

- pressure or volume, conductivity, absorbency of light
- concentration, temperature, catalysis, chemical nature of reactants
- Additional surface area = $18 \times 1 \text{ cm}^2$

$$\text{Total surface area} = 24 \text{ cm}^2$$

$$\text{Proportional change in surface area} = \frac{24 \text{ cm}^2}{6 \text{ cm}^2} = 4$$

The rate would be multiplied by a factor proportional to the surface area change:

$$r = 4 \times 20 \text{ mL/s}$$

$$r = 80 \text{ mL/s}$$

- (a) rate increases
(b) rate decreases
(c) rate increases
(d) rate increases

$$\begin{aligned} 5. \quad (a) \quad r &= \frac{\Delta V}{\Delta t} \\ &= \frac{44.2 \text{ mL}}{30.0 \text{ s}} \\ r &= 1.47 \text{ mL/s} \end{aligned}$$

- (i) With a 5°C increase in temperature, the rate could be doubled and the time halved.
(ii) Without the catalyst, the reaction might be imperceptibly slow.

$$6. \quad (a) \quad r = k [\text{ClO}_{2(\text{aq})}]^2 [\text{OH}_{(\text{aq})}]$$

- This is a third-order reaction.
(c) The rate would quadruple.
(d) The rate would double.

- (a) When we compare Trials 1 and 2, we see that as $[\text{Cl}_2]$ is doubled, rate is multiplied by 2; therefore, rate depends on $[\text{Cl}_2]^1$.

When we compare Trials 2 and 3, we see that as $[\text{NO}]$ is doubled, rate is multiplied by 4; therefore, rate depends on $[\text{NO}]^2$.

$$\text{Overall, } r = k [\text{Cl}_2]^1 [\text{NO}]^2.$$

- The rate-determining step is most likely to be
 $2 \text{ NO}_{(\text{g})} + \text{ Cl}_{2(\text{g})} \rightarrow \text{ product or intermediate}$

$$\begin{aligned} (c) \quad k &= \frac{r}{[\text{NO}]^2 [\text{Cl}_2]} \\ &= \frac{1.8 \times 10^{-2} \text{ mol/(L}\cdot\text{s)}}{(0.10 \text{ mol/L})^2 \times 0.10 \text{ mol/L}} \end{aligned}$$

$$k = 18 \text{ L}^2/(\text{mol}^2\cdot\text{s})$$

$$\begin{aligned} (d) \quad r &= k [\text{NO}]^2 [\text{Cl}_2] \\ &= 18 \text{ L}^2/(\text{mol}^2\cdot\text{s}) (0.30 \text{ mol/L})^2 \times 0.40 \text{ mol/L} \end{aligned}$$

$$r = 0.65 \text{ mol/(L}\cdot\text{s)}$$

14. (c)
15. (a)
16. (b)
17. (d)
18. (b)

CHAPTER 6 REVIEW

(Page 408)

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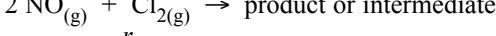
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$$\text{Overall, } r = k [\text{Cl}_2]^1 [\text{NO}]^2$$

- The rate-determining step is most likely to be



$$(c) \quad k = \frac{r}{[\text{NO}]^2 [\text{Cl}_2]}$$

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$$k = 18 \text{ L}^2/(\text{mol}^2\cdot\text{s})$$

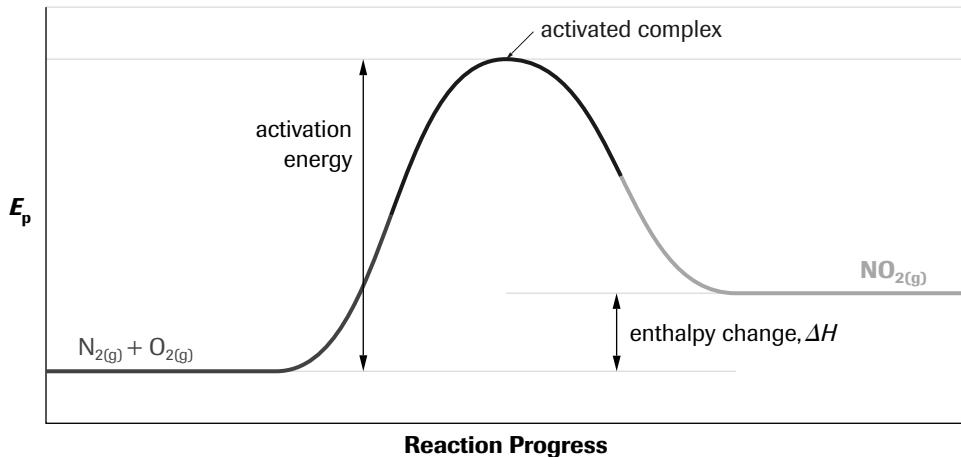
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$$r = 0.65 \text{ mol/(L}\cdot\text{s)}$$

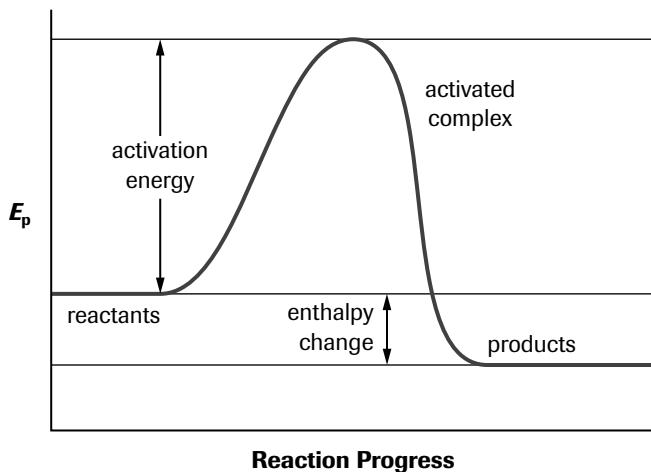
8. (a) Half-life is the amount of time for one-half the mass of a radioisotope to decay.
 (b) 14.0 a is four half-lives. The percentage remaining is $100\% \times (\frac{1}{2})^4 = 6.25\%$.

9.

Potential Energy Diagram of Formation of Nitrogen Dioxide



10. **Potential Energy Diagram of an Exothermic Reaction**

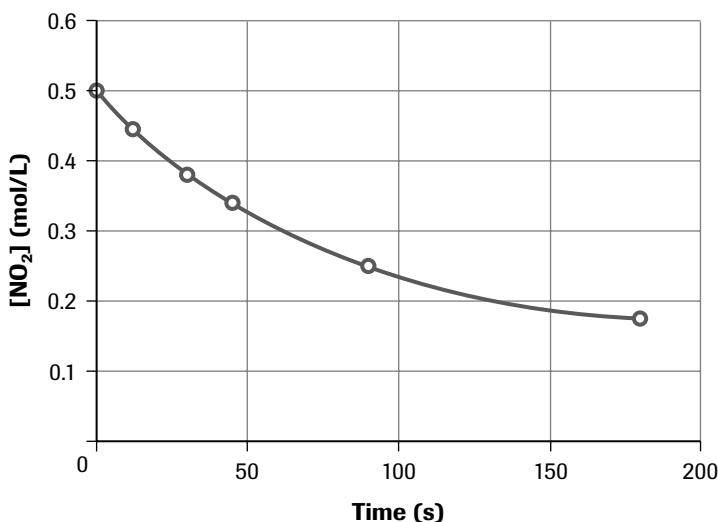


11. (a) There are generally one, two, or three particles involved in each elementary step.
 (b) Collisions of more particles at the same point in time and space are much less probable as the number of particles increases. Four-body collisions are effectively impossible as contributors to a reaction process.
12. (a) A catalyst might be consumed in one step of a mechanism as long as it is regenerated in a subsequent step.
 (b) Homogeneous catalysts, like acid in aqueous solution, are in the same phase as reactants. Heterogeneous catalysts, like platinum in gases, are in different phases from reactants.
13. (a) catalyst (necessary in first step but regenerated): $\text{Cu}^{2+}_{(\text{aq})}$
 intermediates (produced but then consumed): $\text{Cu}^+_{(\text{aq})}, \text{I}^-_{(\text{aq})}, \text{CuSO}_4^+_{(\text{aq})}$
 (b) $\text{S}_2\text{O}_8^{2-}_{(\text{aq})} + 2 \text{I}^-_{(\text{aq})} \rightarrow \text{I}_2_{(\text{aq})} + 2 \text{SO}_4^{2-}_{(\text{aq})}$
 (c) Since the $\text{I}^-_{(\text{aq})}$ is not part of the rate-determining (slow) step, increasing its concentration will have no effect on the overall rate.
 (d) Since the $\text{S}_2\text{O}_8^{2-}_{(\text{aq})}$ is part of the rate-determining (slow) step, increasing its concentration will increase the overall rate.

Applying Inquiry Skills

14. (a)

Graph of $[NO_2]$ Changing Over Time



(b) Average rate, $r_{ave(t=10 - 60)} = \frac{\Delta c}{\Delta t}$
 $= (0.45 - 0.30)/(10 - 60)$

$$r_{ave(t=10 - 60)} = 0.003 \text{ mol/(L}\cdot\text{s)}$$

(c) Instantaneous rate, $r_{ins(c=0.46)} = \frac{\Delta c}{\Delta t}$
 $r_{ins(c=0.46)} = 0.004 \text{ mol/(L}\cdot\text{s)}$

Instantaneous rate, $r_{ins(c=0.23)} = \frac{\Delta c}{\Delta t}$
 $r_{ins(c=0.23)} = 0.001 \text{ mol/(L}\cdot\text{s)}$

(d) As $[NO_2]$ was halved, the rate was multiplied by 1/4, roughly.

(e) The reaction is second order or rate is proportional to $[NO_2]^2$.

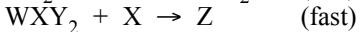
15. (a) When we compare Trials 1 and 2, we see that as $[W]$ is doubled, rate is unchanged; therefore, rate depends on $[W]^0$. When we compare Trials 1 and 3, we see that as $[X]$ is doubled, rate is multiplied by 2; therefore, rate depends on $[X]^1$.

When we compare Trials 1 and 4, we see that as $[Y]$ is doubled, rate is multiplied by 4; therefore, rate depends on $[Y]^2$.

Overall, $r = k[X]^1[Y]^2$.

(b) The rate-determining step is $X + 2Y \rightarrow$ products.

(c) A possible mechanism might be:



Making Connections

16. (a) When we compare Trials 1 and 2, we see that as $[Hbn]$ is doubled, rate is multiplied by 2; therefore, rate depends on $[Hbn]^1$.

When we compare Trials 2 and 3, we see that as $[CO]$ is tripled, rate is multiplied by 3; therefore, rate depends on $[CO]^1$.

(b) The overall order is two.

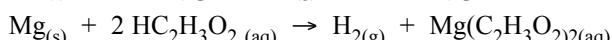
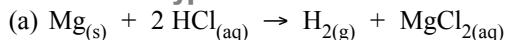
(c) Overall, $r = k[Hbn]^1[CO]^1$.

(d) The carbon monoxide rate constant might be expected to be larger than the oxygen rate constant because it seems to bind so quickly to hemoglobin. On the other hand, as will be discovered in the next unit, the more significant factor is the equilibrium constant for the binding reaction, which is much larger for carbon monoxide than for oxygen.

UNIT 3 PERFORMANCE TASK: ENERGY AND RATES ANALYSIS OF CHEMICAL REACTIONS

(Page 410)

Prediction/Hypothesis



- (b) The molar enthalpy should be about the same for all three acids, since it is expressed “per mole” of magnesium. The largest rate should be with a dibasic strong acid (sulfuric acid) which yields 2 mol of hydrogen ion for each mole of acid, and the smallest with a weak acid (acetic acid) which yields a fraction of a mole of hydrogen ion for each mole of acid.

Experimental Design

- (c) (Answers will vary.) Variables such as temperature and concentrations must be controlled. In the thermochemistry part, maximum temperature of the solution would be measured. In the kinetics part, time for the magnesium ribbon to be consumed might be a possibility, but a better method would be to measure the volume of hydrogen gas trapped in a gas measuring tube, over time.

Materials

- (d) (Answers will vary.)

Styrofoam cups (for calorimetry)

stopwatches (for kinetics)

Procedure

- (e) (Answers will vary. This is a student-designed experiment and considerable opportunity should be provided students to come up with their own procedures, in particular in the measurements of changes of gas production over time. The following is only one possible minimal design.)

1. Place 50 mL of 0.50 mol/L hydrochloric acid in a Styrofoam cup calorimeter. Measure the initial temperature of the acid. Add a measured mass of magnesium to the acid. Record the maximum temperature.
2. Repeat the previous step for separate samples of the other acids.
3. Place 50 mL of hydrochloric acid in an Erlenmeyer flask, stoppered with a one-hole rubber stopper and delivery tube leading to an inverted water-filled graduated cylinder. Measure the time taken for 20 mL of gas to be produced.
4. Repeat the previous step for separate samples of the other acids.

Evidence

- (f) (Sample answers)

Thermochemistry				
Acid	Initial T (°C)	Final T (°C)	Volume of Acid (mL)	Mass of Mg (g)
HCl	24.2	31.0	50	0.075
H ₂ SO ₄	22.0	28.5	50	0.079
HAc	21.2	27.0	50	0.076

Kinetics	
Acid	Time for 20 mL of Gas to Form (s)
HCl	31
H ₂ SO ₄	15
HAc	160

Analysis

- (g) The ΔH_r was about the same for all three acids. For example, for the hydrochloric acid,
- $$q = mc\Delta T$$

$$= 50 \text{ g} \times (31.0 - 24.2)^\circ\text{C} \times 4.18 \text{ J/g} \cdot {}^\circ\text{C}$$

$$q = 1.4 \text{ kJ}$$

The amount of Mg (in moles) was

$$\begin{aligned}n &= m/M \\&= \frac{0.075 \text{ g}}{(24.3 \text{ g/mol})} \\n &= 3.1 \times 10^{-3} \text{ mol}\end{aligned}$$

$$\begin{aligned}\text{Thus, } H_{\text{hydrochloric acid}} &= \frac{q}{n} \\&= \frac{1.4 \text{ kJ}}{3.1 \times 10^{-3} \text{ mol}}\end{aligned}$$

$$\Delta H_{\text{hydrochloric acid}} = -4.6 \times 10^2 \text{ kJ/mol} \text{ (negative sign for exothermic reaction)}$$

Similarly, for sulfuric acid,

$$\Delta H_{\text{sulfuric acid}} = -4.2 \times 10^2 \text{ kJ/mol}$$

and for acetic acid,

$$\Delta H_{\text{acetic acid}} = -4.5 \times 10^2 \text{ kJ/mol}$$

The rates of production of hydrogen gas, expressed as mL H₂ produced per s, varied considerably for the acids.

The rate for hydrochloric acid:

$$r_{\text{hydrochloric acid}} = 20 \text{ mL/31 s}$$

$$r_{\text{hydrochloric acid}} = 0.65 \text{ mL/s}$$

The rate for sulfuric acid:

$$r_{\text{sulfuric acid}} = 20 \text{ mL/15 s}$$

$$r_{\text{sulfuric acid}} = 1.3 \text{ mL/s}$$

The rate for acetic acid:

$$r_{\text{acetic acid}} = 20 \text{ mL/60 s}$$

$$r_{\text{acetic acid}} = 0.33 \text{ mL/s}$$

Evaluation

- (h) The molar enthalpies of reaction are about the same for all three acids. The rate of reaction for sulfuric acid is about double the rate for hydrochloric acid and more than ten times the rate for acetic acid. (The student predictions will vary, but generally, students tend to expect the heat of reaction to be different for the acids.)

Synthesis

- (i) The energy produced by the reaction is a function of the time taken for the roughly fixed mass of magnesium to be consumed. The dibasic sulfuric acid has twice the amount of H⁺ as hydrochloric acid, and reacts roughly twice as fast. The weak organic acetic acid has a much smaller concentration of H⁺ in solution, and reacts much more slowly.
- (j) Possibilities could include solution conductivity, or volume or pressure of gas produced.
- (k) As time passes, the rate increases because solution temperature increases but decreases as reactant concentration decreases.
- (l) (Answers will vary.) The materials used are somewhat toxic for consumer products and the reaction occurs very quickly. Most consumer handwarmers use a slower reaction like the oxidation of iron filings.

UNIT 3 SELF-QUIZ

(Page 412)

1. False: A physical change usually involves a *larger* enthalpy change than does a chemical change.
2. True
3. False: The potential energy of the products is *smaller* than the potential energy of the reactants in an exothermic change.
4. True
5. False: An *endothermic* reaction absorbs heat from the surroundings.
6. True
7. True
8. False: *Three-quarters* of a radioisotope will have changed after two half-lives.
9. False: In an endothermic reaction, *only* the potential *energy* of the chemical system increases.
10. True
11. (b)
12. (c)
13. (e)
14. (a)
15. (e)
16. (c)
17. (b)
18. (d)
19. (b)
20. (e)
21. (b)
22. (a)
23. (c)
24. (c)
25. (e)
26. (c)
27. (b)
28. (d)
29. (c)
30. (d)

UNIT 3 REVIEW

(Page 414)

Understanding Concepts

$$1. \ q_{\text{water}} = mc\Delta T \\ = 1500 \text{ g} \times 4.18 \text{ J/(g}\cdot^{\circ}\text{C)} \times (75 - 20)^{\circ}\text{C}$$

$$q_{\text{water}} = 340 \text{ kJ}$$

$$2. \ M_{\text{Cl}_2} = 70.9 \text{ g/mol} \\ n_{\text{Cl}_2} = 2250 \text{ g} \times \frac{1 \text{ mol}}{70.9 \text{ g}} \\ n_{\text{Cl}_2} = 31.7 \text{ mol} \\ \Delta H = n_{\text{Cl}_2} \Delta H_{\text{vap}} \\ = 31.7 \text{ mol} \times 20.7 \text{ kJ/mol} \\ \Delta H = 657 \text{ kJ}$$

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(Page 412)

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(Page 414)

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$$\begin{aligned}
 3. \text{ (a)} \quad q_{\text{water}} &= mc\Delta T \\
 &= 100.0 \text{ g} \times 4.18 \text{ J/(g}^{\circ}\text{C)} \times 5.6^{\circ}\text{C} \\
 q_{\text{water}} &= 2341 \text{ J} \\
 n_{\text{NaOH}} &= MV \\
 &= 0.700 \text{ mol/L} \times 0.600 \text{ L} \\
 n_{\text{NaOH}} &= 0.420 \text{ mol} \\
 n\Delta H_{\text{neut}} &= q_{\text{water}}
 \end{aligned}$$

$$\begin{aligned}
 \Delta H_{\text{neut}} &= \frac{q_{\text{water}}}{n} \\
 &= \frac{2341 \text{ J}}{0.420 \text{ mol}}
 \end{aligned}$$

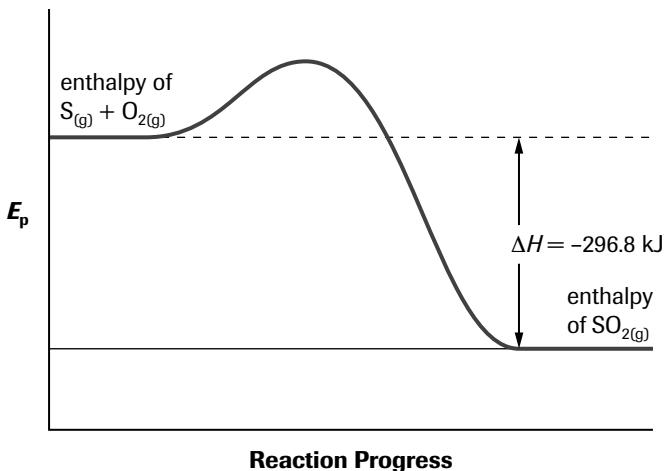
$$\Delta H_{\text{neut}} = 5573 \text{ J/mol, or } 5.57 \text{ kJ/mol}$$

Because the reaction is exothermic, $\Delta H_{\text{neut}} = -5.57 \text{ kJ/mol}$.

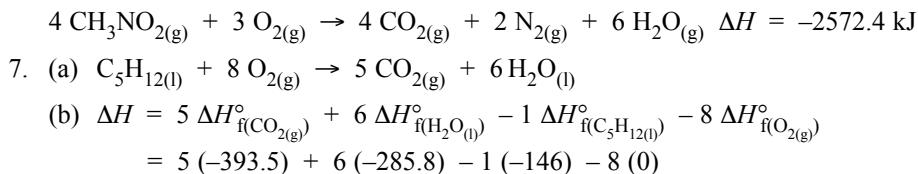
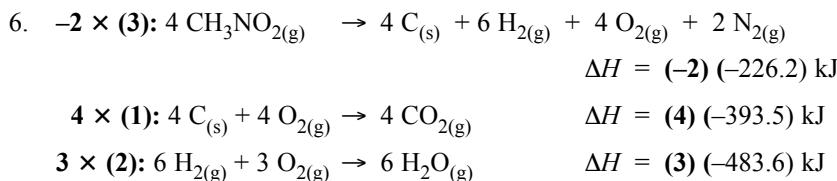
- (b) The assumption is that the reaction went to completion and that all heat from the reaction was absorbed by the water in the calorimeter and not by the calorimeter or surroundings.

4. (a) $2 \text{ C}_{(\text{s})} + \frac{3}{2} \text{ H}_{2(\text{g})} + 1/2 \text{ Cl}_{2(\text{g})} + 37.3 \text{ kJ} \rightarrow \text{C}_2\text{H}_3\text{Cl}_{(\text{g})}$
- (b) $2 \text{ C}_{(\text{s})} + \frac{3}{2} \text{ H}_{2(\text{g})} + 1/2 \text{ Cl}_{2(\text{g})} \rightarrow \text{C}_2\text{H}_3\text{Cl}_{(\text{g})} \quad \Delta H = +37.3 \text{ kJ}$
5. (a) $\text{S}_{(\text{s})} + \text{O}_{2(\text{g})} \rightarrow \text{SO}_{2(\text{g})} \quad \Delta H = -296.8 \text{ kJ}$

(b) **Potential Energy Diagram of the Formation of Sulfur Dioxide**



$$\begin{aligned}
 \text{(c)} \quad M_{\text{SO}_2} &= 64.07 \text{ g/mol} \\
 n_{\text{SO}_2} &= 9.63 \text{ g} \times 1 \text{ mol}/64.07 \text{ g} \\
 n_{\text{SO}_2} &= 0.150 \text{ mol} \\
 q &= n_{\text{SO}_2} \Delta H_f \\
 &= 0.150 \text{ mol} \times 296.8 \text{ kJ} \\
 q &= 44.6 \text{ kJ}
 \end{aligned}$$



$$\begin{aligned}\Delta H &= 5 \Delta H_{\text{f}}^{\circ}(\text{CO}_{2(\text{g})}) + 6 \Delta H_{\text{f}}^{\circ}(\text{H}_2\text{O}_{(\text{l})}) - 1 \Delta H_{\text{f}}^{\circ}(\text{C}_5\text{H}_{12(\text{l})}) - 8 \Delta H_{\text{f}}^{\circ}(\text{O}_{2(\text{g})}) \\ &= 5(-393.5) + 6(-285.8) - 1(-146) - 8(0)\end{aligned}$$

$$\Delta H = -3536.3 \text{ kJ}$$

(c) $M_{\text{pentane}} = 72.0 \text{ g/mol}$

$$n_{\text{pentane}} = 20 \text{ g} \times 1 \text{ mol} / 72.0 \text{ g}$$

$$n_{\text{pentane}} = 0.278 \text{ mol}$$

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

$$= 0.278 \text{ mol} \times 3536.3 \text{ kJ/mol}$$

$$q = 982 \text{ kJ}$$

982 kJ would be released, when 20 g of pentane is burned.

8. Properties include colour, volume or pressure, and conductivity.

9. (a) As 1 mol of $\text{CO}_{(\text{g})}$ is consumed, 1 mol of $\text{CO}_{2(\text{g})}$ is produced.

$$\text{At time } 0, [\text{CO}_{2(\text{g})}] = 0 \text{ mol/L}$$

$$\text{At time } 40, [\text{CO}_{2(\text{g})}] = 0.067 \text{ mol/L}$$

$$\text{At time } 100, [\text{CO}_{2(\text{g})}] = 0.017 \text{ mol/L}$$

(b) As 1 mol of $\text{NO}_{2(\text{g})}$ is consumed, 1 mol of $\text{CO}_{2(\text{g})}$ is produced.

$$\text{In } 80 \text{ s}, \Delta[\text{CO}_{2(\text{g})}] = 0.080 \text{ mol/L. Thus, } \Delta[\text{NO}_{2(\text{g})}] = -0.080 \text{ mol/L.}$$

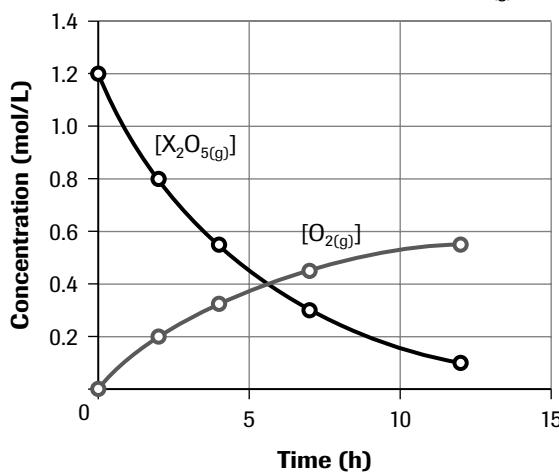
$$[\text{NO}_{2(\text{g})}]_{100 \text{ s}} = 0.250 \text{ mol/L} - 0.080 \text{ mol/L}$$

$$[\text{NO}_{2(\text{g})}]_{100 \text{ s}} = 0.170 \text{ mol/L}$$

10. Newspapers, particularly as they curl while burning and because of air trapped in their pages, expose much more surface area to reaction with air. They therefore start burning more easily, and burn more quickly, than an equivalent quantity of wood.

11. (a)

Graph of Decomposition of $\text{X}_2\text{O}_{5(\text{g})}$



- (b) As 1 mol of $O_{2(g)}$ is produced, 4 mol of $XO_{2(g)}$ are produced. Therefore, the four values for $[XO_{2(g)}]$ (in mol/L) are: 0.80, 1.30, 1.80, and 2.20.

$$(c) \text{ (i)} \quad \frac{-\Delta[X_2O_{5(g)}]}{\Delta t} = \frac{(1.20 - 1.00) \text{ mol/L}}{12.0 \text{ h}} \\ \frac{-\Delta[X_2O_{5(g)}]}{\Delta t} = 0.092 \text{ mol/(L}\cdot\text{h)}$$

In the first 12 h, the overall rate of consumption of $X_2O_{5(g)}$ is 0.092 mol/(L·h).

$$(ii) \quad \frac{+\Delta[O_{2(g)}]}{\Delta t} = \frac{0.55 \text{ mol/L}}{12.0 \text{ h}} \\ \frac{+\Delta[O_{2(g)}]}{\Delta t} = 0.046 \text{ mol/(L}\cdot\text{h)}$$

In the first 12 h, the overall rate of production of $O_{2(g)}$ is 0.046 mol/(L·h).

$$(iii) \quad \frac{+\Delta[XO_{2(g)}]}{\Delta t} = \frac{2.20 \text{ mol/L}}{12.0 \text{ h}} \\ \frac{+\Delta[XO_{2(g)}]}{\Delta t} = 0.183 \text{ mol/(L}\cdot\text{h)}$$

In the first 12 h, the overall rate of production of $XO_{2(g)}$ is 0.183 mol/(L·h).

- (d) When we use tangents to the curve, the rates of consumption of $X_2O_{5(g)}$ at 2.0 h and 7.0 h are 0.14 and 0.058 mol/(L·h), respectively.

- (e) The rate of consumption decreases as the concentration of reactant molecules able to collide and react decreases.
12. Aluminum powder has a much greater surface area, making it react much more quickly with oxygen in the air.

13. (a) The rate would double.

- (b) The rate would be halved.

- (c) Since both initial concentrations would be doubled, the rate would quadruple.

14. (a) This would have to be a multi-step mechanism because it involves six reactant molecules.
(b) Rate of consumption of $O_{2(g)}$:

$$\frac{-\Delta[O_{2(g)}]}{\Delta t} = 5 \times 4.0 \times 10^{-3} \text{ mol/(L}\cdot\text{s)}$$

$$\frac{-\Delta[O_{2(g)}]}{\Delta t} = 2.0 \times 10^{-2} \text{ mol/(L}\cdot\text{s)}$$

Rate of production of $CO_{2(g)}$:

$$\frac{+\Delta[CO_2]}{\Delta t} = 3 \times 4.0 \times 10^{-3} \text{ mol/(L}\cdot\text{s)}$$

$$\frac{+\Delta[CO_2]}{\Delta t} = 1.2 \times 10^{-2} \text{ mol/(L}\cdot\text{s)}$$

15. (a) When we compare Trials 2 and 3, we see that as $[HI]$ is doubled, rate is multiplied by 2; therefore, rate depends on $[HI]^1$.

- (b) When we compare Trials 1 and 2, we see that as $[O_2]$ is doubled, rate is multiplied by 2; therefore, rate depends on $[O_2]^1$.

- (c) The overall order is two.

- (d) $r = k [HI] [O_2]$

$$(e) \quad k = \frac{r}{[HI] [O_2]}$$

$$= \frac{0.0042 \text{ (mol/L}\cdot\text{s)}}{0.010 \text{ mol/L} \times 0.010 \text{ mol/L}}$$

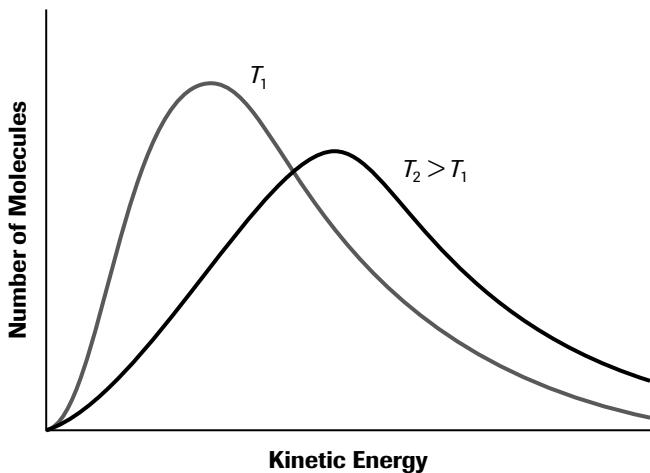
$$k = 42 \text{ L/(mol}\cdot\text{s)}$$

- (f) One molecule each of HI and O_2 are involved: two molecules.

- (g) Five reactant molecules are unlikely to collide in a single step at any appreciable rate.

16. (a) $2 \text{NO}_{(\text{g})} + 2 \text{H}_{2(\text{g})} \rightarrow \text{N}_{2(\text{g})} + 2 \text{H}_2\text{O}_{(\text{g})}$
 (b) The reaction intermediates are $\text{N}_2\text{O}_{2(\text{g})}$ and $\text{N}_2\text{O}_{(\text{g})}$.
 (c) $r = k [\text{NO}]^2$

17.



18. Reaction (a) should be faster because it is homogeneous. In reaction (b), reactions can only occur at the surface of the lead metal.
 19. (a) The activation energy barrier, E_a , for white phosphorus is very low, whereas the E_a for diamond is very high.
 (b) In the potential energy diagram for phosphorus, the activation energy barrier will be very small and the reaction exothermic with a large ΔH ; in the potential energy diagram for diamond, the activation energy barrier will be very large and the reaction exothermic with a very small ΔH .

Applying Inquiry Skills

20. Analysis

$$(a) q_{\text{water}} = mc\Delta T$$

$$= 255 \text{ g} \times 4.18 \text{ J/(g}\cdot^\circ\text{C)} \times 28.8^\circ\text{C}$$

$$q_{\text{water}} = 30.7 \text{ kJ}$$

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

$$= 305 \text{ g} \times 0.385 \text{ J/(g}\cdot^\circ\text{C)} \times 28.8^\circ\text{C}$$

$$q_{\text{copper}} = 3.38 \text{ kJ}$$

$$q_{\text{water}} + q_{\text{copper}} = 34.1 \text{ kJ}$$

$$n\Delta H_{\text{reaction}} = q_{\text{total}}$$

$$m_{\text{C}_3\text{H}_6\text{O}} = 1.01 \text{ g}$$

$$M_{\text{C}_3\text{H}_6\text{O}} = 58.0 \text{ g}$$

$$n_{\text{C}_3\text{H}_6\text{O}} = 1.01 \text{ g} \times \frac{1 \text{ mol}}{58.0 \text{ g}}$$

$$n_{\text{C}_3\text{H}_6\text{O}} = 0.0174 \text{ mol}$$

$$\Delta H_{\text{comb}} = \frac{q_{\text{total}}}{n_{\text{C}_3\text{H}_6\text{O}}}$$

$$= \frac{34.1 \text{ kJ}}{0.0174 \text{ mol}}$$

$$\Delta H_{\text{comb}} = 1958 \text{ kJ/mol propanal}$$

Because the reaction is exothermic, $\Delta H_{\text{comb}} = -1.96 \text{ MJ/mol}$.

21. Analysis

- (a) Assume that 100.0 mL of solution is 100.0 g of water.

$$\begin{aligned} q_{\text{water}} &= mc\Delta T \\ &= 100.0 \text{ g} \times 4.18 \text{ J/(g}\cdot^{\circ}\text{C)} \times (35.6 - 14.5)\text{C}^{\circ} \\ q_{\text{water}} &= 8.82 \text{ kJ} \\ n_{\text{NaOH}_{(s)}} &= 3.40 \text{ g} \times \frac{1 \text{ mol}}{40.0 \text{ g}} \\ n_{\text{NaOH}_{(s)}} &= 0.0850 \text{ mol} \\ n_{\text{HCl}_{(\text{aq})}} &= MV \\ &= 0.850 \text{ mol/L} \times 0.100 \text{ L} \\ n_{\text{HCl}_{(\text{aq})}} &= 0.0850 \text{ mol} \\ n\Delta H_{\text{reaction}} &= q_{\text{water}} \\ \Delta H_{\text{reaction}} &= \frac{q_{\text{water}}}{n} \\ &= \frac{8.82 \text{ kJ}}{0.0850 \text{ mol}} \\ \Delta H_{\text{reaction}} &= 104 \text{ kJ/mol HCl} \end{aligned}$$

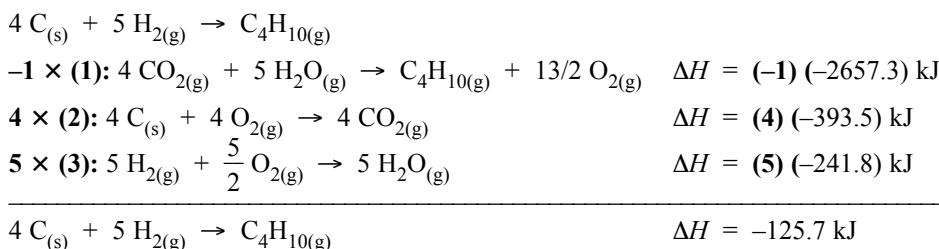
Because the reaction is exothermic, $\Delta H_{\text{reaction}}$ is -104 kJ/mol .

Evaluation

- (b) (Answers will vary.) The Experimental Design is adequate if careful bomb calorimetry is used.

22. Analysis

- (a) The target equation is:



Since this reaction is written for 1 mol of product, the molar enthalpy of formation of butane is -125.7 kJ/mol .

23. Experimental Design

- (a) The rate of reaction in terms of the rate of production of S will be measured by varying, one at a time, the initial concentrations of each of the reactants while controlling the other concentrations.

Analysis

- (b) When we compare Trials 1 and 2, we see that as $[A]$ is doubled, rate is multiplied by 2; therefore, rate depends on $[A]^1$.
When we compare Trials 2 and 3, we see that as $[B]$ is doubled, rate is multiplied by 2; therefore, rate depends on $[B]^1$.
When we compare Trials 3 and 4, we see that as $[C]$ is doubled, rate is multiplied by 1; therefore, rate depends on $[C]^0$.
Overall, $r = k [A]^1[B]^1$.

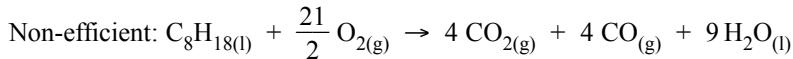
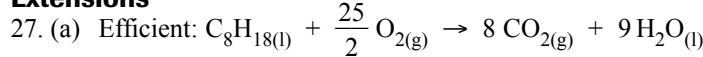
Making Connections

24. (Answers will vary.) Nuclear reactors have higher capital cost, involve reactant fuels that require considerable processing, and have associated serious safety issues related to transportation and storage of radioactive isotopes. Fossil fuels are finite resources, which are nonetheless readily available. The capital cost of plants burning these fuels is relatively low and they can easily be converted to burn a range of fuels. However, fossil fuels are “environmentally

“dirty” energy sources that foul the air with, at best, greenhouse emissions and, at worst, acid-rain-producing sulfur dioxide, particularly when lower grades of coal are used.

25. (Answers will vary.) Carbon-14 and uranium-238 decay can be used to determine the ages of artifacts and ancient rocks. Medical research scientists are interested in the shelf life or rate of decomposition of antibiotics and the rate of retention of environmental toxins in the body after exposure.
26. (a) Increased concentration increases the collision frequency.
 (b) Decreased temperature decreases the fraction of molecules with enough kinetic energy to exceed the activation energy barrier.
 (c) Increased temperature increases the fraction of molecules with enough kinetic energy to exceed the activation energy barrier.
 (d) Reactions require activation energy in order to occur.
 (e) Increased surface area increases the collision frequency.
 (f) Addition of a catalyst lowers the activation energy barrier and increases the fraction of molecules with enough kinetic energy to exceed the activation energy barrier.
 (g) Homogeneous reactions allow much better mixing of reacting molecules, thus increasing the collision frequency.

Extensions



(b) Efficient:

$$\begin{aligned}\Delta H &= 8 \Delta H_{f(\text{CO}_{2(g)})}^\circ + 9 \Delta H_{f(\text{H}_2\text{O}_{(l)})}^\circ - 1 \Delta H_{f(\text{C}_8\text{H}_{18(l)})}^\circ - \frac{25}{2} \Delta H_{f(\text{O}_{2(g)})}^\circ \\ &= 8(-393.5) + 9(-285.8) - 1(-250.1) - 12.5(0)\end{aligned}$$

$$\Delta H = -5470 \text{ kJ}$$

Non-efficient:

$$\begin{aligned}\Delta H &= 4 \Delta H_{f(\text{CO}_{2(g)})}^\circ + 4 \Delta H_{f(\text{CO}_{(g)})}^\circ + 9 \Delta H_{f(\text{H}_2\text{O}_{(l)})}^\circ - 1 \Delta H_{f(\text{C}_8\text{H}_{18(l)})}^\circ - 11.5 \Delta H_{f(\text{O}_{2(g)})}^\circ \\ &= 4(-393.5) + 4(-110.5) + 9(-285.8) - 1(-250.1) - 11.5(0)\end{aligned}$$

$$\Delta H = -4338 \text{ kJ}$$

(c) % waste = $\frac{(5470 \text{ kJ} - 4338 \text{ kJ})}{5470 \text{ kJ}} \times 100\%$

$$\% \text{ waste} = 21\%$$

(d) $q_{\text{water}} = mc\Delta T$

$$= 15\,000 \text{ g} \times 4.18 \text{ J/(g}^\circ\text{C)} \times (95 - (-15))^\circ\text{C}$$

$$q_{\text{water}} = 6.9 \times 10^3 \text{ kJ}$$

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

$$= 200\,000 \text{ g} \times 0.50 \text{ J/(g}^\circ\text{C)} \times (95 - (-15))^\circ\text{C}$$

$$q_{\text{block}} = 1.1 \times 10^4 \text{ kJ}$$

$$q_{\text{total}} = 1.7(9) \times 10^4 \text{ kJ}$$

$$q_{\text{total}} = n_{\text{octane}} \Delta H_{\text{comb}}$$

$$n_{\text{octane}} = \frac{q_{\text{total}}}{\Delta H_{\text{comb}}}$$

$$= \frac{1.7(9) \times 10^4 \text{ kJ}}{5470 \text{ kJ}}$$

$$n_{\text{octane}} = 3.2(7) \text{ mol octane}$$

$$\begin{aligned}
 m_{\text{octane}} &= n_{\text{octane}} M \\
 &= 3.2(7) \text{ mol} \times 114 \text{ g/mol} \\
 m_{\text{octane}} &= 373 \text{ g, or } 3.7 \times 10^2 \text{ g}
 \end{aligned}$$

To raise the temperature of the engine to operating temperature, 373 g of octane must be burned.

- (e) You must assume that all of the energy produced by the burning of octane goes into the sum of temperature changes in the engine and motion of the vehicle.

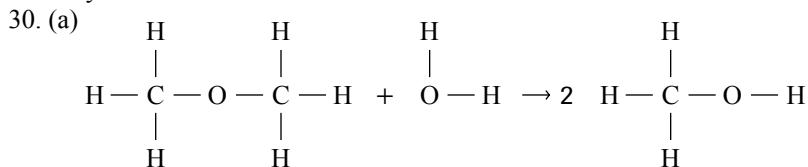
To drive 2 km, when warmed up,

$$\begin{aligned}
 m_{\text{octane}} &= 2 \text{ km} \times 0.150 \text{ L/km} \times 800 \text{ g/L} \\
 m_{\text{octane}} &= 240 \text{ g}
 \end{aligned}$$

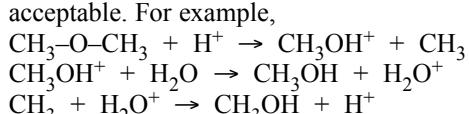
To warm up the engine *and* drive 2 km,

$$\begin{aligned}
 \text{total } m_{\text{octane}} &= 373 + 240 \\
 \text{total } m_{\text{octane}} &= 613 \text{ g, or } 6.1 \times 10^2 \text{ g}
 \end{aligned}$$

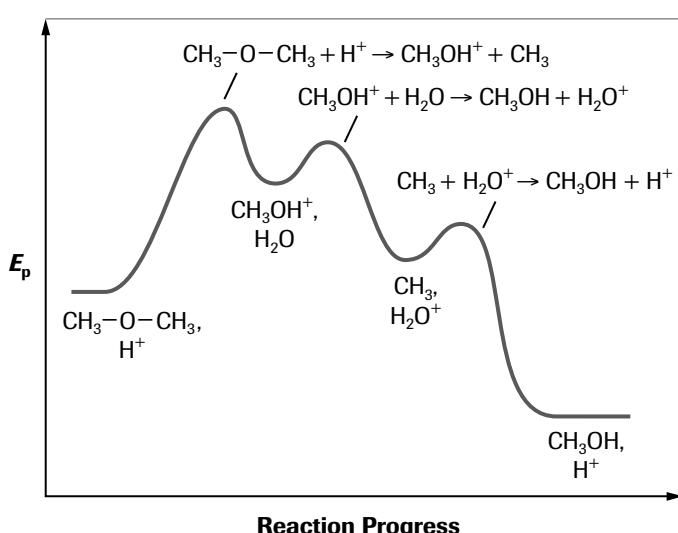
28. (Sample answer) In recent years, there have emerged worldwide infectious bacterial agents that are causing concern. These include: methicillin-resistant *Staphylococcus aureus*, multiple-drug resistant *tuberculosis*, and vancomycin-resistant *enterococci* (VRE). There is extensive evidence that associates these resistances with the use, or abuse, of antibiotics in humans both in hospital and in the community. There is some suggestion that, with VRE, these resistances might originate from the several decades of use of animal feed additives.
29. Plant enzymes or meat marinades have been used for centuries to tenderize meats. For example, food might be wrapped in papaya leaves prior to cooking. Papain is an enzyme derived from these leaves, which catalyzes the breakdown of the muscle tissue, thus making the meat more tender. Figs and pineapples also contain protein-digesting enzymes which are produced as commercial meat tenderizers. These enzymes can only act on the surface of the meat, unless holes are poked in the surface, but the greater resultant fluid loss can be a problem in cooking. Most of these enzymes are most effective from 60–80°C but are denatured and rendered ineffective at boiling temperature.



- (b) The acid is a catalyst.
(c) $\text{CH}_3-\text{O}-\text{CH}_3$ must be in the rate-determining step.
(d) Any series of steps that uses up reactants, produces products, and consumes and regenerates the catalyst will be acceptable. For example,



- (e) **Potential Energy Diagram of a Proposed Three-Step Mechanism for the Hydrolysis of Dimethyl Ether**



Unit 4 Chemical Systems and Equilibrium

ARE YOU READY?

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Knowledge and Understanding

1. (a) solid, liquid, and gas
(b) The system is considered closed because matter cannot flow in or out of the system. Removal of the lid allows water molecules to escape, creating an open system.
(c) The reduction in size of the sugar cube as it dissolves proves that the solution is unsaturated.
(d) The crystal remains the same size because the solution is saturated with sugar. Crystallization and dissolving are both occurring at the same rate.
(e) The solution is saturated. The crystal would shrink in size if the solution was unsaturated.
2. (a) $Mg_{(s)} + 2 HCl_{(aq)} \rightarrow MgCl_{2(aq)} + H_{2(g)}$
(b) $n_{HCl} = v_{HCl} \times c_{HCl}$
 $= 0.250 \text{ L} \times 0.8 \text{ mol/L}$
 $n_{HCl} = 0.2 \text{ mol}$
2:1 mol ratio
 $\therefore n_{MgCl_2} = 0.1 \text{ mol}$
0.1 mol of magnesium chloride is produced.
(c) $c_{MgCl_2} = \frac{0.1 \text{ mol}}{0.250 \text{ L}}$
 $c_{MgCl_2} = 0.4 \text{ mol/L}$
The concentration of the magnesium chloride solution is 0.4 mol/L.
3. (a) A strong base, such as sodium hydroxide, $NaOH_{(aq)}$, raises the pH of water far more than a weak base like aqueous ammonia, $NH_3_{(aq)}$.
(b) An acid is a proton donor while a base is a proton acceptor.
(c) $HPO_{4(aq)}^{2-} + HSO_{4(aq)}^{-} \rightarrow H_2PO_{4(aq)}^{-} + SO_{4(aq)}^{2-}$
 $B_2 \quad \quad \quad A_1 \quad \quad \quad A_2 \quad \quad \quad B_1$
4. $C_3H_{6(g)} + 4.5 O_{2(g)} \rightarrow 3 CO_{2(g)} + 3 H_2O_{(g)}$
 $\Delta H = [3\Delta H_f(CO_{2(g)}) + 3\Delta H_f(H_2O_{(l)})] - [\Delta H_f(C_3H_{6(g)})]$
 $= [3 \text{ mol} \times (-393.5 \text{ kJ/mol}_{CO_{2(g)}}) + 3 \text{ mol} \times (-241.8 \text{ kJ/mol}_{H_2O_{(l)}})] - [+17.8 \text{ kJ/mol}_{C_3H_{6(g)}}]$
 $\Delta H = -1923.7 \text{ kJ/mol}_{C_3H_6}$

Inquiry and Communication

5. **Procedure**
 - (a)
 1. Put on eye protection and a lab apron.
 2. Add about 600 mL of water to a 1-L beaker on a hot plate.
 3. Raise the temperature of the water to 60°C and maintain the temperature at this level.
 4. Add 100 mL of water to a 125-mL flask.
 5. Add 0.020 g of calcium hydroxide to the flask.
 6. Insert a thermometer into the flask.

7. Use water bath to warm the contents of the flask up to 60°C.
8. Note if the calcium hydroxide had dissolved.
9. If the calcium hydroxide did completely dissolve, add another 0.02 g to the flask.
10. Repeat steps 7 through 9 until some calcium hydroxide remains.

Safety Precautions

Wear eye protection and lab aprons.

- (b) If 0.10 g of calcium hydroxide dissolves in 100 mL, then 1.0 g will dissolve in 1 L of water.

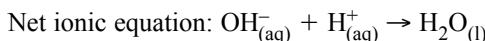
$$\begin{aligned} n_{\text{Ca(OH)}_2\text{(aq)}} &= \frac{1.0 \text{ g}}{74.10 \text{ g/mol}} \\ n_{\text{Ca(OH)}_2\text{(aq)}} &= 0.0135 \text{ mol} \quad (\text{extra digits carried}) \\ [\text{Ca(OH)}_2\text{(aq)}] &= \frac{0.0135 \text{ mol}}{1.0 \text{ L}} \\ [\text{Ca(OH)}_2\text{(aq)}] &= 0.0135 \text{ mol/L} \end{aligned}$$

Since there are two hydroxide ions in each $\text{Ca(OH)}_2\text{(aq)}$

$$\begin{aligned} [\text{OH}^-_{\text{(aq)}}] &= 2 \times [\text{Ca(OH)}_2\text{(aq)}] \\ [\text{OH}^-_{\text{(aq)}}] &= 0.027 \text{ mol/L} \end{aligned}$$

The hydroxide concentration is 0.027 mol/L.

- (c) The calculation assumes that the ionization of water does not contribute a significant amount of hydroxide.
6. (a) Chemical equation: $\text{NaOH}_{\text{(aq)}} + \text{HCl}_{\text{(aq)}} \rightarrow \text{H}_2\text{O}_{\text{(l)}} + \text{NaCl}_{\text{(aq)}}$



- (b) neutralization reaction

- (c) buret

- (d) titration

- (e) an acid–base indicator

- (f) **Procedure**

Add three drops of bromothymol blue indicator to the flask.

- Add base in small increments to the titration flask. Swirl the flask carefully during each addition.
- Continue adding base until a bromothymol blue endpoint.

Safety Precautions

Eye protection and a lab apron must be worn.

- (g) 15.00 mL
- (h) 7
- (i) Test the solution with pH test strips or a pH meter.
- (j) $[\text{H}^+_{\text{(aq)}}] = 1.0 \times 10^{-7} \text{ mol/L}$

$$7. \text{ (a)} \frac{(0.020)(0.030)}{(0.10)x} = 2.3 \times 10^{-4}$$

$$\frac{6.0 \times 10^{-4}}{(0.10)x} = 2.3 \times 10^{-4}$$

$$\frac{6.0}{(0.10)x} = 2.3$$

$$\frac{60}{x} = 2.3$$

$$x = \frac{60}{2.3}$$

$$x = 26$$

$$(b) \quad \frac{(2x)^2}{(x - 0.20)^2} = 49$$

$$\sqrt{\frac{(2x)^2}{(x - 0.20)^2}} = \sqrt{49}$$

$$\frac{2x}{x - 0.20} = 7$$

$$7x - 1.4 = 2x$$

$$5x = 1.4$$

$$x = 0.28$$

$$(c) \quad \frac{(3x)^2}{(x - 1.0)(x - 3.0)} = 2.0$$

$$\frac{9x^2}{(x^2 - 4x + 3)} = 2.0$$

$$9x^2 = 2x^2 - 8x + 6$$

$$7x^2 + 8x - 6 = 0$$

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

$$= \frac{-8 \pm \sqrt{8^2 - 4 \times 7(-6)}}{2 \times 1}$$

$$= 0.52 \text{ or } -1.7$$

8. Since the pH scale is logarithmic, a change in only 1 pH unit represents a 10-fold change in acidity. Sourville's water is on average over 10 times more acidic than neutral water. The August and September readings were approximately 100 times the acidity of neutral water. Although the acidity from the occasional soft drink or salad may not be a health risk, prolonged exposure to excess acid is a potential health risk. For example, below a pH of 5.5, tooth enamel begins to break down. The water commissioner should take the appropriate steps to raise the pH of the town's water supply.

CHAPTER 7 CHEMICAL SYSTEMS IN EQUILIBRIUM

Reflect on Your Learning

(Page 422)

1. This is not an example of dynamic equilibrium because there are no opposing processes taking place – even at the microscopic level. “Dynamic” implies change, or movement.
2. Household examples of dynamic equilibrium are:
 - dissolved carbon dioxide in soft drinks in equilibrium with gaseous carbon dioxide in the air space above the soft drink in the bottle;
 - undissolved sugar at the bottom of a cup of tea in equilibrium with dissolved sugar;
 - the temperature of a house staying steady as the furnace warms the air inside, but heat leaks out through cracks and by radiation.
3. The presence of the iodide ion prevents some of the lead iodide from dissolving.
4. (a) The double arrow implies that two opposite chemical reactions are occurring at the same rate.
(b) Heating the container would decrease the production of carbon dioxide since the reverse reaction consumes the applied heat.
5. (Most students will probably conclude that they are not able to answer the question at this stage.) The reaction should proceed spontaneously as written because its products are in a more random state than the reactant.

Try This Activity: Shakin’ the Blues

(Page 423)

- (a) Some chemical reactions are reversible.
- (b) The solution turns blue after being shaken and then returns to colourless after being allowed to stand for a few moments. This cycle can be repeated.
- (c) The colour changes will continue forever.
- (d) The blue–colourless cycle continues even after 10 cycles. (Note: After a considerable amount of time, the solution turns yellow and the colour changes stop.)

7.1 DYNAMIC EQUILIBRIUM IN CHEMICAL SYSTEMS

Try This Activity: The Coin Exchange: Establishing Dynamic Equilibrium

(Page 425)

- (a) The player with the smaller exchange rate gained pennies until a maximum was reached. The player with the larger exchange rate lost pennies until a minimum number was reached.
- (b) Groups with the largest difference in the initial amount of pennies had the most exchanges before the equilibrium was established. Groups with exchange rates that were similar took longer to reach equilibrium. This is because the pennies from one side were replacing almost all the pennies taken from the other pile.
- (c) The partner with the larger exchange rate always had less pennies. The number of pennies never reaches zero because some are always returned.
- (d) During the course of the activity, the number of pennies approaches a constant value.

Try This Activity: Digesting a Precipitate

(Page 426)

- (a) The settling time decreases over the course of one week.
- (b) The size of the crystals increases.
- (c) For the system to be at equilibrium, two opposing reactions need to be occurring at the same rate in the closed system. The solution had to be saturated because crystals were always present at the bottom of the flask. Over the course of the week the crystals grew, implying that crystallization was still occurring. However, the number of crystals also decreased, proof that dissolving was occurring. If the rate of crystallization and dissolving were not equal, the crystals would have either disappeared or grown in number and size.

CHAPTER 7 CHEMICAL SYSTEMS IN EQUILIBRIUM

Reflect on Your Learning

(Page 422)

1. This is not an example of dynamic equilibrium because there are no opposing processes taking place – even at the microscopic level. “Dynamic” implies change, or movement.
2. Household examples of dynamic equilibrium are:
 - dissolved carbon dioxide in soft drinks in equilibrium with gaseous carbon dioxide in the air space above the soft drink in the bottle;
 - undissolved sugar at the bottom of a cup of tea in equilibrium with dissolved sugar;
 - the temperature of a house staying steady as the furnace warms the air inside, but heat leaks out through cracks and by radiation.
3. The presence of the iodide ion prevents some of the lead iodide from dissolving.
4. (a) The double arrow implies that two opposite chemical reactions are occurring at the same rate.
(b) Heating the container would decrease the production of carbon dioxide since the reverse reaction consumes the applied heat.
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(Page 423)

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PRACTICE

(Page 428)

Understanding Concepts

- Evaporating water molecules cannot escape from the plastic bag. The saturation of the air inside the bag with water vapour prevents the towel from drying completely as a dynamic equilibrium becomes established.
- Dissolution and crystallization continue to occur at the same rate, resulting in no visible changes.
- Stirring removes solute as it dissolves, lowering the concentration in the region of the solute, allowing further dissolution to occur.

Making Connections

- Hot moist air can escape from the clothes dryer through the exhaust vent, to be replaced by drier air.
- Resealing carbonated soft drink bottles prevents carbon dioxide gas from leaving the solution. Equilibrium is quickly reestablished between dissolved CO₂ and gaseous CO₂ in the air space above the soft drink.

PRACTICE

(Page 437)

Understanding Concepts

$$6. [\text{CO}_{2(\text{g})}]_{\text{initial}} = \frac{2.0 \text{ mol}}{5.0 \text{ L}}$$

$$[\text{CO}_{2(\text{g})}]_{\text{initial}} = 0.40 \text{ mol/L}$$

ICE Table for the Decomposition of Carbon Dioxide			
	2 CO _{2(g)} ⇌	2 CO _(g) +	O _{2(g)}
Initial concentration (mol/L)	0.4	0	0
Change in concentration (mol/L)	-2x	+2x	+x
Equilibrium concentration (mol/L)	0.39		

At equilibrium:

$$[\text{CO}_{2(\text{g})}] = 0.40 \text{ mol/L} - 2x$$

$$[\text{CO}_{2(\text{g})}] = 0.39$$

$$2x = 0.01$$

$$[\text{CO}_{(\text{g})}] = 2x$$

$$[\text{CO}_{(\text{g})}] = 0.01 \text{ mol/L}$$

$$[\text{O}_{2(\text{g})}] = x$$

$$x = 0.005$$

The concentration of carbon monoxide is 0.01 mol/L and the concentration of oxygen is 0.005 mol/L.

$$7. [\text{NOCl}_{(\text{g})}]_{\text{initial}} = \frac{2.0 \text{ mol}}{2.0 \text{ L}}$$

$$[\text{NOCl}_{(\text{g})}]_{\text{initial}} = 1.0 \text{ mol/L}$$

ICE Table for the Decomposition of NOCl			
	2 NOCl _(g) ⇌	2 NO _(g) +	Cl _{2(g)}
Initial concentration (mol/L)	1.0		
Change in concentration (mol/L)	-2x	+2x	+x
Equilibrium concentration (mol/L)		0.032	

At equilibrium:

$$[\text{NO}_{(\text{g})}] = 0.32 \text{ mol/L}$$

$$[\text{NO}_{(\text{g})}] = 2x$$

$$x = 0.16 \text{ mol/L}$$

$$[\text{NOC1}_{(\text{g})}] = 1.0 - 2x$$

$$= 1.0 - 0.32$$

$$[\text{NOC1}_{(\text{g})}] = 0.68 \text{ mol/L}$$

$$[\text{Cl2}_{(\text{g})}] = x$$

$$= 0.16 \text{ mol/L}$$

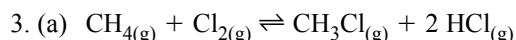
The concentration of $\text{NO}_{(\text{g})}$ and $\text{Cl2}_{(\text{g})}$ are 0.68 mol/L and 0.16 mol/L, respectively.

SECTION 7.1 QUESTIONS

(Page 437)

Understanding Concepts

1. (a) No observable changes occur.
(b) Equilibrium is considered to be “dynamic” because changes are still occurring at the microscopic level.
(c) The rates of the two opposing processes are equal.
2. (Answers will vary. Possible examples include:
 - undissolved sugar at the bottom of cup of tea (dynamic equilibrium)
 - an ice cube floating in water at 0°C (dynamic equilibrium)
 - carbon dioxide gas in equilibrium with dissolved carbon dioxide in soft drinks (dynamic equilibrium)
 - preparing a saturated sugar solution when making “rock” candy (dynamic equilibrium)



(b) percent reaction = $\frac{\text{actual product yield}}{\text{theoretical product yield}} \times 100\%$

$$= \frac{1.4}{2.0} \times 100\%$$

percent reaction = 70%

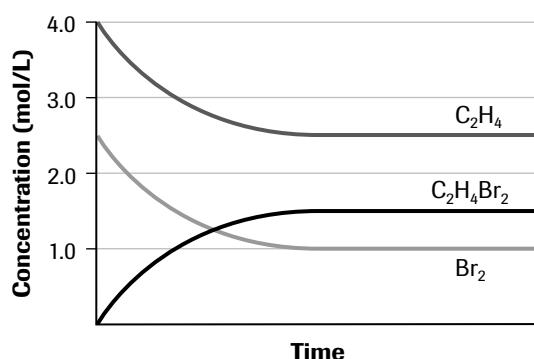
The percent reaction of this equilibrium is 70%. This equilibrium favours the products.

4. (a)

ICE Table for the Reaction $\text{C}_2\text{H}_4_{(\text{g})}$ with $\text{Br}_2_{(\text{g})}$			
	$\text{C}_2\text{H}_4_{(\text{g})}$	$\text{Br}_2_{(\text{g})} \rightleftharpoons$	$\text{C}_2\text{H}_4\text{Br}_2_{(\text{g})}$
Initial concentration (mol/L)	4.00	2.50	0
Change in concentration (mol/L)	-1.50	-1.50	+1.50
Equilibrium concentration (mol/L)	2.50	1.50	1.50

(b)

Reaction of Ethene



$$(c) \text{ percent reaction} = \frac{\text{actual product yield}}{\text{theoretical product yield}} \times 100\% \\ = \frac{1.5}{2.5} \times 100\%$$

percent reaction = 60%

5. (a) $\text{N}_{2(\text{g})} + 3 \text{H}_{(\text{g})} \rightleftharpoons 2 \text{NH}_{3(\text{g})}$ < 50%
- (b) $\text{C}_{(\text{s})} + \text{H}_2\text{O}_{(\text{g})} \rightleftharpoons \text{CO}_{(\text{g})} + \text{H}_{2(\text{g})}$ > 50%
- (c) $2 \text{Ag}_{(\text{aq})} + \text{Cu}_{(\text{s})} \rightleftharpoons 2 \text{Ag}_{(\text{s})} + \text{Cu}_{(\text{aq})}^{2+}$ > 99%
- (d) $2 \text{SO}_{2(\text{g})} + \text{O}_{2(\text{g})} \rightleftharpoons 2 \text{SO}_{3(\text{g})}$ > 50%

6. The addition reactions of halogens and alkenes are generally quantitative, so for the reaction of bromine with ethene (ethylene) a >99% yield of products is predicted.

7. (a) $n_{\text{HI}} = 2.00 \text{ L} \times 0.00 \text{ mol/L}$

$$n_{\text{HI}} = 0.00 \text{ mol}$$

$$n_{\text{H}_2} = 2.00 \text{ L} \times 6.0 \text{ mol/L}$$

$$n_{\text{H}_2} = 12.0 \text{ mol}$$

$$n_{\text{I}_2} = 2.00 \text{ L} \times 6.0 \text{ mol/L}$$

$$n_{\text{I}_2} = 12.0 \text{ mol}$$

(b)

ICE Table for the Reaction of Hydrogen and Iodine

	$\text{H}_{2(\text{g})} +$	$\text{I}_{2(\text{g})} \rightleftharpoons$	$2 \text{HBr}_{(\text{g})}$
Initial concentration (mol/L)	6.0	4.0	0.0
Change in concentration (mol/L)	3.6	3.6	7.2
Equilibrium concentration (mol/L)	2.4	0.4	7.2

At equilibrium, 14.4 mol of hydrogen iodide had formed.

(c) Since iodine is the limiting reagent, the maximum possible yield of hydrogen iodide is calculated as

$$n_{\text{HI}} = 8.0 \text{ mol} \times \frac{2 \text{ mol}}{1 \text{ mol}}$$

$$n_{\text{HI}} = 16.0 \text{ mol}$$

$$\text{percent reaction} = \frac{14.4 \text{ mol}}{16.0 \text{ mol}} \times 100\%$$

$$\text{percent reaction} = 90\%$$

(d) At equilibrium, the rate of the forward reaction is equal to the rate of the reverse reaction. In this case, at equilibrium, the rate of reaction of hydrogen with iodine is equal to the rate of decomposition of hydrogen.

8.

ICE Table for the Decomposition of $\text{PCl}_{5(\text{g})}$

	$\text{PCl}_{5(\text{g})} \rightleftharpoons$	$\text{PCl}_{3(\text{g})} +$	$\text{Cl}_{2(\text{g})}$
Initial concentration (mol/L)	1.00	0	0
Change in concentration (mol/L)	-0.100	+0.100	+0.100
Equilibrium concentration (mol/L)	0.90	0.100	0.100

The concentrations of $\text{PCl}_{3(\text{g})}$ and $\text{Cl}_{2(\text{g})}$ are both 0.100 mol/L.

9. (a)

ICE Table for the Production of Methanol			
	$\text{CO}_{(\text{g})} +$	$2 \text{H}_{2(\text{g})} \rightleftharpoons$	$\text{CH}_3\text{OH}_{(\text{g})}$
Initial concentration (mol/L)	0.100	0.200	0
Change in concentration (mol/L)	-0.040	-0.080	+0.040
Equilibrium concentration (mol/L)	0.060	0.120	0.040

The concentrations of carbon monoxide and methanol are 0.060 mol/L and 0.0400 mol/L, respectively.

$$(b) \text{ percent reaction} = \frac{\text{actual product yield}}{\text{theoretical product yield}} \times 100\% \\ = \frac{0.0400}{0.100} \times 100\%$$

$$\text{percent reaction} = 40\%$$

10. (a) The saturated solution is in a state of dynamic equilibrium. Even though the appearance of the system did not change, the evidence suggests that some radioactive iodine became incorporated into the original sample of iodine. Furthermore, the radioactivity of the solution implies that some radioactive iodine had dissolved.

Making Connections

11. (a) Immediately following a fructose-rich meal, a net amount of diffusion of fructose will occur into the (surrounding) intestinal cells because the concentration of fructose in the intestinal tract is higher than the concentration of fructose in the intestinal cells. Diffusion into the cells continues until the concentration of fructose inside the intestinal cells and the intestinal tract are equal. At this point, a dynamic equilibrium is reached; the rate of fructose diffusing into the cells equals the rate of fructose diffusing out of the cells. Thus, a certain amount of fructose remains in the intestinal tract (unabsorbed).
 (b) Cells use active transport mechanisms to pump nutrient molecules such as glucose and amino acids (digested protein). These systems require the use of cell membrane proteins and cell energy in the form of adenosine triphosphate (ATP). Using energy to actively pump certain nutrients against a concentration gradient ensures that intestinal cells absorb the majority of nutrient molecules.

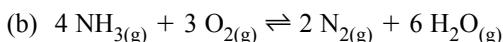
7.2 EQUILIBRIUM LAW IN CHEMICAL REACTIONS

PRACTICE

(Page 442)

Understanding Concepts

$$1. (\text{a}) K = \frac{[\text{SO}_{3(\text{g})}]^2}{[\text{SO}_{2(\text{g})}]^2[\text{O}_{2(\text{g})}]}$$



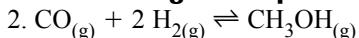
$$K = \frac{[\text{N}_{2(\text{g})}]^2[\text{H}_2\text{O}_{(\text{g})}]^6}{[\text{NH}_{3(\text{g})}]^4[\text{O}_{2(\text{g})}]^3}$$

$$(\text{c}) K = \frac{[\text{NO}_{(\text{g})}]^2[\text{Br}_{2(\text{g})}]}{[\text{NOBr}_{(\text{g})}]^2}$$

PRACTICE

(Page 444)

Understanding Concepts



The concentrations of $\text{PCl}_{3(\text{g})}$ and $\text{Cl}_{2(\text{g})}$ are both 0.100 mol/L.

9. (a)

ICE Table for the Production of Methanol			
	$\text{CO}_{(\text{g})} +$	$2 \text{H}_{2(\text{g})} \rightleftharpoons$	$\text{CH}_3\text{OH}_{(\text{g})}$
Initial concentration (mol/L)	0.100	0.200	0
Change in concentration (mol/L)	-0.040	-0.080	+0.040
Equilibrium concentration (mol/L)	0.060	0.120	0.040

The concentrations of carbon monoxide and methanol are 0.060 mol/L and 0.0400 mol/L, respectively.

$$(b) \text{ percent reaction} = \frac{\text{actual product yield}}{\text{theoretical product yield}} \times 100\% \\ = \frac{0.0400}{0.100} \times 100\%$$

$$\text{percent reaction} = 40\%$$

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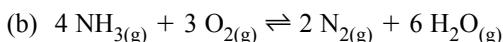
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(Page 442)

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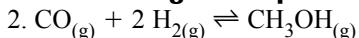
$$K = \frac{[\text{N}_{2(\text{g})}]^2[\text{H}_2\text{O}_{(\text{g})}]^6}{[\text{NH}_{3(\text{g})}]^4[\text{O}_{2(\text{g})}]^3}$$

$$(\text{c}) K = \frac{[\text{NO}_{(\text{g})}]^2[\text{Br}_{2(\text{g})}]}{[\text{NOBr}_{(\text{g})}]^2}$$

PRACTICE

(Page 444)

Understanding Concepts

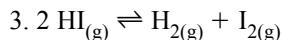


$$K = \frac{[\text{CH}_3\text{OH}_{(\text{g})}]}{[\text{CO}_{(\text{g})}][\text{H}_{2(\text{g})}]^2}$$

$$= \frac{[0.021]}{[0.079][0.158]^2}$$

$$K = 10.6$$

The value of the equilibrium constant for this reaction at 327°C is 10.6.



$$K = \frac{[\text{H}_{2(\text{g})}][\text{I}_{2(\text{g})}]}{[\text{HI}_{(\text{g})}]^2}$$

$$= \frac{[1.065][0.065]}{[1.870]^2}$$

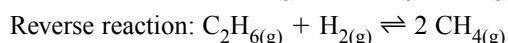
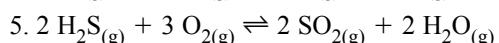
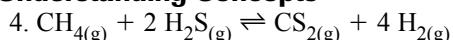
$$K = 0.020$$

The value of the equilibrium constant for this reaction at 440°C is 0.020.

PRACTICE

(Page 444)

Understanding Concepts



$$K' = \frac{[\text{CH}_{4(\text{g})}]^2}{[\text{H}_{2(\text{g})}][\text{C}_2\text{H}_{6(\text{g})}]}$$

$$= \frac{1}{K}$$

$$= \frac{1}{9.5 \times 10^{-13}}$$

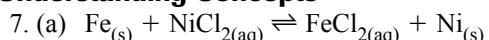
$$K' = 1.1 \times 10^{12}$$

The value of the equilibrium constant for the reverse reaction is 1.1×10^{12} .

PRACTICE

(Page 447)

Understanding Concepts



$$K = \frac{[\text{Fe}_{(\text{aq})}^{2+}]}{[\text{Ni}_{(\text{aq})}^{2+}]}$$

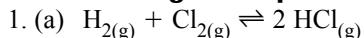
(b) $K = \frac{[\text{Zn}_{(\text{aq})}^{2+}]^3}{[\text{Cr}_{(\text{aq})}^{3+}]^2}$

(c) $K = [\text{H}_2\text{O}_{(\text{g})}][\text{CO}_{2(\text{g})}]$

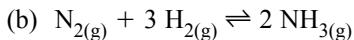
SECTION 7.2 QUESTIONS

(Page 448)

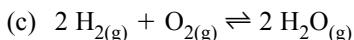
Understanding Concepts



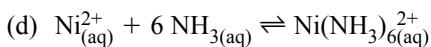
$$K = \frac{[\text{HCl}_{(\text{g})}]^2}{[\text{H}_{2(\text{g})}][\text{Cl}_{2(\text{g})}]}$$



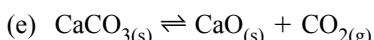
$$K = \frac{[\text{NH}_{3(\text{g})}]^2}{[\text{N}_{2(\text{g})}][\text{H}_{2(\text{g})}]^3}$$



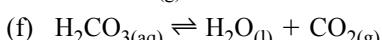
$$K = \frac{[\text{H}_2\text{O}_{(\text{g})}]^2}{[\text{H}_{2(\text{g})}]^2[\text{O}_{2(\text{g})}]}$$



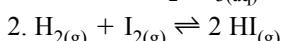
$$K = \frac{[\text{Ni}(\text{NH}_3)_{6(\text{aq})}^{2+}]}{[\text{Ni}_{(\text{aq})}^{2+}][\text{NH}_{3(\text{aq})}]^6}$$



$$K = [\text{CO}_{2(\text{g})}]$$



$$K = \frac{[\text{CO}_{2(\text{g})}]}{[\text{H}_2\text{CO}_{3(\text{aq})}]}$$



$$K = \frac{[\text{HI}_{2(\text{g})}]^2}{[\text{H}_{2(\text{g})}][\text{I}_{2(\text{g})}]}$$

$$= \frac{[3.116]^2}{[0.442][0.442]}$$

$$K = 49.7$$

The value of the equilibrium constant at 485°C is 49.7.

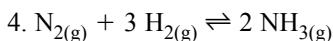


$$K = \frac{[\text{PCl}_{3(\text{g})}][\text{Cl}_{2(\text{g})}]}{[\text{PCl}_{5(\text{g})}]}$$

$$= \frac{[0.014][0.014]}{[4.3 \times 10^{-4}]}$$

$$K = 0.46$$

The value of the equilibrium constant at 200°C is 0.46.



$$K = \frac{[\text{NH}_{3(\text{g})}]^2}{[\text{N}_{2(\text{g})}][\text{H}_{2(\text{g})}]^3}$$

$$K = 8.00 \times 10^{-7}$$

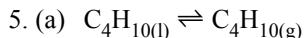
$$[\text{NH}_{3(\text{g})}]^2 = 8.00 \times 10^{-7} \times [\text{N}_{2(\text{g})}][\text{H}_{2(\text{g})}]^3$$

$$= 8.00 \times 10^{-7} [1.50][0.50]^3$$

$$[\text{NH}_{3(\text{g})}]^2 = 1.5 \times 10^{-7}$$

$$[\text{NH}_{3(\text{g})}] = 3.9 \times 10^{-4} \text{ mol/L}$$

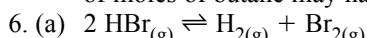
The equilibrium concentration of ammonia is $3.9 \times 10^{-4} \text{ mol/L}$.



$$K = [\text{C}_4\text{H}_{10(\text{g})}]$$

(b) The amount of butane in the gas phase varies directly with the temperature. As the temperature increases, for example, more butane will be found in the gas phase. However, the butane concentration at a particular temperature is a constant. Since the value of the equilibrium constant depends only on $[\text{C}_4\text{H}_{10(\text{g})}]$, it also is constant.

(c) The concentration of butane gas depends only on the temperature and not on the amount of liquid butane. If the volume of liquid butane decreases, there's more space above the liquid for gaseous butane to occupy. The number of moles of butane may have increased but the mol/L remains the same.



$$(b) K = \frac{[\text{H}_{2(\text{g})}][\text{Br}_{2(\text{g})}]}{[\text{HBr}_{(\text{g})}]^2}$$

$$(c) n_{\text{HBr}_{(\text{g})}} = C_{\text{HBr}_{(\text{g})}} \times 2.00 \text{ L}$$

$$= 0.100 \text{ mol/L} \times 2.00 \text{ L}$$

$$n_{\text{HBr}_{(\text{g})}} = 0.200 \text{ mol}$$

0.200 mol of $\text{HBr}_{(\text{g})}$ is present at equilibrium.

(d) $n_{\text{HBr}} = 0.100 \text{ mol/L} \times 2.00 \text{ L}$

$$n_{\text{HBr}} = 0.200 \text{ mol}$$

0.200 mol of hydrogen bromide is present at equilibrium.

$$n_{\text{HBr}_{\text{reacted}}} = n_{\text{HBr}_{\text{initial}}} - n_{\text{HBr}_{\text{equilibrium}}}$$

$$= 1.00 \text{ mol} - 0.200 \text{ mol}$$

$$n_{\text{HBr}_{\text{reacted}}} = 0.800 \text{ mol}$$

0.800 mol of hydrogen bromide reacted.

(e) Given the 2:1 ratio, 0.400 mol of both hydrogen and bromine are produced.

$$(f) [\text{H}_2] = \frac{0.400 \text{ mol}}{2.00 \text{ L}}$$

$$= 0.200 \text{ mol/L}$$

$$[\text{H}_2] = [\text{Br}_2]$$

The concentrations of hydrogen and bromine are both 0.200 mol/L, while the hydrogen bromide concentration is 0.100 mol/L.

$$(g) K = \frac{[\text{H}_{2(\text{g})}][\text{Br}_{2(\text{g})}]}{[\text{HBr}_{(\text{g})}]^2}$$

$$= \frac{[0.20][0.20]}{[0.100]^2}$$

$$K = 4.0$$

The value of the equilibrium constant is 4.00.

7. (a) One could specify either the value of the equilibrium constant or the extent of reaction (as percent reaction).
 (b) Both methods measure the extent to which reactants become products in a closed system. However, percent reaction describes the extent of the reaction as the yield of product at equilibrium compared to the maximum possible yield. The value of the equilibrium constant gives the ratio of products to reactants at equilibrium. Furthermore, the percent reaction is variable, for a given reaction, depending on the concentration of reactants; the equilibrium constant is independent of concentration.
 (c) Both methods are effective in describing the extent of the reaction. However, they also have their limitations. The value of the equilibrium constant is valid only for a given temperature. Percent reaction values depend not only on temperature but on concentration as well.

Applying Inquiry Skills

8. Analysis

$$(a) K = \frac{[\text{SO}_{3(\text{g})}]^2}{[\text{SO}_{2(\text{g})}]^2[\text{O}_{2(\text{g})}]}$$

For trial 1...

$$K = \frac{[3.50 \times 10^{-2}]^2}{[1.50 \times 10^{-1}]^2[1.26 \times 10^{-2}]}$$

$$K = 4.32$$

For trial 2...

$$K = \frac{[2.60 \times 10^{-3}]^2}{[5.90 \times 10^{-2}]^2[4.50 \times 10^{-4}]}$$

$$K = 4.32$$

For trial 3...

$$K = \frac{[3.6 \times 10^{-3}]^2}{[1.00 \times 10^{-2}]^2[3.0 \times 10^{-2}]}$$

$$K = 4.32$$

Making Connections

9. The small value of the equilibrium constant suggests that the equilibrium strongly favours oxygen. Only a negligible amount of ozone is produced by this reaction.

7.3 QUALITATIVE CHANGES IN EQUILIBRIUM SYSTEMS

PRACTICE

(Page 457)

Understanding Concepts

1. The equilibrium will shift to the
 (a) left
 (b) right
 (c) left
 (d) right
 (e) right

7. (a) One could specify either the value of the equilibrium constant or the extent of reaction (as percent reaction).
- (b) Both methods measure the extent to which reactants become products in a closed system. However, percent reaction describes the extent of the reaction as the yield of product at equilibrium compared to the maximum possible yield. The value of the equilibrium constant gives the ratio of products to reactants at equilibrium. Furthermore, the percent reaction is variable, for a given reaction, depending on the concentration of reactants; the equilibrium constant is independent of concentration.
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Applying Inquiry Skills

8. Analysis

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For trial 1...

$$K = \frac{[3.50 \times 10^{-2}]^2}{[1.50 \times 10^{-1}]^2[1.26 \times 10^{-2}]}$$

$$K = 4.32$$

For trial 2...

$$K = \frac{[2.60 \times 10^{-3}]^2}{[5.90 \times 10^{-2}]^2[4.50 \times 10^{-4}]}$$

$$K = 4.32$$

For trial 3...

$$K = \frac{[3.6 \times 10^{-3}]^2}{[1.00 \times 10^{-2}]^2[3.0 \times 10^{-2}]}$$

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Making Connections

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7.3 QUALITATIVE CHANGES IN EQUILIBRIUM SYSTEMS

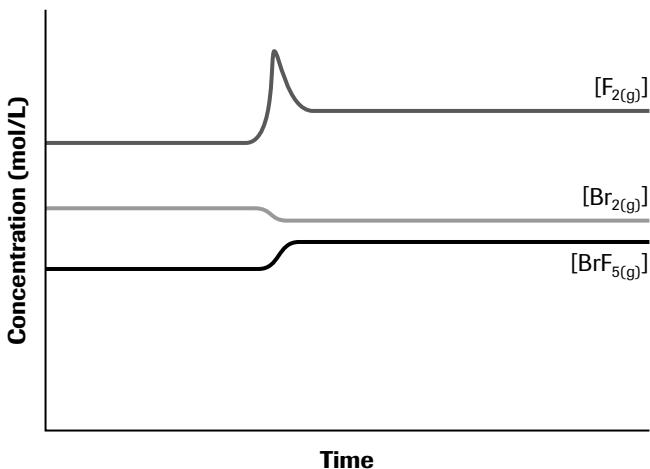
PRACTICE

(Page 457)

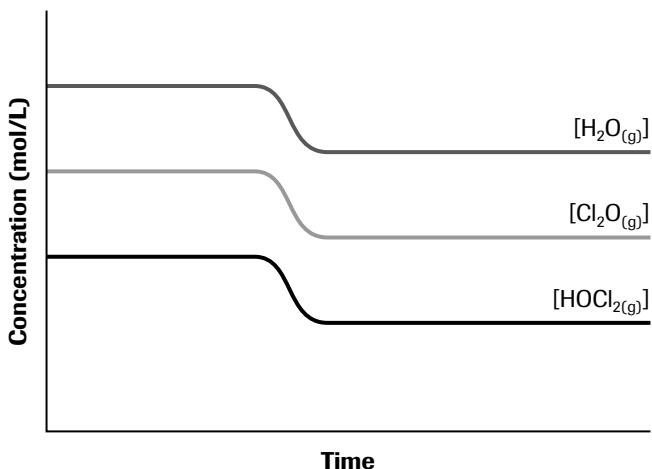
Understanding Concepts

1. The equilibrium will shift to the
- left
 - right
 - left
 - right
 - right

2. (a) **Graph Showing Adjustment of $\text{BrF}_{5(\text{g})}$ Equilibrium**



(b) **Graph Showing Adjustment of FeSCN Equilibrium**



3. (a) The catalyst reduces the time required for the system to reach equilibrium.

(b) The equilibrium concentration of hydrogen would not be affected by the use of a catalyst.

4. The warmer temperatures of summer shift the equilibrium to the left, increasing the concentration of the brown gas, NO_2 .

5. Based on Le Châtelier's principle, the conditions that favour the production of methane include:

- decreasing the pressure on the system
- increasing the concentration of the reactants
- removing the products as they are produced
- cooling the reaction chamber

(In practice, raising the reaction temperature increases the rate of both reactions, thereby increasing the yield of methane.)

6. (a) An increase in acidity would favour the forward reaction, thereby promoting the decomposition of the stalagmites and stalactites.

(b) Water hardness, which results from increased levels of ions such as Ca^{2+} and Mg^{2+} , favours the reverse reaction, promoting the growth of the stalagmites and stalactites.

Applying Inquiry Skills

7. Prediction

(a) The addition of chloride ions will shift the equilibrium to the right.

Analysis

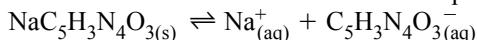
(b) The addition of chloride ions shifts the equilibrium to the right, changing the colour of the solution to green.

Evaluation

- (c) The addition of hydrochloric acid also increased the total volume of the solution, decreasing the concentration of entities in the equilibrium. Smaller volumes of more concentrated HCl or perhaps using solid NaCl would have improved the results.

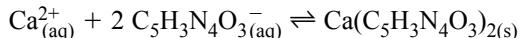
Making Connections

8. (a) One possible dietary recommendation is to reduce the consumption of protein-rich foods. This results in a lower concentration of urate ions in the bloodstream and promotes the dissolving of existing sodium urate crystals.



Alternatively, a reduction in the amount of sodium in the diet (and thus in the blood) would tend to shift the dissociation to the right. The dietitian might recommend that the patient avoid sodium-rich foods, particularly table salt.

- (b) Excess calcium in the blood can combine with the urate ion to precipitate as calcium urate.



- (c) Anti-inflammatory drugs such as indomethacin are commonly used to treat gout.

Non-dietary treatments of gout include:

- Tylenol for pain relief.
- anti-inflammatory drugs such as Indomethacin to help reduce the swelling.
- specific medications, e.g., benemid, that promote the excretion of uric acid in the urine.

SECTION 7.3 QUESTIONS

(Page 459)

Understanding Concepts

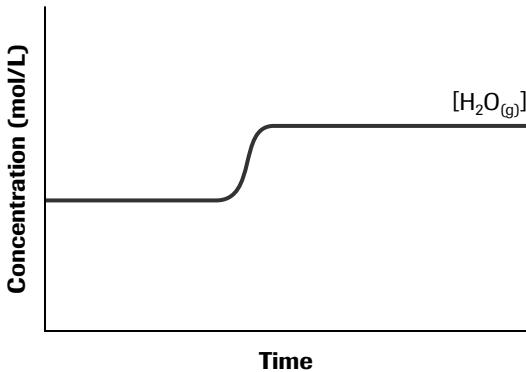
1. (a) temperature: An increase in temperature increases the kinetic energy of the colliding entities in a chemical reaction, increasing the likelihood of a successful collision occurring.

pressure: For systems involving gases, an increase in pressure increases the number of collisions occurring.

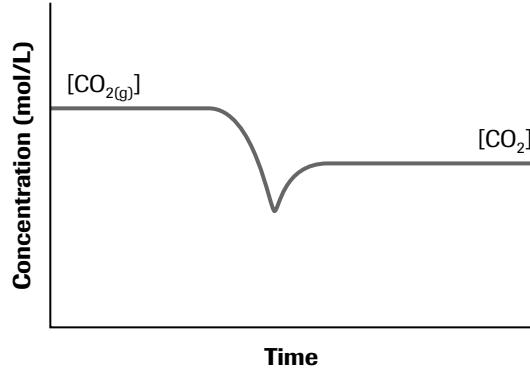
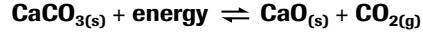
concentration: An increase in concentration generally also increases the number of collisions occurring.

- (b) Catalysts and surface area do not affect the position of equilibrium, and neither does the addition of inert gases.

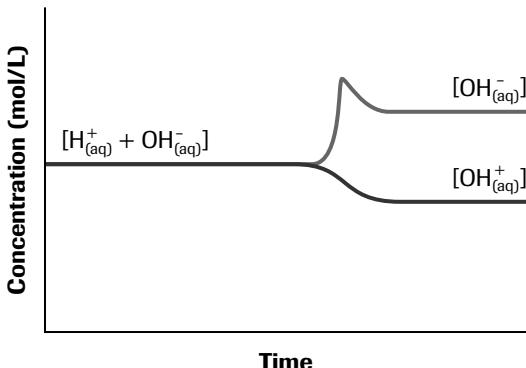
2. (a)



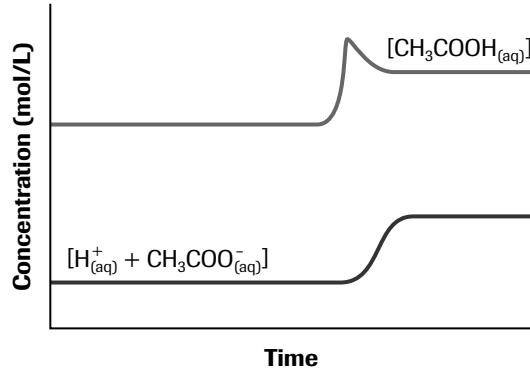
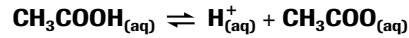
- (c)



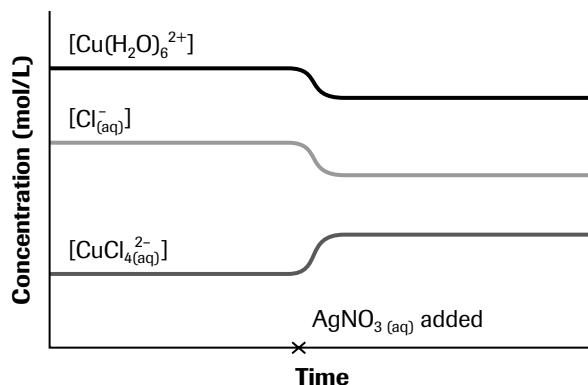
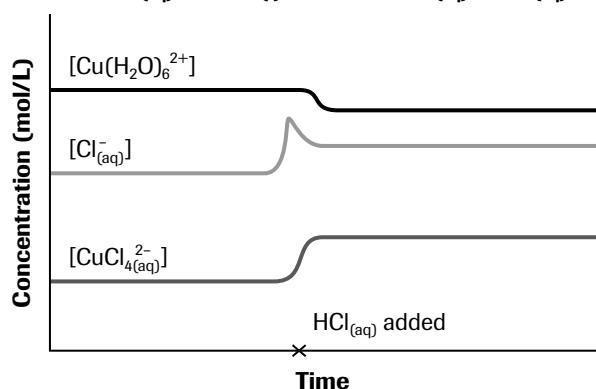
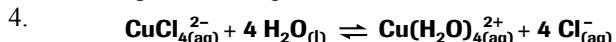
- (b)



- (d)



3. (a) When oxygen is added, the rate of the forward reaction is greater than that of the reverse, shifting the equilibrium to the right.
 (b) When the system is heated, the rate of the reverse reaction is greater than that of the forward, shifting the equilibrium to the left.
 (c) When $\text{NO}_{(\text{g})}$ is removed, the rate of the forward reaction is greater than that of the reverse, shifting the equilibrium to the right.
 (d) When the volume of the reaction vessel is decreased, the rate of the reverse reaction is greater than that of the forward, shifting the equilibrium to the left.
 (e) When an inert gas is added (without changing the volume), the amount/L of reactants and products doesn't change, and no equilibrium shift occurs.



5. Hydroxide ions combine with hydrogen ions to form water. The removal of $\text{H}_{(\text{aq})}^+$ results in the equilibrium shifting to the right.
 6. At A, the pressure of the system is decreased by increasing the volume.
 At B, the temperature is increased.
 At C, $\text{C}_2\text{H}_{6(\text{g})}$ is added to the system.
 At D, no change is apparent (although it is possible that a catalyst or an inert gas was added).
 At E, $\text{H}_{2(\text{g})}$ is added to the system.

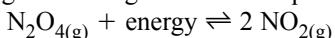
Applying Inquiry Skills

7. Question

- (a) How does increasing the pressure affect the nitrogen–dinitrogen tetroxide equilibrium?

Prediction

- (b) The nitrogen–dinitrogen tetroxide equilibrium is represented by the equation



According to Le Châtelier's principle, increasing the pressure of the nitrogen–dinitrogen tetroxide equilibrium causes the equilibrium to shift to the left, which decreases the number of gas molecules. (Two moles of $\text{NO}_{2(\text{g})}$ produce one mole of $\text{N}_2\text{O}_{4(\text{g})}$)

Experimental Design

- (c) A sample of nitrogen dioxide gas is compressed in a syringe and the intensity of the colour is used as evidence to test the prediction.

Evaluation

- (d) The experimental design should give reproducible qualitative results for this experiment. Given the toxicity of the gases involved, this experiment should only be conducted in a fume hood. The experimental design produced results that provided clear evidence that pressure does affect the nitrogen–dinitrogen tetroxide equilibrium. One flaw in the experimental design is that the experiment should be conducted in a fume hood, given the toxicity of the chemicals involved.

8. Prediction

- (a) (i) The equilibrium shifts to the right, changing colour from yellow to orange.
 (ii) The equilibrium shifts to the left, becoming more yellow.
 (iii) A yellow precipitate of barium chromate is produced, shifting the equilibrium to the left. The solution becomes more yellow.

Synthesis

- (b) An addition of acid to the test tube shifts the equilibrium to the right, dissolving the precipitate. Note: Barium dichromate is much more soluble than barium chromate.

Making Connections

9. (a) The Claus method is one of the most common methods of removing foul-smelling hydrogen sulfide during the processing of crude oil and natural gas. The Claus method occurs in two steps:
1. In the “thermal step,” hydrogen sulfide is burned with oxygen temperatures in excess of 850°C .
 2. During the “catalytic step,” the combustion products from step 1 are cooled and passed over an aluminum oxide catalyst, where the following reaction takes place:
$$2 \text{H}_2\text{S}_{(\text{g})} + \text{SO}_{2(\text{g})} \rightleftharpoons 3 \text{S}_{(\text{s})} + 2 \text{H}_2\text{O}_{(\text{g})}$$
Elemental sulfur is removed as it forms in the process. The remaining gases are passed on to other chambers where more sulfur removal takes place. Step 2 needs to be repeated 2–3 times because equilibrium prevents the reaction from going to completion.
- (b) Immediate removal of sulfur favours the forward reaction in the equilibrium, removing the hydrogen sulfide and sulfur dioxide from the processing plant emissions.
10. The first limitation is the limited oxygen supply on the spacecraft. Secondly, excess carbon dioxide exhaled by the astronauts will consume all the lithium hydroxide in the purification system, forcing the equilibrium to the right and eventually to completion. Without lithium hydroxide, carbon dioxide levels would soon increase, reaching toxic levels.
11. Reducing the pressure of a solution–gas equilibrium (blood and air in the body) reduces the quantity of gas (oxygen) that is dissolved in a solution (blood). At high altitudes, the human body can compensate for the loss of oxygen by increasing the number of red blood cells in the blood. This adaptation to increase the red blood cell count usually takes about three to four weeks, but it can be accelerated by transfusion.
12. Get the victim to fresh air as soon as possible. Administer oxygen with a bottle-fed breathing mask. Breathing 100% oxygen would shift the given equilibrium to the left, displacing carbon monoxide from hemoglobin.

7.4 CASE STUDY: THE HABER PROCESS: AMMONIA FOR FOOD AND BOMBS

PRACTICE

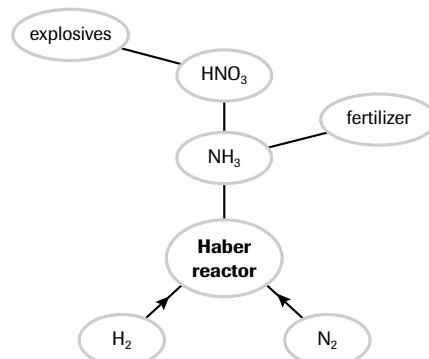
(Page 461)

Understanding Concepts

1. Factors increasing production include:
- removing $\text{NH}_{3(\text{g})}$
 - adding $\text{N}_{2(\text{g})}$
 - adding $\text{H}_{2(\text{g})}$
 - reducing the temperature slightly
 - raising the pressure
 - adding a catalyst (which will have the effect of speeding up both forward and reverse reactions)

Making Connections

2.



Synthesis

- (b) An addition of acid to the test tube shifts the equilibrium to the right, dissolving the precipitate. Note: Barium dichromate is much more soluble than barium chromate.

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7.4 CASE STUDY: THE HABER PROCESS: AMMONIA FOR FOOD AND BOMBS

PRACTICE

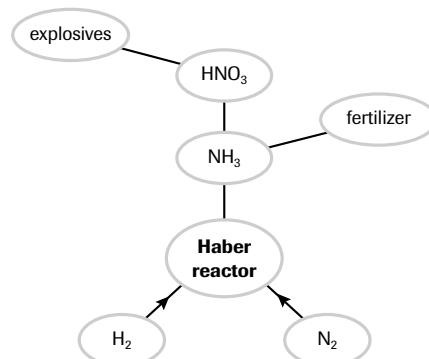
(Page 461)

Understanding Concepts

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Making Connections

2.



PRACTICE

(Page 462)

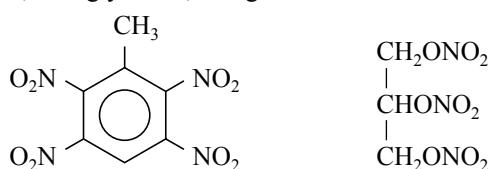
Understanding Concepts

3. Lowering the temperature would have the effect of slowing down the reaction.
4. The catalyst does not affect the position of the equilibrium since it lowers the activation energy for both the forward and reverse reactions. However, using a catalyst allows the manufacturer to run the process at a lower temperature and still maintain yield.

Making Connections

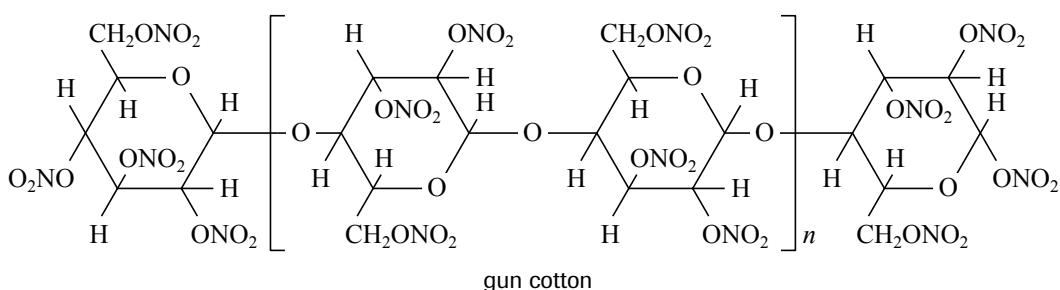
5. (a) TNT, nitroglycerine, and gun cotton

(b)

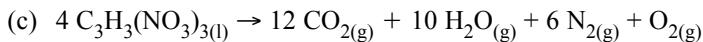


TNT

nitroglycerine



gun cotton



This reaction is explosive because it is highly exothermic ($\Delta H = 1415 \text{ kJ/mol}$ nitroglycerine) and converts four moles of liquid nitroglycerine into 29 moles of gaseous products.

- (d) Gun cotton (nitrocellulose) is a highly explosive nitrated cellulose made by soaking cotton (cellulose) in nitric acid and sulfuric acid; used to make smokeless gunpowder.

SECTION 7.4 QUESTIONS

(Page 462)

Making Connections

1. (a) Decrease the temperature, increase the pressure, increase $[\text{N}_{2(g)}]$, increase $[\text{H}_{2(g)}]$, and remove ammonia from the system.
(b) Decreasing the temperature will shift the equilibrium to the right but makes the reaction uneconomical because the yield of ammonia decreases.
(c) The heat released by the forward reaction can be used to help maintain the temperature of the reaction chamber. The company should also ensure that the equipment is well maintained so that gas leaks in the system do not reduce pressure. They should keep the system insulated to prevent heat loss, and they should use high-efficiency pumps and heaters to save on energy costs. The system should separate and recycle unreacted $\text{H}_{2(g)}$ and $\text{N}_{2(g)}$.
2. (a) Possible sources of these gases are: nitrogen—extraction from the atmosphere, and hydrogen—electrolysis of water.
(b) Hydrogen is produced by reacting methane ($\text{CH}_{4(g)}$, (natural gas)) with steam ($\text{H}_2\text{O}_{(g)}$), producing carbon dioxide ($\text{CO}_{2(g)}$) and hydrogen ($\text{H}_{2(g)}$). Nitrogen ($\text{N}_{2(g)}$) is obtained by the fractional distillation of air (~78% $\text{N}_{2(g)}$). Fractional distillation is a process by which the components in a chemical mixture are separated according to their different boiling points. Vapours from a boiling solution are passed along a cooled column. The temperature of the column gradually decreases along its length. Components with a higher boiling point condense on the column and return to the solution; components with a lower boiling point pass through the column, are condensed, and are collected in a suitable collecting vessel.
3. (a) Bacteria such as *Rhizobium* and *Azotobacter* absorb nitrogen from air and fix it into ammonia through a series of reactions that use an enzyme complex called nitrogenase as a catalyst.

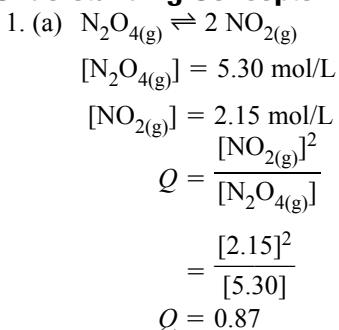
- (b) More nitrogen is fixed naturally (1.75×10^8 tonnes per year) than synthetically (8×10^7 tonnes per year).
- (c) Studies show that high levels of nitrogen fixation caused by nitrogen pollution are likely to cause severe declines in native plant communities by favouring weedy plants that favour high ammonia concentrations in soil. This problem can be reduced by decreasing the use of machines that burn fossil fuels such as automobiles, trucks, buses, planes, leaf blowers, lawn mowers, and jet skis, and by reducing the nitrogen oxide emissions of coal- and oil-burning electricity generating plants and large industries.

7.5 QUANTITATIVE CHANGES IN EQUILIBRIUM SYSTEMS

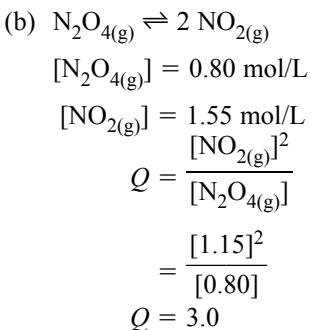
PRACTICE

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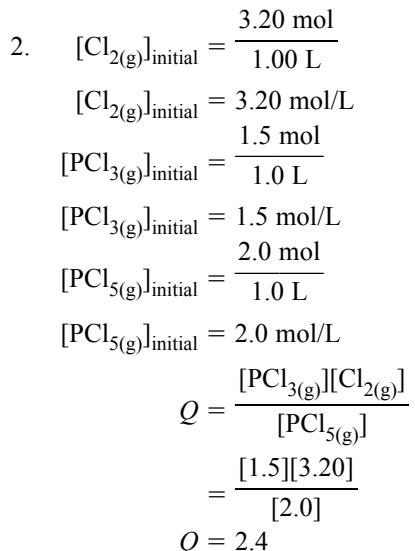
Understanding Concepts



Since the value of Q is equal to the value of K (0.87), the reaction is at equilibrium.



Since the value of Q is larger than the value of K (0.87), the reaction is not at equilibrium. In order to attain equilibrium, the reaction will shift to the left (as written). The concentration of the reactants will increase and the concentration of the products will decrease.



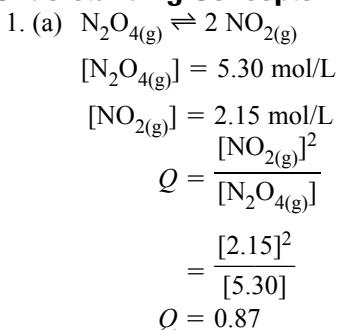
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7.5 QUANTITATIVE CHANGES IN EQUILIBRIUM SYSTEMS

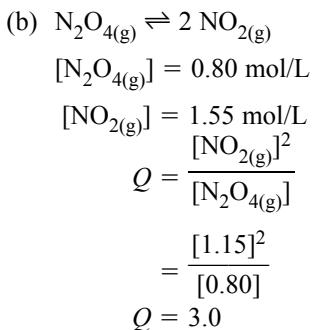
PRACTICE

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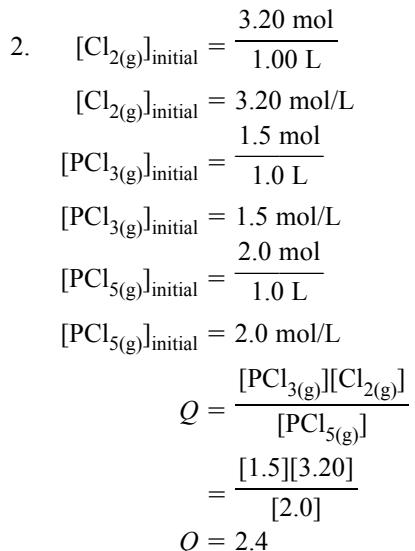
Understanding Concepts



Since the value of Q is equal to the value of K (0.87), the reaction is at equilibrium.



Since the value of Q is larger than the value of K (0.87), the reaction is not at equilibrium. In order to attain equilibrium, the reaction will shift to the left (as written). The concentration of the reactants will increase and the concentration of the products will decrease.



Since the value of Q is smaller than the value of K (12.5), the reaction is not at equilibrium. In order to attain equilibrium, the reaction will shift to the right (as written). The concentration of the reactants will decrease and the concentration of the products will increase.

PRACTICE

(Page 466)

Understanding Concepts

$$3. \quad K = \frac{[\text{NH}_3\text{(g)}]^2}{[\text{N}_2\text{(g)}][\text{H}_2\text{(g)}]^3}$$

$$K = 626$$

$$[\text{N}_2\text{(g)}] = \frac{[\text{NH}_3\text{(g)}]^2}{626[\text{H}_2\text{(g)}]^3}$$

$$= \frac{(0.46)^2}{626(0.50)^3}$$

$$[\text{N}_2\text{(g)}] = 2.7 \times 10^{-3} \text{ mol/L}$$

The equilibrium concentration of nitrogen is 2.7×10^{-3} mol/L.



$$K = \frac{[\text{PCl}_{3(\text{g})}][\text{Cl}_{2(\text{g})}]}{[\text{PCl}_{5(\text{g})}]}$$

$$K = 32$$

$$[\text{PCl}_{5(\text{g})}] = \frac{[\text{PCl}_{3(\text{g})}][\text{Cl}_{2(\text{g})}]}{32}$$

$$= \frac{[0.80][0.70]}{32}$$

$$[\text{PCl}_{5(\text{g})}] = 1.80 \times 10^{-2} \text{ mol/L}$$

The equilibrium concentration of phosphorus pentachloride is 1.8×10^{-3} mol/L.

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5. Initial concentrations...

$$[\text{CO}_{2(\text{g})}] = [\text{H}_{2(\text{g})}]$$

$$= \frac{1.00 \text{ mol}}{10.0 \text{ L}}$$

$$[\text{CO}_{2(\text{g})}] = 0.100 \text{ mol/L}$$

ICE Table for the Reaction of $\text{CO}_{2(\text{g})}$ with $\text{H}_{2(\text{g})}$				
	$\text{CO}_{2(\text{g})} +$	\rightleftharpoons	$\text{CO}_{(\text{g})} +$	$\text{H}_2\text{O}_{(\text{g})}$
Initial concentration (mol/L)	0.100	0.100	0.000	0.000
Change in concentration (mol/L)	$-x$	$-x$	$+x$	$+x$
Equilibrium concentration (mol/L)	$0.100 - x$	$0.100 - x$	x	x

$$K = \frac{[\text{CO}_{(\text{g})}][\text{H}_2\text{O}_{(\text{g})}]}{[\text{CO}_{2(\text{g})}][\text{H}_{2(\text{g})}]}$$

$$\frac{x^2}{(0.100 - x)^2} = 1.60$$

$$\frac{x}{(0.100 - x)} = \sqrt{1.60}$$

$$\frac{x}{(0.100 - x)} = 1.2649 \text{ (extra digits carried)}$$

$$1.2649(0.100 - x) = x$$

$$0.12649 - 1.2649x = x$$

$$0.12649 = 2.2649x$$

$$x = 5.58 \times 10^{-2}$$

$$[\text{CO}_{2(\text{g})}] = [\text{H}_{2(\text{g})}]$$

$$= 0.100 - (5.58 \times 10^{-2})$$

$$[\text{CO}_{2(\text{g})}] = 0.0442 \text{ mol/L}$$

The concentrations of hydrogen and carbon dioxide are both 0.0442 mol/L, and the concentrations of carbon monoxide and water are both 0.0558 mol/L.

6. Initial concentrations...

$$[\text{I}_{2(\text{g})}] = [\text{Cl}_{2(\text{g})}]$$

$$= \frac{0.50 \text{ mol}}{200.0 \text{ L}}$$

$$[\text{I}_{2(\text{g})}] = 0.25 \text{ mol/L}$$

ICE Table for the Reaction of $\text{I}_{2(\text{g})}$ with $\text{Cl}_{2(\text{g})}$			
	$\text{I}_{2(\text{g})} +$	$\text{Cl}_{2(\text{g})} \rightleftharpoons$	$2 \text{ ICl}_{(\text{g})}$
Initial concentration (mol/L)	0.25	0.25	
Change in concentration (mol/L)	$-x$	$-x$	$+2x$
Equilibrium concentration (mol/L)	$0.25 - x$	$0.25 - x$	$2x$

$$K = \frac{[\text{ICl}_{(\text{g})}]^2}{[\text{I}_{2(\text{g})}][\text{Cl}_{2(\text{g})}]}$$

$$\frac{(2x^2)}{(0.25 - x)^2} = 81.9$$

$$\frac{2x}{(0.25 - x)} = \sqrt{81.9}$$

$$\frac{2x}{(0.25 - x)} = 9.05$$

$$9.05(0.25 - x) = 2x$$

$$2.2625 - 9.05x = 2x \quad (\text{extra digits carried})$$

$$2.2625 = 11.05x$$

$$x = 0.2048$$

$$[\text{I}_{2(\text{g})}] = [\text{Cl}_{2(\text{g})}]$$

$$= 0.25 - 0.2251$$

$$[\text{I}_{2(\text{g})}] = 0.045 \text{ mol/L}$$

$$[\text{ICl}_{(\text{g})}] = 2x$$

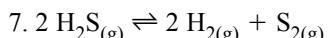
$$[\text{ICl}_{(\text{g})}] = 0.41 \text{ mol/L}$$

At equilibrium, the concentrations of iodine and chlorine are 0.045 mol/L and the concentration of the iodine chloride is 0.41 mol/L.

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ICE Table for the Decomposition of Hydrogen Sulfide			
	$2 \text{ H}_2\text{S}_{(\text{g})} \rightleftharpoons$	$2 \text{ H}_{2(\text{g})} +$	$\text{S}_{2(\text{g})}$
Initial concentration (mol/L)	0.200		
Change in concentration (mol/L)	$-2x$	$+2x$	$+x$
Equilibrium concentration (mol/L)	$0.200 - 2x$	$+2x$	$+x$

$$K = \frac{[\text{H}_{2(\text{g})}]^2[\text{S}_{2(\text{g})}]}{[\text{H}_2\text{S}_{(\text{g})}]^2}$$

$$K = 4.20 \times 10^{-6}$$

$$\frac{[2x]^2[x]}{[0.200 - 2x]^2} = 4.20 \times 10^{-6}$$

$$\frac{4x^3}{[0.200 - 2x]^2} = 4.20 \times 10^{-6}$$

If we assume $0.200 - 2x \doteq 0.200$...

$$\frac{4x^3}{[0.200]^2} \doteq 4.20 \times 10^{-6}$$

$$x^3 \doteq 4.2 \times 10^{-8}$$

$$x \doteq 3.48 \times 10^{-3}$$

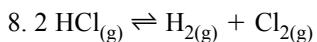
Validate the assumption...

$$\begin{aligned} &= \frac{0.200 - 2 \times 3.48 \times 10^{-3}}{0.200} \times 100 \\ &= 3.48\% \end{aligned}$$

Since $3.48\% < 5\%$, the assumption is justified.

$$\begin{aligned} [\text{S}_{2(\text{g})}] &= x \\ &= 3.48 \times 10^{-3} \text{ mol/L} \end{aligned}$$

The equilibrium concentration of $\text{S}_{2(\text{g})}$ is $3.48 \times 10^{-3} \text{ mol/L}$.



ICE Table for the Decomposition of Hydrogen Chloride			
	$2 \text{HCl}_{(\text{g})} \rightleftharpoons$	$\text{H}_{2(\text{g})} +$	$\text{Cl}_{2(\text{g})}$
Initial concentration (mol/L)	2.00		
Change in concentration (mol/L)	$-2x$	$+x$	$+x$
Equilibrium concentration (mol/L)	$2.00 - 2x$	x	x

$$K = \frac{[\text{H}_{2(\text{g})}][\text{Cl}_{2(\text{g})}]}{[\text{HCl}_{(\text{g})}]^2}$$

$$K = 3.2 \times 10^{-34}$$

$$\begin{aligned} \frac{x^2}{[2.00 - 2x]^2} &= 3.2 \times 10^{-34} \\ \sqrt{\frac{x^2}{[2.00 - 2x]^2}} &= \sqrt{3.2 \times 10^{-34}} \\ \frac{x}{[2.00 - 2x]} &= 1.789 \times 10^{-17} \quad (\text{extra digits carried}) \end{aligned}$$

If we assume that $2.00 - x \doteq 2.00$

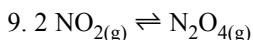
$$\begin{aligned} \frac{x}{2.00} &\doteq 1.789 \times 10^{-17} \\ x &\doteq 3.58 \times 10^{-17} \end{aligned}$$

The equilibrium concentrations of hydrogen and chlorine are 3.58×10^{-17} and the equilibrium concentration of hydrogen chloride is 2.00 mol/L.

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Initial concentrations are

$$[\text{NO}_{2(\text{g})}] = 0.650 \text{ mol/L}$$

$$[\text{N}_{2\text{O}}_{4(\text{g})}] = 0.000 \text{ mol/L}$$

$$\begin{aligned} Q &= \frac{[\text{N}_{2\text{O}}_{4(\text{g})}]}{[\text{NO}_{2(\text{g})}]^2} \\ &= \frac{0.000}{(0.650)^2} \end{aligned}$$

$$Q = 0.000$$

Since Q is less than K , the reaction will proceed to the right.

ICE Table for the Formation of $\text{N}_{2\text{O}}_{4(\text{g})}$		
	$2 \text{NO}_{2(\text{g})} \rightleftharpoons$	$\text{N}_{2\text{O}}_{4(\text{g})}$
Initial concentration (mol/L)	0.650	0.000
Change in concentration (mol/L)	$-2x$	$+x$
Equilibrium concentration (mol/L)	$0.650 - 2x$	$+x$

At equilibrium...

$$K = \frac{[\text{N}_2\text{O}_{4(\text{g})}]}{[\text{NO}_{2(\text{g})}]^2}$$

$$\frac{x}{(0.65 - 2x)^2} = 1.15$$

$$1.15(0.65 - 2x)^2 = x$$

$$1.15(0.4225 - 2.60x + 4x^2) = x \quad (\text{extra digits carried})$$

$$4.60x^2 - 3.99x + 0.486 = 0$$

$$x = \frac{3.99 \pm \sqrt{(-3.99)^2 - 4(4.60)(0.486)}}{2(4.60)}$$

$$x = 0.7209 \text{ or } 0.1465 \quad (\text{extra digits carried})$$

x cannot be equal to 0.7209, since this value will give negative concentrations.

$$x = 0.1465$$

$$[\text{N}_2\text{O}_{4(\text{g})}] = x$$

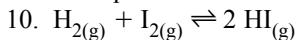
$$= 0.147 \text{ mol/L}$$

$$[\text{NO}_{2(\text{g})}] = 0.65 - 2x$$

$$= 0.65 - 2(0.1465)$$

$$[\text{NO}_{2(\text{g})}] = 0.357 \text{ mol/L}$$

The equilibrium concentrations of $\text{NO}_{2(\text{g})}$ and $\text{N}_2\text{O}_{4(\text{g})}$ are 0.357 mol/L and 0.147 mol/L, respectively.



Initial concentrations are

$$[\text{HI}_{(\text{g})}] = 0.00$$

$$[\text{H}_{2(\text{g})}] = [\text{I}_{2(\text{g})}]$$

$$= \frac{0.40 \text{ mol}}{0.50 \text{ L}}$$

$$[\text{H}_{2(\text{g})}] = 0.80 \text{ mol/L}$$

$$Q = \frac{[\text{HI}_{(\text{g})}]^2}{[\text{H}_{2(\text{g})}][\text{I}_{2(\text{g})}]}$$

$$Q = \frac{0.000}{0.80^2}$$

$$Q = 0.000$$

Since Q is less than K , the reaction will proceed to the right.

ICE Table for the Formation of $\text{HI}_{(\text{g})}$			
	$\text{H}_{2(\text{g})} +$	$\text{I}_{2(\text{g})} \rightleftharpoons$	$2 \text{HI}_{(\text{g})}$
Initial concentration (mol/L)	0.80	0.80	0.000
Change in concentration (mol/L)	$-x$	$-x$	$2x$
Equilibrium concentration (mol/L)	$0.80 - x$	$0.80 - x$	$2x$

At equilibrium...

$$Q = \frac{[\text{HI}_{(\text{g})}]^2}{[\text{H}_{2(\text{g})}][\text{I}_{2(\text{g})}]}$$

$$\frac{(2x)^2}{(0.80 - x)^2} = 46.0$$

$$\sqrt{\frac{(2x)^2}{(0.80 - x)^2}} = \sqrt{46.0}$$

$$\frac{2x}{0.80 - x} = 6.782 \quad (\text{extra digits carried})$$

$$2x = 6.782(0.80 - x)$$

$$x = 0.618$$

$$\begin{aligned} [\text{HI}_{(\text{g})}] &= 2x \\ &= 2(0.618) \end{aligned}$$

$$[\text{HI}_{(\text{g})}] = 1.2 \text{ mol/L}$$

$$\begin{aligned} [\text{H}_{2(\text{g})}] &= [\text{I}_{2(\text{g})}] \\ &= 0.80 - x \end{aligned}$$

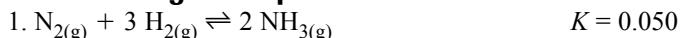
$$[\text{H}_{2(\text{g})}] = 0.18 \text{ mol/L}$$

The equilibrium concentrations of hydrogen, iodine, and hydrogen iodide are 0.18 mol/L, 0.18 mol/L, and 1.2 mol/L, respectively.

SECTION 7.5 QUESTIONS

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$$[\text{N}_{2(\text{g})}] = 2.0 \times 10^{-4} \text{ mol/L}$$

$$[\text{H}_{2(\text{g})}] = 4.0 \times 10^{-3} \text{ mol/L}$$

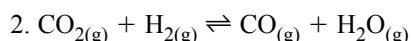
$$[\text{NH}_{3(\text{g})}] = 2.2 \times 10^{-3} \text{ mol/L}$$

$$Q = \frac{[\text{NH}_{3(\text{g})}]^2}{[\text{N}_{2(\text{g})}][\text{H}_{2(\text{g})}]^3}$$

$$= \frac{[2.2 \times 10^{-3}]^2}{[2.0 \times 10^{-4}][4.0 \times 10^{-3}]^3}$$

$$Q = 3.8 \times 10^5$$

Since the value of Q is larger than the value of K (0.050), the reaction is not at equilibrium. In order to attain equilibrium, the reaction will shift to the left (as written). The concentration of the reactants will increase and the concentration of the products will decrease.



$$[\text{H}_2\text{O}_{(\text{g})}]_{\text{initial}} = \frac{0.25 \text{ mol}}{1.00 \text{ L}}$$

$$[\text{H}_2\text{O}_{(\text{g})}]_{\text{initial}} = 0.25 \text{ mol/L}$$

$$[\text{CO}_{(\text{g})}]_{\text{initial}} = \frac{0.20 \text{ mol}}{1.00 \text{ L}}$$

$$[\text{CO}_{(\text{g})}]_{\text{initial}} = 0.20 \text{ mol/L}$$

$$\text{At equilibrium, } [\text{CO}_{2(\text{g})}] = \frac{0.10 \text{ mol}}{1.00 \text{ L}}$$

$$[\text{CO}_{2(\text{g})}] = 0.10 \text{ mol/L}$$

ICE Table for the Reaction of Carbon Dioxide and Hydrogen				
	$\text{CO}_{2(\text{g})}$	$+ \text{H}_{2(\text{g})} \rightleftharpoons$	$\text{CO}_{(\text{g})} +$	$\text{H}_2\text{O}_{(\text{g})}$
Initial concentration (mol/L)	0.00	0.00	0.20	0.25
Change in concentration (mol/L)	+0.10	+0.10	-0.10	-0.10
Equilibrium concentration (mol/L)	0.10	0.10	0.10	0.15

$$K = \frac{[\text{CO}_{(\text{g})}][\text{H}_2\text{O}_{(\text{g})}]}{[\text{CO}_{2(\text{g})}][\text{H}_{2(\text{g})}]}$$

$$= \frac{[0.10][0.15]}{[0.10][0.10]}$$

$$K = 1.5$$

3. (a) $K = \frac{[\text{H}_{2(\text{g})}][\text{Br}_{2(\text{g})}]}{[\text{HBr}_{(\text{g})}]^2}$

$$[\text{H}_{2(\text{g})}]_{\text{initial}} = [\text{Br}_{2(\text{g})}]_{\text{initial}}$$

$$[\text{H}_{2(\text{g})}]_{\text{initial}} = \frac{0.25 \text{ mol}}{0.50 \text{ L}}$$

$$= 0.50 \text{ mol/L}$$

ICE Table for the Decomposition of Hydrogen Bromide			
	$2 \text{ HBr}_{(\text{g})} \rightleftharpoons$	$\text{H}_{2(\text{g})} +$	$\text{Br}_{2(\text{g})}$
Initial concentration (mol/L)	0.00	0.50	0.50
Change in concentration (mol/L)	+2x	-x	-x
Equilibrium concentration (mol/L)	2x	0.50 - x	0.50 - x

$$K = \frac{[\text{H}_{2(\text{g})}][\text{Br}_{2(\text{g})}]}{[\text{HBr}_{(\text{g})}]^2}$$

$$\frac{[0.50 - x][0.50 - x]}{[2x]^2} = 0.020$$

$$\frac{[0.50 - x]^2}{[2x]^2} = 0.020$$

$$\sqrt{\frac{[0.50 - x]^2}{[2x]^2}} = \sqrt{0.020}$$

$$\frac{0.50 - x}{2x} = 0.1414 \quad (\text{extra digits carried})$$

$$0.2828x = 0.50 - x$$

$$x = 0.390$$

$$[\text{HBr}_{(\text{g})}] = 2x \\ = 2(0.390)$$

$$[\text{HBr}_{(\text{g})}] = 0.78 \text{ mol/L} \\ [\text{Br}_{2(\text{g})}] = [\text{H}_{2(\text{g})}] \\ = 0.50 - x \\ = 0.50 - 0.390$$

$$[\text{Br}_{2(\text{g})}] = 0.11 \text{ mol/L} \\ [\text{H}_{2(\text{g})}] = 0.11 \text{ mol/L}$$

The concentrations of hydrogen bromide, hydrogen, and bromine are 0.78 mol/L, 0.11 mol/L, and 0.11 mol/L, respectively.

(b) $n_{\text{HBr}} = (0.78 \text{ mol/L})(0.50 \text{ L})$

$$n_{\text{HBr}} = 0.39 \text{ mol}$$

$$n_{\text{H}_2} = n_{\text{Br}_2} \\ = (0.11 \text{ mol/L})(0.50 \text{ L})$$

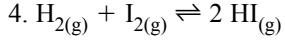
$$n_{\text{H}_2} = 0.055 \text{ mol}$$

$$n_{\text{Br}_2} = 0.055 \text{ mol}$$

There is 0.39 mol of hydrogen bromide, 0.055 mol of hydrogen, and 0.055 mol of bromine present at equilibrium.

$$(c) \text{ percent reaction} = \frac{\text{actual product yield}}{\text{theoretical product yield}} \times 100\% \\ = \frac{0.39}{0.50} \times 100\%$$

$$\text{percent reaction} = 78\%$$



Initial concentrations are

$$K = \frac{[\text{H}_{2(\text{g})}][\text{I}_{2(\text{g})}]}{[\text{HI}_{(\text{g})}]^2}$$

$$K = \frac{[\text{HI}_{(\text{g})}]^2}{[\text{H}_{2(\text{g})}][\text{I}_{2(\text{g})}]}$$

$$[\text{H}_{2(\text{g})}]_{\text{initial}} = \frac{0.20 \text{ mol}}{0.500 \text{ L}}$$

$$[\text{H}_{2(\text{g})}]_{\text{initial}} = 0.40 \text{ mol/L}$$

$$[\text{I}_{2(\text{g})}]_{\text{initial}} = \frac{0.50 \text{ mol}}{0.500 \text{ L}}$$

$$[\text{I}_{2(\text{g})}]_{\text{initial}} = 1.0 \text{ mol/L}$$

$$[\text{HI}_{(\text{g})}]_{\text{initial}} = 0.0 \text{ mol/L}$$

$$Q = \frac{[\text{HI}_{(\text{g})}]^2}{[\text{H}_{2(\text{g})}][\text{I}_{2(\text{g})}]}$$

$$= \frac{0.000}{(0.40)(1.0)}$$

$$Q = 0.000$$

Since Q is less than K , the reaction will proceed to the right.

ICE Table for the Formation of $\text{HI}_{(\text{g})}$			
	$\text{H}_{2(\text{g})} +$	$\text{I}_{2(\text{g})} \rightleftharpoons$	$2 \text{ HI}_{(\text{g})}$
Initial concentration (mol/L)	0.40	1.0	0.00
Change in concentration (mol/L)	$-x$	$-x$	$+2x$
Equilibrium concentration (mol/L)	$0.40 - x$	$1.0 - x$	$2x$

At equilibrium,

$$Q = \frac{[\text{HI}_{(\text{g})}]^2}{[\text{H}_{2(\text{g})}][\text{I}_{2(\text{g})}]}$$

$$\frac{(2x)^2}{(0.40 - x)(1.0 - x)} = 46$$

$$4x^2 = (46)(0.40 - x)(1 - x)$$

$$4x^2 = (46)(0.4 - 1.4x + x^2)$$

$$x^2 = (11.5)(0.40 - x)(1 - x)$$

$$x^2 = 4.6 - 16.1x + 11.5x^2$$

$$10.5x^2 - 16.1x + 4.6 = 0$$

$$x = \frac{16.1 \pm \sqrt{16.1^2 - 4(10.5)(4.6)}}{2(10.5)}$$

$$x = 0.3798 \text{ or } 1.15$$

extra digits carried

The root 1.15 is rejected as it exceeds the initial amount of hydrogen.

$$K = \frac{[\text{HI}_{(\text{g})}]^2}{[\text{H}_{2(\text{g})}][\text{I}_{2(\text{g})}]}$$

$$[\text{HI}_{(\text{g})}] = 2x$$

$$[\text{HI}_{(\text{g})}] = 0.7596 \text{ mol/L}$$

$$[\text{H}_{2(\text{g})}] = 0.40 - x$$

$$= 0.40 - 0.3798$$

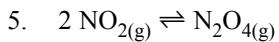
$$[\text{H}_{2(\text{g})}] = 0.020$$

$$[\text{I}_{2(\text{g})}] = 1.0 - x$$

$$= 1.0 - 0.3798$$

$$[\text{I}_{2(\text{g})}] = 0.62 \text{ mol/L}$$

The equilibrium concentrations of hydrogen, iodine, and hydrogen iodide are 0.020 mol/L, 0.62 mol/L, and 0.76 mol/L, respectively.



Initial concentrations are

$$[\text{N}_2\text{O}_{4(\text{g})}] = \frac{4.00 \text{ mol}}{1.00 \text{ L}}$$

$$[\text{N}_2\text{O}_{4(\text{g})}] = 4.00 \text{ mol/L}$$

$$[\text{NO}_{2(\text{g})}] = 0.00 \text{ mol/L}$$

ICE Table for the Formation of $\text{N}_2\text{O}_{4(\text{g})}$		
	$2 \text{NO}_{2(\text{g})} \rightleftharpoons$	$\text{N}_2\text{O}_{4(\text{g})}$
Initial concentration (mol/L)	0.00	4.00
Change in concentration (mol/L)	+2x	-x
Equilibrium concentration (mol/L)	2x	4.00 - x

At equilibrium,

$$K = \frac{[\text{N}_2\text{O}_{4(\text{g})}]}{[\text{NO}_{2(\text{g})}]^2}$$

$$K = 1.15$$

$$\frac{4.00 - x}{(2x)^2} = 1.15$$

$$\frac{4.00 - x}{4x^2} = 1.15$$

$$4 - x = 4.6x^2$$

$$4.6x^2 + x - 4 = 0$$

$$x = \frac{-1 \pm \sqrt{1^2 - 4(4.6)(-4)}}{2(4.6)}$$

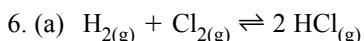
$$x = 0.830 \text{ or } -1.05$$

The negative root is rejected because negative concentrations are impossible.

$$[\text{NO}_{2(\text{g})}] = 2x$$

$$[\text{NO}_{2(\text{g})}] = 1.66 \text{ mol/L}$$

The equilibrium concentration of $\text{NO}_{2(\text{g})}$ is 1.66 mol/L.



Initial concentrations are

$$[\text{HCl}_{(\text{g})}] = 0.00$$

$$[\text{HCl}_{(\text{g})}] = [\text{Cl}_{2(\text{g})}]$$

$$= \frac{1.50 \text{ mol}}{0.750 \text{ L}}$$

$$[\text{H}_{2(\text{g})}] = 2.00 \text{ mol/L}$$

$$[\text{Cl}_{2(\text{g})}] = 2.00 \text{ mol/L}$$

ICE Table for the Formation of $\text{HCl}_{(\text{g})}$			
	$\text{H}_{2(\text{g})} +$	$\text{Cl}_{2(\text{g})} \rightleftharpoons$	$2 \text{HCl}_{(\text{g})}$
Initial concentration (mol/L)	2.00	2.00	0.000
Change in concentration (mol/L)	-x	-x	2x
Equilibrium concentration (mol/L)	2.00 - x	2.00 - x	2x

At equilibrium,

$$K = \frac{[\text{HCl}_{(\text{g})}]^2}{[\text{H}_{2(\text{g})}][\text{Cl}_{2(\text{g})}]}$$

$$\frac{(2x)^2}{(2.00 - x)^2} = 4.4 \times 10^{-2}$$

$$\frac{4x^2}{(2.00 - x)^2} = 4.4 \times 10^{-2}$$

$$\sqrt{\frac{4x^2}{(2.00 - x)^2}} = \sqrt{4.4 \times 10^{-2}}$$

$$\frac{2x}{2.00 - x} = 0.21$$

$$x = 0.19$$

$$[\text{HCl}_{(\text{g})}] = 2x$$

$$[\text{HCl}_{(\text{g})}] = 0.38 \text{ mol/L}$$

$$\begin{aligned} [\text{H}_{2(\text{g})}] &= [\text{Cl}_{2(\text{g})}] \\ &= 2.00 - x \end{aligned}$$

$$[\text{H}_{2(\text{g})}] = 1.81 \text{ mol/L}$$

$$[\text{Cl}_{2(\text{g})}] = 1.81 \text{ mol/L}$$

The equilibrium concentrations of hydrogen, chlorine, and hydrogen chloride are 1.81 mol/L, 1.81 mol/L, and 0.38 mol/L, respectively.

$$(b) n_{\text{H}_2} = (1.81 \text{ mol/L})(0.750 \text{ L})$$

$$n_{\text{H}_2} = 1.36 \text{ mol}$$

$$n_{\text{Cl}_2} = n_{\text{H}_2}$$

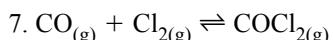
$$n_{\text{Cl}_2} = 1.36 \text{ mol}$$

$$n_{\text{HCl}} = (0.38 \text{ mol/L})(0.750 \text{ L})$$

$$n_{\text{HCl}} = 0.285 \text{ mol/L}$$

$$(c) \text{ percent reaction} = \frac{0.285}{3.00} \times 100\% \\ = 9.50\%$$

The reaction extent is 9.50%.



Initial concentrations are

$$[\text{COCl}_{2(\text{g})}] = \frac{2.5 \text{ mol}}{10.00 \text{ L}}$$

$$= 0.25 \text{ mol/L}$$

ICE Table for the Formation of $\text{COCl}_{2(\text{g})}$			
	$\text{CO}_{(\text{g})} +$	$\text{Cl}_{2(\text{g})} \rightleftharpoons$	$\text{COCl}_{2(\text{g})}$
Initial concentration (mol/L)	0.00	0.00	0.25
Change in concentration (mol/L)	+x	+x	-x
Equilibrium concentration (mol/L)	x	x	0.25 - x

At equilibrium,

$$K = \frac{[\text{COCl}_{2(\text{g})}]}{[\text{CO}_{(\text{g})}][\text{Cl}_{2(\text{g})}]}$$

$$= 8.2 \times 10^{-2}$$

$$\frac{0.25 - x}{x^2} = 8.2 \times 10^{-2}$$

$$8.2 \times 10^{-2} x^2 = 0.25 - x$$

$$8.2 \times 10^{-2} x^2 + x - 0.25 = 0$$

$$x = \frac{-1 \pm \sqrt{1^2 - 4(8.2 \times 10^{-2})(-0.25)}}{2(8.2 \times 10^{-2})}$$

$$= 0.25 \text{ or } -12.4$$

The negative root is rejected because negative concentrations are impossible.

$$[\text{CO}_{(\text{g})}] = [\text{Cl}_{2(\text{g})}] = x \\ = 0.25 \text{ mol/L}$$

The equilibrium concentrations of carbon monoxide and chlorine are 0.25 mol/L.



Initial concentrations are

$$[\text{PCl}_{3(\text{g})}] = \frac{0.500 \text{ mol}}{1.00 \text{ L}}$$

$$[\text{PCl}_{3(\text{g})}] = 0.500 \text{ mol/L}$$

$$[\text{Cl}_{2(\text{g})}] = \frac{0.500 \text{ mol}}{1.00 \text{ L}}$$

$$[\text{Cl}_{2(\text{g})}] = 0.500 \text{ mol/L}$$

ICE Table for the Decomposition of $\text{PCl}_{5(\text{g})}$			
	$\text{PCl}_{5(\text{g})} \rightleftharpoons$	$\text{PCl}_{3(\text{g})} +$	$\text{Cl}_{2(\text{g})}$
Initial concentration (mol/L)	0.00	0.500	0.500
Change in concentration (mol/L)	x	$-x$	$-x$
Equilibrium concentration (mol/L)	x	$0.500 - x$	$0.500 - x$

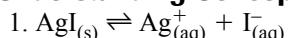
The equilibrium concentrations of phosphorus pentachloride, phosphorus trichloride, and chlorine are 0.0185 mol/L, 0.482 mol/L, and 0.482 mol/L, respectively.

7.6 THE SOLUBILITY PRODUCT CONSTANT

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$$K_{\text{sp}} = [\text{Ag}^+][\text{I}^-]$$

$$K_{\text{sp}} = 1.5 \times 10^{-16}$$

At equilibrium,

$$K = \frac{[\text{COCl}_{2(\text{g})}]}{[\text{CO}_{(\text{g})}][\text{Cl}_{2(\text{g})}]}$$

$$= 8.2 \times 10^{-2}$$

$$\frac{0.25 - x}{x^2} = 8.2 \times 10^{-2}$$

$$8.2 \times 10^{-2} x^2 = 0.25 - x$$

$$8.2 \times 10^{-2} x^2 + x - 0.25 = 0$$

$$x = \frac{-1 \pm \sqrt{1^2 - 4(8.2 \times 10^{-2})(-0.25)}}{2(8.2 \times 10^{-2})}$$

$$= 0.25 \text{ or } -12.4$$

The negative root is rejected because negative concentrations are impossible.

$$[\text{CO}_{(\text{g})}] = [\text{Cl}_{2(\text{g})}] = x \\ = 0.25 \text{ mol/L}$$

The equilibrium concentrations of carbon monoxide and chlorine are 0.25 mol/L.



Initial concentrations are

$$[\text{PCl}_{3(\text{g})}] = \frac{0.500 \text{ mol}}{1.00 \text{ L}}$$

$$[\text{PCl}_{3(\text{g})}] = 0.500 \text{ mol/L}$$

$$[\text{Cl}_{2(\text{g})}] = \frac{0.500 \text{ mol}}{1.00 \text{ L}}$$

$$[\text{Cl}_{2(\text{g})}] = 0.500 \text{ mol/L}$$

ICE Table for the Decomposition of $\text{PCl}_{5(\text{g})}$			
	$\text{PCl}_{5(\text{g})} \rightleftharpoons$	$\text{PCl}_{3(\text{g})} +$	$\text{Cl}_{2(\text{g})}$
Initial concentration (mol/L)	0.00	0.500	0.500
Change in concentration (mol/L)	x	$-x$	$-x$
Equilibrium concentration (mol/L)	x	$0.500 - x$	$0.500 - x$

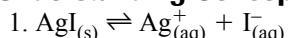
The equilibrium concentrations of phosphorus pentachloride, phosphorus trichloride, and chlorine are 0.0185 mol/L, 0.482 mol/L, and 0.482 mol/L, respectively.

7.6 THE SOLUBILITY PRODUCT CONSTANT

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$$K_{\text{sp}} = [\text{Ag}^+][\text{I}^-]$$

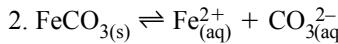
$$K_{\text{sp}} = 1.5 \times 10^{-16}$$

$$[\text{Ag}^+] = [\text{I}^-]$$

$$1.5 \times 10^{-16} = [\text{Ag}^+]^2$$

$$[\text{Ag}^+] = 1.2 \times 10^{-8} \text{ mol/L}$$

The solubility of silver iodide is $1.2 \times 10^{-8} \text{ mol/L}$.



$$K_{\text{sp}} = [\text{Fe}_{(\text{aq})}^{2+}][\text{CO}_{3(\text{aq})}^{2-}]$$

$$K_{\text{sp}} = 3.5 \times 10^{-11}$$

$$[\text{Fe}_{(\text{aq})}^{2+}] = [\text{CO}_{3(\text{aq})}^{2-}]$$

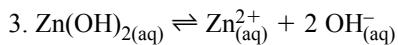
$$3.5 \times 10^{-11} = [\text{Fe}_{(\text{aq})}^{2+}]^2$$

$$[\text{Fe}_{(\text{aq})}^{2+}] = 5.9 \times 10^{-6} \text{ mol/L}$$

$$[\text{FeCO}_{3(\text{aq})}] = [\text{Fe}_{(\text{aq})}^{2+}]$$

$$[\text{FeCO}_{3(\text{aq})}] = 5.9 \times 10^{-6} \text{ mol/L}$$

The solubility of iron(II) carbonate is $5.9 \times 10^{-6} \text{ mol/L}$.



$$K_{\text{sp}} = [\text{Zn}_{(\text{aq})}^{2+}][\text{OH}_{(\text{aq})}^-]$$

$$K_{\text{sp}} = 4.5 \times 10^{-17}$$

$$2[\text{Zn}_{(\text{aq})}^{2+}] = [\text{OH}_{(\text{aq})}^-]$$

$$4.5 \times 10^{-17} = [\text{Zn}_{(\text{aq})}^{2+}][2 \text{Zn}_{(\text{aq})}^{2+}]^2$$

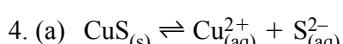
$$4.5 \times 10^{-17} = 4[\text{Zn}_{(\text{aq})}^{2+}]^3$$

$$[\text{Zn}_{(\text{aq})}^{2+}] = 2.2 \times 10^{-6}$$

$$[\text{Zn(OH)}_{2(\text{aq})}] = [\text{Zn}_{(\text{aq})}^{2+}]$$

$$[\text{Zn(OH)}_{2(\text{aq})}] = 2.2 \times 10^{-6} \text{ mol/L}$$

The solubility of zinc hydroxide is $2.2 \times 10^{-6} \text{ mol/L}$.



ICE Table for Calculating K_{sp} from Solubility			
	$\text{CuS}_{(\text{s})} \rightleftharpoons$	$\text{Cu}_{(\text{aq})}^{2+} +$	$\text{S}_{(\text{aq})}^{2-}$
Initial concentration (mol/L)		0	0
Change in concentration (mol/L)		+x	+x
Equilibrium concentration (mol/L)		x	x

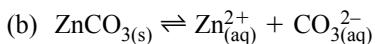
$$x = 8.89 \times 10^{-19} \text{ mol/L}$$

$$K_{\text{sp}} = [\text{Cu}_{(\text{aq})}^{2+}][\text{S}_{(\text{aq})}^{2-}]$$

$$= [8.89 \times 10^{-19}][8.89 \times 10^{-19}]$$

$$K_{\text{sp}} = 7.90 \times 10^{-37}$$

The solubility product of copper(II) sulfide has a value of 7.90×10^{-37} .



ICE Table for Calculating K_{sp} from Solubility			
	$\text{ZnCO}_{3(\text{s})} \rightleftharpoons$	$\text{Zn}_{(\text{aq})}^{2+} +$	$\text{CO}_{3(\text{aq})}^{2-}$
Initial concentration (mol/L)		0	0
Change in concentration (mol/L)		+x	+x
Equilibrium concentration (mol/L)		x	x

$$x = 3.87 \times 10^{-6} \text{ mol/L}$$

$$\begin{aligned} K_{\text{sp}} &= [\text{Zn}_{(\text{aq})}^{2+}][\text{CO}_{3(\text{aq})}^{2-}] \\ &= [3.87 \times 10^{-6}][3.87 \times 10^{-6}] \end{aligned}$$

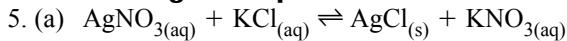
$$K_{\text{sp}} = 1.50 \times 10^{-11}$$

The solubility product of zinc carbonate has a value of 1.50×10^{-11} .

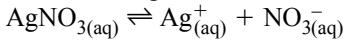
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Before mixing:



$$[\text{AgNO}_{3(\text{aq})}] = [\text{Ag}_{(\text{aq})}^+] = 0.010 \text{ mol/L}$$

$$[\text{KCl}_{(\text{aq})}] = [\text{Cl}_{(\text{aq})}^-] = 0.0050 \text{ mol/L}$$

After mixing:

$$25.0 \text{ mL} + 25.0 \text{ mL} = 50.0 \text{ mL}$$

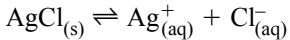
Concentrations after mixing:

$$[\text{Ag}_{(\text{aq})}^+] = 0.010 \text{ mol/L} \times \frac{25.0 \text{ mL}}{50.0 \text{ mL}}$$

$$[\text{Ag}_{(\text{aq})}^+] = 0.005 \text{ mol/L}$$

$$[\text{Cl}_{(\text{aq})}^-] = 0.0050 \text{ mol/L} \times \frac{25.0 \text{ mL}}{50.0 \text{ mL}}$$

$$[\text{Cl}_{(\text{aq})}^-] = 0.0025 \text{ mol/L}$$



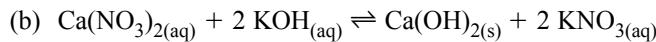
$$Q = [\text{Ag}_{(\text{aq})}^+][\text{Cl}_{(\text{aq})}^-]$$

$$= (0.005 \text{ mol/L})(0.0025 \text{ mol/L})$$

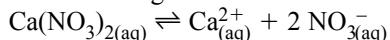
$$Q = 1.25 \times 10^{-5}$$

$$K_{\text{sp}} = 1.8 \times 10^{-10}$$

Q is larger than K_{sp} . Therefore, a precipitate does form.



Before mixing:



$$[\text{Ca}(\text{NO}_3)_{2(\text{aq})}] = [\text{Ca}_{(\text{aq})}^{2+}] = 0.0010 \text{ mol/L}$$

$$[\text{KOH}_{(\text{aq})}] = [\text{OH}_{(\text{aq})}^-] = 0.0020 \text{ mol/L}$$

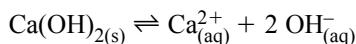
Concentrations after mixing:

$$[\text{Ca}_{(\text{aq})}^{2+}] = \frac{0.0010 \text{ mol/L}}{2}$$

$$[\text{Ca}_{(\text{aq})}^{2+}] = 0.0005 \text{ mol/L}$$

$$[\text{OH}_{(\text{aq})}^-] = \frac{0.0020 \text{ mol/L}}{2}$$

$$[\text{OH}_{(\text{aq})}^-] = 0.0010 \text{ mol/L}$$

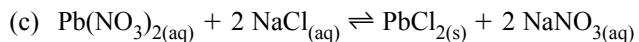


$$\begin{aligned} Q &= [\text{Ca}_{(\text{aq})}^{2+}][\text{OH}_{(\text{aq})}^-]^2 \\ &= (0.0005 \text{ mol/L})(0.0010 \text{ mol/L})^2 \end{aligned}$$

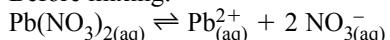
$$Q = 5.0 \times 10^{-10}$$

$$K_{\text{sp}} = 7.9 \times 10^{-6}$$

Q is larger than K_{sp} . Therefore, a precipitate does form.



Before mixing:



$$[\text{Pb}(\text{NO}_3)_{2(\text{aq})}] = [\text{Pb}_{(\text{aq})}^{2+}] = 0.010 \text{ mol/L}$$

$$[\text{NaCl}_{(\text{aq})}] = [\text{Cl}_{(\text{aq})}^-] = 0.10 \text{ mol/L}$$

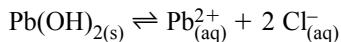
Concentrations after mixing:

$$[\text{Pb}_{(\text{aq})}^{2+}] = \frac{0.010 \text{ mol/L}}{2}$$

$$[\text{Pb}_{(\text{aq})}^{2+}] = 0.005 \text{ mol/L}$$

$$[\text{Cl}_{(\text{aq})}^-] = \frac{0.10 \text{ mol/L}}{2}$$

$$[\text{Cl}_{(\text{aq})}^-] = 0.050 \text{ mol/L}$$



$$\begin{aligned} Q &= [\text{Pb}_{(\text{aq})}^{2+}][\text{Cl}_{(\text{aq})}^-]^2 \\ &= (0.005 \text{ mol/L})(0.050 \text{ mol/L})^2 \end{aligned}$$

$$Q = 1.2 \times 10^{-5}$$

$$K_{\text{sp}} = 1.2 \times 10^{-5}$$

$Q = K_{\text{sp}}$. Therefore, a precipitate just begins to form.

Making Connections

6. The concentration of barium ions in the solution is so low ($1.0 \times 10^{-5} \text{ mol/L}$) that the suspension can be safely consumed.

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Understanding Concepts

7.

ICE Table for the Solubility of Silver Chloride in a Solution Containing $\text{NaCl}_{(\text{aq})}$			
	$\text{AgCl}_{(\text{s})} \rightleftharpoons$	$\text{Ag}_{(\text{aq})}^+ +$	$\text{Cl}_{(\text{aq})}^-$
Initial concentration (mol/L)	—	0.0	0.10
Change in concentration (mol/L)	—	+x	+x
Equilibrium concentration (mol/L)	—	x	0.10 + x

$$K_{\text{sp}} = [\text{Ag}_{(\text{aq})}^+][\text{Cl}_{(\text{aq})}^-]$$

$$K_{\text{sp}} = 1.8 \times 10^{-10}$$

$$0.10 + x \doteq 0.10$$

Therefore,

$$(x)(0.10) = 1.8 \times 10^{-10}$$

$$x = 1.8 \times 10^{-9}$$

The solubility of silver chloride in a 0.10 mol/L solution of sodium chloride is 1.8×10^{-9} mol/L.

8.

ICE Table for the Solubility of CaSO_4 in a Solution Containing $\text{Ca}(\text{NO}_3)_2(\text{aq})$			
	$\text{CaSO}_{4(\text{s})} \rightleftharpoons$	$\text{Ca}_{(\text{aq})}^{2+} +$	$\text{SO}_{4(\text{aq})}^{2-}$
Initial concentration (mol/L)	—	0.010	0.00
Change in concentration (mol/L)	—	+x	+x
Equilibrium concentration (mol/L)	—	0.010 + x	x

$$K_{\text{sp}} = [\text{Ca}_{(\text{aq})}^{2+}][\text{SO}_{4(\text{aq})}^{2-}]$$

$$K_{\text{sp}} = 7.1 \times 10^{-5}$$

$$0.010 + x \doteq 0.010$$

Therefore,

$$(0.010)(x) = 7.1 \times 10^{-5}$$

$$x = 7.1 \times 10^{-3}$$

The solubility of calcium sulfate in a 0.010 mol/L solution of calcium nitrate is 7.1×10^{-3} mol/L.

9. (a)

ICE Table for the Solubility of Ag_2CrO_4 in Water			
	$\text{Ag}_2\text{CrO}_{4(\text{s})} \rightleftharpoons$	$2 \text{Ag}_{(\text{aq})}^+ +$	$\text{CrO}_{4(\text{aq})}^{2-}$
Initial concentration (mol/L)	—	—	—
Change in concentration (mol/L)	—	+2x	+x
Equilibrium concentration (mol/L)	—	2x	x

$$K_{\text{sp}} = [\text{Ag}_{(\text{aq})}^+][\text{CrO}_{4(\text{aq})}^{2-}]$$

$$K_{\text{sp}} = 1.1 \times 10^{-12}$$

$$(2x)^2(x) = 1.1 \times 10^{-12}$$

$$4x^3 = 1.1 \times 10^{-12}$$

$$x = 6.5 \times 10^{-5}$$

The solubility of silver chromate is 6.5×10^{-5} mol/L.

(b)

ICE Table for the Solubility of Ag_2CrO_4 in a Solution of 0.1 mol/L Sodium Chromate			
	$\text{Ag}_2\text{CrO}_{4(\text{s})} \rightleftharpoons$	$2 \text{Ag}_{(\text{aq})}^+ +$	$\text{CrO}_{4(\text{aq})}^{2-}$
Initial concentration (mol/L)		0.0	0.1
Change in concentration (mol/L)		$+2x$	$+x$
Equilibrium concentration (mol/L)		$2x$	$x + 0.1$

$$K_{\text{sp}} = [\text{Ag}_{(\text{aq})}^+]^2[\text{CrO}_{4(\text{aq})}^{2-}]$$

$$K_{\text{sp}} = 1.1 \times 10^{-12}$$

$$(2x)^2(x + 0.10) = 1.1 \times 10^{-12}$$

Assume $x + 0.10 \doteq 0.10$

$$(2x)^2(0.10) = 1.1 \times 10^{-12}$$

$$4x^2 = 1.1 \times 10^{-11}$$

$$x = 1.7 \times 10^{-6}$$

The solubility of silver chromate is 1.7×10^{-6} mol/L.

- (c) The solubility of silver chromate in a solution containing the chromate ion should be lower than its solubility in water. Presence of chromate already in solution shifts the equilibrium to the left, decreasing the amount of silver chromate that dissolves.
10. Soluble compounds containing either barium or sulfate ions would decrease the solubility of barium sulfate. Examples include barium nitrate, $\text{Ba}(\text{NO}_3)_2$, and potassium sulfate, K_2SO_4 .
11. Soluble compounds containing either copper(II) or carbonate ions would decrease the solubility of copper(II) carbonate. Examples include copper(II) sulfate, CuSO_4 , and sodium carbonate, Na_2CO_3 .
12. The reaction of silver ions with thiosulfate removes silver ions from the equilibrium, prompting the forward reaction to predominate, consuming silver chloride.

SECTION 7.6 QUESTIONS

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Understanding Concepts

- The solubility of a salt is the amount of salt that dissolves in a given amount of solvent to give a saturated solution. Solubility product constant is the product of the molar concentrations of the ions in the saturated solution.
- (a) The common ion effect is a reduction in the solubility of a salt caused by the presence of another salt having a common ion.
- (b) For the general dissociation equilibrium equation $B_p C_{c(\text{s})} \rightleftharpoons bB_{(\text{aq})}^+ + cC_{(\text{aq})}^-$, the presence of a common ion $B_{(\text{aq})}^+$ or $C_{(\text{aq})}^-$ will shift the equilibrium to the left, reducing the solubility of the salt $B_p C_c$.
- When the solutions combine, there are more ions in solution than necessary to achieve saturation, resulting in an unstable supersaturated solution. The excess ions precipitate from solution, leaving behind a saturated solution.

4.

ICE Table for the Solubility of Barium Sulfate			
	$\text{BaSO}_{4(\text{s})} \rightleftharpoons$	$\text{Ba}_{(\text{aq})}^{2+} +$	$\text{SO}_{4(\text{aq})}^{2-}$
Initial concentration (mol/L)	—	0	0
Change in concentration (mol/L)	—	$+x$	$+x$
Equilibrium concentration (mol/L)	—	x	x

$$K_{\text{sp}} = [\text{Ba}_{(\text{aq})}^{2+}][\text{SO}_{4(\text{aq})}^{2-}]$$

$$K_{\text{sp}} = 1.1 \times 10^{-10}$$

$$(x)(x) = 1.1 \times 10^{-10}$$

$$x = 1.0 \times 10^{-5}$$

The molar solubility of barium sulfate is 1.0×10^{-5} mol/L.

5.

ICE Table for the Solubility of Silver Bromide			
	$\text{AgBr}_{(\text{s})} \rightleftharpoons$	$\text{Ag}_{(\text{aq})}^+ +$	$\text{Br}_{(\text{aq})}^-$
Initial concentration (mol/L)	—	0	
Change in concentration (mol/L)	—	$+x$	$+x$
Equilibrium concentration (mol/L)	—	x	x

$$K_{\text{sp}} = [\text{Ag}_{(\text{aq})}^+][\text{Br}_{4(\text{aq})}^-]$$

$$K_{\text{sp}} = 5.4 \times 10^{-13}$$

$$x^2 = 5.4 \times 10^{-13}$$

$$x = 7.35 \times 10^{-7} \quad (\text{extra digits carried})$$

molar solubility of silver bromide = 7.35×10^{-7} mol/L

Solubility in g/100 mL ...

mass of silver bromide in 1 L

$$= 7.35 \times 10^{-7} \text{ mol/L} \times 187.77 \text{ g/mol}$$

$$= 1.38 \times 10^{-4} \text{ g/L}$$

mass of silver bromide in 100 mL

$$m = 1.38 \times 10^{-4} \text{ g} \times \frac{100 \text{ mL}}{1000 \text{ mL}}$$

$$m = 1.4 \times 10^{-5} \text{ g}/100 \text{ mL}$$

The solubility of silver bromide is 1.4×10^{-5} g/100 mL.

6.

ICE Table for the Solubility of Strontium Fluoride			
	$\text{SrF}_{2(\text{s})} \rightleftharpoons$	$\text{Sr}_{(\text{aq})}^{2+} +$	$2 \text{ F}_{(\text{aq})}^-$
Initial concentration (mol/L)	—	0	0
Change in concentration (mol/L)	—	$+x$	$+2x$
Equilibrium concentration (mol/L)	—	x	$2x$

$$K_{\text{sp}} = [\text{Sr}_{(\text{aq})}^{2+}][\text{F}_{(\text{aq})}^-]^2$$

$$K_{\text{sp}} = 4.3 \times 10^{-9}$$

$$(x)(2x)^2 = 4.3 \times 10^{-9}$$

$$4x^3 = 4.3 \times 10^{-9}$$

$$x = 1.0 \times 10^{-3}$$

$$[\text{F}_{(\text{aq})}^-] = 2 \times 1.0 \times 10^{-3}$$

$$[\text{F}_{(\text{aq})}^-] = 2.0 \times 10^{-3} \text{ mol/L}$$

The fluoride ion concentration in a saturated solution of strontium fluoride is 2.0×10^{-3} mol/L.

7. If 2.4 g of TlCl dissolves in 100 mL, then 24 g must dissolve in 1.00 L.

$$C_{\text{TlCl}} = \frac{\left(\frac{24 \text{ g}}{239.83 \text{ g/mol}}\right)}{1.00 \text{ L}}$$

$$C_{\text{TlCl}} = 0.10 \text{ mol/L}$$

ICE Table for the Dissolving of Thallium(I) Chloride			
	$\text{TlCl}_{(\text{s})} \rightleftharpoons$	$\text{Tl}^+_{(\text{aq})} +$	$\text{Cl}^-_{(\text{aq})}$
Initial concentration (mol/L)	—	0	0
Change in concentration (mol/L)	—	+0.10	+0.10
Equilibrium concentration (mol/L)	—	0.10	0.10

$$K_{\text{sp}} = [\text{Tl}^+_{(\text{aq})}][\text{Cl}^-_{(\text{aq})}] \\ = [0.10][0.10]$$

$$K_{\text{sp}} = 1.0 \times 10^{-2}$$

The K_{sp} for thallium chloride is 1.0×10^{-2} .

8. If 0.0016 g of CaF_2 dissolves in 100 mL, then 0.016 g dissoves in 1.00 L.

$$C_{\text{CaF}_2} = \frac{\frac{0.016 \text{ g}}{78.08 \text{ g/mol}}}{1.00 \text{ L}}$$

$$C_{\text{CaF}_2} = 2.05 \times 10^{-4} \text{ mol/L} \quad (\text{extra digits carried})$$

ICE Table for the Dissolving of Calcium Fluoride			
	$\text{CaF}_{2(\text{aq})} \rightleftharpoons$	$\text{Ca}^{2+}_{(\text{aq})} +$	$2 \text{ F}^-_{(\text{aq})}$
Initial concentration (mol/L)		0	0
Change in concentration (mol/L)		$+2.05 \times 10^{-4}$	$+4.10 \times 10^{-4}$
Equilibrium concentration (mol/L)		2.05×10^{-4}	4.10×10^{-4}

$$K_{\text{sp}} = [\text{Ca}^{2+}_{(\text{aq})}][\text{F}^-_{(\text{aq})}]^2 \\ = [2.05 \times 10^{-4}][4.10 \times 10^{-4}]^2$$

$$K_{\text{sp}} = 3.4 \times 10^{-11}$$

The K_{sp} for calcium fluoride is 3.4×10^{-11} .

9.

ICE Table for the Dissolving of Mercury(I) Chloride			
	$\text{Hg}_2\text{Cl}_{2(\text{aq})} \rightleftharpoons$	$\text{Hg}_{2(\text{aq})}^{2+} +$	$2 \text{ Cl}^-_{(\text{aq})}$
Initial concentration (mol/L)		0	0
Change in concentration (mol/L)		$+x$	$+2x$
Equilibrium concentration (mol/L)		x	$2x$

$$K_{\text{sp}} = [\text{Hg}_{2(\text{aq})}^{2+}][\text{Cl}^-_{(\text{aq})}]^2$$

$$(x)(2x)^2 = 1.5 \times 10^{-18}$$

$$4x^3 = 1.5 \times 10^{-18}$$

$$x = 7.21 \times 10^{-7} \quad (\text{extra digits carried})$$

The molar solubility of mercury(I) chloride is 7.21×10^{-7} mol/L.

mass of Hg_2Cl_2 required to prepare 1.0 L of solution,

$$m = 7.21 \times 10^{-7} \text{ mol/L} \times 472.08 \text{ g/mol}$$

$$m = 3.40 \times 10^{-4} \text{ g}$$

mass of Hg_2Cl_2 required to prepare 500 mL of solution,

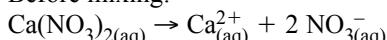
$$m = \frac{3.40 \times 10^{-4} \text{ g}}{2}$$

$$m = 1.7 \times 10^{-4} \text{ g}$$

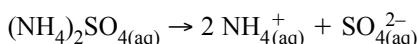
The mass of mercury(I) chloride required is 1.7×10^{-4} g.



Before mixing:



$$[\text{Ca}(\text{NO}_3)_{2(\text{aq})}] = [\text{Ca}_{(\text{aq})}^{2+}] = 0.040 \text{ mol/L}$$



$$[(\text{NH}_4)_2\text{SO}_{4(\text{aq})}] = [\text{SO}_{4(\text{aq})}^{2-}] = 0.080 \text{ mol/L}$$

After mixing:

$$50 \text{ mL} + 150 \text{ mL} = 200 \text{ mL}$$

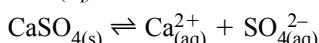
Concentrations after mixing:

$$[\text{Ca}_{(\text{aq})}^{2+}] = 0.040 \text{ mol/L} \times \frac{50 \text{ mL}}{200 \text{ mL}}$$

$$[\text{Ca}_{(\text{aq})}^{2+}] = 0.010 \text{ mol/L}$$

$$[\text{SO}_{4(\text{aq})}^{2-}] = 0.080 \text{ mol/L} \times \frac{150 \text{ mL}}{200 \text{ mL}}$$

$$[\text{SO}_{4(\text{aq})}^{2-}] = 0.060 \text{ mol/L}$$



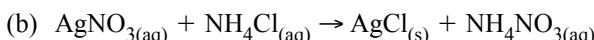
$$Q = [\text{Ca}_{(\text{aq})}^{2+}][\text{SO}_{4(\text{aq})}^{2-}]$$

$$= (0.010)(0.060)$$

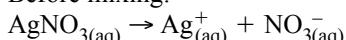
$$Q = 6.0 \times 10^{-4}$$

$$K_{\text{sp}} = 7.1 \times 10^{-5}$$

Q is larger than K_{sp} . Therefore, a precipitate does form.



Before mixing:



$$[\text{AgNO}_{3(\text{aq})}] = [\text{Ag}_{(\text{aq})}^+] = 2.2 \times 10^{-9} \text{ mol/L}$$

$$[\text{NH}_4\text{Cl}_{(\text{aq})}] = [\text{Cl}_{(\text{aq})}^-] = 0.050 \text{ mol/L}$$

After mixing:

$$50 \text{ mL} + 50 \text{ mL} = 100 \text{ mL}$$

Concentrations after mixing:

$$[\text{Ag}_{(\text{aq})}^+] = 2.2 \times 10^{-9} \text{ mol/L} \times \frac{50 \text{ mL}}{100 \text{ mL}}$$

$$[\text{Ag}_{(\text{aq})}^+] = 1.1 \times 10^{-9} \text{ mol/L}$$

$$[\text{Cl}_{(\text{aq})}^-] = 0.050 \text{ mol/L} \times \frac{50 \text{ mL}}{100 \text{ mL}}$$

$$[\text{Cl}_{(\text{aq})}^-] = 0.025 \text{ mol/L}$$



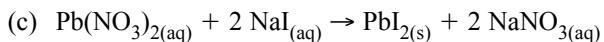
$$Q = [\text{Ag}_{(\text{aq})}^+][\text{Cl}_{(\text{aq})}^-]$$

$$= (1.1 \times 10^{-9})(0.025)$$

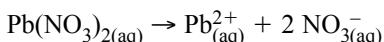
$$Q = 2.8 \times 10^{-11}$$

$$K_{\text{sp}} = 1.8 \times 10^{-10}$$

Q is smaller than K_{sp} . Therefore, a precipitate does not form.



Before mixing:



$$[\text{Pb}(\text{NO}_3)_2(\text{aq})] = [\text{Pb}_{(\text{aq})}^{2+}] = 2.1 \times 10^{-3} \text{ mol/L}$$

$$[\text{NaI}_{(\text{aq})}] = [\text{I}_{(\text{aq})}^-] = 0.006 \text{ mol/L}$$

After mixing:

$$100 \text{ mL} + 50 \text{ mL} = 150 \text{ mL}$$

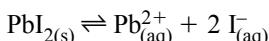
Concentrations after mixing:

$$[\text{Pb}_{(\text{aq})}^{2+}] = 2.1 \times 10^{-3} \text{ mol/L} \times \frac{100 \text{ mL}}{150 \text{ mL}}$$

$$[\text{Pb}_{(\text{aq})}^{2+}] = 1.4 \times 10^{-3} \text{ mol/L}$$

$$[\text{I}_{(\text{aq})}^-] = 0.006 \text{ mol/L} \times \frac{50 \text{ mL}}{150 \text{ mL}}$$

$$[\text{I}_{(\text{aq})}^-] = 2.0 \times 10^{-3} \text{ mol/L}$$



$$Q = [\text{Pb}_{(\text{aq})}^{2+}][\text{I}_{(\text{aq})}^-]^2$$

$$= (1.4 \times 10^{-3})(2.0 \times 10^{-3})^2$$

$$Q = 5.6 \times 10^{-9}$$

$$K_{\text{sp}} = 8.5 \times 10^{-9}$$

Q is smaller than K_{sp} . Therefore, a precipitate does not form.

11.

ICE Table for the Solubility of Lead Iodide in a Solution of 0.1 mol/L Sodium Iodide			
	$\text{PbI}_{2(\text{s})} \rightleftharpoons$	$\text{Pb}_{(\text{aq})}^{2+} +$	$2 \text{I}_{(\text{aq})}^-$
Initial concentration (mol/L)			0.1
Change in concentration (mol/L)	—	+x	+2x
Equilibrium concentration (mol/L)		x	2x + 0.1

$$K_{\text{sp}} = [\text{Pb}_{(\text{aq})}^{2+}][\text{I}_{(\text{aq})}^-]^2$$

$$K_{\text{sp}} = 8.5 \times 10^{-9}$$

$$(x)(2x + 0.1)^2 = 8.5 \times 10^{-9}$$

Assume $2x + 0.10 \doteq 0.10$

$$(x)(0.10)^2 = 8.5 \times 10^{-9}$$

$$x = 8.5 \times 10^{-7}$$

The solubility of lead iodide in a 0.10 mol/L solution of sodium iodide is 8.5×10^{-7} mol/L.

Applying Inquiry Skills

$$12. (a) n_{Zn} = \frac{0.094 \text{ g}}{65.38 \text{ g/mol}}$$

$$n_{Zn} = 1.4 \times 10^{-3} \text{ mol}$$

1.4×10^{-3} mol of zinc reacted.

$$(b) C_{Pb^{2+}} = \frac{1.4 \times 10^{-3} \text{ mol}}{0.100 \text{ L}}$$

$$C_{Pb^{2+}} = 1.4 \times 10^{-2} \text{ mol/L}$$

The molar concentration of the lead ions is 1.4×10^{-2} mol/L.

$$(c) \text{ If } [Pb_{(aq)}^{2+}] = 1.4 \times 10^{-2} \text{ mol/L, then } [Cl_{(aq)}^{-}] = 2.8 \times 10^{-2} \text{ mol/L.}$$

$$\begin{aligned} K_{sp} &= [Pb_{(aq)}^{2+}][Cl_{(aq)}^{-}]^2 \\ &= [1.4 \times 10^{-2}][2.8 \times 10^{-2}]^2 \end{aligned}$$

$$K_{sp} = 1.1 \times 10^{-5}$$

The K_{sp} for lead(II) chloride is 1.1×10^{-5} .

13. Analysis

$$(a) n_{Cu} = \frac{0.16 \text{ g}}{63.55 \text{ g/mol}}$$

$$n_{Cu} = 2.5 \times 10^{-3} \text{ mol}$$

2.5×10^{-3} mol of copper reacted.

$$(b) n_{Ag} = 2n_{Cu}$$

$$= 2 \times 2.5 \times 10^{-3}$$

$$n_{Ag} = 5.0 \times 10^{-3} \text{ mol}$$

5.0×10^{-3} mol of silver was produced.

$$(c) C_{Ag^{+}} = \frac{5.0 \times 10^{-3} \text{ mol}}{0.100 \text{ L}}$$

$$C_{Ag^{+}} = 5.0 \times 10^{-2} \text{ mol/L}$$

The molar concentration of the silver ions is 5.0×10^{-2} mol/L.

$$(d) K_{sp} = [Ag_{(aq)}^{+}][C_2H_3O_2]_{(aq)}$$
$$= [5.0 \times 10^{-2}][5.0 \times 10^{-2}]$$

$$K_{sp} = 2.5 \times 10^{-3}$$

The solubility product for silver acetate is 2.5×10^{-3} .

Evaluation

- (e) The mass of copper observed would be larger than intended, suggesting that not as much silver reacted with it. The silver and acetate concentrations, as a result, would be lower, resulting in a lower value for the solubility product.

The silver residue made the copper heavier. Because of this error, the experimenter would erroneously conclude that less copper metal reacted, implying that there is less silver in solution. The final value for K_{sp} would be lower than expected.

7.7 ENERGY AND EQUILIBRIUM: THE LAWS OF THERMODYNAMICS

PRACTICE

(Page 498)

Understanding Concepts

1. (a) negative
(b) negative
(c) positive
(d) positive

Explore an Issue: Take a Stand: Can We Do Anything About Pollution?

(Page 501)

(There are a variety of positions that students can take as they argue the inevitability of pollution. The following argument is one possible scenario.)

At first glance, manufacturing new complex goods from simpler raw materials appears to contradict the second law of thermodynamics. However, when you consider the energy required to produce these products and the volume of waste materials the process generates, it becomes obvious that the second law remains valid. While the generation of waste materials may be inevitable, we can nevertheless control the type of waste a process generates. For example, an internal combustion engine and a hydrogen fuel cell arguably contribute a similar amount of entropy to the universe. However, the waste product of the fuel cell (steam) is much less harmful to the environment than the combustion products of gasoline.

Try This Activity: Stretching a Point

(Page 503)

- (a) Forward reaction (stretching)
 $\Delta G > 0, \Delta H < 0, \Delta S < 0$
- (b) Reverse reaction (relaxing)
 $\Delta G < 0, \Delta H > 0, \Delta S > 0$
- (c) The rubber molecules become more ordered as the rubber band is stretched (the forward reaction). Stretching the rubber band forces the molecules to align parallel to each other, much like strands of spaghetti in a box. When the rubber band is relaxed, the long rubber molecules become more disordered since the force holding them into regular pattern has been removed.
- (d) Bonds are forming between the polymer chains when the rubber band is being stretched. Conversely, bonds between the polymer chains are broken when the rubber band is relaxed.
- (e) London forces are being affected during the changes.
- (f) The spontaneous contraction of the rubber band is driven by entropy. Since ΔH is positive, the $T\Delta S$ term in the Gibbs free energy equation must be larger than ΔH in order for ΔG to be negative.
- (g) Since $T\Delta S$ is always negative regardless of temperature, ΔG will always be negative as well. Consequently, the contraction process should be spontaneous at all temperatures.
- (h) (Answers may vary. Sample investigation might include students testing their prediction by using rubber bands that have been warmed in a water bath or cooled in the freezer.)

PRACTICE

(Page 508)

Understanding Concepts

2. (a) $\text{NH}_{3(g)} + \text{HCl}_{(g)} \rightarrow \text{NH}_4\text{Cl}_{(s)}$
$$\Delta H^\circ = [\Delta H^\circ_{f(\text{NH}_4\text{Cl}_{(s)})}] - [\Delta H^\circ_{f(\text{NH}_{3(g)})} + \Delta H^\circ_{f(\text{HCl}_{(g)})}]$$
$$= [1 \text{ mol } (-314.4 \text{ kJ/mol})] - [1 \text{ mol } (-45.9 \text{ kJ/mol}) + 1 \text{ mol } (-92.3 \text{ kJ/mol})]$$
$$= [-314.4 \text{ kJ}] - [-45.9 \text{ kJ} - 92.3 \text{ kJ}]$$
$$= [-314.4 \text{ kJ}] - [-138.2 \text{ kJ}]$$

$$\Delta H^\circ = -176.2 \text{ kJ}$$

$$\begin{aligned}\Delta S^\circ &= [S^\circ_{(\text{NH}_4\text{Cl}_{(s)})}] - [S^\circ_{(\text{NH}_3_{(g)})} + S^\circ_{(\text{HCl}_{(g)})}] \\ &= [1 \text{ mol} (94.6 \text{ J/mol}\cdot\text{K})] - [1 \text{ mol} (192.78 \text{ J/mol}\cdot\text{K}) + 1 \text{ mol} (186.9 \text{ J/mol}\cdot\text{K})] \\ &= [94.6 \text{ J/K}] - [192.78 \text{ J/K} + 186.90 \text{ J/K}]\end{aligned}$$

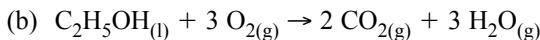
$$\begin{aligned}\Delta S^\circ &= -285.08 \text{ J/K} \\ &= -285.08 \text{ J/K} \times \frac{1 \text{ kJ}}{1000 \text{ J}}\end{aligned}$$

$$\Delta S^\circ = -0.28508 \text{ kJ/K}$$

$$\begin{aligned}\Delta G^\circ &= \Delta H^\circ - T\Delta S^\circ \\ &= -176.2 \text{ kJ} - (298 \text{ K})(-0.28508 \text{ kJ/K})\end{aligned}$$

$$\Delta G^\circ = -91.2 \text{ kJ}$$

The standard Gibbs free energy change associated with this reaction is -91.2 kJ . Since ΔG° is negative, the reaction is spontaneous under standard conditions and will proceed to the right as written. A total of 91.2 kJ of free energy is made available to do useful work for each mole of ammonia that reacts.



$$\begin{aligned}\Delta H^\circ &= [2\Delta H^\circ_{f(\text{CO}_{2(g)})} + 3\Delta H^\circ_{f(\text{H}_2\text{O}_{(g)})}] - [\Delta H^\circ_{f(\text{C}_2\text{H}_5\text{OH}_{(l)})} + 3\Delta H^\circ_{f(\text{O}_{2(g)})}] \\ &= [2 \text{ mol} \times (-393.5 \text{ kJ/mol}) + 3 \text{ mol} \times (-241.8 \text{ kJ/mol})] - [(-235.2 \text{ kJ/mol}) + 3 \text{ mol} \times (0)] \\ &= [-1512.4 \text{ kJ}] - [-235.2 \text{ kJ}]\end{aligned}$$

$$\Delta H^\circ = -1277.2 \text{ kJ}$$

$$\begin{aligned}\Delta S^\circ &= [2S^\circ_{(\text{CO}_{2(g)})} + 3S^\circ_{(\text{H}_2\text{O}_{(g)})}] - [S^\circ_{(\text{C}_2\text{H}_5\text{OH}_{(l)})} + 3S^\circ_{(\text{O}_{2(g)})}] \\ &= [2 \text{ mol} \times (213.78 \text{ J/mol}\cdot\text{K}) + 3 \text{ mol} \times (188.84 \text{ J/mol}\cdot\text{K})] - [(161.0 \text{ J/mol}\cdot\text{K}) + 3 \text{ mol} \times (205.14 \text{ J/mol}\cdot\text{K})] \\ &= [994.08 \text{ J/K}] - [776.42 \text{ J/K}]\end{aligned}$$

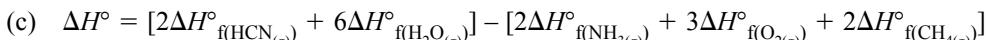
$$\begin{aligned}\Delta S^\circ &= 217.66 \text{ J/K} \\ &= 217.66 \text{ J/K} \times \frac{1 \text{ kJ}}{1000 \text{ J}}\end{aligned}$$

$$\Delta S^\circ = 0.21766 \text{ kJ/K}$$

$$\begin{aligned}\Delta G^\circ &= \Delta H^\circ - T\Delta S^\circ \\ &= -1277.2 \text{ kJ} - (298 \text{ K})(0.21766 \text{ kJ/K})\end{aligned}$$

$$\Delta G^\circ = -1342.1 \text{ kJ}$$

The standard Gibbs free energy change associated with this reaction is -1342.1 kJ . Since ΔG° is negative, the reaction is spontaneous under standard conditions and will proceed to the right as written. A total of 1342.1 kJ of free energy is made available to do useful work for each mole of ethanol that burns.



$$\begin{aligned}&= [2 \text{ mol} \times (+135.1 \text{ kJ/mol}) + 6 \text{ mol} \times (-241.8 \text{ kJ/mol})] - [2 \text{ mol} \times (-45.9 \text{ kJ/mol}) + 3 \text{ mol} \times (0 \text{ kJ/mol}) \\ &\quad + 2 \text{ mol} \times (-74.4 \text{ kJ/mol})] \\ &= [-1180.6 \text{ kJ}] - [-240.6 \text{ kJ}] \\ &= -940.0 \text{ kJ}\end{aligned}$$

$$\begin{aligned}\Delta S^\circ &= [2S^\circ_{(\text{HCN}_{(g)})} + 6S^\circ_{(\text{H}_2\text{O}_{(g)})}] - [2S^\circ_{(\text{NH}_3_{(g)})} + 3S^\circ_{(\text{O}_{2(g)})} + 2S^\circ_{(\text{CH}_4_{(g)})}] \\ &= [2 \text{ mol} \times (201.81 \text{ J/mol}\cdot\text{K}) + 6 \text{ mol} \times (188.84 \text{ J/mol}\cdot\text{K})] - [2 \text{ mol} \times (+192.78 \text{ J/mol}\cdot\text{K}) \\ &\quad + 3 \text{ mol} \times (+205 \text{ J/mol}\cdot\text{K})] \\ &= [1536.66 \text{ J/K}] - [1373.58 \text{ J/K}]\end{aligned}$$

$$\Delta S^\circ = 163.08 \text{ J/K}$$

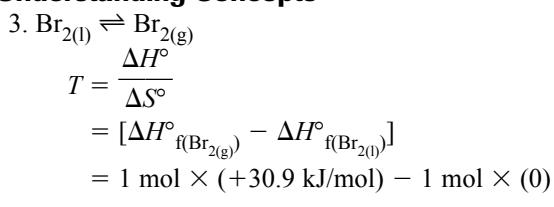
$$\begin{aligned}
 &= 163.08 \text{ J/K} \times \frac{1 \text{ kJ}}{1000 \text{ J}} \\
 \Delta S^\circ &= 0.16308 \text{ kJ/K} \\
 \Delta G^\circ &= \Delta H^\circ - T\Delta S^\circ \\
 &= -940.0 \text{ kJ} - (298 \text{ K})(0.16308 \text{ kJ/K}) \\
 &= -940.0 \text{ kJ} - 48.6 \text{ kJ} \\
 \Delta G^\circ &= -988.6 \text{ kJ}
 \end{aligned}$$

The standard Gibbs free energy change associated with this reaction is -988.6 kJ . Since ΔG° is negative, the reaction is spontaneous under standard conditions and will proceed to the right as written. A total of 988.6 kJ of free energy is made available to do useful work for each mole of ethanol that burns.

PRACTICE

(Page 511)

Understanding Concepts



$$T = +30.9 \text{ kJ}$$

$$\begin{aligned}
 \Delta S^\circ &= [S^\circ_{(\text{Br}_{2(g)})} - S^\circ_{(\text{Br}_{2(l)})}] \\
 &= 1 \text{ mol} \times (+245.47 \text{ J/mol}\cdot\text{K}) - 1 \text{ mol} \times (+152.2 \text{ J/mol}\cdot\text{K}) \\
 &= 245.47 \text{ J/mol}\cdot\text{K} - 152.2 \text{ J/mol}\cdot\text{K}
 \end{aligned}$$

$$\Delta S^\circ = 93.3 \text{ J/mol}\cdot\text{K}$$

$$= 93.3 \text{ J/K} \times \frac{1 \text{ kJ}}{1000 \text{ J}}$$

$$\Delta S^\circ = 0.0933 \text{ kJ/K}$$

$$\begin{aligned}
 T &= \frac{\Delta H^\circ}{\Delta S^\circ} \\
 &= \frac{30.9 \text{ kJ}}{0.0933 \text{ kJ/K}}
 \end{aligned}$$

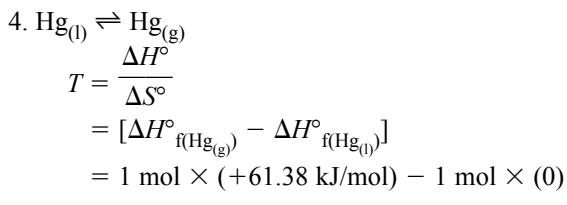
$$T = 331 \text{ K}$$

$$t = (T - 273^\circ\text{C})$$

$$= (331 \text{ K} - 273^\circ\text{C})$$

$$t = 58^\circ\text{C}$$

The boiling point of bromine is 58°C .



$$T = +61.38 \text{ kJ}$$

$$\begin{aligned}
 \Delta S^\circ &= [S^\circ_{(\text{Hg}_{(g)})} - S^\circ_{(\text{Hg}_{(l)})}] \\
 &= 1 \text{ mol} \times (+174.97 \text{ J/mol}\cdot\text{K}) - 1 \text{ mol} \times (+75.90 \text{ J/mol}\cdot\text{K})
 \end{aligned}$$

$$= 174.97 \text{ J/mol}\cdot\text{K} - 75.90 \text{ J/mol}\cdot\text{K}$$

$$\Delta S^\circ = 99.07 \text{ J/mol}\cdot\text{K}$$

$$= 99.07 \text{ J/K} \times \frac{1 \text{ kJ}}{1000 \text{ J}}$$

$$\Delta S^\circ = 0.09907 \text{ kJ/K}$$

$$T = \frac{\Delta H^\circ}{\Delta S^\circ}$$

$$= \frac{61.38 \text{ kJ}}{0.09907 \text{ kJ/K}}$$

$$T = 620 \text{ K}$$

$$t = (T - 273^\circ\text{C})$$

$$= (620 \text{ K} - 273^\circ\text{C})$$

$$t = 347^\circ\text{C}$$

The boiling point of mercury is 347°C.

SECTION 7.7 QUESTIONS

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Understanding Concepts

1. Given the necessary activation energy to begin, a spontaneous change occurs without outside assistance. A change in entropy measures the change in disorder or randomness of a system while a change in enthalpy measures a change in the energy that flows in or out of a system.
2. Change in enthalpy refers to the difference between the enthalpies of products and reactants while a change in entropy measures the difference in randomness or disorder between products and reactants.
3. (a) positive
(b) negative
(c) positive
4. (a) All changes either directly or indirectly increase the entropy of the universe.
(b) The likelihood or probability of dropping the puzzle parts onto the floor and having them land in a random state is far greater than having them land assembled.
(c) Although school can be considered a highly structured environment, the operation of the school still obeys the second law of thermodynamics. For example, a considerable amount of energy is used to transport students to the school. Furthermore, a great deal of energy is involved in the manufacture of all the materials that are used in school – everything from the paper this text is printed on to the food in the cafeteria. The heat released from these processes, as well as the waste generated, increases entropy.

5. (a) $\Delta H < 0, \Delta S > 0$

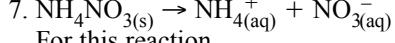
- (b) $\Delta H > 0, \Delta S < 0$

6. (a) $\Delta H < 0, \Delta S > 0$

- (b) Given that

$$\begin{aligned}\Delta G^\circ &= \Delta H^\circ - T\Delta S^\circ \\ &= (-) - (+)(+)\end{aligned}$$

This combination of negative ΔH° and positive ΔS° will always result in a negative value for ΔG° , implying that the reaction is spontaneous.



For this reaction,

$\Delta H^\circ > 0$, since the dissolving of ammonium nitrate is endothermic.

$\Delta S^\circ > 0$, since the entropy of the system increases as the reaction proceeds.

Therefore,

$$\begin{aligned}\Delta G^\circ &= \Delta H^\circ - T\Delta S^\circ \\ &= (+) - (T)(+)\end{aligned}$$

If the reaction is spontaneous at room temperature, $\Delta G^\circ < 0$. Consequently, T must be sufficiently large so that $T\Delta S^\circ > \Delta H^\circ$.

8. The rate of a chemical reaction cannot be inferred from the standard free energy of the reaction. The rate of a reaction can only be determined experimentally.
9. The decomposition of a compound into its elements is an endothermic process ($\Delta H > 0$), resulting in an increase in entropy, $\Delta S > 0$.

Given that

$$\begin{aligned}\Delta G &= \Delta H - T\Delta S \\ &= (+) - (T)(+)\end{aligned}$$

Since T is always positive, there must exist a temperature at which $T\Delta S > \Delta H$, resulting in the spontaneous decomposition of the compound.

10. (a) negative

- (b) negative

- (c) positive



$$\begin{aligned}\Delta H^\circ &= [\Delta H^\circ_{f(\text{CaSO}_{4(s)})} + 2\Delta H^\circ_{f(\text{H}_2\text{O}_{(l)})}] - [\Delta H^\circ_{f(\text{Ca}(\text{OH})_{2(s)})} + \Delta H^\circ_{f(\text{H}_2\text{SO}_{4(l)})}] \\ &= [1 \text{ mol} \times (-1434.1 \text{ kJ/mol}) + 2 \text{ mol} \times (-285.8 \text{ kJ/mol})] - [1 \text{ mol} \times (-986.1 \text{ kJ/mol}) + 1 \text{ mol} \times (-814.0 \text{ kJ/mol})] \\ &= [-2005.7 \text{ kJ}] - [-1800.1 \text{ kJ}]\end{aligned}$$

$$\Delta H^\circ = -205.6 \text{ kJ}$$

$$\begin{aligned}\Delta S^\circ &= [S^\circ_{(\text{CaSO}_{4(s)})} + 2S^\circ_{(\text{H}_2\text{O}_{(l)})}] - [S^\circ_{(\text{Ca}(\text{OH})_{2(s)})} + S^\circ_{(\text{H}_2\text{SO}_{4(l)})}] \\ &= [1 \text{ mol} \times (+108.4 \text{ J/mol}\cdot\text{K}) + 2 \text{ mol} \times (+69.95 \text{ J/mol}\cdot\text{K})] - [1 \text{ mol} \times (+83.4 \text{ J/mol}\cdot\text{K}) + 1 \text{ mol} \times (+156.90 \text{ J/mol}\cdot\text{K})] \\ &= [248.3 \text{ J/K}] - [240.3 \text{ J/K}]\end{aligned}$$

$$\begin{aligned}\Delta S^\circ &= 8.0 \text{ J/K} \\ &= 8.0 \text{ J/K} \times \frac{1 \text{ kJ}}{1000 \text{ J}}\end{aligned}$$

$$\Delta S^\circ = 0.0080 \text{ kJ/K}$$

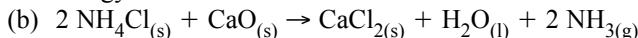
$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

$$= -205.6 \text{ kJ} - (298 \text{ K})(0.0080 \text{ kJ/K})$$

$$= -205.6 \text{ kJ} - 2.4 \text{ kJ}$$

$$\Delta G^\circ = -208.0 \text{ kJ}$$

The standard Gibbs free energy change associated with this reaction is -208.0 kJ . Since ΔG° is negative, the reaction is spontaneous under standard conditions and will proceed to the right as written. A total of 208.0 kJ of free energy is made available to do useful work for each mole of calcium hydroxide that reacts.



$$\begin{aligned}\Delta H^\circ &= [\Delta H^\circ_{f(\text{CaCl}_{2(aq)})} + \Delta H^\circ_{f(\text{H}_2\text{O}_{(l)})} + 2\Delta H^\circ_{f(\text{NH}_3_{(g)})}] - [2\Delta H^\circ_{f(\text{NH}_4\text{Cl}_{(s)})} + \Delta H^\circ_{f(\text{CaO}_{(s)})}] \\ &= [1 \text{ mol} \times (-795.8 \text{ kJ/mol}) + 1 \text{ mol} \times (-285.8 \text{ kJ/mol}) + 2 \text{ mol} \times (-45.9 \text{ kJ/mol})] - [2 \text{ mol} \times (-314.1 \text{ kJ/mol})] \\ &= [-1173.4 \text{ kJ}] - [-1263.7 \text{ kJ}]\end{aligned}$$

$$\Delta H^\circ = +90.3 \text{ kJ}$$

$$\begin{aligned}\Delta S^\circ &= [S^\circ_{(\text{CaCl}_{2(aq)})} + S^\circ_{(\text{H}_2\text{O}_{(l)})} + 2S^\circ_{(\text{NH}_3_{(g)})}] - [2S^\circ_{(\text{NH}_4\text{Cl}_{(s)})} + S^\circ_{(\text{CaO}_{(s)})}] \\ &= [1 \text{ mol} \times (+104.6 \text{ J/mol}\cdot\text{K}) + 1 \text{ mol} \times (+69.95 \text{ J/mol}\cdot\text{K}) + 2 \text{ mol} \times (+192.78 \text{ J/mol}\cdot\text{K})] - [2 \text{ mol} \times (+83.4 \text{ J/mol}\cdot\text{K})] \\ &= [560.11 \text{ J/K}] - [227.3 \text{ J/K}]\end{aligned}$$

$$\begin{aligned}\Delta S^\circ &= 332.8 \text{ J/K} \\ &= 332.8 \text{ J/K} \times \frac{1 \text{ kJ}}{1000 \text{ J}}\end{aligned}$$

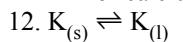
$$\Delta S^\circ = 0.3328 \text{ kJ/K}$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

$$= +90.3 \text{ kJ} - (298 \text{ K})(0.3328 \text{ kJ/K})$$

$$\Delta G^\circ = +803.8 \text{ kJ}$$

The standard Gibbs free energy change associated with this reaction is +803.8 kJ. Since ΔG° is positive, the reaction is not spontaneous under standard conditions. A total of 803.8 kJ of free energy must be provided per mole of calcium oxide to make the reaction proceed according to the balanced equation.



$$T = \frac{\Delta H^\circ}{\Delta S^\circ}$$

$$= [\Delta H^\circ_{f(\text{K}_{(l)})} - \Delta H^\circ_{f(\text{K}_{(s)})}]$$

$$= 1 \text{ mol} \times (+2.284 \text{ kJ/mol}) - 1 \text{ mol} \times (0)$$

$$T = +2.284 \text{ kJ}$$

$$\Delta S^\circ = [S^\circ_{(\text{K}_{(l)})} - S^\circ_{(\text{K}_{(s)})}]$$

$$= 1 \text{ mol} \times (+71.46 \text{ J/mol}\cdot\text{K}) - 1 \text{ mol} \times (+64.68 \text{ J/mol}\cdot\text{K})$$

$$= 71.46 \text{ J/mol}\cdot\text{K} - 64.68 \text{ J/mol}\cdot\text{K}$$

$$\Delta S^\circ = 6.78 \text{ J/mol}\cdot\text{K}$$

$$= 6.78 \text{ J/K} \times \frac{1 \text{ kJ}}{1000 \text{ J}}$$

$$\Delta S^\circ = 0.00678 \text{ kJ/K}$$

$$T = \frac{\Delta H^\circ}{\Delta S^\circ}$$

$$= \frac{2.284 \text{ kJ}}{0.00678 \text{ kJ/K}}$$

$$T = 337 \text{ K}$$

$$t = (T - 273^\circ\text{C})$$

$$= (337 \text{ K} - 273^\circ\text{C})$$

$$t = 64^\circ\text{C}$$

The melting point of potassium is 64°C.

13. (a) $\Delta H^\circ > 0$. Reactions involving bond formation tend to be endothermic.

$\Delta S^\circ > 0$. Solid ammonium is far more ordered than the gaseous reactants.

$\Delta G^\circ < 0$. The picture provides evidence that the reaction occurs spontaneously. Therefore, $\Delta G^\circ < 0$.



$$\Delta H^\circ = [\Delta H^\circ_{f(\text{NH}_4\text{Cl}_{(s)})}] - [\Delta H^\circ_{f(\text{NH}_{3(g)})} + \Delta H^\circ_{f(\text{HCl}_{(g)})}]$$

$$= [1 \text{ mol} (-314.4 \text{ kJ/mol})] - [1 \text{ mol} (-45.9 \text{ kJ/mol}) + 1 \text{ mol} (-92.3 \text{ kJ/mol})]$$

$$= [-314.4 \text{ kJ}] - [-45.9 \text{ kJ} - 92.3 \text{ kJ}]$$

$$= [-314.4 \text{ kJ}] - [-138.2 \text{ kJ}]$$

$$\Delta H^\circ = -176.2 \text{ kJ}$$

$$\Delta S^\circ = [S^\circ_{(\text{NH}_4\text{Cl}_{(s)})}] - [S^\circ_{(\text{NH}_{3(g)})} + S^\circ_{(\text{HCl}_{(g)})}]$$

$$= [1 \text{ mol} (94.6 \text{ J/mol}\cdot\text{K})] - [1 \text{ mol} (192.78 \text{ J/mol}\cdot\text{K}) + 1 \text{ mol} (186.9 \text{ J/mol}\cdot\text{K})]$$

$$= [94.6 \text{ J/K}] - [192.78 \text{ J/K} + 186.90 \text{ J/K}]$$

$$\Delta S^\circ = -285.08 \text{ J/K}$$

$$= -285.08 \text{ J/K} \times \frac{1 \text{ kJ}}{1000 \text{ J}}$$

$$\Delta S^\circ = -0.28508 \text{ kJ/K}$$

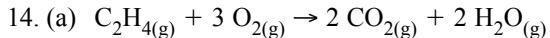
$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

$$= -176.2 \text{ kJ} - (298 \text{ K})(-0.28508 \text{ kJ/K})$$

$$\Delta G^\circ = -91.2 \text{ kJ}$$

The standard Gibbs free energy change associated with this reaction is -91.2 kJ .

- (c) All the calculated values agreed with the predicted values except ΔH° . The enthalpy change for this reaction is negative. Since ΔG° is negative, the reaction is spontaneous under standard conditions and will proceed to the right as written. A total of 91.2 kJ of free energy is made available to do useful work for each mole of ammonia that reacts.



$$\Delta H^\circ = [2\Delta H^\circ_{f(\text{CO}_{2(g)})} + 2\Delta H^\circ_{f(\text{H}_2\text{O}_{(g)})}] - [\Delta H^\circ_{f(\text{C}_2\text{H}_{4(g)})} + 3\Delta H^\circ_{f(\text{O}_{2(g)})}]$$

$$= [2 \text{ mol} \times (-393.5 \text{ kJ/mol}) + 2 \text{ mol} \times (-241.8 \text{ kJ/mol})] - [(+52.5 \text{ kJ/mol}) + 3 \text{ mol} \times (0)]$$

$$= [-1270.6 \text{ kJ}] - [+52.5 \text{ kJ}]$$

$$\Delta H^\circ = -1323.1 \text{ kJ}$$

$$\Delta S^\circ = [2S^\circ_{(\text{CO}_{2(g)})} + 2S^\circ_{(\text{H}_2\text{O}_{(g)})}] - [S^\circ_{(\text{C}_2\text{H}_{4(g)})} + 3S^\circ_{(\text{O}_{2(g)})}]$$

$$= [2 \text{ mol} \times (213.78 \text{ J/mol}\cdot\text{K}) + 2 \text{ mol} \times (188.84 \text{ J/mol}\cdot\text{K})] - [(219.3 \text{ J/mol}\cdot\text{K}) + 3 \text{ mol} \times (+205.14 \text{ J/mol}\cdot\text{K})]$$

$$= [+805.24 \text{ J/K}] - [+834.42 \text{ J/K}]$$

$$\Delta S^\circ = 29.18 \text{ J/K}$$

$$= -29.18 \text{ J/K} \times \frac{1 \text{ kJ}}{1000 \text{ J}}$$

$$\Delta S^\circ = -0.02918 \text{ kJ/K}$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

$$= -1323.1 \text{ kJ} - (298 \text{ K})(-0.02918 \text{ kJ/K})$$

$$\Delta G^\circ = -1314.4 \text{ kJ}$$

The standard Gibbs free energy change associated with this reaction is -1314.4 kJ .

- (b) Since ΔG° is negative, the reaction is spontaneous under standard conditions and will proceed to the right as written. A total of 1314.4 kJ of free energy is made available to do useful work for each mole of ethene that burns.

15. Once a system reaches equilibrium in a closed system, $\Delta G = 0$.

Making Connections

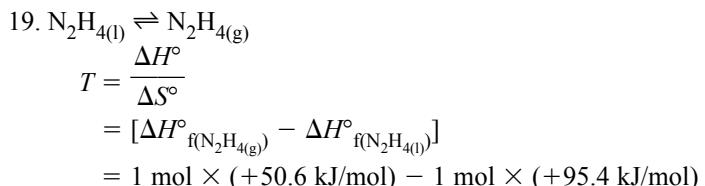
16. (a) (Sample answers) dissolving sugar, burning a candle, melting ice, making a sandwich, charging a battery, pumping water

17. There are a number of processes involved in the operation of a car that increase the entropy of the universe. For example:

- The combustion of fuel takes the large ordered molecules in gasoline and converts them into many smaller molecules with considerable kinetic energy.
- After an oil change, clean oil gradually becomes dirty as it accumulates engine residue.
- Left unprotected, the metallic components of a car rust.
- There are many different types of fluids pumped throughout a network of hoses in the car. Leaks are inevitable.

18. Chemical reactions used in the home include:

- The combustion of natural gas: $\text{CH}_{4(g)} + 2 \text{O}_{2(g)} \rightarrow \text{CO}_{2(g)} + 2 \text{H}_2\text{O}_{(g)}$. Free energy from this reaction is used to increase the kinetic energy of air molecules drawn into the furnace. The warm air is then blown throughout the house.
- The dissolving of cleaning products such as lye (sodium hydroxide): $\text{NaOH}_{(s)} \rightarrow \text{Na}_{(aq)}^+ + \text{OH}_{(aq)}^-$. Free energy released from this reaction is used to help dissolve organic matter that accumulates in plumbing.



$$T = -44.8 \text{ kJ}$$

$$\Delta S^\circ = [S^\circ_{(\text{N}_2\text{H}_{4(\text{g})})} - S^\circ_{(\text{N}_2\text{H}_{4(\text{l})})}]$$

$$= 1 \text{ mol} \times (+237.11 \text{ J/mol}\cdot\text{K}) - 1 \text{ mol} \times (+121.21 \text{ J/mol}\cdot\text{K})$$

$$= 237.11 \text{ J/mol}\cdot\text{K} - 121.21 \text{ J/mol}\cdot\text{K}$$

$$\Delta S^\circ = 115.9 \text{ J/mol}\cdot\text{K}$$

$$= 115.9 \text{ J/K} \times \frac{1 \text{ kJ}}{1000 \text{ J}}$$

$$\Delta S^\circ = 0.1159 \text{ kJ/K}$$

$$T = \frac{\Delta H^\circ}{\Delta S^\circ}$$

$$= \frac{-44.8 \text{ kJ}}{0.1159 \text{ kJ/K}}$$

$$T = 387 \text{ K}$$

$$t = (T - 273^\circ\text{C})$$

$$= (387 \text{ K} - 273^\circ\text{C})$$

$$t = 114^\circ\text{C}$$

The boiling point of hydrazine is 114°C.

- (b) Hydrazine is used mainly as a chemical intermediate in the production of agricultural chemicals, and spandex fibres. It is also a rocket fuel. Hydrazine is also used for plating metals on glass and plastics and as a component of photographic developers.

CHAPTER 7 LAB ACTIVITIES

INVESTIGATION 7.1.1 DISCOVERING THE EXTENT OF A CHEMICAL REACTION

(Page 513)

Prediction

- (a) The reaction is quantitative since equimolar amounts of both reactants are combined.

Experimental Design

- (b) $\text{CaCl}_{2(\text{aq})} + \text{Na}_2\text{SO}_{4(\text{aq})} \rightarrow \text{CaSO}_{4(\text{s})} + 2 \text{NaCl}_{(\text{aq})}$
- (c) $\text{Ca}^{2+}_{(\text{aq})} + \text{SO}^{2-}_{4(\text{aq})} \rightarrow \text{CaSO}_{4(\text{s})}$

Procedure

(d)

1. Measure 10 mL (or 5 mL) of $\text{CaCl}_{2(\text{aq})}$ in a clean graduated cylinder.
2. Pour the solution into a clean 50-mL or 100-mL beaker.
3. Measure 5 mL (or 10 mL) of $\text{Na}_2\text{SO}_{4(\text{aq})}$ in a clean graduated cylinder.
4. Slowly add this quantity of $\text{Na}_2\text{SO}_{4(\text{aq})}$ to the $\text{CaCl}_{2(\text{aq})}$ while stirring.
5. Filter the precipitate from the mixture.
6. Collect about 5 mL of the filtrate into a small clean test tube.
7. Test the filtrate by adding a few drops of $\text{Na}_2\text{CO}_{3(\text{aq})}$.

7.7 ENERGY AND EQUILIBRIUM: THE LAWS OF THERMODYNAMICS

PRACTICE

(Page 498)

Understanding Concepts

1. (a) negative
(b) negative
(c) positive
(d) positive

Explore an Issue: Take a Stand: Can We Do Anything About Pollution?

(Page 501)

(There are a variety of positions that students can take as they argue the inevitability of pollution. The following argument is one possible scenario.)

At first glance, manufacturing new complex goods from simpler raw materials appears to contradict the second law of thermodynamics. However, when you consider the energy required to produce these products and the volume of waste materials the process generates, it becomes obvious that the second law remains valid. While the generation of waste materials may be inevitable, we can nevertheless control the type of waste a process generates. For example, an internal combustion engine and a hydrogen fuel cell arguably contribute a similar amount of entropy to the universe. However, the waste product of the fuel cell (steam) is much less harmful to the environment than the combustion products of gasoline.

Try This Activity: Stretching a Point

(Page 503)

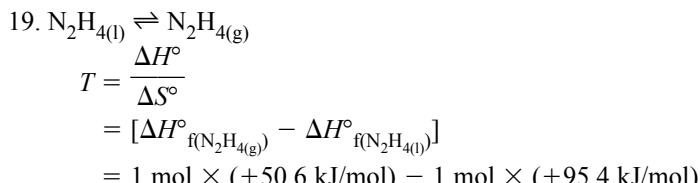
- (a) Forward reaction (stretching)
 $\Delta G > 0, \Delta H < 0, \Delta S < 0$
- (b) Reverse reaction (relaxing)
 $\Delta G < 0, \Delta H > 0, \Delta S > 0$
- (c) The rubber molecules become more ordered as the rubber band is stretched (the forward reaction). Stretching the rubber band forces the molecules to align parallel to each other, much like strands of spaghetti in a box. When the rubber band is relaxed, the long rubber molecules become more disordered since the force holding them into regular pattern has been removed.
- (d) Bonds are forming between the polymer chains when the rubber band is being stretched. Conversely, bonds between the polymer chains are broken when the rubber band is relaxed.
- (e) London forces are being affected during the changes.
- (f) The spontaneous contraction of the rubber band is driven by entropy. Since ΔH is positive, the $T\Delta S$ term in the Gibbs free energy equation must be larger than ΔH in order for ΔG to be negative.
- (g) Since $T\Delta S$ is always negative regardless of temperature, ΔG will always be negative as well. Consequently, the contraction process should be spontaneous at all temperatures.
- (h) (Answers may vary. Sample investigation might include students testing their prediction by using rubber bands that have been warmed in a water bath or cooled in the freezer.)

PRACTICE

(Page 508)

Understanding Concepts

2. (a) $\text{NH}_{3(g)} + \text{HCl}_{(g)} \rightarrow \text{NH}_4\text{Cl}_{(s)}$
$$\Delta H^\circ = [\Delta H^\circ_{f(\text{NH}_4\text{Cl}_{(s)})}] - [\Delta H^\circ_{f(\text{NH}_{3(g)})} + \Delta H^\circ_{f(\text{HCl}_{(g)})}]$$
$$= [1 \text{ mol } (-314.4 \text{ kJ/mol})] - [1 \text{ mol } (-45.9 \text{ kJ/mol}) + 1 \text{ mol } (-92.3 \text{ kJ/mol})]$$
$$= [-314.4 \text{ kJ}] - [-45.9 \text{ kJ} - 92.3 \text{ kJ}]$$
$$= [-314.4 \text{ kJ}] - [-138.2 \text{ kJ}]$$



$$T = -44.8 \text{ kJ}$$

$$\Delta S^\circ = [S^\circ_{(\text{N}_2\text{H}_{4(\text{g})})} - S^\circ_{(\text{N}_2\text{H}_{4(\text{l})})}]$$

$$= 1 \text{ mol} \times (+237.11 \text{ J/mol}\cdot\text{K}) - 1 \text{ mol} \times (+121.21 \text{ J/mol}\cdot\text{K})$$

$$= 237.11 \text{ J/mol}\cdot\text{K} - 121.21 \text{ J/mol}\cdot\text{K}$$

$$\Delta S^\circ = 115.9 \text{ J/mol}\cdot\text{K}$$

$$= 115.9 \text{ J/K} \times \frac{1 \text{ kJ}}{1000 \text{ J}}$$

$$\Delta S^\circ = 0.1159 \text{ kJ/K}$$

$$T = \frac{\Delta H^\circ}{\Delta S^\circ}$$

$$= \frac{-44.8 \text{ kJ}}{0.1159 \text{ kJ/K}}$$

$$T = 387 \text{ K}$$

$$t = (T - 273^\circ\text{C})$$

$$= (387 \text{ K} - 273^\circ\text{C})$$

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CHAPTER 7 LAB ACTIVITIES

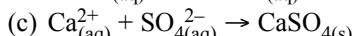
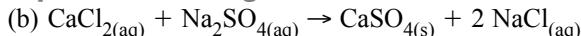
INVESTIGATION 7.1.1 DISCOVERING THE EXTENT OF A CHEMICAL REACTION

(Page 513)

Prediction

- (a) The reaction is quantitative since equimolar amounts of both reactants are combined.

Experimental Design



Procedure

(d)

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2. Pour the solution into a clean 50-mL or 100-mL beaker.
3. Measure 5 mL (or 10 mL) of $\text{Na}_2\text{SO}_{4(\text{aq})}$ in a clean graduated cylinder.
4. Slowly add this quantity of $\text{Na}_2\text{SO}_{4(\text{aq})}$ to the $\text{CaCl}_{2(\text{aq})}$ while stirring.
5. Filter the precipitate from the mixture.
6. Collect about 5 mL of the filtrate into a small clean test tube.
7. Test the filtrate by adding a few drops of $\text{Na}_2\text{CO}_{3(\text{aq})}$.

8. Collect another 5 mL of the filtrate in step 5 into a test tube and test with $\text{Ba}(\text{NO}_3)_2$ _(aq).
 9. Repeat the experiment again if time and supplies permit.

Analysis

- (e) A white precipitate formed by mixing solutions of $\text{CaCl}_{2(\text{aq})}$ and $\text{Na}_2\text{SO}_{4(\text{aq})}$. White precipitates formed in both diagnostic tests of the filtrate. The same evidence was obtained when the experiment was repeated.
 (f) According to the net ionic equation, $\text{Ca}_{(\text{aq})}^{2+}$ and $\text{SO}_{4(\text{aq})}^{2-}$ combine in a 1:1 ratio. It is logical to assume that if an excess of $\text{Ca}_{(\text{aq})}^{2+}$, for example, is used, then $\text{SO}_{4(\text{aq})}^{2-}$ should be totally consumed by the reaction. However, a white precipitate of $\text{BaSO}_{4(\text{s})}$ was observed in all samples.

Evaluation

- (g) The Experimental Design (combining precipitation with diagnostic tests for excess ions) is adequate since clear evidence was obtained to answer the question. Because the experiment required little time, it was repeated. To make the testing complete, at least one diagnostic test for one ion from each reactant is performed. Testing for sodium and chloride ions is not appropriate since these ions are expected to be in the filtrate regardless of the quantitative nature of the reaction.

The prediction is falsified since the evidence indicates the presence of both reactants after the reaction was completed. The assumption of a quantitative reaction is judged to be unacceptable for this reaction.

- (h) One improvement to the Experimental Design would be to assess the purity of the reagents. An impurity could have caused the unexpected positive diagnostic tests. Furthermore, the precipitate did not form immediately. Perhaps a pair of chemicals that do precipitate immediately would be a more appropriate test of the question.
 (i) The use of the terms “limiting” and “excess reagents” does not seem appropriate since $\text{Ca}_{(\text{aq})}^{2+}$ and $\text{SO}_{4(\text{aq})}^{2-}$ were detected in all samples.

LAB EXERCISE 7.2.1 DEVELOP AN EQUILIBRIUM LAW

(Page 514)

Analysis

- (a) The only relationship that gives a constant is #3.

Relationship	Trial 1	Trial 2	Trial 3	Trial 4	Trial 5
1. $[\text{Fe}^{3+}] [\text{SCN}^{-}] [\text{FeSCN}^{2+}]$	2.89×10^{-11}	2.34×10^{-9}			
2. $[\text{Fe}^{3+}] + [\text{SCN}^{-}] + [\text{FeSCN}^{2+}]$	4.01×10^{-2}	1.58×10^{-2}	6.37×10^{-2}		
3. $\frac{[\text{FeSCN}^{2+}]}{[\text{Fe}^{3+}] [\text{SCN}^{-}]}$	294	293	288	306	296
4. $\frac{[\text{Fe}^{3+}]}{[\text{FeSCN}^{2+}]}$	42.4	17.9	9.23		
5. $\frac{[\text{SCN}^{-}]}{[\text{FeSCN}^{2+}]}$	0.0870	0.231	0.555	1.52	

- (b) This relationship is the concentration of the reaction product divided by the concentrations of the reactants multiplied together.

INVESTIGATION 7.3.1 TESTING LE CHÂTELIER'S PRINCIPLE

(Page 514)

Predictions

- (a) I. According to Le Châtelier's principle,
 (a) placing the flasks into a cold-water mixture will shift the equilibrium to the left.
 (b) placing the flasks into a hot-water mixture will shift the equilibrium to the right.
 II. According to Le Châtelier's principle, an increase in pressure will shift the equilibrium to the left.
 III. According to Le Châtelier's principle,
 (a) adding water will shift the equilibrium to the right.
 (b) adding saturated silver nitrate will shift the equilibrium to the right.

8. Collect another 5 mL of the filtrate in step 5 into a test tube and test with $\text{Ba}(\text{NO}_3)_2$ _(aq).
 9. Repeat the experiment again if time and supplies permit.

Analysis

- (e) A white precipitate formed by mixing solutions of $\text{CaCl}_{2(\text{aq})}$ and $\text{Na}_2\text{SO}_{4(\text{aq})}$. White precipitates formed in both diagnostic tests of the filtrate. The same evidence was obtained when the experiment was repeated.
 (f) According to the net ionic equation, $\text{Ca}_{(\text{aq})}^{2+}$ and $\text{SO}_{4(\text{aq})}^{2-}$ combine in a 1:1 ratio. It is logical to assume that if an excess of $\text{Ca}_{(\text{aq})}^{2+}$, for example, is used, then $\text{SO}_{4(\text{aq})}^{2-}$ should be totally consumed by the reaction. However, a white precipitate of $\text{BaSO}_{4(\text{s})}$ was observed in all samples.

Evaluation

- (g) The Experimental Design (combining precipitation with diagnostic tests for excess ions) is adequate since clear evidence was obtained to answer the question. Because the experiment required little time, it was repeated. To make the testing complete, at least one diagnostic test for one ion from each reactant is performed. Testing for sodium and chloride ions is not appropriate since these ions are expected to be in the filtrate regardless of the quantitative nature of the reaction.

The prediction is falsified since the evidence indicates the presence of both reactants after the reaction was completed. The assumption of a quantitative reaction is judged to be unacceptable for this reaction.

- (h) One improvement to the Experimental Design would be to assess the purity of the reagents. An impurity could have caused the unexpected positive diagnostic tests. Furthermore, the precipitate did not form immediately. Perhaps a pair of chemicals that do precipitate immediately would be a more appropriate test of the question.
 (i) The use of the terms “limiting” and “excess reagents” does not seem appropriate since $\text{Ca}_{(\text{aq})}^{2+}$ and $\text{SO}_{4(\text{aq})}^{2-}$ were detected in all samples.

LAB EXERCISE 7.2.1 DEVELOP AN EQUILIBRIUM LAW

(Page 514)

Analysis

- (a) The only relationship that gives a constant is #3.

Relationship	Trial 1	Trial 2	Trial 3	Trial 4	Trial 5
1. $[\text{Fe}^{3+}] [\text{SCN}^{-}] [\text{FeSCN}^{2+}]$	2.89×10^{-11}	2.34×10^{-9}			
2. $[\text{Fe}^{3+}] + [\text{SCN}^{-}] + [\text{FeSCN}^{2+}]$	4.01×10^{-2}	1.58×10^{-2}	6.37×10^{-2}		
3. $\frac{[\text{FeSCN}^{2+}]}{[\text{Fe}^{3+}] [\text{SCN}^{-}]}$	294	293	288	306	296
4. $\frac{[\text{Fe}^{3+}]}{[\text{FeSCN}^{2+}]}$	42.4	17.9	9.23		
5. $\frac{[\text{SCN}^{-}]}{[\text{FeSCN}^{2+}]}$	0.0870	0.231	0.555	1.52	

- (b) This relationship is the concentration of the reaction product divided by the concentrations of the reactants multiplied together.

INVESTIGATION 7.3.1 TESTING LE CHÂTELIER'S PRINCIPLE

(Page 514)

Predictions

- (a) I. According to Le Châtelier's principle,
 (a) placing the flasks into a cold-water mixture will shift the equilibrium to the left.
 (b) placing the flasks into a hot-water mixture will shift the equilibrium to the right.
 II. According to Le Châtelier's principle, an increase in pressure will shift the equilibrium to the left.
 III. According to Le Châtelier's principle,
 (a) adding water will shift the equilibrium to the right.
 (b) adding saturated silver nitrate will shift the equilibrium to the right.

8. Collect another 5 mL of the filtrate in step 5 into a test tube and test with $\text{Ba}(\text{NO}_3)_2$ _(aq).
 9. Repeat the experiment again if time and supplies permit.

Analysis

- (e) A white precipitate formed by mixing solutions of $\text{CaCl}_{2(\text{aq})}$ and $\text{Na}_2\text{SO}_{4(\text{aq})}$. White precipitates formed in both diagnostic tests of the filtrate. The same evidence was obtained when the experiment was repeated.
 (f) According to the net ionic equation, $\text{Ca}_{(\text{aq})}^{2+}$ and $\text{SO}_{4(\text{aq})}^{2-}$ combine in a 1:1 ratio. It is logical to assume that if an excess of $\text{Ca}_{(\text{aq})}^{2+}$, for example, is used, then $\text{SO}_{4(\text{aq})}^{2-}$ should be totally consumed by the reaction. However, a white precipitate of $\text{BaSO}_{4(\text{s})}$ was observed in all samples.

Evaluation

- (g) The Experimental Design (combining precipitation with diagnostic tests for excess ions) is adequate since clear evidence was obtained to answer the question. Because the experiment required little time, it was repeated. To make the testing complete, at least one diagnostic test for one ion from each reactant is performed. Testing for sodium and chloride ions is not appropriate since these ions are expected to be in the filtrate regardless of the quantitative nature of the reaction.

The prediction is falsified since the evidence indicates the presence of both reactants after the reaction was completed. The assumption of a quantitative reaction is judged to be unacceptable for this reaction.

- (h) One improvement to the Experimental Design would be to assess the purity of the reagents. An impurity could have caused the unexpected positive diagnostic tests. Furthermore, the precipitate did not form immediately. Perhaps a pair of chemicals that do precipitate immediately would be a more appropriate test of the question.
 (i) The use of the terms “limiting” and “excess reagents” does not seem appropriate since $\text{Ca}_{(\text{aq})}^{2+}$ and $\text{SO}_{4(\text{aq})}^{2-}$ were detected in all samples.

LAB EXERCISE 7.2.1 DEVELOP AN EQUILIBRIUM LAW

(Page 514)

Analysis

- (a) The only relationship that gives a constant is #3.

Relationship	Trial 1	Trial 2	Trial 3	Trial 4	Trial 5
1. $[\text{Fe}^{3+}] [\text{SCN}^-] [\text{FeSCN}^{2+}]$	2.89×10^{-11}	2.34×10^{-9}			
2. $[\text{Fe}^{3+}] + [\text{SCN}^-] + [\text{FeSCN}^{2+}]$	4.01×10^{-2}	1.58×10^{-2}	6.37×10^{-2}		
3. $\frac{[\text{FeSCN}^{2+}]}{[\text{Fe}^{3+}] [\text{SCN}^-]}$	294	293	288	306	296
4. $\frac{[\text{Fe}^{3+}]}{[\text{FeSCN}^{2+}]}$	42.4	17.9	9.23		
5. $\frac{[\text{SCN}^-]}{[\text{FeSCN}^{2+}]}$	0.0870	0.231	0.555	1.52	

- (b) This relationship is the concentration of the reaction product divided by the concentrations of the reactants multiplied together.

INVESTIGATION 7.3.1 TESTING LE CHÂTELIER'S PRINCIPLE

(Page 514)

Predictions

- (a) I. According to Le Châtelier's principle,
 (a) placing the flasks into a cold-water mixture will shift the equilibrium to the left.
 (b) placing the flasks into a hot-water mixture will shift the equilibrium to the right.
 II. According to Le Châtelier's principle, an increase in pressure will shift the equilibrium to the left.
 III. According to Le Châtelier's principle,
 (a) adding water will shift the equilibrium to the right.
 (b) adding saturated silver nitrate will shift the equilibrium to the right.

- (c) adding heat will shift the equilibrium to the left.
- IV. According to Le Châtelier's principle,
- adding $\text{HCl}_{(\text{aq})}$ will shift the equilibrium to the left.
 - adding $\text{NaOH}_{(\text{aq})}$ will shift the equilibrium to the right.
- V. According to Le Châtelier's principle,
- adding $\text{Fe}(\text{NO}_3)_3\text{ (aq)}$ will shift the equilibrium to the right.
 - adding $\text{KSCN}_{(\text{aq})}$ will shift the equilibrium to the right.
 - adding $\text{NaOH}_{(\text{aq})}$ will shift the equilibrium to the left.
- VI. According to Le Châtelier's principle,
- adding $\text{NH}_3\text{ (aq)}$ will shift the equilibrium to the right.
 - adding $\text{HCl}_{(\text{aq})}$ will shift the equilibrium to the left.
- VII. According to Le Châtelier's principle,
- adding $\text{NaOH}_{(\text{aq})}$ will shift the equilibrium to the left.
 - adding $\text{HCl}_{(\text{aq})}$ will shift the equilibrium to the right.
 - adding $\text{Ba}(\text{NO}_3)_2\text{ (aq)}$ will shift the equilibrium to the left.
- In each case, the equilibrium will shift to try to undo what was done to the initial equilibrium.
- (b) According to the colour-change evidence gathered in this experiment, the systems are affected in the same way as predicted above.
- (c)

Equilibrium System	Stress Applied	Colour Change Observed
1.	(a) cold (b) heat	lighter darker
2.	increase in pressure	solution changes from green/blue to yellow
3.	(a) adding more water (b) adding silver nitrate (c) adding heat	solution became more pink solution became more pink solution became more blue
4.	(a) adding $\text{HCl}_{(\text{aq})}$ (b) adding $\text{NaOH}_{(\text{aq})}$	yellow solution turned red yellow solution turned blue
5.	(a) adding $\text{Fe}(\text{NO}_3)_3\text{ (aq)}$ (b) adding $\text{KSCN}_{(\text{aq})}$ (c) adding $\text{NaOH}_{(\text{aq})}$	solution became more red solution became more red solution became more yellow
6.	(a) adding $\text{NH}_3\text{ (aq)}$ (b) adding $\text{HCl}_{(\text{aq})}$	solution became less blue solution became more blue
7.	(a) adding $\text{NaOH}_{(\text{aq})}$ (b) adding $\text{HCl}_{(\text{aq})}$ (c) adding $\text{Ba}(\text{NO}_3)_2\text{ (aq)}$	solution became more yellow solution became more orange solution became more yellow

INVESTIGATION 7.6.1 DETERMINING THE K_{SP} OF CALCIUM OXALATE

(Page 517)

Evidence

(a) (See Table 3 in the text.)

Analysis

(b) to (g)

- (c) adding heat will shift the equilibrium to the left.
- IV. According to Le Châtelier's principle,
- adding $\text{HCl}_{(\text{aq})}$ will shift the equilibrium to the left.
 - adding $\text{NaOH}_{(\text{aq})}$ will shift the equilibrium to the right.
- V. According to Le Châtelier's principle,
- adding $\text{Fe}(\text{NO}_3)_3\text{ (aq)}$ will shift the equilibrium to the right.
 - adding $\text{KSCN}_{(\text{aq})}$ will shift the equilibrium to the right.
 - adding $\text{NaOH}_{(\text{aq})}$ will shift the equilibrium to the left.
- VI. According to Le Châtelier's principle,
- adding $\text{NH}_3\text{ (aq)}$ will shift the equilibrium to the right.
 - adding $\text{HCl}_{(\text{aq})}$ will shift the equilibrium to the left.
- VII. According to Le Châtelier's principle,
- adding $\text{NaOH}_{(\text{aq})}$ will shift the equilibrium to the left.
 - adding $\text{HCl}_{(\text{aq})}$ will shift the equilibrium to the right.
 - adding $\text{Ba}(\text{NO}_3)_2\text{ (aq)}$ will shift the equilibrium to the left.
- In each case, the equilibrium will shift to try to undo what was done to the initial equilibrium.
- (b) According to the colour-change evidence gathered in this experiment, the systems are affected in the same way as predicted above.
- (c)

Equilibrium System	Stress Applied	Colour Change Observed
1.	(a) cold (b) heat	lighter darker
2.	increase in pressure	solution changes from green/blue to yellow
3.	(a) adding more water (b) adding silver nitrate (c) adding heat	solution became more pink solution became more pink solution became more blue
4.	(a) adding $\text{HCl}_{(\text{aq})}$ (b) adding $\text{NaOH}_{(\text{aq})}$	yellow solution turned red yellow solution turned blue
5.	(a) adding $\text{Fe}(\text{NO}_3)_3\text{ (aq)}$ (b) adding $\text{KSCN}_{(\text{aq})}$ (c) adding $\text{NaOH}_{(\text{aq})}$	solution became more red solution became more red solution became more yellow
6.	(a) adding $\text{NH}_3\text{ (aq)}$ (b) adding $\text{HCl}_{(\text{aq})}$	solution became less blue solution became more blue
7.	(a) adding $\text{NaOH}_{(\text{aq})}$ (b) adding $\text{HCl}_{(\text{aq})}$ (c) adding $\text{Ba}(\text{NO}_3)_2\text{ (aq)}$	solution became more yellow solution became more orange solution became more yellow

INVESTIGATION 7.6.1 DETERMINING THE K_{SP} OF CALCIUM OXALATE

(Page 517)

Evidence

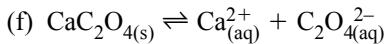
(a) (See Table 3 in the text.)

Analysis

(b) to (g)

Well #	A	B	C	D	E
1	1.0×10^{-1}	1×10^{-1}	5.00×10^{-2}	5.00×10^{-2}	3×10^{-3}
2	5.00×10^{-2}	1×10^{-1}	2.50×10^{-2}	5.00×10^{-2}	1×10^{-3}
3	2.50×10^{-2}	1×10^{-1}	1.25×10^{-2}	5.00×10^{-2}	6×10^{-4}
4	1.25×10^{-2}	1×10^{-1}	6.25×10^{-3}	5.00×10^{-2}	3×10^{-4}
5	6.25×10^{-3}	1×10^{-1}	3.13×10^{-3}	5.00×10^{-2}	2×10^{-4}
6	3.13×10^{-3}	1×10^{-1}	1.56×10^{-3}	5.00×10^{-2}	8×10^{-5}
7	1.56×10^{-3}	1×10^{-1}	7.81×10^{-4}	5.00×10^{-2}	4×10^{-5}
8	7.81×10^{-4}	1×10^{-1}	3.91×10^{-4}	5.00×10^{-2}	2×10^{-5}
9	3.91×10^{-4}	1×10^{-1}	1.95×10^{-4}	5.00×10^{-2}	1×10^{-5}
10	1.95×10^{-4}	1×10^{-1}	9.77×10^{-5}	5.00×10^{-2}	5×10^{-6}
11	9.77×10^{-5}	1×10^{-1}	4.88×10^{-5}	5.00×10^{-2}	2×10^{-6}
12	4.88×10^{-5}	1×10^{-1}	2.44×10^{-5}	5.00×10^{-2}	1×10^{-6}

(extra digits carried in the calculation of columns A, C, and D)



$$K_{\text{sp}} = [\text{Ca}^{2+}_{(\text{aq})}][\text{C}_2\text{O}_{4(\text{aq})}^{2-}]$$

(g) Well #11 was the last well in which a precipitate was observed. Therefore, the actual value of K_{sp} must lie between 1×10^{-6} and 2×10^{-6} .

Evaluation

- (i) Air bubbles can easily be drawn into the pipet. This decreases the volume of solutions transferred to the next well. Doubling the volumes of all solutions initially should reduce the risk of drawing into the pipet without affecting the calculations.
- (j) The accepted value of K_{sp} for calcium oxalate is 2.3×10^{-9} . The result obtained from this experiment is approximately 1000 times larger than the accepted value. Since similar results were obtained by most of my classmates, I have confidence in my data.

INVESTIGATION 7.6.2 DETERMINING K_{sp} FOR CALCIUM HYDROXIDE

(Page 519)

Question

- (a) What is the K_{sp} for calcium hydroxide?

Prediction

- (b) The accepted value for the solubility product of calcium hydroxide is 7.9×10^{-6} .

Experimental Design

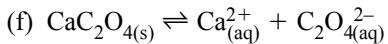
- (c) A filtered solution of calcium hydroxide is titrated with a hydrochloric acid solution of known concentration to a bromophenol blue endpoint.

Materials

- (d) 0.10 mol/L hydrochloric acid, $\text{HCl}_{(\text{aq})}$
 bromophenol blue indicator
 filtered calcium hydroxide
 buret, stand, and clamp
 125-mL Erlenmeyer flask
 funnel
 two 250-mL beakers
 10-mL pipet and filler

Well #	A	B	C	D	E
1	1.0×10^{-1}	1×10^{-1}	5.00×10^{-2}	5.00×10^{-2}	3×10^{-3}
2	5.00×10^{-2}	1×10^{-1}	2.50×10^{-2}	5.00×10^{-2}	1×10^{-3}
3	2.50×10^{-2}	1×10^{-1}	1.25×10^{-2}	5.00×10^{-2}	6×10^{-4}
4	1.25×10^{-2}	1×10^{-1}	6.25×10^{-3}	5.00×10^{-2}	3×10^{-4}
5	6.25×10^{-3}	1×10^{-1}	3.13×10^{-3}	5.00×10^{-2}	2×10^{-4}
6	3.13×10^{-3}	1×10^{-1}	1.56×10^{-3}	5.00×10^{-2}	8×10^{-5}
7	1.56×10^{-3}	1×10^{-1}	7.81×10^{-4}	5.00×10^{-2}	4×10^{-5}
8	7.81×10^{-4}	1×10^{-1}	3.91×10^{-4}	5.00×10^{-2}	2×10^{-5}
9	3.91×10^{-4}	1×10^{-1}	1.95×10^{-4}	5.00×10^{-2}	1×10^{-5}
10	1.95×10^{-4}	1×10^{-1}	9.77×10^{-5}	5.00×10^{-2}	5×10^{-6}
11	9.77×10^{-5}	1×10^{-1}	4.88×10^{-5}	5.00×10^{-2}	2×10^{-6}
12	4.88×10^{-5}	1×10^{-1}	2.44×10^{-5}	5.00×10^{-2}	1×10^{-6}

(extra digits carried in the calculation of columns A, C, and D)



$$K_{\text{sp}} = [\text{Ca}^{2+}_{(\text{aq})}][\text{C}_2\text{O}_{4(\text{aq})}^{2-}]$$

(g) Well #11 was the last well in which a precipitate was observed. Therefore, the actual value of K_{sp} must lie between 1×10^{-6} and 2×10^{-6} .

Evaluation

- (i) Air bubbles can easily be drawn into the pipet. This decreases the volume of solutions transferred to the next well. Doubling the volumes of all solutions initially should reduce the risk of drawing into the pipet without affecting the calculations.
- (j) The accepted value of K_{sp} for calcium oxalate is 2.3×10^{-9} . The result obtained from this experiment is approximately 1000 times larger than the accepted value. Since similar results were obtained by most of my classmates, I have confidence in my data.

INVESTIGATION 7.6.2 DETERMINING K_{sp} FOR CALCIUM HYDROXIDE

(Page 519)

Question

- (a) What is the K_{sp} for calcium hydroxide?

Prediction

- (b) The accepted value for the solubility product of calcium hydroxide is 7.9×10^{-6} .

Experimental Design

- (c) A filtered solution of calcium hydroxide is titrated with a hydrochloric acid solution of known concentration to a bromophenol blue endpoint.

Materials

- (d) 0.10 mol/L hydrochloric acid, $\text{HCl}_{(\text{aq})}$
 bromophenol blue indicator
 filtered calcium hydroxide
 buret, stand, and clamp
 125-mL Erlenmeyer flask
 funnel
 two 250-mL beakers
 10-mL pipet and filler

Safety Precautions

The solutions in this experiment are corrosive. Eye protection and a laboratory apron must be worn. Leftover acid or base should be disposed of in a container provided by the teacher.

Procedure

- (e) 1. Clean the buret with water. Check that the buret drains appropriately.
2. Fill the buret with the acid solution.
3. Pipet 10.00 mL of calcium hydroxide into the flask.
4. Add about 20 mL of distilled water to the flask.
5. Add 3 drops of bromophenol blue indicator to the flask.
6. Titrate the base to a bromophenol blue endpoint.
7. Repeat the titration until reproducible results are obtained.
8. Dispose of the solutions as directed by the teacher.

Analysis

(f) Average volume of 0.10 mol/L HCl used: 2.50 mL

volume of calcium hydroxide: 10.00 mL

$$n_{\text{HCl}_{(\text{aq})}} = 0.10 \text{ mol/L} \times 2.50 \text{ mL}$$

$$= 0.25 \text{ mmol}$$

$$= n_{\text{OH}_{(\text{aq})}^-}$$

$$C_{\text{OH}_{(\text{aq})}^-} = \frac{0.25 \text{ mmol}}{10.00 \text{ mL}}$$

$$C_{\text{OH}_{(\text{aq})}^-} = 0.025 \text{ mol/L}$$

$$C_{\text{Ca}_{(\text{aq})}^{2+}} = \frac{C_{\text{OH}_{(\text{aq})}^-}}{2}$$

$$C_{\text{Ca}_{(\text{aq})}^{2+}} = 0.0125 \text{ mol/L} \text{ (extra digits carried)}$$

$$[\text{Ca}_{(\text{aq})}^{2+}][\text{OH}_{(\text{aq})}^-]^2 = (0.0125)(0.025)^2$$

$$[\text{Ca}_{(\text{aq})}^{2+}][\text{OH}_{(\text{aq})}^-]^2 = 7.8 \times 10^{-6}$$

The solubility product for calcium hydroxide is 7.8×10^{-6} .

Evaluation

$$(g) \% \text{ difference} = \frac{7.9 \times 10^{-6} - 7.8 \times 10^{-6}}{7.9 \times 10^{-6}} \times 100\%$$

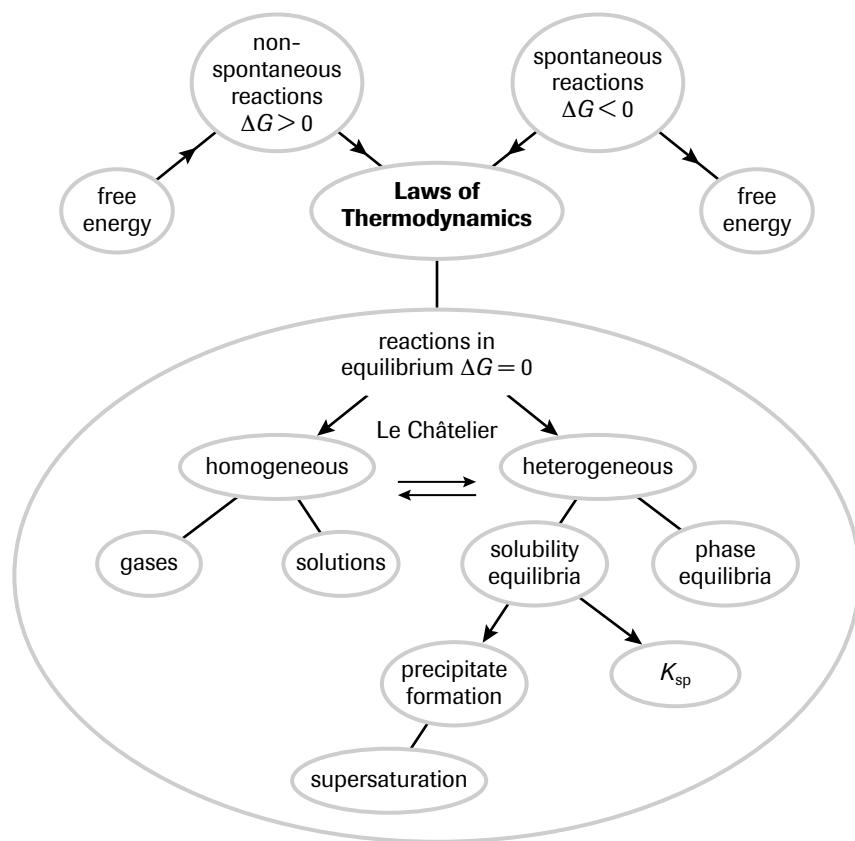
$$\% \text{ difference} = 1.3\%$$

- (h) The experimental value is judged to be acceptable because it is very close to the reference value for calcium hydroxide. Some error in the lab could be attributed to concentration of the hydrochloric acid solution. The concentration of the solution could be first determined experimentally by titrating the acid with a primary standard such as potassium hydrogen phthalate.

CHAPTER 7 SUMMARY

MAKE A SUMMARY

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CHAPTER 7 SELF-QUIZ

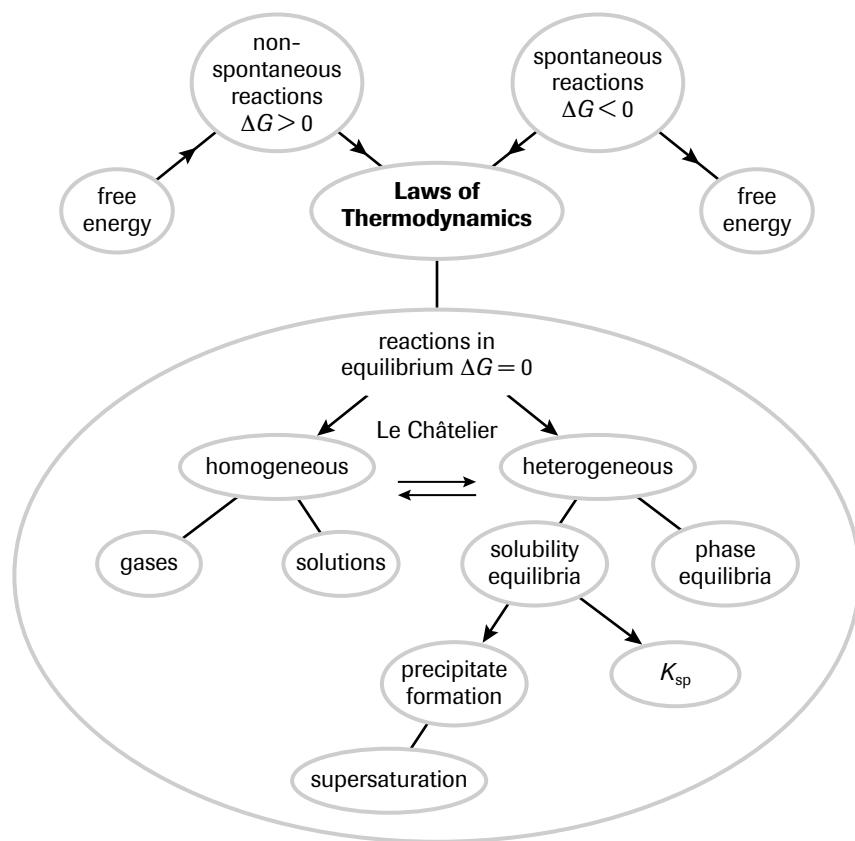
(Page 522)

1. False. Chemical equilibrium involves two opposing reactions occurring at the same rate.
2. True
3. False. A catalyst does not shift either reaction. A catalyst speeds up the time required to reach equilibrium.
4. True
5. False. Exothermic reactions shift to the left when heated.
6. False. If trial ion product is greater than K_{sp} , a precipitate will form.
7. False. The reaction will be spontaneous only at low temperatures.
8. True
9. True
10. True
11. (e)
12. (a)
13. (e)
14. (b)
15. (d)
16. (a)
17. (a)

CHAPTER 7 SUMMARY

MAKE A SUMMARY

(Page 521)



CHAPTER 7 SELF-QUIZ

(Page 522)

1. False. Chemical equilibrium involves two opposing reactions occurring at the same rate.
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9. True
10. True
11. (e)
12. (a)
13. (e)
14. (b)
15. (d)
16. (a)
17. (a)

18. (a)

19. (c)

20. (a)

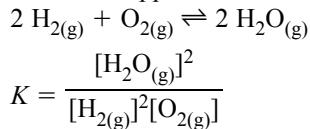
CHAPTER 7 REVIEW

(Page 523)

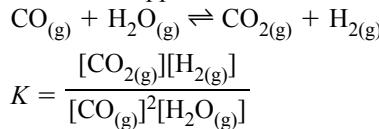
Understanding Concepts

1. (a) Chemical equilibrium is a dynamic equilibrium between the reactants and products of a chemical reaction in a closed system.
(b) Chemical equilibrium depends on the rate of the two opposing processes being equal.
2. Two ways to describe the relative amounts of reactants and products are percent reaction and the equilibrium law expression.
3. (a) A soft drink is in a non-equilibrium state when it is open.
(b) A soft drink is in an equilibrium state when it is closed.
4. When a chemical system at equilibrium is disturbed by a change in a property, the system adjusts in a way that opposes the change.
5. Given the size of the equilibrium constant, the amount of water present at equilibrium far exceeds the amount of hydrogen and oxygen. For all practical purposes, this reaction is complete.
6. Variables commonly manipulated to shift the position of the equilibrium include: concentration, temperature, volume/pressure.
7. An increase in volume of a container results in a decrease in pressure. Conversely, a decrease in volume results in an increase in pressure.
8. An increase in the concentration of reactants as well as a decrease in the concentration of products can improve yield.

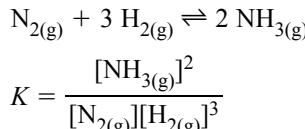
9. (a) approx. 100%



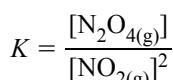
- (b) approx. 67%



- (c) <10%



10. (a) $2 \text{NO}_{2(\text{g})} \rightleftharpoons \text{N}_2\text{O}_{4(\text{g})}$



$$\frac{[\text{N}_2\text{O}_{4(\text{g})}]}{[0.050]^2} = 1.15$$

$$[\text{N}_2\text{O}_{4(\text{g})}] = 2.9 \times 10^{-3} \text{ mol/L}$$

The concentration of dinitrogen tetroxide is $2.9 \times 10^{-3} \text{ mol/L}$.

- (c) An increase in the nitrogen dioxide concentration will shift the equilibrium to the right.

11. (a) left

- (b) left

- (c) right

- (d) no effect

- (e) no effect

18. (a)

19. (c)

20. (a)

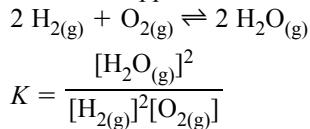
CHAPTER 7 REVIEW

(Page 523)

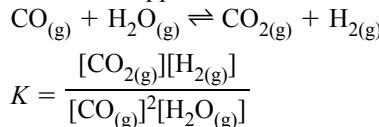
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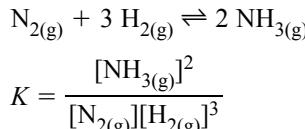
9. (a) approx. 100%



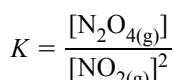
- (b) approx. 67%



- (c) <10%



10. (a) $2 \text{NO}_{2(\text{g})} \rightleftharpoons \text{N}_2\text{O}_{4(\text{g})}$



$$\frac{[\text{N}_2\text{O}_{4(\text{g})}]}{[0.050]^2} = 1.15$$

$$[\text{N}_2\text{O}_{4(\text{g})}] = 2.9 \times 10^{-3} \text{ mol/L}$$

The concentration of dinitrogen tetroxide is $2.9 \times 10^{-3} \text{ mol/L}$.

- (c) An increase in the nitrogen dioxide concentration will shift the equilibrium to the right.

11. (a) left

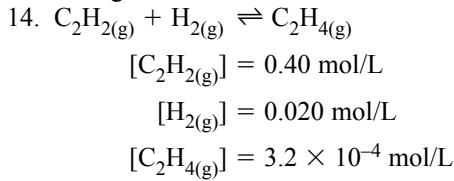
- (b) left

- (c) right

- (d) no effect

- (e) no effect

12. (a) Conditions that would increase the yield of ethene include:
- increasing the temperature.
 - decreasing the pressure on the system, or conversely, increasing the volume.
 - increasing the concentration of ethane.
 - removing the products as quickly as they form.
- (b) Conditions that would increase the yield of methanol include:
- decreasing the temperature.
 - increasing the pressure on the system, or conversely, decreasing the volume.
 - increasing the concentration of the reactants.
 - removing methanol as quickly as it forms.
13. (a) The addition of CuSO_4 increases the concentration of copper(II) ions. The system shifts to the right to remove excess copper(II) ions.
- (b) The reverse reaction is favoured when the temperature is decreased, causing the system to shift to the left.
- (c) The addition of a solid has no effect on the equilibrium because condensed phases are not included in the equilibrium law expression.
- (d) A decrease in volume (increase in pressure) favours the reverse reaction, shifting the equilibrium to the left.
- (e) Silver ions from the silver nitrate combine with chloride ions from the equilibrium to produce a silver chloride precipitate. The system adjusts by favouring the forward reaction, which produces more chloride.
- (f) A volume change has no effect on this equilibrium because the same number of moles of gas are on each side of the chemical equation.
- (g) Iron(III) ions released from $\text{Fe}(\text{NO}_3)_3$ favour the formation of more $\text{FeSCN}_{(\text{aq})}^{2+}$, shifting the equilibrium to the right.

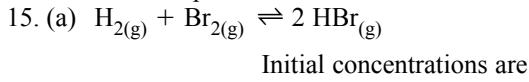


$$Q = \frac{[\text{C}_2\text{H}_{4(\text{g})}]}{[\text{C}_2\text{H}_{2(\text{g})}][\text{H}_{2(\text{g})}]}$$

$$= \frac{[3.2 \times 10^{-4}]}{[0.40][0.020]}$$

$$Q = 0.040$$

Since the value of Q is less than the value of K (0.072), the reaction is not at equilibrium. In order to attain equilibrium, the reaction will shift to the right (as written). The concentration of the reactants will decrease and the concentration of the products will increase.



$$[\text{HBr}_{2(\text{g})}] = 0.00$$

$$[\text{H}_{2(\text{g})}] = [\text{Br}_{2(\text{g})}]$$

$$= \frac{8.00 \text{ mol}}{2.00 \text{ L}}$$

$$[\text{H}_{2(\text{g})}] = 4.00 \text{ mol/L}$$

ICE Table for the Formation of $\text{HBr}_{(\text{g})}$			
	$\text{H}_{2(\text{g})} +$	$\text{Br}_{2(\text{g})} \rightleftharpoons$	$2 \text{ HBr}_{(\text{g})}$
Initial concentration (mol/L)	4.00	4.00	0.00
Change in concentration (mol/L)	$-x$	$-x$	$-2x$
Equilibrium concentration (mol/L)	$4.00 - x$	$4.00 - x$	$2x$

At equilibrium,

$$K = \frac{[\text{HBr}_{(\text{g})}]^2}{[\text{H}_2(\text{g})][\text{Br}_2(\text{g})]}$$

$$\frac{(2x)^2}{(4.00 - x)^2} = 12.0$$

$$\sqrt{\frac{(2x)^2}{(4.00 - x)^2}} = \sqrt{12.0}$$

$$\frac{2x}{4.00 - x} = 3.464 \quad (\text{extra digits carried})$$

$$2x = 3.464 (4.00 - x)$$

$$x = 2.536$$

$$\begin{aligned} [\text{HBr}_{(\text{g})}] &= 2x \\ &= 2(2.536) \end{aligned}$$

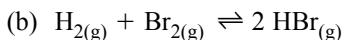
$$[\text{HBr}_{(\text{g})}] = 5.07 \text{ mol/L}$$

$$[\text{H}_2(\text{g})] = [\text{Br}_2(\text{g})]$$

$$= 4.00 - x$$

$$[\text{H}_2(\text{g})] = 1.46 \text{ mol/L}$$

The equilibrium concentrations of hydrogen, bromine, and hydrogen bromide are 1.46 mol/L, 1.46 mol/L, and 5.07 mol/L, respectively.



Initial concentrations are

$$[\text{HBr}_{(\text{g})}] = 0.00$$

$$[\text{H}_2(\text{g})] = [\text{Br}_2(\text{g})]$$

$$= \frac{12.00 \text{ mol}}{2.00 \text{ L}}$$

$$[\text{H}_2(\text{g})] = 6.00 \text{ mol/L}$$

ICE Table for the Formation of $\text{HBr}_{(\text{g})}$			
	$\text{H}_{2(\text{g})} +$	$\text{Br}_{2(\text{g})} \rightleftharpoons$	$2 \text{ HBr}_{(\text{g})}$
Initial concentration (mol/L)	6.00	6.00	0.000
Change in concentration (mol/L)	$-x$	$-x$	$+2x$
Equilibrium concentration (mol/L)	$6.00 - x$	$6.00 - x$	$2x$

At equilibrium,

$$K = \frac{[\text{HBr}_{(\text{g})}]^2}{[\text{H}_2(\text{g})][\text{Br}_2(\text{g})]}$$

$$\frac{(2x)^2}{(6.00 - x)^2} = 12.0$$

$$\sqrt{\frac{(2x)^2}{(6.00 - x)^2}} = \sqrt{12.0}$$

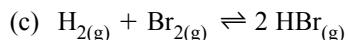
$$\frac{2x}{6.00 - x} = 3.464 \quad (\text{extra digits carried})$$

$$2x = 3.464 (6.00 - x)$$

$$x = 3.804$$

$$\begin{aligned} [\text{HBr}_{(\text{g})}] &= 2x \\ &= 2(3.804) \\ [\text{HBr}_{(\text{g})}] &= 7.61 \text{ mol/L} \\ [\text{H}_{2(\text{g})}] &= [\text{Br}_{2(\text{g})}] \\ &= 6.00 - x \\ [\text{H}_{2(\text{g})}] &= 2.20 \text{ mol/L} \end{aligned}$$

The equilibrium concentrations of hydrogen, bromine, and hydrogen bromide are 2.20 mol/L, 2.20 mol/L, and 7.61 mol/L, respectively.



Initial concentrations are

$$\begin{aligned} [\text{HBr}_{(\text{g})}] &= 0.00 \\ [\text{H}_{2(\text{g})}] &= \frac{12.00 \text{ mol}}{2.00 \text{ L}} \\ [\text{H}_{2(\text{g})}] &= 6.00 \text{ mol/L} \\ [\text{Br}_{2(\text{g})}] &= \frac{8.00 \text{ mol}}{2.00 \text{ L}} \\ [\text{Br}_{2(\text{g})}] &= 4.00 \text{ mol/L} \end{aligned}$$

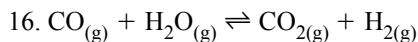
ICE Table for the Formation of $\text{HBr}_{(\text{g})}$			
	$\text{H}_{2(\text{g})} +$	$\text{Br}_{2(\text{g})} \rightleftharpoons$	$2 \text{ HBr}_{(\text{g})}$
Initial concentration (mol/L)	6.00	4.00	0.00
Change in concentration (mol/L)	$-x$	$-x$	$+2x$
Equilibrium concentration (mol/L)	$6.00 - x$	$4.00 - x$	$2x$

At equilibrium,

$$\begin{aligned} K &= \frac{[\text{HBr}_{(\text{g})}]^2}{[\text{H}_{2(\text{g})}][\text{Br}_{2(\text{g})}]} \\ \frac{(2x)^2}{(6.00 - x)(4.00 - x)} &= 12.0 \\ \frac{4x^2}{(6.00 - x)(4.00 - x)} &= 12.0 \\ 12.0(6.00 - x)(4.00 - x) &= 4x^2 \quad (\text{extra digits carried}) \\ 3(6.00 - x)(4.00 - x) &= x^2 \\ 3(24 - 10x + x^2) &= x^2 \\ 2x^2 - 30x + 72 &= 0 \\ x^2 - 15x + 36 &= 0 \\ x &= \frac{15 \pm \sqrt{15^2 - 4(1)(36)}}{2(1)} \\ x &= 12.0 \text{ or } 3.00 \\ x &= 12.0 \text{ gives a negative concentration, which is meaningless.} \\ \therefore x &= 3.00 \\ [\text{HBr}_{(\text{g})}] &= 2x \end{aligned}$$

$$\begin{aligned}
&= 2(3.00) \\
&= 6.00 \text{ mol/L} \\
&[\text{H}_{2(\text{g})}][\text{Br}_{2(\text{g})}] \\
&= 6.00 - x \\
&[\text{HBr}_{(\text{g})}] = 3.00 \text{ mol/L} \\
&[\text{Br}_{2(\text{g})}] = 4.00 - x \\
&[\text{Br}_{2(\text{g})}] = 1.00 \text{ mol/L}
\end{aligned}$$

The equilibrium concentrations of hydrogen, bromine, and hydrogen bromide are 3.00 mol/L, 1.00 mol/L, and 6.00 mol/L, respectively.



$$[\text{CO}_{(\text{g})}] = 4.00 \text{ mol/L}$$

$$[\text{H}_2\text{O}_{(\text{g})}] = 2.00 \text{ mol/L}$$

$$[\text{CO}_{2(\text{g})}] = 4.00 \text{ mol/L}$$

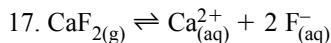
$$[\text{H}_{2(\text{g})}] = 2.00 \text{ mol/L}$$

$$Q = \frac{[\text{CO}_{2(\text{g})}][\text{H}_{2(\text{g})}]}{[\text{CO}_{(\text{g})}][\text{H}_2\text{O}_{(\text{g})}]}$$

$$= \frac{[4.00][2.00]}{[4.00][2.00]}$$

$$Q = 1$$

Since the value of Q is less than the value of K (4.00), the reaction is not at equilibrium. In order to attain equilibrium, the reaction will shift to the right (as written). The concentration of the reactants will decrease and the concentration of the products will increase.



$$n_{\text{CaF}_{2(\text{s})}} = \frac{26.76 \times 10^{-3} \text{ g}}{78.08 \text{ g/mol}}$$

$$n_{\text{CaF}_{2(\text{s})}} = 3.4273 \times 10^{-4} \text{ mol} \quad (\text{extra digits carried})$$

$$[\text{CaF}_{2(\text{aq})}] = [\text{Ca}_{(\text{aq})}^{2+}]$$

$$= \frac{3.4273 \times 10^{-4} \text{ mol}}{1.00 \text{ L}}$$

$$[\text{CaF}_{2(\text{aq})}] = 3.4273 \times 10^{-4} \text{ mol/L}$$

$$[\text{F}_{(\text{aq})}^-] = 2[\text{Ca}_{(\text{aq})}^{2+}]$$

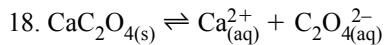
$$[\text{F}_{(\text{aq})}^-] = 6.8546 \times 10^{-4} \text{ mol/L}$$

$$K_{\text{sp}} = [\text{Ca}_{(\text{aq})}^{2+}][\text{F}_{(\text{aq})}^-]^2$$

$$= [3.4273 \times 10^{-4}][6.8546 \times 10^{-4}]^2$$

$$K_{\text{sp}} = 1.61 \times 10^{-10}$$

The K_{sp} for calcium fluoride is 1.61×10^{-10} .



$$K_{\text{sp}} = [\text{Ca}_{(\text{aq})}^{2+}][\text{C}_2\text{O}_{4(\text{aq})}^{2-}]$$

$$K_{\text{sp}} = 2.3 \times 10^{-9}$$

$$[\text{Ca}_{(\text{aq})}^{2+}] = [\text{C}_2\text{O}_{4(\text{aq})}^{2-}]$$

$$2.3 \times 10^{-9} = [\text{Ca}_{(\text{aq})}^{2+}]^2$$

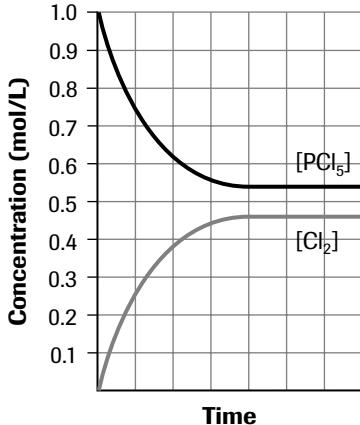
$$[\text{Ca}_{(\text{aq})}^{2+}] = 4.8 \times 10^{-5} \text{ mol/L}$$

$$[\text{CaC}_2\text{O}_{4(\text{aq})}] = [\text{Ca}^{2+}_{(\text{aq})}] \\ = 4.8 \times 10^{-5} \text{ mol/L}$$

The molar solubility of calcium oxalate is 4.8×10^{-5} mol/L.

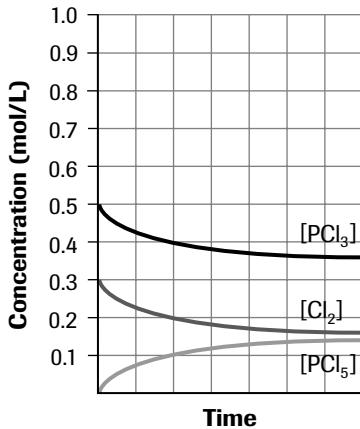
Applying Inquiry Skills

19. (a)



The concentrations of PCl₅ and Cl₂ both begin at zero, increase, and level off at 0.46 mol/L.

(b)

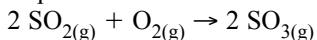


20. (a) The addition of a common ion (chloride) will shift a system in the direction that consumes the common ion.
 (b) Both hydrochloric acid and sodium chloride had a similar effect on the equilibrium. Although the amounts of both chemicals increased in regular increments, the concentration of the chloride ion does not increase regularly. The addition of the solid NaCl increases the chloride solution at a faster rate than adding a solution of hydrochloric acid because the total volume does not change. An improvement to the experiment could be to use two solids, such as NaCl and NaBr, or two solutions, such as HCl_(aq) and HBr_(aq).

Making Connections

21. The tungsten and iodine reaction to produce tungsten(II) iodide is exothermic. A high temperature of the system forces the equilibrium to shift to the left, depositing tungsten on the filament. This deposition reverses the tendency of the tungsten to be lost gradually from the filament. The presence of the halogen (iodine) helps to establish an equilibrium, which at high temperature, restores the filament.
22. The unreacted reagents should be pumped back into the process to make more ammonia.
23. Most of the sulfuric acid manufactured is produced using the Contact Process, a process involving the catalytic oxidation of sulfur dioxide, SO₂, to sulfur trioxide, SO_{3(g)}.
- I. S_(s) + O_{2(g)} → SO_{2(g)}
 - II. 2 SO_{2(g)} + O_{2(g)} → 2 SO_{3(g)}
 - III. SO_{3(g)} + H₂SO_{4(l)} → H₂S₂O_{7(l)}
 - IV. H₂S₂O_{7(l)} + H₂O_(l) → 2 H₂SO_{4(l)}

The oxidation of sulfur dioxide to sulfur trioxide in step III above is an exothermic reaction, and according to Le Châtelier's principle, higher temperatures will force the equilibrium position to shift to the left, favouring the production of sulfur dioxide. Lower temperatures would favour the production of sulfur trioxide and result in a higher yield. However, the rate of reaching equilibrium at the lower temperatures is extremely low. A higher temperature would mean equilibrium is established more rapidly but the yield of sulfur trioxide is lower. A temperature of 450°C is a compromise, whereby a faster reaction rate results in a slightly lower yield. Similarly, at higher pressures, the equilibrium position shifts to the side of the equation in which there are the least numbers of gaseous molecules.



According to Le Châtelier's principle, higher pressure favours the right-hand side. Higher pressure results in a higher yield of sulfur trioxide. A vanadium catalyst is also used in this reaction in order to speed up the rate of the reaction.

24. (a) The increase in pressure as the diver descends, shifts the equilibrium to the right, forcing more gaseous nitrogen into solution.
- (b) The decrease in water pressure on the diver as he/she ascends, shifts the equilibrium to the left, favouring gaseous nitrogen.

Extension

25. An increase in temperature shifts this equilibrium to the left, increasing the concentration of nitrogen dioxide and decreasing the concentration of dinitrogen tetroxide. As a result, high temperatures are associated with lower values of the equilibrium constant. $K = 1250$ corresponds to 0°C and $K = 200$ corresponds to 25°C.

CHAPTER 8 ACID-BASE EQUILIBRIUM

Reflect on Your Learning

(Page 526)

1. The concentration of the hydrogen ion in pure water at SATP is equal to 1.0×10^{-7} mol/L.

$$\text{pH} = -\log [\text{H}_{(\text{aq})}^+]$$

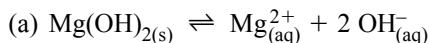
$$= -\log [1.0 \times 10^{-7}]$$

$$\text{pH} = 7$$

2. The pH of hydrochloric acid is lower because $\text{HCl}_{(\text{aq})}$ is a stronger acid than acetic acid.
3. The products for the neutralization of $\text{HCl}_{(\text{aq})}$ and $\text{NaOH}_{(\text{aq})}$ are $\text{NaCl}_{(\text{aq})}$ and water. Neither the sodium ion nor chloride hydrolyze to change the pH of water. However, the neutralization of acetic acid with sodium hydroxide produces water and sodium acetate. The acetate ion is a stronger base than chloride and hydrolyzes to release hydroxide ions in solution. The production of hydroxide accounts for why the resulting solution is basic.
4. The blood contains a variety of buffering agents, which resist changes in pH.

Try This Activity: Antacid Equilibrium

(Page 527)



- (b) The equilibrium shifts to the right when hydrochloric acid is added. The evidence is the observation that the solution becomes clear, indicating that all the magnesium hydroxide had dissolved.

8.1 THE NATURE OF ACID-BASE EQUILIBRIA

PRACTICE

(Page 532)

Understanding Concepts

1. (a) $\text{HCO}_{3(\text{aq})}^- / \text{CO}_{3(\text{aq})}^{2-}$ $\text{HS}_{(\text{aq})}^- / \text{S}_{(\text{aq})}^{2-}$
(b) $\text{H}_2\text{CO}_{3(\text{aq})} / \text{HCO}_{3(\text{aq})}^-$ $\text{H}_2\text{O}_{(\text{l})} / \text{OH}_{(\text{aq})}^-$
(c) $\text{HSO}_{4(\text{aq})}^- / \text{SO}_{4(\text{aq})}^{2-}$ $\text{H}_2\text{PO}_{4(\text{aq})}^- / \text{HPO}_{4(\text{aq})}^{2-}$
(d) $\text{H}_2\text{O}_{(\text{l})} / \text{OH}_{(\text{aq})}^-$ $\text{H}_3\text{O}_{(\text{aq})}^+ / \text{H}_2\text{O}_{(\text{l})}$

2. Amphoteric substances in question 1 are $\text{H}_2\text{O}_{(\text{l})}$, $\text{HCO}_{3(\text{aq})}^-$.

3. $\text{H}_2\text{CO}_{3(\text{aq})} / \text{HCO}_{3(\text{aq})}^-$ $\text{HCO}_{3(\text{aq})}^- / \text{CO}_{3(\text{aq})}^{2-}$

PRACTICE

(Page 537)

Understanding Concepts

4. (a) 0 mol/L
(b) $[\text{OH}^-] = \frac{1.0 \times 10^{-14}}{0.30} = 3.3 \times 10^{-14}$ mol/L
5. $n_{\text{HCl}} = \frac{0.37 \text{ g}}{36.46 \text{ g/mol}}$
 $n_{\text{HCl}} = 0.010 \text{ mol}$
 $[\text{H}^+] = \frac{0.010 \text{ mol}}{250 \times 10^{-3} \text{ L}}$

CHAPTER 8 ACID-BASE EQUILIBRIUM

Reflect on Your Learning

(Page 526)

1. The concentration of the hydrogen ion in pure water at SATP is equal to 1.0×10^{-7} mol/L.

$$\text{pH} = -\log [\text{H}_{(\text{aq})}^+]$$

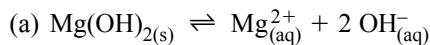
$$= -\log [1.0 \times 10^{-7}]$$

$$\text{pH} = 7$$

2. The pH of hydrochloric acid is lower because $\text{HCl}_{(\text{aq})}$ is a stronger acid than acetic acid.
3. The products for the neutralization of $\text{HCl}_{(\text{aq})}$ and $\text{NaOH}_{(\text{aq})}$ are $\text{NaCl}_{(\text{aq})}$ and water. Neither the sodium ion nor chloride hydrolyze to change the pH of water. However, the neutralization of acetic acid with sodium hydroxide produces water and sodium acetate. The acetate ion is a stronger base than chloride and hydrolyzes to release hydroxide ions in solution. The production of hydroxide accounts for why the resulting solution is basic.
4. The blood contains a variety of buffering agents, which resist changes in pH.

Try This Activity: Antacid Equilibrium

(Page 527)



- (b) The equilibrium shifts to the right when hydrochloric acid is added. The evidence is the observation that the solution becomes clear, indicating that all the magnesium hydroxide had dissolved.

8.1 THE NATURE OF ACID-BASE EQUILIBRIA

PRACTICE

(Page 532)

Understanding Concepts

1. (a) $\text{HCO}_{3(\text{aq})}^- / \text{CO}_{3(\text{aq})}^{2-}$ $\text{HS}_{(\text{aq})}^- / \text{S}_{(\text{aq})}^{2-}$
(b) $\text{H}_2\text{CO}_{3(\text{aq})} / \text{HCO}_{3(\text{aq})}^-$ $\text{H}_2\text{O}_{(\text{l})} / \text{OH}_{(\text{aq})}^-$
(c) $\text{HSO}_{4(\text{aq})}^- / \text{SO}_{4(\text{aq})}^{2-}$ $\text{H}_2\text{PO}_{4(\text{aq})}^- / \text{HPO}_{4(\text{aq})}^{2-}$
(d) $\text{H}_2\text{O}_{(\text{l})} / \text{OH}_{(\text{aq})}^-$ $\text{H}_3\text{O}_{(\text{aq})}^+ / \text{H}_2\text{O}_{(\text{l})}$

2. Amphoteric substances in question 1 are $\text{H}_2\text{O}_{(\text{l})}$, $\text{HCO}_{3(\text{aq})}^-$.

3. $\text{H}_2\text{CO}_{3(\text{aq})} / \text{HCO}_{3(\text{aq})}^-$ $\text{HCO}_{3(\text{aq})}^- / \text{CO}_{3(\text{aq})}^{2-}$

PRACTICE

(Page 537)

Understanding Concepts

4. (a) 0 mol/L
(b) $[\text{OH}^-] = \frac{1.0 \times 10^{-14}}{0.30} = 3.3 \times 10^{-14}$ mol/L
5. $n_{\text{HCl}} = \frac{0.37 \text{ g}}{36.46 \text{ g/mol}}$
 $n_{\text{HCl}} = 0.010 \text{ mol}$
 $[\text{H}^+] = \frac{0.010 \text{ mol}}{250 \times 10^{-3} \text{ L}}$

$$[\text{H}^+] = 0.040 \text{ mol/L}$$

$$\begin{aligned} [\text{OH}^-] &= \frac{K_w}{[\text{H}^+]} \\ &= \frac{1.0 \times 10^{-14}}{0.040} \end{aligned}$$

$$[\text{OH}^-] = 2.5 \times 10^{-13} \text{ mol/L}$$

The hydroxide ion concentration is $2.5 \times 10^{-13} \text{ mol/L}$.

6. $[\text{H}^+] = 4.40 \times 10^{-3} \text{ mol/L}$

$$\begin{aligned} [\text{OH}^-] &= \frac{K_w}{[\text{H}^+]} \\ &= \frac{1.0 \times 10^{-14}}{4.40 \times 10^{-3} \text{ mol/L}} \end{aligned}$$

$$[\text{OH}^-] = 2.3 \times 10^{-12} \text{ mol/L}$$

The hydroxide ion concentration in the effluent is $2.3 \times 10^{-12} \text{ mol/L}$.

Applying Inquiry Skills

7. Prediction

An increase in the hydrogen ion concentration should shift the equilibrium to the right.

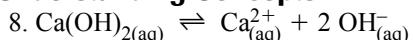
Experimental Design

1. Half-fill one test tube with 0.1 mol/L potassium chromate, K_2CrO_4 .
2. Add 5 drops of 1.0 mol/L hydrochloric acid, HCl, to the test tube. Stopper the test tube and carefully mix its contents.
3. Continue adding acid, if necessary, until a colour change is observed.

PRACTICE

(Page 540)

Understanding Concepts



$$[\text{Ca(OH)}_{2(\text{aq})}] = 6.9 \times 10^{-3} \text{ mol/L}$$

$$[\text{OH}^-] = 2[\text{Ca(OH)}_{2(\text{aq})}]$$

$$[\text{OH}^-] = 1.38 \times 10^{-2} \text{ mol/L}$$

$$\begin{aligned} [\text{H}^+] &= \frac{K_w}{[\text{OH}^-]} \\ &= \frac{1.0 \times 10^{-14}}{1.38 \times 10^{-2} \text{ mol/L}} \end{aligned}$$

$$[\text{H}^+] = 7.2 \times 10^{-13} \text{ mol/L}$$

9. $[\text{OH}^-] = 0.299 \times 10^{-3} \text{ mol/L}$

$$\begin{aligned} [\text{H}^+] &= \frac{K_w}{[\text{OH}^-]} \\ &= \frac{1.00 \times 10^{-14}}{0.299 \times 10^{-3} \text{ mol/L}} \end{aligned}$$

$$[\text{H}^+] = 3.34 \times 10^{-11} \text{ mol/L}$$

The hydrogen ion concentration in the cleaning solution is $3.34 \times 10^{-11} \text{ mol/L}$.

$$10. \quad n_{\text{KOH}} = \frac{20.0 \text{ g}}{56.11 \text{ g/mol}}$$

$$n_{\text{KOH}} = 0.356 \text{ mol}$$

$$[\text{OH}^-] = \frac{0.356 \text{ mol}}{0.500 \text{ L}}$$

$$[\text{OH}^-] = 0.713 \text{ mol/L}$$

$$\begin{aligned} [\text{H}^+] &= \frac{K_w}{[\text{OH}^-]} \\ &= \frac{1.00 \times 10^{-14}}{0.713} \end{aligned}$$

$$[\text{H}^+] = 1.40 \times 10^{-14} \text{ mol/L}$$

The hydrogen ion concentration is $1.40 \times 10^{-14} \text{ mol/L}$.

$$11. \quad n_{\text{H}_2\text{O}} \text{ in } 1.000 \text{ L} = \frac{1000 \text{ g}}{18.02 \text{ g/mol}}$$

$$n_{\text{H}_2\text{O}} = 55.5 \text{ mol}$$

$$[\text{H}_2\text{O}] = \frac{55.5 \text{ mol}}{1.000 \text{ L}}$$

$$[\text{H}_2\text{O}] = 55.5 \text{ mol/L}$$

$$\begin{aligned} \text{percent dissociation} &= \frac{[\text{H}^+]}{[\text{H}_2\text{O}]} \times 100 \\ &= \frac{1.00 \times 10^{-7} \text{ mol/L}}{55.5 \text{ mol/L}} \times 100 \end{aligned}$$

$$\text{percent dissociation} = 1.80 \times 10^{-7}\%$$

The percent dissociation of water is $1.80 \times 10^{-7}\%$.

Try This Activity: Magic Markers

(Page 544)

Source	Colour (as is)	Colour with distilled water (neutral pH)	Colour with dilute baking soda (basic pH)	Colour with vinegar (acidic pH)	Colour with "magic" marker
Marker	Blue	Blue	Cyan	Blue	Cyan
Marker	Yellow	Yellow	Magenta	Yellow	Magenta
Marker	Red	Red	Red	Red	Red
Marker	Green	Green	Purple	Green	Purple
Marker	Black	Black	Orange	Black	Orange
Marker	Purple	Purple	Pink	Purple	Pink
Red cabbage leaf	Purple	Purple	Green	Blue	Green

- (a) The changes in colour that occurred with baking soda correspond to those that occurred with the "magic" marker in the case of blue, yellow, green, black, and purple inks, and red cabbage juice. This indicates that the "magic" marker most likely contains a clear, colourless basic solution.
- (b) The tip of the "magic" marker could be touched to litmus paper to determine whether the solution is acidic or basic, or it can be touched to wide-range pH paper to estimate its pH.
- (c) (See table, above.)

PRACTICE

(Page 546)

Understanding Concepts

$$12. (a) \quad \text{pH} = -\log [\text{H}^+]$$
$$= -\log [0.006]$$

$$\text{pH} = 2.2$$

$$\text{pOH} = 14.0 - \text{pH}$$
$$= 14.0 - 2.2$$

$$\text{pOH} = 11.8$$

$$[\text{OH}^-] = 10^{-\text{pOH}}$$
$$= 10^{-11.8}$$

$$[\text{OH}^-] = 2 \times 10^{-12} \text{ mol/L}$$

$$(b) \quad \text{pH} = -\log [\text{H}^+]$$
$$= -\log [0.025]$$

$$\text{pH} = 1.60$$

$$\text{pOH} = 14.0 - \text{pH}$$
$$= 14.00 - 1.60$$

$$\text{pOH} = 12.40$$

$$[\text{OH}^-] = 10^{-\text{pOH}}$$
$$= 10^{-12.40}$$

$$[\text{OH}^-] = 4.0 \times 10^{-13} \text{ mol/L}$$

$$(c) \quad \text{pH} = -\log [\text{H}^+]$$
$$= -\log [0.010]$$

$$\text{pH} = 2.00$$

$$\text{pOH} = 14.0 - \text{pH}$$
$$= 14.00 - 2.00$$

$$\text{pOH} = 12.00$$

$$[\text{OH}^-] = 10^{-\text{pOH}}$$
$$= 10^{-12.00}$$

$$[\text{OH}^-] = 1.0 \times 10^{-12} \text{ mol/L}$$

$$13. \quad n_{\text{NaOH}} = \frac{26 \text{ g}}{40.00 \text{ g/mol}}$$

$$n_{\text{NaOH}} = 0.65 \text{ mol}$$

$$[\text{NaOH}] = \frac{0.65 \text{ mol}}{0.150 \text{ L}}$$

$$[\text{NaOH}] = 4.33333333 \text{ mol/L}$$

$$\text{pOH} = -\log [\text{OH}^-]$$

$$= -\log [4.333333]$$

$$\text{pOH} = -0.64$$

$$\text{pH} = 14.00 - \text{pOH}$$

$$= 14.00 - (-0.64)$$

$$\text{pH} = 14.64$$

14. $\text{pOH} = 14.0 - 11.5$

$$\text{pOH} = 2.5$$

$$[\text{OH}^-] = 3 \times 10^{-3} \text{ mol/L}$$

$$n_{\text{KOH}} = [3 \times 10^{-3} \text{ mol/L}][0.5 \text{ L}]$$

$$n_{\text{KOH}} = 1.5 \times 10^{-3} \text{ mol}$$

$$m_{\text{KOH}} = [1.5 \times 10^{-3} \text{ mol}][56.11 \text{ g/mol}]$$

$$m_{\text{KOH}} = 0.09 \text{ g}$$

Making Connections

15. (a) (Solution provided for oranges. Calculations for other fruits are similar.)

Oranges:

$$[\text{OH}^-] = \frac{1.0 \times 10^{-14}}{5.5 \times 10^{-3}}$$

$$[\text{OH}^-] = 1.8 \times 10^{-12} \text{ mol/L}$$

$$\text{pOH} = -\log [\text{OH}^-]$$

$$= -\log [1.8 \times 10^{-12}]$$

$$\text{pOH} = 11.74$$

$$\text{pH} = 14.00 - \text{pOH}$$

$$= 14.00 - 11.74$$

$$\text{pH} = 2.26$$

Food	$[\text{H}_{(\text{aq})}^+]$	$[\text{OH}_{(\text{aq})}^-]$	pH	pOH
Oranges	5.5×10^{-3}	1.8×10^{-12}	2.26	11.74
Asparagus	4×10^{-9}	3×10^{-6}	8.4	5.6
Olives	5.0×10^{-4}	2.0×10^{-11}	3.30	10.70
Blackberries	4.0×10^{-4}	2.5×10^{-11}	3.40	10.60

- (b) Oranges and olives would taste the most sour because they have the lowest pH.
(c) Blackberries may relieve heartburn caused by excess stomach acid because they are basic.
(d) Diet suggestions: The speed of movement of sperm decreases with increasing acidity. Vaginal secretions are slightly acidic while uterine secretions are slightly alkaline – a more favourable environment to sperm. Foods that result in an increase in the acidity of vaginal secretions should be avoided.

16. (a) The hydrogen ion concentration increases after the change in pH.
(b) The stomach is made up of layers of tissue, each with a specific function. The outermost layer, called the serosa, is tough and acid resistant. Specialized cells in an inner layer of the stomach called the epithelium secrete mucus, which protects the epithelium and underlying tissues from attack by stomach acid and digestive proteins.

PRACTICE

(Page 549)

Understanding Concepts

17. $[\text{OH}^-_{(\text{aq})}] = 0.15 \text{ mol/L}$

$\text{pOH} = -\log 0.15$

$\text{pOH} = 0.8239 \quad (\text{extra digits carried})$

$\text{pH} = 14 - \text{pOH}$

$= 14 - 0.8239$

$\text{pH} = 13.18$

The pH of the sodium hydroxide solution is 13.18.

18. $[\text{OH}^-_{(\text{aq})}] = 2 \times [\text{Ba}(\text{OH})_2]_{(\text{aq})}$

$= 2 \times 0.032 \text{ mol/L}$

$[\text{OH}^-_{(\text{aq})}] = 0.064 \text{ mol/L}$

$\text{pOH} = -\log 0.064$

$\text{pOH} = 1.194 \quad (\text{extra digits carried})$

$\text{pH} = 14 - \text{pOH}$

$= 14 - 1.194$

$\text{pH} = 12.81$

The pH of the barium hydroxide solution is 12.81.

19. $n_{\text{Ca}(\text{OH})_2} = \frac{0.80 \text{ g}}{74.10 \text{ g/mol}}$

$n_{\text{Ca}(\text{OH})_2} = 0.0108 \text{ mol} \quad (\text{extra digits carried})$

$[\text{Ca}(\text{OH})_2] = \frac{0.0108 \text{ mol}}{0.100 \text{ L}}$

$[\text{Ca}(\text{OH})_2] = 0.108 \text{ mol/L}$

$[\text{OH}^-] = 2 \times [\text{Ca}(\text{OH})_2]$

$= 2 \times 0.108$

$[\text{OH}^-] = 0.216 \text{ mol/L}$

$\text{pOH} = -\log 0.216$

$\text{pOH} = 0.666$

$\text{pH} = 14 - 0.666$

$\text{pH} = 13.33$

The pH of the barium hydroxide solution is 13.33.

SECTION 8.1 QUESTIONS

(Page 549)

Understanding Concepts

1. (a) Hydrogen ion concentration is equal to the hydroxide ion concentration.
(b) Hydrogen ion concentration is greater than the hydroxide ion concentration.
(c) Hydrogen ion concentration is less than the hydroxide ion concentration.
2. Two diagnostic tests to distinguish a weak acid from a strong acid are:
 - (i) Measure the pH with indicators, pH test strips, or a pH meter. Strong acids have a lower pH than weak acids.
 - (ii) Reactivity with active metals. A strip of magnesium bubbles more vigorously in a strong acid than in a weak acid.
3. According to Arrhenius's theory, all bases contain hydroxide.
4. $\text{pOH} = 14.00 - 10.35$

$$\text{pOH} = 3.65$$

$$[\text{OH}^-] = 10^{-\text{pOH}}$$

$$= 10^{-3.65}$$

$$[\text{OH}^-] = 2.24 \times 10^{-4} \text{ mol/L}$$

$$n_{\text{NaOH}} = (2.24 \times 10^{-4} \text{ mol/L})(2.00 \text{ L})$$

$$n_{\text{NaOH}} = 4.48 \times 10^{-4} \text{ mol}$$

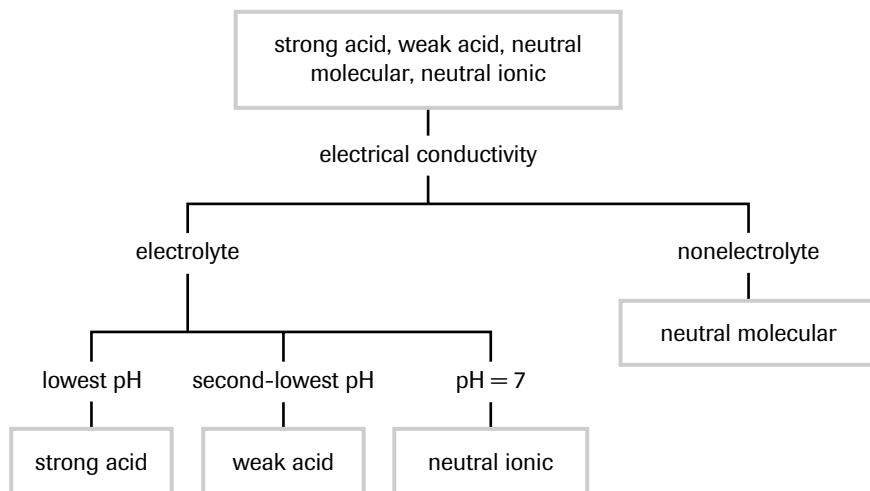
$$m_{\text{NaOH}} = (4.48 \times 10^{-4} \text{ mol})(40.00 \text{ g/mol})$$

$$m_{\text{NaOH}} = 0.018 \text{ g}$$

5. (a) blue
(b) yellow
6. (a) less than 6
(b) greater than 10
(c) greater than 3.8
(d) 7
7. (a) pH 5
(b) $[\text{H}^+] = 1 \times 10^{-5} \text{ mol/L}$

Applying Inquiry Skills

8. Experimental Design



1. Test all solutions with pH test strips. The strong acid has the lowest pH, the weak acid has the next lowest pH, and the remaining solutions have pH 7.
2. Test the pH 7 solutions with a conductivity tester. The neutral ionic solution will test positive while the neutral molecular solution will test negative.

Making Connections

9. (a) Gastroesophageal reflux disease (GERD) is a condition that results in the movement of stomach or duodenal contents into the esophagus.
 (b) GERD can affect all age groups.
 (c) A thin spaghetti-like tube containing a tiny pH probe is passed down the throat to the esophagus where it measures acidity over a 24-h period. Data from the probe is recorded on a recording device. Hospitalization is usually required while the test is being done.
 (d) Treatments currently available include
 Monitoring diet: the following foods can aggravate acid reflux: deep-fried foods, whole milk, chocolate, creamy foods. The following foods can aggravate an already-inflamed lower esophagus: coffee and other caffeinated beverages, carbonated soft drinks, citric juices like orange and grapefruit juice.
 Surgery: the lower portion of the esophagus is surgically tightened, the end result being a one-way valve, which allows food to enter the stomach while preventing stomach contents from flowing upward.
10. (a) Prior to the 19th century, paper was handmade from linen or rags. To meet the skyrocketing demand for paper in the 19th century, chemists found that large quantities of paper could be made economically from wood pulp. During this process, alum (aluminum sulfate) was added to the paper to fill the microscopic holes in the paper. This procedure is known as sizing. Sizing prevents ink from bleeding across the paper. The acidity of the aluminum ion catalyzes the degradation of cellulose strands of the paper. Over a long period of time, acidic paper becomes extremely brittle. Acid-free paper is manufactured often with alkaline sizing agents such as alkyl ketene dimers (AKD).
 (b) Acid-free paper is used for important documents that must last a long time, such as birth certificates, marriage licences, photograph album pages, archival records, etc.
 (c) Acid-free paper lasts considerably longer and is stronger than regular acidic paper. It also requires less energy and fresh water to manufacture. Paper made from this process can be recycled more easily. One disadvantage of acid-free paper is that the sizing agents tend to form sticky deposits on the paper-making equipment, and sometimes on the paper itself.

8.2 WEAK ACIDS AND BASES

PRACTICE

(Page 554)

Understanding Concepts

$$1. \quad [\text{H}_{(\text{aq})}^+] = 10^{-2.54}$$

$$[\text{H}_{(\text{aq})}^+] = 2.88 \times 10^{-3} \text{ mol/L}$$

$$[\text{H}_{(\text{aq})}^+] = \frac{P}{100} \times [\text{HC}_2\text{H}_3\text{O}_2]$$

$$P = \frac{[\text{H}_{(\text{aq})}^+]}{[\text{HC}_2\text{H}_3\text{O}_2]} \times 100\%$$

$$= \frac{2.88 \times 10^{-3} \text{ mol/L}}{[0.46 \text{ mol/L}]} \times 100\%$$

$$P = 0.63\%$$

$$2. \quad [\text{H}_{(\text{aq})}^+] = 10^{-2.00}$$

$$[\text{H}_{(\text{aq})}^+] = 1.0 \times 10^{-2} \text{ mol/L}$$

$$[\text{H}_{(\text{aq})}^+] = \frac{P}{100} \times [\text{HF}_{(\text{aq})}]$$

1. Test all solutions with pH test strips. The strong acid has the lowest pH, the weak acid has the next lowest pH, and the remaining solutions have pH 7.
2. Test the pH 7 solutions with a conductivity tester. The neutral ionic solution will test positive while the neutral molecular solution will test negative.

Making Connections

9. (a) Gastroesophageal reflux disease (GERD) is a condition that results in the movement of stomach or duodenal contents into the esophagus.
 (b) GERD can affect all age groups.
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10. (a) Prior to the 19th century, paper was handmade from linen or rags. To meet the skyrocketing demand for paper in the 19th century, chemists found that large quantities of paper could be made economically from wood pulp. During this process, alum (aluminum sulfate) was added to the paper to fill the microscopic holes in the paper. This procedure is known as sizing. Sizing prevents ink from bleeding across the paper. The acidity of the aluminum ion catalyzes the degradation of cellulose strands of the paper. Over a long period of time, acidic paper becomes extremely brittle. Acid-free paper is manufactured often with alkaline sizing agents such as alkyl ketene dimers (AKD).
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8.2 WEAK ACIDS AND BASES

PRACTICE

(Page 554)

Understanding Concepts

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$$[\text{H}_{(\text{aq})}^+] = 2.88 \times 10^{-3} \text{ mol/L}$$

$$[\text{H}_{(\text{aq})}^+] = \frac{P}{100} \times [\text{HC}_2\text{H}_3\text{O}_2]$$

$$P = \frac{[\text{H}_{(\text{aq})}^+]}{[\text{HC}_2\text{H}_3\text{O}_2]} \times 100\%$$

$$= \frac{2.88 \times 10^{-3} \text{ mol/L}}{[0.46 \text{ mol/L}]} \times 100\%$$

$$P = 0.63\%$$

$$2. \quad [\text{H}_{(\text{aq})}^+] = 10^{-2.00}$$

$$[\text{H}_{(\text{aq})}^+] = 1.0 \times 10^{-2} \text{ mol/L}$$

$$[\text{H}_{(\text{aq})}^+] = \frac{P}{100} \times [\text{HF}_{(\text{aq})}]$$

$$p = \frac{[\text{H}_{(\text{aq})}^+]}{[\text{HF}_{(\text{aq})}]} \times 100\%$$

$$= \frac{1.0 \times 10^{-2} \text{ mol/L}}{[0.15 \text{ mol/L}]} \times 100\%$$

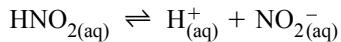
$$p = 6.7\%$$

PRACTICE

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Understanding Concepts

3. 5.8%



$$K_a = \frac{[\text{H}_{(\text{aq})}^+][\text{NO}_{2(\text{aq})}^-]}{[\text{HNO}_{2(\text{aq})}]}$$

$$x = 200 \text{ mol/L} \times 0.058$$

$$x = 0.0116 \text{ mol/L} \quad (\text{extra digits carried})$$

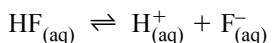
ICE Table for the Ionization of $\text{HNO}_{2(\text{aq})}$			
	$\text{HNO}_{2(\text{aq})} \rightleftharpoons$	$\text{H}_{(\text{aq})}^+ +$	$\text{NO}_{2(\text{aq})}^-$
Initial concentration (mol/L)	0.200		
Change in concentration (mol/L)	- 0.0116	+0.0116	+0.0116
Equilibrium concentration (mol/L)	0.188 mol/L	0.0116	0.0116

$$K_a = \frac{[\text{H}_{(\text{aq})}^+][\text{NO}_{2(\text{aq})}^-]}{[\text{HNO}_{2(\text{aq})}]}$$

$$= \frac{(0.0116)^2}{0.188}$$

$$K_a = 7.1 \times 10^{-4}$$

4. (a) 7.8%



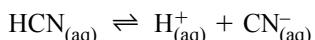
$$K_a = \frac{[\text{H}_{(\text{aq})}^+][\text{F}_{(\text{aq})}^-]}{[\text{HF}_{(\text{aq})}]}$$

$$x = 0.100 \text{ mol/L} \times 0.078$$

$$x = 0.0078 \text{ mol/L}$$

$$[\text{H}_{(\text{aq})}^+] = 7.8 \times 10^{-3} \text{ mol/L}$$

(b) 0.0078%



$$K_a = \frac{[\text{H}_{(\text{aq})}^+][\text{CN}_{(\text{aq})}^-]}{[\text{HCN}_{(\text{aq})}]}$$

$$x = 0.100 \text{ mol/L} \times 7.8 \times 10^{-4}$$

$$x = 7.8 \times 10^{-6} \text{ mol/L}$$

$$[\text{H}_{(\text{aq})}^+] = 7.8 \times 10^{-6} \text{ mol/L}$$

(c) The hydrofluoric solution (a) is more acidic.

$$5. \quad [\text{H}_{(\text{aq})}^+] = \frac{p}{100} \times [\text{HA}_{(\text{aq})}]$$

$$p = \frac{[\text{H}_{(\text{aq})}^+]}{[\text{HA}_{(\text{aq})}]} \times 100\%$$

$$= \frac{1.16 \times 10^{-3} \text{ mol/L}}{[0.100 \text{ mol/L}]} \times 100\%$$

$$p = 1.16\%$$

The percent ionization of propanoic acid is 1.16%.

PRACTICE

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Understanding Concepts

$$6. \text{ (a)} \quad K_w = 1.0 \times 10^{-14}$$

$$K_a = 2.9 \times 10^{-8}$$

$$K_a K_b = K_w$$

$$K_b = \frac{K_w}{K_a}$$

$$= \frac{1.0 \times 10^{-14}}{2.9 \times 10^{-8}}$$

$$K_b = 3.4 \times 10^{-7}$$

The base dissociation constant for the hypochlorite ion is 3.4×10^{-7} .

$$\text{(b)} \quad K_w = 1.0 \times 10^{-14}$$

$$K_a = 7.2 \times 10^{-4}$$

$$K_a K_b = K_w$$

$$K_b = \frac{K_w}{K_a}$$

$$= \frac{1.0 \times 10^{-14}}{7.2 \times 10^{-4}}$$

$$K_b = 1.4 \times 10^{-11}$$

The base dissociation constant for the nitrite ion is 1.4×10^{-11} .

$$\text{(c)} \quad K_w = 1.0 \times 10^{-14}$$

$$K_a = 6.3 \times 10^{-5}$$

$$K_a K_b = K_w$$

$$K_b = \frac{K_w}{K_a}$$

$$= \frac{1.0 \times 10^{-14}}{6.3 \times 10^{-5}}$$

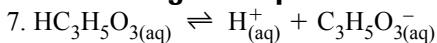
$$K_b = 1.6 \times 10^{-10}$$

The base dissociation constant for the benzoate ion is 1.6×10^{-10} .

PRACTICE

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Understanding Concepts



$$K_a = \frac{[\text{H}_{(\text{aq})}^+][\text{C}_3\text{H}_5\text{O}_{3(\text{aq})}^-]}{[\text{HC}_3\text{H}_5\text{O}_{3(\text{aq})}]}$$

$$K_a = 1.4 \times 10^{-4}$$

Predict whether a simplifying assumption is justified:

$$\frac{[\text{HA}]_{\text{initial}}}{K_a} = \frac{0.0010 \text{ mol/L}}{1.4 \times 10^{-4}}$$

$$\frac{[\text{HA}]_{\text{initial}}}{K_a} = 7.14$$

Since $7.14 < 100$, we may not assume that $0.0010 - x \doteq 0.0010$.

ICE Table for the Ionization of $\text{HC}_3\text{H}_5\text{O}_{3(\text{aq})}$			
	$\text{HC}_3\text{H}_5\text{O}_{3(\text{aq})} \rightleftharpoons$	$\text{H}_{(\text{aq})}^+ +$	$\text{C}_3\text{H}_5\text{O}_{3(\text{aq})}^-$
Initial concentration (mol/L)	0.0010	0.0000	0.0000
Change in concentration (mol/L)	$-x$	$+x$	$+x$
Equilibrium concentration (mol/L)	$0.0010 - x$	x	x

$$\frac{x^2}{(0.0010 - x)} = 1.4 \times 10^{-4}$$

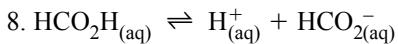
$$x^2 = 1.4 \times 10^{-4}(0.0010 - x)$$

$$x = \frac{-1.4x \times 10^{-4} \pm \sqrt{(1.4x \times 10^{-4})^2 - 4(-1.4 \times 10^{-7})}}{2}$$

$$x = 3.1 \times 10^{-4}$$

$$\begin{aligned}\text{pH} &= -\log [\text{H}_{(\text{aq})}^+] \\ &= -\log [3.1 \times 10^{-4}]\end{aligned}$$

$$\text{pH} = 3.51$$



$$K_a = \frac{[\text{H}_{(\text{aq})}^+][\text{HCO}_2\text{H}_{(\text{aq})}^-]}{[\text{HCO}_2\text{H}_{(\text{aq})}]}$$

$$K_a = 1.8 \times 10^{-4}$$

Predict whether a simplifying assumption is justified:

$$\frac{[\text{HA}]_{\text{initial}}}{K_a} = \frac{0.150 \text{ mol/L}}{1.8 \times 10^{-4}}$$

$$\frac{[\text{HA}]_{\text{initial}}}{K_a} = 830$$

Since $830 > 100$, we may assume that $0.150 - x = 0.150$.

The equilibrium expression becomes

$$\frac{x^2}{0.150} \doteq 1.8 \times 10^{-4}$$

which yields

$$x^2 \doteq 2.7 \times 10^{-5}$$

$$x \doteq 5.2 \times 10^{-3}$$

Validation of the approximation:

In general, the approximation is valid if

$$\frac{x}{[\text{HA}]_{\text{initial}}} \times 100\% \leq 5\%$$

$$[\text{HA}]_{\text{initial}} = 0.15 \text{ mol/L}$$

$$\frac{x}{[\text{HA}]_{\text{initial}}} \times 100\% = \frac{5.2 \times 10^{-3}}{0.15} \times 100\%$$

$$\frac{x}{[\text{HA}]_{\text{initial}}} = 3.5\%$$

Since $3.5\% < 5\%$, the assumption is valid.

Therefore,

$$[\text{H}_{(\text{aq})}^+] = 5.2 \times 10^{-3} \text{ mol/L}$$

$$\text{pH} = -\log 5.2 \times 10^{-3}$$

$$\text{pH} = 2.28$$

PRACTICE

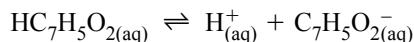
(Page 570)

Understanding Concepts

9. pH = 2.40

$$\begin{aligned} [\text{H}_{(\text{aq})}^+] &= 10^{-\text{pH}} \\ &= 10^{-2.40} \end{aligned}$$

$$[\text{H}_{(\text{aq})}^+] = 3.98 \times 10^{-3} \text{ mol/L}$$



$$K_a = \frac{[\text{H}_{(\text{aq})}^+][\text{C}_7\text{H}_5\text{O}_{2(\text{aq})}^-]}{[\text{HC}_7\text{H}_5\text{O}_{2(\text{aq})}]}$$

$$[\text{H}_{(\text{aq})}^+] = [\text{C}_7\text{H}_5\text{O}_{2(\text{aq})}^-]$$

$$[\text{H}_{(\text{aq})}^+] = 3.98 \times 10^{-3} \text{ mol/L}$$

$$K_a = \frac{(3.98 \times 10^{-3})^2}{0.25}$$

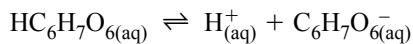
$$K_a = 6.3 \times 10^{-5}$$

The K_a for benzoic acid is 6.3×10^{-5} .

10. pH = 2.40

$$\begin{aligned} [\text{H}_{(\text{aq})}^+] &= 10^{-\text{pH}} \\ &= 10^{-2.40} \end{aligned}$$

$$[\text{H}_{(\text{aq})}^+] = 3.98 \times 10^{-3} \text{ mol/L}$$



$$K_a = \frac{[\text{H}_{(\text{aq})}^+][\text{C}_6\text{H}_7\text{O}_{6(\text{aq})}^-]}{[\text{HC}_6\text{H}_7\text{O}_{6(\text{aq})}]}$$

$$[\text{H}_{(\text{aq})}^+] = [\text{C}_6\text{H}_7\text{O}_{6(\text{aq})}^-]$$

$$[\text{H}_{(\text{aq})}^+] = 3.98 \times 10^{-3} \text{ mol/L}$$

$$K_a = \frac{(3.98 \times 10^{-3})^2}{0.20}$$

$$K_a = 7.9 \times 10^{-5}$$

The K_a for ascorbic acid is 7.9×10^{-5} .

Applying Inquiry Skills

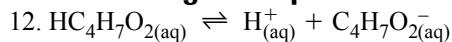
11. Experimental Design

1. Calibrate the pH following the manufacturer's instructions.
2. Add 25 mL of acetic acid to a 100-mL beaker.
3. Measure the pH of the solution using the pH meter.
4. Rinse the pH meter as directed by your teacher.
5. Discard the acetic acid solution as directed by your teacher.

PRACTICE

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Understanding Concepts



$$K_a = \frac{[\text{H}_{(\text{aq})}^+][\text{C}_4\text{H}_7\text{O}_{2(\text{aq})}^-]}{[\text{HC}_4\text{H}_7\text{O}_{2(\text{aq})}]}$$

$$K_a = 1.8 \times 10^{-4}$$

Predict whether a simplifying assumption is justified:

$$\frac{[\text{HA}]_{\text{initial}}}{K_a} = \frac{0.150 \text{ mol/L}}{1.8 \times 10^{-4}}$$

$$\frac{[\text{HA}]_{\text{initial}}}{K_a} = 830$$

Since $830 > 100$, we may assume that $0.150 - x \doteq 0.150$.

The equilibrium expression becomes

$$\frac{x^2}{0.150} \doteq 1.8 \times 10^{-4}$$

which yields

$$x^2 \doteq 2.7 \times 10^{-5}$$

$$x \doteq 5.2 \times 10^{-3}$$

Validation of the approximation:

In general, the approximation is valid if

$$\frac{x}{[\text{HA}]_{\text{initial}}} \times 100\% \leq 5\%$$

$$[\text{HA}]_{\text{initial}} = 0.15 \text{ mol/L}$$

$$\frac{x}{[\text{HA}]_{\text{initial}}} \times 100\% = \frac{5.2 \times 10^{-3}}{0.15} \times 100\%$$

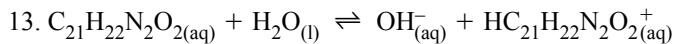
$$\frac{x}{[\text{HA}]_{\text{initial}}} = 3.5\%$$

Since $3.5\% < 5\%$, the assumption is valid.
Therefore,

$$[\text{H}_{(\text{aq})}^+] = 5.2 \times 10^{-3} \text{ mol/L}$$

$$\text{pH} = -\log 5.2 \times 10^{-3}$$

$$\text{pH} = 2.28$$



$$K_b = \frac{[\text{HC}_{21}\text{H}_{22}\text{N}_2\text{O}_{2(\text{aq})}^+][\text{OH}_{(\text{aq})}^-]}{[\text{C}_{21}\text{H}_{22}\text{N}_2\text{O}_{2(\text{aq})}]}$$

$$K_b = 1.0 \times 10^{-6}$$

ICE Table for the Ionization of $\text{C}_{21}\text{H}_{22}\text{N}_2\text{O}_{2(\text{aq})}$			
	$\text{C}_{21}\text{H}_{22}\text{N}_2\text{O}_{2(\text{aq})} +$	$\text{H}_2\text{O}_{(\text{l})} \rightleftharpoons \text{OH}_{(\text{aq})}^- +$	$\text{HC}_{21}\text{H}_{22}\text{N}_2\text{O}_{2(\text{aq})}^+$
Initial concentration (mol/L)	0.001	0.000	0.000
Change in concentration (mol/L)	x	$+x$	$+x$
Equilibrium concentration (mol/L)	$0.001 - x$	x	x

$$K_b = \frac{[\text{HC}_{21}\text{H}_{22}\text{N}_2\text{O}_{2(\text{aq})}^+][\text{OH}_{(\text{aq})}^-]}{[\text{C}_{21}\text{H}_{22}\text{N}_2\text{O}_{2(\text{aq})}]}$$

$$K_b = 1.0 \times 10^{-6}$$

$$\frac{x^2}{(0.001 - x)} = 1.0 \times 10^{-6}$$

Predicting the validity of the assumption ...

$$\frac{0.001}{1.0 \times 10^{-6}} = 1000$$

Since $1000 > 100$, we may assume that $0.001 - x \doteq 0.001$.

The equilibrium expression becomes

$$\frac{x^2}{0.001} \doteq 1.0 \times 10^{-6}$$

which yields

$$x^2 \doteq 1.0 \times 10^{-9}$$

$$x \doteq 3.2 \times 10^{-5}$$

Justifying the simplification assumption ...

$$\frac{3.2 \times 10^{-5}}{0.001} \times 100\% = 3.2\%$$

Since $3.2\% < 5\%$, the assumption is valid.

Therefore,

$$[\text{OH}_{(\text{aq})}^-] = 3.2 \times 10^{-5} \text{ mol/L}$$

$$\text{pOH} = \log 3.2 \times 10^{-5}$$

$$\text{pOH} = 4.5$$

$$\text{pH} = 14 - \text{pOH}$$

$$= 14.0 - 4.5$$

$$\text{pH} = 9.5$$

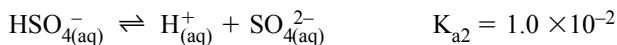
The pH of a 0.001 mol/L solution of strychnine is 9.5.

PRACTICE

(Page 578)

Understanding Concepts

14. (a) Since $\text{H}_2\text{SO}_{4(\text{aq})}$ is a strong acid, the hydrogen ion concentration from $K_{\text{a}1}$ is 1.00 mol/L.



ICE Table for the Ionization of $\text{HSO}_{4(\text{aq})}^-$			
	$\text{HSO}_{4(\text{aq})}^- \rightleftharpoons$	$\text{H}_{(\text{aq})}^+ +$	$\text{SO}_{4(\text{aq})}^{2-}$
Initial concentration (mol/L)	1.00	0.00	0.00
Change in concentration (mol/L)	$-x$	$+x$	$+x$
Equilibrium concentration (mol/L)	$1.00 - x$	x	x

$$K_a = \frac{[\text{H}_{(\text{aq})}^+][\text{HSO}_{4(\text{aq})}^-]}{[\text{SO}_{4(\text{aq})}^{2-}]}$$

$$\frac{x^2}{1.00 - x} = 1.0 \times 10^{-2}$$

Predicting whether $1.00 - x \doteq 1.00 \dots$

$$\frac{[\text{HA}]_{\text{initial}}}{K_a} = \frac{1.00 \text{ mol/L}}{1.0 \times 10^{-2}}$$

$$\frac{[\text{HA}]_{\text{initial}}}{K_a} = 100$$

Since $100 = 100$, we can assume that $1.00 - x \doteq 1.00$.

$$\frac{x^2}{(1.00 - x)} = 1.0 \times 10^{-2}$$

$$x^2 \doteq 1.0 \times 10^{-2}$$

$$x = 1.0 \times 10^{-1}$$

$$x = 0.10$$

Validating the assumption ...

$$\frac{1.0 \times 10^{-2}}{1.00} \times 100\% = 1.0\%$$

Since $1.0\% < 5.0\%$, the assumption is valid.

$$[\text{H}_{(\text{aq})}^+] = 0.10 + 1.00$$

$$[\text{H}_{(\text{aq})}^+] = 1.1 \text{ mol/L}$$

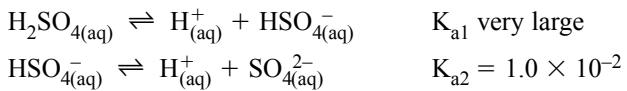
$$\text{pH} = -\log[\text{H}_{(\text{aq})}^+]$$

$$= -\log[1.10]$$

$$\text{pH} = -0.0414$$

The pH of a 0.001 mol/L solution of sulfuric acid is -0.0414.

(b) Since $\text{H}_2\text{SO}_{4(\text{aq})}$ is a strong acid, the hydrogen ion concentration from $K_{\text{a}1}$ is 0.001 mol/L.



ICE Table for the Ionization of $\text{HSO}_{4(\text{aq})}^-$			
	$\text{HSO}_{4(\text{aq})}^- \rightleftharpoons$	$\text{H}_{(\text{aq})}^+ +$	$\text{SO}_{4(\text{aq})}^{2-}$
Initial concentration (mol/L)	0.001	0.000	0.000
Change in concentration (mol/L)	$-x$	$+x$	$+x$
Equilibrium concentration (mol/L)	$0.001 - x$	x	x

$$K_a = \frac{[\text{H}_{(\text{aq})}^+][\text{HSO}_{4(\text{aq})}^-]}{[\text{SO}_{4(\text{aq})}^{2-}]}$$

$$\frac{x^2}{0.001 - x} = 1.0 \times 10^{-2}$$

Predicting whether $0.001 - x \doteq 0.001 \dots$

$$\frac{[\text{HA}]_{\text{initial}}}{K_a} = \frac{0.001 \text{ mol/L}}{1.0 \times 10^{-2}}$$

$$\frac{[\text{HA}]_{\text{initial}}}{K_a} = 0.1$$

Since $0.1 < 100$, we cannot assume that $0.001 - x \doteq 0.001$.

$$\frac{x^2}{(0.001 - x)} = 1.0 \times 10^{-2}$$

$$x^2 = 1.0 \times 10^{-2}(0.001 - x)$$

$$x^2 = 1(1.0 \times 10^{-2}x) - (1.0 \times 10^{-5}x)$$

$$x^2 + (1.0 \times 10^{-2}x) - (1.0 \times 10^{-5}x) = 0$$

$$x = \frac{-1.0 \times 10^{-2} \pm \sqrt{(1.0 \times 10^{-2})^2 - 4(-1.0 \times 10^{-5})}}{2}$$

$$x = 9 \times 10^{-4}$$

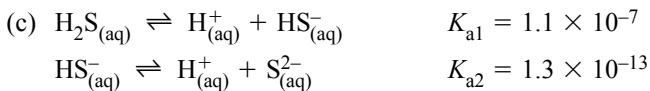
$$[\text{H}_{(\text{aq})}^+] = 0.001 + (9 \times 10^{-4})$$

$$[\text{H}_{(\text{aq})}^+] = 0.0019$$

$$\begin{aligned} \text{pH} &= -\log[\text{H}_{(\text{aq})}^+] \\ &= -\log[0.0019] \end{aligned}$$

$$\text{pH} = 2.7$$

The pH of a 0.001 mol/L solution of sulfuric acid is 2.7.



Since $\text{H}_2\text{S}_{(\text{aq})}$ is a much stronger acid than $\text{HS}_{(\text{aq})}^-$, it will dominate the production of $\text{H}_{(\text{aq})}^+$.

$$K_{\text{a}1} = \frac{[\text{H}_{(\text{aq})}^+][\text{HS}_{(\text{aq})}^-]}{[\text{H}_2\text{S}_{(\text{aq})}]}$$

ICE Table for the Ionization of $\text{H}_2\text{S}_{(\text{aq})}$			
	$\text{H}_2\text{S}_{(\text{aq})} \rightleftharpoons$	$\text{H}_{(\text{aq})}^+ +$	$\text{HS}_{(\text{aq})}^-$
Initial concentration (mol/L)	0.010	0.00	0.00
Change in concentration (mol/L)	$-x$	$+x$	$+x$
Equilibrium concentration (mol/L)	$0.010 - x$	x	x

$$K_a = \frac{[\text{H}_{(\text{aq})}^+][\text{HS}_{(\text{aq})}^-]}{[\text{H}_2\text{S}_{(\text{aq})}]}$$

$$\frac{x^2}{0.010 - x} = 1.1 \times 10^{-7}$$

Predicting whether $0.010 - x \doteq 0.010 \dots$

$$\frac{[\text{HA}]_{\text{initial}}}{K_a} = \frac{0.010 \text{ mol/L}}{1.1 \times 10^{-7}}$$

$$\frac{[\text{HA}]_{\text{initial}}}{K_a} = 9.0 \times 10^5$$

Since $9.0 \times 10^5 > 100$, we can assume that $0.010 - x \doteq 0.010$.

$$\frac{x^2}{(0.010)} \doteq 1.0 \times 10^{-2}$$

$$x^2 \doteq 1.0 \times 10^{-9}$$

$$x = 3.3 \times 10^{-5}$$

Validating the assumption ...

$$\frac{3.3 \times 10^{-5}}{0.010} \times 100\% = 0.33\%$$

Since $0.33\% < 5.0\%$, the assumption is valid.

$$[\text{H}_{(\text{aq})}^+] = 3.3 \times 10^{-5} \text{ mol/L}$$

$$\text{pH} = -\log[\text{H}_{(\text{aq})}^+]$$

$$= -\log[3.3 \times 10^{-5}]$$

$$\text{pH} = 4.48$$

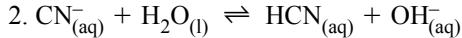
The pH of a 0.010 mol/L solution of hydrosulfuric acid is 4.48.

SECTION 8.2 QUESTIONS

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Understanding Concepts

1. A dilute solution of a strong acid and a solution of a weak acid may have similar pH values but differ in the degree of ionization that occurs. Strong acids are fully ionized while weak acids are only partially ionized.



$$K_b = \frac{[\text{CN}_{(\text{aq})}^-][\text{OH}_{(\text{aq})}^-]}{[\text{HCN}_{(\text{aq})}]}$$

ICE Table for the Ionization of $\text{CN}^-_{(\text{aq})}$				
	$\text{CN}^-_{(\text{aq})} +$	$\text{H}_2\text{O}_{(\text{l})} \rightleftharpoons$	$\text{HCN}_{(\text{aq})} +$	$\text{OH}^-_{(\text{aq})}$
Initial concentration (mol/L)	0.18	—	0	0
Change in concentration (mol/L)	$-x$	—	$+x$	$+x$
Equilibrium concentration (mol/L)	$0.18 - x$	—	x	x

$$K_b = \frac{1.0 \times 10^{-14}}{K_a}$$

$$= \frac{1.0 \times 10^{-14}}{6.2 \times 10^{-10}}$$

$$K_b = 1.6 \times 10^{-5}$$

$$\frac{x^2}{0.18 - x} = 1.6 \times 10^{-5}$$

Predicting whether $0.18 - x \doteq 0.18 \dots$

$$\frac{0.18}{1.6 \times 10^{-5}} = 1.1 \times 10^4$$

Since $1.1 \times 10^4 > 100$, we assume that $0.18 - x \doteq 0.18$.

$$\frac{x^2}{(0.18)} \doteq 1.6 \times 10^{-5}$$

$$x^2 \doteq 2.9 \times 10^{-6}$$

$$x = 1.7 \times 10^{-3}$$

Validating the assumption ...

$$\frac{1.7 \times 10^{-3}}{0.18} \times 100\% = 0.94\%$$

Since $0.94\% < 5.0\%$, the assumption is valid.

$$[\text{OH}^-_{(\text{aq})}] = 1.7 \times 10^{-3} \text{ mol/L}$$

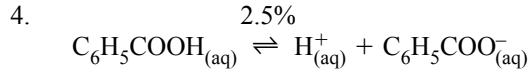
$$\begin{aligned} \text{pOH} &= -\log[\text{OH}^-_{(\text{aq})}] \\ &= -\log[1.7 \times 10^{-3}] \end{aligned}$$

$$\text{pOH} = 2.77$$

$$\begin{aligned} \text{pH} &= 14 - \text{pOH} \\ &= 14 - 2.77 \end{aligned}$$

$$\text{pH} = 11.23$$

The pH of a 0.18 mol/L cyanide solution is 11.23.



$$K_a = \frac{[\text{H}^+_{(\text{aq})}][\text{C}_6\text{H}_5\text{COO}^-_{(\text{aq})}]}{[\text{C}_6\text{H}_5\text{COOH}_{(\text{aq})}]}$$

$$x = 0.100 \text{ mol/L} \times 0.0025$$

$$x = 2.5 \times 10^{-3}$$

ICE Table for the Ionization of $C_6H_5COOH_{(aq)}$			
	$C_6H_5COOH_{(aq)} \rightleftharpoons$	$H^+_{(aq)} +$	$C_6H_5COO^-_{(aq)}$
Initial concentration (mol/L)	0.100	0.00	0.00
Change in concentration (mol/L)	-2.5×10^{-3}	$+2.5 \times 10^{-3}$	$+2.5 \times 10^{-3}$
Equilibrium concentration (mol/L)	0.098	2.5×10^{-3}	2.5×10^{-3}

$$K_a = \frac{[H^+]_{(aq)}[C_6H_5COO^-_{(aq)}]}{[C_6H_5COOH_{(aq)}]}$$

$$= \frac{(2.5 \times 10^{-3})^2}{0.098}$$

$$K_a = 6.4 \times 10^{-5}$$

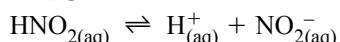
The K_a of benzoic acid is 6.4×10^{-5} .

5. $pH = 2.1$

$$[H^+]_{(aq)} = 10^{-pH}$$

$$= 10^{-2.1}$$

$$[H^+]_{(aq)} = 8 \times 10^{-3} \text{ mol/L}$$



$$K_a = \frac{[H^+]_{(aq)}[NO_2^-_{(aq)}]}{[HNO_2_{(aq)}]}$$

ICE Table for the Ionization of $HNO_2_{(aq)}$			
	$HNO_2_{(aq)} \rightleftharpoons$	$H^+_{(aq)} +$	$NO_2^-_{(aq)}$
Initial concentration (mol/L)	0.100	0	0
Change in concentration (mol/L)	-8×10^{-3}	$+8 \times 10^{-3}$	$+8 \times 10^{-3}$
Equilibrium concentration (mol/L)	0.09	8×10^{-3}	8×10^{-3}

$$K_a = \frac{[H^+]_{(aq)}[NO_2^-_{(aq)}]}{[HNO_2_{(aq)}]}$$

$$= \frac{(8 \times 10^{-3})^2}{0.09}$$

$$K_a = 7 \times 10^{-4}$$

The K_a for nitrous acid is 7×10^{-4} .

6. $HBrO_{(aq)} \rightleftharpoons H^+_{(aq)} + BrO^-_{(aq)}$

$$K_a = \frac{[H^+]_{(aq)}[BrO^-_{(aq)}]}{[HBrO_{(aq)}]}$$

$$K_a = 2.5 \times 10^{-9}$$

Since $2.5 \times 10^{-9} > 100$, we can assume that $0.200 - x \doteq 0.200$.

Predict whether a simplifying assumption is justified:

$$\frac{[\text{HA}]_{\text{initial}}}{K_a} = \frac{0.200}{2.5 \times 10^{-9}}$$

$$\frac{[\text{HA}]_{\text{initial}}}{K_a} = 1.3 \times 10^9$$

The equilibrium expression becomes

$$\frac{x^2}{0.200} \doteq 2.5 \times 10^{-9}$$

which yields

$$x^2 \doteq 5.0 \times 10^{-10}$$

$$x \doteq 2.2 \times 10^{-5}$$

Validation of the approximation:

In general, the approximation is valid if

$$\frac{x}{[\text{HA}]_{\text{initial}}} \times 100\% \leq 5\%$$

$$[\text{HA}]_{\text{initial}} = 0.200 \text{ mol/L}$$

$$\frac{x}{[\text{HA}]_{\text{initial}}} \times 100\% = \frac{2.2 \times 10^{-5}}{0.200} \times 100\%$$

$$\frac{x}{[\text{HA}]_{\text{initial}}} \times 100\% = 0.011\%$$

Since $0.011\% < 5\%$, the assumption is valid.

Therefore,

$$[\text{H}_{(\text{aq})}^+] = 2.2 \times 10^{-5} \text{ mol/L}$$

$$\text{pH} = -\log 2.2 \times 10^{-5}$$

$$= 2.28$$

$$\text{pH} = 4.65$$

The pH of the hypobromous acid solution is 4.65.

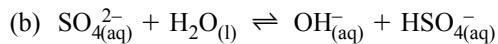
7. (a) $\text{HCN}_{(\text{aq})}$, $\text{HCO}_2\text{H}_{(\text{aq})}$, $\text{HF}_{(\text{aq})}$, $\text{HNO}_3_{(\text{aq})}$
 (b) Approximate pH of 1.0 mol/L solutions:

Acid	Approximate pH
$\text{HCN}_{(\text{aq})}$	5
$\text{HCO}_2\text{H}_{(\text{aq})}$	4
$\text{HF}_{(\text{aq})}$	2
$\text{HNO}_3_{(\text{aq})}$	0

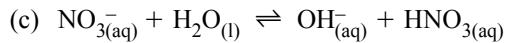
8. (a) (strongest acid) $\text{H}_3\text{PO}_4_{(\text{aq})}$, $\text{HNO}_2_{(\text{aq})}$, $\text{HC}_2\text{H}_3\text{O}_2_{(\text{aq})}$, $\text{H}_2\text{S}_{(\text{aq})}$, $\text{NH}_4^+_{(\text{aq})}$ (weakest acid)
 (b) (highest pH) $\text{NH}_4^+_{(\text{aq})}$, $\text{H}_2\text{S}_{(\text{aq})}$, $\text{HC}_2\text{H}_3\text{O}_2_{(\text{aq})}$, $\text{HNO}_2_{(\text{aq})}$, $\text{H}_3\text{PO}_4_{(\text{aq})}$ (lowest pH)
 (c) (strongest base) $\text{NH}_3_{(\text{aq})}$, $\text{HS}^-_{(\text{aq})}$, $\text{C}_2\text{H}_3\text{O}_2^-_{(\text{aq})}$, $\text{NO}_2^-_{(\text{aq})}$, $\text{H}_2\text{PO}_4^-_{(\text{aq})}$ (weakest base)

9. (a) $\text{CN}^-_{(\text{aq})} + \text{H}_2\text{O}_{(\text{l})} \rightleftharpoons \text{OH}^-_{(\text{aq})} + \text{HCN}_{(\text{aq})}$

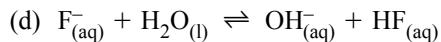
$$K_b = \frac{[\text{HCN}_{(\text{aq})}][\text{OH}^-_{(\text{aq})}]}{[\text{CN}^-_{(\text{aq})}]}$$



$$K_b = \frac{[\text{HSO}_{4(\text{aq})}^-][\text{OH}_{(\text{aq})}^-]}{[\text{SO}_{4(\text{aq})}^{2-}]}$$



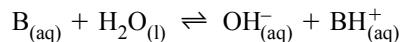
$$K_b = \frac{[\text{HNO}_{3(\text{aq})}][\text{OH}_{(\text{aq})}^-]}{[\text{NO}_{3(\text{aq})}^-]}$$



$$K_b = \frac{[\text{HF}_{(\text{aq})}][\text{OH}_{(\text{aq})}^-]}{[\text{F}_{(\text{aq})}^-]}$$

10. (a) (weakest base) morphine, erythromycin, atropine (strongest base)

(b) **pH of morphine ...**



$$K_b = \frac{[\text{BH}_{(\text{aq})}^+][\text{OH}_{(\text{aq})}^-]}{[\text{B}_{(\text{aq})}]}$$

$$K_b = 7.9 \times 10^{-7}$$

ICE Table for the Ionization of the Base Atropine $\text{B}_{(\text{aq})}$				
	$\text{B}_{(\text{aq})}^+$	$\text{H}_2\text{O}_{(\text{l})} \rightleftharpoons$	$\text{OH}_{(\text{aq})}^- +$	$\text{BH}_{(\text{aq})}^+$
Initial concentration (mol/L)	0.1	—	0	0
Change in concentration (mol/L)	$-x$	—	$+x$	$+x$
Equilibrium concentration (mol/L)	$0.1 - x$	—	x	x

Since $0.3\% < 5\%$, the assumption is valid.

Therefore,

$$[\text{OH}_{(\text{aq})}^-] = 2.8 \times 10^{-4} \text{ mol/L}$$

$$\text{pOH} = -\log 2.8 \times 10^{-4}$$

$$\text{pOH} = 3.6$$

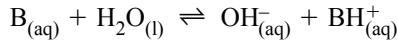
$$\text{pH} = 14 - \text{pOH}$$

$$= 14.0 - 3.6$$

$$\text{pH} = 10.4$$

The pH of a 0.1 mol/L solution of morphine is 10.4.

pH of erythromycin ...



$$K_b = \frac{[\text{BH}_{(\text{aq})}^+][\text{OH}_{(\text{aq})}^-]}{[\text{B}_{(\text{aq})}]}$$

$$K_b = 6.3 \times 10^{-6}$$

ICE Table for the Ionization of the Base Erythromycin $\text{B}_{(\text{aq})}$				
	$\text{B}_{(\text{aq})}^+$	$\text{H}_2\text{O}_{(\text{l})} \rightleftharpoons$	$\text{OH}_{(\text{aq})}^- +$	$\text{BH}_{(\text{aq})}^+$
Initial concentration (mol/L)	0.1	—	0.0	0.0
Change in concentration (mol/L)	$-x$	—	$+x$	$+x$
Equilibrium concentration (mol/L)	$0.1 - x$	—	x	x

Since $0.8\% < 5\%$, the assumption is valid.

Therefore,

$$[\text{OH}_{(\text{aq})}^-] = 8.0 \times 10^{-4} \text{ mol/L}$$

$$\text{pOH} = -\log 8.0 \times 10^{-4}$$

$$\text{pOH} = 3.1$$

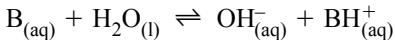
$$\text{pH} = 14 - \text{pOH}$$

$$= 14.0 - 3.1$$

$$\text{pH} = 10.9$$

The pH of a 0.1 mol/L solution of erythromycin is 10.9.

pH of atropine ...



$$K_b = \frac{[\text{BH}_{(\text{aq})}^+][\text{OH}_{(\text{aq})}^-]}{[\text{B}_{(\text{aq})}]}$$

$$K_b = 3.2 \times 10^{-5}$$

ICE Table for the Ionization of the Base Atropine $\text{B}_{(\text{aq})}$

	$\text{B}_{(\text{aq})}^+$	$\text{H}_2\text{O}_{(\text{l})} \rightleftharpoons$	$\text{OH}_{(\text{aq})}^- +$	$\text{BH}_{(\text{aq})}^+$
Initial concentration (mol/L)	0.1	—	0.0	0.0
Change in concentration (mol/L)	$-x$	—	$+x$	$+x$
Equilibrium concentration (mol/L)	$0.1 - x$	—	x	x

Since $2\% < 5\%$, the assumption is valid.

Therefore,

$$[\text{OH}_{(\text{aq})}^-] = 2 \times 10^{-3} \text{ mol/L}$$

$$\text{pOH} = -\log 2 \times 10^{-3}$$

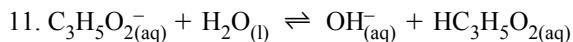
$$\text{pOH} = 2.7$$

$$\text{pH} = 14 - \text{pOH}$$

$$= 14.0 - 2.7$$

$$\text{pH} = 11.3$$

The pH of a 0.1 mol/L solution of atropine is 11.3.



$$K_b = \frac{[\text{HC}_3\text{H}_5\text{O}_{2(\text{aq})}][\text{OH}_{(\text{aq})}^-]}{[\text{C}_3\text{H}_5\text{O}_{2(\text{aq})}^-]}$$

ICE Table for the Ionization of $\text{C}_3\text{H}_5\text{O}_{2(\text{aq})}^-$

	$\text{C}_3\text{H}_5\text{O}_{2(\text{aq})}^- +$	$\text{H}_2\text{O}_{(\text{l})} \rightleftharpoons$	$\text{OH}_{(\text{aq})}^- +$	$\text{HC}_3\text{H}_5\text{O}_{2(\text{aq})}$
Initial concentration (mol/L)	0.157	—	0.000	0.000
Change in concentration (mol/L)	-1.1×10^{-5}	—	$+1.1 \times 10^{-5}$	$+1.1 \times 10^{-5}$
Equilibrium concentration (mol/L)	0.157	—	1.1×10^{-5}	1.1×10^{-5}

$$K_b = \frac{[\text{HC}_3\text{H}_5\text{O}_{2(\text{aq})}][\text{OH}_{(\text{aq})}^-]}{[\text{C}_3\text{H}_5\text{O}_{2(\text{aq})}^-]}$$

$$= \frac{(1.1 \times 10^{-5})^2}{0.157}$$

$$K_b = 7.7 \times 10^{-10}$$

The base ionization constant of the propanoate ion is 7.7×10^{-10} .

12. $K_w = 1.0 \times 10^{-14}$

$$K_a = 7.2 \times 10^{-4}$$

$$K_a K_b = K_w$$

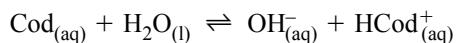
$$K_b = \frac{K_w}{K_a}$$

$$= \frac{1.0 \times 10^{-14}}{7.2 \times 10^{-4}}$$

$$K_b = 1.4 \times 10^{-11}$$

The base dissociation constant for the nitrite ion is 1.4×10^{-11} .

13. **pH of codeine ...**



$$K_b = \frac{[\text{HCod}_{(\text{aq})}^+][\text{OH}_{(\text{aq})}^-]}{[\text{Cod}_{(\text{aq})}]}$$

$$K_b = 1.73 \times 10^{-6}$$

ICE Table for the Base $\text{Cod}_{(\text{aq})}$				
	$\text{Cod}_{(\text{aq})}^+$	$\text{H}_2\text{O}_{(\text{l})} \rightleftharpoons$	$\text{OH}_{(\text{aq})}^-$	$\text{HCod}_{(\text{aq})}^+$
Initial concentration (mol/L)	0.020	—	0.000	0.000
Change in concentration (mol/L)	$-x$	—	$+x$	$+x$
Equilibrium concentration (mol/L)	$0.020 - x$	—	x	x

Since $0.93\% < 5\%$, the assumption is valid.

Therefore,

$$[\text{OH}_{(\text{aq})}^-] = 1.9 \times 10^{-4} \text{ mol/L}$$

$$\text{pOH} = -1.9 \times 10^{-4}$$

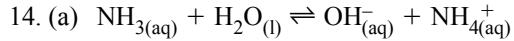
$$\text{pOH} = 3.73$$

$$\text{pH} = 14 - \text{pOH}$$

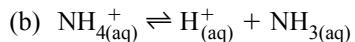
$$= 14.0 - 3.73$$

$$\text{pH} = 10.27$$

The pH of a 0.020 mol/L solution of codeine is 10.27.



$$K_b = \frac{[\text{NH}_4_{(\text{aq})}^+][\text{OH}_{(\text{aq})}^-]}{[\text{NH}_3_{(\text{aq})}]}$$

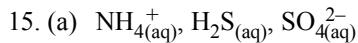


$$K_a = \frac{[\text{H}_{(\text{aq})}^+][\text{NH}_3_{(\text{aq})}]}{[\text{NH}_4_{(\text{aq})}^+]}$$

$$(c) \frac{[\text{H}_{(\text{aq})}^+][\text{NH}_3_{(\text{aq})}]}{[\text{NH}_4^+_{(\text{aq})}]} \times \frac{[\text{NH}_4^+_{(\text{aq})}][\text{OH}_{(\text{aq})}^-]}{[\text{NH}_3_{(\text{aq})}]} = [\text{H}_{(\text{aq})}^+][\text{OH}_{(\text{aq})}^-] = K_w$$

Numerically...

$$[5.80 \times 10^{-10}][1.72 \times 10^{-5}] = 1.00 \times 10^{-14}$$



(b) $\text{NH}_3 : K_b = 1.7 \times 10^{-5}$

$$\text{HS}_{(\text{aq})}^- : K_b = 9.1 \times 10^{-8}$$

$$\text{SO}_4^{2-}_{(\text{aq})} : K_b = 1.0 \times 10^{-12}$$

16. $\text{pH} = 10.10$

$$\text{pOH} = 14 - \text{pH}$$

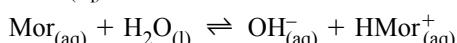
$$= 14.0 - 10.10$$

$$\text{pOH} = 3.90$$

$$[\text{OH}_{(\text{aq})}^-] = 10^{-\text{pOH}}$$

$$= 10^{-3.90}$$

$$[\text{OH}_{(\text{aq})}^-] = 1.26 \times 10^{-4} \text{ mol/L}$$



$$K_b = \frac{[\text{HMor}^+_{(\text{aq})}][\text{OH}_{(\text{aq})}^-]}{[\text{Mor}_{(\text{aq})}]}$$

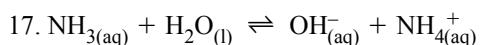
ICE Table for the Ionization of Morphine $\text{Mor}_{(\text{aq})}$				
	$\text{Mor}_{(\text{aq})}$	$+ \text{H}_2\text{O}_{(\text{l})} \rightleftharpoons$	$\text{OH}_{(\text{aq})}^- +$	$\text{HMor}^+_{(\text{aq})}$
Initial concentration (mol/L)	0.010	—	0.000	0.000
Change in concentration (mol/L)	-1.26×10^{-4}	—	$+1.26 \times 10^{-4}$	$+1.26 \times 10^{-4}$
Equilibrium concentration (mol/L)	9.87×10^{-3}	—	1.26×10^{-4}	1.26×10^{-4}

$$K_b = \frac{[\text{HMor}^+_{(\text{aq})}][\text{OH}_{(\text{aq})}^-]}{[\text{Mor}_{(\text{aq})}]}$$

$$= \frac{(1.26 \times 10^{-4})^2}{9.87 \times 10^{-3}}$$

$$K_b = 1.6 \times 10^{-6}$$

The K_b for morphine is 1.6×10^{-6} .



$$K_b = \frac{[\text{NH}_4^+_{(\text{aq})}][\text{OH}_{(\text{aq})}^-]}{[\text{NH}_3_{(\text{aq})}]}$$

$$K_b = 1.77 \times 10^{-5}$$

ICE Table for the Ionization of Ammonia				
	$\text{NH}_3_{(\text{aq})} +$	$\text{H}_2\text{O}_{(\text{l})} \rightleftharpoons$	$\text{OH}_{(\text{aq})}^- +$	$\text{NH}_4^+_{(\text{aq})}$
Initial concentration (mol/L)	0.100	—	0.000	0.000
Change in concentration (mol/L)	$-x$	—	$+x$	$+x$
Equilibrium concentration (mol/L)	$0.100 - x$	—	x	x

Since $1.33\% < 5\%$, the assumption is valid.

Therefore,

$$[\text{OH}_{(\text{aq})}^-] = 1.33 \times 10^{-3} \text{ mol/L}$$

$$\text{pOH} = -\log 1.33 \times 10^{-3}$$

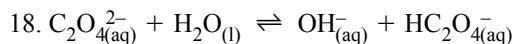
$$\text{pOH} = 2.877$$

$$\text{pH} = 14 - \text{pOH}$$

$$= 14.0 - 2.877$$

$$\text{pH} = 11.123$$

The pH of a 0.100 mol/L solution of ammonia is 11.123.



$$K_b = \frac{[\text{HC}_2\text{O}_{4(\text{aq})}^-][\text{OH}_{(\text{aq})}^-]}{[\text{C}_2\text{O}_{4(\text{aq})}^{2-}]}$$

$$K_b = 1.7 \times 10^{-10}$$

ICE Table for the Hydrolysis of Oxalate				
	$\text{C}_2\text{O}_{4(\text{aq})}^{2-} +$	$\text{H}_2\text{O}_{(\text{l})} \rightleftharpoons$	$\text{OH}_{(\text{aq})}^- +$	$\text{HC}_2\text{O}_{4(\text{aq})}^-$
Initial concentration (mol/L)	0.0500	—	0.000	0.000
Change in concentration (mol/L)	$-x$	—	$+x$	$+x$
Equilibrium concentration (mol/L)	$0.0500 - x$	—	x	x

Since $5.83 \times 10^{-3} \% < 5\%$, the assumption is valid.

Therefore,

$$[\text{OH}_{(\text{aq})}^-] = 2.9 \times 10^{-6} \text{ mol/L}$$

$$\text{pOH} = -\log 2.9 \times 10^{-6}$$

$$\text{pOH} = 5.54$$

$$\text{pH} = 14 - \text{pOH}$$

$$= 14.0 - 5.54$$

$$\text{pH} = 8.46$$

The pH of a 0.0500 mol/L sodium oxalate solution is 8.460.

Applying Inquiry Skills

19. Strong bases have a higher pH than weaker bases. Weak bases that are molecular produce solutions that do not conduct electricity well.

20. Analysis

Solution 1: $\text{HBr}_{(\text{aq})}$

Solution 2: $\text{C}_{12}\text{H}_{22}\text{O}_{11(\text{aq})}$

Solution 3: $\text{HC}_2\text{H}_3\text{O}_{2(\text{aq})}$

Solution 4: $\text{NaCl}_{(\text{aq})}$

Making Connections

21. (a) pH = 10.10

$$\text{pOH} = 14 - \text{pH}$$

$$= 14.0 - 8.81$$

$$\text{pOH} = 5.19$$

$$[\text{OH}_{(\text{aq})}^-] = 10^{-\text{pOH}}$$

$$= 10^{-5.19}$$

$$[\text{OH}_{(\text{aq})}^-] = 6.5 \times 10^{-6} \text{ mol/L}$$

- (b) (Answers may vary. Answers might include the following information.) Aniline dyes are dyes derived from coal tar products. William Perkin accidentally discovered Mauvein, the first synthetic dye, while he was a 17-year-old student at the Royal College of Chemistry in London in 1856. Perkin's chemistry professor assigned him the task of synthesizing quinine, a drug to treat malaria. Perkin's first attempt ended in failure. Instead of quinine, Perkin had produced a seemingly useless black paste. Being the curious chemist, Perkin investigated the properties of this new material and found that it produced a brilliant purple colour when dissolved in alcohol. He also discovered that this dye had adhered to fabrics well, making it ideal as a fabric dye. In the nineteenth century, most fabric dyes came from natural sources. Purple, for example, came from the shell of a rare mollusk. Since hundreds of shells needed to be pulverized to produce a small amount of dye, purple dyes were very expensive. Because of its scarcity, purple was a popular colour among Europe's nobility. Realizing the potential of his new discovery, Perkin promptly left the College, patented the process for manufacturing aniline, and established a manufacturing facility in 1857.

ICE Table for the Ionization of Aniline				
	$\text{C}_6\text{H}_5\text{NH}_{2(\text{aq})}^+$	$\text{H}_2\text{O}(\text{l}) \rightleftharpoons$	$\text{OH}_{(\text{aq})}^- +$	$\text{HC}_6\text{H}_5\text{NH}_{2(\text{aq})}^+$
Initial concentration (mol/L)	0.010	—	0.000	0.000
Change in concentration (mol/L)	-6.5×10^{-6}	—	$+6.5 \times 10^{-6}$	$+6.5 \times 10^{-6}$
Equilibrium concentration (mol/L)	0.010	—	6.5×10^{-6}	6.5×10^{-6}

$$K_b = \frac{[\text{HC}_6\text{H}_5\text{NH}_{2(\text{aq})}^+][\text{OH}_{(\text{aq})}^-]}{[\text{C}_6\text{H}_5\text{NH}_{2(\text{aq})}]}$$

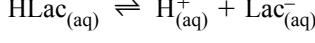
$$= \frac{(6.5 \times 10^{-6})^2}{0.10}$$

$$K_b = 4.2 \times 10^{-10}$$

The K_b for aniline is 4.2×10^{-10} .

22. (a) The high concentration of hydrogen ions in stomach fluid pushes the Aspirin equilibrium to the left, resulting in most of the Aspirin being in its un-ionized form.
 (b) Since this region of the stomach is of lower acidity, the forward reaction of the Aspirin equilibrium predominates to produce more hydrogen ions. This acidity is the cause of the irritation.
 (c) (Answers may vary, but may include the following information.) The enteric coating delays the release of Aspirin long enough for the tablet to pass through the stomach and into the intestine. This alleviates the potential irritation that Aspirin can cause.

23. (a) Let HLac represent the chemical formula for lactic acid.



$$K_a = \frac{[\text{H}_{(\text{aq})}^+][\text{Lac}_{(\text{aq})}^-]}{[\text{HLac}_{(\text{aq})}]}$$

$$K_a = 7.98 \times 10^{-5}$$

ICE Table for the Ionization of $\text{HC}_3\text{H}_5\text{O}_3(\text{aq})$			
	$\text{HLac}_{(\text{aq})} \rightleftharpoons$	$\text{H}_{(\text{aq})}^+ +$	$\text{Lac}_{(\text{aq})}^-$
Initial concentration (mol/L)	5.6×10^{-3}	0	0
Change in concentration (mol/L)	$-x$	$+x$	$+x$
Equilibrium concentration (mol/L)	$5.6 \times 10^{-3} - x$	x	x

$$\frac{x^2}{(5.6 \times 10^{-3} - x)} = 7.94 \times 10^{-5}$$

Predict whether a simplifying assumption is justified ...

$$\frac{[\text{HA}]_{\text{initial}}}{K_a} = \frac{5.6 \times 10^{-3}}{7.94 \times 10^{-5}}$$

$$\frac{[\text{HA}]_{\text{initial}}}{K_a} = 70$$

Since $70 < 100$, we may not assume that $5.6 \times 10^{-3} - x \doteq 5.6 \times 10^{-3}$.

$$\frac{x^2}{(5.6 \times 10^{-3} - x)} = 7.94 \times 10^{-5}$$

$$x^2 = 7.94 \times 10^{-5} (5.6 \times 10^{-3} - x)$$

$$x^2 + (7.94 \times 10^{-5} x) - (4.45 \times 10^{-7}) = 0$$

$$x = \frac{-7.94 \times 10^{-5} \pm \sqrt{(7.94 \times 10^{-5})^2 - 4(-4.45 \times 10^{-7})}}{2}$$

$$x = 6.29 \times 10^{-4} \text{ mol/L}$$

$$\begin{aligned}\text{pH} &= -\log[\text{H}_{(\text{aq})}^+] \\ &= -\log[6.29 \times 10^{-4}]\end{aligned}$$

$$\text{pH} = 3.20$$

The pH of the lactic acid in the runner's muscles is 3.20.

- (b) Lactic acid buildup in muscles causes fatigue, pain, and muscle stiffness.
- (c) Muscles can oxidize glucose aerobically or anaerobically to release energy. The energy released is stored temporarily in the molecule ATP that can then be used by muscles to do mechanical work. Anaerobic oxidation of glucose, however, is not very efficient. In a sprint, for example, a great deal of energy is required in a short period of time. Anaerobic oxidation supplies most of this energy but is very inefficient. Short-term energy reserves are depleted quickly and lactic acid accumulates.

Muscles used in long-distance running rely more on aerobic oxidation of glucose for their energy. When running at a comfortable pace, both systems of oxidation are used but the ratio of anaerobic: aerobic is low enough to prevent lactic acid from accumulating. As the pace increases, the anaerobic: aerobic ratio increases to the point where lactic acid begins to accumulate in the blood. This is known as the lactic acid threshold. In order to improve performance, long-distance runners try to train at the speed at which the lactic acid threshold occurs. This serves to increase the threshold and overall performance.

8.3 ACID-BASE PROPERTIES OF SALT SOLUTIONS

PRACTICE

(Page 588)

Understanding Concepts

1. (a) The ammonium ion is a weak acid with $K_a = 5.8 \times 10^{-10}$. The phosphate ion is a base with $K_b = 2.4 \times 10^{-2}$. Since K_b is larger than K_a , an ammonium phosphate solution is basic.
 (b) The ammonium ion is a weak acid with $K_a = 5.8 \times 10^{-10}$. The sulfate ion is a base with $K_b = 1.0 \times 10^{-12}$. Since K_a is larger than K_b , an ammonium sulfate solution is slightly acidic.
 (c) Magnesium oxide reacts with water to form magnesium hydroxide (a base).
 (d) $\text{MgO}_{(\text{s})} + \text{H}_2\text{O}_{(\text{l})} \rightarrow \text{Mg}_{(\text{aq})}^{2+} + 2 \text{OH}_{(\text{aq})}^-$. This makes a solution of magnesium oxide basic.
2. A solution of sodium sulfite will be basic.
3. $\text{NH}_4\text{NO}_3_{(\text{aq})} \rightarrow \text{NH}_{(\text{aq})}^+ + \text{NO}_3^-$

$$\frac{x^2}{(5.6 \times 10^{-3} - x)} = 7.94 \times 10^{-5}$$

Predict whether a simplifying assumption is justified ...

$$\frac{[\text{HA}]_{\text{initial}}}{K_a} = \frac{5.6 \times 10^{-3}}{7.94 \times 10^{-5}}$$

$$\frac{[\text{HA}]_{\text{initial}}}{K_a} = 70$$

Since $70 < 100$, we may not assume that $5.6 \times 10^{-3} - x \doteq 5.6 \times 10^{-3}$.

$$\frac{x^2}{(5.6 \times 10^{-3} - x)} = 7.94 \times 10^{-5}$$

$$x^2 = 7.94 \times 10^{-5} (5.6 \times 10^{-3} - x)$$

$$x^2 + (7.94 \times 10^{-5} x) - (4.45 \times 10^{-7}) = 0$$

$$x = \frac{-7.94 \times 10^{-5} \pm \sqrt{(7.94 \times 10^{-5})^2 - 4(-4.45 \times 10^{-7})}}{2}$$

$$x = 6.29 \times 10^{-4} \text{ mol/L}$$

$$\begin{aligned}\text{pH} &= -\log[\text{H}_{(\text{aq})}^+] \\ &= -\log[6.29 \times 10^{-4}]\end{aligned}$$

$$\text{pH} = 3.20$$

The pH of the lactic acid in the runner's muscles is 3.20.

- (b) Lactic acid buildup in muscles causes fatigue, pain, and muscle stiffness.
- (c) Muscles can oxidize glucose aerobically or anaerobically to release energy. The energy released is stored temporarily in the molecule ATP that can then be used by muscles to do mechanical work. Anaerobic oxidation of glucose, however, is not very efficient. In a sprint, for example, a great deal of energy is required in a short period of time. Anaerobic oxidation supplies most of this energy but is very inefficient. Short-term energy reserves are depleted quickly and lactic acid accumulates.

Muscles used in long-distance running rely more on aerobic oxidation of glucose for their energy. When running at a comfortable pace, both systems of oxidation are used but the ratio of anaerobic: aerobic is low enough to prevent lactic acid from accumulating. As the pace increases, the anaerobic: aerobic ratio increases to the point where lactic acid begins to accumulate in the blood. This is known as the lactic acid threshold. In order to improve performance, long-distance runners try to train at the speed at which the lactic acid threshold occurs. This serves to increase the threshold and overall performance.

8.3 ACID-BASE PROPERTIES OF SALT SOLUTIONS

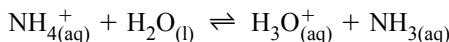
PRACTICE

(Page 588)

Understanding Concepts

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 (c) Magnesium oxide reacts with water to form magnesium hydroxide (a base).
 (d) $\text{MgO}_{(\text{s})} + \text{H}_2\text{O}_{(\text{l})} \rightarrow \text{Mg}_{(\text{aq})}^{2+} + 2 \text{OH}_{(\text{aq})}^-$. This makes a solution of magnesium oxide basic.
2. A solution of sodium sulfite will be basic.
3. $\text{NH}_4\text{NO}_3_{(\text{aq})} \rightarrow \text{NH}_{(\text{aq})}^+ + \text{NO}_3^-$

Since NO_3^- is the conjugate base of a strong acid, it will not affect the pH of the solution. NH_4^+ is the conjugate acid of a weak base NH_3 , so it will hydrolyze according to the equation:



$$K_a = \frac{[\text{H}_3\text{O}^+][\text{NH}_3]}{[\text{NH}_4^+]}$$

$$K_a = 5.8 \times 10^{-10}$$

ICE Table for the Hydrolysis of NH_4^+				
	$\text{NH}_4^+ +$	$\text{H}_2\text{O}_{(l)} \rightleftharpoons$	$\text{H}_3\text{O}^+ +$	NH_3
Initial concentration (mol/L)	0.30	—	0.00	0.00
Change in concentration (mol/L)	$-x$	—	$+x$	$+x$
Equilibrium concentration (mol/L)	$0.30 - x$	—	x	x

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{NH}_3]}{[\text{NH}_4^+]}$$

$$K_a = 5.8 \times 10^{-10}$$

$$\frac{x^2}{0.30 - x} = 5.8 \times 10^{-10}$$

Predicting whether $0.30 - x \doteq 0.30$...

$$\frac{[\text{HA}]_{\text{initial}}}{K_a} = \frac{0.30}{5.8 \times 10^{-10}}$$

$$\frac{[\text{HA}]_{\text{initial}}}{K_a} = 5.2 \times 10^8$$

Since $5.2 \times 10^8 > 100$, we may assume that $0.30 - x \doteq 0.30$.

$$\frac{x^2}{0.30} \doteq 5.8 \times 10^{-10}$$

$$x^2 \doteq 1.7 \times 10^{-10}$$

$$x \doteq 1.3 \times 10^{-5}$$

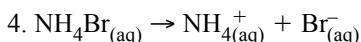
$$\text{Since } x = [\text{H}_3\text{O}^+]$$

$$[\text{H}_3\text{O}^+] = 1.3 \times 10^{-5} \text{ mol/L}$$

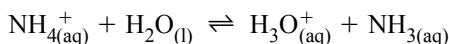
$$\text{pH} = -\log 1.3 \times 10^{-5}$$

$$\text{pH} = 4.88$$

The pH of a 0.30 mol/L ammonium nitrate solution is 4.88.



Since $\text{Br}_-(aq)$ is the conjugate base of a strong acid, it will not affect the pH of the solution. NH_4^+ hydrolyzes according to the equation:



$$K_a = \frac{[\text{H}_3\text{O}^+][\text{NH}_3]}{[\text{NH}_4^+]}$$

$$K_a = 5.8 \times 10^{-10}$$

ICE Table for the Hydrolysis of $\text{NH}_{4(aq)}^+$				
	$\text{NH}_{4(aq)}^+ +$	$\text{H}_2\text{O}_{(l)} \rightleftharpoons$	$\text{H}_3\text{O}_{(aq)}^+ +$	$\text{NH}_{3(aq)}$
Initial concentration (mol/L)	0.25	—	0.00	0.00
Change in concentration (mol/L)	$-x$	—	$+x$	$+x$
Equilibrium concentration (mol/L)	$0.25 - x$	—	x	x

$$K_a = \frac{[\text{H}_3\text{O}_{(aq)}^+][\text{NH}_{3(aq)}]}{[\text{NH}_{4(aq)}^+]}$$

$$K_a = 5.8 \times 10^{-10}$$

$$\frac{x^2}{0.25 - x} = 5.8 \times 10^{-10}$$

Predicting whether $0.25 - x \doteq 0.25 \dots$

$$\frac{[\text{HA}]_{\text{initial}}}{K_a} = \frac{0.25}{5.8 \times 10^{-10}}$$

$$\frac{[\text{HA}]_{\text{initial}}}{K_a} = 5.2 \times 10^8$$

Since $5.2 \times 10^8 > 100$, we may assume that $0.25 - x \doteq 0.25$.

$$\frac{x^2}{0.25} \doteq 5.8 \times 10^{-10}$$

$$x^2 \doteq 1.5 \times 10^{-10}$$

$$x \doteq 1.2 \times 10^{-5}$$

$$\text{Since } x = [\text{H}_3\text{O}_{(aq)}^+]$$

$$[\text{H}_3\text{O}_{(aq)}^+] = 1.2 \times 10^{-5} \text{ mol/L}$$

$$\text{pH} = -\log 1.2 \times 10^{-5}$$

$$\text{pH} = 4.92$$

The pH of a 0.25 mol/L ammonium bromide solution is 4.92.

5. $\text{NH}_4\text{C}_2\text{H}_3\text{O}_{2(aq)} \rightarrow \text{NH}_{4(aq)}^+ + \text{C}_2\text{H}_3\text{O}_{2-}$. The ammonium ion is a weak acid with $K_a = 5.8 \times 10^{-10}$. The acetate ion is a weak base with $K_b = 5.6 \times 10^{-10}$. Since K_b and K_a are similar, an ammonium acetate solution is essentially neutral.

Making Connections

6. Fertilizers containing ammonium compounds, which hydrolyze to produce acidic solutions, are ideal for evergreens.

PRACTICE

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Understanding Concepts

7. $\text{HCO}_{3(aq)}^-$, $\text{HS}_{(aq)}^-$, $\text{HPO}_{4(aq)}^{2-}$, $\text{H}_2\text{PO}_{4(aq)}^-$, $\text{HSO}_{4(aq)}^-$, $\text{HSO}_{3(aq)}^-$, $\text{HC}_2\text{O}_{4(aq)}^-$

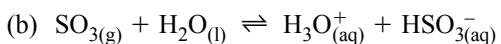
8. (a) acidic
(b) basic

PRACTICE

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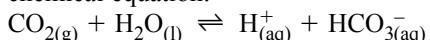
Understanding Concepts

9. (a) $\text{Na}_2\text{O}_{(s)} + \text{H}_2\text{O}_{(l)} \rightleftharpoons 2 \text{Na}_{(aq)}^+ + 2 \text{OH}_{(aq)}^-$

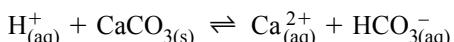


Making Connections

10. (a) Carbon dioxide exhaled by the visitors can increase the acidity of the moisture in the caves, according to the chemical equation:



The increased acidity can accelerate the dissolving of the cave structures:



- (b) Possible solutions include providing air circulation systems or large fans that would prevent carbon dioxide gas from accumulating.

11. Arguments supporting the use of fluoride:

- Some studies of large populations suggest that water fluoridation does prevent tooth decay.

Arguments against the use of fluoride:

- Some other studies suggest that the evidence to support that water fluoridation prevents tooth decay is inconclusive.
- The risks associated with long-term exposure to trace amounts of fluoride have not been established.
- The effects of fluoride on aquatic life have not been thoroughly studied.
- Some studies suggest that prolonged exposure to fluoride is associated with a condition known as skeletal fluorosis – a gradual deterioration of bone.
- Fluoride can be administered in more direct ways that do not threaten the environment.

PRACTICE

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Understanding Concepts

12. (a) Lewis acid: $\text{H}_{(\text{aq})}^+$; Lewis base: $\text{OH}_{(\text{aq})}^-$

- (b) Lewis acid: $\text{H}_{(\text{aq})}^+$; Lewis base: $\text{NH}_{3(\text{aq})}$

SECTION 8.3 QUESTIONS

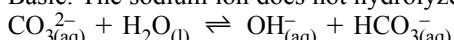
(Page 594)

Understanding Concepts

1. (a) Neutral. The sodium ion, being a member of Group 1, does not hydrolyze. The chloride ion is an extremely weak base and therefore also does not hydrolyze.

- (b) Acidic. Chloride does not hydrolyze. Aluminum ions will hydrolyze according to the equation
$$\text{Al}(\text{H}_2\text{O})_{6(\text{aq})}^{3+} \rightleftharpoons \text{Al}(\text{H}_2\text{O})_5(\text{OH})_{(\text{aq})}^{2+} + \text{H}_{(\text{aq})}^+$$

- (c) Basic. The sodium ion does not hydrolyze. Carbonate will hydrolyze to release hydroxide ions.



2. The ammonium ion is a weak acid with $K_a = 5.8 \times 10^{-10}$. The carbonate ion is a base with $K_b = 2.1 \times 10^{-4}$. Since K_b is larger than K_a , an ammonium carbonate solution is basic.

3. According to Table C7 in the Appendix, the strongest possible acid is perchloric acid and the strongest possible base is the hydroxide ion, $\text{OH}_{(\text{aq})}^-$ – the base released when the hydroxide ion dissociates. However, for all practical purposes, the concentration of oxide in a solution of the hydroxide ion is zero.

4. $\text{BeCl}_{2(\text{aq})}$ will turn litmus red because the $\text{Be}_{(\text{aq})}^{2+}$ hydrolyzes to release $\text{H}_{(\text{aq})}^+$.

5. (a) acidic
(b) basic

Applying Inquiry Skills

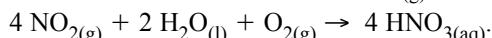
6. Analysis

$\text{Na}_2\text{O}_{(\text{s})}$	basic
$\text{MgO}_{(\text{s})}$	basic

$\text{As}_2\text{O}_{3(s)}$	insoluble – no solution produced. The water remains neutral.
$\text{SiO}_{2(s)}$	insoluble – no solution produced. The water remains neutral.
$\text{P}_2\text{O}_{3(s)}$	acidic
$\text{SO}_{3(g)}$	acidic
$\text{Cl}_2\text{O}_{(g)}$	acidic

Extension

7. Rainwater containing dissolved $\text{NO}_{2(g)}$ is acidic because of the formation of nitric acid in this reaction:



8.4 ACID–BASE TITRATION

PRACTICE

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Understanding Concepts

1. (a) pH 7
 (b) Since this is a titration of a strong acid with a strong base, the equivalence point occurs at pH 7. Any indicator with pH 7 within its range would be suitable, e.g., bromothymol blue, litmus, neutral red, phenol red.

$$\begin{aligned} 2. \quad n_{\text{HI}} &= V_{\text{HI}} \times C_{\text{HI}} \\ &= 11 \text{ mL} \times 0.18 \text{ mol/L} \\ &= 1.98 \text{ mmol} \quad (\text{extra digits carried}) \end{aligned}$$

$$n_{\text{HI}} = n_{\text{NaOH}} \text{ required}$$

$$C_{\text{NaOH}} = \frac{n_{\text{NaOH}}}{V_{\text{NaOH}}}$$

$$V_{\text{NaOH}} = \frac{n_{\text{NaOH}}}{C_{\text{NaOH}}}$$

$$= \frac{1.98 \text{ mmol}}{0.23 \text{ mol/L}}$$

$$V_{\text{NaOH}} = 8.6 \text{ mL}$$

8.6 mL of 0.23 mol/L sodium hydroxide is required to reach the equivalence point.

Applying Inquiry Skills

3. (a) The last drop is washed into the flask because the titrant volume level in the buret already includes the volume of the drop.
 (b) The results of the titration depend only on the moles of acid or base present, not their concentration. Adding water changes concentration but not the moles present.

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Understanding Concepts

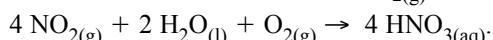
4. (a)

ICE Table for the Ionization of $\text{HCO}_2\text{H}_{(aq)}$			
	$\text{HCO}_2\text{H}_{(aq)} \rightleftharpoons$	$\text{H}_{(aq)}^+ +$	$\text{CO}_2\text{H}_{(aq)}^-$
Initial concentration (mol/L)	0.20	0.00	0.00
Change in concentration (mol/L)	$-x$	$+x$	$+x$
Equilibrium concentration (mol/L)	$0.20 - x$	x	x

$\text{As}_2\text{O}_{3(s)}$	insoluble – no solution produced. The water remains neutral.
$\text{SiO}_{2(s)}$	insoluble – no solution produced. The water remains neutral.
$\text{P}_2\text{O}_{3(s)}$	acidic
$\text{SO}_{3(g)}$	acidic
$\text{Cl}_2\text{O}_{(g)}$	acidic

Extension

7. Rainwater containing dissolved $\text{NO}_{2(g)}$ is acidic because of the formation of nitric acid in this reaction:



8.4 ACID–BASE TITRATION

PRACTICE

(Page 599)

Understanding Concepts

1. (a) pH 7
 (b) Since this is a titration of a strong acid with a strong base, the equivalence point occurs at pH 7. Any indicator with pH 7 within its range would be suitable, e.g., bromothymol blue, litmus, neutral red, phenol red.

$$\begin{aligned} 2. \quad n_{\text{HI}} &= V_{\text{HI}} \times C_{\text{HI}} \\ &= 11 \text{ mL} \times 0.18 \text{ mol/L} \\ &= 1.98 \text{ mmol} \quad (\text{extra digits carried}) \end{aligned}$$

$$n_{\text{HI}} = n_{\text{NaOH}} \text{ required}$$

$$C_{\text{NaOH}} = \frac{n_{\text{NaOH}}}{V_{\text{NaOH}}}$$

$$V_{\text{NaOH}} = \frac{n_{\text{NaOH}}}{C_{\text{NaOH}}} \\ = \frac{1.98 \text{ mmol}}{0.23 \text{ mol/L}}$$

$$V_{\text{NaOH}} = 8.6 \text{ mL}$$

8.6 mL of 0.23 mol/L sodium hydroxide is required to reach the equivalence point.

Applying Inquiry Skills

3. (a) The last drop is washed into the flask because the titrant volume level in the buret already includes the volume of the drop.
 (b) The results of the titration depend only on the moles of acid or base present, not their concentration. Adding water changes concentration but not the moles present.

PRACTICE

(Page 607)

Understanding Concepts

4. (a)

ICE Table for the Ionization of $\text{HCO}_2\text{H}_{(aq)}$			
	$\text{HCO}_2\text{H}_{(aq)} \rightleftharpoons$	$\text{H}_{(aq)}^+ +$	$\text{CO}_2\text{H}_{(aq)}^-$
Initial concentration (mol/L)	0.20	0.00	0.00
Change in concentration (mol/L)	$-x$	$+x$	$+x$
Equilibrium concentration (mol/L)	$0.20 - x$	x	x

$$K_a = \frac{[H_{(aq)}^+][CO_2H_{(aq)}^-]}{[HCO_2H_{(aq)}]}$$

$$\frac{x^2}{0.20 - x} = 1.8 \times 10^{-4}$$

Predicting whether $0.20 - x \doteq 0.20 \dots$

$$\frac{[HA]_{\text{initial}}}{K_a} = \frac{0.20 \text{ mol/L}}{1.8 \times 10^{-4}}$$

$$= 1100$$

Since $1100 > 100$, we assume that $0.20 - x \doteq 0.20$.

$$\frac{x^2}{(0.20)} \doteq 1.8 \times 10^{-4}$$

$$x^2 \doteq 3.6 \times 10^{-5}$$

$$x \doteq 6.0 \times 10^{-3}$$

Validating the assumption ...

$$\frac{6.0 \times 10^{-3}}{0.20} \times 100\% = 3.0\%$$

Since $3.0\% < 5.0\%$, the assumption is valid.

$$[H_{(aq)}^+] = 6.0 \times 10^{-3} \text{ mol/L}$$

$$\begin{aligned} \text{pH} &= -\log [H_{(aq)}^+] \\ &= -\log [6.0 \times 10^{-3}] \end{aligned}$$

$$\text{pH} = 2.22$$

The pH of the 0.20 mol/L formic acid solution is 2.22.

$$\begin{aligned} \text{(b)} \quad V_{HCO_2H_{(aq)}} &= 25.00 \text{ mL} \\ C_{HCO_2H_{(aq)}} &= 0.20 \text{ mol/L} \\ n_{HCO_2H_{(aq)}} &= V_{HCO_2H_{(aq)}} \times C_{HCO_2H_{(aq)}} \\ &= 25.00 \text{ mL} \times 0.20 \text{ mol/L} \end{aligned}$$

$$n_{HCO_2H_{(aq)}} = 5.0 \text{ mmol}$$

$$\begin{aligned} V_{NaOH_{(aq)}} &= 10.00 \text{ mL} \\ C_{NaOH_{(aq)}} &= 0.20 \text{ mol/L} \\ n_{NaOH_{(aq)}} &= V_{NaOH_{(aq)}} \times C_{NaOH_{(aq)}} \\ &= 10.00 \text{ mL} \times 0.20 \text{ mol/L} \end{aligned}$$

$$n_{NaOH_{(aq)}} = 2.0 \text{ mmol}$$

$n_{HCO_2H_{(aq)}}$ remaining ...

$$n_{HCO_2H_{(aq)}} = 5.0 \text{ mmol} - 2.0 \text{ mmol}$$

$$n_{HCO_2H_{(aq)}} = 3.0 \text{ mmol}$$

$$\begin{aligned} \text{Total volume} &= 25.00 \text{ mL} + 10.00 \text{ mL} \\ &= 35.00 \text{ mL} \end{aligned}$$

$$C_{HCO_2H_{(aq)}} = \frac{3.0 \text{ mmol}}{35.00 \text{ mL}}$$

$$C_{\text{HCO}_2\text{H}_{(\text{aq})}} = 0.08571 \text{ mol/L} \quad (\text{extra digits carried})$$

$$C_{\text{CO}_2\text{H}_{(\text{aq})}^-} = \frac{2.0 \text{ mmol}}{35.00 \text{ mL}}$$

$$C_{\text{CO}_2\text{H}_{(\text{aq})}^-} = 0.05714 \text{ mol/L} \quad (\text{extra digits carried})$$

Let x represent the changes in concentration that occur as the system reestablishes equilibrium.

ICE Table for the Ionization of $\text{HCO}_2\text{H}_{(\text{aq})}$			
	$\text{HCO}_2\text{H}_{(\text{aq})} \rightleftharpoons$	$\text{H}_{(\text{aq})}^+ +$	$\text{CO}_2\text{H}_{(\text{aq})}^-$
Initial concentration (mol/L)	0.08571	0.00	0.05714
Change in concentration (mol/L)	$-x$	$+x$	$+x$
Equilibrium concentration (mol/L)	$0.08571 - x$	x	$0.05714 + x$

$$\frac{[\text{H}_{(\text{aq})}^+][\text{CO}_2\text{H}_{(\text{aq})}^-]}{[\text{HCO}_2\text{H}_{(\text{aq})}]} = K_a$$

$$\frac{x(0.05714 + x)}{0.08571 - x} = 1.8 \times 10^{-4}$$

Checking whether an approximation is warranted:

$$\frac{[\text{HCO}_2\text{H}_{(\text{aq})}]_{\text{initial}}}{K_a} = \frac{0.08571}{1.8 \times 10^{-4}}$$

$$\frac{[\text{HCO}_2\text{H}_{(\text{aq})}]_{\text{initial}}}{K_a} = 480$$

Since $480 > 100$, we can assume that

$$0.08571 - x \doteq 0.08571 \text{ and that}$$

$$0.05714 + x \doteq 0.05714$$

The equilibrium simplifies to

$$\frac{x(0.05714)}{0.08571} = 1.8 \times 10^{-4}$$

$$x = 2.70 \times 10^{-4}$$

Verifying the assumption with the 5% rule:

$$\frac{2.70 \times 10^{-4}}{0.20} \times 100\% = 0.14\%$$

Since $0.14\% < 5\%$, the simplifying assumption is justified.

$$[\text{H}_{(\text{aq})}^+] \doteq 2.70 \times 10^{-4} \text{ mol/L}$$

$$\text{pH} \doteq -\log[2.70 \times 10^{-4}]$$

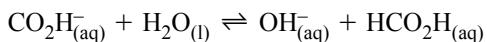
$$\text{pH} = 3.569$$

The pH after the addition of 10.00 mL of $\text{NaOH}_{(\text{aq})}$ is 3.57.

- (c) At the equivalence point, 25.00 mL of 0.20 mol/L $\text{NaOH}_{(\text{aq})}$ were added.

Entities remaining in solution: $\text{Na}_{(\text{aq})}^+$, $\text{CO}_2\text{H}_{(\text{aq})}^-$, $\text{H}_2\text{O}_{(\text{l})}$

Since $\text{Na}_{(\text{aq})}^+$ does not hydrolyze, the pH of the solution is determined by the methanoate ion.



$$\frac{[\text{HCO}_2\text{H}_{(\text{aq})}][\text{OH}_{(\text{aq})}^-]}{[\text{CO}_2\text{H}_{(\text{aq})}^-]} = K_b$$

$$K_a = 1.8 \times 10^{-4}$$

$$K_b = \frac{K_w}{K_a}$$

$$= \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-4}}$$

$$K_b = 5.6 \times 10^{-11}$$

Therefore,

$$\frac{[\text{HCO}_2\text{H}_{(\text{aq})}][\text{OH}_{(\text{aq})}^-]}{[\text{CO}_2\text{H}_{(\text{aq})}^-]} = 5.6 \times 10^{-11}$$

At the equivalence point, the total volume = 50.00 mL.

Since 5.00 mmol of $\text{HCO}_2\text{H}_{(\text{aq})}$ was present initially,

5.00 mmol of $\text{CO}_2\text{H}_{(\text{aq})}^-$ is present at the equivalence point.

$$[\text{CO}_2\text{H}_{(\text{aq})}^-] = \frac{5.00 \text{ mmol}}{50.00 \text{ mL}}$$

$$[\text{CO}_2\text{H}_{(\text{aq})}^-] = 0.100 \text{ mol/L}$$

ICE Table for the Hydrolysis of $\text{CO}_2\text{H}_{(\text{aq})}^-$				
	$\text{CO}_2\text{H}_{(\text{aq})}^- +$	$\text{H}_2\text{O}_{(\text{l})} \rightleftharpoons$	$\text{HCO}_2\text{H}_{(\text{aq})} +$	$\text{OH}_{(\text{aq})}^-$
Initial concentration (mol/L)	0.100	–	0.000	0.000
Change in concentration (mol/L)	$-x$	–	$+x$	$+x$
Equilibrium concentration (mol/L)	$0.100 - x$	–	x	x

$$\frac{[\text{HCO}_2\text{H}_{(\text{aq})}][\text{OH}_{(\text{aq})}^-]}{[\text{CO}_2\text{H}_{(\text{aq})}^-]} = 5.6 \times 10^{-11}$$

$$\frac{x^2}{0.100 - x} = 5.6 \times 10^{-11}$$

Checking whether an approximation is warranted:

$$\frac{[\text{CO}_2\text{H}_{(\text{aq})}]_{\text{initial}}}{K} = \frac{0.10}{5.6 \times 10^{-11}}$$

$$\frac{[\text{CO}_2\text{H}_{(\text{aq})}]_{\text{initial}}}{K} = 1.8 \times 10^9$$

Since $1.8 \times 10^9 > 100$, we can assume that

$$0.100 - x \doteq 0.100$$

The equilibrium simplifies to $\frac{x^2}{0.100} = 5.6 \times 10^{-11}$

$$x = 2.37 \times 10^{-6}$$

Verifying the assumption with the 5% rule:

$$\frac{2.37 \times 10^{-6}}{0.100} \times 100\% = 2.4 \times 10^{-3}\%$$

Since $2.4 \times 10^{-3\%} < 5\%$, the simplifying assumption is justified.

$$[\text{OH}_{(\text{aq})}^-] \doteq 2.37 \times 10^{-6} \text{ mol/L}$$

$$\text{pOH} \doteq -\log[2.37 \times 10^{-6}]$$

$$\text{pOH} = 5.625$$

$$\text{pH} = 14 - \text{pOH}$$

$$\text{pH} = 8.37$$

The pH at the equivalence point is 8.37.

$$\begin{aligned} 5. \quad V_{\text{HOCN}_{(\text{aq})}} &= 30.00 \text{ mL} \\ C_{\text{HOCN}_{(\text{aq})}} &= 0.17 \text{ mol/L} \\ n_{\text{HOCN}_{(\text{aq})}} &= V_{\text{HOCN}_{(\text{aq})}} \times C_{\text{HOCN}_{(\text{aq})}} \\ &= 30.00 \text{ mL} \times 0.17 \text{ mol/L} \end{aligned}$$

$$\begin{aligned} n_{\text{HOCN}_{(\text{aq})}} &= 5.1 \text{ mmol} \\ V_{\text{NaOH}_{(\text{aq})}} &= 10.00 \text{ mL} \\ C_{\text{NaOH}_{(\text{aq})}} &= 0.250 \text{ mol/L} \\ n_{\text{NaOH}_{(\text{aq})}} &= V_{\text{NaOH}_{(\text{aq})}} \times C_{\text{NaOH}_{(\text{aq})}} \\ &= 10.00 \text{ mL} \times 0.250 \text{ mol/L} \end{aligned}$$

$$\begin{aligned} n_{\text{NaOH}_{(\text{aq})}} &= 2.50 \text{ mmol} \\ n_{\text{HCON}_{(\text{aq})}} &\text{ remaining ...} \\ n_{\text{HOCN}_{(\text{aq})}} &= 5.1 \text{ mmol} - 2.50 \text{ mmol} \\ n_{\text{HOCN}_{(\text{aq})}} &= 2.6 \text{ mmol} \end{aligned}$$

$$\text{Total volume} = 30.00 \text{ mL} + 10.00 \text{ mL}$$

$$\begin{aligned} &= 40.00 \text{ mL} \\ C_{\text{HOCN}_{(\text{aq})}} &= \frac{2.6 \text{ mmol}}{40.00 \text{ mL}} \\ C_{\text{HOCN}_{(\text{aq})}} &= 0.0625 \text{ mol/L} \\ C_{\text{OCN}_{(\text{aq})}} &= \frac{2.5 \text{ mmol}}{40.00 \text{ mL}} \\ C_{\text{OCN}_{(\text{aq})}^-} &= 0.0625 \text{ mol/L} \end{aligned}$$

Let x represent the changes in concentration that occur as the system reestablishes equilibrium.

ICE Table for the Ionization of $\text{HOCN}_{(\text{aq})}$			
	$\text{HOCN}_{(\text{aq})} \rightleftharpoons$	$\text{H}_{(\text{aq})}^+ +$	$\text{OCN}_{(\text{aq})}^-$
Initial concentration (mol/L)	0.0625	0.00	0.0625
Change in concentration (mol/L)	$-x$	$+x$	$+x$
Equilibrium concentration (mol/L)	$0.0625 - x$	x	$0.0625 + x$

$$\frac{[\text{H}_{(\text{aq})}^+][\text{OCN}_{(\text{aq})}^-]}{[\text{HO}\text{CN}_{(\text{aq})}]} = K_a$$

$$\frac{x(0.0625 + x)}{0.0625 - x} = 3.5 \times 10^{-4}$$

Checking whether an approximation is warranted:

$$\frac{[\text{HO}\text{CN}_{(\text{aq})}]_{\text{initial}}}{K_a} = \frac{0.0625}{3.5 \times 10^{-4}}$$

$$\frac{[\text{HO}\text{CN}_{(\text{aq})}]_{\text{initial}}}{K_a} = 180$$

Since $180 > 100$, we can assume that

$0.0625 + x \doteq 0.0625$ and that $0.0625 - x \doteq 0.0625$

The equilibrium simplifies to

$$\frac{x(0.0625)}{0.0625} = 1.8 \times 10^{-4}$$

$$x = 1.8 \times 10^{-4}$$

Verifying the assumption with the 5% rule:

$$\frac{1.8 \times 10^{-4}}{0.0625} \times 100\% = 0.29\%$$

Since $0.29\% < 5\%$, the simplifying assumption is justified.

$$[\text{H}_{(\text{aq})}^+] \doteq 1.8 \times 10^{-4} \text{ mol/L}$$

$$\text{pH} \doteq -\log[1.8 \times 10^{-4}]$$

$$\text{pH} = 3.74$$

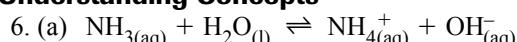
The $\text{OCN}_{(\text{aq})}$ is such a weak base ($K_b = 2.10 \times 10^{-12}$) that any hydrolysis to produce $\text{OH}_{(\text{aq})}^-$ is insignificant.

The pH of the resulting solution is 3.74.

PRACTICE

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Understanding Concepts



$$K_b = \frac{[\text{NH}_{4(\text{aq})}^+][\text{OH}_{(\text{aq})}^-]}{[\text{NH}_{3(\text{aq})}]}$$

$$K_b = 1.8 \times 10^{-5}$$

ICE Table for the Ionization of Ammonia				
	$\text{NH}_{3(\text{aq})}^+$	$\text{H}_2\text{O}_{(\text{l})} \rightleftharpoons$	$\text{NH}_{4(\text{aq})}^+$	$\text{OH}_{(\text{aq})}^-$
Initial concentration (mol/L)	0.15	-	0.00	0.00
Change in concentration (mol/L)	$-x$	-	$+x$	$+x$
Equilibrium concentration (mol/L)	$0.15 - x$	-	x	x

$$K_b = \frac{[\text{NH}_4^+_{(\text{aq})}][\text{OH}^-_{(\text{aq})}]}{[\text{NH}_3_{(\text{aq})}]}$$

$$K_b = 1.8 \times 10^{-5}$$

$$\frac{x^2}{0.15 - x} = 1.8 \times 10^{-5}$$

Predicting the validity of the assumption ...

$$\frac{0.15}{1.8 \times 10^{-5}} = 8300$$

Since $8300 > 100$, we may assume that $0.15 - x \doteq 0.15$.

The equilibrium expression becomes

$$\frac{x^2}{0.15} \doteq 1.8 \times 10^{-5}$$

which yields

$$x^2 \doteq 2.7 \times 10^{-6}$$

$$x \doteq 1.643 \times 10^{-3} \quad (\text{extra digits carried})$$

Justifying the simplification assumption ...

$$\frac{1.643 \times 10^{-3}}{0.15} \times 100\% = 1.1\%$$

Since $1.1\% < 5\%$, the assumption is justified.

Therefore,

$$[\text{OH}^-_{(\text{aq})}] = 1.643 \times 10^{-3} \text{ mol/L}$$

$$\text{pOH} = -\log[1.643 \times 10^{-3}]$$

$$\text{pOH} = 2.7844 \quad (\text{extra digits carried})$$

$$\text{pH} = 14 - \text{pOH}$$

$$= 14.0 - 2.7844$$

$$\text{pH} = 11.216$$

The pH before any $\text{HI}_{(\text{aq})}$ is added is 11.22.

(b) At the equivalence point, the entities remaining in solution are $\text{NH}_4^+_{(\text{aq})}$, $\text{I}^-_{(\text{aq})}$, and $\text{H}_2\text{O}_{(\text{l})}$.

Since $\text{I}^-_{(\text{aq})}$ does not hydrolyze, the pH of the solution is determined by the ammonium ion.

$$C_{\text{NH}_3_{(\text{aq})}} = 0.1500 \text{ mol/L}$$

$$n_{\text{NH}_3_{(\text{aq})}} = V_{\text{NH}_3_{(\text{aq})}} \times C_{\text{NH}_3_{(\text{aq})}}$$

$$= 20.0 \text{ mL} \times 0.1500 \text{ mol/L}$$

$$n_{\text{NH}_3_{(\text{aq})}} = 3.00 \text{ mmol} \quad (\text{amount of } \text{NH}_4^+_{(\text{aq})} \text{ produced})$$

Final volume = 40.0 mL

$$[\text{NH}_4^+_{(\text{aq})}] = \frac{3.00 \text{ mmol}}{40.0 \text{ mL}}$$

$$[\text{NH}_4^+_{(\text{aq})}] = 0.075 \text{ mol/L}$$

$$K_a = \frac{[\text{H}^+_{(\text{aq})}][\text{NH}_4^+_{(\text{aq})}]}{[\text{NH}_3_{(\text{aq})}]}$$

$$\frac{x^2}{0.075 - x} = 5.8 \times 10^{-10}$$

Predicting whether $0.075 - x \doteq 0.075$:

$$\frac{[\text{HA}]_{\text{initial}}}{K_a} = \frac{0.075 \text{ mol/L}}{5.8 \times 10^{-10}}$$

$$\frac{[\text{HA}]_{\text{initial}}}{K_a} = 1.3 \times 10^9$$

Since $1.3 \times 10^9 > 100$, we assume that $0.075 - x \doteq 0.075$.

$$\frac{x^2}{(0.075)} \doteq 5.8 \times 10^{-10}$$

$$x \doteq 6.595 \times 10^{-6} \quad (\text{extra digits carried})$$

$$[\text{H}_{(\text{aq})}^+] = 6.595 \times 10^{-6} \text{ mol/L}$$

$$\begin{aligned} \text{pH} &= -\log[\text{H}_{(\text{aq})}^+] \\ &= -\log[6.595 \times 10^{-6}] \end{aligned}$$

$$\text{pH} = 5.181$$

The pH at the equivalence point is 5.18.

PRACTICE

(Page 611)

Understanding Concepts

7. Since this is a titration of a weak base with a strong acid, the equivalence point will occur at pH less than 7. Alizarin yellow's pH range is 10.1–12.0, beyond the required equivalence point.
8. Indicators are weak acids in equilibrium with their conjugate base. At the endpoint some titrant is required to “neutralize” the indicator. A small volume of indicator solution is used to keep the titrant volume required to produce the colour change insignificant to the results of the titration.
9. Since this is a titration of a weak acid with a strong base, the equivalence point will occur at pH greater than 7. However, methyl red has a pH range of 4.8–6.0, well below the equivalence point. As a result, the endpoint of the titration occurs before the equivalence point is reached.

PRACTICE

(Page 613)

Understanding Concepts

10. (a) $\text{PO}_{4(\text{aq})}^{3-} + \text{H}_{(\text{aq})}^+ \rightarrow \text{HPO}_{4(\text{aq})}^{2-}$
 $\text{HPO}_{4(\text{aq})}^{2-} + \text{H}_{(\text{aq})}^+ \rightarrow \text{H}_2\text{PO}_{4(\text{aq})}^-$
 $\text{H}_2\text{PO}_{4(\text{aq})}^- + \text{H}_{(\text{aq})}^+ \rightarrow \text{H}_3\text{PO}_{4(\text{aq})}$
- (b) 25 mL and 50 mL
- (c) The hydrogen phosphate ion, $\text{HPO}_{4(\text{aq})}^{2-}$, is an extremely weak acid ($K_a = 4.2 \times 10^{-13}$) and does not lose its proton quantitatively. Only quantitative reactions produce detectable endpoints in an acid–base titration.

SECTION 8.4 QUESTIONS

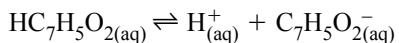
(Page 613)

Understanding Concepts

1. (a) The endpoint is at pH 9 and the equivalence point is at 26 mL.
(b) Phenolphthalein
(c) $\text{HC}_2\text{H}_3\text{O}_{2(\text{aq})} + \text{OH}_{(\text{aq})}^- \rightarrow \text{C}_2\text{H}_3\text{O}_{2(\text{aq})}^- + \text{H}_2\text{O}_{(\text{l})}$
2. (a) 7
(b) >7

- (c) 7
 (d) <7
3. (a) <7
 (b) >7
 (c) =7
4. A pH curve is used to determine the pH of the solution at the equivalence point of a titration, so that a suitable indicator that will change colour at that endpoint can be chosen.
5. (a) pink
 (b) yellow
 (c) blue
 (d) red-orange
6. (a)

ICE Table for the Ionization of $\text{HC}_7\text{H}_5\text{O}_{2(\text{aq})}$			
	$\text{HC}_7\text{H}_5\text{O}_{2(\text{aq})} \rightleftharpoons$	$\text{H}_{(\text{aq})}^+$ +	$\text{C}_7\text{H}_5\text{O}_{2(\text{aq})}^-$
Initial concentration (mol/L)	0.100	0.000	0.000
Change in concentration (mol/L)	$-x$	$+x$	$+x$
Equilibrium concentration (mol/L)	$0.100 - x$	x	x



$$K_a = \frac{[\text{H}_{(\text{aq})}^+][\text{C}_7\text{H}_5\text{O}_{2(\text{aq})}^-]}{[\text{HC}_7\text{H}_5\text{O}_{2(\text{aq})}]}$$

$$\frac{x^2}{0.100 - x} = 6.3 \times 10^{-5}$$

Predicting whether $0.100 - x \doteq 0.100 \dots$

$$\frac{[\text{HA}]_{\text{initial}}}{K_a} = \frac{0.100 \text{ mol/L}}{6.3 \times 10^{-5}}$$

$$\frac{[\text{HA}]_{\text{initial}}}{K_a} = 1580$$

Since $1580 > 100$, we assume that $0.100 - x \doteq 0.100$.

$$\frac{x^2}{(0.100)} \doteq 6.3 \times 10^{-5}$$

$$x^2 \doteq 6.3 \times 10^{-6}$$

$$x = 2.51 \times 10^{-3} \quad (\text{extra digits carried})$$

The 5% rule justifies the assumption.

$$[\text{H}_{(\text{aq})}^+] = 2.51 \times 10^{-3} \text{ mol/L}$$

$$\text{pH} = -\log [\text{H}_{(\text{aq})}^+]$$

$$= -\log [2.51 \times 10^{-3}]$$

$$\text{pH} = 2.600$$

The pH of the solution is 2.600.

- (b) $V_{\text{HC}_7\text{H}_5\text{O}_{2(\text{aq})}} = 25.00 \text{ mL}$
 $C_{\text{HC}_7\text{H}_5\text{O}_{2(\text{aq})}} = 0.100 \text{ mol/L}$
 $n_{\text{HC}_7\text{H}_5\text{O}_{2(\text{aq})}} = V_{\text{HC}_7\text{H}_5\text{O}_{2(\text{aq})}} \times C_{\text{HC}_7\text{H}_5\text{O}_{2(\text{aq})}}$
 $= 25.00 \text{ mL} \times 0.100 \text{ mol/L}$
 $n_{\text{HC}_7\text{H}_5\text{O}_{2(\text{aq})}} = 2.50 \text{ mmol}$

$$\begin{aligned}V_{\text{NaOH}_{(\text{aq})}} &= 10.00 \text{ mL} \\C_{\text{NaOH}_{(\text{aq})}} &= 0.100 \text{ mol/L} \\n_{\text{NaOH}_{(\text{aq})}} &= V_{\text{NaOH}_{(\text{aq})}} \times C_{\text{NaOH}_{(\text{aq})}} \\&= 10.00 \text{ mL} \times 0.100 \text{ mol/L}\end{aligned}$$

$$\begin{aligned}n_{\text{NaOH}_{(\text{aq})}} &= 1.00 \text{ mmol} \\n_{\text{HC}_7\text{H}_5\text{O}_{2(\text{aq})}} &\text{ remaining } \dots\end{aligned}$$

$$n_{\text{HC}_7\text{H}_5\text{O}_{2(\text{aq})}} = 2.50 \text{ mmol} - 1.00 \text{ mmol}$$

$$n_{\text{HC}_7\text{H}_5\text{O}_{2(\text{aq})}} = 1.50 \text{ mmol}$$

$$\text{Total volume} = 25.00 \text{ mL} + 10.00 \text{ mL}$$

$$= 35.00 \text{ mL}$$

$$C_{\text{HC}_7\text{H}_5\text{O}_{2(\text{aq})}} = \frac{1.50 \text{ mmol}}{35.00 \text{ mL}}$$

$$C_{\text{HC}_7\text{H}_5\text{O}_{2(\text{aq})}} = 0.04286 \text{ mol/L} \quad (\text{extra digits carried})$$

$$C_{\text{C}_7\text{H}_5\text{O}_{2(\text{aq})}^-} = \frac{1.00 \text{ mmol}}{35.00 \text{ mL}}$$

$$C_{\text{C}_7\text{H}_5\text{O}_{2(\text{aq})}^-} = 0.02857 \text{ mol/L} \quad (\text{extra digits carried})$$

Let x represent the changes in concentration that occur as the system reestablishes equilibrium.

ICE Table for the Ionization of $\text{HC}_7\text{H}_5\text{O}_{2(\text{aq})}$			
	$\text{HC}_7\text{H}_5\text{O}_{2(\text{aq})} \rightleftharpoons$	$\text{H}_{(\text{aq})}^+ +$	$\text{C}_7\text{H}_5\text{O}_{2(\text{aq})}^-$
Initial concentration (mol/L)	0.04286	0.000	0.02857
Change in concentration (mol/L)	$-x$	$+x$	$+x$
Equilibrium concentration (mol/L)	$0.04286 - x$	x	$0.02857 + x$

$$\frac{[\text{H}_{(\text{aq})}^+][\text{C}_7\text{H}_5\text{O}_{2(\text{aq})}^-]}{[\text{HC}_7\text{H}_5\text{O}_{2(\text{aq})}]} = K_a$$

$$\frac{x(0.02857 + x)}{0.04286 - x} = 6.3 \times 10^{-5}$$

Checking whether an approximation is warranted:

$$\begin{aligned}\frac{[\text{HC}_7\text{H}_5\text{O}_{2(\text{aq})}]_{\text{initial}}}{K_a} &= \frac{0.100}{6.3 \times 10^{-5}} \\&= 1600\end{aligned}$$

Since $1600 > 100$, we can assume that $0.04286 - x \doteq 0.04286$ and that $0.02857 + x \doteq 0.02857$.

The equilibrium simplifies to

$$\begin{aligned}\frac{x(0.02857)}{0.04286} &= 6.3 \times 10^{-5} \\x &= 9.45 \times 10^{-5}\end{aligned}$$

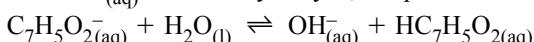
The 5% rule validates the assumption:

$$\begin{aligned}[\text{H}_{(\text{aq})}^+] &\doteq 9.45 \times 10^{-5} \text{ mol/L} \\-\log[\text{H}_{(\text{aq})}^+] &\doteq -\log[9.45 \times 10^{-5}] \\-\log[\text{H}_{(\text{aq})}^+] &\doteq 4.03\end{aligned}$$

- (c) At the equivalence point, 25.00 mL of 0.100 mol/L $\text{NaOH}_{(\text{aq})}$ were added.

Entities remaining in solution: $\text{Na}^+_{(\text{aq})}$, $\text{C}_7\text{H}_5\text{O}_2^-_{(\text{aq})}$, $\text{H}_2\text{O}_{(\text{l})}$

Since $\text{Na}^+_{(\text{aq})}$ does not hydrolyze, the pH is determined by the benzoate ion.



$$\frac{[\text{OH}^-_{(\text{aq})}][\text{HC}_7\text{H}_5\text{O}_2_{(\text{aq})}]}{[\text{C}_7\text{H}_5\text{O}_2^-_{(\text{aq})}]} = K_b$$

$$K_a = 6.3 \times 10^{-5}$$

$$\begin{aligned} K_b &= \frac{K_w}{K_a} \\ &= \frac{1.0 \times 10^{-14}}{6.3 \times 10^{-5}} \end{aligned}$$

$$K_b = 1.587 \times 10^{-10} \quad (\text{extra digits carried})$$

Therefore,

$$\frac{[\text{OH}^-_{(\text{aq})}][\text{HC}_7\text{H}_5\text{O}_2_{(\text{aq})}]}{[\text{C}_7\text{H}_5\text{O}_2^-_{(\text{aq})}]} = 1.587 \times 10^{-10}$$

At the equivalence point, the total volume is 50 mL.

Since 2.50 mmol of $\text{HC}_7\text{H}_5\text{O}_2_{(\text{aq})}$ was present initially, 2.50 mmol of $\text{C}_7\text{H}_5\text{O}_2^-_{(\text{aq})}$ is present at the equivalence point.

$$[\text{C}_7\text{H}_5\text{O}_2^-_{(\text{aq})}] = \frac{2.50 \text{ mmol}}{50.00 \text{ mL}}$$

$$[\text{C}_7\text{H}_5\text{O}_2^-_{(\text{aq})}] = 0.0500 \text{ mol/L}$$

ICE Table for the Hydrolysis of $\text{C}_7\text{H}_5\text{O}_2^-_{(\text{aq})}$				
	$\text{C}_7\text{H}_5\text{O}_2^-_{(\text{aq})} +$	$\text{H}_2\text{O}_{(\text{l})} \rightleftharpoons$	$\text{OH}^-_{(\text{aq})} +$	$\text{HC}_7\text{H}_5\text{O}_2_{(\text{aq})}$
Initial concentration (mol/L)	0.0500	–	0.000	0.000
Change in concentration (mol/L)	$-x$	–	$+x$	$+x$
Equilibrium concentration (mol/L)	$0.0500 - x$	–	x	x

$$\frac{[\text{HC}_7\text{H}_5\text{O}_2_{(\text{aq})}][\text{OH}^-_{(\text{aq})}]}{[\text{C}_7\text{H}_5\text{O}_2^-_{(\text{aq})}]} = 1.587 \times 10^{-10}$$

$$\frac{x^2}{0.0500 - x} = 1.587 \times 10^{-10}$$

Checking whether an approximation is warranted:

$$\begin{aligned} \frac{[\text{C}_7\text{H}_5\text{O}_2^-_{(\text{aq})}]_{\text{initial}}}{K} &= \frac{0.0500}{1.587 \times 10^{-10}} \\ &= 3.2 \times 10^8 \end{aligned}$$

Since $3.2 \times 10^8 > 100$, we can assume that $0.0500 - x \doteq 0.0500$.

The equilibrium simplifies to

$$\frac{x^2}{0.0500} = 1.587 \times 10^{-10}$$

$$x = 2.82 \times 10^{-6}$$

(The 5% rule verifies the assumption.)

$$[\text{OH}_{(\text{aq})}^-] \doteq 2.82 \times 10^{-6} \text{ mol/L}$$

$$\text{pOH} \doteq -\log[2.82 \times 10^{-6}]$$

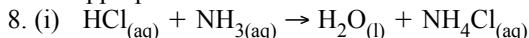
$$\text{pOH} = 5.550$$

$$\text{pH} = 14 - \text{pOH}$$

$$\text{pH} = 8.450$$

The pH at the equivalence point is 8.450.

7. An appropriate indicator for this titration is alizarin yellow.



At the equivalence point, $n_{\text{acid}} = n_{\text{base}}$

$$\begin{aligned} \therefore C_{\text{acid}} V_{\text{acid}} &= C_{\text{base}} V_{\text{base}} \\ V_{\text{HCl}_{(\text{aq})}\text{ required}} &= \frac{C_{\text{NH}_3_{(\text{aq})}} \times V_{\text{NH}_3_{(\text{aq})}}}{C_{\text{HCl}_{(\text{aq})}}} \\ &= \frac{0.100 \text{ mol/L} \times 20.0 \text{ mL}}{0.200 \text{ mol/L}} \end{aligned}$$

$$V_{\text{HCl}_{(\text{aq})}\text{ required}} = 10.0 \text{ mL NaOH}$$

Final solution volume = 30.0 mL

Entities in solution at the equivalence point: $\text{Cl}_{(\text{aq})}^-$, $\text{NH}_4^+_{(\text{aq})}$, $\text{H}_2\text{O}_{(\text{l})}$

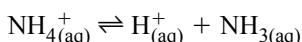
Since $\text{Cl}_{(\text{aq})}^-$ does not hydrolyze, pH is determined by the ammonium ion.



Since 2.00 mmol of $\text{NH}_3_{(\text{aq})}$ was present initially, 2.00 mmol of $\text{NH}_4^+_{(\text{aq})}$ is present at the equivalence point.

$$[\text{NH}_4^+_{(\text{aq})}] = \frac{2.00 \text{ mmol}}{30.0 \text{ mL}}$$

$$[\text{NH}_4^+_{(\text{aq})}] = 0.0667 \text{ mol/L}$$



$$\frac{[\text{H}^+_{(\text{aq})}][\text{NH}_3_{(\text{aq})}]}{[\text{NH}_4^+_{(\text{aq})}]} = 5.8 \times 10^{-10}$$

ICE Table for the Hydrolysis of $\text{NH}_4^+_{(\text{aq})}$			
	$\text{NH}_4^+_{(\text{aq})} \rightleftharpoons$	$\text{H}^+_{(\text{aq})} +$	$\text{NH}_3_{(\text{aq})}$
Initial concentration (mol/L)	0.0667	0.000	0.000
Change in concentration (mol/L)	$-x$	$+x$	$+x$
Equilibrium concentration (mol/L)	$0.0667 - x$	x	x

$$\frac{[\text{H}^+_{(\text{aq})}][\text{NH}_3_{(\text{aq})}]}{[\text{NH}_4^+_{(\text{aq})}]} = 5.8 \times 10^{-10}$$

$$\frac{x^2}{0.0667 - x} = 5.8 \times 10^{-10}$$

Checking whether an approximation is warranted:

$$\frac{[\text{NH}_4^+_{(\text{aq})}]_{\text{initial}}}{K_a} = \frac{0.0667}{5.8 \times 10^{-10}} > 100$$

The equilibrium simplifies to

$$\frac{x^2}{0.0667} = 5.8 \times 10^{-10}$$

$$x = 6.22 \times 10^{-6}$$

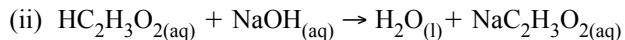
The 5% rule verifies the assumption.

$$[\text{H}_{(\text{aq})}^+] \doteq 6.22 \times 10^{-6} \text{ mol/L}$$

$$\text{pH} \doteq -\log[6.22 \times 10^{-6}]$$

$$\text{pH} = 5.206$$

The pH at the equivalence point is 5.206.

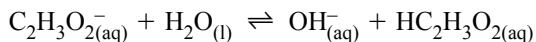


$$\begin{aligned} V_{\text{NaOH required}} &= \frac{C_{\text{HC}_2\text{H}_3\text{O}_{2(\text{aq})}} \times V_{\text{HC}_2\text{H}_3\text{O}_{2(\text{aq})}}}{C_{\text{NaOH}}} \\ &= \frac{0.350 \text{ mol/L} \times 10.0 \text{ mL}}{0.150 \text{ mol/L}} \end{aligned}$$

$$V_{\text{NaOH required}} = 23.3 \text{ mL NaOH}$$

Entities remaining in solution at the equivalence point: $\text{Na}_{(\text{aq})}^+$, $\text{C}_2\text{H}_3\text{O}_{2(\text{aq})}^-$, $\text{H}_2\text{O}_{(\text{l})}$

Since $\text{Na}_{(\text{aq})}^+$ does not hydrolyze, the pH of the solution is determined by the acetate ion.



$$\frac{[\text{OH}_{(\text{aq})}^-][\text{HC}_2\text{H}_3\text{O}_{2(\text{aq})}]}{[\text{C}_2\text{H}_3\text{O}_{2(\text{aq})}^-]} = K_b$$

$$K_b = 1.8 \times 10^{-5}$$

$$\begin{aligned} K_b &= \frac{K_w}{K_a} \\ &= \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} \end{aligned}$$

$$K_b = 5.555 \times 10^{-10} \quad (\text{extra digits carried})$$

Therefore,

$$\frac{[\text{OH}_{(\text{aq})}^-][\text{HC}_2\text{H}_3\text{O}_{2(\text{aq})}]}{[\text{C}_2\text{H}_3\text{O}_{2(\text{aq})}^-]} = 5.555 \times 10^{-10}$$

At the equivalence point, the total volume = 33.33 mL.

Since 3.50 mmol of $\text{HC}_2\text{H}_3\text{O}_{2(\text{aq})}$ was present initially, 3.50 mmol of $\text{C}_2\text{H}_3\text{O}_{2(\text{aq})}^-$ is present at the equivalence point.

$$[\text{C}_2\text{H}_3\text{O}_{2(\text{aq})}^-] = \frac{3.50 \text{ mmol}}{33.33 \text{ mL}}$$

$$[\text{C}_2\text{H}_3\text{O}_{2(\text{aq})}^-] = 0.105 \text{ mol/L}$$

ICE Table for the Hydrolysis of $\text{C}_2\text{H}_3\text{O}_{2(\text{aq})}^-$				
	$\text{C}_2\text{H}_3\text{O}_{2(\text{aq})}^- +$	$\text{H}_2\text{O}_{(\text{l})} \rightleftharpoons$	$\text{OH}_{(\text{aq})}^- +$	$\text{HC}_2\text{H}_3\text{O}_{2(\text{aq})}$
Initial concentration (mol/L)	0.105	-	0.000	0.000
Change in concentration (mol/L)	$-x$	-	$+x$	$+x$
Equilibrium concentration (mol/L)	$0.105 - x$	-	x	x

$$\frac{[\text{HC}_2\text{H}_3\text{O}_{2(\text{aq})}][\text{OH}_{(\text{aq})}^-]}{[\text{C}_2\text{H}_3\text{O}_{2(\text{aq})}^-]} = 5.556 \times 10^{-10}$$

$$\frac{x^2}{0.105 - x} = 5.556 \times 10^{-10}$$

Checking whether an approximation is warranted:

$$\frac{[\text{C}_2\text{H}_3\text{O}_{2(\text{aq})}]_{\text{initial}}}{K} = \frac{0.105}{5.556 \times 10^{-10}} > 100$$

The equilibrium simplifies to

$$\frac{x^2}{0.105} = 5.556 \times 10^{-10}$$

$$x = 7.64 \times 10^{-6}$$

The 5% rule verifies the assumption.

$$[\text{OH}_{(\text{aq})}] \doteq 7.64 \times 10^{-6} \text{ mol/L}$$

$$\text{pOH} \doteq -\log[7.64 \times 10^{-6}]$$

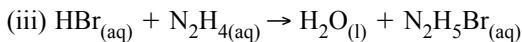
$$= 5.117$$

$$\text{pH} = 14 - \text{pOH}$$

$$= 14 - 5.117$$

$$\text{pH} = 8.883$$

The pH at the equivalence point is 8.883.



at the equivalence point, $n_{\text{acid}} = n_{\text{base}}$

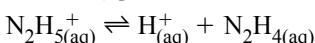
$$\begin{aligned} V_{\text{HBr}_{(\text{aq})} \text{ required}} &= \frac{C_{\text{N}_2\text{H}_4_{(\text{aq})}} \times V_{\text{N}_2\text{H}_4_{(\text{aq})}}}{C_{\text{HBr}_{(\text{aq})}}} \\ &= \frac{0.150 \text{ mol/L} \times 15.0 \text{ mL}}{0.250 \text{ mol/L}} \end{aligned}$$

$$V_{\text{HBr}_{(\text{aq})} \text{ required}} = 9.00 \text{ mL HBr}_{(\text{aq})}$$

Final solution volume = 24.0 mL

Entities remaining in solution at the equivalence point: $\text{Br}_{(\text{aq})}^-$, N_2H_5^+ , $\text{H}_2\text{O}_{(\text{l})}$

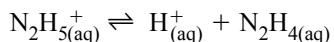
Since $\text{Br}_{(\text{aq})}^-$ does not hydrolyze, the pH of the solution is determined by N_2H_5^+ .



Since 2.25 mmol of $\text{N}_2\text{H}_4_{(\text{aq})}$ was present initially, 2.25 mmol of N_2H_5^+ is present at the equivalence point.

$$[\text{N}_2\text{H}_{5(\text{aq})}^+] = \frac{2.25 \text{ mmol}}{24.0 \text{ mL}}$$

$$[\text{N}_2\text{H}_{5(\text{aq})}^+] = 0.0938 \text{ mol/L}$$



$$\begin{aligned}\frac{[\text{H}_{(\text{aq})}^+][\text{N}_2\text{H}_{4(\text{aq})}]}{[\text{N}_2\text{H}_{5(\text{aq})}^+]} &= \frac{K_w}{K_b} \\ &= \frac{1.0 \times 10^{-14}}{9.6 \times 10^{-7}} \\ &= 1.04 \times 10^{-8} \quad (\text{extra digits carried})\end{aligned}$$

ICE Table for the Hydrolysis of $\text{N}_2\text{H}_{5(\text{aq})}^+$				
	$\text{N}_2\text{H}_{5(\text{aq})}^+ +$	$\text{H}_2\text{O}_{(\text{l})} \rightleftharpoons$	$\text{OH}_{(\text{aq})}^- +$	$\text{N}_2\text{H}_{4(\text{aq})}$
Initial concentration (mol/L)	0.0938	-	0.000	0.000
Change in concentration (mol/L)	$-x$	-	$+x$	$+x$
Equilibrium concentration (mol/L)	$0.0938 - x$	-	x	x



$$\begin{aligned}\frac{[\text{H}_{(\text{aq})}^+][\text{N}_2\text{H}_{4(\text{aq})}]}{[\text{N}_2\text{H}_{5(\text{aq})}^+]} &= 1.04 \times 10^{-8} \\ \frac{x^2}{0.0938 - x} &= 1.04 \times 10^{-8}\end{aligned}$$

Checking whether an approximation is warranted:

$$\frac{[\text{N}_2\text{H}_{5(\text{aq})}^+]_{\text{initial}}}{K_a} = \frac{0.0938}{1.04 \times 10^{-8}} > 100$$

The equilibrium simplifies to

$$\frac{x^2}{0.0938} = 1.04 \times 10^{-8}$$

$$x = 3.12 \times 10^{-5}$$

The 5% rule verifies the assumption.

$$[\text{H}_{(\text{aq})}^+] \doteq 3.12 \times 10^{-5} \text{ mol/L}$$

$$\text{pH} \doteq -\log[3.12 \times 10^{-5}]$$

$$\text{pH} = 4.505$$

The pH at the equivalence point is 4.505.

(b) Appropriate indicators: methyl orange, bromophenol blue.

$$9. \quad V_{\text{HC}_2\text{H}_3\text{O}_{2(\text{aq})}} = 45.00 \text{ mL}$$

$$C_{\text{HC}_2\text{H}_3\text{O}_{2(\text{aq})}} = 0.10 \text{ mol/L}$$

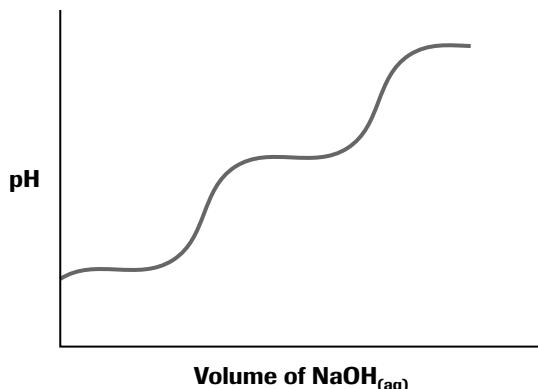
$$\begin{aligned}
 n_{\text{HC}_2\text{H}_3\text{O}_2\text{(aq)}} &= V_{\text{HC}_2\text{H}_3\text{O}_2\text{(aq)}} \times C_{\text{HC}_2\text{H}_3\text{O}_2\text{(aq)}} \\
 &= 45.00 \text{ mL} \times 0.10 \text{ mol/L} \\
 n_{\text{HC}_2\text{H}_3\text{O}_2\text{(aq)}} &= 4.5 \text{ mmol} \\
 V_{\text{NaOH}_{\text{(aq)}}} &= 25.00 \text{ mL} \\
 C_{\text{NaOH}_{\text{(aq)}}} &= 0.23 \text{ mol/L} \\
 n_{\text{NaOH}_{\text{(aq)}}} &= V_{\text{NaOH}_{\text{(aq)}}} \times C_{\text{NaOH}_{\text{(aq)}}} \\
 &= 25.00 \text{ mL} \times 0.23 \text{ mol/L} \\
 n_{\text{NaOH}_{\text{(aq)}}} &= 5.75 \text{ mmol} \quad (\text{extra digit carried}) \\
 n_{\text{NaOH}_{\text{(aq)}}} &\text{ remaining ...} \\
 n_{\text{NaOH}_{\text{(aq)}}} &= 5.75 \text{ mmol} - 4.5 \text{ mmol} \\
 n_{\text{NaOH}_{\text{(aq)}}} &= 1.25 \text{ mmol} \\
 \text{Total volume} &= 25.00 \text{ mL} + 45.00 \text{ mL} \\
 &= 70.00 \text{ mL} \\
 C_{\text{NaOH}_{\text{(aq)}}} &= \frac{1.25 \text{ mmol}}{70.00 \text{ mL}} \\
 C_{\text{NaOH}_{\text{(aq)}}} &= 0.0179 \text{ mol/L} \quad (\text{extra digits carried}) \\
 [\text{OH}^-_{\text{(aq)}}] &= 0.0179 \text{ mol/L} \\
 \text{pOH} &= -\log(0.0179) \\
 \text{pOH} &= 1.748 \\
 \text{pH} &= 12.25
 \end{aligned}$$

The pH of the resulting solution is 12.25.

10. (a) The pH is between 5.6 and 6.0.
 (b) The pH is approximately 6, which corresponds to a $[\text{H}^+_{\text{(aq)}}]$ of 1.0×10^{-6} mol/L.

Applying Inquiry Skills

11. Oxalic Acid Reacted with Sodium Hydroxide



12. A: between 4.4 and 4.8
 B: between 6.0 and 6.6
 C: between 2.8 and 3.2

13. The three solutions are tested with bromocresol green indicator. The pH 3.5 solution is the only solution that is yellow in bromocresol green indicator. The two remaining solutions are tested with cresol red indicator. The pH 7.8 solution is the only solution that is red in cresol red indicator. The remaining solution must be pH 5.8. This can be verified by testing the solution with litmus and bromophenol blue. It should be red in litmus and blue-violet in bromophenol blue.
14. From strongest to weakest: nitric and hydrochloric acid are identical, hydrofluoric acid, methanoic acid, acetic acid, and hydrocyanic acid.

8.5 BUFFERS

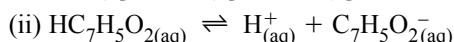
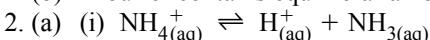
PRACTICE

(Page 620)

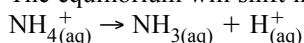
Understanding Concepts

1. (a) A good buffer solution maintains a nearly constant pH when diluted or when a strong acid or base is added.

(b) A buffer contains equimolar amounts of a weak acid and its conjugate base.

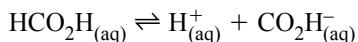


(b) The equilibrium will shift in the direction of the conjugate acid:



3. $[\text{CO}_2\text{H}_\text{(aq)}^-] = 1.5 \text{ mol/L}$

$$[\text{HCO}_2\text{H}_\text{(aq)}] = 1.5 \text{ mol/L}$$



$$\frac{[\text{H}_\text{(aq)}^+][\text{CO}_2\text{H}_\text{(aq)}^-]}{[\text{HCO}_2\text{H}_\text{(aq)}]} = 1.8 \times 10^{-4}$$

$$[\text{H}_\text{(aq)}^+] = K_a \frac{[\text{HCO}_2\text{H}_\text{(aq)}]}{[\text{CO}_2\text{H}_\text{(aq)}^-]}$$

$$= 1.8 \times 10^{-4} \times \frac{1.5 \text{ mol/L}}{1.5 \text{ mol/L}}$$

$$[\text{H}_\text{(aq)}^+] = 1.8 \times 10^{-4}$$

$$\text{pH} = -\log[1.8 \times 10^{-4}]$$

$$\text{pH} = 3.74$$

The addition of $\text{H}_\text{(aq)}^+$...

$$[\text{H}_\text{(aq)}^+]_{\text{added}} = 0.13 \text{ mol/L}$$

$$[\text{HCO}_2\text{H}_\text{(aq)}]_{\text{final}} = (1.5 + 0.13) \text{ mol/L}$$

$$[\text{HCO}_2\text{H}_\text{(aq)}]_{\text{final}} = 1.63 \text{ mol/L}$$

$$[\text{CO}_2\text{H}_\text{(aq)}^-]_{\text{final}} = (1.5 - 0.13) \text{ mol/L}$$

$$[\text{CO}_2\text{H}_\text{(aq)}^-]_{\text{final}} = 1.37 \text{ mol/L}$$

$$[\text{H}_\text{(aq)}^+] = K_a \frac{[\text{HCO}_2\text{H}_\text{(aq)}]}{[\text{CO}_2\text{H}_\text{(aq)}^-]}$$

$$= 1.8 \times 10^{-4} \times \frac{1.63}{1.37}$$

$$[\text{H}_\text{(aq)}^+] = 2.1 \times 10^{-4}$$

$$\text{pH} = 3.67$$

13. The three solutions are tested with bromocresol green indicator. The pH 3.5 solution is the only solution that is yellow in bromocresol green indicator. The two remaining solutions are tested with cresol red indicator. The pH 7.8 solution is the only solution that is red in cresol red indicator. The remaining solution must be pH 5.8. This can be verified by testing the solution with litmus and bromophenol blue. It should be red in litmus and blue-violet in bromophenol blue.
14. From strongest to weakest: nitric and hydrochloric acid are identical, hydrofluoric acid, methanoic acid, acetic acid, and hydrocyanic acid.

8.5 BUFFERS

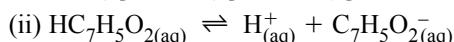
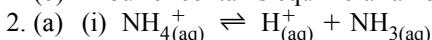
PRACTICE

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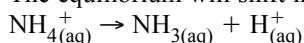
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(b) A buffer contains equimolar amounts of a weak acid and its conjugate base.

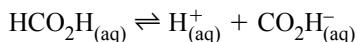


(b) The equilibrium will shift in the direction of the conjugate acid:



3. $[\text{CO}_2\text{H}_\text{(aq)}^-] = 1.5 \text{ mol/L}$

$$[\text{HCO}_2\text{H}_\text{(aq)}] = 1.5 \text{ mol/L}$$



$$\frac{[\text{H}_\text{(aq)}^+][\text{CO}_2\text{H}_\text{(aq)}^-]}{[\text{HCO}_2\text{H}_\text{(aq)}]} = 1.8 \times 10^{-4}$$

$$[\text{H}_\text{(aq)}^+] = K_a \frac{[\text{HCO}_2\text{H}_\text{(aq)}]}{[\text{CO}_2\text{H}_\text{(aq)}^-]}$$

$$= 1.8 \times 10^{-4} \times \frac{1.5 \text{ mol/L}}{1.5 \text{ mol/L}}$$

$$[\text{H}_\text{(aq)}^+] = 1.8 \times 10^{-4}$$

$$\text{pH} = -\log[1.8 \times 10^{-4}]$$

$$\text{pH} = 3.74$$

The addition of $\text{H}_\text{(aq)}^+$...

$$[\text{H}_\text{(aq)}^+]_{\text{added}} = 0.13 \text{ mol/L}$$

$$[\text{HCO}_2\text{H}_\text{(aq)}]_{\text{final}} = (1.5 + 0.13) \text{ mol/L}$$

$$[\text{HCO}_2\text{H}_\text{(aq)}]_{\text{final}} = 1.63 \text{ mol/L}$$

$$[\text{CO}_2\text{H}_\text{(aq)}^-]_{\text{final}} = (1.5 - 0.13) \text{ mol/L}$$

$$[\text{CO}_2\text{H}_\text{(aq)}^-]_{\text{final}} = 1.37 \text{ mol/L}$$

$$[\text{H}_\text{(aq)}^+] = K_a \frac{[\text{HCO}_2\text{H}_\text{(aq)}]}{[\text{CO}_2\text{H}_\text{(aq)}^-]}$$

$$= 1.8 \times 10^{-4} \times \frac{1.63}{1.37}$$

$$[\text{H}_\text{(aq)}^+] = 2.1 \times 10^{-4}$$

$$\text{pH} = 3.67$$

$$\Delta \text{pH} = 3.74 - 3.67$$

$$\Delta \text{pH} = 0.07$$

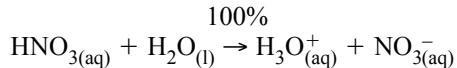
The change in pH is 0.07.

SECTION 8.5 QUESTIONS

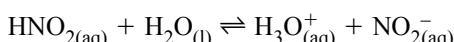
(Page 620)

Understanding Concepts

1. A buffer is a mixture of a conjugate acid–base pair that maintains a nearly constant pH when diluted or when a strong acid or base is added.
2. Phosphate and carbonate buffers help maintain a normal pH level in the human body.
3. (a) $\text{H}_2\text{CO}_{3(\text{aq})} \rightarrow \text{H}_{(\text{aq})}^+ + \text{HCO}_{3(\text{aq})}^-$
(b) $\text{H}_{(\text{aq})}^+ + \text{HCO}_{3(\text{aq})}^- \rightarrow \text{H}_2\text{CO}_{3(\text{aq})}$
(c) $\text{H}_2\text{CO}_{3(\text{aq})} + \text{OH}_{(\text{aq})}^- \rightarrow \text{H}_2\text{O}_{(\text{l})} + \text{HCO}_{3(\text{aq})}^-$
4. A large excess of strong acid or base can drive the buffer equilibrium to completion. For example, the addition of $\text{HCl}_{(\text{aq})}$ to the carbonate buffer shifts the equilibrium in question 3(a) completely to the left.
5. $\text{HC}_2\text{H}_3\text{O}_{2(\text{aq})} \rightleftharpoons \text{H}_{(\text{aq})}^+ + \text{C}_2\text{H}_3\text{O}_{2(\text{aq})}^-$
 - (a) The addition of a small amount of $\text{HCl}_{(\text{aq})}$ shifts the equilibrium to the left, consuming some acetate.
 - (b) $\text{NaOH}_{(\text{aq})}$ consumes $\text{H}_{(\text{aq})}^+$, which causes the equilibrium to shift to the right.
6. (a) base
(b) acid
(c) neutral
(d) base
Lowest pH: (b), (c), (d), (a)
7. (a) and (c) will not form effective buffers because they consist of strong acids and bases. Conversely, (b) and (d) will form buffer systems because these mixtures consist of weak acids and their conjugate bases.
8. (a) The pH of nitric acid is much lower than that of nitrous acid.
(b) Nitric acid is such a strong acid that it completely donates its hydrogen to water:

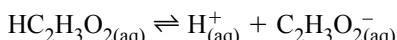


Nitrous acid only partially donates its hydrogen to water. Some molecular nitrous acid remains.



$$[\text{C}_2\text{H}_3\text{O}_{2(\text{aq})}^-] = 0.25 \text{ mol/L}$$

$$[\text{HC}_2\text{H}_3\text{O}_{2(\text{aq})}] = 0.25 \text{ mol/L}$$



$$[\text{H}_{(\text{aq})}^+] [\text{C}_2\text{H}_3\text{O}_{2(\text{aq})}^-] = 1.8 \times 10^{-5}$$

$$[\text{H}_{(\text{aq})}^+] = K_a \frac{[\text{HC}_2\text{H}_3\text{O}_{2(\text{aq})}]}{[\text{C}_2\text{H}_3\text{O}_{2(\text{aq})}^-]}$$

$$= 1.8 \times 10^{-5} \times \frac{0.25 \text{ mol/L}}{0.25 \text{ mol/L}}$$
$$= 1.8 \times 10^{-5}$$

$$\text{pH} = -\log[1.8 \times 10^{-5}]$$

$$\text{pH} = 4.74$$

The addition of hydroxide ...

$$[\text{OH}_{(\text{aq})}]_{\text{added}} = 0.15 \text{ mol/L}$$

$$[\text{HC}_2\text{H}_3\text{O}_{2(\text{aq})}]_{\text{final}} = (0.25 - 0.15) \text{ mol/L}$$

$$[\text{HC}_2\text{H}_3\text{O}_{2(\text{aq})}]_{\text{final}} = 0.10 \text{ mol/L}$$

$$[\text{C}_2\text{H}_3\text{O}_{2(\text{aq})}^-]_{\text{final}} = (0.25 + 0.15) \text{ mol/L}$$

$$[\text{C}_2\text{H}_3\text{O}_{2(\text{aq})}^-]_{\text{final}} = 0.40 \text{ mol/L}$$

$$[\text{H}_{(\text{aq})}^+] = K_a \frac{[\text{HC}_2\text{H}_3\text{O}_{2(\text{aq})}]}{[\text{C}_2\text{H}_3\text{O}_{2(\text{aq})}^-]}$$

$$= 1.8 \times 10^{-5} \times \frac{0.10}{0.40}$$

$$[\text{H}_{(\text{aq})}^+] = 4.5 \times 10^{-6}$$

$$\text{pH} = 5.35$$

$$\Delta\text{pH} = 5.35 - 4.74$$

$$\Delta\text{pH} = 0.61$$

The change in pH is 0.61.

8.6 CASE STUDY: THE SCIENCE OF ACID DEPOSITION

PRACTICE

(Page 624)

Understanding Concepts

- Acid deposition is suspected as one of the causes of forest decline, particularly in forests at high altitudes and colder latitudes. (Sample table)

Evidence of acid rain damage	Alternative interpretations
The evidence clearly demonstrates that the Black Forest, for example, receives as much as 30 times more acid than if the rain fell through clean air. Damage to the trees includes yellowing, premature needle loss, and eventual death. Study of the tree rings shows that trees grow more slowly in areas subject to acid deposition.	Other scientists question the link between tree growth and acid deposition. They propose conflicting evidence that seedlings actually grow better in an acidic environment. They counter that the reduction in tree growth rate is more directly due to the reduction in mean annual temperature in the regions in question. This hypothesis is supported by empirical data. Other researchers indicate that ground-level ozone, rather than acid deposition, is implicated in the damage to the forests.

- (a) Scientific research on catalysis assisted the development of catalytic converter technology.
(b) Sensitive detection devices have helped scientific research in the reduction of sulfur oxide emissions.
(c) The technology that produces sulfur oxides (smelting and power generating) has a harmful impact on human health.
(d) Society provides the resources, through government funding, that enable scientific research on the causes and effects of acid deposition.
(e) Society affects technology by purchasing its products, such as cars with catalytic converters.

$$[\text{OH}_{(\text{aq})}]_{\text{added}} = 0.15 \text{ mol/L}$$

$$[\text{HC}_2\text{H}_3\text{O}_{2(\text{aq})}]_{\text{final}} = (0.25 - 0.15) \text{ mol/L}$$

$$[\text{HC}_2\text{H}_3\text{O}_{2(\text{aq})}]_{\text{final}} = 0.10 \text{ mol/L}$$

$$[\text{C}_2\text{H}_3\text{O}_{2(\text{aq})}^-]_{\text{final}} = (0.25 + 0.15) \text{ mol/L}$$

$$[\text{C}_2\text{H}_3\text{O}_{2(\text{aq})}^-]_{\text{final}} = 0.40 \text{ mol/L}$$

$$[\text{H}_{(\text{aq})}^+] = K_a \frac{[\text{HC}_2\text{H}_3\text{O}_{2(\text{aq})}]}{[\text{C}_2\text{H}_3\text{O}_{2(\text{aq})}^-]}$$

$$= 1.8 \times 10^{-5} \times \frac{0.10}{0.40}$$

$$[\text{H}_{(\text{aq})}^+] = 4.5 \times 10^{-6}$$

$$\text{pH} = 5.35$$

$$\Delta\text{pH} = 5.35 - 4.74$$

$$\Delta\text{pH} = 0.61$$

The change in pH is 0.61.

8.6 CASE STUDY: THE SCIENCE OF ACID DEPOSITION

PRACTICE

(Page 624)

Understanding Concepts

- Acid deposition is suspected as one of the causes of forest decline, particularly in forests at high altitudes and colder latitudes. (Sample table)

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- (a) Scientific research on catalysis assisted the development of catalytic converter technology.
(b) Sensitive detection devices have helped scientific research in the reduction of sulfur oxide emissions.
(c) The technology that produces sulfur oxides (smelting and power generating) has a harmful impact on human health.
(d) Society provides the resources, through government funding, that enable scientific research on the causes and effects of acid deposition.
(e) Society affects technology by purchasing its products, such as cars with catalytic converters.

Making Connections

3. (a)

ICE Table for the Formation of Carbonic Acid			
	$\text{CO}_{2(\text{aq})} +$	$\text{H}_2\text{O}_{(\text{l})} \rightleftharpoons$	$\text{H}_2\text{CO}_{3(\text{aq})}$
Initial concentration (mol/L)	1.2×10^{-5}	-	0.00
Change in concentration (mol/L)	$-x$	-	$+x$
Equilibrium concentration (mol/L)	$1.2 \times 10^{-5} - x$	-	x

$$\frac{x}{1.2 \times 10^{-5} - x} = 3.3 \times 10^{-2}$$

$$x = 4.541 \times 10^{-7} \quad (\text{extra digits carried})$$

$$x = [\text{H}_2\text{CO}_{3(\text{aq})}]$$

ICE Table for the Ionization of Carbonic Acid			
	$\text{H}_2\text{CO}_{3(\text{aq})} \rightleftharpoons$	$\text{H}_{(\text{aq})}^+ +$	$\text{HCO}_{3(\text{aq})}^-$
Initial concentration (mol/L)	4.541×10^{-7}	-	0.00
Change in concentration (mol/L)	$-x$	-	$+x$
Equilibrium concentration (mol/L)	$4.541 \times 10^{-7} - x$	-	x

$$\frac{x^2}{4.541 \times 10^{-7} - x} = 4.4 \times 10^{-4}$$

$$x^2 + 4.4 \times 10^{-4} x - 2.0 \times 10^{-13} = 0$$

$$x = 2.78 \times 10^{-7}$$

$$x = [\text{H}_{(\text{aq})}^+]$$

$$\text{pH} = -\log 2.78 \times 10^{-7}$$

$$\text{pH} = 6.55$$

The pH of natural rain is 6.55.

- (b) Carbonate or bicarbonate ions consume hydrogen from the rain, shifting the given equilibria to the right.
- (c) (Answers may vary. Answers might include the following:) Some of the effects of acid deposition can be temporarily relieved by adding large quantities of lime, calcium hydroxide, to the lakes. The long-term solution to the problem, of course, is to eliminate the source of the acid.

Explore an Issue: Take a Stand: Acting to Reduce the Effects

(Page 624)

- (a) Possible action plans include:

- creating a SO_x tax – industries are taxed on the level of their sulfur emissions.
- increasing the cost of gasoline by \$0.10/L.
- These sources of revenue could be used to research cleaner fuels.

- (b) Perspectives

Economic

For legislation: Acid deposition is endangering fishing tourism, agriculture, and forestry.

Against legislation: Regulations could severely hinder economic growth.

Social

For legislation: Failure to reduce acid rain will destroy the social fabric of fishing and logging communities.

Against legislation: Shutting down acid-rain-producing industries will severely affect the social fabric of communities depending on these industries.

Legal

For legislation: Both the Canadian and the American governments have passed legislation to reduce the discharge of sulfur and nitrogen oxides.

Against legislation: Passing laws will not solve the problem but only create difficulties for companies.

Ecological

For legislation: Sulfuric and sulfurous acids cause considerable damage when they fall to Earth in the form of acid deposition. Some environmental groups claimed that 14 000 Canadian lakes have been damaged by acid deposition. Acid deposition is also suspected as one of the causes of forest decline, particularly in forests at high altitudes and colder latitudes.

Against legislation: Some researchers report that acid deposition painted on seedlings in soil with inadequate nutrients actually has a beneficial effect on growth.

Scientific

For legislation: Empirical work indicates that the main causes of acid deposition in North America are sulfur dioxide, SO_2 , and nitrogen oxides, NO_x . In the atmosphere, SO_2 reacts with water to produce sulfurous acid, $\text{H}_2\text{SO}_3(\text{aq})$.

Against legislation: A 1988 U.S. federal task force maintained that damage to human health, crops, and forests by acid deposition is yet to be proven.

(c) and (d) (Answers will vary widely.)

PRACTICE

(Page 625)

Making Connections

1. Many medications require that the **hospital pharmacist** has a thorough knowledge of acids and base chemistry. For example, there are several antacid medications for treating peptic ulcer. Some pain relievers are weak acids that potentially can irritate the stomach of patients. The blood must be maintained within a very narrow pH range for the body to function properly. The pharmacist must be aware of the effects of medication on blood pH.

The **quality-control chemist** must ensure that product specifications are maintained during the manufacturing process. For example, samples of shampoo are checked regularly during a manufacturing process to ensure that their pH falls within required limits. Many pain relievers are weak acids. The amount of acid in a given tablet can be determined by conducting an acid–base titration to ensure that the tablet contains the required amount.

The **inorganic laboratory analyst** could design and test specific procedures for handling industrial chemicals and processes. For example, coiled steel is often “pickled” or cleaned using a dip tank of sulfuric acid. The strength of the acid bath needs to be monitored regularly to ensure it can clean the steel effectively. Once the acid has been depleted, the analyst must oversee the proper treatment and disposal of the sludge remaining in a dip tank.

The **environmental chemist** monitors the testing of samples taken from specific sites. Acids and bases are commonly used in the preparation of samples for analysis. Sometimes the chemist is required to determine the specific concentration of an acid or base spill in the environment and perhaps monitor its cleanup. Knowledge of acid–base properties will help the chemist to determine the best way for containing and treating the spill.

2. (a) The only university in Ontario that has an undergraduate program specifically designed to train analytical chemists is York University.
- (b) At the time of publication of this text, the undergraduate tuition for York University was \$915 per full course.
- (c) A variety of scholarships and bursaries is available. Consult the York web site for further details.

CHAPTER 8 LAB ACTIVITIES

ACTIVITY 8.1.1 DETERMINING THE pH OF COMMON SUBSTANCES

(Page 626)

- (a) acids: vinegar, soft drinks, shampoo, orange juice, milk
neutral: tap water, milk

basic: antacid, household ammonia, liquid soap

- (b) Based on the evidence gathered in this activity, the pH of many foods is generally less than 7 (acidic) and the pH of cleaning solutions is generally greater than 7 (basic). These generalizations are based upon a limited number of foods and cleaners tested.

Making Connections

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	$\text{CO}_{2(\text{aq})} +$	$\text{H}_2\text{O}_{(\text{l})} \rightleftharpoons$	$\text{H}_2\text{CO}_{3(\text{aq})}$
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Equilibrium concentration (mol/L)	$1.2 \times 10^{-5} - x$	-	x

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Change in concentration (mol/L)	$-x$	-	$+x$
Equilibrium concentration (mol/L)	$4.541 \times 10^{-7} - x$	-	x

$$\frac{x^2}{4.541 \times 10^{-7} - x} = 4.4 \times 10^{-4}$$

$$x^2 + 4.4 \times 10^{-4} x - 2.0 \times 10^{-13} = 0$$

$$x = 2.78 \times 10^{-7}$$

$$x = [\text{H}_{(\text{aq})}^+]$$

$$\text{pH} = -\log 2.78 \times 10^{-7}$$

$$\text{pH} = 6.55$$

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(Page 624)

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Against legislation: Passing laws will not solve the problem but only create difficulties for companies.

Ecological

For legislation: Sulfuric and sulfurous acids cause considerable damage when they fall to Earth in the form of acid deposition. Some environmental groups claimed that 14 000 Canadian lakes have been damaged by acid deposition. Acid deposition is also suspected as one of the causes of forest decline, particularly in forests at high altitudes and colder latitudes.

Against legislation: Some researchers report that acid deposition painted on seedlings in soil with inadequate nutrients actually has a beneficial effect on growth.

Scientific

For legislation: Empirical work indicates that the main causes of acid deposition in North America are sulfur dioxide, SO_2 , and nitrogen oxides, NO_x . In the atmosphere, SO_2 reacts with water to produce sulfurous acid, $\text{H}_2\text{SO}_3(\text{aq})$.

Against legislation: A 1988 U.S. federal task force maintained that damage to human health, crops, and forests by acid deposition is yet to be proven.

(c) and (d) (Answers will vary widely.)

PRACTICE

(Page 625)

Making Connections

1. Many medications require that the **hospital pharmacist** has a thorough knowledge of acids and base chemistry. For example, there are several antacid medications for treating peptic ulcer. Some pain relievers are weak acids that potentially can irritate the stomach of patients. The blood must be maintained within a very narrow pH range for the body to function properly. The pharmacist must be aware of the effects of medication on blood pH.

The **quality-control chemist** must ensure that product specifications are maintained during the manufacturing process. For example, samples of shampoo are checked regularly during a manufacturing process to ensure that their pH falls within required limits. Many pain relievers are weak acids. The amount of acid in a given tablet can be determined by conducting an acid–base titration to ensure that the tablet contains the required amount.

The **inorganic laboratory analyst** could design and test specific procedures for handling industrial chemicals and processes. For example, coiled steel is often “pickled” or cleaned using a dip tank of sulfuric acid. The strength of the acid bath needs to be monitored regularly to ensure it can clean the steel effectively. Once the acid has been depleted, the analyst must oversee the proper treatment and disposal of the sludge remaining in a dip tank.

The **environmental chemist** monitors the testing of samples taken from specific sites. Acids and bases are commonly used in the preparation of samples for analysis. Sometimes the chemist is required to determine the specific concentration of an acid or base spill in the environment and perhaps monitor its cleanup. Knowledge of acid–base properties will help the chemist to determine the best way for containing and treating the spill.

2. (a) The only university in Ontario that has an undergraduate program specifically designed to train analytical chemists is York University.
- (b) At the time of publication of this text, the undergraduate tuition for York University was \$915 per full course.
- (c) A variety of scholarships and bursaries is available. Consult the York web site for further details.

CHAPTER 8 LAB ACTIVITIES

ACTIVITY 8.1.1 DETERMINING THE pH OF COMMON SUBSTANCES

(Page 626)

- (a) acids: vinegar, soft drinks, shampoo, orange juice, milk
neutral: tap water, milk

basic: antacid, household ammonia, liquid soap

- (b) Based on the evidence gathered in this activity, the pH of many foods is generally less than 7 (acidic) and the pH of cleaning solutions is generally greater than 7 (basic). These generalizations are based upon a limited number of foods and cleaners tested.

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- (c) Litmus paper only provides a quick, inexpensive test to classify substances as being acidic, basic, or neutral. Wide-range pH test paper is useful when comparing the acidity of a wide range of substances. The advantage of the pH meter over test paper is that it can provide specific pH readings, useful when comparing solutions that have similar pH values, indistinguishable by the wide-range pH test paper.
- (d) Calibration to a specific pH is necessary to ensure that the initial reading of the meter is correct.

INVESTIGATION 8.3.1 THE pH OF SALT SOLUTIONS

(Page 627)

Prediction

- (a) According to the concept of hydrolysis, the pH of the salts tested in order from lowest to highest is:

1. $\text{NaHSO}_{4(\text{aq})}$	pH = 1.50
2. $\text{Fe}(\text{SO})_{4(\text{aq})}$	pH > 1.76
3. $\text{FeCl}_{3(\text{aq})}$	pH = 1.91
4. $\text{Al}_2(\text{SO}_4)_{3(\text{aq})}$	pH > 2.85
5. $\text{AlCl}_{3(\text{aq})}$	pH = 3.00
6. $\text{CuSO}_{4(\text{aq})}$	pH > 4.50
7. $\text{NH}_4\text{Cl}_{(\text{aq})}$	pH = 5.12
8. $\text{NaCl}_{(\text{aq})}$	pH = 7.00
9. $(\text{NH}_4)_2\text{SO}_{4(\text{aq})}$	pH < 7.50
10. $\text{K}_2\text{SO}_{4(\text{aq})}$	pH = 7.50
11. $(\text{NH}_4)_2\text{OOCCOO}_{(\text{aq})}$	pH < 8.63
12. $\text{NH}_4\text{CH}_3\text{COO}_{(\text{aq})}$	pH < 8.87
13. $\text{NaHCO}_{3(\text{aq})}$	pH < 9.68
14. $(\text{NH}_4)_2\text{CO}_{3(\text{aq})}$	pH < 11.66
15. $\text{Na}_2\text{CO}_{3(\text{aq})}$	pH = 11.66
16. $\text{Na}_3\text{PO}_{4(\text{aq})}$	pH = 12.69

The reasoning behind the above prediction is provided in the examples below.

For $\text{NaHSO}_{4(\text{aq})}$, $\text{HSO}_{4(\text{aq})}^-$ is amphoteric but $\text{HSO}_{4(\text{aq})}^-$ is a weaker base than water. Therefore, a calculation involving $\text{HSO}_{4(\text{aq})}^-$ being only an acid is justified.

$$\begin{aligned} [\text{H}_{(\text{aq})}^+] &= \sqrt{K_a [\text{HSO}_{4(\text{aq})}^+]} \\ &= \sqrt{\frac{1.0 \times 10^{-2} \text{ mol}}{1 \text{ L}} \times \frac{0.10 \text{ mol}}{1 \text{ L}}} \end{aligned}$$

$$[\text{H}_{(\text{aq})}^+] = 3.1 \times 10^{-2} \text{ mol}$$

$$\begin{aligned} \text{pH} &= -\log[\text{H}_{(\text{aq})}^+] \\ &= -\log(3.1 \times 10^{-2} \text{ mol}) \end{aligned}$$

$$\text{pH} = 1.50$$

Procedure

(b)

1. Dip a strip of pH paper into the 1.0 mol/L solution for a controlled period of time.
2. Observe and record the pH.
3. Repeat steps 1 and 2 for each of the salt solutions.
4. Dispose of all solutions into the sink and flush with plenty of water.

- (c) Litmus paper only provides a quick, inexpensive test to classify substances as being acidic, basic, or neutral. Wide-range pH test paper is useful when comparing the acidity of a wide range of substances. The advantage of the pH meter over test paper is that it can provide specific pH readings, useful when comparing solutions that have similar pH values, indistinguishable by the wide-range pH test paper.
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$$[\text{H}_{(\text{aq})}^+] = 3.1 \times 10^{-2} \text{ mol}$$

$$\begin{aligned} \text{pH} &= -\log[\text{H}_{(\text{aq})}^+] \\ &= -\log(3.1 \times 10^{-2} \text{ mol}) \end{aligned}$$

$$\text{pH} = 1.50$$

Procedure

(b)

1. Dip a strip of pH paper into the 1.0 mol/L solution for a controlled period of time.
2. Observe and record the pH.
3. Repeat steps 1 and 2 for each of the salt solutions.
4. Dispose of all solutions into the sink and flush with plenty of water.

Evidence

pH of Various Salts			
Salt	pH	Salt	pH
$\text{Na}_2\text{CO}_{3(\text{aq})}$	11.8	$(\text{NH}_4)_2\text{CO}_{3(\text{aq})}$	11.3
$\text{Na}_3\text{PO}_{4(\text{aq})}$	12.4	$(\text{NH}_4)_2\text{SO}_{4(\text{aq})}$	7.4
$\text{Al}_2(\text{SO}_4)_{3(\text{aq})}$	3.0	$\text{K}_2\text{SO}_{4(\text{aq})}$	7.6
$\text{AlCl}_{3(\text{aq})}$	3.0	$\text{CuSO}_{4(\text{aq})}$	4.9
$\text{NaCl}_{(\text{aq})}$	6.8	$\text{Fe}(\text{SO})_{4(\text{aq})}$	2.1
$\text{NH}_4\text{Cl}_{(\text{aq})}$	5.3	$\text{FeCl}_{3(\text{aq})}$	2.1
$(\text{NH}_4)_2\text{OOCCOO}_{(\text{aq})}$	8.2	$\text{NaHCO}_{3(\text{aq})}$	9.5
$\text{NH}_4\text{CH}_3\text{COO}_{(\text{aq})}$	8.5	$\text{NaHSO}_{4(\text{aq})}$	1.9

Analysis

(c) According to the evidence gathered in this experiment, the order of pH from lowest to highest is:

1. $\text{NaHSO}_{4(\text{aq})}$ pH = 1.50
2. $\text{Fe}(\text{SO})_{4(\text{aq})}$ pH > 1.76
3. $\text{FeCl}_{3(\text{aq})}$ pH = 1.91
4. $\text{Al}_2(\text{SO}_4)_{3(\text{aq})}$ pH > 2.85
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15. $\text{Na}_2\text{CO}_{3(\text{aq})}$ pH = 11.66
16. $\text{Na}_3\text{PO}_{4(\text{aq})}$ pH = 12.69

Evaluation

(d) The experimental design is judged to be adequate because it is simple, efficient, and economical with adequate controls. Without controlling the time, the results might be different. The temperature has to be assumed as controlled although there was no thermometer monitoring the temperature change during the experiment. The procedure is judged to be adequate because the evidence was reliably (consistently) collected. (If a pH meter is shared among the solutions, the Procedure needs to include the step of rinsing the pH meter between uses.) The skills employed are adequate because they are simple and have been practised before. (If one or more pH meters are used, more practice with a pH meter may be necessary.) There is sufficient confidence in the evidence provided by the design, procedure, and skills to proceed with judging the prediction and the hydrolysis concept.

The prediction is judged to be verified because the relative pH found is consistent with the prediction (in over 90% of the cases). The concept of hydrolysis is judged to be acceptable because the prediction, which is based upon the concept of hydrolysis, is verified. The concept of hydrolysis has survived another test and should be able to be used with more confidence in the future.

ACTIVITY 8.4.1 QUANTITATIVE TITRATION

(Page 627)

Evidence

Part I

mass $\text{KHC}_8\text{H}_4\text{O}_{4(\text{s})}$ used: 0.400 g

average volume of $\text{NaOH}_{(\text{aq})}$ used : 19.20 mL

Part II

2.00 mL vinegar

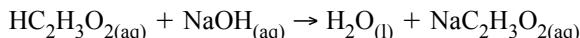
average volume of $\text{NaOH}_{(\text{aq})}$ used : 17.50 mL

Analysis

$$\begin{aligned} \text{(a)} \quad C_{\text{NaOH}(\text{aq})} &= \frac{19.6 \times 10^{-3} \text{ mol}}{19.20 \times 10^{-3} \text{ L}} \\ &= 0.102 \text{ mol/L} \end{aligned}$$

The molar concentration of the sodium hydroxide solution was 0.102 mol/L.

- (b) $\text{KHC}_8\text{H}_4\text{O}_{4(\text{s})}$ is commonly used in standardization titrations because it is a weak acid and because a known amount (in moles) of it can conveniently and accurately be determined using a balance. Furthermore, potassium hydrogen phthalate can be obtained to a high degree of purity. (The degree of purity is given on the reagent bottle.)
- (c) Shaking the solution before titrating dissolves more carbon dioxide into the solution, which then produces carbonic acid. This would slightly increase the acidity of the solution—an unnecessary source of error.
- (d) Boiling the water removes dissolved carbon dioxide from the solution.
- (e) For the titration of vinegar:



$$n_{\text{NaOH}_{(\text{aq})}} = 17.50 \text{ mL} \times 0.102 \text{ mol/L}$$

$$n_{\text{NaOH}_{(\text{aq})}} = 1.785 \text{ mmol} \quad (\text{extra digit carried})$$

$$C_{\text{HC}_2\text{H}_3\text{O}_{2(\text{aq})}} = \frac{1.785 \text{ mmol}}{2.00 \text{ mL}}$$

$$C_{\text{HC}_2\text{H}_3\text{O}_{2(\text{aq})}} = 0.893 \text{ mol/L}$$

The molar concentration of acetic acid in vinegar is also 0.893 mol/L.

Evaluation

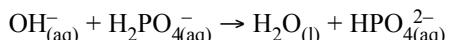
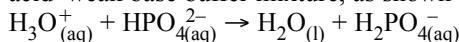
- (g) The Procedure is judged to be adequate because the concentration of the unknown acid was determined with no obvious flaws. One minor improvement would be to use a more concentrated sodium hydroxide solution. This would allow for a larger sample of vinegar to be titrated.

INVESTIGATION 8.5.1 BUFFER ACTION

(Page 629)

Prediction

- (a) According to the empirical definition of a buffer, the addition of small amounts of a strong acid or strong base produces only a slight change in the pH of the mixture until the capacity of the buffer is exceeded. The reasoning is that the added hydronium ion or hydroxide ion is quantitatively removed by reacting with a component of the weak acid–weak base buffer mixture, as shown below.



Both of the above reactions are predicted to be quantitative.

Experimental Design

- (b) A $\text{H}_2\text{PO}_{4(\text{aq})}^-/\text{HPO}_{4(\text{aq})}^{2-}$ buffer is prepared and then tested by adding small amounts of $\text{HCl}_{(\text{aq})}$ and $\text{NaHO}_{(\text{aq})}$, one drop at a time. Indicators are used to indicate a sudden change in pH. A $\text{NaCl}_{(\text{aq})}$ solution is tested as a control. The independent variable is the volume (number of drops) of acid or base added. The dependent variable is the colour of the

ACTIVITY 8.4.1 QUANTITATIVE TITRATION

(Page 627)

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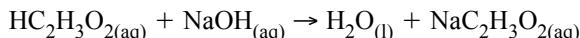
average volume of $\text{NaOH}_{(\text{aq})}$ used : 17.50 mL

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- (c) Shaking the solution before titrating dissolves more carbon dioxide into the solution, which then produces carbonic acid. This would slightly increase the acidity of the solution—an unnecessary source of error.
- (d) Boiling the water removes dissolved carbon dioxide from the solution.
- (e) For the titration of vinegar:



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$$n_{\text{NaOH}_{(\text{aq})}} = 1.785 \text{ mmol} \quad (\text{extra digit carried})$$

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Evaluation

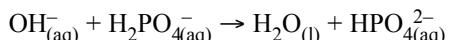
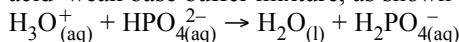
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Both of the above reactions are predicted to be quantitative.

Experimental Design

- (b) A $\text{H}_2\text{PO}_{4(\text{aq})}^-/\text{HPO}_{4(\text{aq})}^{2-}$ buffer is prepared and then tested by adding small amounts of $\text{HCl}_{(\text{aq})}$ and $\text{NaHO}_{(\text{aq})}$, one drop at a time. Indicators are used to indicate a sudden change in pH. A $\text{NaCl}_{(\text{aq})}$ solution is tested as a control. The independent variable is the volume (number of drops) of acid or base added. The dependent variable is the colour of the

indicator (the pH). The controlled variables are temperature, volume, and concentration of buffer used, and volume and concentration of added acid or base.

Materials

- (c) lab apron
- eye protection
- distilled or deionized water
- 0.10 mol/L $\text{KH}_2\text{PO}_4\text{(aq)}$
- 0.10 mol/L $\text{NaOH}\text{(aq)}$
- 0.10 mol/L $\text{NaCl}\text{(aq)}$
- 0.10 mol/L $\text{HCl}\text{(aq)}$
- two 50-mL graduated cylinders
- 150-mL beaker
- 4 small test tubes or spot plate

Evidence

(d)

Colour of bromocresol green in buffer solution						
Volume of $\text{HCl}\text{(aq)}$ (drops)	0	2	4	6	8	10
Colour of buffer solution	blue	blue	blue	blue	blue	blue
Colour of salt solution	blue	green	yellow	yellow	yellow	yellow

Colour of phenolphthalein in buffer solution						
Volume of $\text{NaOH}\text{(aq)}$ (drops)	0	2	4	6	8	10
Colour of buffer solution	blue	blue	blue	blue	blue	blue
Colour of salt solution	colourless	pink	red	red	red	red

Analysis

- (e) Based on the evidence gathered in this investigation, the slow addition of a strong acid or a strong base to a $\text{H}_2\text{PO}_4^-\text{(aq)}/\text{HPO}_4^{2-}\text{(aq)}$ buffer does not change the pH significantly.

Evaluation

- (f) The Experimental Design is judged to be adequate because there was clearly one independent variable and one dependent variable, and all necessary controls were employed. Using the salt solution as a control was even better than using distilled water. A universal indicator or pH paper might have provided more precise information as to the pH change. The procedure is judged to be adequate because it was simple and efficient. Perhaps the pH of the prepared buffer could be checked with an indicator, pH paper, and pH meter to provide more certainty, and the droppers used to add the strong acid and strong base could be calibrated to give more quantitative evidence. The skills used to carry out the investigation are judged to be adequate because they are very simple. The precision of the measurements is not crucial. Overall I am confident in the evidence gathered by the use of the experimental design, procedure, and skills employed herein.
- (g) The Prediction based upon the empirical definition of a buffer is judged to be verified because the evidence supported the predicted effects on the pH. The pH of the buffer solution, as predicted, did not change significantly when a strong acid or base was added. The empirical definition of a buffer is judged to be acceptable because the prediction was veri-

fied. The prediction based upon the empirical definition of a buffer was accurate. It appears that we can continue to have confidence in this concept.

CHAPTER 8 SUMMARY

MAKE A SUMMARY

(Page 630)

(Answers may vary, but should include a page for each of the following six sections: The Nature of Acid–Base Equilibria; Weak Acids and Bases; Acid–Base Properties of Salt Solutions; Acid–Base Titration; Buffers; and The Science of Acid Deposition.)

CHAPTER 8 SELF-QUIZ

(Page 631)

1. False. The stronger a Brønsted–Lowry acid is, the weaker its conjugate base.
2. False. Group I metal ions produce neutral solutions.
3. True
4. True
5. False. A solution of the bicarbonate ion is basic.
6. False. The pH of water would be less than 7.
7. True
8. False. Most dyes that act as acid–base indicators are weak acids.
9. True
10. (b)
11. (b)
12. (e)
13. (a)
14. (b)
15. (c)
16. (e)
17. (a)
18. (b)
19. (a)

CHAPTER 8 REVIEW

(Page 632)

Understanding Concepts

$$1. \ n_{\text{NaOH}} = \frac{8.50 \text{ g}}{40.00 \text{ g/mol}}$$

$$n_{\text{NaOH}} = 0.2125 \text{ mol} \quad (\text{extra digits carried})$$

$$[\text{OH}^-] = \frac{0.2125 \text{ mol}}{0.500 \text{ L}}$$

$$[\text{OH}^-] = 0.425 \text{ mol/L}$$

$$\text{pOH} = -\log 0.425$$

$$\text{pOH} = -0.372$$

The pOH of sodium hydroxide is –0.372.

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CHAPTER 8 SUMMARY

MAKE A SUMMARY

(Page 630)

(Answers may vary, but should include a page for each of the following six sections: The Nature of Acid–Base Equilibria; Weak Acids and Bases; Acid–Base Properties of Salt Solutions; Acid–Base Titration; Buffers; and The Science of Acid Deposition.)

CHAPTER 8 SELF-QUIZ

(Page 631)

1. False. The stronger a Brønsted–Lowry acid is, the weaker its conjugate base.
2. False. Group I metal ions produce neutral solutions.
3. True
4. True
5. False. A solution of the bicarbonate ion is basic.
6. False. The pH of water would be less than 7.
7. True
8. False. Most dyes that act as acid–base indicators are weak acids.
9. True
10. (b)
11. (b)
12. (e)
13. (a)
14. (b)
15. (c)
16. (e)
17. (a)
18. (b)
19. (a)

CHAPTER 8 REVIEW

(Page 632)

Understanding Concepts

$$1. \ n_{\text{NaOH}} = \frac{8.50 \text{ g}}{40.00 \text{ g/mol}}$$

$$n_{\text{NaOH}} = 0.2125 \text{ mol} \quad (\text{extra digits carried})$$

$$[\text{OH}^-] = \frac{0.2125 \text{ mol}}{0.500 \text{ L}}$$

$$[\text{OH}^-] = 0.425 \text{ mol/L}$$

$$\text{pOH} = -\log 0.425$$

$$\text{pOH} = -0.372$$

The pOH of sodium hydroxide is -0.372 .

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The pOH of sodium hydroxide is -0.372 .

$$2. (a) n_{\text{HCl}} = \frac{3.05 \times 10^4 \text{ g}}{36.46 \text{ g/mol}}$$

$$n_{\text{HCl}} = 836.5 \text{ mol} \quad (\text{extra digits carried})$$

$$[\text{H}^+] = \frac{836.5 \text{ mol}}{806 \text{ L}}$$

$$[\text{H}^+] = 1.038 \text{ mol/L}$$

$$\text{pH} = -\log 1.038$$

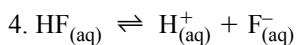
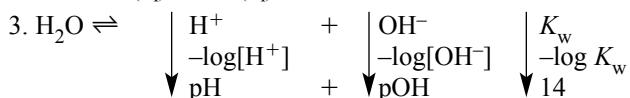
$$\text{pH} = 0.016$$

$$\text{pOH} = 14 - 0.016$$

$$\text{pOH} = 13.984$$

The pH and pOH of the hydrochloric acid are 0.016 and 13.984, respectively.

- (b) Assumptions are that the temperature remains constant, and that water does not contribute a significant amount of $\text{H}_{(\text{aq})}^+$ or $\text{OH}_{(\text{aq})}^-$.



$$K_a = \frac{[\text{H}_{(\text{aq})}^+][\text{F}_{(\text{aq})}^-]}{[\text{HF}_{(\text{aq})}]}$$

ICE Table for the Dissociation of Hydrofluoric Acid			
	$\text{HF}_{(\text{aq})} \rightleftharpoons$	$\text{H}_{(\text{aq})}^+$	$+ \text{F}_{(\text{aq})}^-$
Initial concentration (mol/L)	2.0	0.0	0.0
Change in concentration (mol/L)	$-x$	$+x$	$+x$
Equilibrium concentration (mol/L)	$2.0 - x$	x	x

$$K_a = \frac{[\text{H}_{(\text{aq})}^+][\text{F}_{(\text{aq})}^-]}{[\text{HF}_{(\text{aq})}]}$$

$$K_a = 6.6 \times 10^{-4}$$

Predict whether a simplifying assumption is justified:

$$\frac{[\text{HA}]_{\text{initial}}}{K_a} = \frac{2.0}{6.6 \times 10^{-4}}$$

$$\frac{[\text{HA}]_{\text{initial}}}{K_a} = 3000$$

Since $3000 > 100$, we may assume that $2.0 - x \doteq 2.0$.

The equilibrium expression becomes

$$\frac{x^2}{2.00} \doteq 6.6 \times 10^{-4}$$

$$x \doteq 0.036$$

The 5% rule justifies the assumption that $2.0 - x \doteq 2.0$.

$$[\text{H}_{(\text{aq})}^+] = [\text{F}_{(\text{aq})}^-] = 0.036 \text{ mol/L}$$

The concentrations of hydrogen and fluoride in a 2.0 mol/L hydrofluoric acid solution are 0.036 mol/L.

$$5. \quad [H^+] = \frac{K_w}{[OH^-]} \\ = \frac{1.0 \times 10^{-14}}{2.5 \times 10^{-7}}$$

$$[H^+] = 4.0 \times 10^{-8} \text{ mol/L}$$

$$pH = -\log 4.0 \times 10^{-8}$$

$$pH = 7.40$$

The hydrogen ion concentration and pH of blood are 4.0×10^{-8} mol/L and 7.40, respectively.

$$6. \quad n_{HC_2H_3O_2(aq)} = \frac{60\,000 \text{ g}}{60.06 \text{ g/mol}}$$

$$n_{HC_2H_3O_2(aq)} = 999 \text{ mol}$$

$$C_{HC_2H_3O_2(aq)} = \frac{999 \text{ mol}}{1250 \text{ L}}$$

$$C_{HC_2H_3O_2(aq)} = 0.799 \text{ mol/L}$$

ICE Table for the Dissociation of Acetic Acid			
	$HC_2H_3O_2(aq) \rightleftharpoons$	$H_{(aq)}^+ +$	$C_2H_3O_2^-(aq)$
Initial concentration (mol/L)	0.799	0.0	0.0
Change in concentration (mol/L)	$-x$	$+x$	$+x$
Equilibrium concentration (mol/L)	$0.799 - x$	x	x

$$\frac{[H_{(aq)}^+][C_2H_3O_2^-(aq)]}{[HC_2H_3O_2(aq)]} = 1.8 \times 10^{-5}$$

$$\frac{x^2}{0.799 - x} = 1.8 \times 10^{-5}$$

Predicting whether $0.799 - x \doteq 0.799 - x \dots$

$$\frac{[HA]_{\text{initial}}}{K_a} = \frac{0.799 \text{ mol/L}}{1.8 \times 10^{-5}}$$

$$\frac{[HA]_{\text{initial}}}{K_a} = 44400$$

Since $44400 > 100$, we assume that $0.799 - x \doteq 0.799$

$$\frac{x^2}{0.799} \doteq 1.8 \times 10^{-5}$$

$$x = 1.8 \times 10^{-5} \quad (\text{extra digits carried})$$

The 5% rule justifies the assumption.

$$[H_{(aq)}^+] = 3.795 \times 10^{-3} \text{ mol/L}$$

$$pH = -\log [H_{(aq)}^+]$$

$$= -\log [3.795 \times 10^{-3}]$$

$$pH = 2.421$$

$$pOH = 14 - 2.421$$

$$pOH = 11.579$$

The pH and pOH of the acetic acid solution are 2.421 and 11.579.

7. (a)

ICE Table for the Ionization of ASA			
	$\text{HC}_{10}\text{H}_7\text{CO}_{4(\text{aq})} \rightleftharpoons$	$\text{H}_{(\text{aq})}^+ +$	$\text{C}_{10}\text{H}_7\text{CO}_{4(\text{aq})}^-$
Initial concentration (mol/L)	0.018	0.0	0.0
Change in concentration (mol/L)	$-x$	$+x$	$+x$
Equilibrium concentration (mol/L)	$0.018 - x$	x	x

$$\frac{[\text{H}_{(\text{aq})}^+][\text{C}_{10}\text{H}_7\text{CO}_{4(\text{aq})}^-]}{[\text{HC}_{10}\text{H}_7\text{CO}_{4(\text{aq})}]} = 3.27 \times 10^{-4}$$

$$\frac{x^2}{0.018 - x} = 3.27 \times 10^{-4}$$

Predicting whether $0.018 - x \doteq 0.018$...

$$\frac{[\text{HA}]_{\text{initial}}}{K_a} = \frac{0.018 \text{ mol/L}}{3.27 \times 10^{-4}}$$

$$\frac{[\text{HA}]_{\text{initial}}}{K_a} = 55$$

Since $55 < 100$, we cannot assume that $0.018 - x \doteq 0.018$.

$$\frac{x^2}{0.018} \doteq 3.27 \times 10^{-4}$$

$$\frac{x^2}{0.018 - x} = 3.27 \times 10^{-4}$$

$$(0.018 - x)(3.27 \times 10^{-4}) = x^2$$

$$5.89 \times 10^{-6} - 3.27 \times 10^{-4}x = x^2$$

$$x^2 + 3.27 \times 10^{-4}x - 5.89 \times 10^{-6} = 0$$

$$x = \frac{-3.27 \times 10^{-4} \pm \sqrt{(3.27 \times 10^{-4})^2 - 4(1)(-5.89 \times 10^{-6})}}{2(1)}$$

$$= \frac{-3.27 \times 10^{-4} \pm 4.86 \times 10^{-3}}{2}$$

$$x = 2.27 \times 10^{-3} \text{ or } -8.13 \times 10^{-4}$$

Since negative concentrations are meaningless,

$$x = 2.27 \times 10^{-3}$$

$$[\text{H}_{(\text{aq})}^+] = 2.27 \times 10^{-3} \text{ mol/L}$$

$$\text{pH} = -\log[\text{H}_{(\text{aq})}^+]$$

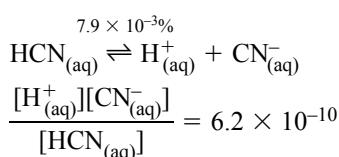
$$\text{pH} = -\log[2.27 \times 10^{-3}]$$

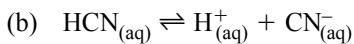
$$\text{pH} = 2.644$$

The pH of the ASA solution is 2.644.

- (b) An increase in temperature shifts the autoionization equilibrium of water to the right, producing more $\text{H}_{(\text{aq})}^+$. As a result, the pH of the solution would decrease.

8. (a)





$$\frac{[\text{H}_{(\text{aq})}^+][\text{CN}_{(\text{aq})}^-]}{[\text{HCN}_{(\text{aq})}]} = 6.2 \times 10^{-10}$$

$$\frac{x^2}{0.10 - x} = 6.2 \times 10^{-10}$$

Predicting whether $0.10 - x \doteq 0.10$...

$$\frac{[\text{HA}]_{\text{initial}}}{K_a} = \frac{0.10 \text{ mol/L}}{6.2 \times 10^{-10}}$$

$$\frac{[\text{HA}]_{\text{initial}}}{K_a} \doteq 10^9$$

Since $10^9 > 100$, we assume that $0.10 - x \doteq 0.10$.

$$\frac{x^2}{(0.10)} \doteq 6.2 \times 10^{-10}$$

$$x = 7.9 \times 10^{-6}$$

The 5% rule justifies the assumption.

$$[\text{H}_{(\text{aq})}^+] = 7.9 \times 10^{-6} \text{ mol/L}$$

$$\begin{aligned} \text{pH} &= -\log[\text{H}_{(\text{aq})}^+] \\ &= -\log[7.9 \times 10^{-6}] \end{aligned}$$

$$\text{pH} = 5.10$$

The pH of the hydrocyanic acid is 5.10.

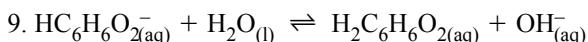
Calculating percent ionization ...

$$[\text{H}_{(\text{aq})}^+] = \frac{P}{100} \times [\text{HA}_{(\text{aq})}]$$

$$P = \frac{[\text{H}_{(\text{aq})}^+]}{[\text{HA}_{(\text{aq})}]} \times 100\%$$

$$\begin{aligned} &= \frac{7.9 \times 10^{-6} \text{ mol/L}}{0.100 \text{ mol/L}} \times 100\% \\ &= 7.9 \times 10^{-3}\% \end{aligned}$$

The percent ionization of hydrocyanic acid is $7.9 \times 10^{-3}\%$.



$$\text{pH} = 8.65$$

$$\text{pOH} = 5.35$$

$$[\text{OH}_{(\text{aq})}^+] = 10^{-5.35}$$

$$= 4.47 \times 10^{-6} \text{ mol/L} \text{ (extra digits carried)}$$

$$[\text{OH}_{(\text{aq})}^+] = [\text{H}_2\text{C}_6\text{H}_6\text{O}_{2(\text{aq})}]$$

ICE Table for the Ionization of Ascorbate				
	$\text{HC}_6\text{H}_6\text{O}_2^- +$	$\text{H}_2\text{O}_{(\text{l})} \rightleftharpoons$	$\text{H}_2\text{C}_6\text{H}_6\text{O}_{2(\text{aq})} +$	$\text{OH}_{(\text{aq})}^-$
Initial concentration (mol/L)	0.15	-	0.00	0.00
Change in concentration (mol/L)	-4.47×10^{-6}	-	4.47×10^{-6}	4.47×10^{-6}
Equilibrium concentration (mol/L)	$0.15 - (4.47 \times 10^{-6})$	-	4.47×10^{-6}	4.47×10^{-6}

$$\frac{[\text{H}_2\text{C}_6\text{H}_6\text{O}_{2(\text{aq})}][\text{OH}_{(\text{aq})}^-]}{[\text{HC}_6\text{H}_6\text{O}_{2(\text{aq})}^-]} = K_b$$

$$\frac{(4.47 \times 10^{-6})^2}{0.15 - 4.47 \times 10^{-6}} = K_b$$

Assume that $0.15 - 4.47 \times 10^{-6} \doteq 0.15$.

$$\frac{(4.47 \times 10^{-6})^2}{0.15} = 1.3 \times 10^{-10}$$

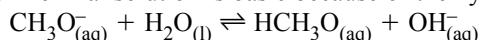
K_b for the ascorbate ion is 1.3×10^{-10} .

10. (a)

acid	conjugate base	acid	conjugate base
$(\text{C}_6\text{H}_5)_3\text{CH}$	$(\text{C}_6\text{H}_5)\text{C}^-$	$\text{C}_4\text{H}_4\text{NH}$	$\text{C}_4\text{H}_4\text{N}^-$
$\text{HC}_2\text{H}_3\text{O}_2$	$\text{C}_2\text{H}_3\text{O}_2^-$	H_2S	HS^-
$(\text{C}_6\text{H}_5)_3\text{CH}$	$(\text{C}_6\text{H}_5)\text{C}^-$	OH^-	O^{2-}
$\text{C}_4\text{H}_4\text{NH}$	$\text{C}_4\text{H}_4\text{N}^-$	H_2S	HS^-

(b) (strongest acid) $\text{HC}_2\text{H}_3\text{O}_2$; H_2S ; $\text{C}_4\text{H}_4\text{NH}$; $(\text{C}_6\text{H}_5)_3\text{CH}$ (weakest acid)

11. The final solution is basic because of the hydrolysis of the methanoate ion:



12.

Ionic			Molecular		
neutral	acidic	basic	neutral	acidic	basic
CaCl_2	NH_4Cl	NaOH	$\text{C}_6\text{H}_{12}\text{O}_6$	HCl	NH_3
NaNO_3	$\text{Al}(\text{NO}_3)_3$	Na_2CO_3	O_2	H_2S	N_2H_4

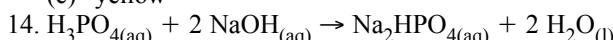
13. (a) yellow

(b) red

(c) yellow-green

(d) colourless

(e) yellow



$$\begin{array}{ll} 25.0 \text{ mL} & 17.9 \text{ mL} \\ C & 1.5 \text{ mol/L} \end{array}$$

$$n_{\text{NaOH}_{(\text{aq})}} = 17.9 \text{ mL} \times \frac{1.50 \text{ mol}}{1 \text{ L}}$$

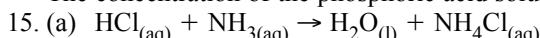
$$n_{\text{NaOH}_{(\text{aq})}} = 26.9 \text{ mmol}$$

$$n_{\text{H}_3\text{PO}_{4(\text{aq})}} = 26.9 \text{ mmol} \times \frac{1}{2} = 13.4 \text{ mmol}$$

$$C_{\text{H}_3\text{PO}_{4(\text{aq})}} = \frac{13.4 \text{ mmol}}{25.0 \text{ mL}}$$

$$C_{\text{H}_3\text{PO}_{4(\text{aq})}} = 0.537 \text{ mol/L}$$

The concentration of the phosphoric acid solution is 0.537 mol/L.



$$n_{\text{NH}_3_{(\text{aq})}} = C_{\text{NH}_3_{(\text{aq})}} \times V_{\text{NH}_3_{(\text{aq})}}$$

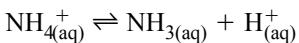
$$= 0.10 \text{ mol/L} \times 10.0 \text{ mL}$$

$$n_{\text{NH}_3_{(\text{aq})}} = 1.0 \text{ mmol}$$

Final solution volume = 20.0 mL

Entities remaining in solution at the equivalence point: $\text{Cl}^-_{(\text{aq})}$, $\text{NH}_4^+_{(\text{aq})}$, $\text{H}_2\text{O}_{(\text{l})}$

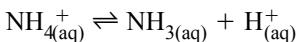
Since $\text{Cl}^-_{(\text{aq})}$ does not hydrolyze, the pH of the solution is determined by $\text{NH}_4^+_{(\text{aq})}$.



Since 1.0 mmol of $\text{NH}_3_{(\text{aq})}$ was present initially, 1.0 mmol of $\text{NH}_4^+_{(\text{aq})}$ is present at the equivalence point.

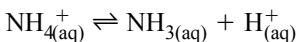
$$[\text{NH}_4^+] = \frac{1.0 \text{ mmol}}{20.0 \text{ mL}}$$

$$[\text{NH}_4^+] = 0.050 \text{ mol/L}$$



$$\frac{[\text{H}^+] [\text{NH}_3_{(\text{aq})}]}{[\text{NH}_4^+]} = 5.8 \times 10^{-10}$$

ICE Table for the Hydrolysis of $\text{NH}_4^+_{(\text{aq})}$			
	$\text{NH}_4^+ \rightleftharpoons$	$\text{H}^+_{(\text{aq})} +$	$\text{NH}_3_{(\text{aq})}$
Initial concentration (mol/L)	0.050	0.000	0.000
Change in concentration (mol/L)	$-x$	$+x$	$+x$
Equilibrium concentration (mol/L)	$0.050 - x$	x	x



$$\frac{[\text{H}^+] [\text{NH}_3_{(\text{aq})}]}{[\text{NH}_4^+]} = 5.8 \times 10^{-10}$$

$$\frac{x^2}{0.050 - x} = 5.8 \times 10^{-10}$$

Applying the hundred rule ...

$$\frac{[\text{NH}_4^+]_{\text{initial}}}{K_a} = \frac{0.050}{5.8 \times 10^{-10}} > 100$$

The equilibrium simplifies to

$$\frac{x^2}{0.050} = 5.8 \times 10^{-10}$$
$$x = 5.385 \times 10^{-6} \quad (\text{extra digits carried})$$

The 5% rule verifies the assumption.

$$[\text{H}^+] \doteq 5.385 \times 10^{-6} \text{ mol/L}$$

$$\text{pH} \doteq -\log [5.385 \times 10^{-6}]$$

$$\text{pH} = 5.27$$

The pH of the solution at the equivalence point is 5.27.

$$(b) K_b = \frac{[\text{NH}_4^+] [\text{OH}^-_{(\text{aq})}]}{[\text{NH}_3_{(\text{aq})}]}$$

$$K_b = 1.8 \times 10^{-5}$$

$$\frac{x^2}{0.10 - x} = 1.8 \times 10^{-5}$$

Predicting the validity of the assumption ...

$$\frac{0.10}{1.8 \times 10^{-5}} > 100$$

\therefore we may assume that $0.10 - x \doteq 0.10$

The equilibrium expression becomes

$$\frac{x^2}{0.10} \doteq 1.8 \times 10^{-5}$$

$$x \doteq 1.342 \times 10^{-3} \quad (\text{extra digits carried})$$

The 5% rule verifies the simplification assumption.

$$[\text{OH}_{(\text{aq})}] = 1.342 \times 10^{-3} \text{ mol/L}$$

$$\text{pOH} = -\log[1.342 \times 10^{-3}]$$

$$\text{pOH} = 2.872$$

$$\text{pH} = 14 - \text{pOH}$$

$$= 14.0 - 2.872$$

$$\text{pH} = 11.13$$

The initial pH of the ammonia solution is 11.13.

$$\begin{aligned} (\text{c}) \quad V_{\text{HCl}_{(\text{aq})}} &= 5.00 \text{ mL} \\ C_{\text{HCl}_{(\text{aq})}} &= 0.100 \text{ mol/L} \\ n_{\text{HCl}_{(\text{aq})}} &= V_{\text{HCl}_{(\text{aq})}} \times C_{\text{HCl}_{(\text{aq})}} \\ &= 5.00 \text{ mL} \times 0.100 \text{ mol/L} \end{aligned}$$

$$n_{\text{HCl}_{(\text{aq})}} = 0.50 \text{ mmol}$$

$$V_{\text{NH}_3(\text{aq})} = 10.00 \text{ mL}$$

$$C_{\text{NH}_3(\text{aq})} = 0.100 \text{ mol/L}$$

$$n_{\text{NH}_3(\text{aq})} = V_{\text{NH}_3(\text{aq})} \times C_{\text{NH}_3(\text{aq})}$$

$$n_{\text{NH}_3(\text{aq})} = 10.00 \text{ mL} \times 0.100 \text{ mol/L}$$

$$n_{\text{NH}_3(\text{aq})} = 1.00 \text{ mmol}$$

$$n_{\text{NH}_3(\text{aq})} \text{ remaining} \dots$$

$$n_{\text{NH}_3(\text{aq})} = 1.00 \text{ mmol} - 0.50 \text{ mmol}$$

$$n_{\text{NH}_3(\text{aq})} = 0.50 \text{ mmol}$$

Total volume = 5.00 mL + 10.00 mL = 15.00 mL

$$C_{\text{NH}_3(\text{aq})} = \frac{0.50 \text{ mmol}}{15.00 \text{ mL}}$$

$$C_{\text{NH}_3(\text{aq})} = 0.0333 \text{ mol/L} \quad (\text{extra digits carried})$$

$$C_{\text{NH}_4^+(\text{aq})} = \frac{0.50 \text{ mmol}}{15.00 \text{ mL}}$$

$$C_{\text{NH}_4^+(\text{aq})} = 0.0333 \text{ mol/L} \quad (\text{extra digits carried})$$

Let x represent the changes in concentration that occur as the system reestablishes equilibrium.

ICE Table for the Ionization of Ammonia				
	$\text{NH}_3\text{(aq)}$	$+ \text{H}_2\text{O}_{(\text{l})} \rightleftharpoons$	$\text{OH}_{(\text{aq})}^- +$	$\text{NH}_4^+_{(\text{aq})}$
Initial concentration (mol/L)	0.0333	-	0.00	0.0333
Change in concentration (mol/L)	$-x$	-	$+x$	$+x$
Equilibrium concentration (mol/L)	$0.0333 - x$	-	x	$0.0333 + x$

$$\frac{[\text{NH}_4^+]_{(\text{aq})} [\text{OH}_{(\text{aq})}^-]}{[\text{NH}_3\text{(aq)}]} = K_b$$

$$\frac{x(0.0333 + x)}{0.0333 - x} = 1.8 \times 10^{-5}$$

Applying the hundred rule ...

$$\frac{[\text{NH}_3\text{(aq)}]_{\text{initial}}}{K_a} = \frac{0.0333}{1.8 \times 10^{-5}}$$

$$\frac{[\text{NH}_3\text{(aq)}]_{\text{initial}}}{K_a} = 1850$$

Since $1850 > 100$, we can assume that $0.0333 + x \doteq 0.0333$ and that $0.0333 - x \doteq 0.0333$

The equilibrium simplifies to

$$\frac{x(0.0333)}{0.0333} = 1.8 \times 10^{-5}$$

$$x = 1.8 \times 10^{-5}$$

The 5% rule validates the assumption.

$$[\text{OH}_{(\text{aq})}^-] \doteq 1.8 \times 10^{-5} \text{ mol/L}$$

$$\text{pOH} \doteq -\log [1.8 \times 10^{-5}]$$

$$= 4.7445 \quad (\text{extra digits carried})$$

$$\text{pH} = 9.26$$

The pH after adding 5.0 mL of HCl is 9.26.

- (d) Entities at the equivalence point are: $\text{H}_2\text{O}_{(\text{l})}$, $\text{NH}_4^+_{(\text{aq})}$, $\text{Cl}^-_{(\text{aq})}$
 (e) The equivalence point is reached after 10.0 mL of $\text{HCl}_{(\text{aq})}$ is added. The pH of this solution is 5.27. (See calculation in (a).)

$$(f) \quad n_{\text{HCl}_{(\text{aq})}} = V_{\text{HCl}_{(\text{aq})}} \times C_{\text{HCl}_{(\text{aq})}}$$

$$= 15.0 \text{ mL} \times 0.10 \text{ mol/L}$$

$$n_{\text{HCl}_{(\text{aq})}} = 1.5 \text{ mmol} \quad (\text{extra digits carried})$$

$$n_{\text{NH}_3\text{(aq)}} = V_{\text{NH}_3\text{(aq)}} \times C_{\text{NH}_3\text{(aq)}}$$

$$n_{\text{NH}_3\text{(aq)}} = 10.0 \text{ mL} \times 0.10 \text{ mol/L}$$

$$= 1.0 \text{ mmol}$$

$$n_{\text{HCl}_{(\text{aq})}} \text{ remaining} = 1.5 \text{ mmol} - 1.0 \text{ mmol}$$

$$= 0.5 \text{ mmol}$$

$$C_{\text{HCl}_{(\text{aq})}} = \frac{n_{\text{HCl}_{(\text{aq})}}}{V_{\text{HCl}_{(\text{aq})}}}$$

$$= \frac{0.5 \text{ mmol}}{25 \text{ mL}}$$

$$C_{\text{HCl}_{(\text{aq})}} = 0.020 \text{ mol/L}$$

$$[\text{H}_{(\text{aq})}^+] = 0.020 \text{ mol/L}$$

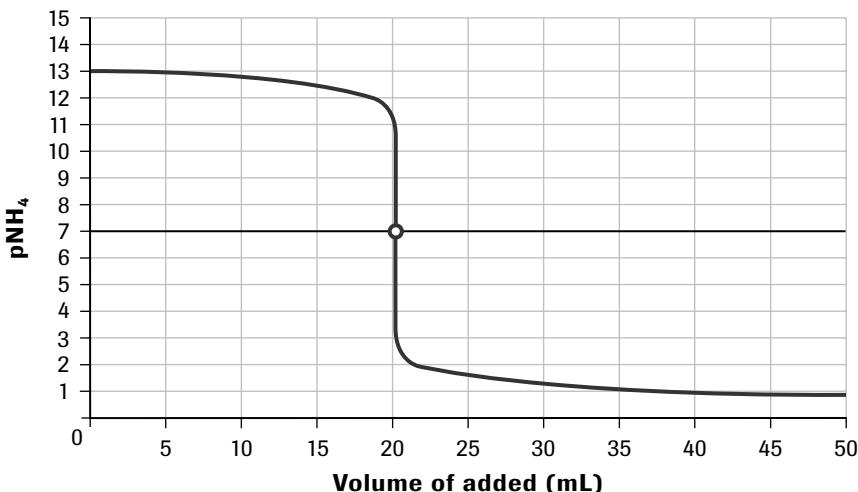
$$\text{pH} = -\log 0.020$$

$$\text{pH} = 1.70$$

After 15.0 mL of acid is added, the pH of the solution is 1.70.

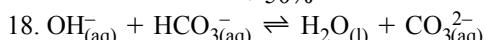
- (g) A suitable indicator for this titration would be methyl red (pH range 4.4–6.2).
16. (a) NH_4^+
(b) NH_2^-
(c) $2 \text{NH}_3 \rightleftharpoons \text{NH}_4^+ + \text{NH}_2^-$
(d)

Titration Curve for Titrating NH_2^- with NH_4^+

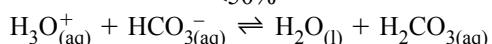


17. The pH would be between 5.0 and 5.4. An estimate of the hydrogen ion concentration is 1×10^{-5} mol/L.

>50%



<50%



Applying Inquiry Skills

19. (i) Test the solutions with a pH meter. The strongest bases have the largest pH values.
(ii) Test the solutions with universal indicator. Compare the indicator colour with a colour chart to determine the approximate pH.
20. (a) (i) neutral
(ii) basic
(iii) basic
(iv) <7
(v) <7
(vi) basic
(vii) <7
- (b) The predictions could be tested with a pH meter. (The meter should be carefully calibrated, and rinsed between solutions.)
21. (Sample answer—there are many possible correct solutions to this problem.) If the solutions are tested with a pH meter, and the pH values are ordered from smallest to largest, then the solutions are sulfuric acid, hydrochloric acid, acetic acid, ethanediol, ammonia, sodium hydroxide, and barium hydroxide, respectively.

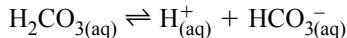
Diagnostic Tests on the Unlabelled Solutions			
Litmus	Conductivity	Acid/Base titration	Analysis
red	low	one volume	$\text{CH}_3\text{COOH}_{(\text{aq})}$
blue	very high	two volumes	$\text{Ba}(\text{OH})_2_{(\text{aq})}$
blue	low	one volume	$\text{NH}_3_{(\text{aq})}$
no change	none	not applicable	$\text{C}_2\text{H}_4(\text{OH})_2_{(\text{aq})}$
red	higher	two volumes	$\text{H}_2\text{SO}_4_{(\text{aq})}$
red	high	one volume	$\text{HCl}_{(\text{aq})}$
blue	high	one volume	$\text{NaOH}_{(\text{aq})}$

22. (a) There is no third pH endpoint and therefore, no third equivalence point in this titration.
 (b) Removing the hydroxide ions by precipitation will cause the equilibrium to shift to the right, producing more hydroxide ions.
 (c) Hydrochloric acid is not a primary standard.
 (d) Both reactants and products form basic solutions and litmus cannot be used to distinguish among basic solutions.
 (e) Cobalt chloride paper is used in a diagnostic test for the production of water in a strong acid–strong base reaction.
 (f) The strength of an acid is determined by titration.

Making Connections



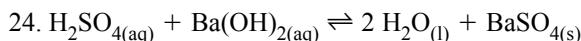
(b) Alkalosis is based on the carbonic acid/bicarbonate equilibrium:



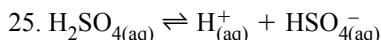
During alkalosis, an increase in blood levels of the bicarbonate ion removes hydrogen ions, thereby increasing blood pH. Symptoms of alkalosis include vomiting, headache, and nausea.

(c) Hydroxide-based antacids are very common.

Extension



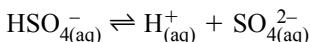
Place an accurately measured volume of $\text{Ba}(\text{OH})_{2(\text{aq})}$ into a beaker and immerse the leads from a conductivity meter in the solution. Measure and record the initial conductivity reading. Titrate with standardized $\text{H}_2\text{SO}_{4(\text{aq})}$ and record the conductivity readings. A sudden drop in the conductivity serves as the endpoint of the titration. This drop in conductivity corresponds to the removal of most of the ions through the production of water and insoluble barium sulfate. When the $\text{H}_2\text{SO}_{4(\text{aq})}$ is added in excess, the conductivity increases due to the ions present in the acid.



From the first ionization:

Since sulfuric acid is a strong acid $[\text{H}_{(\text{aq})}^+] = 1.0 \times 10^{-2} \text{ mol/L}$

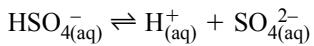
From the second ionization:



$$K_a = \frac{[\text{H}_{(\text{aq})}^+][\text{HSO}_{4(\text{aq})}^-]}{[\text{HSO}_{4(\text{aq})}^-]}$$

$$K_a = 1.0 \times 10^{-2}$$

ICE Table for the Ionization of the Hydrogen Sulfate Ion			
	$\text{HSO}_{4(\text{aq})}^- \rightleftharpoons$	$\text{H}_{(\text{aq})}^+ +$	$\text{SO}_{4(\text{aq})}^{2-}$
Initial concentration (mol/L)	0.010	0.00	0.00
Change in concentration (mol/L)	$-x$	$+x$	$+x$
Equilibrium concentration (mol/L)	$0.010 - x$	x	x



$$K_a = \frac{[\text{H}^+_{\text{(aq)}}][\text{HSO}_4^{\text{-}}_{\text{(aq)}}]}{[\text{HSO}_4^{\text{-}}_{\text{(aq)}}]} = 1.0 \times 10^{-2}$$

$$\frac{x^2}{0.010 - x} = 1.0 \times 10^{-2}$$

Predict whether a simplifying assumption is justified ...

$$\frac{[\text{HA}]_{\text{initial}}}{K_a} = \frac{0.010}{1.0 \times 10^{-2}}$$
$$= 1$$

Therefore, we may not assume that $0.010 - x \doteq 0.010$.

$$\frac{x^2}{0.010 - x} = 1.0 \times 10^{-2}$$

$$x^2 + 0.01x - 0.0001 = 0$$

$$x = \frac{-0.01 \pm \sqrt{(0.01)^2 - 4(-0.0001)}}{2}$$

The only positive root is $x = 6.18 \times 10^{-3}$ (extra digits carried)

$$\begin{aligned}\text{Total } [\text{H}^+_{\text{(aq)}}] &= 6.18 \times 10^{-3} \text{ mol/L} + 1.0 \times 10^{-2} \text{ mol/L} \\ &= 1.618 \times 10^{-2} \text{ mol/L}\end{aligned}$$

$$\text{pH} = 1.79$$

The pH of the sulfuric acid solution is 1.79.

UNIT 4 PERFORMANCE TASK: CHEMICAL ANALYST FOR A DAY

(Page 634)

Prediction

- (a) After the experimental sample is passed through a Brita water filter (or similar ion-exchange resin), the $[Ca_{(aq)}^{2+}]$ should be lower.

Materials

(b)

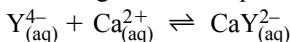
- Brita water filter (or similar ion-exchange resin)
- funnel
- two 250-mL beakers
- ring clamp and stand

Procedure

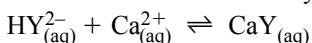
- (c) Two identical samples of hard water are obtained. One is kept as the control; the other is passed through the Brita water filter and collected.

Analysis

- (d) The chemical formula of the EDTA ion can be written as $Y_{(aq)}^{4-}$. EDTA chelates (or binds) metal ions by forming up to six attractions with the metal ion (see Figure 1): four attractions with the oxygen ends of EDTA and two with the nitrogen atoms. During the titration, EDTA, in the form $Y_{(aq)}^{4-}$ combines in a 1:1 ratio with calcium as given by the following chemical equation:



EDTA is also commonly available as the disodium salt. If this version of EDTA is used, the equilibrium becomes:



(e)

	Tap water	Treated water
volume of 0.0100 mol/L EDTA:	4.40 mL	1.60 mL

Tap water analysis:

$$\begin{aligned} n_{EDTA_{(aq)}} &= C_{EDTA_{(aq)}} \times V_{EDTA_{(aq)}} \\ &= 0.0100 \text{ mol/L} \times 4.40 \text{ mL} \\ n_{EDTA_{(aq)}} &= 4.40 \times 10^{-2} \text{ mol/L} \end{aligned}$$

Treated water analysis:

$$\begin{aligned} n_{EDTA_{(aq)}} &= 0.0100 \text{ mol/L} \times 1.60 \text{ mL} \\ n_{EDTA_{(aq)}} &= 1.60 \times 10^{-2} \text{ mol/L} \end{aligned}$$

The calcium ion concentration in tap water decreased from 4.40×10^{-2} mol/L to 1.60×10^{-2} mol/L after being passed through a Brita water filter.

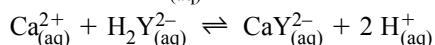
Evaluation

- (f) There were no obvious flaws or sources of error in the experimental design. One minor improvement would be to use a fresh supply of indicator to ensure that the colour change is as crisp as possible.
- (g) The prediction is judged to be adequate because the concentration of the water sample was lower as a result of being passed through the water filter.

Synthesis

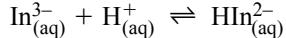
- (h) Both types of titrations involve indicators that are weak acids. The endpoint of each type of titration is signalled by an equilibrium shift of the indicator. However, the colour changes involved in EDTA titrations tend to be more sluggish than acid-base titration endpoints.

- (i) (This answer assumes the disodium salt of EDTA was used in the experiment.) During the titration, $\text{H}_2\text{Y}_{(\text{aq})}^{2-}$ chelates (binds) free $\text{Ca}_{(\text{aq})}^{2+}$ ions in solution, shifting the following equilibrium to the right:

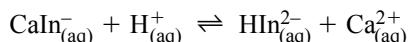


Performing this titration in a basic solution shifts this equilibrium to the right, ensuring that all the calcium in the sample has been complexed with EDTA. This is particularly important because calcium–EDTA complexes are weak as compared to metal–EDTA complexes.

Erichrome black T is a dark dye used to signal the endpoint of an EDTA titration. Like acid–base indicators, Erichrome black T is a weak acid (abbrev. $\text{HIn}_{(\text{aq})}^{2-}$) which is in equilibrium with its conjugate base, $\text{In}_{(\text{aq})}^{3-}$:



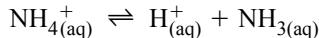
Initially, in the titration, there is a large excess of $\text{Ca}_{(\text{aq})}^{2+}$. Some calcium combines with the indicator to produce a red-coloured complex, $\text{CaIn}_{(\text{aq})}^{-}$.



(red) (blue)

At the endpoint, chelation of the last trace of free $\text{Ca}_{(\text{aq})}^{2+}$ shifts the Erichrome black T equilibrium to the right, resulting in the endpoint colour change.

- (j) The sharpness of the endpoint increases with pH. However, there is an upper limit to how high the pH can be. If the pH is too high, calcium and magnesium ions begin to precipitate out of solution as $\text{CaCO}_{3(\text{s})}$ and $\text{Mg(OH)}_{2(\text{s})}$. As a result, a compromise of pH 10 is used for this titration. To maintain a constant pH during the titration, an ammonia/ammonium buffer solution is used. The buffering equilibrium involved is:



Small amounts of acid ($\text{H}_{(\text{aq})}^+$) produced in the flask are consumed by the forward reaction. Small excesses of base ($\text{OH}_{(\text{aq})}^-$) are consumed by the reverse reaction.

- (k) EDTA can be found in a large variety of consumer and pharmaceutical products:

Soaps – EDTA is sometimes added to soap to act as a water-softening agent. EDTA softens water by chelating calcium and magnesium from the water.

Canned fruits and vegetables – Metals are sometimes introduced into canned vegetables either from the soil or from harvesting or processing machinery. Metals can degrade food by catalyzing the oxidation of fat. EDTA chelates metals, preventing them from decomposing food.

Meat products – EDTA prevents the discoloration of some meat products.

Chelation therapy – EDTA is useful in the treatment of a variety of disorders, such as

- arteriosclerosis (hardening of the arteries). EDTA removes calcium deposits, making the arteries flexible again.
- metal poisoning. EDTA chelates the metal (e.g., lead), which can then be eliminated from the body in urine.
- kidney stones (which consist primarily of calcium compounds such as calcium oxalate). EDTA chelates calcium, which helps to shrink the stones.

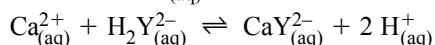
- (l) The medical use of EDTA is not without risk. Large doses of EDTA can damage the kidneys. Also, EDTA can cause a drop in the blood sugar levels. This is a particular concern for diabetics who use zinc-based insulin.

UNIT 4 SELF-QUIZ

(Page 636)

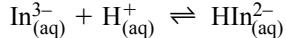
1. False: The equilibrium concentrations depend on the value of the equilibrium constant at any given temperature.
2. True
3. True
4. False: Catalysts lower the activation energy for both the forward and reverse reactions.
5. False: Inert gases have no effect on equilibrium concentrations.
6. False: The value of the equilibrium constant will decrease.
7. False: Calcium fluoride is more soluble.
8. True
9. False: The activation energy depends on whether the reaction is endothermic or exothermic.

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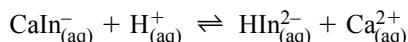


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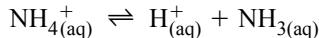
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- (j) The sharpness of the endpoint increases with pH. However, there is an upper limit to how high the pH can be. If the pH is too high, calcium and magnesium ions begin to precipitate out of solution as $\text{CaCO}_{3(\text{s})}$ and $\text{Mg(OH)}_{2(\text{s})}$. As a result, a compromise of pH 10 is used for this titration. To maintain a constant pH during the titration, an ammonia/ammonium buffer solution is used. The buffering equilibrium involved is:



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- kidney stones (which consist primarily of calcium compounds such as calcium oxalate). EDTA chelates calcium, which helps to shrink the stones.

- (l) The medical use of EDTA is not without risk. Large doses of EDTA can damage the kidneys. Also, EDTA can cause a drop in the blood sugar levels. This is a particular concern for diabetics who use zinc-based insulin.

UNIT 4 SELF-QUIZ

(Page 636)

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7. False: Calcium fluoride is more soluble.
8. True
9. False: The activation energy depends on whether the reaction is endothermic or exothermic.

10. False: The spontaneity of a reaction depends on enthalpy changes as well as entropy changes.
 11. False: The pH of acetic acid is greater than 1.
 12. False: The hypochlorite ion is a weaker base than ammonia.
 13. False: Metal oxides form basic solutions while nonmetal oxides form acidic solutions.
 14. False: Potassium sulfate forms a neutral solution.
 15. True
 16. True
 17. False: The pH at the equivalence point depends on the type of acid and base involved.
 18. True
 19. False: Buffering action occurs during the flat portions of the graph.
 20. True
 21. False: An effective acid–base buffer contains approximately equal amounts of a weak acid and its conjugate base.
 22. True
 23. (b)
 24. (b)
 25. (e)
 26. (b)
 27. (b)
 28. (c)
 29. (b)
 30. (e)
 31. (c)
 32. (c)
 33. (d)
 34. (c)
 35. (e)
 36. (c)
 37. (b)
 38. (a)
 39. (d)
 40. (d)
 41. (e)

UNIT 4 REVIEW

(Page 639)

Understanding Concepts

$$1. \frac{[\text{SO}_{2(\text{g})}]^2 [\text{O}_{2(\text{g})}]}{[\text{SO}_{3(\text{g})}]^2} = K$$

$$= \frac{1}{279}$$

$$K = 3.58 \times 10^{-3}$$

The equilibrium constant for the given reaction has a value of 3.58×10^{-3} .

$$2. K = \frac{[\text{NO}_{(\text{g})}]^2}{[\text{N}_{2(\text{g})}][\text{O}_{2(\text{g})}]}$$

$$= \frac{[0.15]^2}{[0.63][0.21]}$$

$$K = 1.7 \times 10^{-3}$$

The equilibrium constant is 1.7×10^{-3} .

3. (a) $[\text{CO}]$ decreases
 (b) $[\text{CO}]$ decreases
 (c) $[\text{CO}]$ increases

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 31. (c)
 32. (c)
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 34. (c)
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UNIT 4 REVIEW

(Page 639)

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The equilibrium constant for the given reaction has a value of 3.58×10^{-3} .

$$2. K = \frac{[\text{NO}_{(\text{g})}]^2}{[\text{N}_{2(\text{g})}][\text{O}_{2(\text{g})}]} \\ = \frac{[0.15]^2}{[0.63][0.21]} \\ K = 1.7 \times 10^{-3}$$

The equilibrium constant is 1.7×10^{-3} .

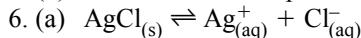
3. (a) $[\text{CO}]$ decreases
 (b) $[\text{CO}]$ decreases
 (c) $[\text{CO}]$ increases

- (d) [CO] no effect
- (e) [CO] no effect
- (f) [CO] increases
- (g) [CO] decreases

4. (Sample answers) The equilibrium methanol concentration can be increased by:

- removing methanol as it is produced,
- increasing the concentration of the reactants,
- increasing the pressure on the system,
- decreasing the volume of the reaction chamber,
- cooling the reaction chamber.

5. (a) An increase in pressure shifts the equilibrium to the right, favouring the production of ammonium carbamate.
 (b) An increase in temperature and a reduction of pressure favour the production of urea.



$$K_{\text{sp}} = [\text{Ag}_{(\text{aq})}^+][\text{Cl}_{(\text{aq})}^-]$$

$$K_{\text{sp}} = 1.8 \times 10^{-10}$$

$$[\text{Ag}_{(\text{aq})}^+] = [\text{Cl}_{(\text{aq})}^-]$$

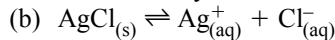
$$1.8 \times 10^{-10} = [\text{Ag}_{(\text{aq})}^+]^2$$

$$[\text{Ag}_{(\text{aq})}^+] = 1.8 \times 10^{-5} \text{ mol/L}$$

$$[\text{AgCl}_{(\text{aq})}] = [\text{Ag}_{(\text{aq})}^+]$$

$$[\text{AgCl}_{(\text{aq})}] = 1.3 \times 10^{-5} \text{ mol/L}$$

The solubility of silver chloride is 1.3×10^{-5} .



$$K_{\text{sp}} = [\text{Ag}_{(\text{aq})}^+][\text{Cl}_{(\text{aq})}^-]$$

$$K_{\text{sp}} = 1.8 \times 10^{-10}$$

$$\text{If } [\text{Cl}_{(\text{aq})}^-] = 0.015 \text{ mol/L}$$

$$1.8 \times 10^{-10} = [\text{Ag}_{(\text{aq})}^+][0.015]$$

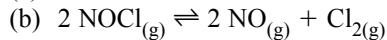
$$[\text{Ag}_{(\text{aq})}^+] = 1.2 \times 10^{-8} \text{ mol/L}$$

$$[\text{AgCl}_{(\text{aq})}] = [\text{Ag}_{(\text{aq})}^+]$$

The solubility of silver chloride in 0.015 mol/L $\text{NaCl}_{(\text{aq})}$ is 1.2×10^{-8} .

7. The synthesis of ammonia is exothermic. An increase in temperature results in a decrease in the value of the equilibrium constant. This observation implies that the concentration of ammonia decreases and the concentrations of nitrogen and hydrogen increase with a temperature increase. This result can only occur if the energy term is on the right side of the chemical equation.

8. (a) reactants

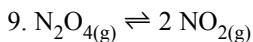


$$\frac{[\text{NO}_{(\text{g})}]^2[\text{Cl}_{2(\text{g})}]}{[\text{NOCl}_{(\text{g})}]^2} = 1.60 \times 10^{-5}$$

$$\frac{[0.10]^2[0.10]}{[\text{NOCl}_{(\text{g})}]^2} = 1.60 \times 10^{-5}$$

$$[\text{NOCl}_{(\text{g})}] = 7.91 \text{ mol/L}$$

The equilibrium concentration of $\text{NOCl}_{(\text{g})}$ is 7.91 mol/L.

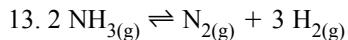


$$\frac{[\text{NO}_{2(\text{g})}]^2}{[\text{N}_2\text{O}_{4(\text{g})}]} = 6.13 \times 10^{-3}$$

$$\begin{aligned} Q &= \frac{[\text{NO}_{2(\text{g})}]^2}{[\text{N}_2\text{O}_{4(\text{g})}]} \\ &= \frac{[4.00 \times 10^{-3}]^2}{[8.00 \times 10^{-4}]} \end{aligned}$$

$$Q = 0.0200$$

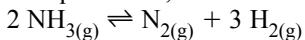
Since $Q \neq 6.13 \times 10^{-3}$, the system is not at equilibrium. The system will become less reddish-brown as it shifts to approach equilibrium.



$$\frac{[\text{N}_{2(\text{g})}][\text{H}_{2(\text{g})}]^3}{[\text{NH}_{3(\text{g})}]^2} = 1.60 \times 10^{-3}$$

ICE Table for the Decomposition of Ammonia			
	$2 \text{NH}_{3(\text{g})} \rightleftharpoons$	$\text{N}_{2(\text{g})} +$	$3 \text{H}_{2(\text{g})}$
Initial concentration (mol/L)	0.20	0.00	0.00
Change in concentration (mol/L)	$-2x$	$+x$	$+3x$
Equilibrium concentration (mol/L)	$0.20 - 2x$	x	$3x$

At equilibrium,



$$\frac{[\text{N}_{2(\text{g})}][\text{H}_{2(\text{g})}]^3}{[\text{NH}_{3(\text{g})}]^2} = 1.60 \times 10^{-3}$$

$$\frac{[x][3x]^3}{[0.20 - 2x]^2} = 1.60 \times 10^{-3}$$

$$\frac{x^4}{(0.20 - 2x)^2} = 5.926 \times 10^{-3} \text{ (extra digits carried)}$$

$$\sqrt{\frac{x^4}{(0.20 - 2x)^2}} = \sqrt{5.926 \times 10^{-3}}$$

$$\frac{x^2}{0.20 - 2x} = 0.770$$

$$x^2 + 0.154x - 0.00154 = 0$$

$$x = \frac{-0.154 \pm \sqrt{(0.154)^2 - 4(1)(-0.00154)}}{2(1)}$$

$$x = 0.3229$$

$$\begin{aligned} [\text{NH}_{3(\text{g})}] &= 0.20 - 2x \\ &= 0.20 - 2(0.3229) \end{aligned}$$

$$[\text{NH}_{3(\text{g})}] = 0.14 \text{ mol/L}$$

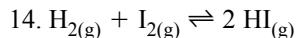
$$\begin{aligned} [\text{H}_{2(\text{g})}] &= 3x \\ &= 3(0.3229) \end{aligned}$$

$$[\text{H}_{2(\text{g})}] = 0.097 \text{ mol/L}$$

$$[\text{N}_{2(\text{g})}] = 2x$$

$$[\text{N}_{2(\text{g})}] = 0.32 \text{ mol/L}$$

The equilibrium concentrations of nitrogen, hydrogen, and ammonia are 0.32 mol/L, 0.097 mol/L, and 0.14 mol/L.



$$K = \frac{[\text{HI}_{(\text{g})}]^2}{[\text{H}_{2(\text{g})}][\text{I}_{2(\text{g})}]}$$

Initial concentrations are

$$[\text{H}_{2(\text{g})}]_{\text{initial}} = \frac{2.00 \text{ mol}}{5.00 \text{ L}}$$

$$[\text{H}_{2(\text{g})}]_{\text{initial}} = 0.400 \text{ mol/L}$$

$$[\text{I}_{2(\text{g})}]_{\text{initial}} = \frac{1.00 \text{ mol}}{5.00 \text{ L}}$$

$$[\text{I}_{2(\text{g})}]_{\text{initial}} = 0.200 \text{ mol/L}$$

$$[\text{HI}_{(\text{g})}]_{\text{initial}} = 0.0 \text{ mol/L}$$

ICE Table for the Formation of $\text{HI}_{(\text{g})}$			
	$\text{H}_{2(\text{g})} +$	$\text{I}_{2(\text{g})} \rightleftharpoons$	$2 \text{HI}_{(\text{g})}$
Initial concentration (mol/L)	0.400	0.200	0.000
Change in concentration (mol/L)	$-x$	$-x$	$+2x$
Equilibrium concentration (mol/L)	$0.400 - x$	$0.200 - x$	$2x$

At equilibrium,

$$K = \frac{[\text{HI}_{(\text{g})}]^2}{[\text{H}_{2(\text{g})}][\text{I}_{2(\text{g})}]}$$

$$\frac{(2x)^2}{(0.400 - x)(0.200 - x)} = 49.7$$

$$4x^2 = (49.7)(0.400 - x)(0.200 - x)$$

$$x^2 = (12.425)(0.0800 - 0.6x + x^2) \quad (\text{extra digits carried})$$

$$x^2 - 0.6525x + 0.0870 = 0$$

$$x = \frac{0.6525 \pm \sqrt{0.6525^2 - 4(0.0870)(1)}}{2(1)}$$

$$x = 0.46565 \text{ or } 0.18725 \quad (\text{extra digits carried})$$

The root 0.46565 is rejected as it exceeds the initial amount of hydrogen.

$$K = \frac{[\text{HI}_{(\text{g})}]^2}{[\text{H}_{2(\text{g})}][\text{I}_{2(\text{g})}]}$$

$$[\text{HI}_{(\text{g})}] = 2x$$

$$= 2 \times 0.18725$$

$$[\text{HI}_{(\text{g})}] = 0.375 \text{ mol/L}$$

$$[\text{H}_{2(\text{g})}] = 0.400 - x$$

$$= 0.400 - 0.18725$$

$$\begin{aligned} [\text{H}_{2(\text{g})}] &= 0.213 \text{ mol/L} \\ [\text{I}_{2(\text{g})}] &= 0.200 - x \\ &= 0.200 - 0.18725 \\ [\text{I}_{2(\text{g})}] &= 0.013 \text{ mol/L} \end{aligned}$$

The equilibrium concentrations of hydrogen, iodine, and hydrogen iodide are 0.213 mol/L, 0.013 mol/L, and 0.375 mol/L, respectively.

15. At equilibrium,

$$\begin{aligned} 2 \text{SO}_{3(\text{g})} &\rightleftharpoons 2 \text{SO}_{2(\text{g})} + \text{O}_{2(\text{g})} \\ \frac{[\text{SO}_{2(\text{g})}]^2 [\text{O}_{2(\text{g})}]}{[\text{SO}_{3(\text{g})}]^2} &= 6.9 \times 10^{-7} \\ \frac{[2x]^2 [x]}{[0.200 - 2x]^2} &= 6.9 \times 10^{-7} \\ \frac{4x^3}{(0.200 - 2x)^2} &= 6.9 \times 10^{-7} \end{aligned}$$

Assuming $0.200 - 2x \doteq 0.200 \dots$

$$\begin{aligned} \frac{4x^3}{(0.200)^2} &\doteq 6.9 \times 10^{-7} \\ \frac{4x^3}{0.040} &\doteq 6.9 \times 10^{-7} \\ 100x^3 &\doteq 6.9 \times 10^{-7} \\ x^3 &\doteq 6.9 \times 10^{-5} \\ x &= 1.904 \times 10^{-3} \quad (\text{extra digits carried}) \end{aligned}$$

$$\begin{aligned} [\text{SO}_{3(\text{g})}] &= 0.200 - 2x \\ &= 0.200 - 2(1.904 \times 10^{-3}) \\ [\text{SO}_{3(\text{g})}] &= 0.20 \text{ mol/L} \\ [\text{O}_{2(\text{g})}] &= 1.9 \times 10^{-3} \text{ mol/L} \\ [\text{SO}_{2(\text{g})}] &= 2(1.904 \times 10^{-3}) \\ [\text{SO}_{2(\text{g})}] &= 3.8 \times 10^{-3} \text{ mol/L} \end{aligned}$$

The equilibrium concentrations of sulfur trioxide, oxygen, and sulfur dioxide are 0.20 mol/L, 1.9×10^{-3} mol/L, and 3.8×10^{-3} mol/L, respectively.

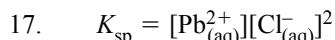
$$\begin{aligned} 16. K_{\text{sp}} &= [\text{Ca}^{2+}_{(\text{aq})}][\text{SO}_4^{2-}_{(\text{aq})}] \\ K_{\text{sp}} &= 7.1 \times 10^{-5} \\ x^2 &= 7.1 \times 10^{-5} \\ x &= 8.4 \times 10^{-3} \end{aligned}$$

The molar solubility of calcium sulfate is 8.4×10^{-3} mol/L.

ICE Table for the Dissolving of Calcium Sulfate			
	$\text{CaSO}_{4(\text{s})} \rightleftharpoons$	$\text{Ca}^{2+}_{(\text{aq})} +$	$\text{SO}_4^{2-}_{(\text{aq})}$
Initial concentration (mol/L)			
Change in concentration (mol/L)		$+x$	$+x$
Equilibrium concentration (mol/L)			

$$x = 8.4 \times 10^{-3} \text{ mol/L}$$

The molar solubility of calcium sulfate is 8.4×10^{-3} mol/L.



$$K_{\text{sp}} = 1.2 \times 10^{-5}$$

$$(x)(2x)^2 = 1.2 \times 10^{-5}$$

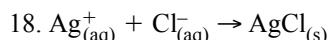
$$4x^3 = 1.2 \times 10^{-5}$$

$$x = 0.01442 \quad (\text{extra digits carried})$$

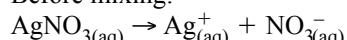
$$[\text{Cl}_{(\text{aq})}^-] = 2 \times 0.01442$$

$$[\text{Cl}_{(\text{aq})}^-] = 0.029 \text{ mol/L}$$

The molar concentration of chloride ions is 0.029 mol/L.



Before mixing:



$$[\text{AgNO}_3_{(\text{aq})}] = [\text{Ag}_{(\text{aq})}^+]$$

$$[\text{AgNO}_3_{(\text{aq})}] = 0.010 \text{ mol/L}$$

$$[\text{Cl}_{(\text{aq})}^-] = 2.2 \times 10^{-4} \text{ mol/L}$$

After mixing:

$$250.0 \text{ mL} + 250.0 \text{ mL} = 500.0 \text{ mL}$$

Concentrations after mixing:

$$[\text{Ag}_{(\text{aq})}^+] = 0.010 \text{ mol/L} \times \frac{250.0 \text{ mL}}{500.0 \text{ mL}}$$

$$[\text{Ag}_{(\text{aq})}^+] = 0.0050 \text{ mol/L}$$

$$[\text{Cl}_{(\text{aq})}^-] = 2.2 \times 10^{-4} \text{ mol/L} \times \frac{250.0 \text{ mL}}{500.0 \text{ mL}}$$

$$[\text{Cl}_{(\text{aq})}^-] = 1.1 \times 10^{-4} \text{ mol/L}$$

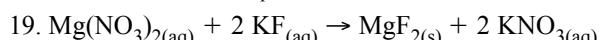


$$Q = [\text{Ag}_{(\text{aq})}^+][\text{Cl}_{(\text{aq})}^-] \\ = (0.0050)(1.1 \times 10^{-4})$$

$$Q = 5.5 \times 10^{-7}$$

$$K_{\text{sp}} = 1.8 \times 10^{-10}$$

Q is greater than K_{sp} . Therefore, a precipitate will form.



Before mixing:



$$[\text{Mg}(\text{NO}_3)_2_{(\text{aq})}] = [\text{Mg}_{(\text{aq})}^{2+}]$$

$$[\text{Mg}(\text{NO}_3)_2_{(\text{aq})}] = 0.015 \text{ mol/L}$$

$$[\text{KF}_{(\text{aq})}] = [\text{F}_{(\text{aq})}^-]$$

$$[\text{KF}_{(\text{aq})}] = 0.10 \text{ mol/L}$$

After mixing:

$$300 \text{ mL} + 100 \text{ mL} = 400 \text{ mL}$$

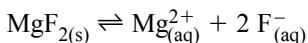
Concentrations after mixing:

$$[\text{Mg}_{(\text{aq})}^{2+}] = 0.015 \text{ mol/L} \times \frac{100 \text{ mL}}{400 \text{ mL}}$$

$$[\text{Mg}_{(\text{aq})}^{2+}] = 3.75 \times 10^{-3} \text{ mol/L} \quad (\text{extra digits carried})$$

$$[\text{F}_{(\text{aq})}^-] = 0.10 \text{ mol/L} \times \frac{300 \text{ mL}}{400 \text{ mL}}$$

$$[\text{F}_{(\text{aq})}^-] = 0.075 \text{ mol/L}$$



$$Q = [\text{Mg}_{(\text{aq})}^{2+}][\text{F}_{(\text{aq})}^-]^2$$

$$= (3.75 \times 10^{-3})(0.075)^2$$

$$Q = 2.1 \times 10^{-5}$$

$$K_{\text{sp}} = 6.4 \times 10^{-9}$$

Q is larger than K_{sp} . Therefore, a precipitate does form.

20. Solubility refers to the amount of a compound that dissolves in a given volume of solution. The solubility product, however, is the product of the concentration of the ions released when a compound dissolves.
21. Compounds that release calcium or sulfate ions will decrease the solubility of calcium sulfate. Some examples are calcium chloride, calcium nitrate, sodium sulfate, and potassium sulfate.
22. (a) Entropy is positive. The liquid state is more random than the solid state.
(b) Entropy is negative. The products are less random due to the formation of the precipitate.
(c) Entropy is negative. The formation of two molecules of the same substance HOCl is more ordered than the left side.
(d) Entropy is positive. The gases on the right side of the equation are more randomly arranged than solid ammonium chloride.
23. $2 \text{NaCl}_{(\text{s})} \rightarrow 2 \text{Na}_{(\text{g})} + \text{Cl}_{2(\text{g})}$

The decomposition of sodium chloride is endothermic ($\Delta H > 0$). The entropy change is positive, $\Delta S > 0$, since the products are more random than the reactant.

$$\Delta G = \Delta H - T\Delta S$$

$$\Delta G = + - (+)(+)$$

Since the reaction does not occur spontaneously at room temperature, ΔG must be positive. Consequently, the temperature must be small enough so that the ΔH term in the equation is greater than $T\Delta S$.

$$\begin{aligned} 24. \Delta H^\circ &= [\Delta H^\circ_{\text{f}(\text{NH}_4\text{Cl}_{(\text{aq})})}] - [\Delta H^\circ_{\text{f}(\text{NH}_4\text{Cl}_{(\text{s})})}] \\ &= [1 \text{ mol} (-299.7 \text{ kJ/mol})] - [1 \text{ mol} (-314.4 \text{ kJ/mol})] \\ &= [-299.7 \text{ kJ}] - [-314.4 \text{ kJ}] \end{aligned}$$

$$\Delta H^\circ = +14.7 \text{ kJ}$$

$$\begin{aligned} \Delta S^\circ &= [S^\circ_{(\text{NH}_4\text{Cl}_{(\text{aq})})}] - [S^\circ_{(\text{NH}_4\text{Cl}_{(\text{s})})}] \\ &= [1 \text{ mol} (169.9 \text{ J/mol}\cdot\text{K})] - [1 \text{ mol} (94.6 \text{ J/mol}\cdot\text{K})] \\ &= [169.9 \text{ J/K}] - [94.6 \text{ J/K}] \end{aligned}$$

$$\Delta S^\circ = 75.3 \text{ J/K}$$

$$\Delta S^\circ = 75.3 \text{ J/K} \times \frac{1 \text{ kJ}}{1000 \text{ J}}$$

$$\Delta S^\circ = 0.0753 \text{ kJ/K}$$

$$\begin{aligned} \Delta G^\circ &= \Delta H^\circ - T\Delta S^\circ \\ &= 14.7 \text{ kJ} - (298 \text{ K})(0.0753 \text{ kJ/K}) \end{aligned}$$

$$\Delta G^\circ = -7.7 \text{ kJ}$$

The standard Gibbs free energy change associated with this reaction is -7.7 kJ . Since ΔG° is negative, the reaction is spontaneous under standard conditions and will proceed to the right as written. A total of -7.7 kJ of free energy is made available to do useful work for each mole of solid ammonium chloride that reacts.

$$\begin{aligned} 25. \Delta H^\circ &= [\Delta H^\circ_{f(\text{CO}_{2(\text{g})})} + 2 \Delta H^\circ_{f(\text{H}_2\text{O}_{(\text{g})})}] - [\Delta H^\circ_{f(\text{CH}_{4(\text{g})})} + 2 \Delta H^\circ_{f(\text{O}_{2(\text{g})})}] \\ &= [1 \text{ mol} + (-393.5 \text{ kJ/mol}) + 2 \text{ mol} \times (-241.8 \text{ kJ/mol})] - [(-74.4 \text{ kJ/mol}) + 2 \text{ mol} \times (0)] \\ &= [-877.1 \text{ kJ/mol}] - [-74.4 \text{ kJ}] \end{aligned}$$

$$\Delta H^\circ = -802.7 \text{ kJ}$$

$$\begin{aligned} \Delta S^\circ &= [S^\circ_{(\text{CO}_{2(\text{g})})} + 2 S^\circ_{(\text{H}_2\text{O}_{(\text{g})})}] - [S^\circ_{(\text{CH}_{4(\text{g})})} + 2 S^\circ_{(\text{O}_{2(\text{g})})}] \\ &= [1 \text{ mol} \times (213.78 \text{ J/mol}\cdot\text{K}) + 2 \text{ mol} \times (188.84 \text{ J/mol}\cdot\text{K})] - [(186.3 \text{ J/mol}\cdot\text{K}) + 2 \text{ mol} \times (205.14 \text{ J/mol}\cdot\text{K})] \\ &= [591.46 \text{ J/K}] - [596.58 \text{ J/K}] \end{aligned}$$

$$\Delta S^\circ = -5.12 \text{ J/K}$$

$$\Delta S^\circ = -5.12 \text{ J/K} \times \frac{1 \text{ kJ}}{1000 \text{ J}}$$

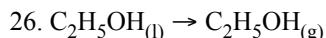
$$\Delta S^\circ = -0.00512 \text{ kJ/K}$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

$$= -802.7 \text{ kJ} - (298\text{K})(-0.00512 \text{ kJ/K})$$

$$\Delta G^\circ = -801.2 \text{ kJ}$$

The standard Gibbs free energy change associated with this reaction is -801.2 kJ . Since ΔG° is negative, the reaction is spontaneous under standard conditions and will proceed to the right as written. A total of -801.2 kJ of free energy is made available to do useful work for each mole of methane that burns.



$$\begin{aligned} T &= \frac{\Delta H^\circ}{\Delta S^\circ} \\ &= [\Delta H^\circ_{f(\text{C}_2\text{H}_5\text{OH}_{(\text{g})})} - \Delta H^\circ_{f(\text{C}_2\text{H}_5\text{OH}_{(\text{l})})}] \\ &= (-235.2 \text{ kJ/mol}) - (-277.7 \text{ kJ/mol}) \end{aligned}$$

$$T = 42.5 \text{ kJ}$$

$$\begin{aligned} \Delta S^\circ &= [S^\circ_{(\text{C}_2\text{H}_5\text{OH}_{(\text{g})})} - S^\circ_{(\text{C}_2\text{H}_5\text{OH}_{(\text{l})})}] \\ &= (+282.70 \text{ J/mol}\cdot\text{K}) - (+160.7 \text{ J/mol}\cdot\text{K}) \end{aligned}$$

$$\Delta S^\circ = 122 \text{ J/mol}\cdot\text{K}$$

$$\Delta S^\circ = 122 \text{ J/K} \times \frac{1 \text{ kJ}}{1000 \text{ J}}$$

$$\Delta S^\circ = 0.122 \text{ kJ/K}$$

$$\begin{aligned} T &= \frac{\Delta H^\circ}{\Delta S^\circ} \\ &= \frac{42.5 \text{ kJ}}{0.122 \text{ kJ/K}} \end{aligned}$$

$$T = 348 \text{ K}$$

$$t = (T - 273^\circ\text{C})$$

$$= (348 \text{ K} - 273^\circ\text{C})$$

$$t = 75^\circ\text{C}$$

The normal condensation point of ethanol is 75°C .

- $\text{HNO}_{2(\text{aq})} + \text{SO}_{4(\text{aq})}^{2-} \rightleftharpoons \text{HSO}_{4(\text{aq})}^- + \text{NO}_{2(\text{aq})}^-$
- $\text{HCO}_{3(\text{aq})}^- + \text{NH}_{4(\text{aq})}^+ \rightleftharpoons \text{NH}_{3(\text{g})} + \text{H}_2\text{CO}_{3(\text{aq})}$
- $\text{NH}_{3(\text{g})} + \text{HS}_{(\text{aq})}^- \rightleftharpoons \text{NH}_{4(\text{aq})}^+ + \text{S}_{(\text{aq})}^{2-}$

28. (a) endothermic
 (b) The increase in K_w with temperature implies that the hydrogen ion concentration also increases. Consequently, the pH decreases.

29. $[H_{(aq)}^+]_{\text{rainwater}} = 10^{-5.6}$
 $[H_{(aq)}^+]_{\text{rainwater}} = 2.51 \times 10^{-6} \text{ mol/L}$ (extra digits carried)

$$[H_{(aq)}^+]_{\text{acidic rainwater}} = 10^{-4.0}$$

$$[H_{(aq)}^+]_{\text{acidic rainwater}} = 1 \times 10^{-4} \text{ mol/L}$$

$$\frac{1 \times 10^{-4} \text{ mol/L}}{2.51 \times 10^{-6} \text{ mol/L}} = 40$$

The acidic rainwater is 40 times more acidic than normal rainwater.

30. $[H_{(aq)}^+]_{\text{cola}} = 10^{-2.7}$
 $[H_{(aq)}^+]_{\text{cola}} = 2 \times 10^{-3} \text{ mol/L}$
 $\text{pOH} = 14 - 2.7$
 $\text{pOH} = 11.3$
 $[OH_{(aq)}^-]_{\text{cola}} = 10^{-11.3}$
 $[OH_{(aq)}^-]_{\text{cola}} = 5 \times 10^{-12} \text{ mol/L}$

The hydrogen and hydroxide ion concentrations in cola are $2 \times 10^{-3} \text{ mol/L}$ and $5 \times 10^{-12} \text{ mol/L}$, respectively.

31. 5.9%
 $\text{HOCl}_{(\text{aq})} \rightleftharpoons H_{(\text{aq})}^+ + \text{OCl}_{(\text{aq})}^-$
 $K_a = \frac{[H_{(\text{aq})}^+][\text{OCl}_{(\text{aq})}^-]}{[\text{HOCl}_{(\text{aq})}]}$
 $[H_{(\text{aq})}^+] = (5.9 \times 10^{-3})(0.100 \text{ mol/L})$
 $[H_{(\text{aq})}^+] = 5.9 \times 10^{-4}$

ICE Table for the Ionization of $\text{HOCl}_{(\text{aq})}$			
	$\text{HOCl}_{(\text{aq})} \rightleftharpoons$	$H_{(\text{aq})}^+ +$	$\text{OCl}_{(\text{aq})}^-$
Initial concentration (mol/L)	0.100	0.000	0.000
Change in concentration (mol/L)	-5.9×10^{-4}	5.9×10^{-4}	5.9×10^{-4}
Equilibrium concentration (mol/L)	$0.100 - 5.9 \times 10^{-4}$	5.9×10^{-4}	5.9×10^{-4}

$$K_a = \frac{[H_{(\text{aq})}^+][\text{OCl}_{(\text{aq})}^-]}{[\text{HOCl}_{(\text{aq})}]}$$

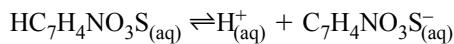
$$= \frac{(5.9 \times 10^{-4})^2}{0.100 - 5.9 \times 10^{-4}}$$

$$K_a = 3.5 \times 10^{-6}$$

The K_a for cyanic acid is 3.5×10^{-6} .

32.

ICE Table for the Ionization of $\text{HC}_7\text{H}_4\text{NO}_3\text{S}_{(\text{aq})}$			
	$\text{HC}_7\text{H}_4\text{NO}_3\text{S}_{(\text{aq})} \rightleftharpoons$	$H_{(\text{aq})}^+ +$	$\text{C}_7\text{H}_4\text{NO}_3\text{S}_{(\text{aq})}^-$
Initial concentration (mol/L)	0.500	0.000	0.000
Change in concentration (mol/L)	$-x$	$+x$	$+x$
Equilibrium concentration (mol/L)	$0.500 - x$	x	x



$$K_a = \frac{[\text{H}_{(\text{aq})}^+][\text{C}_7\text{H}_4\text{NO}_3\text{S}_{(\text{aq})}^-]}{[\text{HC}_7\text{H}_4\text{NO}_3\text{S}_{(\text{aq})}]}$$

$$\frac{x^2}{0.500 - x} = 2.1 \times 10^{-12}$$

Predicting whether $0.100 - x \doteq 0.100 \dots$

$$\frac{[\text{HA}]_{\text{initial}}}{K_a} = \frac{0.100 \text{ mol/L}}{2.1 \times 10^{-12}}$$

>100

Therefore, we assume that $0.500 - x \doteq 0.500$.

$$\frac{x^2}{(0.500)} \doteq 2.1 \times 10^{-12}$$

$$x^2 \doteq 1.05 \times 10^{-12} \text{ (extra digits carried)}$$

$$x = 1.1 \times 10^{-6}$$

The 5% rule justifies the assumption.

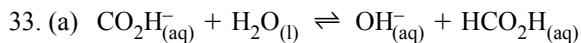
$$[\text{H}_{(\text{aq})}^+] = 1.1 \times 10^{-6} \text{ mol/L}$$

$$\text{pH} = -\log[\text{H}_{(\text{aq})}^+]$$

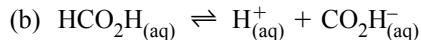
$$= -\log[1.1 \times 10^{-6}]$$

$$\text{pH} = 5.99$$

The pH of the saccharin solution is 5.99.



$$\frac{[\text{HCO}_2\text{H}_{(\text{aq})}][\text{OH}_{(\text{aq})}^-]}{[\text{CO}_2\text{H}_{(\text{aq})}^-]}$$

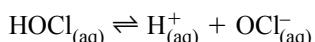


$$\frac{[\text{H}_{(\text{aq})}^+][\text{CO}_2\text{H}_{(\text{aq})}^-]}{[\text{HCO}_2\text{H}_{(\text{aq})}]}$$

(c) $\frac{[\text{H}_{(\text{aq})}^+][\text{CO}_2\text{H}_{(\text{aq})}^-]}{[\text{HCO}_2\text{H}_{(\text{aq})}]} \times \frac{[\text{HCO}_2\text{H}_{(\text{aq})}][\text{OH}_{(\text{aq})}^-]}{[\text{CO}_2\text{H}_{(\text{aq})}^-]} = [\text{H}_{(\text{aq})}^+][\text{OH}_{(\text{aq})}^-] = K_w$

34.

ICE Table for the Ionization of $\text{HOCl}_{(\text{aq})}$			
	$\text{HOCl}_{(\text{aq})} \rightleftharpoons$	$\text{H}_{(\text{aq})}^+ +$	$\text{OCl}_{(\text{aq})}^-$
Initial concentration (mol/L)	0.100	0.000	0.000
Change in concentration (mol/L)	$-x$	$+x$	$+x$
Equilibrium concentration (mol/L)	$0.100 - x$	x	x



$$K_a = \frac{[\text{H}_{(\text{aq})}^+][\text{OCl}_{(\text{aq})}^-]}{[\text{HOCl}_{(\text{aq})}]}$$

$$\frac{x^2}{0.100 - x} = 2.9 \times 10^{-8}$$

Predicting whether $0.100 - x \doteq 0.100$...

$$\frac{[\text{HA}]_{\text{initial}}}{K_a} = \frac{0.100 \text{ mol/L}}{2.9 \times 10^{-8}}$$

>100

Therefore, we assume that $0.100 - x \doteq 0.100$.

$$\frac{x^2}{(0.100)} \doteq 2.9 \times 10^{-8}$$

$$x^2 \doteq 2.9 \times 10^{-8}$$

$$x = 5.39 \times 10^{-5} \quad (\text{extra digits carried})$$

The 5% rule justifies the assumption.

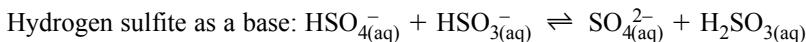
$$[\text{H}_{(\text{aq})}^+] = 5.4 \times 10^{-5} \text{ mol/L}$$

$$\text{pH} = -\log[\text{H}_{(\text{aq})}^+]$$

$$= -\log[5.39 \times 10^{-5}]$$

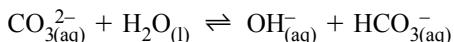
$$\text{pH} = 4.27$$

The pH of the hypochlorous acid solution is 4.27.

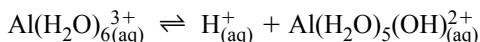


36. Despite having identical molar concentrations, solutions of these compounds differ in pH because the hydrogen sulfite ion, $\text{HSO}_{4(\text{aq})}^-$, is a stronger acid than the hydrogen sulfite ion, $\text{HSO}_{3(\text{aq})}^-$.

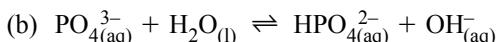
37. (a) Calcium carbonate would raise soil pH because the hydrolysis of the carbonate ion releases hydroxide ions:



(b) Alum lowers soil pH due to the hydrolysis of the aluminum ion:



38. (a) Sodium phosphate solution is likely to be basic.



ICE Table for the Hydrolysis of Phosphate				
	$\text{PO}_{4(\text{aq})}^{3-} +$	$\text{H}_2\text{O}_{(\text{l})} \rightleftharpoons$	$\text{HPO}_{4(\text{aq})}^{2-} +$	$\text{OH}_{(\text{aq})}^-$
Initial concentration (mol/L)	0.10	-	0.00	0.00
Change in concentration (mol/L)	$-x$	-	$+x$	$+x$
Equilibrium concentration (mol/L)	$0.10 - x$	-	x	x

$$K_b = \frac{K_w}{K_a}$$

$$= \frac{1.0 \times 10^{-14}}{4.2 \times 10^{-13}}$$

$$K_b = 2.3 \times 10^{-2}$$

$$K_b = \frac{[\text{HPO}_{4(\text{aq})}^{2-}][\text{OH}_{(\text{aq})}^-]}{[\text{PO}_{4(\text{aq})}^{3-}]}$$

$$K_b = 2.3 \times 10^{-2}$$

$$\frac{x^2}{0.10 - x} = 2.3 \times 10^{-2}$$

$$x^2 = 2.3 \times 10^{-2} (0.10 - x)$$

$$x^2 = 2.3 \times 10^{-3} - 2.3 \times 10^{-2}x$$

$$x^2 + 2.3 \times 10^{-2}x - 2.3 \times 10^{-3} = 0$$

$$x = \frac{-2.3 \times 10^{-2} \pm \sqrt{(2.3 \times 10^{-2})^2 - 4(-2.3 \times 10^{-3})}}{2}$$

$$x = 0.0378 \text{ (the only positive root)} \quad (\text{extra digits carried})$$

$$[\text{OH}_{(\text{aq})}^-] = 0.0378 \text{ mol/L}$$

$$\text{pOH} = -\log[0.0378]$$

$$= 1.42$$

$$\text{pH} = 14 - \text{pOH}$$

$$= 14.0 - 1.42$$

$$\text{pH} = 12.58$$

The pH of the phosphate solution is 12.58.

39. (a) (i) $\text{HPO}_{4(\text{aq})}^{2-} + \text{H}_2\text{O}_{(\text{l})} \rightleftharpoons \text{H}_3\text{O}_{(\text{aq})}^+ + \text{PO}_{4(\text{aq})}^{3-}$
(ii) $\text{HPO}_{4(\text{aq})}^{2-} + \text{H}_2\text{O}_{(\text{l})} \rightleftharpoons \text{OH}_{(\text{aq})}^- + \text{H}_2\text{PO}_{4(\text{aq})}^-$
- (b) $\text{HPO}_{4(\text{aq})}^{2-}; K_a = 4.2 \times 10^{-13}$
 $\text{HPO}_{4(\text{aq})}^{2-}; K_b = 2.4 \times 10^{-2}$
 K_b for the hydrogen phosphate ion is larger than K_a .
- (c) Since $K_b > K_a$, a solution of Na_2HPO_4 is basic.

40. (a) <7
(b) >7
(c) <7
(d) >7
(e) >7
(f) 7

41.

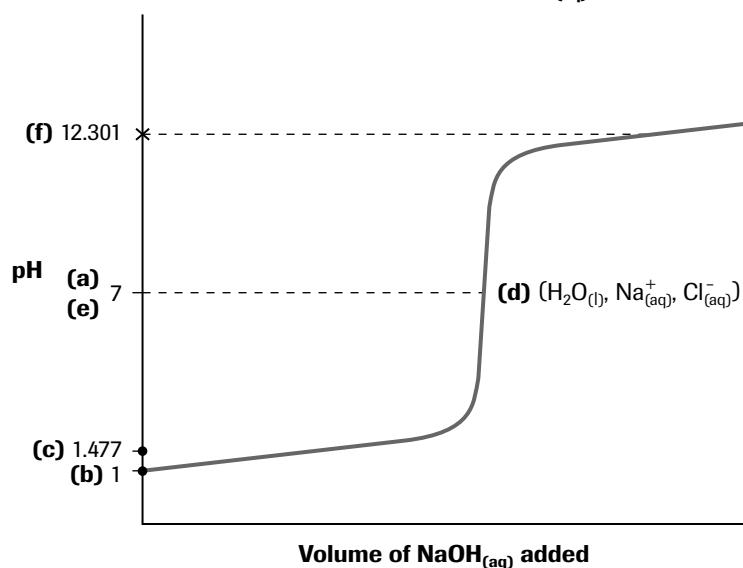
	Lewis acid:	Lewis base:
(a)	$\text{HCl}_{(\text{g})}$	$\text{NH}_{3(\text{g})}$
(b)	$\text{Cu}_{(\text{aq})}^{2+}$	$\text{H}_2\text{O}_{(\text{l})}$
(c)	$\text{Al}(\text{OH})_3$	$\text{OH}_{(\text{aq})}^-$

42.

Type of titration	pH at equivalence point
strong acid/strong base	7
strong acid/weak base	6
weak acid/strong base	9

43.

Titration of 0.100 mol/L HCl_(aq) with 0.100 mol/L NaOH_(aq)



(a) 7

(b) 1

(c) $V_{\text{HCl remaining}} = 5.00 \text{ mL}$

$$C_{\text{HCl after addition of NaOH}} = 0.100 \text{ mol/L} \times \frac{5 \text{ mL}}{15 \text{ mL}}$$

$$C_{\text{HCl after addition of NaOH}} = 0.0333 \text{ mol/L}$$

$$\text{pH} = -\log 0.0333$$

$$\text{pH} = 1.477$$

The pH after adding 5.00 mL of base is 1.477.

(d) H₂O_(l), Cl⁻_(aq), Na⁺_(aq)

(e) 7

(f) $V_{\text{NaOH remaining}} = 5.00 \text{ mL}$

$$C_{\text{NaOH}} = 0.100 \text{ mol/L} \times \frac{5.00 \text{ mL}}{25.00 \text{ mL}}$$
$$= 0.0200 \text{ mol/L}$$

$$\text{pOH} = -\log 0.0200$$

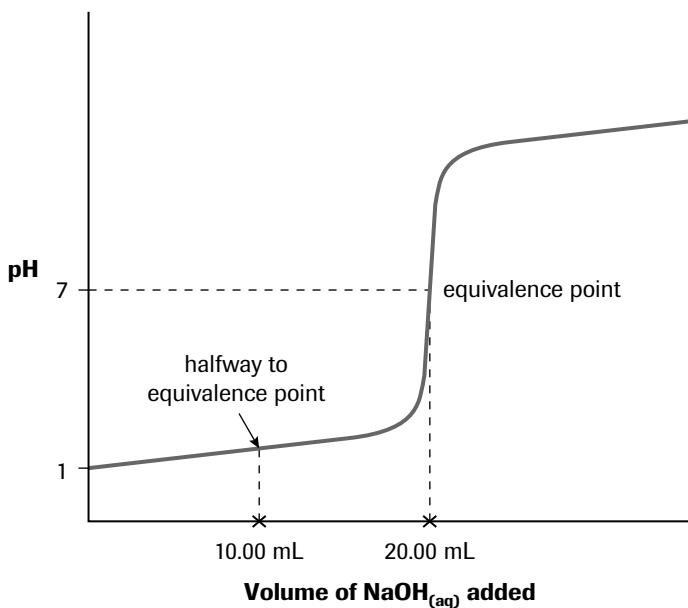
$$\text{pOH} = 1.699$$

$$\text{pH} = 12.301$$

The pH after adding 15.00 mL of base is 12.301.

44.

**Titration of 0.100 mol/L HCl_(aq)
with 0.100 mol/L NaOH_(aq)**



(a) 1

(b) $V_{\text{HCl remaining}} = 10.00 \text{ mL}$

$$C_{\text{HCl after addition of NaOH}} = 0.100 \text{ mol/L} \times \frac{10.00 \text{ mL}}{30.00 \text{ mL}}$$

$$C_{\text{HCl after addition of NaOH}} = 0.0333 \text{ mol/L}$$

$$\text{pH} = -\log 0.0333$$

$$\text{pH} = 1.477$$

The pH after adding 10.00 mL of base is 1.477.

(c) $V_{\text{HCl remaining}} = 0.10 \text{ mL}$

$$C_{\text{HCl after addition of NaOH}} = 0.100 \text{ mol/L} \times \frac{0.10 \text{ mL}}{39.90 \text{ mL}}$$

$$C_{\text{HCl after addition of NaOH}} = 2.506 \times 10^{-4} \text{ mol/L} \quad (\text{extra digits carried})$$

$$\text{pH} = -\log 2.506 \times 10^{-4}$$

$$\text{pH} = 3.601$$

The pH after adding 19.90 mL of base is 3.601.

(d) $V_{\text{HCl remaining}} = 0.01 \text{ mL}$

$$C_{\text{HCl after addition of NaOH}} = 0.01 \text{ mol/L} \times \frac{0.01 \text{ mL}}{39.99 \text{ mL}}$$

$$C_{\text{HCl after addition of NaOH}} = 2.5006 \times 10^{-6} \text{ mol/L} \quad (\text{extra digits carried})$$

$$\text{pH} = -\log 2.5006 \times 10^{-6}$$

$$\text{pH} = 4.602$$

The pH after adding 19.99 mL of base is 4.602.

(e) $V_{\text{NaOH remaining}} = 0.01 \text{ mL}$

$$C_{\text{NaOH}} = 0.100 \text{ mol/L} \times \frac{0.01 \text{ mL}}{40.01 \text{ mL}}$$

$$C_{\text{NaOH}} = 2.499 \times 10^{-5} \text{ mol/L} \quad (\text{extra digits carried})$$

$$\text{pOH} = -\log 2.499 \times 10^{-5}$$

$$pOH = 4.600$$

$$pH = 9.400$$

The pH after adding 20.01 mL of base is 9.400.

(f) $V_{NaOH \text{ remaining}} = 5.00 \text{ mL}$

$$C_{NaOH} = 0.100 \text{ mol/L} \times \frac{5.00 \text{ mL}}{45.00 \text{ mL}}$$

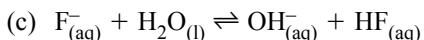
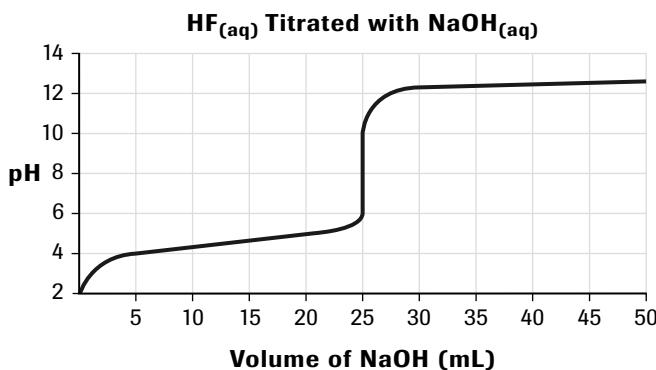
$$C_{NaOH} = 11 \times 10^{-2} \text{ mol/L}$$

$$pOH = 1.954$$

$$pH = 12.046$$

The pH after adding 25.00 mL of base is 12.046.

45. (a) $\text{HF}_{(aq)} + \text{NaOH}_{(aq)} \rightleftharpoons \text{H}_2\text{O}_{(l)} + \text{NaF}_{(aq)}$
(b)



Small additions of hydroxide are consumed by the reverse reaction of the equilibrium.

- (d) The pH at the equivalence point will be greater than 7: basic.

46. (a) The bottom curve represents the titration of a strong acid with sodium hydroxide solution. The strongest acid has the lowest initial pH.
(b) The top curve represents the titration of the acid with the smallest K_a value. The weakest acid will have the highest initial pH.
(c) At the equivalence point, the moles of acid present equal the moles of base added.

47.

methyl red	orange (red in transition to yellow)
thymolphthalein	colourless
bromothymol blue	green (blue in transition to yellow)
indigo carmine	yellow

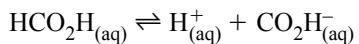
48. Thymolphthalein

49. The molar concentration of sodium acetate should also be 0.5 mol/L. Dissolve 1.5 g of anhydrous sodium acetate in enough distilled water to make 50 mL of solution. Combine this solution with 50 mL of 0.5 mol/L acetic acid.

50. (a) Bromothymol blue changes colour during the steep portion of the graph.
(b) The colour change of phenolphthalein is within the steep portion of the graph.
51. (a) Equilibrium shifts to the left.
(b) Equilibrium shifts to the right.
(c) Equilibrium shifts to the left.

52. $[CO_2H_{(aq)}^-] = 0.15 \text{ mol/L}$

$$[HCO_2H_{(aq)}] = 0.25 \text{ mol/L}$$



$$\frac{[H_{(aq)}^+][CO_2H_{(aq)}^-]}{[HCO_2H_{(aq)}]} = 1.8 \times 10^{-4}$$

$$\begin{aligned} [H_{(aq)}^+] &= K_a \frac{[HCO_2H_{(aq)}]}{[CO_2H_{(aq)}^-]} \\ &= 1.8 \times 10^{-4} \times \frac{0.25 \text{ mol/L}}{0.15 \text{ mol/L}} \end{aligned}$$

$$[H_{(aq)}^+] = 3.0 \times 10^{-4}$$

$$pH = -\log [1.8 \times 10^{-4}]$$

$$pH = 3.52$$

The addition of $H_{(aq)}^+$...

$$[H_{(aq)}^+]_{\text{added}} = 0.10 \text{ mol/L}$$

$$[HCO_2H_{(aq)}]_{\text{final}} = (0.25 + 0.10) \text{ mol/L}$$

$$[HCO_2H_{(aq)}]_{\text{final}} = 0.35 \text{ mol/L}$$

$$[CO_2H_{(aq)}^-]_{\text{final}} = (0.15 - 0.10) \text{ mol/L}$$

$$[CO_2H_{(aq)}^-]_{\text{final}} = 0.05 \text{ mol/L}$$

$$\begin{aligned} [H_{(aq)}^+] &= K_a \frac{[HCO_2H_{(aq)}]}{[CO_2H_{(aq)}^-]} \\ &= 1.8 \times 10^{-4} \times \frac{0.35}{0.05} \\ [H_{(aq)}^+] &= 1.26 \times 10^{-3} \quad (\text{extra digits carried}) \end{aligned}$$

$$pH = 2.90$$

The change in pH is $3.52 - 2.90$.

$$\Delta pH = 0.62$$

53. (a) $n_{Ag_2SO_4} = \frac{0.25 \text{ g}}{311.80 \text{ g/mol}}$

$$n_{Ag_2SO_4} = 8.0 \times 10^{-4} \text{ mol}$$

(b) molar solubility of Ag_2SO_4

$$= \frac{8.0 \times 10^{-4} \text{ mol}}{50.00 \times 10^{-3}}$$

$$= 0.016 \text{ mol/L}$$

(c) $[Ag_{(aq)}^+] = 0.032 \text{ mol/L}$

(d) $[SO_{4(aq)}^{2-}] = 0.016 \text{ mol/L}$

(e) $K_{sp} = [Ag_{(aq)}^+]^2[SO_{4(aq)}^{2-}]$

(f) $K_{sp} = [Ag_{(aq)}^+]^2[SO_{4(aq)}^{2-}]$

$$= [0.032]^2[0.016]$$

$$K_{sp} = 1.6 \times 10^{-5}$$

- (g) The accepted value for the solubility product of silver sulfate is 1.2×10^{-5} . The perfect difference between the calculated value and the accepted value is 33%. Given the large difference, the calculated value is judged to be unacceptable. (Note: Large errors in K_{sp} experiments are quite common.)
54. (a) Volume of unreacted acid = 17.40 mL

$$C_{\text{HCl}} = 17.40 \text{ mL} \times 1.00 \text{ mol/L}$$

$$C_{\text{HCl}} = 17.4 \text{ mmol}$$

The amount of unreacted acid is 17.4 mmol.

- (b) 7.60 mL of HCl reacted.

$$n_{\text{HCl}} = 7.60 \text{ mL} \times 1.00 \text{ mol/L}$$

$$n_{\text{HCl}} = 7.60 \text{ mmol}$$

2:1 ratio, therefore

$$n_{\text{CaCO}_3} = 3.80 \text{ mmol}$$

The amount of calcium carbonate in the shell was 3.80 mmol.

- (c) $m_{\text{CaCO}_3} = 3.80 \text{ mmol} \times 100.09 \text{ g/mol}$

$$m_{\text{CaCO}_3} = 0.380 \text{ g}$$

The mass of calcium carbonate in the shell was 0.380 g.

$$\% \text{CaCO}_3 = \frac{0.38}{0.45}$$

$$\% \text{CaCO}_3 = 84\%$$

The percent by mass of calcium carbonate in the shell is 84%.

- (d) Grinding the shell increases its surface area, allowing the reaction with acid to occur more quickly.
 (e) The contents of the flask are boiled to remove dissolved carbon dioxide from the solution and to ensure that the reaction with the acid is complete.
 (f) The addition of water dilutes the acid but does not alter the moles of acid present. The amount of base added depends only on the amount of acid.

55. (a) $n_{\text{KH}(\text{IO}_3)_2} = \frac{1.00 \text{ g}}{263.01 \text{ g/mol}}$

$$n_{\text{KH}(\text{IO}_3)_2} = 3.802 \times 10^{-3} \text{ mol}$$

$$n_{\text{KH}(\text{IO}_3)_2} = n_{\text{NaOH used}}$$

$$C_{\text{NaOH}} = \frac{3.802 \times 10^{-3} \text{ mol}}{25.54 \times 10^{-3} \text{ mol}}$$

$$C_{\text{NaOH}} = 0.185 \text{ mol/L}$$

The concentration of the sodium hydroxide solution is 0.185 mol/L.

- (b) Since this is a titration of a strong acid with a strong base, the pH change at the equivalence point is large. The pH range of both indicators falls well within the pH change that occurs.
 (c) Boiling the water removes dissolved carbon dioxide that could combine with the hydroxide ions.
 (d) The test tube prevents atmospheric carbon dioxide from dissolving into the solution.
56. (a) Maintaining a high pressure inside the washing machine forces the equilibrium to shift to the right – the side with fewer gas molecules.
 (b) Fresh-air circulation systems must be installed in CO₂ dry-cleaning facilities to ensure that workers and customers are not exposed to excessive levels of carbon dioxide. Periodic monitoring of carbon dioxide levels should occur on a regular basis. In the extreme, a sudden leak of CO₂ could suffocate everyone in the facility.
 (c) Carbon dioxide is an ideal dry-cleaning solvent. It is a nonpolar molecule that is just as effective in dissolving grease and oil as the organic solvents currently used in the dry-cleaning process. It is nonflammable, almost chemically inert, and does not harm the ozone layer as many dry-cleaning solvents do. Once the washing cycle is complete, carbon dioxide can be evaporated, leaving behind the residue of the cleaning process. The “clean”

gas is then collected and can be used for the next cleaning cycle. The clean clothing can be packaged immediately because no drying is required, saving considerable time.

57. (a) Assuming only Au^{3+} is present ...



Concentrations after mixing:

$$[\text{Au}_{(\text{aq})}^{3+}] = 5.6 \times 10^{-11} \text{ mol/L} \times \frac{1}{2}$$

$$[\text{Au}_{(\text{aq})}^{3+}] = 2.8 \times 10^{-11} \text{ mol/L}$$

$$[\text{Cl}_{(\text{aq})}^-] = 0.100 \text{ mol/L} \times \frac{1}{2}$$

$$[\text{Cl}_{(\text{aq})}^-] = 5.0 \times 10^{-2} \text{ mol/L}$$

$$Q = [\text{Au}_{(\text{aq})}^{3+}][\text{Cl}_{(\text{aq})}^-]^2 \\ = (2.8 \times 10^{-11})(5.0 \times 10^{-2})^3$$

$$Q = 3.5 \times 10^{-15}$$

$$K_{\text{sp}} = 3.2 \times 10^{-25}$$

Q is larger than K_{sp} . Therefore, a precipitate does form.

- (b) There is so little gold dissolved in seawater that huge quantities of water would have to be processed to extract a measurable amount of gold. This would require investment in an extremely large filtration system. Assuming the gold precipitates could be separated from all the other particulates that are found in seawater, we would then have to extract the gold from the precipitate. Another complication is that the amount of gold that has already precipitated with the existing chloride ions in seawater is unknown. In summary, the extraction of gold from seawater using precipitation is not feasible.

58. (a) $n_{\text{NaOH}} = \frac{24.88 \text{ g}}{40.00 \text{ g/mol}}$

$$n_{\text{NaOH}} = 0.6000 \text{ mol}$$

$$C_{\text{NaOH}_{(\text{aq})}} = \frac{0.6000 \text{ mol}}{0.750 \text{ L}}$$

$$C_{\text{NaOH}_{(\text{aq})}} = 0.800 \text{ mol/L}$$

$$\text{pOH} = -\log 0.800$$

$$\text{pOH} = 0.0969$$

$$\text{pH} = 14 - \text{pOH}$$

$$\text{pH} = 13.903$$

- (b) Safety goggles and chemical-resistant gloves and apron should be worn when preparing this solution.
59. (a) The approximately 2-mm-thick enamel layer that protects teeth is a mineral that has a very low K_{sp} — $\text{Ca}_5(\text{PO}_4)_3\text{OH}_{(\text{s})}$. The action of bacteria, particularly on the sweets we consume, can produce acetic and lactic acids. If the pH drops below 5.5, hydroxide ions are removed from enamel, resulting in demineralization.
- (b) Tooth decay can be prevented by:
- regular brushing to remove food particles, which become nutrients for bacteria, from teeth;
 - flossing to remove trapped food particles and plaque in places that the toothbrush cannot reach;
 - using toothpastes and fluoride treatments, which add $\text{F}_{(\text{aq})}^-$ ions to replace the $\text{OH}_{(\text{aq})}^-$ ions, to remineralize teeth with $\text{Ca}_5(\text{PO}_4)_3\text{F}_{(\text{s})}$;
 - avoiding sticky, sweet foods because they remain on teeth, providing bacteria with a trapped supply of sugar.
 - Some foods, such as milk and other dairy products, actually raise the pH of saliva. They are also rich in calcium and phosphorus and can help remineralize teeth.
60. (a) A decrease in pH corresponds to an increase in the hydrogen ion concentration in the pool water. In response, the system shifts to the left in an effort to consume the excess acid. This produces more hypochlorous acid, which is an eye irritant.

- (b) Raising the pH removes hydrogen ions from the equilibrium. The system responds by producing more hydrogen hypochlorite ions via the forward reaction. The concentration of hypochlorite increases.
- (c) A “shock treatment” involves adding a larger than normal amount of an oxidizing compound like sodium hypochlorite to the pool. These compounds oxidize organic contaminants or ammonia and other nitrogen compounds and sanitize the water.
- (d) A “shock treatment” introduces excess hypochlorite ions to the pool that cause the hypochlorous acid–hypochlorite equilibrium to shift to the left, consuming hydrogen ions in the process. The reduction of hydrogen ions increases the pH of the water.
61. The addition of calcium hydroxide or “slaked lime” has been useful in temporarily reducing the effects of acid deposition in lakes. Calcium hydroxide is relatively inexpensive, readily available in Ontario, nontoxic, and it dissolves readily in water. However, liming a lake can only be a temporary solution. If acid deposition continues, it is not economically feasible to be continually adding calcium hydroxide to lakes. Also, the already existing metal contaminants of the lake pose a possible toxic risk to aquatic life. An alternative strategy would be to reduce the amount of acid deposition contaminating the lakes in the first place.

Extension/Challenge

62. (a) The large value of K suggests that the reaction strongly favours the products of this reaction. Consequently, very little hydrogen sulfide or sulfur dioxide is released.
- (b) An increase in pressure shifts the equilibrium to the side having fewer gas molecules – the right side. The efficiency of the reaction should increase with increasing pressure.
- (c) An increase in temperature favours the reverse reaction, which would decrease the efficiency of the reaction.
63. (a) (i) An increase in pressure increases the yield of sulfur trioxide.
(ii) The removal of sulfur trioxide increases the yield of sulfur trioxide.
(iii) Continually adding $\text{SO}_{2(\text{g})}$ and $\text{O}_{2(\text{g})}$ increases the yield of sulfur trioxide.
- (b) The use of a catalyst does not affect the position of the equilibrium because the catalyst increases the rate of both forward and reverse reactions. However, a catalyst does allow more SO_3 to be produced in a given period of time – an increase in the rate of production.
- (c) An increase in temperature shifts the equilibrium to the left. However, it also increases the rate of both reactions, resulting in more SO_3 being produced.
64. (a)

ICE Table for the Solubility of Calcium Carbonate			
	$\text{CaCO}_{3(\text{s})} \rightleftharpoons$	$\text{Ca}_{(\text{aq})}^{2+} +$	$\text{CO}_{3(\text{aq})}^{2-}$
Initial concentration (mol/L)	–	0.00	0.00
Change in concentration (mol/L)	–	+ x	+ x
Equilibrium concentration (mol/L)	–	x	x

$$K_{\text{sp}} = [\text{Ca}_{(\text{aq})}^{2+}][\text{CO}_{3(\text{aq})}^{2-}]$$

$$= 5.0 \times 10^{-9}$$

$$(x)(x) = 5.0 \times 10^{-9}$$

$$x = 7.1 \times 10^{-5}$$

The molar solubility of calcium carbonate is 7.1×10^{-5} mol/L.

$$(b) \quad n_{\text{CaCO}_3} = \frac{5.00 \text{ g}}{100.0 \text{ g/mol}}$$

$$n_{\text{CaCO}_3} = 0.050 \text{ mol}$$

$$\text{molar solubility} = 7.1 \times 10^{-5} \text{ mol/L}$$

$$V_{\text{water required}} = \frac{0.050 \text{ mol}}{7.1 \times 10^{-5} \text{ mol/L}}$$

$$V_{\text{water required}} = 700 \text{ L}$$

Since the kettle holds 2.0 L of water, it would have to be filled 350 times to dissolve the calcium carbonate scale. This assumes that more scale deposits do not form and that the existing calcium carbonate does not break off during this process.

- (c) Precipitation of calcium carbonate occurs because water cannot hold as much solute when its temperature decreases.
- (d) This is a common problem in hot-water pipes and hot-water heaters.

Unit 5 Electrochemistry

ARE YOU READY?

(Page 648)

Safety and Technical Skills

1. Check all connections and make sure that the equipment is in good condition with no frayed cords or damaged plugs.
2. To handle electrical equipment safely, water or wet hands should never be used near electrical equipment and wires and cords should not be placed where someone could trip over them.

Knowledge and Understanding

3. When a metal atom forms an ion, the atom loses electrons to form a positively charged ion.
4. When a nonmetal atom forms an ion, the atom gains electrons to form a negatively charged ion.
- 5.

Table 1 Reactivity of Elements

Category	Groups or examples
most reactive metals	alkali metals
least reactive metals	precious metals, i.e., silver, gold, platinum
most reactive nonmetals	halogens
least reactive nonmetals	noble gases

6. (a) $\text{K}^+ \left[: \ddot{\text{Cl}} : \right]^-$
- :Cl:
- (b) :Cl: P :Cl:
- (c) In part (a), the potassium atom transfers one electron to the chlorine atom, forming a potassium ion and a chloride ion.
In part (b), the phosphorus atom shares two electrons with each of three chlorine atoms, thereby forming a neutral molecule.
- (d) According to bonding theory, the difference in electronegativity between two atoms is believed to determine whether they will transfer or share electrons.
7. (a) element + compound → element + compound
(b) The product is the same class of element as the reactant; that is, the product is a metal when the reactant element is a metal, and the product is a nonmetal when the reactant element is a nonmetal.
8. (a) $\text{Zn}_{(s)} + 2 \text{AgNO}_{3(aq)} \rightarrow 2 \text{Ag}_{(s)} + \text{Zn}(\text{NO}_3)_{2(aq)}$
(b) $\text{Cl}_{2(aq)} + 2 \text{KBr}_{(aq)} \rightarrow \text{Br}_{2(aq)} + 2 \text{KCl}_{(aq)}$
(c) $2 \text{Al}_{(s)} + 6 \text{HCl}_{(aq)} \rightarrow 3 \text{H}_{2(g)} + 2 \text{AlCl}_{3(aq)}$
(d) $\text{C}_3\text{H}_{8(g)} + 5 \text{O}_{2(g)} \rightarrow 3 \text{CO}_{2(g)} + 4 \text{H}_2\text{O}_{(g)}$

Inquiry and Communication

9. (a) Iodine is likely present.
(b) Bromine is likely present.
(c) The solution is acidic.
(d) The solution is basic.
(e) Copper(II) ions are likely present.
(f) Sodium ions are likely present.

CHAPTER 9 ELECTRIC CELLS

Reflect On Your Learning

(Page 650)

1. [Likely initial answer] Chemical reactions occur that produce electricity.
[More complete answer] The substance with the greatest tendency to gain electrons (i.e., with the most positive reduction potential) pulls electrons via the external circuit from another substance with the greatest tendency to lose electrons (i.e., with the most negative reduction potential). Ions transfer electric charge within the electrolyte to complete the internal circuit.
2. [Likely initial answer] The ability to transfer electrons is the key scientific concept.
[More complete answer] The relative strengths of oxidizing and reducing agents as measured by reduction potentials is a key concept to explain why electrons are transferred. Oxidation states help to understand and describe the chemical changes that accompany the gain and loss of electrons. Other concepts such as electronegativities and ion mobility are also part of the explanation.
3. [Likely initial answer] Cells come in a variety of sizes; some cells are rechargeable and some are not. There are also different chemicals that are used such as nickel–cadmium (NiCad) and lead acid. Cells have a great impact because of their use in cars and portable electronic devices such as CD and DVD players.
[More complete answer] Cells generally fall into three categories: primary, secondary, and fuel cells. Each has different characteristics and uses. Primary cells are not rechargeable, are relatively inexpensive, and are used in flashlights and small electronic devices. Secondary cells are rechargeable and are very useful for mobile phones, laptop computers, and small electronic devices. Fuel cells use a continuously supplied fuel and can be used for small power-generating stations and probably (in the near future) in cars. All of these cells significantly affect our lives in terms of convenience, new opportunities, and environmental effects.

Try This Activity: A Simple Electric Cell

(Page 651)

- (a) The copper strip was momentarily connected to the positive (red) terminal of the voltmeter and the zinc strip to the negative (black) terminal. The needle of the voltmeter deflected briefly from zero to positive values (or the digital meter briefly registered a positive value). When the leads were reversed, the needle tried to go backwards below zero (or the digital meter briefly registered a negative value).
- (b) Yes. (Depending on the fruit or vegetable, two may be needed, connected in series.)
- (c) The orange with the two metal strips acted like a cell or battery. There must be some chemical reactions occurring that produce electricity.
- (d) Yes.
- (e) All fruits and vegetables contain some kind of juice as long as they are relatively fresh and not dried out.
- (f) The electric cell could be improved with a more compact and convenient design. Instead of using some fruit or vegetable, use the essential chemicals inside the fruit or vegetable and put them in some kind of container.

9.1 OXIDATION AND REDUCTION

PRACTICE

(Page 653)

Understanding Concepts

1. (a) Reduction was used to describe a reaction producing a metal from its naturally occurring compound.
- (b) Oxidation was used to describe reactions of substances such as metals or fuels with oxygen.
- (c) An oxidizing agent is a substance that causes or promotes the oxidation of another substance.
- (d) A reducing agent is a substance that causes or promotes the reduction of another substance.
- (e) Metallurgy is the science and technology of extracting metals from their naturally occurring compounds and adapting these metals for useful purposes.
- (f) Corrosion is the adverse reaction of human-made items with chemicals in the environment, usually metals reacting to form oxides, carbonates, or sulfides.

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(Page 653)

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2. (a) oxidation of iron; oxygen is the oxidizing agent
 (b) reduction of lead(II) oxide; carbon is the reducing agent
 (c) reduction of nickel(II) oxide; hydrogen is the reducing agent
 (d) oxidation of tin; bromine is the oxidizing agent
 (e) reduction of iron(III) oxide; carbon monoxide is the reducing agent
 (f) oxidation of copper; nitric acid is the oxidizing agent
3. Three reducing agents used in metallurgy are carbon, carbon monoxide, and hydrogen.
4. Nonmetals serve as oxidizing agents for metals.

Making Connections

5. In the history of metallurgy, technological applications came before scientific understanding. Methods for refining and alloying gold, copper, silver, lead, mercury, tin, and iron were developed over 3000 years ago, long before atomic theory.

Extension

6. Archaeometallurgists are concerned with what metals are present in metallic objects, where the metal ores were mined, and where the metals were reduced from the ore. The metals most studied are copper, tin, and lead, as found in bronze objects made during the time period from 3000 B.C. to 1000 B.C. (the “Bronze Age”). Samples of the same metal from different mines can be distinguished from each other by the ratios of the lead isotopes that are present. Establishing the place where a metal was mined helps archaeologists to reconstruct the trade patterns of ancient societies.

PRACTICE

(Page 656)

Understanding Concepts

7. (a) A redox reaction is a chemical reaction involving a transfer of electrons.
 (b) Reduction is a chemical process involving a gain of electrons.
 (c) Oxidation is a chemical process involving a loss of electrons.
8. (a) $\text{Zn}_{(\text{s})} \rightarrow \text{Zn}_{(\text{aq})}^{2+} + 2 \text{e}^-$
 $\text{Cu}_{(\text{aq})}^{2+} + 2 \text{e}^- \rightarrow \text{Cu}_{(\text{s})}$
- (b) $\text{Mg}_{(\text{s})} \rightarrow \text{Mg}_{(\text{aq})}^{2+} + 2 \text{e}^-$
 $2 \text{H}_{(\text{aq})}^+ + 2 \text{e}^- \rightarrow \text{H}_{2(\text{g})}$
9. (a) $\text{Ni}_{(\text{s})} \rightarrow \text{Ni}_{(\text{aq})}^{2+} + 2 \text{e}^-$ oxidation
 $\text{Cu}_{(\text{aq})}^{2+} + 2 \text{e}^- \rightarrow \text{Cu}_{(\text{s})}$ reduction
- (b) $\text{Pb}_{(\text{s})} \rightarrow \text{Pb}_{(\text{aq})}^{2+} + 2 \text{e}^-$ oxidation
 $\text{Cu}_{(\text{aq})}^{2+} + 2 \text{e}^- \rightarrow \text{Cu}_{(\text{s})}$ reduction
- (c) $2 \text{H}_{(\text{aq})}^+ + 2 \text{e}^- \rightarrow \text{H}_{2(\text{g})}$ reduction
 $\text{Ca}_{(\text{s})} \rightarrow \text{Ca}_{(\text{aq})}^{2+} + 2 \text{e}^-$ oxidation
- (d) $\text{Fe}_{(\text{s})}^{3+} + 3 \text{e}^- \rightarrow \text{Fe}_{(\text{l})}$ reduction
 $\text{Al}_{(\text{s})} \rightarrow \text{Al}_{(\text{aq})}^{3+} + 3 \text{e}^-$ oxidation
10. $\text{Cl}_{2(\text{aq})} + 2 \text{e}^- \rightarrow 2 \text{Cl}_{(\text{aq})}^-$
 $2 \text{I}_{(\text{aq})} \rightarrow \text{I}_{2(\text{s})} + 2 \text{e}^-$

11. The presence of the same ions in the reactants and products indicates that no electrons have been transferred. Therefore, a redox reaction has not taken place.

PRACTICE

(Page 659)

Understanding Concepts

12. (a) +4

(b) +7

(c) +6

(d) +6

(e) -1

(f) -1

13. (a) +1

(b) +2

(c) +4

(d) -3

(e) -2

(f) +5

(g) 0

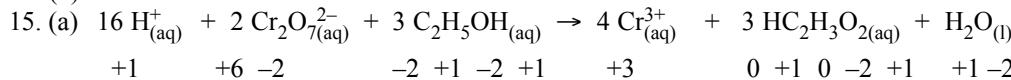
(h) -3

14. (a) 0

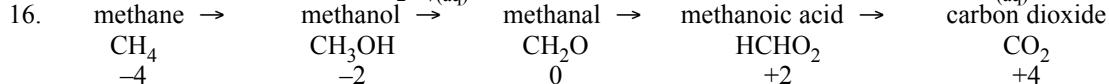
(b) 0

(c) +4

(d) +2



(b) The orange colour of the $\text{Cr}_2\text{O}_{7(\text{aq})}^{2-}$ should be replaced by the green colour of the $\text{Cr}_{(\text{aq})}^{3+}$.



Extension

17. (a) The oxidation number of iron in Fe_3O_4 is calculated to be $\frac{8}{3}$.

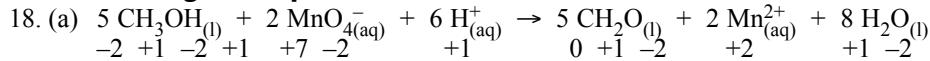
(b) The fractional value of the answer is unusual because it would involve a fractional number of electrons which is not possible.

(c) The formula, Fe_3O_4 , might represent a compound involving a combination of iron(II) oxide and iron(III) oxide, which could be written $\text{FeO} \cdot \text{Fe}_2\text{O}_3$.

PRACTICE

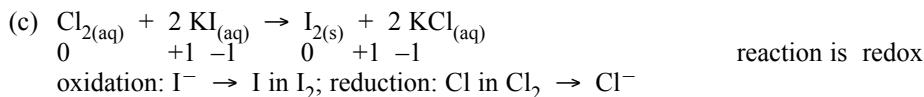
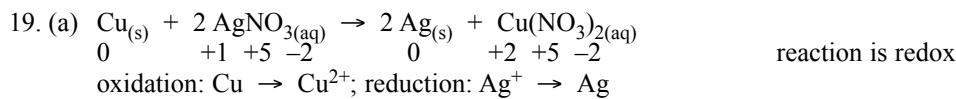
(Page 662)

Understanding Concepts



(b) Carbon is oxidized from -2 to 0; $\text{CH}_3\text{OH} \xrightarrow{\text{oxidation}} \text{CH}_2\text{O}$

(c) Manganese is reduced from +7 to +2; $\text{MnO}_4^- \xrightarrow{\text{reduction}} \text{Mn}^{2+}$



(d) $2 \text{NaCl}_{(l)} \rightarrow 2 \text{Na}_{(l)} + \text{Cl}_{2(g)}$	reaction is redox
oxidation: $\text{Cl}^- \rightarrow \text{Cl}$ in Cl_2 ; reduction: $\text{Na}^+ \rightarrow \text{Na}$	
(e) $\text{HCl}_{(aq)} + \text{NaOH}_{(aq)} \rightarrow \text{HOH}_{(l)} + \text{NaCl}_{(aq)}$	reaction is not redox
$\begin{array}{ccccccc} +1 & -1 & +1 & -2 & +1 & +1 & -1 \\ \text{HCl}_{(aq)} & & \text{NaOH}_{(aq)} & & \text{HOH}_{(l)} & + & \text{NaCl}_{(aq)} \end{array}$	
(f) $2 \text{Al}_{(s)} + 3 \text{Cl}_{2(g)} \rightarrow 2 \text{AlCl}_{3(s)}$	reaction is redox
$\begin{array}{ccccc} 0 & 0 & +3 & -1 \\ \text{Al}_{(s)} & \text{Cl}_{2(g)} & & & \text{AlCl}_{3(s)} \end{array}$	
oxidation: $\text{Al} \rightarrow \text{Al}^{3+}$; reduction: Cl in $\text{Cl}_2 \rightarrow \text{Cl}^-$	
(g) $2 \text{C}_4\text{H}_{10(g)} + 13 \text{O}_{2(g)} \rightarrow 8 \text{CO}_{2(g)} + 10 \text{H}_2\text{O}_{(l)}$	reaction is redox
$\begin{array}{ccccc} -2.5 & +1 & 0 & +4 & -2 \\ \text{C}_4\text{H}_{10(g)} & & \text{O}_{2(g)} & & \text{CO}_{2(g)} \\ & & & +1 & -2 \\ & & & \text{H}_2\text{O}_{(l)} & \end{array}$	
oxidation: C in C_4H_{10} \rightarrow C in CO_2 ; reduction: O in $\text{O}_2 \rightarrow$ O in CO_2 and H_2O	
(h) $2 \text{H}_2\text{O}_{2(l)} \rightarrow 2 \text{H}_2\text{O}_{(l)} + \text{O}_{2(g)}$	reaction is redox
$\begin{array}{ccccc} +1 & -1 & +1 & -2 & 0 \\ \text{H}_2\text{O}_{2(l)} & & \text{H}_2\text{O}_{(l)} & + & \text{O}_{2(g)} \end{array}$	
oxidation: O in H_2O_2 to O in O_2 ; reduction: O in H_2O_2 to O in H_2O	

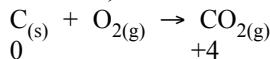
20. (a) single displacement
 (b) double displacement
 (c) single displacement
 (d) decomposition
 (e) double displacement
 (f) formation
 (g) combustion
 (h) decomposition

Double displacement reactions do not appear to be redox reactions.

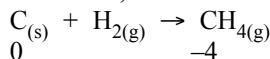
21. The oxygen atoms in hydrogen peroxide, $\text{H}_2\text{O}_{2(l)}$, have an oxidation number of -1 , and can be either oxidized to $\text{O}_{2(g)}$, (oxidation number of 0), or reduced to an oxidation state of -2 (as in $\text{H}_2\text{O}_{(l)}$ or metallic oxides).

Making Connections

22. On Earth, carbon is easily oxidized to carbon dioxide by a combustion reaction.



On Saturn, carbon would likely undergo the following reduction reaction.



SECTION 9.1 QUESTIONS

(Page 663)

Understanding Concepts

1.

	Electron transfer	Oxidation states
oxidation	loss of electrons	increases (becomes more positive)
reduction	gain of electrons	decreases (becomes more negative)

2. (a) $\text{Cu}_{(aq)}^{2+} + 2 \text{e}^- \rightarrow \text{Cu}_{(s)}$ reduction
 $\text{Pb}_{(s)} \rightarrow \text{Pb}_{(aq)}^{2+} + 2 \text{e}^-$ oxidation
 (b) $\text{Cl}_{2(aq)} + 2 \text{e}^- \rightarrow 2 \text{Cl}_{(aq)}^-$ reduction
 $2 \text{Br}_{(aq)}^- \rightarrow \text{Br}_{2(l)} + 2 \text{e}^-$ oxidation

3. An oxidation number is a positive or negative number corresponding to the apparent charge that an atom in a molecule or ion would have if the electron pairs in covalent bonds belonged entirely to the more electronegative atom.

4. A redox reaction can be recognized using a chemical reaction equation by

- looking for examples of formation, decomposition, single displacement, and combustion reactions;

- comparing the oxidation states of atoms/ions on the reactant side of the equation with those of atoms/ions of the same elements on the product side.
5. (a) When an atom is oxidized, its oxidation number increases, i.e., becomes more positive.
 (b) When an atom is reduced, its oxidation number decreases, i.e., becomes more negative.
6. (a) carbon +2; oxygen -2
 (b) oxygen 0
 (c) nitrogen -3; hydrogen +1; chloride -1
 (d) hydrogen +1; phosphorus +5; oxygen -2
 (e) sodium +1; sulfur +2; oxygen -2
 (f) sodium +1; phosphorus +5; oxygen -2
7. (a) $\text{MnO}_4^{\text{-}}_{\text{(aq)}} + \text{C}_2\text{O}_4^{2-}_{\text{(aq)}} + \text{H}^{\text{+}}_{\text{(aq)}} \rightarrow \text{Mn}^{2+}_{\text{(aq)}} + \text{H}_2\text{O}_{\text{(l)}} + \text{CO}_2_{\text{(g)}}$
 $+7 \quad -2 \quad +3 \quad -2 \quad +1 \quad +2 \quad +1 \quad -2 \quad +4 \quad -2$
- (b) Carbon is oxidized. Its oxidation number changes from +3 to +4.
 (c) Manganese is reduced. Its oxidation number changes from +7 to +2.
8. (a) $\text{H}_2\text{O}_{\text{(l)}} + \text{CO}_2_{\text{(g)}} \rightarrow \text{H}_2\text{CO}_3_{\text{(aq)}}$
 (b) This is not a redox reaction. The oxidation numbers of all of the atoms remain unchanged.

Applying Inquiry Skills

9. Clean the surface of the copper and zinc strips thoroughly using steel wool. Rinse, dry, and measure the mass of each metal strip. Then insert the strips into an orange (or other fruit) and connect the strips directly with a wire. Let the cell operate for a period of time. Remove electrodes, rinse and dry, and measure the mass of each electrode.

Making Connections

10. (a) $3 \text{Ag}_2\text{S}_{\text{(s)}} + 2 \text{Al}_{\text{(s)}} \rightarrow \text{Al}_2\text{S}_3_{\text{(s)}} + 6 \text{Ag}_{\text{(s)}}$
 (b) Aluminum is oxidized (0 to +3) and silver is reduced (+1 to 0).
 (c) This is a better method of cleaning silver than polishing or scrubbing because it does not remove silver from the object the way that polishing and scrubbing do.
11. The Breathalyzer measures the alcohol content of exhaled breath, which is assumed to be proportional to the blood alcohol content. Inside the device, the alcohol in the breath sample is oxidized by acidic potassium dichromate, a process that produces a colour change that is measured by a colorimeter.
 The Intoxilyzer uses infrared absorption spectroscopy to pass infrared light through the breath sample, and then measures how much absorption is caused by the presence of alcohol.
 The technology of the Breathalyzer is based on the redox reaction between ethanol and acidic potassium dichromate, while the Intoxilyzer is based on infrared absorption spectroscopy, which does not involve a redox reaction.

9.2 BALANCING REDOX EQUATIONS

PRACTICE

(Page 668)

Understanding Concepts

- The oxidation number of an atom is calculated by counting shared electrons as belonging to the more electronegative atom. Therefore, the gain or loss of electrons by an atom is reflected by a change in the oxidation number equal to the number of electrons transferred.
2. (a) $\text{Cr}_2\text{O}_7^{2-}_{\text{(aq)}} + 6 \text{Cl}^-_{\text{(aq)}} + 14 \text{H}^+_{\text{(aq)}} \rightarrow 2 \text{Cr}^{3+}_{\text{(aq)}} + 3 \text{Cl}_2_{\text{(aq)}} + 7 \text{H}_2\text{O}_{\text{(l)}}$
 (b) $2 \text{IO}_3^-_{\text{(aq)}} + 5 \text{HSO}_3^-_{\text{(aq)}} \rightarrow 5 \text{SO}_4^{2-}_{\text{(aq)}} + \text{I}_2_{\text{(s)}} + 3 \text{H}^+_{\text{(aq)}} + \text{H}_2\text{O}_{\text{(l)}}$
 (c) $2 \text{HBr}_{\text{(aq)}} + \text{H}_2\text{SO}_4_{\text{(aq)}} \rightarrow \text{SO}_2_{\text{(g)}} + \text{Br}_2_{\text{(l)}} + 2 \text{H}_2\text{O}_{\text{(l)}}$
3. (a) $2 \text{MnO}_4^-_{\text{(aq)}} + 3 \text{SO}_3^{2-}_{\text{(aq)}} + \text{H}_2\text{O}_{\text{(l)}} \rightarrow 3 \text{SO}_4^{2-}_{\text{(aq)}} + 2 \text{MnO}_2_{\text{(s)}} + 2 \text{OH}^-_{\text{(aq)}}$
 (b) $4 \text{ClO}_3^-_{\text{(aq)}} + 3 \text{N}_2\text{H}_4_{\text{(aq)}} \rightarrow 6 \text{NO}_{\text{(g)}} + 4 \text{Cl}^-_{\text{(aq)}} + 6 \text{H}_2\text{O}_{\text{(l)}}$
4. $4 \text{NH}_3_{\text{(g)}} + 7 \text{O}_2_{\text{(g)}} \rightarrow 4 \text{NO}_2_{\text{(g)}} + 6 \text{H}_2\text{O}_{\text{(g)}}$

- comparing the oxidation states of atoms/ions on the reactant side of the equation with those of atoms/ions of the same elements on the product side.
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 $+7 \quad -2 \quad +3 \quad -2 \quad +1 \quad +2 \quad +1 \quad -2 \quad +4 \quad -2$
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Applying Inquiry Skills

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 (b) Aluminum is oxidized (0 to +3) and silver is reduced (+1 to 0).
 (c) This is a better method of cleaning silver than polishing or scrubbing because it does not remove silver from the object the way that polishing and scrubbing do.
11. The Breathalyzer measures the alcohol content of exhaled breath, which is assumed to be proportional to the blood alcohol content. Inside the device, the alcohol in the breath sample is oxidized by acidic potassium dichromate, a process that produces a colour change that is measured by a colorimeter.
 The Intoxilyzer uses infrared absorption spectroscopy to pass infrared light through the breath sample, and then measures how much absorption is caused by the presence of alcohol.
 The technology of the Breathalyzer is based on the redox reaction between ethanol and acidic potassium dichromate, while the Intoxilyzer is based on infrared absorption spectroscopy, which does not involve a redox reaction.

9.2 BALANCING REDOX EQUATIONS

PRACTICE

(Page 668)

Understanding Concepts

- The oxidation number of an atom is calculated by counting shared electrons as belonging to the more electronegative atom. Therefore, the gain or loss of electrons by an atom is reflected by a change in the oxidation number equal to the number of electrons transferred.
2. (a) $\text{Cr}_2\text{O}_7^{2-}(\text{aq}) + 6 \text{Cl}^-(\text{aq}) + 14 \text{H}^+(\text{aq}) \rightarrow 2 \text{Cr}^{3+}(\text{aq}) + 3 \text{Cl}_2(\text{aq}) + 7 \text{H}_2\text{O}(\text{l})$
 (b) $2 \text{IO}_3^-(\text{aq}) + 5 \text{HSO}_3^-(\text{aq}) \rightarrow 5 \text{SO}_4^{2-}(\text{aq}) + \text{I}_2(\text{s}) + 3 \text{H}^+(\text{aq}) + \text{H}_2\text{O}(\text{l})$
 (c) $2 \text{HBr}(\text{aq}) + \text{H}_2\text{SO}_4(\text{aq}) \rightarrow \text{SO}_2(\text{g}) + \text{Br}_2(\text{l}) + 2 \text{H}_2\text{O}(\text{l})$
3. (a) $2 \text{MnO}_4^-(\text{aq}) + 3 \text{SO}_3^{2-}(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightarrow 3 \text{SO}_4^{2-}(\text{aq}) + 2 \text{MnO}_2(\text{s}) + 2 \text{OH}^-(\text{aq})$
 (b) $4 \text{ClO}_3^-(\text{aq}) + 3 \text{N}_2\text{H}_4(\text{aq}) \rightarrow 6 \text{NO}(\text{g}) + 4 \text{Cl}^-(\text{aq}) + 6 \text{H}_2\text{O}(\text{l})$
4. $4 \text{NH}_3(\text{g}) + 7 \text{O}_2(\text{g}) \rightarrow 4 \text{NO}_2(\text{g}) + 6 \text{H}_2\text{O}(\text{g})$

PRACTICE

(Page 671)

Understanding Concepts

5. (a) $\text{N}_2\text{O}_{(\text{g})} + 2 \text{H}_{(\text{aq})}^+ + 2 \text{e}^- \rightarrow \text{N}_{2(\text{g})} + \text{H}_2\text{O}_{(\text{l})}$ reduction
(b) $\text{NO}_{2(\text{aq})}^- + 2 \text{OH}_{(\text{aq})}^- \rightarrow \text{NO}_{3(\text{aq})}^- + \text{H}_2\text{O}_{(\text{l})} + 2 \text{e}^-$ oxidation
(c) $\text{Ag}_2\text{O}_{(\text{s})} + \text{H}_2\text{O}_{(\text{l})} + 2 \text{e}^- \rightarrow 2 \text{Ag}_{(\text{s})} + 2 \text{OH}_{(\text{aq})}^-$ reduction
(d) $\text{NO}_{3(\text{aq})}^- + 3 \text{H}_{(\text{aq})}^+ + 2 \text{e}^- \rightarrow \text{HNO}_{2(\text{aq})} + \text{H}_2\text{O}_{(\text{l})}$ reduction
(e) $\text{H}_{2(\text{g})} + 2 \text{OH}_{(\text{aq})}^- \rightarrow 2 \text{H}_2\text{O}_{(\text{l})} + 2 \text{e}^-$ oxidation

PRACTICE

(Page 673)

Understanding Concepts

6. (a)
$$\begin{array}{r} 4 [\text{Zn}_{(\text{s})} \rightarrow \text{Zn}_{(\text{aq})}^{2+} + 2 \text{e}^-] \\ \text{NO}_{3(\text{aq})}^- + 10 \text{H}_{(\text{aq})}^+ + 8 \text{e}^- \rightarrow \text{NH}_{4(\text{aq})}^+ + 3 \text{H}_2\text{O}_{(\text{l})} \\ \hline 4 \text{Zn}_{(\text{s})} + \text{NO}_{3(\text{aq})}^- + 10 \text{H}_{(\text{aq})}^+ \rightarrow 4 \text{Zn}_{(\text{aq})}^{2+} + \text{NH}_{4(\text{aq})}^+ + 3 \text{H}_2\text{O}_{(\text{l})} \end{array}$$

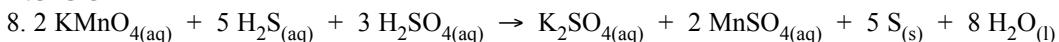
(b)
$$\begin{array}{r} \text{Cl}_{2(\text{aq})} + 2 \text{e}^- \rightarrow 2 \text{Cl}_{(\text{aq})}^- \\ \text{SO}_{2(\text{g})} + 2 \text{H}_2\text{O}_{(\text{l})} \rightarrow \text{SO}_{4(\text{aq})}^{2-} + 4 \text{H}_{(\text{aq})}^+ + 2 \text{e}^- \\ \hline \text{Cl}_{2(\text{aq})} + \text{SO}_{2(\text{g})} + 2 \text{H}_2\text{O}_{(\text{l})} \rightarrow 2 \text{Cl}_{(\text{aq})}^- + \text{SO}_{4(\text{aq})}^{2-} + 4 \text{H}_{(\text{aq})}^+ \end{array}$$

7. (a)
$$\begin{array}{r} 2 [\text{MnO}_{4(\text{aq})}^- + 2 \text{H}_2\text{O}_{(\text{l})} + 3 \text{e}^- \rightarrow \text{MnO}_{2(\text{s})} + 4 \text{OH}_{(\text{aq})}^-] \\ 3 [2 \text{I}_{(\text{aq})}^- \rightarrow \text{I}_{2(\text{s})} + 2 \text{e}^-] \\ \hline 2 \text{MnO}_{4(\text{aq})}^- + 4 \text{H}_2\text{O}_{(\text{l})} + 6 \text{I}_{(\text{aq})}^- \rightarrow 2 \text{MnO}_{2(\text{s})} + 8 \text{OH}_{(\text{aq})}^- + 3 \text{I}_{2(\text{s})} \end{array}$$

(b)
$$\begin{array}{r} 3 [\text{CN}_{(\text{aq})}^- + 2 \text{OH}_{(\text{aq})}^- \rightarrow \text{CNO}_{(\text{aq})}^- + \text{H}_2\text{O}_{(\text{l})} + 2 \text{e}^-] \\ \text{IO}_{3(\text{aq})}^- + 3 \text{H}_2\text{O}_{(\text{l})} + 6 \text{e}^- \rightarrow \text{I}_{(\text{aq})}^- + 6 \text{OH}_{(\text{aq})}^- \\ \hline 3 \text{CN}_{(\text{aq})}^- + \text{IO}_{3(\text{aq})}^- \rightarrow 3 \text{CNO}_{(\text{aq})}^- + \text{I}_{(\text{aq})}^- \end{array}$$

(c)
$$\begin{array}{r} 2 [\text{OCl}_{(\text{aq})}^- + \text{H}_2\text{O}_{(\text{l})} + 2 \text{e}^- \rightarrow \text{Cl}_{(\text{aq})}^- + 2 \text{OH}_{(\text{aq})}^-] \\ \text{OCl}_{(\text{aq})}^- + 4 \text{OH}_{(\text{aq})}^- \rightarrow \text{ClO}_{3(\text{aq})}^- + 2 \text{H}_2\text{O}_{(\text{l})} + 4 \text{e}^- \\ \hline 3 \text{OCl}_{(\text{aq})}^- \rightarrow 2 \text{Cl}_{(\text{aq})}^- + \text{ClO}_{3(\text{aq})}^- \end{array}$$

Extension

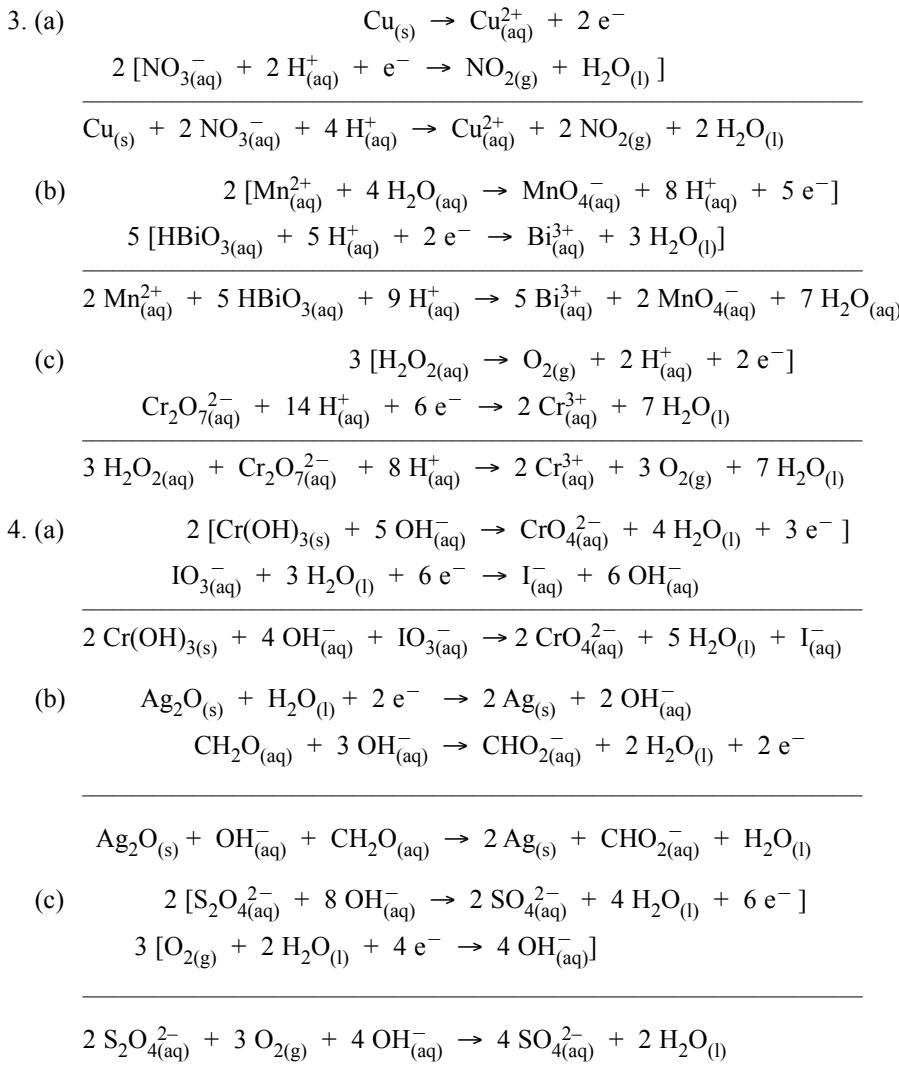


SECTION 9.2 QUESTIONS

(Page 673)

Understanding Concepts

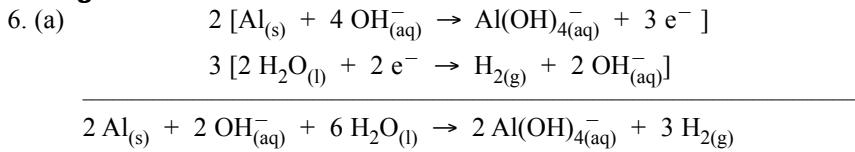
- Both methods of balancing redox equations are based on the conservation of electrons, i.e., the number of electrons gained by the oxidizing agent must equal the number of electrons lost by the reducing agent.
- Oxidation: increase in oxidation number; loss of electrons
Reduction: decrease in oxidation number; gain of electrons



Applying Inquiry Skills

5. Two general experimental designs that could help determine the balancing of the main species in a redox reaction are gravimetric stoichiometry (mass measurement) and volumetric stoichiometry (titration).

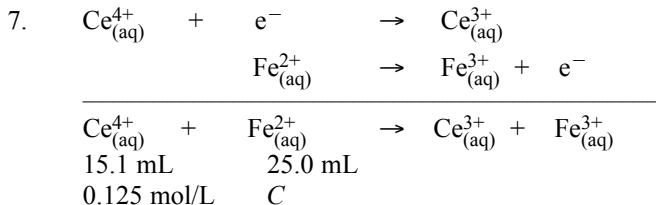
Making Connections



(b) Some possible health and safety issues associated with the use of solid drain cleaners are:

- Sodium hydroxide is very caustic and should be handled with gloves and eye protection.
- Flushing aluminum compounds down the drain has an impact on the environment because aluminum ions are toxic to fish and other aquatic organisms.

Extension



$$n_{\text{Ce}^{4+}} = 15.1 \text{ mL} \times 0.125 \frac{\text{mol}}{\text{L}}$$

$$n_{\text{Ce}^{4+}} = 1.89 \text{ mmol}$$

$$n_{\text{Fe}^{2+}} = 1.89 \text{ mmol Ce}^{4+} \times \frac{1 \text{ mol Fe}^{2+}}{1 \text{ mol Ce}^{4+}}$$

$$n_{\text{Fe}^{2+}} = 1.89 \text{ mmol}$$

$$C_{\text{Fe}^{2+}} = \frac{1.89 \text{ mmol}}{25.0 \text{ mL}}$$

$$= 0.0755 \text{ mol/L}$$

$$C_{\text{Fe}^{2+}} = 75.5 \text{ mmol/L}$$

The concentration of iron(II) ions in the sample is 75.5 mmol/L.

9.3 PREDICTING REDOX REACTIONS

PRACTICE

(Page 676)

Understanding Concepts

- Oxidation and reduction are processes that work together in the transfer of electrons that takes place in many chemical reactions. Oxidation is the process of losing electrons while reduction is the process of gaining electrons. Oxidizing agents and reducing agents are the substances directly involved in the transfer of electrons in a redox reaction. Oxidizing agents remove electrons from reducing agents, causing the reducing agent to be oxidized (loss of electrons) and the oxidizing agent to be reduced (gain of electrons).
- If a substance is a very strong oxidizing agent it has a very strong attraction for electrons.
- If a substance is a very strong reducing agent, its electrons are weakly attracted, and are easily removed.
- According to Table 1, lead and zinc react spontaneously with a copper(II) ion solution.
- According to Table 1, silver and copper did not appear to react with a copper(II) ion solution.
- The metals, $\text{Pb}_{(s)}$ and $\text{Zn}_{(s)}$, which react spontaneously with $\text{Cu}^{2+}_{(\text{aq})}$, both appear below the $\text{Cu}^{2+}_{(\text{aq})}$ line in a table of reduction half-reactions.
- Only zinc metal reacts spontaneously with lead(II) ions; silver, copper, and lead metals did not react with lead(II) ions. The metal, $\text{Zn}_{(s)}$, which reacts spontaneously with $\text{Pb}^{2+}_{(\text{aq})}$, appears below the $\text{Pb}^{2+}_{(\text{aq})}$ line in a table of reduction half-reactions.

Applying Inquiry Skills

- Metal ions react spontaneously with metals listed below them in a table of reduction half-reactions. According to Table 3, the predictions are correct and the hypothesis is verified.
- The following table of reduction half-reaction equations is based on the evidence presented in Table 4.

Relative Strengths of Oxidizing and Reducing Agents

decreasing reactivity of oxidizing agents	SOA	$\text{Cl}_{2(\text{aq})} + 2 \text{e}^- \rightleftharpoons 2 \text{Cl}_{(\text{aq})}^-$	\uparrow	decreasing reactivity of reducing agents
	\downarrow	$\text{Br}_{2(\text{aq})} + 2 \text{e}^- \rightleftharpoons 2 \text{Br}_{(\text{aq})}^-$	\uparrow	
	\downarrow	$\text{I}_{2(\text{aq})} + 2 \text{e}^- \rightleftharpoons 2 \text{I}_{(\text{aq})}^-$	SRA	

$$n_{\text{Ce}^{4+}} = 15.1 \text{ mL} \times 0.125 \frac{\text{mol}}{\text{L}}$$

$$n_{\text{Ce}^{4+}} = 1.89 \text{ mmol}$$

$$n_{\text{Fe}^{2+}} = 1.89 \text{ mmol Ce}^{4+} \times \frac{1 \text{ mol Fe}^{2+}}{1 \text{ mol Ce}^{4+}}$$

$$n_{\text{Fe}^{2+}} = 1.89 \text{ mmol}$$

$$C_{\text{Fe}^{2+}} = \frac{1.89 \text{ mmol}}{25.0 \text{ mL}}$$

$$= 0.0755 \text{ mol/L}$$

$$C_{\text{Fe}^{2+}} = 75.5 \text{ mmol/L}$$

The concentration of iron(II) ions in the sample is 75.5 mmol/L.

9.3 PREDICTING REDOX REACTIONS

PRACTICE

(Page 676)

Understanding Concepts

- Oxidation and reduction are processes that work together in the transfer of electrons that takes place in many chemical reactions. Oxidation is the process of losing electrons while reduction is the process of gaining electrons. Oxidizing agents and reducing agents are the substances directly involved in the transfer of electrons in a redox reaction. Oxidizing agents remove electrons from reducing agents, causing the reducing agent to be oxidized (loss of electrons) and the oxidizing agent to be reduced (gain of electrons).
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Applying Inquiry Skills

- Metal ions react spontaneously with metals listed below them in a table of reduction half-reactions. According to Table 3, the predictions are correct and the hypothesis is verified.
- The following table of reduction half-reaction equations is based on the evidence presented in Table 4.

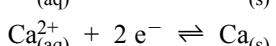
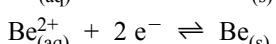
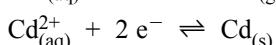
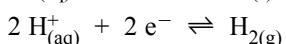
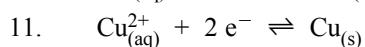
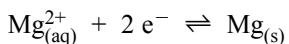
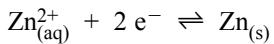
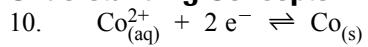
Relative Strengths of Oxidizing and Reducing Agents

decreasing reactivity of oxidizing agents	SOA	$\text{Cl}_{2(\text{aq})} + 2 \text{e}^- \rightleftharpoons 2 \text{Cl}_{(\text{aq})}^-$	\uparrow	decreasing reactivity of reducing agents
	\downarrow	$\text{Br}_{2(\text{aq})} + 2 \text{e}^- \rightleftharpoons 2 \text{Br}_{(\text{aq})}^-$	\uparrow	
	\downarrow	$\text{I}_{2(\text{aq})} + 2 \text{e}^- \rightleftharpoons 2 \text{I}_{(\text{aq})}^-$	SRA	

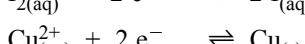
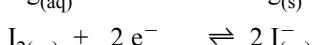
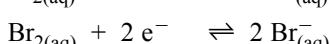
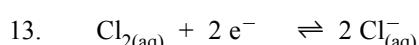
PRACTICE

(Page 678)

Understanding Concepts



12. The redox spontaneity rule is empirical because it is based directly on observations of redox reactions.



PRACTICE

(Page 679)

Understanding Concepts

14. $\text{Ag}_{(\text{aq})}^+$, $\text{Cu}_{(\text{aq})}^{2+}$, $\text{Pb}_{(\text{aq})}^{2+}$, $\text{Zn}_{(\text{aq})}^{2+}$. This order agrees with the evidence presented in Table 3 (text page 676).

15. (a) Metal ions, nonmetals, and a variety of acidic solutions usually behave as oxidizing agents.

(b) Nonmetal ions, metals, and basic solutions of various entities usually behave as reducing agents.

16. According to atomic theory, nonmetal atoms have almost filled valence energy levels and tend to attract electrons to attain a noble gas-like electronic structure. Metal atoms, however, have few electrons in their valence energy levels, have weak attractions for the valence electrons, and tend to lose electrons to attain a noble gas-like electronic structure. This is consistent with the empirically determined table which shows that nonmetals tend to act as oxidizing agents (electron acceptors) and that metals tend to act as reducing agents (electron donors).

17. Since fluorine is the most reactive nonmetal, and nonmetals are generally oxidizing agents, fluorine is expected to be the strongest oxidizing agent. Fluorine is the most reactive nonmetal because it has the greatest attraction for electrons. This reason relates the observed reactivity to the theoretical definition of an oxidizing agent.

Some further “why” questions are as follows. Why does fluorine have the greatest attraction for electrons? Why does fluorine have the highest electronegativity? Why do atoms with almost-filled energy levels have higher electronegativities than those without? (It should soon become obvious that the theory presented, to this point, can provide only a limited explanation of the redox table.)

18. Tin(II), copper(II), and chromium(II) ions can act as both oxidizing and reducing agents. These entities can gain or lose electrons. For example, tin(II) ions can either lose electrons to produce tin(IV) ions or gain electrons to produce tin atoms. The explanation for copper(II) and chromium(II) ions is similar, but there is no simple explanation for the behaviour of water molecules, which can also act as both oxidizing and reducing agents.

19. (a) spontaneous

(b) nonspontaneous

(c) nonspontaneous

(d) spontaneous

(e) spontaneous

(f) spontaneous

Applying Inquiry Skills

20. (I) Mix all combinations of oxidizing and reducing agents from a list of elements and their ions. The oxidizing agent that reacts spontaneously with the greatest number of reducing agents is the strongest. The oxidizing agent that reacts with the next greatest number of reducing agents is the next strongest, etc. From this information, the order of reactivity and the half-reaction equations can be determined.
- (II) Selected mixtures of oxidizing agents and reducing agents are studied and the spontaneity rule is used to order the oxidizing and reducing agents in each reactant mixture. The individual results are combined to form a final table of half-reactions. (If n half-reaction equations are to be placed in a table, a minimum of $n - 1$ reactions must be studied.)

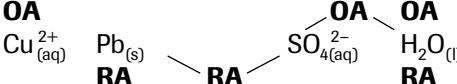
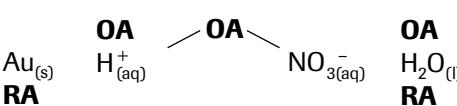
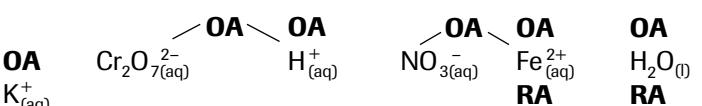
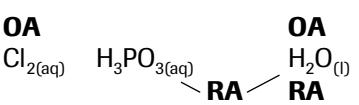
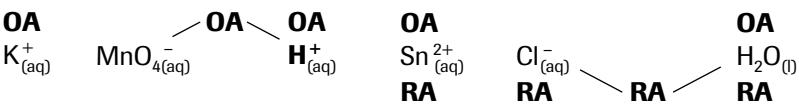
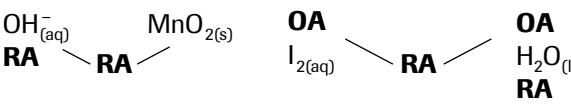
Making Connections

21. Gold and silver (and platinum) are commonly found as metals, while sodium and potassium are never found in their elemental form. Gold and silver are listed near the top of the table of relative strengths of oxidizing and reducing agents and are very weak reducing agents (relatively unreactive). Sodium and potassium are listed near the bottom of the table of relative strengths of oxidizing and reducing agents and are very strong reducing agents (very reactive).
22. The empirical way of knowing has been most useful to this point in predicting the spontaneity of redox reactions because the construction of tables of relative strengths of oxidizing and reducing agents is based on observations of reactions. The theory presented to this point can barely provide an initial explanation after the fact, and has little predictive power.

PRACTICE

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Understanding Concepts

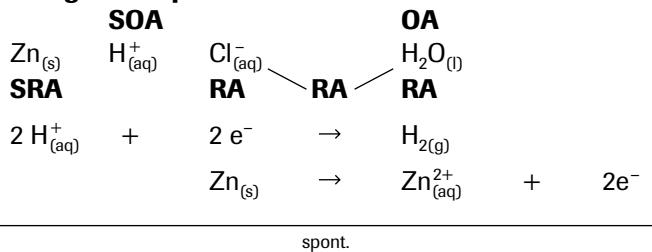
23. (a) 
OA $\text{Cu}^{2+}_{(\text{aq})}$ RA $\text{Pb}_{(\text{s})}$ OA $\text{SO}_4^{2-}_{(\text{aq})}$ RA $\text{H}_2\text{O}_{(\text{l})}$
- (b) 
OA $\text{Au}_{(\text{s})}$ RA $\text{H}^+_{(\text{aq})}$ OA $\text{NO}_3^-_{(\text{aq})}$ RA $\text{H}_2\text{O}_{(\text{l})}$
- (c) 
OA $\text{Cr}_2\text{O}_7^{2-}_{(\text{aq})}$ RA $\text{K}^+_{(\text{aq})}$ OA $\text{H}^+_{(\text{aq})}$ OA $\text{NO}_3^-_{(\text{aq})}$ OA $\text{Fe}^{2+}_{(\text{aq})}$ RA $\text{H}_2\text{O}_{(\text{l})}$
- (d) 
OA $\text{Cl}_2_{(\text{aq})}$ RA $\text{H}_3\text{PO}_3^{2-}_{(\text{aq})}$ OA $\text{H}_2\text{O}_{(\text{l})}$
- (e) 
OA $\text{K}^+_{(\text{aq})}$ RA $\text{MnO}_4^-_{(\text{aq})}$ OA $\text{H}^+_{(\text{aq})}$ OA $\text{Sn}^{2+}_{(\text{aq})}$ RA $\text{Cl}^-_{(\text{aq})}$ RA $\text{H}_2\text{O}_{(\text{l})}$
- (f) 
OA $\text{OH}^-_{(\text{aq})}$ RA $\text{MnO}_2_{(\text{s})}$ OA $\text{I}_2_{(\text{aq})}$ RA $\text{H}_2\text{O}_{(\text{l})}$

PRACTICE

(Page 682)

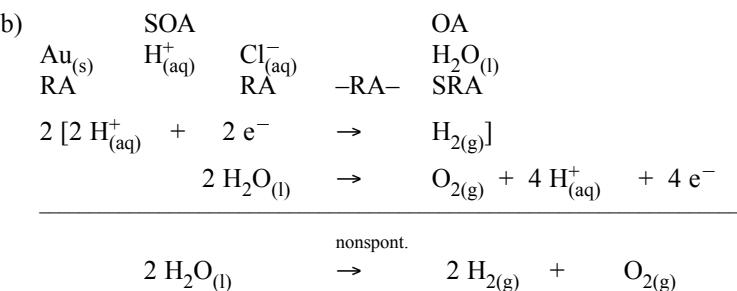
Understanding Concepts

24. (a)

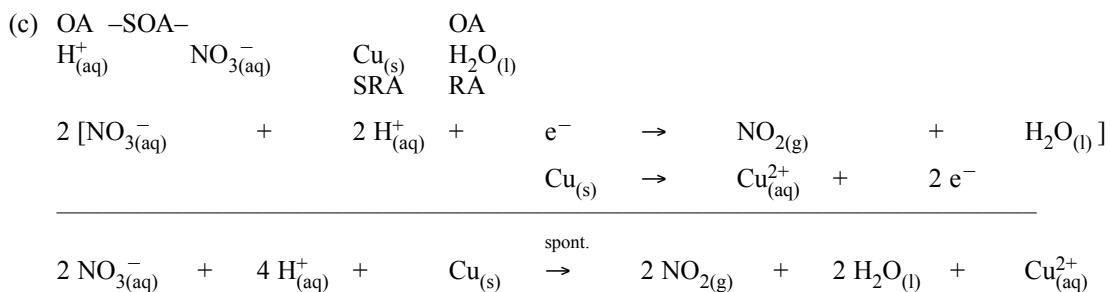


If a flame is inserted into a sample of the gas produced and a “pop” sound is heard, then hydrogen gas is likely present. (Other diagnostic tests include pre- and post-tests for pH, mass measurement of zinc, and a flame test for Zn²⁺.)

(b)



(c)

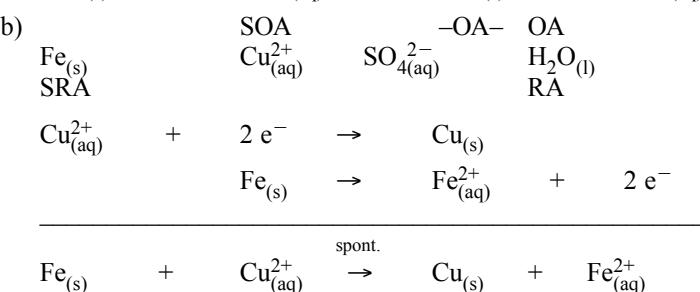


If the colour of the final solution near the copper surface is blue, then it is likely that copper(II) ions are produced. If a brown gas is produced during the course of the reaction, then nitrogen dioxide is likely produced. (Other diagnostic tests include pre- and post-tests for pH, mass measurement of copper, and a flame test for Cu²⁺.)

25. (a) 2 Fe_(s) + 3 CuSO_{4(aq)} → 3 Cu_(s) + Fe₂(SO₄)_{3(aq)} (assuming common ion, Fe³⁺)

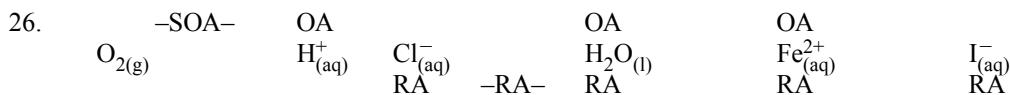
2 Fe_(s) + 3 Cu²⁺_(aq) → 3 Cu_(s) + 2 Fe³⁺ (net ionic)

(b)

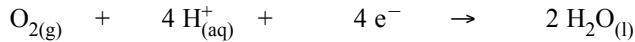


(c) Both predictions cannot be correct; either iron(III) ions are formed or iron(II). The redox table and rules are more likely to be correct because these are based on extensive observations of relative strengths of oxidizing and

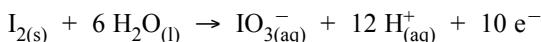
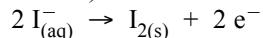
reducing agents supported by the idea of electron transfer. The single displacement rule is a generalization that has been useful in the past but does not have the same empirical basis or any theoretical justification.



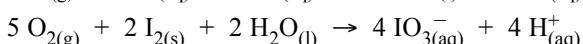
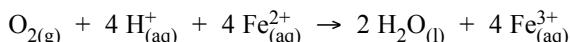
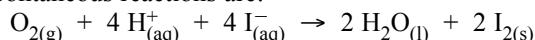
Because an excess of acid is present, $O_{2(g)}$ and $H_{(aq)}^+$ will remain as the strongest oxidizing agent throughout all of the reactions.



Oxygen in an acidic solution will spontaneously oxidize (in order) iodide ions, iron(II) ions, and lastly iodine (product of the iodide oxidation).



The spontaneous reactions are:



Applying Inquiry Skills

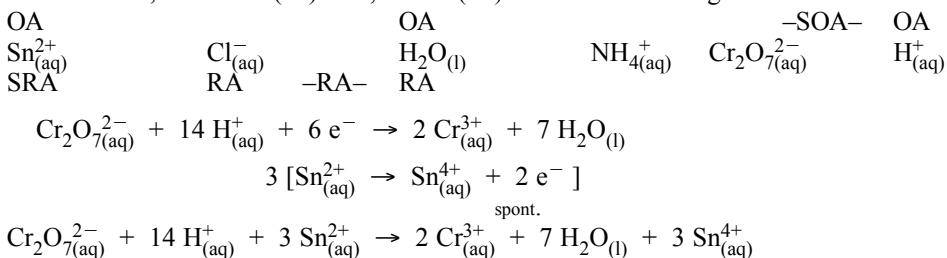
27. Qualitatively, one could ensure complete reaction of the blue copper(II) solution and then observe the colour of the solution. If the iron(III) ion is produced, the solution should be light yellow, but if the iron(II) ion is produced, the solution should be light green.

Quantitatively, one could measure the mass of iron reacted and the mass of copper metal produced. Convert the masses to amounts and calculate the ratio of the amount of copper produced to the amount of iron reacted. If the ratio is 3:2, then iron(III) is produced, but if the ratio is 1:1, then iron(II) is produced.

28. (Sample response)

Prediction

According to redox concepts and the table of relative strengths of oxidizing and reducing agents, the products of the reaction are water, chromium(III) ions, and tin(IV) ions. The reasoning is shown below.



Experimental Design

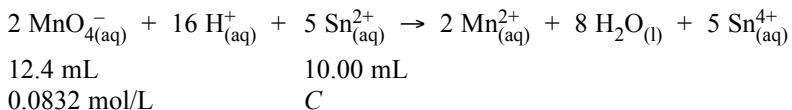
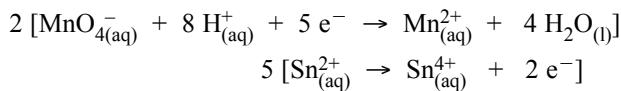
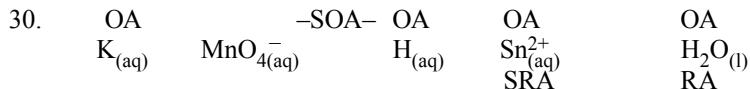
An excess of tin(II) chloride is added to the acidic ammonium dichromate solution. If the colour of the mixture is observed before and after the reaction, and the reaction changes from orange to green, then chromium(III) ions are likely produced.

Making Connections

29. Although aluminum is a reactive metal it does not corrode readily. When aluminum is exposed to air, a microscopically thin impermeable layer of aluminum oxide immediately forms on the surface, protecting it from further oxidation. The small pits that develop in aluminum cooking pots could be due to the reaction of aluminum with hydrogen ions, where the metal is exposed by scratching during stirring. The process is slow because the protective layer of aluminum oxide soon re-forms.

(Note: The presence of chloride ions (from salt) accelerates the pitting process, because chloride ions replace oxygens in the protective coating and reduce its protective integrity.)

Extensions



$$n_{MnO_4^-} = 12.4 \text{ mL} \times 0.0832 \frac{\text{mol}}{\text{L}}$$

$$n_{MnO_4^-} = 1.03 \text{ mmol}$$

$$n_{Sn^{2+}} = 1.03 \text{ mmol} \cancel{MnO_4^-} \times \frac{5 \text{ mol } Sn^{2+}}{2 \text{ mol } \cancel{MnO_4^-}}$$

$$n_{Sn^{2+}} = 2.58 \text{ mmol}$$

$$C_{Sn^{2+}} = \frac{2.58 \text{ mmol}}{10.00 \text{ mL}}$$

$$C_{Sn^{2+}} = 0.258 \text{ mol/L}$$

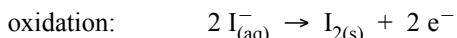
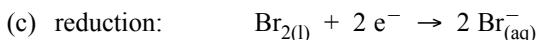
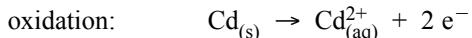
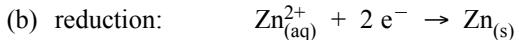
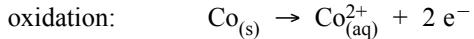
According to the evidence and stoichiometric analysis, the concentration of tin(II) ions is 0.258 mol/L.

SECTION 9.3 QUESTIONS

(Page 683)

Understanding Concepts

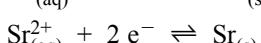
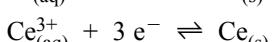
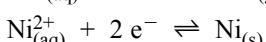
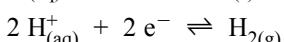
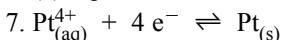
1. The transfer of electrons between chemical entities is the key idea used to explain a redox reaction.
2. Oxidation is a process in which electrons are lost (LEO).
Reduction is a process in which electrons are gained (GER).
3. Oxidation refers to the process of losing electrons, while oxidizing agent refers to the chemical entity that causes the oxidation of another entity by removing electrons from it.
4. Reduction refers to the process of gaining electrons, while reducing agent refers to the chemical entity that causes the reduction of another entity by donating electrons to it.

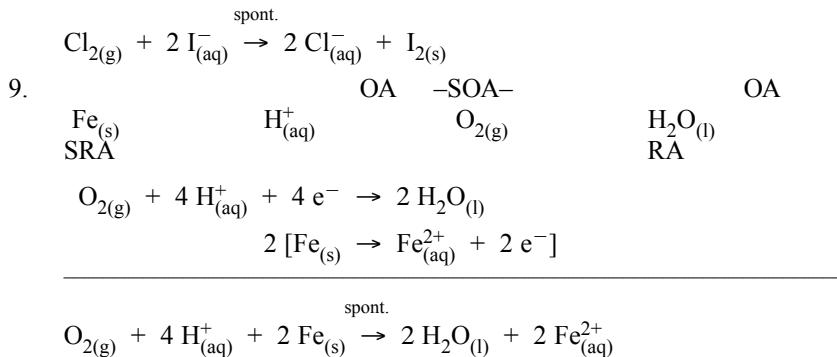
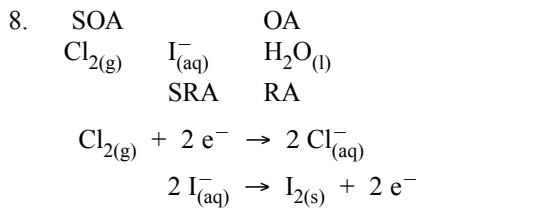


6. (a) spontaneous

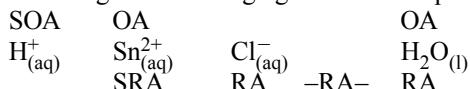
- (b) nonspontaneous

- (c) spontaneous

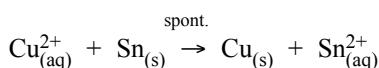
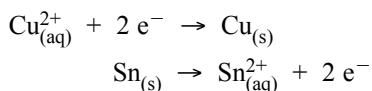
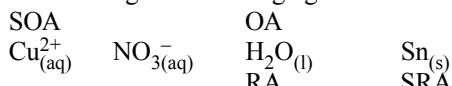




10. (a) The solution will be stable, because no spontaneous reaction occurs according to the table of relative strengths of oxidizing and reducing agents and the spontaneity rule.

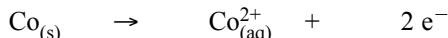


- (b) The solution will not be stable, because a spontaneous reaction occurs according to the table of relative strengths of oxidizing and reducing agents and the spontaneity rule.

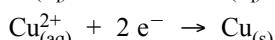
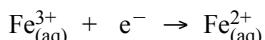
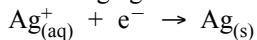


- | | | | | |
|-----|-------------------|-----------------------------|--------------------------------|---------------------------------|
| 11. | OA | OA | OA | OA |
| | $\text{Co}_{(s)}$ | $\text{Ag}^+_{(\text{aq})}$ | $\text{Fe}^{3+}_{(\text{aq})}$ | $\text{Cu}^{2+}_{(\text{aq})}$ |
| | SRA | | | H ₂ O _(l) |
| | | | | RA |

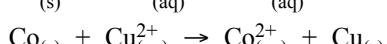
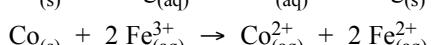
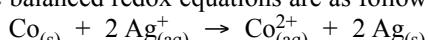
Because cobalt metal is in excess and it is the strongest reducing agent present, it will be the reducing agent in all reactions.



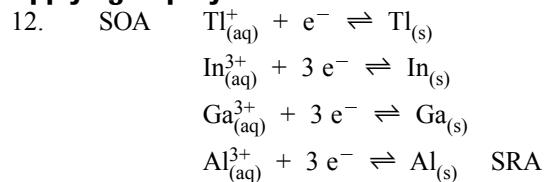
The oxidizing agents that will spontaneously react, in order of decreasing strength, are: $\text{Ag}^{+}_{(\text{aq})}$, $\text{Fe}^{3+}_{(\text{aq})}$, $\text{Cu}^{2+}_{(\text{aq})}$.



The balanced redox equations are as follows:



Applying Inquiry Skills



Making Connections

13. Ursula Franklin specializes in the structure of metals and alloys and has pioneered the study of metallurgy in ancient cultures. In her view, science and technology have a side-by-side relationship, stimulating and utilizing each other. She has voiced serious concerns about Canada's lack of support for research in science and technology. She is a tireless worker for Science for Peace, and has worked to improve opportunities for women in science and to make scientific information understandable and accessible to the public.

9.4 TECHNOLOGY OF CELLS AND BATTERIES

PRACTICE

(Page 687)

Understanding Concepts

1. A simple electric cell contains two solid conductors (electrodes) and an aqueous conductor (electrolyte).
2. An electrode is a solid conductor and an electrolyte is an aqueous conductor. An anode is the negative electrode in an electric cell. A cathode is the positive electrode in an electric cell.
3. Four cells are needed. ($6 \text{ V} \times 1.5 \text{ V/cell} = 4 \text{ cells}$)
4. Electric current is a measure of the rate of flow of charge past a point in an electric circuit. Voltage is a measure of the energy difference per unit charge.

Making Connections

5. From a scientific perspective, a diagram shows where the electrons are believed to enter and exit the device. From a technological perspective, a diagram shows how the batteries should be placed in the device to make it work and to avoid damaging certain components.

PRACTICE

(Page 690)

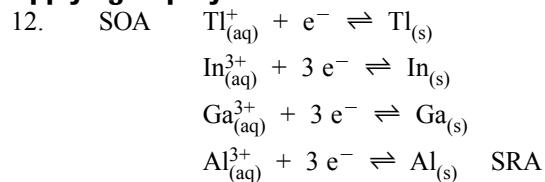
Understanding Concepts

6. Scientific knowledge may be used to describe, explain, or predict the parts or operation of a device. Technological problem solving is used to develop a device that works based on established criteria.
7. The steps involved in technological problem solving are:
 - Develop a general design, for example, select variables to manipulate and control.
 - Follow several prediction–procedure–evidence–analysis cycles, manipulating and systematically studying one variable at a time.
 - Complete an evaluation on criteria such as efficiency, reliability, cost, and simplicity.
8. A technical and safety problem is the possible leakage of the liquid electrolyte. The electrolyte should be changed to a moist paste to reduce this problem.
9. Primary cells, such as the alkaline dry cell or mercury cell, cannot in practice be recharged. Secondary cells, such as the Ni–Cad cell, NiMH cell, or lead–acid cell, can be recharged repeatedly.
10. Advantages of the zinc chloride dry cell include simplicity, reliability, and relatively low cost. The main disadvantage is that the cell is not rechargeable and must be discarded when depleted. Other possible disadvantages for certain uses include short shelf life, relatively low current produced, and constancy of voltage.

Making Connections

11. The AA, C, and D cells differ in size, current produced, and longevity of the cell, but the cell potential remains the same in each cell size. The smaller the cell, the smaller the electrodes and the smaller the current produced.
12. Both designs use containers that are consumed as they are used.

Applying Inquiry Skills



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PRACTICE

(Page 687)

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PRACTICE

(Page 690)

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Making Connections

11. The AA, C, and D cells differ in size, current produced, and longevity of the cell, but the cell potential remains the same in each cell size. The smaller the cell, the smaller the electrodes and the smaller the current produced.
12. Both designs use containers that are consumed as they are used.

13. (a) Some of the requirements for cells used in electronic devices are:
- long life
 - small size
 - constant voltage during its active life
 - reliable for many recharges
 - inexpensive
- (b) The storage capacity of some rechargeable batteries is reduced if they are recharged before being totally drained, because they then may only discharge to the point where they were recharged previously. Such batteries are sometimes referred to as having a “memory.”
14. The original Molicel featured a “jelly roll” design in which sheets of a lithium metal foil (anode), molybdenum disulfide coated on aluminum foil (cathode), and a microporous separator were coiled up and inserted into a steel can. A non-aqueous, liquid electrolyte solution (containing lithium ions) was added to the can and the can was sealed. The original design has been modified to produce a safer cell. Some of the advantages of Molicels (and other lithium ion batteries) compared to other types of secondary cells are: higher current, lighter weight, more energy, and ability to work over a wider temperature range.

PRACTICE

(Page 693)

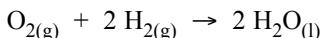
Understanding Concepts

15.

Perspective	Advantage	Disadvantage
technological	<ul style="list-style-type: none"> • high efficiency • high-energy density • lightweight 	<ul style="list-style-type: none"> • requires constant supply of fuel • some cells require pressurized gases
economic		<ul style="list-style-type: none"> • high cost
environmental	<ul style="list-style-type: none"> • very little pollution 	

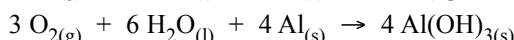
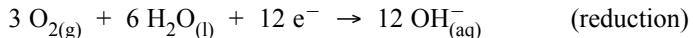
16. Some potential uses of fuel cells are in electric cars, electric buses, and for large-scale commercial and industrial electricity generation.

Hydrogen–oxygen fuel cell:



(Half-reactions in Table 2 refer to an alkaline hydrogen–oxygen fuel cell as used by NASA.)

Aluminum–air fuel cell:



18. Some problems that must be solved before the Ballard cell sees widespread use are:

- finding an inexpensive and abundant source of hydrogen gas
- developing a safe way to store hydrogen in a vehicle
- if the first two problems can't be solved, finding a substitute for hydrogen fuel
- reducing the cost of the cells

19. Some advantages of methanol over hydrogen or natural gas are:

- easy transportation and storage
- industrial manufacture of methanol is well established
- relatively inexpensive
- renewable resource

Making Connections

20. (a) anode: $\text{Pb}_{(s)}$; cathode: $\text{PbO}_{2(s)}$; electrolyte: $\text{H}_2\text{SO}_{4(aq)}$
(b) The large currents are produced by designing electrodes with a large surface area.
(c) The main social impact of this battery is to enable widespread use of motor vehicles for personal transportation.
(d) The lead and acid in used car batteries can have a negative impact on the environment.
21. Plastic batteries are unique in having electrodes made of conducting “doped” polymers rather than metallic materials. In some recent plastic cells, the electrolyte as well is made of a polymer material — resulting in a “leakproof” battery that contains no liquid. Charging involves ion migration to the electrodes, but the electrodes themselves do not charge, making such cells theoretically rechargeable through a very large number of cycles. The cells are very lightweight, may be almost any shape, and have high-energy density and power density characteristics, making them of great interest to designers of satellites. A significant advantage is that such cells operate through a very wide range of temperatures without much change in their electrical properties. Another strong social advantage is that they contain no environmentally harmful materials. Currently, such cells are very expensive and do not store very large quantities of energy, but development continues.

Explore an Issue: Debate: Hydrogen Fuel Cells

(Page 694)

(a) (Sample points to consider ...)

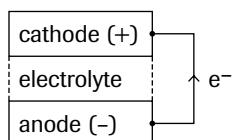
- Most current proposals will use hydrogen stripped from methanol or gasoline, although natural gas is another potential hydrogen source.
- If some fossil fuel is used as a source of hydrogen, carbon dioxide is still produced in the cell and there may be substantial environmental effects of producing the hydrogen-rich fuels, such as methanol and gasoline.
- The cost of fuel-cell cars will be quite high until mass production lowers the unit cost. The economic effects on communities that depend on the well-established oil and gas industry, and internal-combustion vehicle production for employment may be significant. Political issues such as taxation, environmental regulations, and lobbies from special interest groups need to be considered.
- Some alternatives include hybrid vehicles; generating hydrogen from renewable, nonpolluting sources such as sunlight and wind; and storing hydrogen in carbon nanotubes or graphite fibres.

SECTION 9.4 QUESTIONS

(Page 694)

Understanding Concepts

1.



- The chemical changes that occur at the electrodes provide the evidence that an electric cell involves a redox reaction. Reduction always occurs at the cathode (e.g., aqueous metal ions changing to solid metal), and oxidation always occurs at the anode (e.g., solid metal changing to aqueous metal ions).
- The three types of electric cells used in consumer and commercial operations are primary cells, secondary cells, and fuel cells. Primary cells cannot in practice be recharged. Secondary cells can be recharged repeatedly. Fuel cells produce electricity by the reaction of a fuel that is continuously supplied to keep the cell operating.
- Two common examples of consumer cells are alkaline dry cells, which are used in flashlights and radios, and Ni–Cad cells, which are used in power tools, shavers, and portable computers.
- (a) The electrons flow from the zinc to the silver in the external circuit.
(b) Zinc is the anode and silver is the cathode.
(c) $\text{Ag}_2\text{O}_{(s)} + \text{H}_2\text{O}_{(l)} + \text{Zn}_{(s)} \rightarrow 2 \text{Ag}_{(s)} + \text{Zn}(\text{OH})_{2(s)}$

Making Connections

- If cells and batteries did not exist, we would have to live without many commonplace conveniences, such as portable radios, flashlights, and flash cameras. Portable electronic devices, such as cordless phones, cellular phones, laptop computers, disc players, and digital cameras, would not exist. Starting a vehicle would have to be done the old-fashioned way—with a hand crank!

7. (a) Internal-combustion engines are a major source of pollution and environmental damage. Electric cars powered by hydrogen fuel cells are seen as “pollution free.”
- (b) The number of lead-acid batteries needed to power an electric car would make the car very heavy. Used lead-acid batteries are a major source of lead pollution.
- (c) Advances in hydrogen fuel cells could make electric cars the “green” solution to pollution from internal-combustion engines.
8. Consumer magazines are a good source of information on cells and batteries, regarding their reliability, cost, simplicity of use, safety (leakage), size (volume), shelf life, active life, energy density, power capacity, maintenance, disposal, environmental impact, and ability to be recharged.
9. Lithium–iodine batteries are commonly used in pacemakers, but some are powered by radioactive isotopes. Conventional pacemaker batteries last from four to eight years, depending how much the heart uses the pacemaker. A doctor tracks signals from the pacemaker to ascertain when the battery is nearing the end of its life. Rechargeable batteries generally hold less energy, and would need to be replaced more often.

9.5 GALVANIC CELLS

PRACTICE

(Page 700)

Understanding Concepts

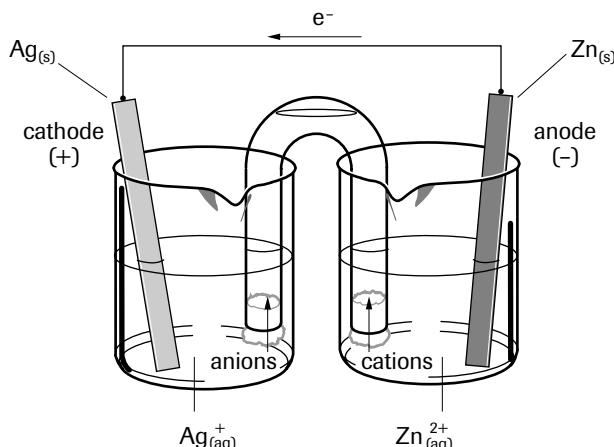
1. A galvanic cell is an arrangement of two half-cells that spontaneously produces electricity.
A half-cell is an electrode–electrolyte combination forming one-half of a complete cell.
A porous boundary is a barrier that separates electrolytes while still permitting the movement of ions.
An inert electrode is a solid conductor that serves as an anode or a cathode in a voltaic cell, but is chemically unreactive.
2. A cathode is the electrode where reduction occurs.
An anode is the electrode where oxidation occurs.
3. (a) cathode
(b) anode
(c) anode
(d) cathode
4. An inert electrode is used in a half-cell where no conducting solid is involved in the half-reaction equation.
5. The solution in a salt bridge must be a “spectator” electrolyte chemically; that is, its ions must not react with the half-cell ions that pass through.
6. (a) SOA

$$\text{Ag}_{(s)} | \text{Ag}^+_{(\text{aq})} \parallel \text{Zn}^{2+}_{(\text{aq})} | \text{Zn}_{(s)}$$

SRA

cathode	$2[\text{Ag}^+_{(\text{aq})} + \text{e}^- \rightarrow \text{Ag}_{(s)}$
anode	$\text{Zn}_{(s)} \rightarrow \text{Zn}^{2+}_{(\text{aq})} + 2\text{e}^-$

net	$2\text{Ag}^+_{(\text{aq})} + \text{Zn}_{(s)} \rightarrow \text{Ag}_{(s)} + \text{Zn}^{2+}_{(\text{aq})}$
-----	---



Making Connections

20. (a) anode: $\text{Pb}_{(s)}$; cathode: $\text{PbO}_{2(s)}$; electrolyte: $\text{H}_2\text{SO}_{4(aq)}$
(b) The large currents are produced by designing electrodes with a large surface area.
(c) The main social impact of this battery is to enable widespread use of motor vehicles for personal transportation.
(d) The lead and acid in used car batteries can have a negative impact on the environment.
21. Plastic batteries are unique in having electrodes made of conducting “doped” polymers rather than metallic materials. In some recent plastic cells, the electrolyte as well is made of a polymer material — resulting in a “leakproof” battery that contains no liquid. Charging involves ion migration to the electrodes, but the electrodes themselves do not charge, making such cells theoretically rechargeable through a very large number of cycles. The cells are very lightweight, may be almost any shape, and have high-energy density and power density characteristics, making them of great interest to designers of satellites. A significant advantage is that such cells operate through a very wide range of temperatures without much change in their electrical properties. Another strong social advantage is that they contain no environmentally harmful materials. Currently, such cells are very expensive and do not store very large quantities of energy, but development continues.

Explore an Issue: Debate: Hydrogen Fuel Cells

(Page 694)

(a) (Sample points to consider ...)

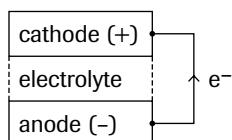
- Most current proposals will use hydrogen stripped from methanol or gasoline, although natural gas is another potential hydrogen source.
- If some fossil fuel is used as a source of hydrogen, carbon dioxide is still produced in the cell and there may be substantial environmental effects of producing the hydrogen-rich fuels, such as methanol and gasoline.
- The cost of fuel-cell cars will be quite high until mass production lowers the unit cost. The economic effects on communities that depend on the well-established oil and gas industry, and internal-combustion vehicle production for employment may be significant. Political issues such as taxation, environmental regulations, and lobbies from special interest groups need to be considered.
- Some alternatives include hybrid vehicles; generating hydrogen from renewable, nonpolluting sources such as sunlight and wind; and storing hydrogen in carbon nanotubes or graphite fibres.

SECTION 9.4 QUESTIONS

(Page 694)

Understanding Concepts

1.



- The chemical changes that occur at the electrodes provide the evidence that an electric cell involves a redox reaction. Reduction always occurs at the cathode (e.g., aqueous metal ions changing to solid metal), and oxidation always occurs at the anode (e.g., solid metal changing to aqueous metal ions).
- The three types of electric cells used in consumer and commercial operations are primary cells, secondary cells, and fuel cells. Primary cells cannot in practice be recharged. Secondary cells can be recharged repeatedly. Fuel cells produce electricity by the reaction of a fuel that is continuously supplied to keep the cell operating.
- Two common examples of consumer cells are alkaline dry cells, which are used in flashlights and radios, and Ni–Cad cells, which are used in power tools, shavers, and portable computers.
- (a) The electrons flow from the zinc to the silver in the external circuit.
(b) Zinc is the anode and silver is the cathode.
(c) $\text{Ag}_2\text{O}_{(s)} + \text{H}_2\text{O}_{(l)} + \text{Zn}_{(s)} \rightarrow 2 \text{Ag}_{(s)} + \text{Zn}(\text{OH})_{2(s)}$

Making Connections

- If cells and batteries did not exist, we would have to live without many commonplace conveniences, such as portable radios, flashlights, and flash cameras. Portable electronic devices, such as cordless phones, cellular phones, laptop computers, disc players, and digital cameras, would not exist. Starting a vehicle would have to be done the old-fashioned way—with a hand crank!

7. (a) Internal-combustion engines are a major source of pollution and environmental damage. Electric cars powered by hydrogen fuel cells are seen as “pollution free.”
- (b) The number of lead-acid batteries needed to power an electric car would make the car very heavy. Used lead-acid batteries are a major source of lead pollution.
- (c) Advances in hydrogen fuel cells could make electric cars the “green” solution to pollution from internal-combustion engines.
8. Consumer magazines are a good source of information on cells and batteries, regarding their reliability, cost, simplicity of use, safety (leakage), size (volume), shelf life, active life, energy density, power capacity, maintenance, disposal, environmental impact, and ability to be recharged.
9. Lithium–iodine batteries are commonly used in pacemakers, but some are powered by radioactive isotopes. Conventional pacemaker batteries last from four to eight years, depending how much the heart uses the pacemaker. A doctor tracks signals from the pacemaker to ascertain when the battery is nearing the end of its life. Rechargeable batteries generally hold less energy, and would need to be replaced more often.

9.5 GALVANIC CELLS

PRACTICE

(Page 700)

Understanding Concepts

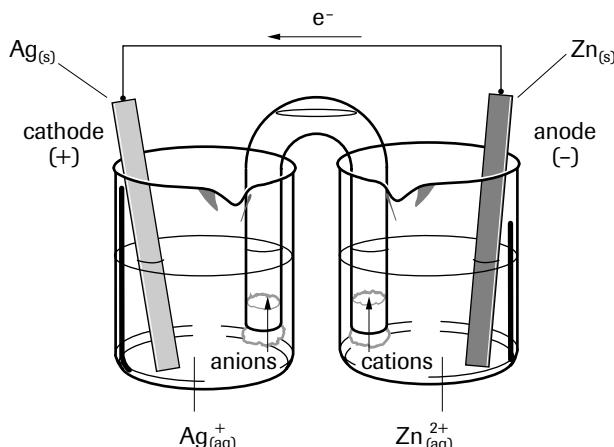
1. A galvanic cell is an arrangement of two half-cells that spontaneously produces electricity.
A half-cell is an electrode–electrolyte combination forming one-half of a complete cell.
A porous boundary is a barrier that separates electrolytes while still permitting the movement of ions.
An inert electrode is a solid conductor that serves as an anode or a cathode in a voltaic cell, but is chemically unreactive.
2. A cathode is the electrode where reduction occurs.
An anode is the electrode where oxidation occurs.
3. (a) cathode
(b) anode
(c) anode
(d) cathode
4. An inert electrode is used in a half-cell where no conducting solid is involved in the half-reaction equation.
5. The solution in a salt bridge must be a “spectator” electrolyte chemically; that is, its ions must not react with the half-cell ions that pass through.
6. (a) SOA

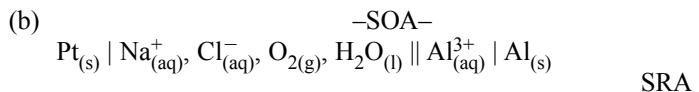
$$\text{Ag}_{(s)} | \text{Ag}^+_{(\text{aq})} \parallel \text{Zn}^{2+}_{(\text{aq})} | \text{Zn}_{(s)}$$

SRA

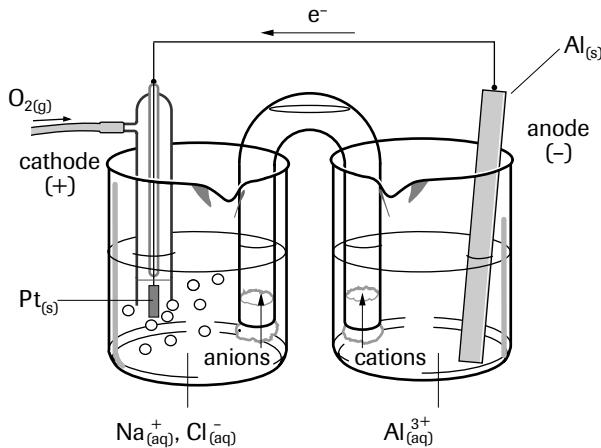
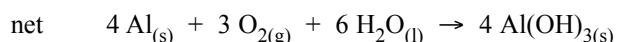
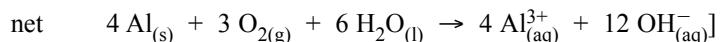
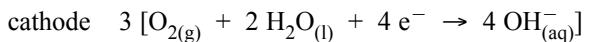
cathode	$2[\text{Ag}^+_{(\text{aq})} + \text{e}^- \rightarrow \text{Ag}_{(s)}$
anode	$\text{Zn}_{(s)} \rightarrow \text{Zn}^{2+}_{(\text{aq})} + 2\text{e}^-$

net	$2\text{Ag}^+_{(\text{aq})} + \text{Zn}_{(s)} \rightarrow \text{Ag}_{(s)} + \text{Zn}^{2+}_{(\text{aq})}$
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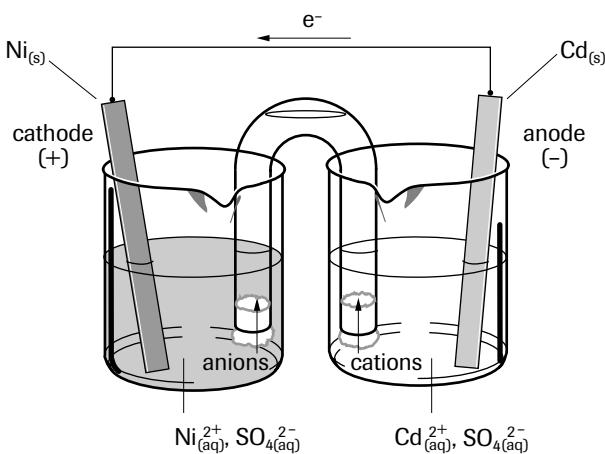
SRA



7. (a) Ions move to maintain electrical neutrality at each electrode. In a simple voltaic (galvanic) cell composed of metals and metal ions, reduction removes positive ions from the solution around the cathode, and oxidation adds positive ions to the solution around the anode. Anions move toward the anode to balance the excess positive charge in the solution around the anode, while cations move toward the cathode to replace the positive charge being removed from the solution around the cathode. Meanwhile, electrons move externally from the anode to the cathode.

- (b) Cations move toward the cathode and anions move toward the anode.

8.

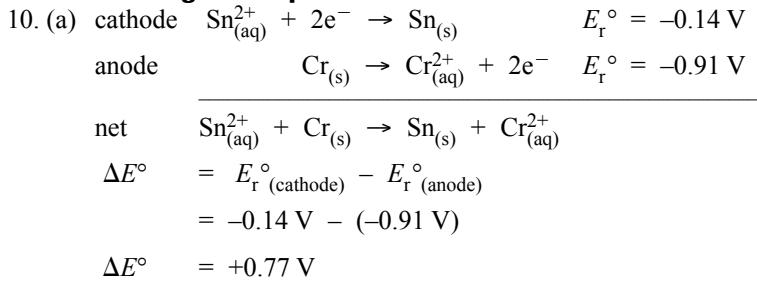


9. The nickel cathode could be replaced by any inert conducting material such as carbon or platinum. The anode solution could be replaced with an inert aqueous electrolyte such as aqueous potassium sulfate.

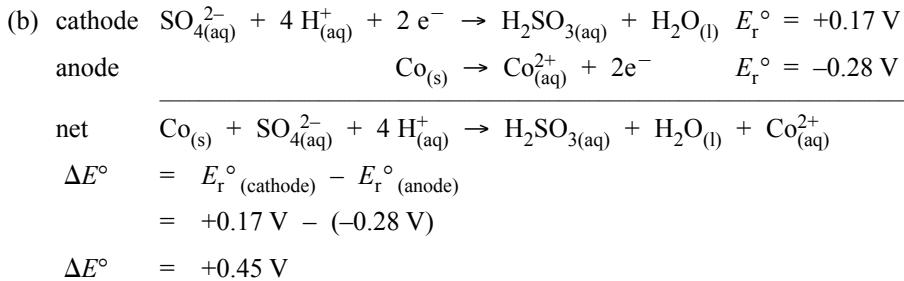
PRACTICE

(Page 708)

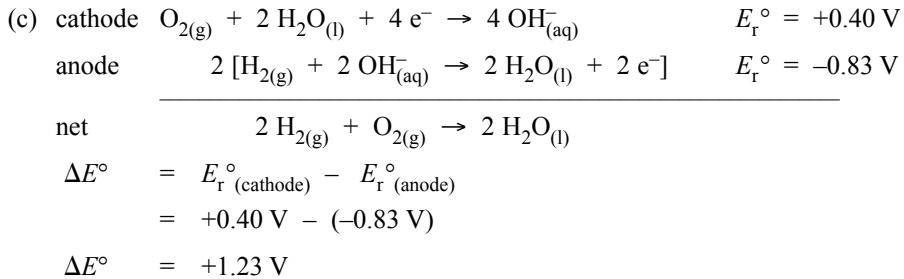
Understanding Concepts



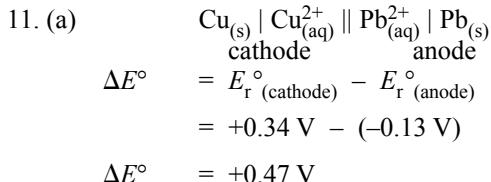
The standard cell potential is +0.77 V.



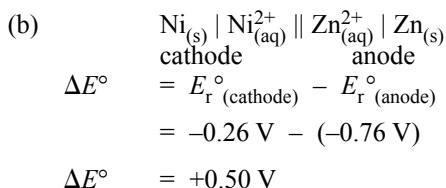
The standard cell potential is +0.45 V.



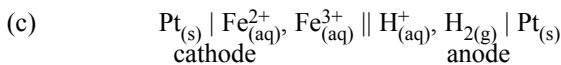
The standard cell potential is +1.23 V.



The standard cell potential is +0.47 V.



The standard cell potential is +0.50 V.

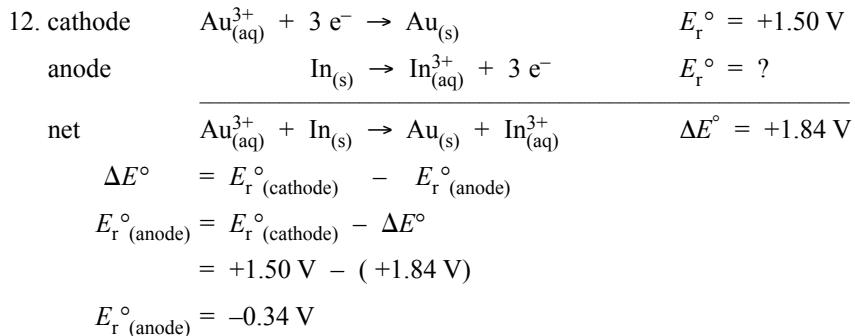


$$\Delta E^\circ = E_r^\circ (\text{cathode}) - E_r^\circ (\text{anode})$$

$$\Delta E^\circ = +0.77 \text{ V} - (0.00 \text{ V})$$

$$\Delta E^\circ = +0.77 \text{ V}$$

The standard cell potential is +0.77 V.



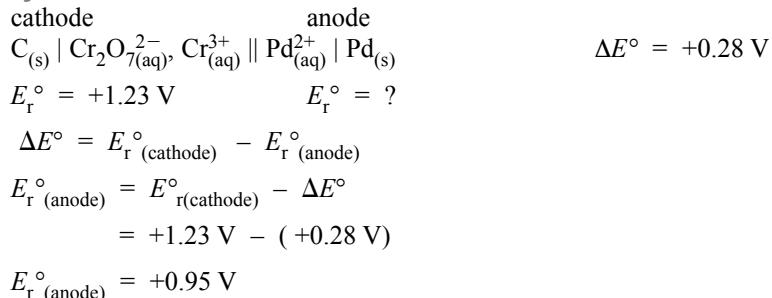
The standard reduction potential for the $\text{In}_{(\text{aq})}^{3+} | \text{In}_{(\text{s})}$ half-cell is -0.34 V.

13. If the standard lithium cell is chosen as the reference half-cell with its reduction potential defined as 0.00 V, then 3.04 V must be added to each reduction potential in the table. Therefore, the reduction potential for the copper half-cell becomes +3.38 V and the reduction potential for the zinc half-cell becomes +2.28 V.

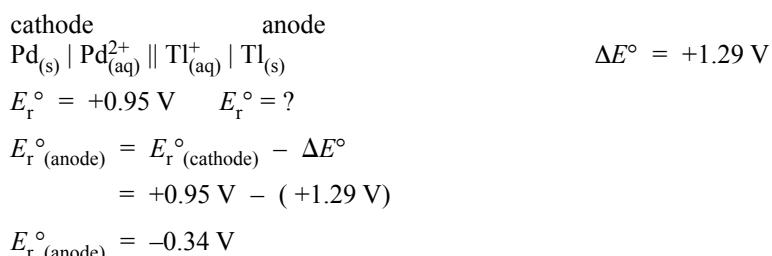
14. The chemical system has come to equilibrium.

Applying Inquiry Skills

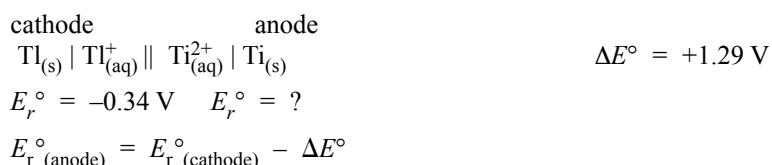
15. Analysis



The standard reduction potential for the $\text{Pd}_{(\text{aq})}^{2+} | \text{Pd}_{(\text{s})}$ half-cell is +0.95 V.



The standard reduction potential for the $\text{Tl}_{(\text{aq})}^+ | \text{Tl}_{(\text{s})}$ half-cell is -0.34 V.

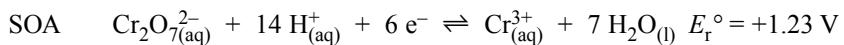


$$= -0.34 \text{ V} - (+1.29 \text{ V})$$

$$E_r^\circ_{\text{(anode)}} = -1.63 \text{ V}$$

The standard reduction potential for the $\text{Ti}_{(\text{aq})}^{2+} \mid \text{Ti}_{(\text{s})}$ half-cell is -1.63 V .

According to the evidence, the relative strength of the four oxidizing agents, in decreasing order of E_r° , is:



16. Prediction

Since the two cells are connected in series, the total electric potential difference of the two cells is predicted to equal the sum of the ΔE° values of each cell.

copper–silver cell

$$\Delta E^\circ = E_r^\circ_{\text{(cathode)}} - E_r^\circ_{\text{(anode)}}$$

$$= +0.80 \text{ V} - (+0.34 \text{ V})$$

$$\Delta E^\circ = +0.46 \text{ V}$$

copper–zinc cell

$$\Delta E^\circ = E_r^\circ_{\text{(cathode)}} - E_r^\circ_{\text{(anode)}}$$

$$= +0.34 \text{ V} - (-0.76 \text{ V})$$

$$\Delta E^\circ = +1.10 \text{ V}$$

The predicted voltmeter reading is: $+0.46 \text{ V} + (+1.10 \text{ V}) = +1.56 \text{ V}$

SECTION 9.5 QUESTIONS

(Page 709)

Understanding Concepts

1. (a) The cell potential is predicted from the standard reduction potential values.

$$\Delta E^\circ = E_r^\circ_{\text{(cathode)}} - E_r^\circ_{\text{(anode)}}$$

- (b) This prediction is restricted to cells containing all entities shown in the half-reaction equations and operating at standard conditions, i.e., SATP using 1.0 mol/L solutions.

2. A positive cell potential indicates a spontaneous reaction and a negative cell potential indicates a nonspontaneous reaction.

3. Galvanic cells are designed with two different half-cells each containing an electrode and electrolyte. Therefore, a spontaneous combination will always exist.

4. The standard hydrogen half-cell is at 25°C and consists of an inert platinum electrode immersed in a 1.00 mol/L solution of hydrogen ions, with hydrogen gas at 100 kPa bubbling over the electrode. Standard reduction potentials for all other half-cells are measured relative to that of the standard hydrogen half-cell, defined as exactly zero volts.

5. A reference half-cell is necessary because it is impossible to determine the reduction potential of a single half-cell. A voltmeter can only measure a potential difference, ΔE° .

6. (a) $\Delta E^\circ = E_r^\circ_{\text{(cathode)}} - E_r^\circ_{\text{(anode)}}$

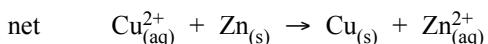
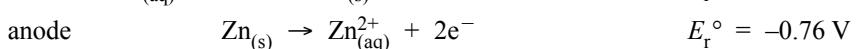
$$= -0.28 \text{ V} - (-0.76 \text{ V})$$

$$\Delta E^\circ = +0.48 \text{ V}$$

The potential of a standard cobalt–zinc cell is $+0.48 \text{ V}$.

- (b) The theoretical interpretation of this cell potential is the cobalt(II) ions have a stronger attraction for electrons than zinc ions. The 0.48 V is a measure of the difference in their abilities to attract electrons.

7. (a) SOA: $\text{Cu}^{2+}_{(\text{aq})}$, SRA: $\text{Zn}_{(\text{s})}$

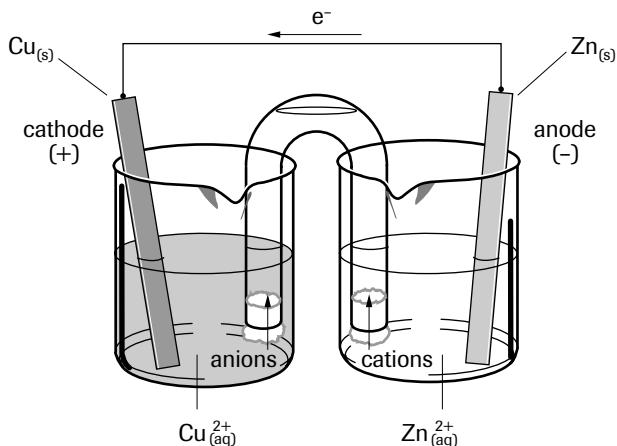


$$\Delta E^\circ = E_r^\circ (\text{cathode}) - E_r^\circ (\text{anode})$$

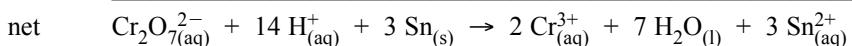
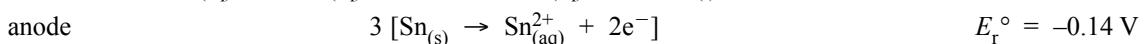
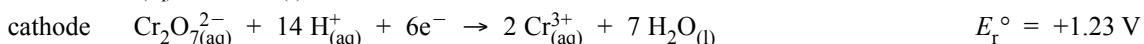
$$= +0.34 \text{ V} - (-0.76 \text{ V})$$

$$\Delta E^\circ = +1.10 \text{ V}$$

The potential of this cell is +1.10 V.



(b) SOA: $\text{Cr}_2\text{O}_7^{2-}_{(\text{aq})}$, SRA: $\text{Sn}_{(\text{s})}$

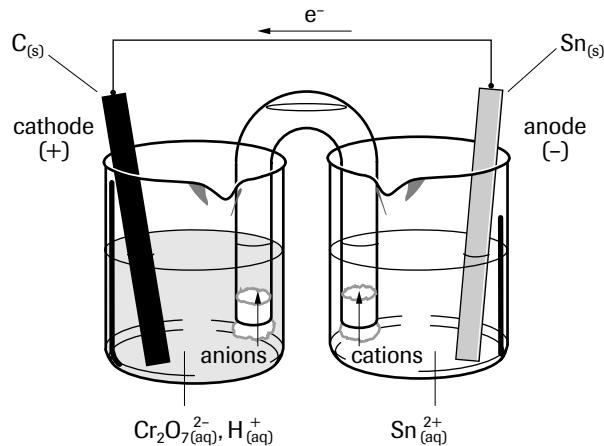


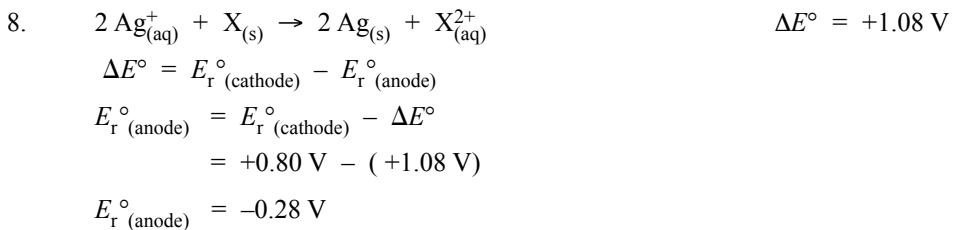
$$\Delta E^\circ = E_r^\circ (\text{cathode}) - E_r^\circ (\text{anode})$$

$$= +1.23 \text{ V} - (-0.14 \text{ V})$$

$$\Delta E^\circ = +1.37 \text{ V}$$

The potential of this cell is +1.37 V.





The reduction potential for the $\text{X}_{(\text{aq})}^{2+} | \text{X}_{(\text{s})}$ half-cell is -0.28 V , which could represent $\text{Co}_{(\text{aq})}^{2+} | \text{Co}_{(\text{s})}$.

9.6 CORROSION

Try This Activity: Home Corrosion Experiment

(Page 711)

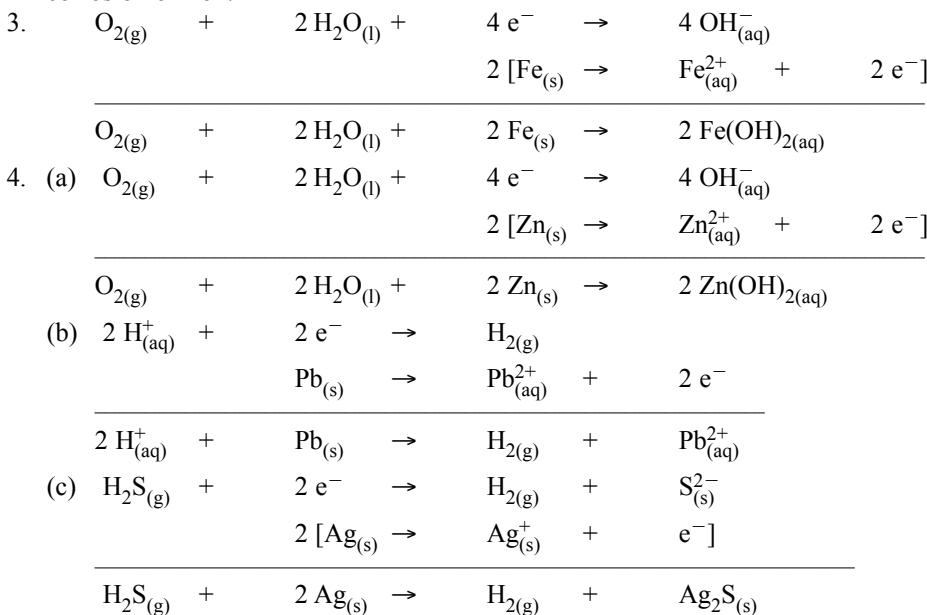
- (a) According to the labels, 7-Up has more kinds of acids and electrolytes (carbonic acid, malic acid, and citric acid) than Coca-Cola (carbonic acid and phosphoric acid). This might suggest that the iron in the steel nail would corrode more in the 7-Up than in the Coca-Cola.
- After about 20 h, the nail in the 7-Up changed from the initial shiny, silvery-grey metal to a slightly darker grey appearance. The change was uniform and the nail was still smooth.
 - After about 20 h, the nail in the Coca-Cola changed from the initial shiny, silvery-grey metal to a darker grey, speckled appearance throughout the whole nail. Some dark brown blotches were evident on the nail only where it was near the surface of the liquid.
- (b) It appears that the nail in the Coca-Cola corroded more than the one in the 7-Up but a longer observation period would be necessary to confirm this. The concentrations of each of the acids are not given on the label. Qualitatively, it may be possible that phosphoric acid in Coca-Cola has a major effect. The initial prediction appears to be false but the reasons for this are not clear.

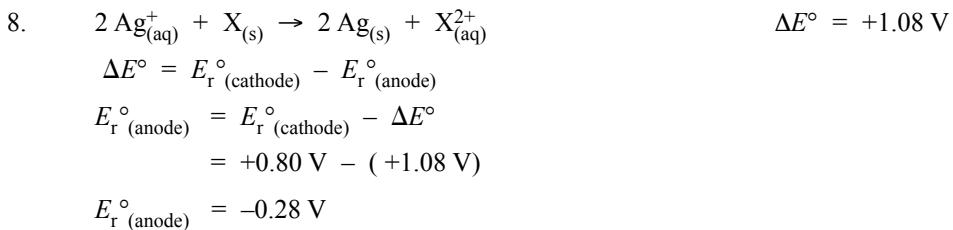
SECTION 9.6 QUESTIONS

(Page 714)

Understanding Concepts

- For the corrosion of iron an oxidizing agent, most commonly oxygen and water, must be present and in contact with the iron.
- The presence of acidic solutions, electrolytes, mechanical stresses, and contact with less active metals accelerate the corrosion of iron.





The reduction potential for the $\text{X}_{(\text{aq})}^{2+} | \text{X}_{(\text{s})}$ half-cell is -0.28 V , which could represent $\text{Co}_{(\text{aq})}^{2+} | \text{Co}_{(\text{s})}$.

9.6 CORROSION

Try This Activity: Home Corrosion Experiment

(Page 711)

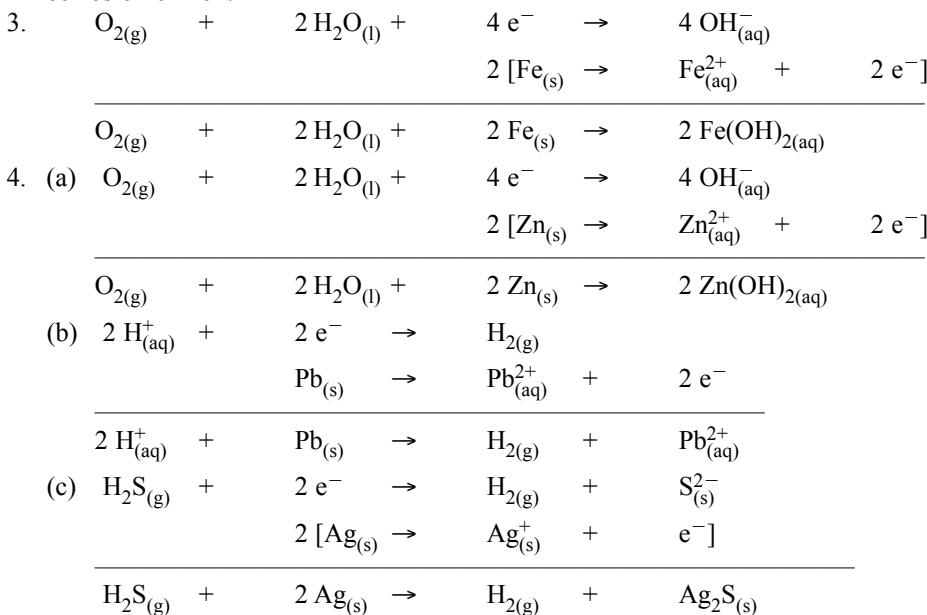
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SECTION 9.6 QUESTIONS

(Page 714)

Understanding Concepts

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- The presence of acidic solutions, electrolytes, mechanical stresses, and contact with less active metals accelerate the corrosion of iron.



5. (a) The painted surface is blistered, providing evidence for damage extending well beyond the break in the paint.
 (b) Moisture may be trapped between the steel and the paint, setting up an electrochemical cell. The iron below the paint is oxidized, releasing electrons that travel through the steel to the edge of the crack where both oxygen and water are present to pick up these electrons.
6. Since hydroxide ions (either alone or in combination with other ions) often act as reducing agents, a basic solution might prevent or slow down the corrosion of iron.
7. A zinc coating on iron is better than a tin coating because zinc is more easily oxidized than iron and the zinc will corrode first. Tin is less active than iron and will promote the oxidation of iron.
8. Impressed current and sacrificial anode are two methods of cathodic protection. They are similar in that both methods force the iron to become the cathode by supplying it with electrons.

Applying Inquiry Skills

9. (a) The independent variable is the oxidizing agent.
 The dependent variable is the extent of any corrosion.
 The controlled variables are temperature, concentration of oxidizing agent, and length of time exposed.

(b) Materials

7 pieces of copper (same size and shape)	0.10 mol/L $\text{HCl}_{(\text{aq})}$
7 large test tubes with stoppers	0.10 mol/L $\text{HNO}_3_{(\text{aq})}$
test-tube rack	0.10 mol/L $\text{H}_2\text{SO}_4_{(\text{aq})}$
source of oxygen gas	0.10 mol/L $\text{H}_3\text{PO}_4_{(\text{aq})}$
5 100-mL beakers	distilled water
steel wool	

Procedure

1. Wear safety glasses and rinse with cool water if any acid is spilled.
2. Clean each piece of copper with steel wool, rinse with water, and dry thoroughly.
3. Place each piece of copper in a different test tube, labelled 1 to 7.
4. Seal test tube #1 with a stopper and note this is the control.
5. Add oxygen gas to the bottom of test tube #2 for about 1 min and then seal test tube.
6. Pour 50 mL of each of the following liquids into a different 100-mL beaker:
 distilled water, $\text{HCl}_{(\text{aq})}$, $\text{HNO}_3_{(\text{aq})}$, $\text{H}_2\text{SO}_4_{(\text{aq})}$, $\text{H}_3\text{PO}_4_{(\text{aq})}$.
7. Bubble oxygen gas through each solution for 1.0 min.
8. Pour each oxygenated solution into a different test tube containing a copper strip, filling the test tube completely.
9. Carefully observe the contents of each test tube after five minutes, thirty minutes, and one day. Note, in particular, any differences compared with the control.
10. Dispose of all liquids into the sink while running water to rinse down the drain. Clean and recycle the pieces of copper.

Making Connections

10. (a) Zinc is being used as a sacrificial anode to protect the pipeline. Zinc is a more active metal than iron. A spontaneous electric cell is established with iron as the cathode and zinc as the anode.
 (b) Protective layers are always used and impressed currents may also be used.
 (c) The environmental and safety issues associated with not protecting pipelines come from the possibility of the pipe corroding so badly that it breaks, allowing gas and/or oil to escape into the environment. In addition to the risk of a catastrophic fire, oil and gas leaks can be very harmful to plants and animals. The environmental and safety issues associated with protecting pipelines are considerably less, although the oxidation of sacrificial anodes can release metal ions into ground water.
11. Some examples of metal corrosion are:
 - Corrosion of oil and/or gas pipelines and storage tanks (environmental, health, and safety issues)
 - Corrosion of steel bridges and towers (health and safety issues)
 - Corrosion of reinforcing steel in concrete structures (environmental, health, and safety issues)
 - Corrosion of the bodies of motor vehicles, boats, and airplanes (health and safety issues)
 Some examples of desirable metal corrosion are: self-protecting metals, e.g., aluminum and zinc; attractive patina forming on copper roofs and bronze statues; and corrosion of sacrificial anodes to protect buried pipes and tanks.
12. (Different results will be found with different search engines, with over 100 000 titles a typical result.)
 general site: <http://www.cp.umist.ac.uk/> “Corrosion Infomation Server”
 Classes of iron corrosion: pitting corrosion, stress corrosion, corrosion in molten salts, corrosion in metal-cooled nuclear reactors, displacement, and hydrogen embrittlement.

CHAPTER 9 LAB ACTIVITIES

INVESTIGATION 9.1.1 SINGLE DISPLACEMENT REACTIONS

(Page 715)

Prediction

(a) According to the single displacement reaction generalization, the products are as follows:

1. $\text{Cu}_{(s)} + 2 \text{AgNO}_{3(aq)} \rightarrow 2 \text{Ag}_{(s)} + \text{Cu}(\text{NO}_3)_{2(aq)}$
2. $\text{Cl}_{2(aq)} + 2 \text{NaBr}_{(aq)} \rightarrow \text{Br}_{2(l)} + 2 \text{NaCl}_{(aq)}$
3. $\text{Mg}_{(s)} + 2 \text{HCl}_{(aq)} \rightarrow \text{H}_{2(g)} + \text{MgCl}_{2(aq)}$
4. $\text{Zn}_{(s)} + \text{CuSO}_{4(aq)} \rightarrow \text{Cu}_{(s)} + \text{ZnSO}_{4(aq)}$
5. $\text{Cl}_{2(aq)} + 2 \text{KI}_{(aq)} \rightarrow \text{I}_{2(s)} + 2 \text{KCl}_{(aq)}$

Experimental Design

(b) For reaction 1, silver metal is identified by its silvery appearance and copper(II) nitrate is identified by its blue colour in solution. For reaction 2, bromine is identified by the orange colour in the halogen diagnostic test. For reaction 3, hydrogen gas is identified by the “pop” sound in the hydrogen diagnostic test. For reaction 4, copper metal is identified by its appearance. For reaction 5, iodine is identified by the violet colour in the halogen diagnostic test.

Evidence

(c)

#	Test procedure	Observations
1.	mixture observed	<ul style="list-style-type: none">initially black and later silver-grey crystals on copper stripblue-coloured solution
2.	mixture observed before and after adding hexane	<ul style="list-style-type: none">initial yellow-brown colour of the solutionorange colour in organic layer
3.	gas collected and a flame inserted	<ul style="list-style-type: none">a squeaky “pop” sound heard in the test tube
4.	mixture observed	<ul style="list-style-type: none">initially, a black deposit which later appeared reddish-brown
5.	mixture observed before and after adding hexane	<ul style="list-style-type: none">initial yellow-brown colour of the solutionviolet colour in organic layer

Analysis

(d) In reaction 1, the silver-grey crystals suggest the presence of silver metal and the blue solution colour agrees with the formation of copper(II) nitrate. In reaction 2, the orange colour in the organic layer confirms the presence of bromine in the final mixture. In reaction 3, the “pop” sound when the gas was ignited confirms the presence of hydrogen. In reaction 4, the appearance of a reddish-brown precipitate suggests copper metal has formed. In reaction 5, the violet colour in the organic layer confirms the presence of iodine.

Evaluation

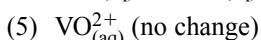
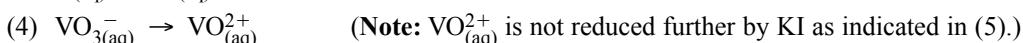
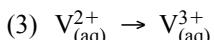
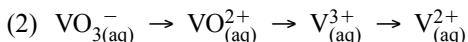
- (e) The experimental design was barely adequate to answer the problem with the materials provided. In most cases, only one product was tested and some of the tests were not very specific. The design could be improved by including additional diagnostic tests which would require additional materials. The procedure was adequate for collecting the evidence indicated in the design.
- (f) The quality of evidence was variable. Some evidence like the halogen and hydrogen tests clearly showed the presence of the predicted product. Other evidence such as the observations of a precipitate were of low quality. In all cases, more evidence is required to check for the presence of a second product.
- (g) I am only moderately confident in the answers obtained. The initial appearance of dark precipitates in reactions 1 and 4 cannot be explained, although the final appearance seemed to agree with the predicted product.
- (h) All predictions are judged to be verified because they generally agree with the results obtained and no significant contradictory evidence was obtained for any of the reactions.

LAB EXERCISE 9.1.1 OXIDATION STATES OF VANADIUM

(Page 716)

Analysis

(a) (1) $\text{VO}_{3(\text{aq})}^-$ (vanadate(V) ion from the dissociation of ammonium vanadate(V))



(b) (1) no reaction

(2) vanadium is being reduced from +5 to +4 to +3 to +2

(3) vanadium is being oxidized from +2 to +3

(4) vanadium is being reduced from +5 to +4

(5) no change in oxidation number

(6) vanadium is being oxidized from +2 to +3 to +4 to +5

(c) (3) The $\text{V}_{(\text{aq})}^{2+}$ is slowly changed to $\text{V}_{(\text{aq})}^{3+}$. This is an oxidation probably caused by the reaction of oxygen in the air with $\text{V}_{(\text{aq})}^{2+}$.

(4) The $\text{VO}_{3(\text{aq})}^-$ is likely reduced to $\text{VO}_{(\text{aq})}^{2+}$, which is blue. At the same time, iodide ions are likely being oxidized to iodine, which is yellow-brown in aqueous solution. The combination of blue and yellow-brown would produce a very dark coloured mixture.

(5) Iodide ions are not able to reduce $\text{VO}_{(\text{aq})}^{2+}$.

(6) Permanganate ions are able to successively oxidize $\text{V}_{(\text{aq})}^{2+}$ to $\text{V}_{(\text{aq})}^{3+}$ to $\text{VO}_{(\text{aq})}^{2+}$ and finally, to $\text{VO}_{3(\text{aq})}^-$.

(d) This equilibrium does not alter the analysis based on oxidation numbers. The oxidation number for vanadium in both $\text{VO}_{3(\text{aq})}^-$ and $\text{VO}_{2(\text{aq})}^+$ is +5.

INVESTIGATION 9.3.1 SPONTANEITY OF REDOX REACTIONS

(Page 716)

Prediction

(a) Based on previous assumptions for chemical reactions and stoichiometry, all combinations that result in products different from reactants are spontaneous. Therefore, all metals should react with compounds of other metal ions.

Procedure

- (b) 1. Clean one side of each of the four metal strips, using steel wool.
2. Add 1 drop of $\text{Cu}(\text{NO}_3)_{2(\text{aq})}$ on each of the four metals.
3. Repeat step 2, using $\text{Pb}(\text{NO}_3)_{2(\text{aq})}$, AgNO_3 , and $\text{Zn}(\text{NO}_3)_{2(\text{aq})}$ on different parts of the metal strips.
4. Rinse the lead and silver solutions into a labelled waste container and clean the metal strips for reuse.

Evidence

(c) **Reactions of Metals and Their Ions**

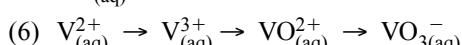
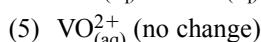
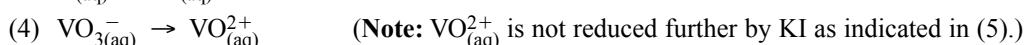
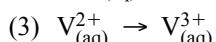
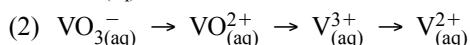
	$\text{Cu}_{(\text{s})}$	$\text{Pb}_{(\text{s})}$	$\text{Ag}_{(\text{s})}$	$\text{Zn}_{(\text{s})}$
$\text{Cu}_{(\text{aq})}^{2+}$	slightly cleaner metal surface	red-brown precipitate	no change	red-brown precipitate
$\text{Pb}_{(\text{aq})}^{2+}$	no change	no change	no change	black precipitate
$\text{Ag}_{(\text{aq})}^+$	silver crystals	silver crystals	no change	silver crystals
$\text{Zn}_{(\text{aq})}^{2+}$	no change	no change	no change	no change

LAB EXERCISE 9.1.1 OXIDATION STATES OF VANADIUM

(Page 716)

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(d) This equilibrium does not alter the analysis based on oxidation numbers. The oxidation number for vanadium in both $\text{VO}_{3(\text{aq})}^-$ and $\text{VO}_{2(\text{aq})}^+$ is +5.

INVESTIGATION 9.3.1 SPONTANEITY OF REDOX REACTIONS

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Prediction

(a) Based on previous assumptions for chemical reactions and stoichiometry, all combinations that result in products different from reactants are spontaneous. Therefore, all metals should react with compounds of other metal ions.

Procedure

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Evidence

(c) **Reactions of Metals and Their Ions**

	$\text{Cu}_{(\text{s})}$	$\text{Pb}_{(\text{s})}$	$\text{Ag}_{(\text{s})}$	$\text{Zn}_{(\text{s})}$
$\text{Cu}_{(\text{aq})}^{2+}$	slightly cleaner metal surface	red-brown precipitate	no change	red-brown precipitate
$\text{Pb}_{(\text{aq})}^{2+}$	no change	no change	no change	black precipitate
$\text{Ag}_{(\text{aq})}^+$	silver crystals	silver crystals	no change	silver crystals
$\text{Zn}_{(\text{aq})}^{2+}$	no change	no change	no change	no change

Analysis

- (d) The evidence obtained is consistent with spontaneous, single displacement reactions for only the combinations of:
- copper metal and silver ions;
 - lead metal and copper(II) ions;
 - lead metal and silver ions; and
 - zinc metal and each of copper(II), silver, and lead(II) ions.

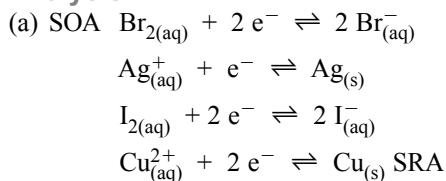
Evaluation

- (e) The experimental design was adequate to answer the problem since only evidence for a reaction (not the identity of the product) was required. The materials and procedure were adequate, although the short observation time did create a little uncertainty for those combinations that did not appear to react.
- (f) Two aspects of this experiment could be improved. The combinations that did not appear to react could be left longer in case there was a slow reaction. Some diagnostic tests could be done to determine the identity of any products produced.
- (g) Overall, the prediction is judged to be falsified since six out of the twelve predicted spontaneous reactions did not give any evidence of a chemical change. The mixture of a metal and a solution of its own ion was predicted to be nonspontaneous and this was verified with the possible exception of the copper system, which would require further testing.
- (h) The assumption of spontaneous reactions is judged to be unacceptable since the prediction was clearly falsified. The assumption will need to be restricted, revised, or discarded.

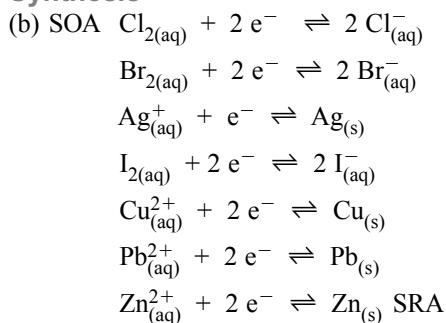
LAB EXERCISE 9.3.1 BUILDING A REDOX TABLE

(Page 717)

Analysis



Synthesis

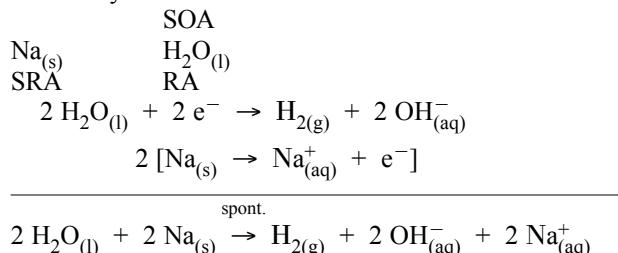


INVESTIGATION 9.3.2 THE REACTION OF SODIUM WITH WATER

(Page 718)

Prediction

- (a) According to the method for predicting redox reactions, the products of the reaction are hydrogen gas and aqueous sodium hydroxide as shown below.



Analysis

- (d) The evidence obtained is consistent with spontaneous, single displacement reactions for only the combinations of:
- copper metal and silver ions;
 - lead metal and copper(II) ions;
 - lead metal and silver ions; and
 - zinc metal and each of copper(II), silver, and lead(II) ions.

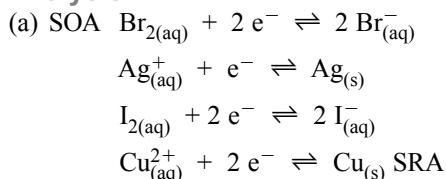
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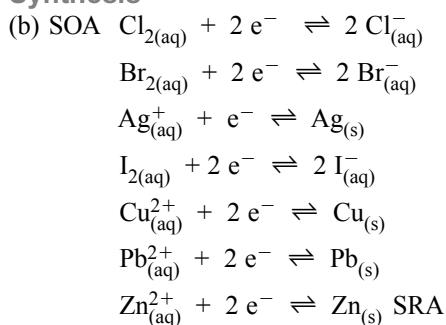
LAB EXERCISE 9.3.1 BUILDING A REDOX TABLE

(Page 717)

Analysis



Synthesis

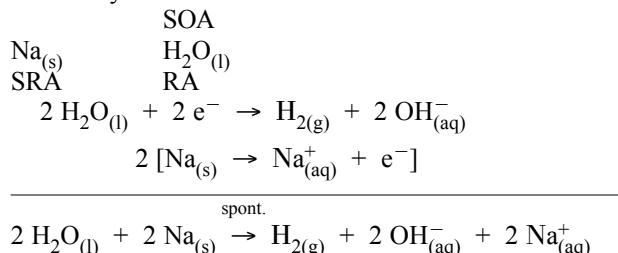


INVESTIGATION 9.3.2 THE REACTION OF SODIUM WITH WATER

(Page 718)

Prediction

- (a) According to the method for predicting redox reactions, the products of the reaction are hydrogen gas and aqueous sodium hydroxide as shown below.



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- (d) The evidence obtained is consistent with spontaneous, single displacement reactions for only the combinations of:
- copper metal and silver ions;
 - lead metal and copper(II) ions;
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LAB EXERCISE 9.3.1 BUILDING A REDOX TABLE

(Page 717)

Analysis

- (a) SOA $\text{Br}_{2(\text{aq})} + 2 \text{e}^- \rightleftharpoons 2 \text{Br}_{(\text{aq})}^-$
- $$\text{Ag}_{(\text{aq})}^+ + \text{e}^- \rightleftharpoons \text{Ag}_{(\text{s})}$$
- $$\text{I}_{2(\text{aq})} + 2 \text{e}^- \rightleftharpoons 2 \text{I}_{(\text{aq})}^-$$
- $$\text{Cu}_{(\text{aq})}^{2+} + 2 \text{e}^- \rightleftharpoons \text{Cu}_{(\text{s})} \text{ SRA}$$

Synthesis

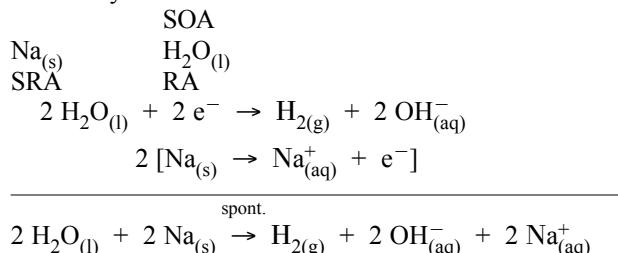
- (b) SOA $\text{Cl}_{2(\text{aq})} + 2 \text{e}^- \rightleftharpoons 2 \text{Cl}_{(\text{aq})}^-$
- $$\text{Br}_{2(\text{aq})} + 2 \text{e}^- \rightleftharpoons 2 \text{Br}_{(\text{aq})}^-$$
- $$\text{Ag}_{(\text{aq})}^+ + \text{e}^- \rightleftharpoons \text{Ag}_{(\text{s})}$$
- $$\text{I}_{2(\text{aq})} + 2 \text{e}^- \rightleftharpoons 2 \text{I}_{(\text{aq})}^-$$
- $$\text{Cu}_{(\text{aq})}^{2+} + 2 \text{e}^- \rightleftharpoons \text{Cu}_{(\text{s})}$$
- $$\text{Pb}_{(\text{aq})}^{2+} + 2 \text{e}^- \rightleftharpoons \text{Pb}_{(\text{s})}$$
- $$\text{Zn}_{(\text{aq})}^{2+} + 2 \text{e}^- \rightleftharpoons \text{Zn}_{(\text{s})} \text{ SRA}$$

INVESTIGATION 9.3.2 THE REACTION OF SODIUM WITH WATER

(Page 718)

Prediction

- (a) According to the method for predicting redox reactions, the products of the reaction are hydrogen gas and aqueous sodium hydroxide as shown below.



Experimental Design

(b-d) A small piece of clean sodium metal is added to pure water. The following diagnostic tests are conducted first on pure water (as a control) and then on the final reaction mixture. If a flame is inserted into a sample of the gas above the water, and a squeal or “pop” sound is heard, then hydrogen is likely present. If pieces of red and blue litmus paper are immersed in the solution, and the red paper turns blue, then hydroxide ions are likely present. If a flame test is conducted on the liquid, and the flame is bright yellow, then sodium ions are likely present.

Evidence

(e) Reaction of Sodium with Water

Diagnostic test	Pure water control	Reaction mixture
hydrogen test	no sound heard	high, squeaky “pop” heard
litmus test	no colour change	red litmus turned blue
flame test	pale yellow flame	bright yellow flame

Analysis

(f) According to the evidence from the diagnostic tests, hydrogen gas, sodium ions, and hydroxide ions were produced in the reaction of sodium metal with water.

Evaluation

(g) The prediction is verified because it clearly agrees with the evidence obtained.

(h) Because the prediction is verified, the method of writing redox reactions appears to be acceptable for this reaction.

(i) One test cannot be sufficient to provide a reliable evaluation. Many other reactions should be predicted and then tested.

ACTIVITY 9.4.1 DEVELOPING AN ELECTRIC CELL

(Page 719)

Evidence

(a) Testing of several cells showed that the aluminum can must always be the negative (black) electrode in order to obtain a positive voltage reading. Scraping the coating to expose the aluminum metal gave better results. However, the voltages were often erratic and slowly changed. In all cases, the voltages slowly increased the longer the cell was assembled.

(b) Developing an Electric Cell Using Different Electrodes and Electrolytes

Electrode	Initial voltages (V)			Final voltages (V)		
	$\text{NaCl}_{(\text{aq})}$	$\text{NaOH}_{(\text{aq})}$	$\text{HCl}_{(\text{aq})}$	$\text{NaCl}_{(\text{aq})}$	$\text{NaOH}_{(\text{aq})}$	$\text{HCl}_{(\text{aq})}$
copper	0.5	0.4	0.6	1.1	2.4	1.2
carbon	0.4	1.5	0.9	1.5	3.8	2.4

Analysis

(c) According to the evidence collected, the largest voltage of an aluminum-can cell is 3.8 V. This voltage is obtained with a carbon electrode as the positive electrode in a 0.5 mol/L sodium hydroxide electrolyte left sitting in the aluminum can (negative electrode) for a long period of time.

Evaluation

(d) Overall, the quality of the evidence was not very high if accurate and reliable voltages are desired. The evidence did clearly show that some cell designs were better than others. Sources of experimental error or uncertainty include the electrical connection between the clip and the aluminum can, the influence of the coating on the inside of the can on the operation of the cell, the purity of the electrodes and solutions, and the time the electrolyte is left in contact with the components of the cell.

(e) The aluminum can would be cleaned or scraped down to the bare metal, both inside and outside where the wire is connected. Electrolytes would be left sitting in the can for a period of time before measuring the voltage. Finally, other electrodes and electrolytes would be tested.

(f) The $\text{C}_{(\text{s})} \mid \text{NaOH}_{(\text{aq})} \mid \text{Al}_{(\text{s})}$ electric cell is judged according to these criteria: reliability, economy, and simplicity. The cell appears reliable since it produced a voltage immediately. However, if a constant voltage is required, this cell may

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(e) Reaction of Sodium with Water

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ACTIVITY 9.4.1 DEVELOPING AN ELECTRIC CELL

(Page 719)

Evidence

(a) Testing of several cells showed that the aluminum can must always be the negative (black) electrode in order to obtain a positive voltage reading. Scraping the coating to expose the aluminum metal gave better results. However, the voltages were often erratic and slowly changed. In all cases, the voltages slowly increased the longer the cell was assembled.

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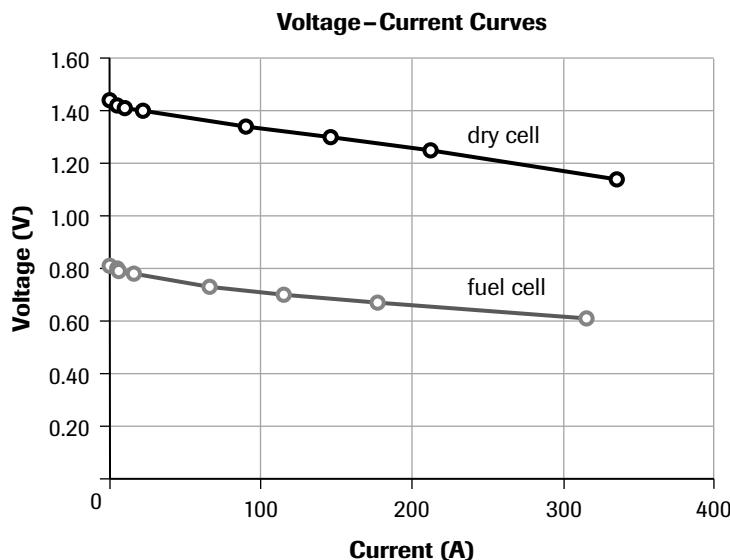
not function reliably. More trials are required to investigate long-term reliability and the time it takes the thin wall of the aluminum can to disintegrate. The economics of the cell would depend largely on the cost of aluminum and the cell's ability to be recharged. Recycled aluminum would be a significant economic advantage. Certainly, there does not appear to be a shortage of empty aluminum cans. The cell is simple as it does not have any complex parts or technical design. Further trials are needed using a moist, basic electrolyte paste to obtain a cell that will not easily leak its contents.

LAB EXERCISE 9.4.1 CHARACTERISTICS OF A HYDROGEN FUEL CELL

(Page 720)

Analysis

(a)



(b) For both cells, the voltage of the cell slowly decreases as the current increases. The behaviour of the hydrogen fuel cell appears similar, although it starts at a lower initial voltage.

(c)

Power Curve Comparison

Dry cell			Hydrogen fuel cell		
Voltage (V)	Current (mA)	Power (mW)	Voltage (V)	Current (mA)	Power (mW)
1.44	0	0	0.81	0	0
1.42	5	7	0.80	5	4
1.41	10	14	0.79	6	5
1.40	22	31	0.78	16	12
1.34	90	120	0.73	66	48
1.30	146	190	0.70	115	80
1.25	212	265	0.67	177	120
1.14	335	382	0.61	315	190

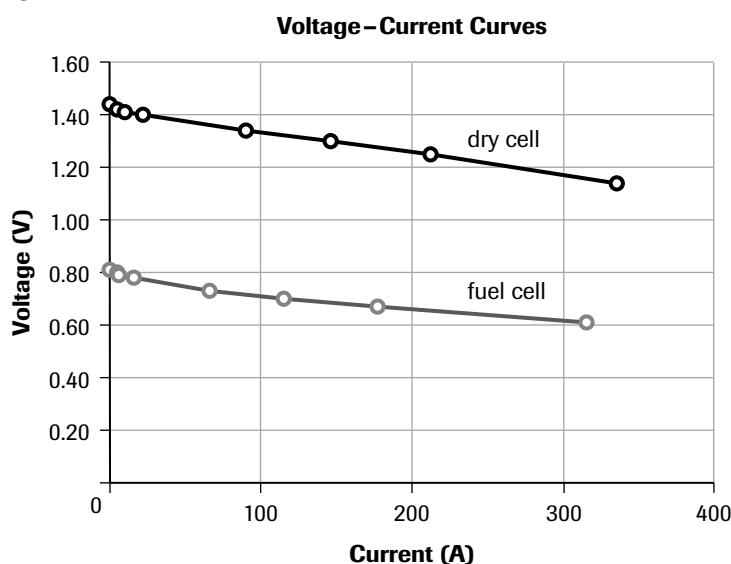
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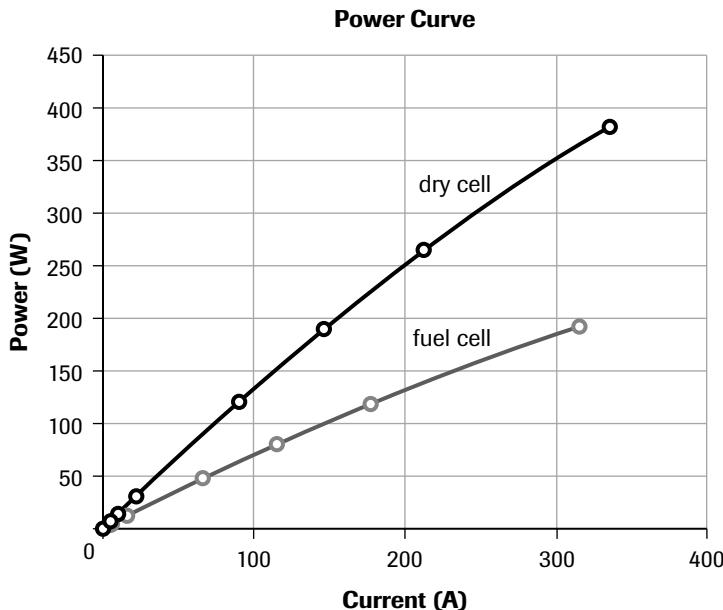
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1.42	5	7	0.80	5	4
1.41	10	14	0.79	6	5
1.40	22	31	0.78	16	12
1.34	90	120	0.73	66	48
1.30	146	190	0.70	115	80
1.25	212	265	0.67	177	120
1.14	335	382	0.61	315	190

(d)



The power curve for the hydrogen fuel cell follows a similar pattern to that of the dry cell. However, the slope of the curve is noticeably less steep for the fuel cell. This means that, as the current increases, the power output of the fuel cell increases less rapidly than that of the dry cell.

- (e) Based on the evidence collected, the trends of the voltage–current and power–current graphs are very similar for a hydrogen fuel cell compared to a typical dry cell.

Synthesis

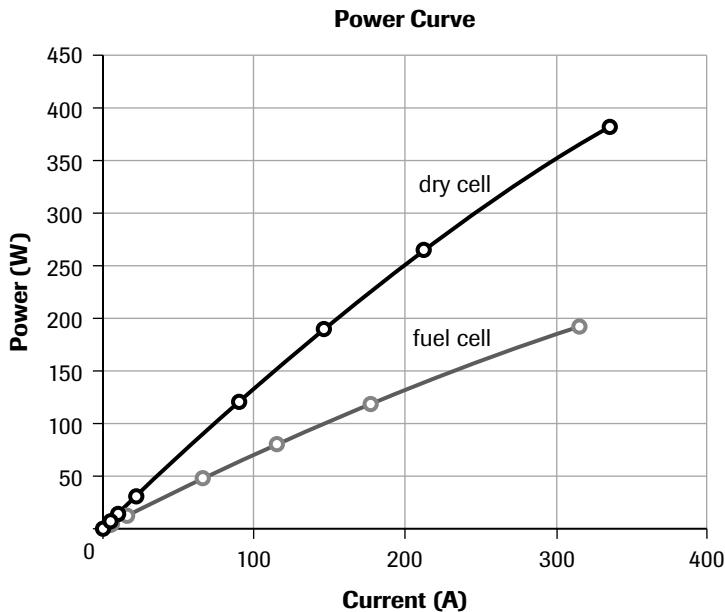
- (f) Both cells have two electrodes, an electrolyte, and chemicals that are consumed as the cell operates. In the case of the dry cell, there is a limited amount of reactant present and the cell will eventually stop producing electricity when the reactants are used up. In the fuel cell, the reactants are continuously supplied to the cell and the cell would only stop operating if the fuel is no longer provided.
- (g) A fuel cell is like a gasoline motor; both operate using a continuous supply of fuel. As long as you keep fuel “in the tank,” you can drive the car. Primary or even secondary cells have a limited quantity of “fuel” sealed inside their containers. The car can only travel a limited distance before the cell has to be recharged. (With present-day cells, this is not a very great distance unless a large battery — with unreasonable size and weight — of cells is present.)

ACTIVITY 9.5.1 GALVANIC CELL DESIGN

(Page 721)

- (a) The first design with the single electrolyte is most like Volta’s invention. All three designs have the same two metal electrodes and at least one electrolyte. Two of the cells have separate half-cells with the metal immersed in an electrolyte of its own ion and the half-cells separated by some porous boundary. The difference between these two designs is in the nature of the porous boundary. One has a salt bridge containing an inert electrolyte separating the two half-cell electrolytes and the other has a porous (porcelain) cup separating the electrolytes.
- (b) In all cells, the silver metal is the cathode (positive electrode) and the copper metal is the anode (negative electrode). (Cell (a) had a voltage of 0.15 V; cell (b) was 0.45 V; and cell (c) was 0.46 V.)
- (c) Each metal in contact with an electrolyte has a different electric potential determined by the nature of the metal atoms. As shown by a redox table, silver and copper have different strengths as reducing agents. Therefore, the answer to (a) should be the same if the two metals are the same.
- (d) The two cells comprised of half-cells both contain the same oxidized and reduced species: e.g., $\text{Cu}_{(s)} \mid \text{Cu}_{(\text{aq})}^{2+}$. The single electrolyte cell contains only an inert electrolyte.
- (e) Removing one of the parts of the cell interrupts or breaks the electrical circuit. (Removing either electrode from the solution, removing the salt bridge, or removing the porous cup immediately produced a zero volt reading. Replacing the removed part restored the original voltmeter reading.)
- (f) A common light switch also breaks or disconnects the electrical circuit.

(d)



The power curve for the hydrogen fuel cell follows a similar pattern to that of the dry cell. However, the slope of the curve is noticeably less steep for the fuel cell. This means that, as the current increases, the power output of the fuel cell increases less rapidly than that of the dry cell.

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- No evidence of reaction was visible after several minutes. After several days, long silvery crystals formed on the silver electrode in cells (b) and (c), the copper solution appeared darker, and some blue-coloured solution had moved toward the silver side of the cell. The voltage of the cell slowly decreased until, after several weeks, the voltage of the cell was almost zero volts.

- (g) A suitable control would be an identical cell with no electrical connection (wire) between the electrodes.
 (h) Silver half-cell: Test the concentration of silver ions several times by removing a known volume of the solution and precipitating the silver ions as silver chloride. Measure the mass of the silver electrode at the beginning and at the end. Copper half-cell: Using colour standards (or a spectrophotometer), determine the concentration of copper ions several times using a sample of the solution. (Alternatively, the concentration of copper ions could be determined by precipitation.) Measure the mass of the copper electrode at the beginning and at the end.
 Salt bridge: Note the colour changes in the solution.
 (i) Nitrates are spectator ions and should be the same for all cells as a control.

INVESTIGATION 9.5.1 INVESTIGATING GALVANIC CELLS

(Page 722)

Prediction

- (a) According to redox concepts and the table of redox half-reactions ...

Cathode (+)			Anode (-)			Cell potential (V)	
Cu _(s)		Cu ²⁺ _(aq)		Pb ²⁺ _(aq)		Pb _(s)	+0.47
Ag _(s)		Ag ⁺ _(aq)		Cu ²⁺ _(aq)		Cu _(s)	+0.46
Cu _(s)		Cu ²⁺ _(aq)		Zn ²⁺ _(aq)		Zn _(s)	+1.10
Ag _(s)		Ag ⁺ _(aq)		Pb ²⁺ _(aq)		Pb _(s)	+0.93
Pb _(s)		Pb ²⁺ _(aq)		Zn ²⁺ _(aq)		Zn _(s)	+0.63
Ag _(s)		Ag ⁺ _(aq)		Zn ²⁺ _(aq)		Zn _(s)	+1.56

Experimental Design

- (b) Individual metal–metal ion half-cells are constructed. Different combinations are connected with a salt bridge and the electrodes, and the cell potentials are determined. The independent variable is the combination of half-cells and the dependent variable is the cell potential. Controlled variables are temperature and electrolyte concentration.

Procedure

- Clean metal strips with steel wool and rinse with distilled water.
- Assemble two of the four metal–metal ion half-cells, for example, copper and lead.
- Connect the copper half-cell with the lead half-cell using the salt bridge.
- Use the voltmeter and connecting wires to determine the cathode and anode of the cell.
- With the voltmeter connected to the cell, measure the initial voltmeter reading.
- Remove and rinse the salt bridge.
- Repeat steps 1 to 5 for the remaining combinations of half-cells.
- Clean and return the metal strips and recycle the electrolyte solutions.

Evidence/Analysis

(d)

Cathode (+)			Anode (-)			Predicted potential (V)	Measured potential (V)	Percent diff. (%)
Cu _(s)		Cu ²⁺ _(aq)		Pb ²⁺ _(aq)		Pb _(s)	+0.47	+0.46
Ag _(s)		Ag ⁺ _(aq)		Cu ²⁺ _(aq)		Cu _(s)	+0.46	+0.45
Cu _(s)		Cu ²⁺ _(aq)		Zn ²⁺ _(aq)		Zn _(s)	+1.10	+1.06
Ag _(s)		Ag ⁺ _(aq)		Pb ²⁺ _(aq)		Pb _(s)	+0.93	+0.88
Pb _(s)		Pb ²⁺ _(aq)		Zn ²⁺ _(aq)		Zn _(s)	+0.63	+0.59
Ag _(s)		Ag ⁺ _(aq)		Zn ²⁺ _(aq)		Zn _(s)	+1.56	+1.47

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Ag _(s)		Ag ⁺ _(aq)		Zn ²⁺ _(aq)		Zn _(s)	+1.56	+1.47

(e) The measured cell potentials were all lower than the predicted values.

Evaluation

- (f) Sources of experimental error or uncertainty include small measurement uncertainties in the solution preparation and the voltmeter readings, cleanliness of the metal strips, purity of the metals and solutions, and the non-standard conditions of temperature. Without knowing the value of all of these uncertainties, but guessing that they will be relatively small, we can see that the overall quality of the evidence is about medium.
- (g) In each case, the prediction of the cathode and anode was correct.
- (h) The agreement between the predicted and measured potentials appears to be acceptable but they are either less than, equal to, or only slightly greater than 5%.
- (i) All measured cell potentials are less than the predicted values. This suggests some systematic error for all cells. Perhaps this is because the temperature was less than the standard 25°C and/or the metals or solutions were not completely pure. The voltmeter could also be reading consistently low.
- (j) The design is adequate to answer the problem with no obvious flaws. However, the procedure used does have some inadequacies. The temperature was controlled, but was not set at the standard value. This should be improved to eliminate some uncertainties in the results. The purity of the metals and accuracy of the solution concentration are not known, but otherwise, the materials appear adequate.

INVESTIGATION 9.6.1 THE CORROSION OF IRON

(Page 723)

Prediction

- (a) According to my experience and a table of relative strengths of oxidizing and reducing agents, the presence of oxygen, water, electrolytes, acidic solutions, and other metals may affect the rate of corrosion of iron. It is general knowledge that air and water are required and that iron rusts faster if ordinary salt is present. Furthermore, if any oxidizing agents that appear above iron in the table of relative strengths of oxidizing and reducing agents are present, then a spontaneous corrosion or reaction should take place; e.g., oxygen and water, and oxygen in an acidic solution.

Materials

- (b) lab apron
eye protection
bottle of distilled water
8 small test tubes with stoppers
2 50-mL beakers
test-tube rack
masking tape
tweezers
10 pieces of iron wire or nails (5–6 cm)
fine sandpaper or steel wool
1 piece of magnesium ribbon (5–6 cm)
1 piece of copper wire (5–6 cm)
2 small carbon rods
2 9-V batteries
4 connecting wires
de aerated water (freshly boiled)
about 50 mL of alcohol (or acetone) in a 250-mL beaker
0.10 mol/L HCl_(aq), NaCl_(aq), and NaOH_(aq)

Procedure

(c)

1. Clean each piece of iron thoroughly with fine sandpaper or steel wool until the iron is silvery in appearance.
2. Drop all of the cleaned iron pieces into a beaker with alcohol and swirl for a few seconds. Remove the iron pieces using tweezers and place the pieces on a clean paper towel. As much as possible, avoid directly handling the iron.
3. Label 8 small, clean test tubes.
4. For test tube 1, make sure it is dry, add a piece of iron, and stopper.
5. Fill test tube 2 with boiled distilled water (de aerated water) and then add a piece of iron and stopper.
6. For test tubes 3–6, add about 2–3 cm depth of the specified liquid and a piece of iron, and then stopper: 3, with distilled water; 4, HCl_(aq); 5, NaCl_(aq); 6, NaOH_(aq).

(e) The measured cell potentials were all lower than the predicted values.

Evaluation

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7. For test tube 7, firmly wrap a piece of cleaned magnesium ribbon around the iron. Add this to 2–3 cm of distilled water in the test tube and then stopper.
8. For test tube 8, firmly wrap a piece of cleaned copper wire around the iron. Add this to 2–3 cm of distilled water in the test tube and then stopper.
9. Tape a 9-V battery to the side of each of two small beakers so that the bottom of the beaker and the battery coincide. Approximately half-fill each beaker with distilled water.
10. Use two connecting wires to connect an iron piece to the negative terminal of one battery and a carbon rod to the positive terminal. Be sure that the two electrodes do not touch. Label this setup as 9.
11. Use two connecting wires to connect an iron piece to the positive terminal and a carbon rod to the negative terminal of the other battery. Be sure that the two electrodes do not touch. Label this setup as 10.
12. Record any observations for each of the 10 containers.
13. Record further observations in two days.
14. When all observations are completed, dispose of all liquids into the sink and return the iron and other materials.

Evidence

(d)

#	Substances/Conditions	Observations – Day 1	Observations – Day 3
1	Fe in dry, empty test tube	no change	no change
2	Fe in deaerated water (full)	no change	very slight yellow-brown tinge in water; little change in iron
3	Fe in distilled water	some slight yellow-brown colour near wire	some yellow-brown solid on wire and at bottom of test tube
4	Fe in $\text{HCl}_{(\text{aq})}$	gas bubbles rising from iron	iron appears mostly clean in liquid but some dark deposits on the part of iron above liquid; stopper popped off
5	Fe in NaCl	some slight yellow-brown colour in water	extensive yellow-brown and dark brown deposit at bottom of test tube and some on iron
6	Fe in NaOH	no change	no change
7	Mg-wrapped Fe in distilled water	tiny gas bubbles	no change to iron; dark deposit on magnesium and grey-black deposit at bottom of test tube
8	Cu-wrapped Fe in distilled water	dark colour on iron; yellow-brown colour near wire	yellow-brown precipitate on iron and at bottom; copper wire still very shiny
9	Fe connected to negative terminal of a battery	no change	no change to iron; few dark bits of material at bottom of beaker
10	Fe connected to positive terminal	slightly darker iron	considerable yellow-brown and dark solid on iron and throughout beaker; dark froth at carbon electrode

Analysis

- (e) According to the evidence, the corrosion of iron is accelerated by the presence of both water and air, salt in the water, contact with copper metal, and connection to the positive terminal of a battery.
- (f) Little or no corrosion appears if: no water is present, no air is present, the solution is basic, iron is in contact with magnesium, and iron is connected to the negative terminal of a battery. The result for hydrochloric acid is uncertain. It appears that both air and water need to be present for significant corrosion to occur. When these are present, a basic solution, contact with magnesium, or a connection to a negative terminal all appear to counteract the effect of air and water.

Evaluation

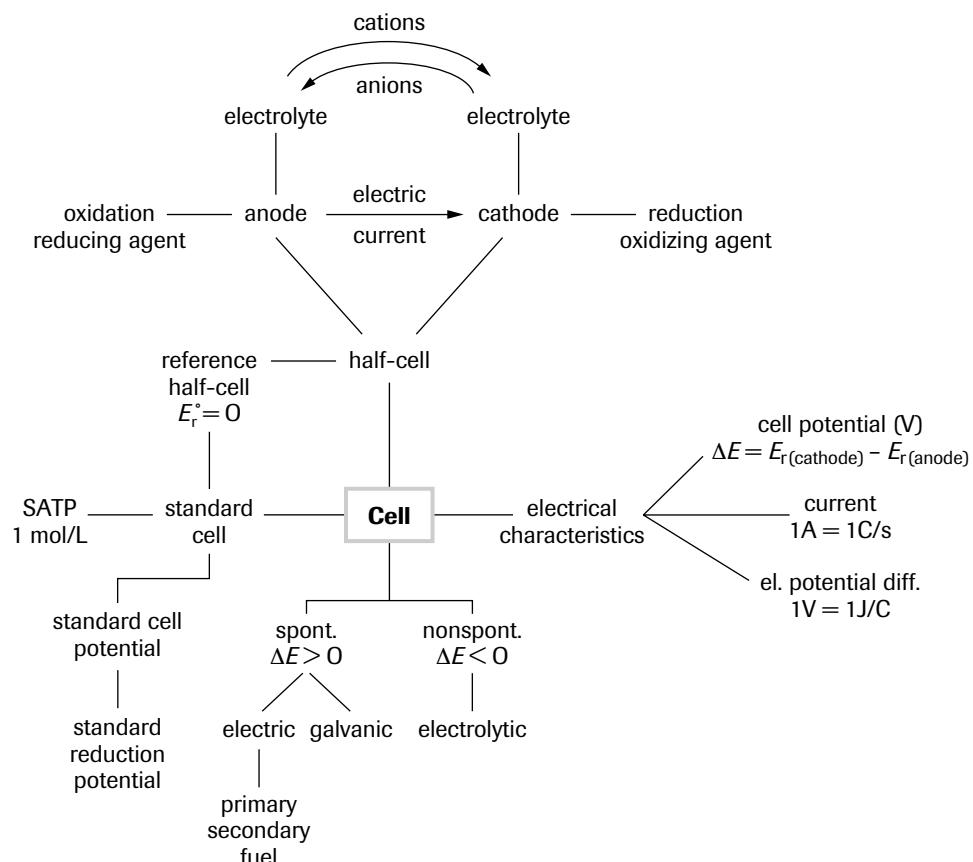
- (g) The design of this experiment is adequate to answer the general question asked in the problem with no major flaws. The design could be improved by clearly specifying the variables and controls in this experiment and adding more specific tests such as a test for iron ions in the solutions and precipitates. This would make the results more certain.

- (h) Both the procedure and materials appear to be adequate to obtain the kind of information required by the problem. An improvement in the procedure would be to find a more efficient method of cleaning the iron before the experiment. A better way of assessing the extent of corrosion would also be useful. Perhaps the iron wire could be examined under a microscope to look for evidence of corrosion. Also, evidence for the presence of iron ions could be obtained.
- (i) The main sources of experimental error or uncertainty include the purity and cleanliness of the iron wire, how well water or air was eliminated in # 1 and # 2, and the qualitative judgment of any corrosion.
- (j) Overall, the evidence seems to be reasonably good for an initial laboratory study of corrosion and I am fairly confident of the results obtained.
- (k) Most of the prediction appears to be qualitatively verified. However, the results obtained were much more specific than predicted, with a few unexpected results; e.g., with acidic and basic solutions. No prediction was made for the effect of an external power supply. Experimenting with a battery provided a starting point but is unacceptable for detailed predictions.
- (l) Personal experience and the table of relative strengths of oxidizing and reducing agents appear somewhat useful but other factors also play an unexpected role. To make better predictions of all factors, especially electrical factors, requires more empirical and theoretical knowledge about electrochemistry and corrosion.

CHAPTER 9 SUMMARY

MAKE A SUMMARY

(Page 724)

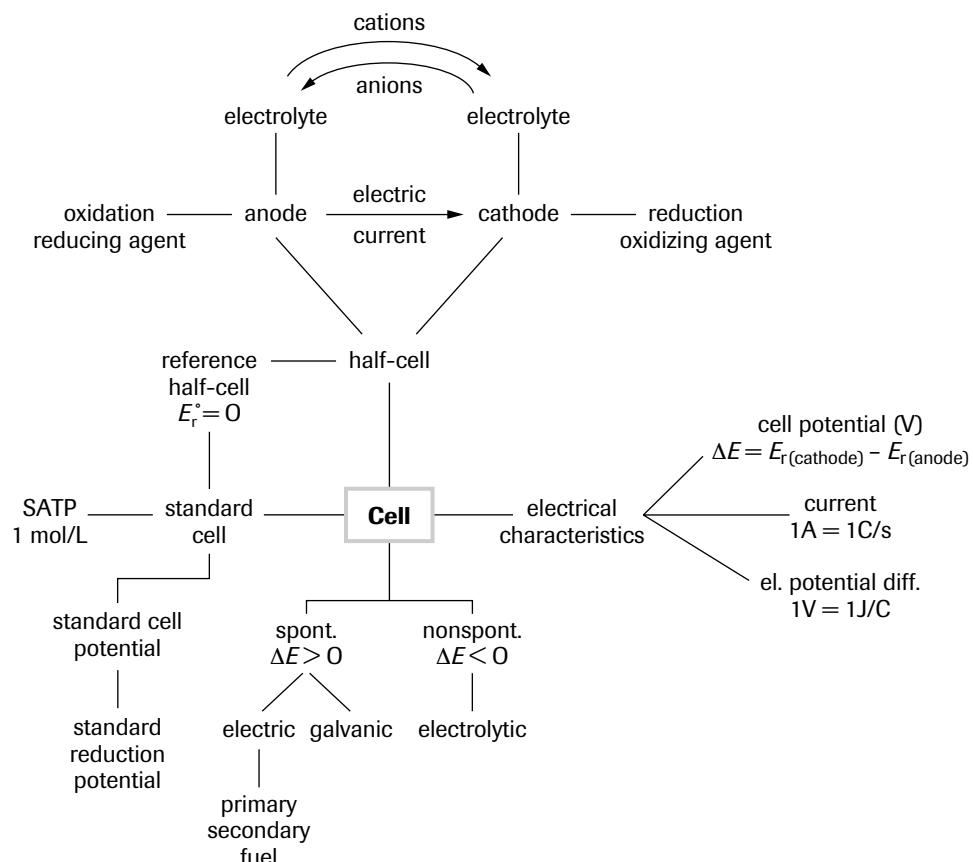


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CHAPTER 9 SUMMARY

MAKE A SUMMARY

(Page 724)



CHAPTER 9 SELF-QUIZ

(Page 725)

1. True
2. False: **Reduction Oxidation** is a process in which electrons are lost or donated by an atom or ion in a redox reaction.
3. True
4. False: The strongest oxidizing agent in a galvanic cell is above the strongest reducing agent in the redox table producing a cell potential that is **negative positive**.
5. False: The **cathode anode** of a cell is the electrode where electrons are lost or given up by the reducing agent.
6. True
7. False: The cell potential of a standard lead–nickel cell is **-0.39 +0.13 V**.
8. True
9. True
10. (a)
11. (d)
12. (c)
13. (a)
14. (b)
15. (d)
16. (c)
17. (c)
18. (b)

CHAPTER 9 REVIEW

(Page 726)

Understanding Concepts

1. (a) Oxidation is a chemical process involving a loss of electrons and an increase in oxidation number.
(b) Reduction is a chemical process involving a gain of electrons and a decrease in oxidation number.
(c) A redox reaction is the transfer of electrons from a reducing agent to an oxidizing agent.
2. (a) $\text{Fe}_{(\text{aq})}^{3+} + \text{e}^- \rightarrow \text{Fe}_{(\text{aq})}^{2+}$ (reduction)
 $\text{Ni}_{(\text{s})} \rightarrow \text{Ni}_{(\text{aq})}^{2+} + 2 \text{e}^-$ (oxidation)
(b) $\text{Br}_{2(\text{aq})} + 2 \text{e}^- \rightarrow 2 \text{Br}_{(\text{aq})}^-$ (reduction)
 $2 \text{I}_{(\text{aq})}^- \rightarrow \text{I}_{2(\text{s})} + 2 \text{e}^-$ (oxidation)
(c) $\text{Pd}_{(\text{aq})}^{2+} + 2 \text{e}^- \rightarrow \text{Pd}_{(\text{s})}$ (reduction)
 $\text{Sn}_{(\text{aq})}^{2+} \rightarrow \text{Sn}_{(\text{aq})}^{4+} + 2 \text{e}^-$ (oxidation)
3. (a) 0
(b) -1
(c) +1
(d) +1
(e) -1
4. (a) $\begin{array}{ccccccc} 0 & +3 & -2 & 0 & +3 & -2 \\ 2 \text{Al}_{(\text{s})} + \text{Fe}_2\text{O}_{3(\text{s})} & \rightarrow & 2 \text{Fe}_{(\text{s})} + \text{Al}_2\text{O}_{3(\text{s})} \end{array}$
 $\text{Al}_{(\text{s})}$ is oxidized, $\text{Fe}_{(\text{s})}^{3+}$ is reduced
(b) $\begin{array}{ccccccc} 0 & +1 & +3 & 0 \\ \text{In}_{(\text{s})} + 3 \text{Tl}_{(\text{aq})}^+ & \rightarrow & \text{In}_{(\text{aq})}^{3+} + 3 \text{Tl}_{(\text{s})} \end{array}$
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CHAPTER 9 SELF-QUIZ

(Page 725)

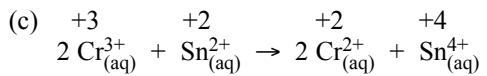
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9. True
10. (a)
11. (d)
12. (c)
13. (a)
14. (b)
15. (d)
16. (c)
17. (c)
18. (b)

CHAPTER 9 REVIEW

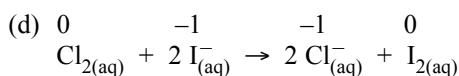
(Page 726)

Understanding Concepts

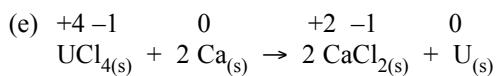
1. (a) Oxidation is a chemical process involving a loss of electrons and an increase in oxidation number.
(b) Reduction is a chemical process involving a gain of electrons and a decrease in oxidation number.
(c) A redox reaction is the transfer of electrons from a reducing agent to an oxidizing agent.
2. (a) $\text{Fe}_{(\text{aq})}^{3+} + \text{e}^- \rightarrow \text{Fe}_{(\text{aq})}^{2+}$ (reduction)
 $\text{Ni}_{(\text{s})} \rightarrow \text{Ni}_{(\text{aq})}^{2+} + 2 \text{e}^-$ (oxidation)
(b) $\text{Br}_{2(\text{aq})} + 2 \text{e}^- \rightarrow 2 \text{Br}_{(\text{aq})}^-$ (reduction)
 $2 \text{I}_{(\text{aq})}^- \rightarrow \text{I}_{2(\text{s})} + 2 \text{e}^-$ (oxidation)
(c) $\text{Pd}_{(\text{aq})}^{2+} + 2 \text{e}^- \rightarrow \text{Pd}_{(\text{s})}$ (reduction)
 $\text{Sn}_{(\text{aq})}^{2+} \rightarrow \text{Sn}_{(\text{aq})}^{4+} + 2 \text{e}^-$ (oxidation)
3. (a) 0
(b) -1
(c) +1
(d) +1
(e) -1
4. (a) $\begin{array}{ccccccc} 0 & +3 & -2 & 0 & +3 & -2 \\ 2 \text{Al}_{(\text{s})} + \text{Fe}_2\text{O}_{3(\text{s})} & \rightarrow & 2 \text{Fe}_{(\text{s})} + \text{Al}_2\text{O}_{3(\text{s})} \end{array}$
 $\text{Al}_{(\text{s})}$ is oxidized, $\text{Fe}_{(\text{s})}^{3+}$ is reduced
(b) $\begin{array}{ccccccc} 0 & +1 & +3 & 0 \\ \text{In}_{(\text{s})} + 3 \text{Tl}_{(\text{aq})}^+ & \rightarrow & \text{In}_{(\text{aq})}^{3+} + 3 \text{Tl}_{(\text{s})} \end{array}$
 $\text{In}_{(\text{s})}$ is oxidized, $\text{Tl}_{(\text{aq})}^+$ is reduced



$\text{Cr}_{(\text{aq})}^{3+}$ is reduced, $\text{Sn}_{(\text{aq})}^{2+}$ is oxidized

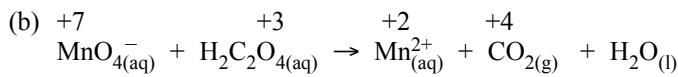
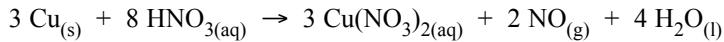
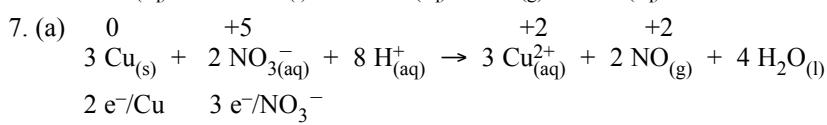
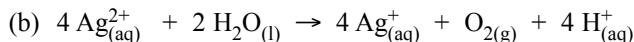
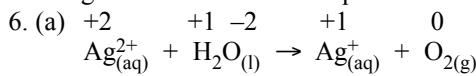


$\text{Cl}_{2(\text{aq})}$ is reduced, $\text{I}_{(\text{aq})}^{-}$ is oxidized

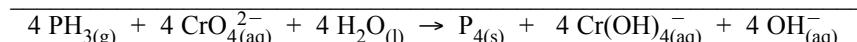
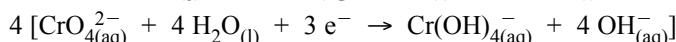
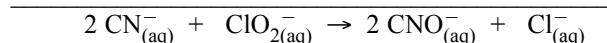
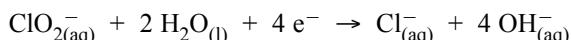
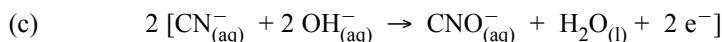
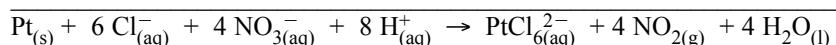
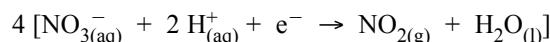
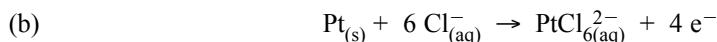
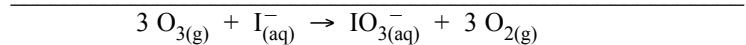
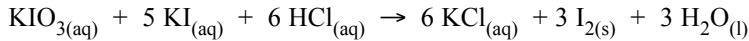
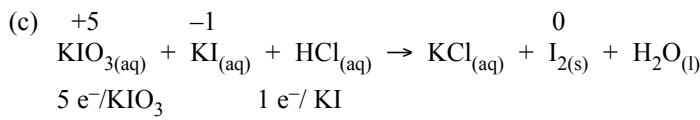
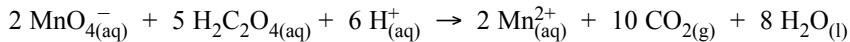


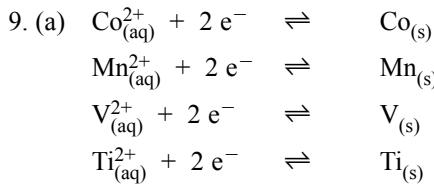
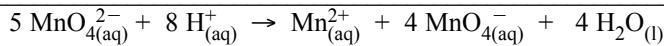
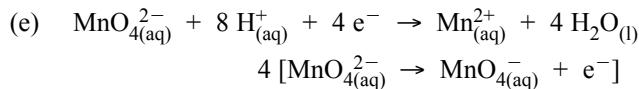
$\text{U}_{(\text{s})}^{4+}$ is reduced, $\text{Ca}_{(\text{s})}$ is oxidized

5. A net ionic equation is balanced in terms of the numbers of different kinds of atoms or ions and the total electric charge on each side of the equation.

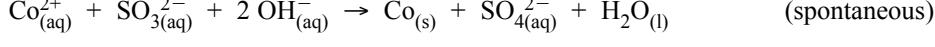
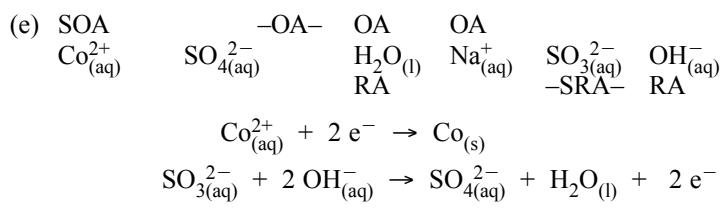
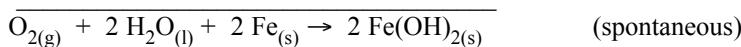
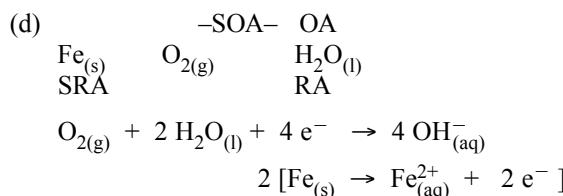
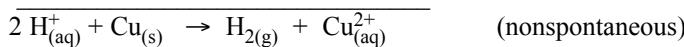
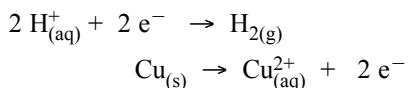
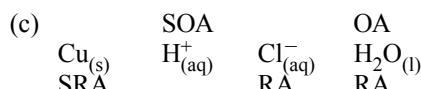
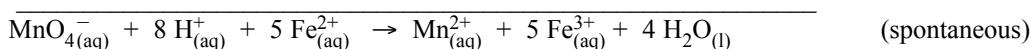
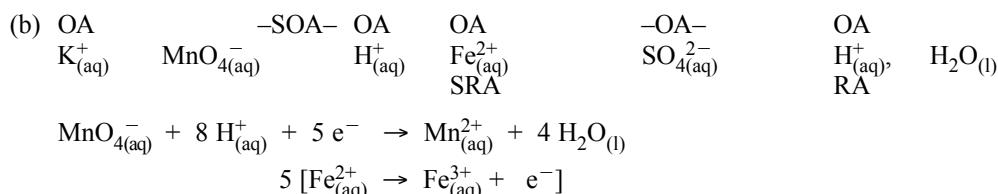
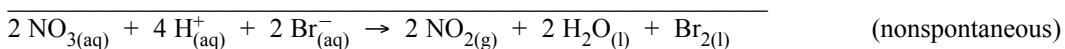
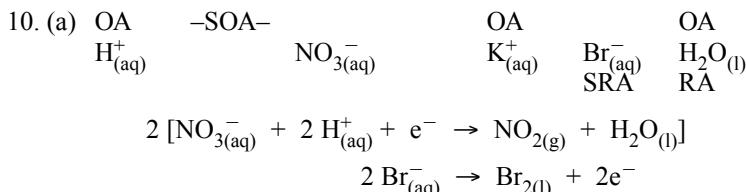


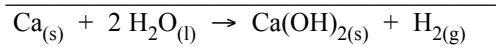
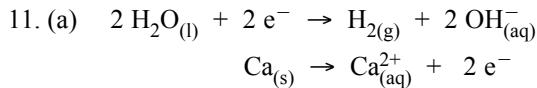
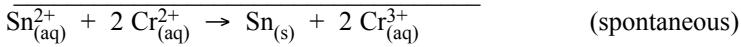
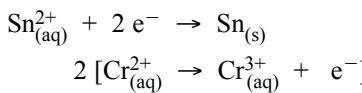
$5 \text{e}^{-}/\text{MnO}_4^{-} \quad 2 \text{e}^{-}/\text{H}_2\text{C}_2\text{O}_4$



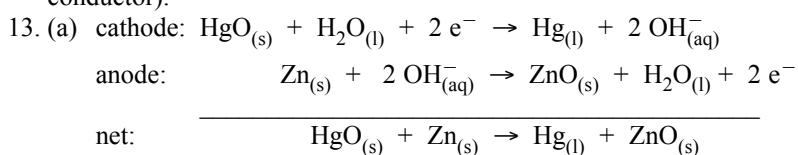


(b) In this table the strongest oxidizing agent is $\text{Co}_{(\text{aq})}^{2+}$ and the strongest reducing agent is $\text{Ti}_{(\text{s})}$.

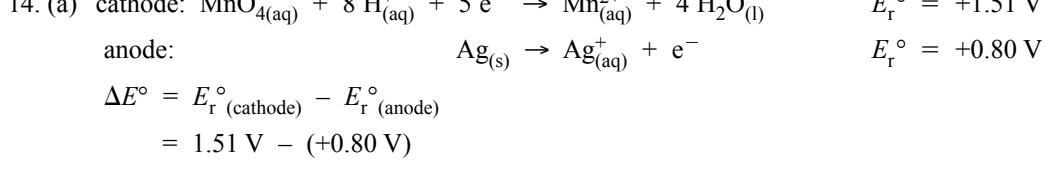




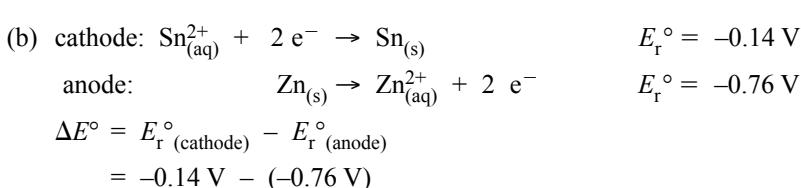
- (b) If a gas is collected and exposed to a flame, and a “pop” sound is heard, then hydrogen gas was likely produced. If a piece of red litmus paper is placed into the reaction mixture and the litmus turns blue, then hydroxide ions were likely produced (slight dissociation of calcium hydroxide precipitate). If a sample of the final solution is placed into a burner flame and a yellow-red colour is produced, then calcium ions were likely produced.
12. The three essential components of an electric cell are two electrodes (solid conductors) and an electrolyte (aqueous conductor).



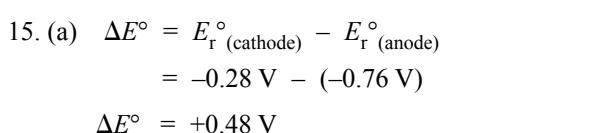
- (b) The electrons flow from zinc to mercury, because they are released by the zinc and gained by the mercury(II) oxide.
- (c) Mercury oxide (in a conducting paste) is likely the cathode and zinc metal the anode.



The predicted cell potential is +0.71 V.



The predicted cell potential is +0.62 V.



The predicted standard cell potential is +0.48 V.

$$(b) \Delta E^\circ = E_r^\circ(\text{cathode}) - E_r^\circ(\text{anode}) \\ = +0.34 \text{ V} - (-0.14 \text{ V})$$

$$\Delta E^\circ = +0.48 \text{ V}$$

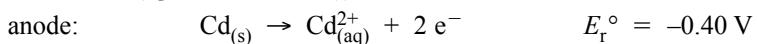
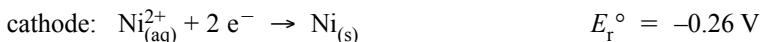
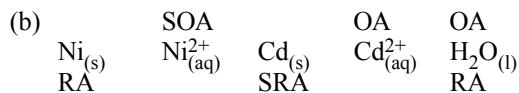
The predicted standard cell potential is +0.48 V.

$$(c) \Delta E^\circ = E_r^\circ(\text{cathode}) - E_r^\circ(\text{anode}) \\ = +1.51 \text{ V} - (-0.26 \text{ V})$$

$$\Delta E^\circ = +1.77 \text{ V}$$

The predicted standard cell potential is +1.77 V.

16. (a) Nickel will be the cathode because it is immersed in the strongest oxidizing agent, $\text{Ni}_{(\text{aq})}^{2+}$. Cadmium will be the anode because $\text{Cd}_{(\text{s})}$ is the strongest reducing agent.

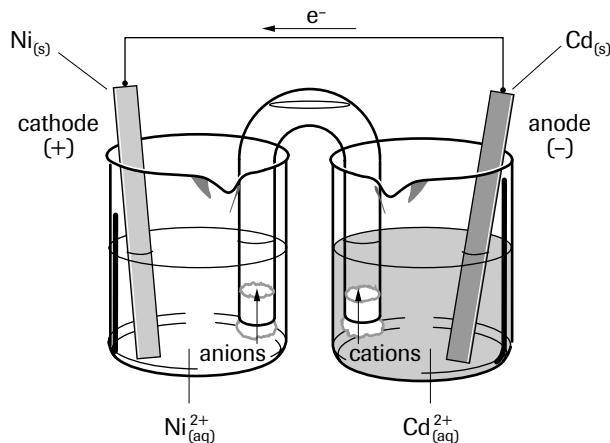


$$\begin{aligned} \Delta E^\circ &= E_r^\circ(\text{cathode}) - E_r^\circ(\text{anode}) \\ &= -0.26 \text{ V} - (-0.40 \text{ V}) \end{aligned}$$

$$\Delta E^\circ = +0.14 \text{ V}$$

The predicted standard cell potential is +0.14 V.

(c)



17. Standard reduction potentials for all other half-cells are measured relative to that of the standard hydrogen half-cell, defined as zero volts. The standard hydrogen half-cell consists of an inert platinum electrode immersed in a 1.00 mol/L solution of hydrogen ions, with hydrogen gas at 1.00 kPa bubbling over the electrode, and at 25°C.

$$18. \Delta E^\circ = E_r^\circ(\text{cathode}) - E_r^\circ(\text{anode})$$

$$\begin{aligned} E_r^\circ(\text{cathode}) &= \Delta E^\circ + E_r^\circ(\text{anode}) \\ &= +1.94 \text{ V} + (-0.40 \text{ V}) \end{aligned}$$

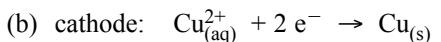
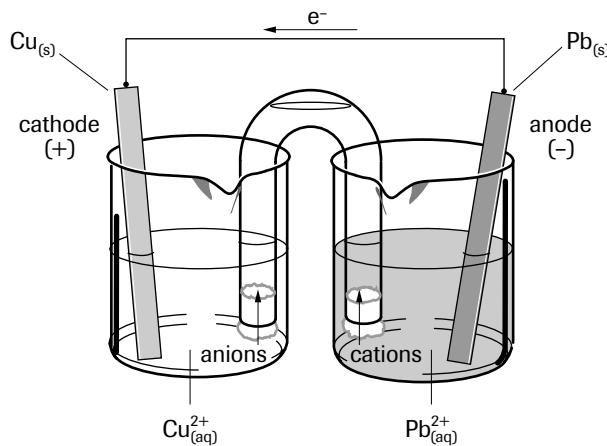
$$E_r^\circ(\text{cathode}) = +1.54 \text{ V}$$

The standard reduction potential for the $\text{Ce}_{(\text{aq})}^{3+} \mid \text{Ce}_{(\text{s})}$ half-cell is +1.54 V.

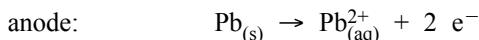
19. A “dead” galvanic cell has a voltage of zero and has reached an equilibrium state.
20. (a) Tin coatings adhere well to iron and provide a strong shiny coating. As long as the tin coating remains intact, the iron underneath is protected; but if the surface coating breaks, the iron beneath corrodes quickly because iron is a stronger reducing agent than tin.
- (b) Zinc coatings adhere well to iron and provide a strong coating that oxidizes to a silver-grey colour. The zinc reaction coating is basic zinc carbonate, which protects zinc and the iron underneath. If the zinc coating is broken, the zinc is preferentially oxidized compared to iron, resealing the opening and preventing the corrosion of the iron.
21. (a) The impressed current method of cathodic protection uses a battery or DC generator to supply electrons to the iron object being protected. The negative terminal of the power supply is connected to the iron object and the positive terminal is connected to an inert carbon electrode. The iron is forced to become the cathode and is protected from corroding.
- (b) The sacrificial anode method of cathodic protection uses a metal that is more easily oxidized than iron, such as zinc or magnesium. The sacrificial anode is connected to the iron object being protected, forming a galvanic cell with iron as the cathode.

Applying Inquiry Skills

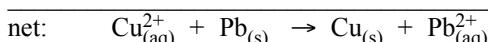
22. (a)



$$E_r^\circ = +0.34 \text{ V}$$



$$E_r^\circ = -0.13 \text{ V}$$



(c) $\Delta E^\circ = E_r^\circ (\text{cathode}) - E_r^\circ (\text{anode})$

$$= +0.34 \text{ V} - (-0.13 \text{ V})$$

$$\Delta E^\circ = +0.47 \text{ V}$$

The predicted cell potential is +0.47 V.

23. (a) **Procedure**

- Clean three small strips of zinc with steel wool.
- Add a few millilitres of each unknown solution into separate, clean test tubes.
- Place a strip of zinc metal into each solution and record evidence of reaction.
- For each solution that was unreactive with zinc, add a few millilitres of each solution to separate test tubes.
- To each of these test tubes, add a few drops of sodium carbonate solution and record evidence of reaction.
- Dispose of all solutions in the waste beaker.

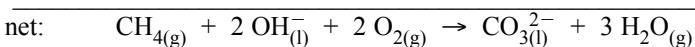
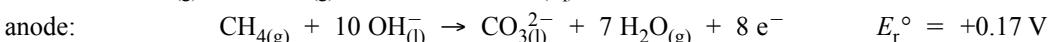
(b) **Evidence/Analysis**

- For step 3, two solutions showed no change with zinc. A dark precipitate formed on the metal in the third solution, which must therefore be the lead(II) nitrate solution, because lead(II) ions react spontaneously with zinc.
- For step 5, one solution showed no change when sodium carbonate was added. One solution produced a white precipitate, so that solution must be calcium nitrate (because calcium carbonate is a low-solubility compound). (Several other procedures are also possible.)

Making Connections

24. (a) The Ballard fuel cell consists of an anode and a cathode separated by a polymer membrane electrolyte. Hydrogen fuel admitted through a porous anode is then converted into hydrogen ions (protons) and free electrons in the presence of a catalyst at the anode. An external circuit conducts the free electrons and produces the desired electric current. Water and heat are produced when the protons, after migrating through the polymer membrane to the cathode, react both with oxygen molecules from the air and with the free electrons from the external circuit.

(b) The widespread use of electric cars could significantly reduce air pollution from internal-combustion engines, thereby reducing both photochemical smog and acid rain. The main social impact of the widespread use of electric cars is likely in employment opportunities as transportation technology shifts from a gasoline base to a hydrogen base.



$$\begin{aligned}\Delta E^\circ &= E_r^\circ (\text{cathode}) - E_r^\circ (\text{anode}) \\ &= +0.40 \text{ V} - (+0.17 \text{ V})\end{aligned}$$

$$\Delta E^\circ = +0.23 \text{ V}$$

The approximate cell potential is +0.23 V.

(b) Advantages: fuel cell using readily available natural gas; high efficiency; does not produce greenhouse gas
Disadvantages: likely relatively expensive; storage and distribution of the gas may be a problem

CHAPTER 10 ELECTROLYtic CELLS

Reflect on Your Learning

(Page 728)

- [*Likely initial answer*] If the cell potential is a negative value, this might mean that the reaction goes in reverse or maybe does not happen at all.
[*More complete answer*] A negative cell potential indicates that the predicted cell reaction is nonspontaneous and requires an external power supply to force the reaction to occur.
- [*Likely initial answer*] Elements are produced by decomposing naturally occurring substances using heat or electricity or using a single displacement reaction.
[*More complete answer*] Most elements are produced or refined in industrial processes using aqueous, nonaqueous, or molten salt electrolysis.
- [*Likely initial answer*] There is probably some relationship but it is not clear what that might be.
[*More complete answer*] The coefficients in the half-reaction equation provide the mole ratio of electrons to the product at the electrode.
- [*Likely initial answer*] All of these are interrelated with science and technology producing useful products and processes for society.
[*More complete answer*] The technology of electrolytic cells preceded any scientific understanding of the processes. Eventually, atomic and redox theories developed to explain known electrolytic cells. Further scientific investigation of electrolytic cells led to new technologies that were very useful to society, which in turn encouraged more research. Today, the continuing cycle of scientific understanding and technological development continues.

Try This Activity: A Nonspontaneous Reaction

(Page 729)

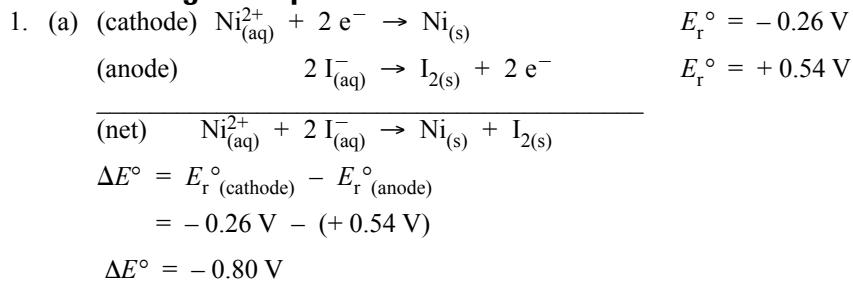
- There is no initial evidence of reaction.
- Near the positive terminal of the battery, the colourless solution changes to a yellow-brown solution (with some black precipitate). Near the negative terminal of the battery, bubbles of gas form.
- The evidence for chemical reaction is both the colour change and gas formation. (A precipitate may also be observed.)
- The battery supplies energy to cause the reaction.
- The colour change means at least one new substance (and probably two substances) is/are formed at the negative battery terminal.
- The two substances might be hydrogen or oxygen (the gas) and iodine (the brown colour). Diagnostic tests for hydrogen and oxygen can be done with a lit or glowing splint. A diagnostic test for iodine can be done by dissolving it in a nonpolar liquid like a hydrocarbon. (Appendix A6)
- To improve this design, the gas produced should be collected by downward displacement of water.
- Forcing a nonspontaneous reaction to occur is a way of producing new substances.

10.1 ELECTROLYSIS

PRACTICE

(Page 735)

Understanding Concepts



The minimum applied potential difference required to make this cell operate at standard conditions is 0.80 V.

CHAPTER 10 ELECTROLYtic CELLS

Reflect on Your Learning

(Page 728)

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- [*Likely initial answer*] All of these are interrelated with science and technology producing useful products and processes for society.
[*More complete answer*] The technology of electrolytic cells preceded any scientific understanding of the processes. Eventually, atomic and redox theories developed to explain known electrolytic cells. Further scientific investigation of electrolytic cells led to new technologies that were very useful to society, which in turn encouraged more research. Today, the continuing cycle of scientific understanding and technological development continues.

Try This Activity: A Nonspontaneous Reaction

(Page 729)

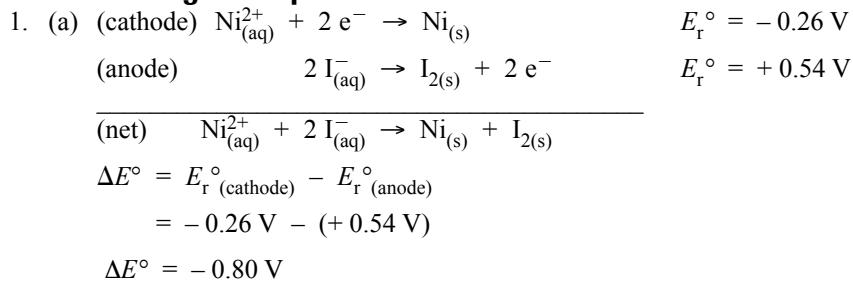
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- (d) The battery supplies energy to cause the reaction.
- (e) The colour change means at least one new substance (and probably two substances) is/are formed at the negative battery terminal.
- (f) The two substances might be hydrogen or oxygen (the gas) and iodine (the brown colour). Diagnostic tests for hydrogen and oxygen can be done with a lit or glowing splint. A diagnostic test for iodine can be done by dissolving it in a nonpolar liquid like a hydrocarbon. (Appendix A6)
- (g) To improve this design, the gas produced should be collected by downward displacement of water.
- (h) Forcing a nonspontaneous reaction to occur is a way of producing new substances.

10.1 ELECTROLYSIS

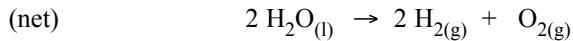
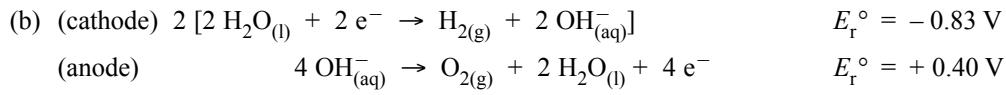
PRACTICE

(Page 735)

Understanding Concepts



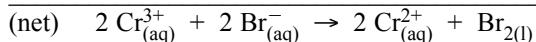
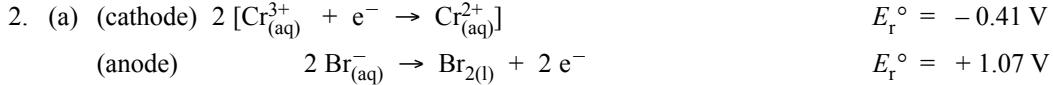
The minimum applied potential difference required to make this cell operate at standard conditions is 0.80 V.



$$\Delta E^\circ = E_r^\circ (\text{cathode}) - E_r^\circ (\text{anode}) \\ = -0.83 \text{ V} - (+0.40 \text{ V})$$

$$\Delta E^\circ = -1.23 \text{ V}$$

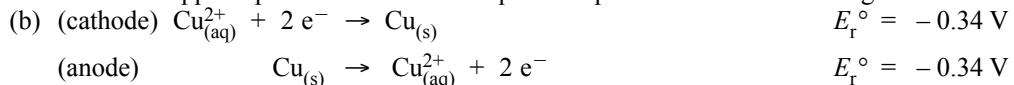
The minimum applied potential difference required to make this cell operate at standard conditions is 1.23 V.



$$\Delta E^\circ = E_r^\circ (\text{cathode}) - E_r^\circ (\text{anode}) \\ = -0.41 \text{ V} - (+1.07 \text{ V})$$

$$\Delta E^\circ = -1.48 \text{ V}$$

The minimum applied potential difference required to produce a chemical change is 1.48 V.

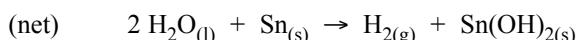
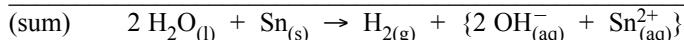
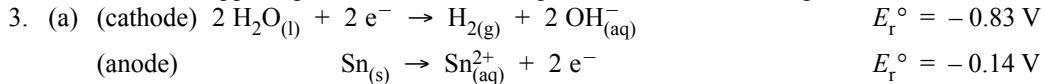


(net) no net (overall) reaction occurs

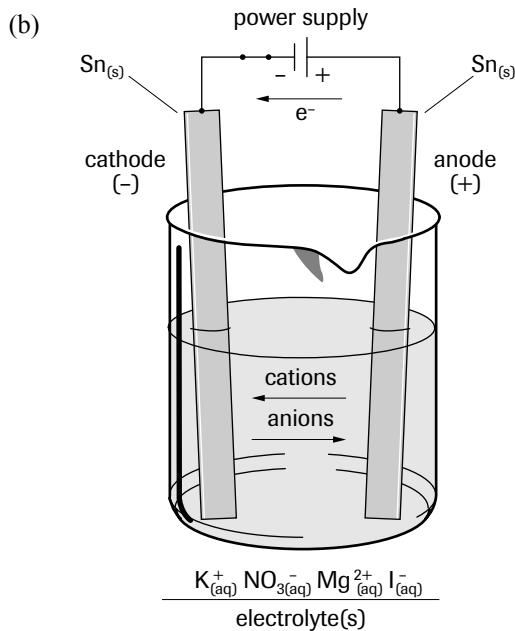
$$\Delta E^\circ = E_r^\circ (\text{cathode}) - E_r^\circ (\text{anode}) \\ = -0.34 \text{ V} - (-0.34 \text{ V})$$

$$\Delta E^\circ = 0.00 \text{ V}$$

The minimum applied potential difference required to make this cell operate at standard conditions is 0.00 V.



Note: Simultaneous production of Sn^{2+} and OH^- aqueous ions forms (low-soluble) solid tin(II) hydroxide, Sn(OH)_2 .



- (c) A 1.5-V cell should be more than enough potential difference to power this reaction, since calculation indicates the minimum required is only 0.69 V at standard conditions.

$$\begin{aligned}\Delta E^\circ &= E_r^\circ(\text{cathode}) - E_r^\circ(\text{anode}) \\ &= -0.83 \text{ V} - (-0.14 \text{ V})\end{aligned}$$

$$\Delta E^\circ = -0.69 \text{ V}$$

The minimum applied potential difference required to produce a chemical change is 0.69 V.

4. The cell would not have a spontaneous reaction. The strongest oxidizing agent present in this cell is water; and it has an E_r° well below that of the strongest reducing agent present, sulfate and lead. The calculated ΔE° value at standard conditions is -0.47 V .

Making Connections

5. A specific consumer product that is used sometimes as an electric cell and sometimes as an electrolytic cell is a rechargeable battery of any type.

SECTION 10.1 QUESTIONS

(Page 736)

Understanding Concepts

- At the cathode of an electrolytic cell, the oxidizing agent reacts by gaining electrons. At the anode of an electrolytic cell, the reducing agent reacts by losing electrons.
- The cathode and anode of an electrolytic cell are labelled with signs opposite to those in a galvanic cell. (The common convention (used in this text) labels the anode of a galvanic cell “negative” because it is a source of electrons and the cell is an electrical power supply. The anode of an electrolytic cell is labelled “negative” because it is not a power source, rather it is an electrical load. For electrical loads, the electrode sign is assigned using the sign of the electrode of a power supply to which it is attached.)
- In an electrolytic cell, electrons move through the external circuit from the anode to the cathode. Within the cell, cations move toward the cathode and anions move toward the anode.
- A power supply is required for an electrolytic cell because the reaction is nonspontaneous, which means that the oxidizing agent cannot attract or remove electrons from the reducing agent. A potential difference must be supplied to move electrons from one to the other.
- (a) $\Delta E^\circ = E_r^\circ(\text{Cr}^{2+}/\text{Cr}) - E_r^\circ(\text{Cr}^{3+}/\text{Cr}^{2+})$
 $= -0.91 \text{ V} - (-0.41 \text{ V})$
 $\Delta E^\circ = -0.50 \text{ V}$

The cell potential value, $\Delta E^\circ = -0.50 \text{ V}$, indicates this reaction is nonspontaneous.

$$(b) \Delta E^\circ = E_r^\circ (\text{Fe}^{3+}/\text{Fe}^{2+}) - E_r^\circ (\text{Ag}^+/\text{Ag}) \\ = +0.77 \text{ V} - (+0.80 \text{ V})$$

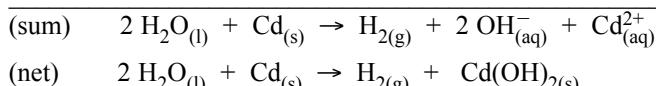
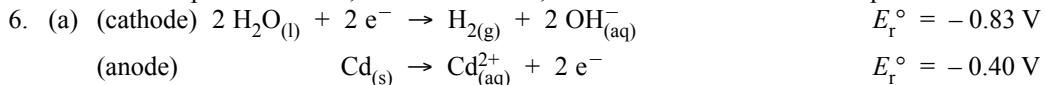
$$\Delta E^\circ = -0.03 \text{ V}$$

The cell potential value, $\Delta E^\circ = -0.03 \text{ V}$, indicates this reaction is nonspontaneous.

$$(c) \Delta E^\circ = E_r^\circ (\text{Pb}^{2+}/\text{Pb}) - E_r^\circ (\text{Cu}^{2+}/\text{Cu}) \\ = -0.13 \text{ V} - (+0.34 \text{ V})$$

$$\Delta E^\circ = -0.47 \text{ V}$$

The cell potential value, $\Delta E^\circ = -0.47 \text{ V}$, indicates this reaction is nonspontaneous.

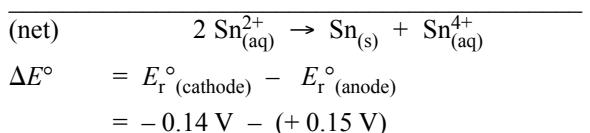
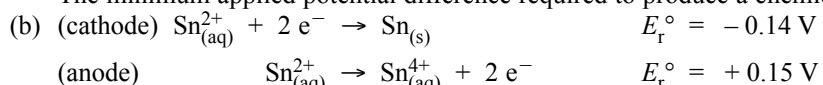


Note: Cd^{2+} and OH^- aqueous ions form (low-soluble) solid cadmium(II) hydroxide, Cd(OH)_2 .

$$\Delta E^\circ = E_r^\circ (\text{cathode}) - E_r^\circ (\text{anode}) \\ = -0.83 \text{ V} - (-0.40 \text{ V})$$

$$\Delta E^\circ = -0.43 \text{ V}$$

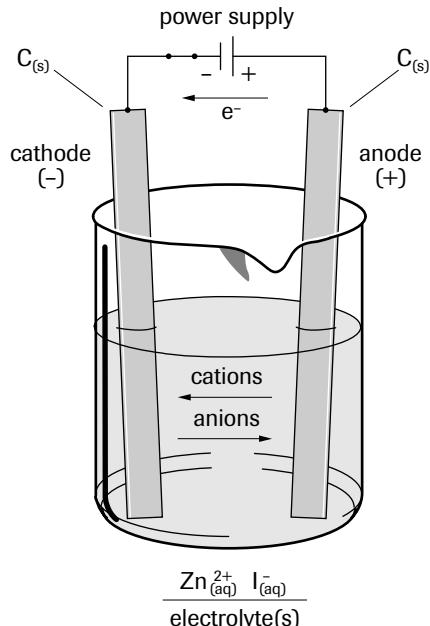
The minimum applied potential difference required to produce a chemical change is 0.43 V.

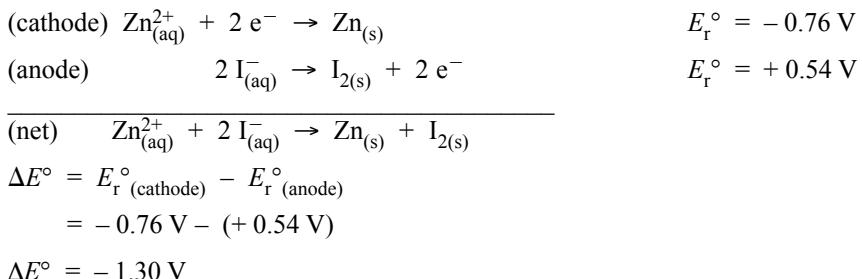


$$\Delta E^\circ = -0.29 \text{ V}$$

The minimum applied potential difference required to produce a chemical change is 0.29 V.

7.





The cell potential is -1.30 V .

8. (a) As the applied voltage is slowly increased, half-reactions occur at the anode in the following order:

1. $\text{Zn}_{(\text{s})} \rightarrow \text{Zn}_{(\text{aq})}^{2+} + 2 \text{e}^-$
2. $\text{Ni}_{(\text{s})} \rightarrow \text{Ni}_{(\text{aq})}^{2+} + 2 \text{e}^-$
3. $\text{Cu}_{(\text{s})} \rightarrow \text{Cu}_{(\text{aq})}^{2+} + 2 \text{e}^-$

(Whether copper oxidizes to copper(I) ion or to copper(II) ion can be controlled by the potential applied.)

(b) At the platinum cathode, the following half-reaction occurs: $2 \text{H}_2\text{O}_{(\text{l})} + 2 \text{e}^- \rightarrow \text{H}_{2(\text{g})} + 2 \text{OH}_{(\text{aq})}^-$.

9. No spontaneous reaction should occur in the cell, because theoretically, the E_r° values at both electrodes are the same, giving a cell potential of zero. Thus, a potential difference *greater* than zero must be applied to cause any reaction.

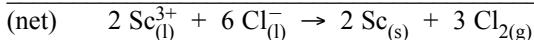
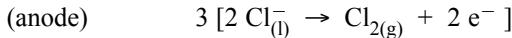
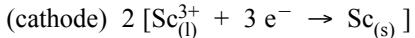
10.2 SCIENCE AND TECHNOLOGY OF ELECTROLYSIS

PRACTICE

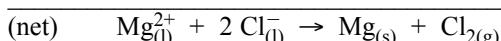
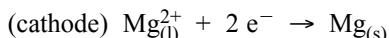
(Page 741)

Understanding Concepts

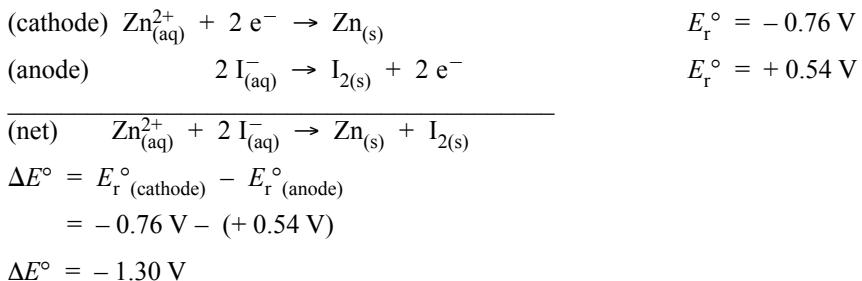
1. (a) Producing active metals by electrolysis of their aqueous compounds is a problem because water will react at the cathode before the metal ions will. As well, many ionic compounds of these metals have low solubility.
 (b) These problems can be overcome by performing the electrolysis in the absence of water (e.g., using molten ionic compounds) or sometimes by using high potential to “overpower” the slower reaction of water.
2. The ions present in the electrolysis cell are $\text{Sc}_{(\text{l})}^{3+}$ and $\text{Cl}_{(\text{l})}^-$.



3. (a) $\text{Ca(OH)}_{2(\text{s})} + \text{MgCl}_{2(\text{aq})} \rightarrow \text{Mg(OH)}_{2(\text{s})} + \text{CaCl}_{2(\text{aq})}$
 (b) $\text{Mg(OH)}_{2(\text{s})} + 2 \text{HCl}_{(\text{aq})} \rightarrow \text{MgCl}_{2(\text{aq})} + 2 \text{H}_2\text{O}_{(\text{l})}$
 (c) The ions present in the electrolysis cell are $\text{Mg}_{(\text{l})}^{2+}$ and $\text{Cl}_{(\text{l})}^-$.



- (d) Dolomite has the advantage of being a more concentrated source of magnesium than seawater and may require fewer initial reactions before the electrolysis. A possible disadvantage is that it is more difficult and requires more energy to mine the solid than to pump the seawater. Another disadvantage is that the seas contain an almost limitless supply of magnesium salts, whereas dolomite is likely present in more limited and localized quantities.



The cell potential is -1.30 V .

8. (a) As the applied voltage is slowly increased, half-reactions occur at the anode in the following order:

1. $\text{Zn}_{(\text{s})} \rightarrow \text{Zn}_{(\text{aq})}^{2+} + 2 \text{e}^-$
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3. $\text{Cu}_{(\text{s})} \rightarrow \text{Cu}_{(\text{aq})}^{2+} + 2 \text{e}^-$

(Whether copper oxidizes to copper(I) ion or to copper(II) ion can be controlled by the potential applied.)

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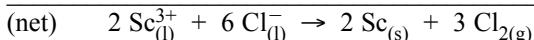
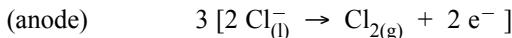
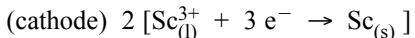
10.2 SCIENCE AND TECHNOLOGY OF ELECTROLYSIS

PRACTICE

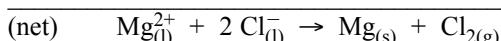
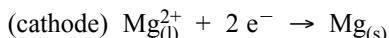
(Page 741)

Understanding Concepts

1. (a) Producing active metals by electrolysis of their aqueous compounds is a problem because water will react at the cathode before the metal ions will. As well, many ionic compounds of these metals have low solubility.
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 (c) The ions present in the electrolysis cell are $\text{Mg}_{(\text{l})}^{2+}$ and $\text{Cl}_{(\text{l})}^-$.



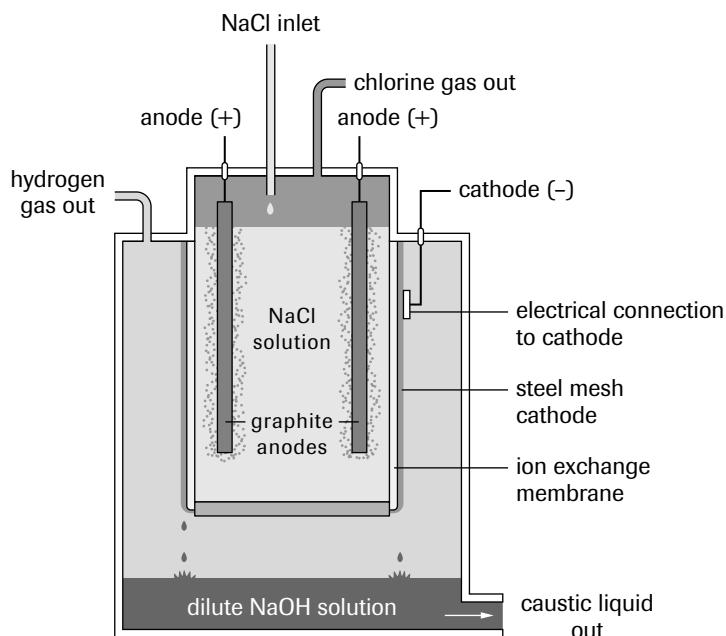
- (d) Dolomite has the advantage of being a more concentrated source of magnesium than seawater and may require fewer initial reactions before the electrolysis. A possible disadvantage is that it is more difficult and requires more energy to mine the solid than to pump the seawater. Another disadvantage is that the seas contain an almost limitless supply of magnesium salts, whereas dolomite is likely present in more limited and localized quantities.

Making Connections

4. Caustic drain cleaners and chlorine bleaches may come from a chlor-alkali process.
5. Recycling metals such as aluminum lessens the need for mining, and thus benefits the environment. It helps to reduce the cost of the metal and thus benefits the consumer. It also encourages the process of recycling and waste management, helping to foster the idea of sustainable lifestyles.
6. Uses for aluminum listed on this site include jewellery, sculpture, furniture, fabrics (fashionable or protective), cars, trains, aircraft, containers (cans), cookware, and stereo components. All make use of aluminum's light weight, high strength, and corrosion resistance.

Extension

7. The new chlor-alkali cell design eliminates the use of mercury as a cathode, or of diaphragm designs that incorporate asbestos. Both of the older designs use toxic/dangerous materials. The membrane design requires the aqueous sodium ions to pass through a fluoropolymer membrane before reacting at the steel-mesh cathode. The hydrogen gas formed by the cathode half-reaction is thus separated from the chlorine that is formed at the anodes inside the cell—a critical point, as these gases are explosively reactive when mixed! The membrane design is really an example of molecular design—it is structured at a molecular level to allow sodium ions and water molecules through only when attracted by a negative charge on the other side.



Explore an Issue: Take a Stand: The Case For and Against Chlorine (Page 742)

- (a) (A typical student report will contain information such as some of the following.)

Production of chlorine is primarily by chlor-alkali electrolysis of brine solutions. Chlorine is made in huge quantities: in 1985 it was ninth in the list of chemicals produced (in volume) in North America. The chemical is normally stored as a liquid under pressure (about 8 atm). Chlorine is transported by ship in sealed tanks; and overland in railway tank cars, in tanker trucks, and by pipeline. Chlorine has a huge variety of uses. It is used in bleaching of paper products and in laundering fabrics; in making pharmaceuticals; for air-conditioning and refrigerating fluids; in manufacturing vinyl plastics; and in water purification and disinfecting. Chlorine is very corrosive, and a very strong oxidizing agent. The chemical is harmful to humans by skin contact and especially harmful by breathing the vapour. Edema of the lungs and chronic bronchitis may result from exposure by inhalation. Many groups concerned with chlorine's potential for harm to the environment and to human health are actively campaigning to have its use in water treatment and the pulp industry replaced by other chemicals. Some chlorine compounds are now banned. While these compounds initially seemed chemically inert, it has been discovered that they accelerate the breakdown of ozone in the stratosphere — “thinning” the ozone layer that absorbs some of our sun's harmful UV radiation.

- (b) (Answers will vary, depending on the issue assessed, but should include a presentation of findings, and a strongly reasoned argument for the chosen position.)

PRACTICE

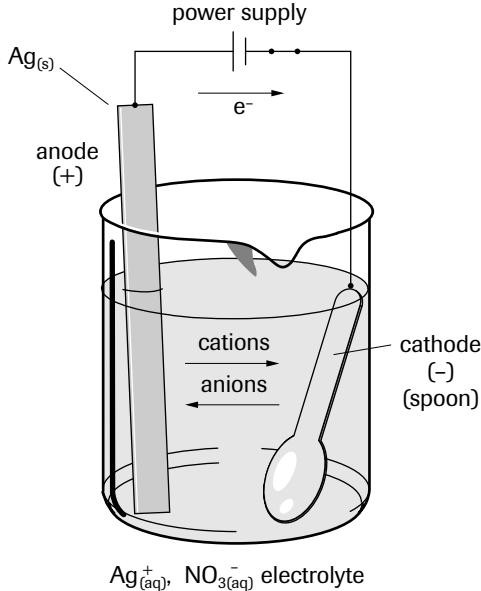
(Page 744)

Understanding Concepts

8. A metal product must form at the cathode during electrolysis because metal ions are positively charged, and must gain electrons (be reduced) to become atoms of metal.
9. (a) Impure copper is placed at the anode to oxidize copper atoms to copper ions, which dissolve in solution.
 (b) The minimum electric potential difference required for this cell is theoretically zero.
 (c) The minimum potential difference is a theoretical minimum and would mean a very long reaction time. A higher voltage is used to get the reaction to occur rapidly. (Note that the choice of voltage is also influenced by the cost of electricity.)
10. A reduction potentials table may be used to predict which metals might be refined from an aqueous solution. Metal ions that are weaker oxidizing agents (lower) than water cannot be easily refined from solution.
11. Electroplating is done usually to coat a strong base metal with a surface that is more attractive, or corrosion resistant, or both. Other metals are commonly plated with silver and gold for appearance, nickel for corrosion resistance, and chromium for both appearance and corrosion resistance.

Applying Inquiry Skills

12. (a)



- (b) Some variables that need to be considered when planning the electrolysis include the selection, solubility, and concentration of the electrolyte, the potential difference that will be applied and the current to be used, the time the cell will operate, and the mass of silver. (Some of these variables are related to each other.)

Making Connections

13. (a) A copper wire is attached to a shoe or other nonconducting object. A conductive lacquer paint, containing copper, is then sprayed onto the object which becomes the cathode of the electrolytic cell.
 (b) The object is first washed and dried, and then sprayed with a lacquer, shellac, or varnish. A copper wire is attached and the object is sprayed with two coats of a conductive lacquer. The object is plated at 1 V for about 30 min and then at 1.5 to 2 V for additional time required to produce a coating of the desired thickness (0.025 mm of copper per hour). One particular kit with all equipment and supplies costs \$460.

14.

Type of waste	Potential hazard
heavy metal waste (Cd, Cr, Pb, Hg)	toxic
alkaline and acidic solutions	environmental damage
solvents	carcinogen, greenhouse gas destroys ozone layer
cyanide waste	toxic

Companies reduce electroplating wastes by getting the most life out of their plating baths, recycling solutions, minimizing rinse water, and letting objects drain completely. Electroplating wastes can be recovered using special processes to extract metals such as copper from a solution, using solvent extraction. Treatment of wastes can use various processes such as precipitation and reverse osmosis.

15. To make an aluminum can, aluminum ingots are rolled into sheets of metal. Shallow cups are punched out and then ironed out to the full can size of the desired thickness. The end is trimmed and the open can is cleaned, coated, and labelled. The top of the can is punched out of a sheet of aluminum and then seated and sealed on the open end of the can.

Aluminum cans were first used in 1965 and the main change in the can is the thickness of the aluminum. Improved technology means that the number of cans per kilogram of aluminum has increased from 48 in 1972 to 70 in 1998. Using recycled aluminum is much better than using new aluminum because of the savings in energy and natural resources and the reduction of waste.

PRACTICE

(Page 745)

Making Connections

16. (Answers will vary depending on the career chosen, but should include a general description of the job, the necessary education, and current opportunities and salaries.)

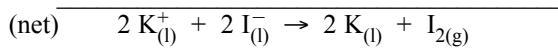
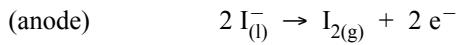
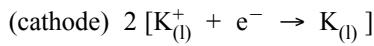
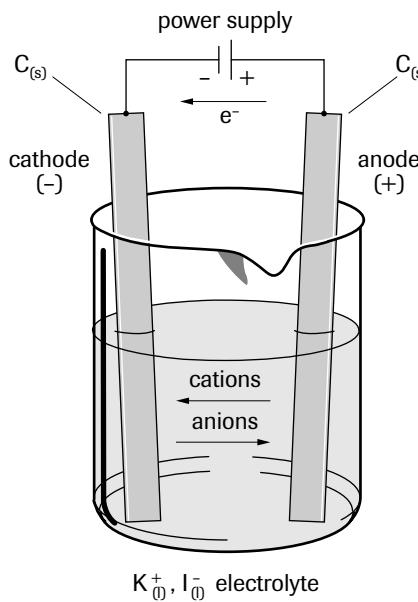
SECTION 10.2 QUESTIONS

(Page 746)

Understanding Concepts

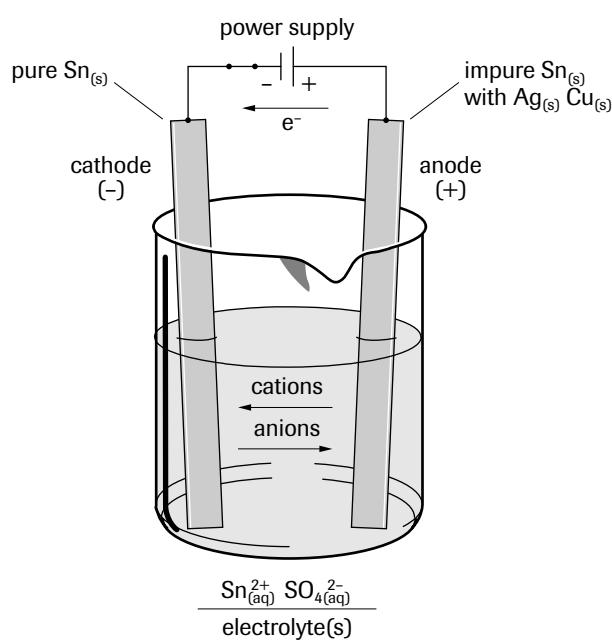
- Electrolytic cells in industry are used to produce chemicals, to refine metals, and for electroplating.
- Many metals were discovered only after the invention of the electric cell because they are too reactive to exist naturally and their compounds were too stable to be decomposed by heat.
- The only metals that occur naturally are those that are very weak reducing agents, appearing near the top right of the redox table.
- A compound with a very high melting point can be mixed with an inert substance to produce a mixture with a lower melting point. Sodium chloride mixed with calcium chloride and aluminum oxide mixed with cryolite are two examples.
- In the solid state, the ions in ionic compounds cannot move to transfer electric charge in a cell.

6.

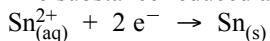


7. (a) The pure metal piece should be the cathode and the impure metal piece should be the anode. According to redox theory, the anode metals will lose electrons and dissolve into solution as ions, while the potential difference applied will be controlled so that only tin(II) ions will gain electrons and plate onto the cathode.

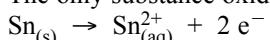
(b)



- (c) The substance reduced at the cathode will be tin(II) ions.



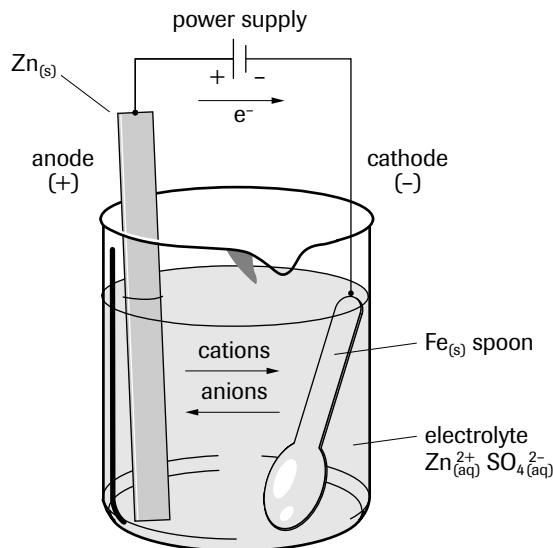
- (d) The only substance oxidized will be tin, at the anode.



- (e) The applied potential difference can be between 0 V and 0.48 V. At or above 0.48 V, the copper atoms in the impure tin anode will oxidize $[+0.34 \text{ V} - (-0.14 \text{ V})]$, and some of the resulting copper(II) ions in solution will then react at the cathode, making the tin deposit impure. At even higher voltages (0.94 V), silver will behave similarly.
- (f) The silver and copper metals will fall to the bottom of the cell as the tin in the anode oxidizes.

Applying Inquiry Skills

8.



9. (a) The nickel(II) ion solution is the electrolyte in an electrolytic cell with inert (e.g., platinum) electrodes. The ions plate out as solid pure nickel metal on the inert cathode.
- (b) Typical questions might include: What effect will other ions in the solution have? How expensive are inert electrodes? How long will the process take? What is the toxicity of nickel(II) ions? What chemical disposal regulations apply? Is there a faster, cheaper, non-electrolysis recovery method available?

Making Connections

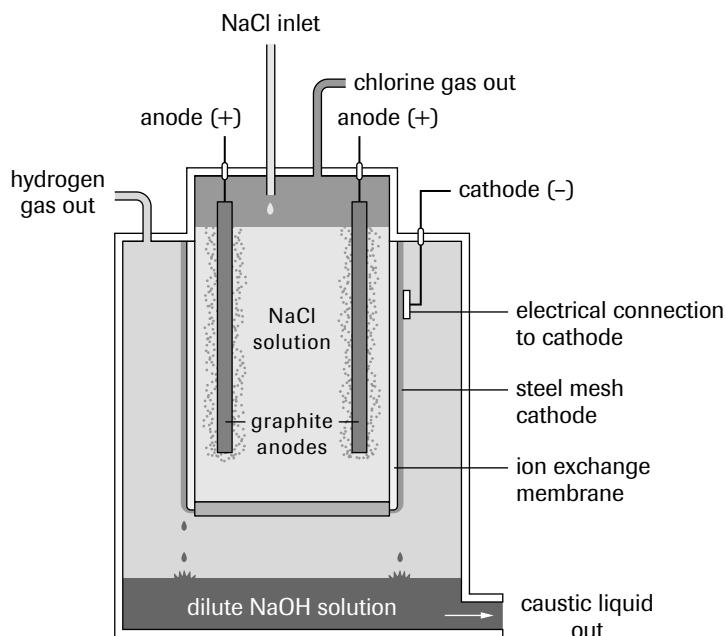
10. The production of zinc metal involves electrolysis of an acidic aqueous solution of zinc ions. The production of galvanized (zinc-plated) objects is often accomplished by electroplating the zinc onto a metal object that is the cathode of an electrolytic cell.
11. (a) A pure nickel core (called a blank) is electroplated with a copper–tin bronze alloy, $\text{Cu}_{88}\text{Sn}_{12}$.
- (b) The golden aureate finish is created by a diffusion heat treatment of the plated bronze alloy. The bronze plating is about 20–25 μm thick on the face and 40–70 μm thick on the edges.
- (c) The master dies for the original design were lost by a courier delivering these to Winnipeg. Therefore, a new design featuring the loon was created as a replacement.

Making Connections

4. Caustic drain cleaners and chlorine bleaches may come from a chlor-alkali process.
5. Recycling metals such as aluminum lessens the need for mining, and thus benefits the environment. It helps to reduce the cost of the metal and thus benefits the consumer. It also encourages the process of recycling and waste management, helping to foster the idea of sustainable lifestyles.
6. Uses for aluminum listed on this site include jewellery, sculpture, furniture, fabrics (fashionable or protective), cars, trains, aircraft, containers (cans), cookware, and stereo components. All make use of aluminum's light weight, high strength, and corrosion resistance.

Extension

7. The new chlor-alkali cell design eliminates the use of mercury as a cathode, or of diaphragm designs that incorporate asbestos. Both of the older designs use toxic/dangerous materials. The membrane design requires the aqueous sodium ions to pass through a fluoropolymer membrane before reacting at the steel-mesh cathode. The hydrogen gas formed by the cathode half-reaction is thus separated from the chlorine that is formed at the anodes inside the cell—a critical point, as these gases are explosively reactive when mixed! The membrane design is really an example of molecular design—it is structured at a molecular level to allow sodium ions and water molecules through only when attracted by a negative charge on the other side.



Explore an Issue: Take a Stand: The Case For and Against Chlorine (Page 742)

- (a) (A typical student report will contain information such as some of the following.)

Production of chlorine is primarily by chlor-alkali electrolysis of brine solutions. Chlorine is made in huge quantities: in 1985 it was ninth in the list of chemicals produced (in volume) in North America. The chemical is normally stored as a liquid under pressure (about 8 atm). Chlorine is transported by ship in sealed tanks; and overland in railway tank cars, in tanker trucks, and by pipeline. Chlorine has a huge variety of uses. It is used in bleaching of paper products and in laundering fabrics; in making pharmaceuticals; for air-conditioning and refrigerating fluids; in manufacturing vinyl plastics; and in water purification and disinfecting. Chlorine is very corrosive, and a very strong oxidizing agent. The chemical is harmful to humans by skin contact and especially harmful by breathing the vapour. Edema of the lungs and chronic bronchitis may result from exposure by inhalation. Many groups concerned with chlorine's potential for harm to the environment and to human health are actively campaigning to have its use in water treatment and the pulp industry replaced by other chemicals. Some chlorine compounds are now banned. While these compounds initially seemed chemically inert, it has been discovered that they accelerate the breakdown of ozone in the stratosphere — “thinning” the ozone layer that absorbs some of our sun's harmful UV radiation.

- (b) (Answers will vary, depending on the issue assessed, but should include a presentation of findings, and a strongly reasoned argument for the chosen position.)

PRACTICE

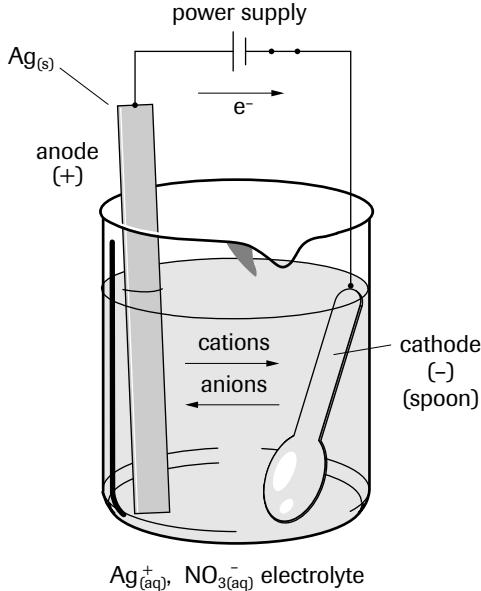
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Understanding Concepts

8. A metal product must form at the cathode during electrolysis because metal ions are positively charged, and must gain electrons (be reduced) to become atoms of metal.
9. (a) Impure copper is placed at the anode to oxidize copper atoms to copper ions, which dissolve in solution.
 (b) The minimum electric potential difference required for this cell is theoretically zero.
 (c) The minimum potential difference is a theoretical minimum and would mean a very long reaction time. A higher voltage is used to get the reaction to occur rapidly. (Note that the choice of voltage is also influenced by the cost of electricity.)
10. A reduction potentials table may be used to predict which metals might be refined from an aqueous solution. Metal ions that are weaker oxidizing agents (lower) than water cannot be easily refined from solution.
11. Electroplating is done usually to coat a strong base metal with a surface that is more attractive, or corrosion resistant, or both. Other metals are commonly plated with silver and gold for appearance, nickel for corrosion resistance, and chromium for both appearance and corrosion resistance.

Applying Inquiry Skills

12. (a)



- (b) Some variables that need to be considered when planning the electrolysis include the selection, solubility, and concentration of the electrolyte, the potential difference that will be applied and the current to be used, the time the cell will operate, and the mass of silver. (Some of these variables are related to each other.)

Making Connections

13. (a) A copper wire is attached to a shoe or other nonconducting object. A conductive lacquer paint, containing copper, is then sprayed onto the object which becomes the cathode of the electrolytic cell.
 (b) The object is first washed and dried, and then sprayed with a lacquer, shellac, or varnish. A copper wire is attached and the object is sprayed with two coats of a conductive lacquer. The object is plated at 1 V for about 30 min and then at 1.5 to 2 V for additional time required to produce a coating of the desired thickness (0.025 mm of copper per hour). One particular kit with all equipment and supplies costs \$460.

10.3 STOICHIOMETRY OF CELL REACTIONS

PRACTICE

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Understanding Concepts

1. $I = 1.5 \text{ A} = 1.5 \text{ C/s}$

$t = 30 \text{ s}$

$$\begin{aligned} q &= It \\ &= 1.5 \frac{\text{C}}{\text{s}} \times 30 \text{ s} \\ q &= 45 \text{ C} \end{aligned}$$

The charge transferred is 45 C.

2. $q = 87.6 \text{ C}$

$t = 22.5 \text{ s}$

$$\begin{aligned} q &= It \\ I &= \frac{q}{t} \\ &= \frac{87.6 \text{ C}}{22.5 \text{ s}} \\ &= 3.89 \text{ C/s} \end{aligned}$$

$I = 3.89 \text{ A}$

The average electric current is 3.89 A.

3. $I = 250 \text{ mA} = 250 \times 10^{-3} \text{ C/s}$

$t = 28.5 \text{ s}$

$$\begin{aligned} q &= It \\ &= 250 \times 10^{-3} \frac{\text{C}}{\text{s}} \times 28.5 \text{ s} \\ q &= 7.13 \text{ C} \end{aligned}$$

The charge transferred is 7.13 C.

4. $I = 1.60 \text{ A} = 1.60 \text{ C/s}$

$q = 375 \text{ C}$

$$\begin{aligned} q &= It \\ t &= \frac{q}{I} \\ &= \frac{375 \text{ C}}{1.60 \frac{\text{C}}{\text{s}}} \\ &= 234 \text{ s} \\ &= 234 \text{ s} \times \frac{1 \text{ min}}{60 \text{ s}} \\ t &= 3.91 \text{ min} \end{aligned}$$

The charge is transferred in a time of 3.91 min.

PRACTICE
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Understanding Concepts

5. $I = 1.9 \text{ A} = 1.9 \text{ C/s}$

$$t = 35 \cancel{\text{min}} \times \frac{60 \text{ s}}{1 \cancel{\text{min}}} = 2.1 \times 10^3 \text{ s}$$

$$F = 9.65 \times 10^4 \text{ C/mol}$$

$$n_{\text{e}^-} = \frac{q}{F}$$

$$\begin{aligned} &= \frac{It}{F} \\ &= \frac{1.9 \frac{\cancel{\text{C}}}{\text{s}} \times 2.1 \times 10^3 \text{ s}}{9.65 \times 10^4 \frac{\cancel{\text{C}}}{\text{mol}}} \end{aligned}$$

$$n_{\text{e}^-} = 0.041 \text{ mol} = 41 \text{ mmol}$$

The amount of electrons transferred is 0.041 mol or 41 mmol.

6. $I = 1.24 \text{ A} = 1.24 \text{ C/s}$

$$n_{\text{e}^-} = 0.146 \text{ mol}$$

$$F = 9.65 \times 10^4 \text{ C/mol}$$

$$n_{\text{e}^-} = \frac{q}{F}$$

$$n_{\text{e}^-} = \frac{It}{F}$$

$$\begin{aligned} t &= \frac{n_{\text{e}} F}{I} \\ &= \frac{0.146 \cancel{\text{mol}} \times 9.65 \times 10^4 \frac{\text{C}}{\cancel{\text{mol}}}}{1.24 \frac{\text{C}}{\text{s}}} \end{aligned}$$

$$t = 1.13 \times 10^4 \text{ s} \times \frac{1 \text{ h}}{3600 \text{ s}} = 3.16 \text{ h}$$

The time of cell operation is 3.16 h.

7. $t = 20 \cancel{\text{min}} \times \frac{60 \text{ s}}{1 \cancel{\text{min}}} = 1.2 \times 10^3 \text{ s}$

$$n_{\text{e}^-} = 0.015 \text{ mol}$$

$$F = 9.65 \times 10^4 \text{ C/mol}$$

$$n_{\text{e}^-} = \frac{q}{F}$$

$$n_{\text{e}^-} = \frac{It}{F}$$

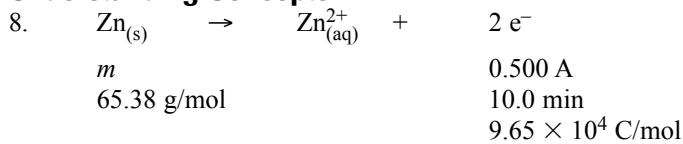
$$\begin{aligned} I &= \frac{n_{\text{e}} F}{t} \\ &= \frac{0.015 \cancel{\text{mol}} \times 9.65 \times 10^4 \frac{\text{C}}{\cancel{\text{mol}}}}{1.2 \times 10^3 \text{ s}} \end{aligned}$$

$$I = 1.2 \text{ C/s} = 1.2 \text{ A}$$

The current required is 1.2 A.

PRACTICE

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Understanding Concepts

$$I = 0.500 \text{ A} = 0.500 \text{ C/s}$$

$$t = 10.0 \cancel{\text{min}} \times \frac{60 \text{ s}}{1 \cancel{\text{min}}} = 600 \text{ s}$$

$$n_{\text{e}^-} = \frac{q}{F}$$

$$= \frac{It}{F}$$

$$= \frac{0.500 \frac{\text{C}}{\text{s}} \times 600 \cancel{\text{s}}}{\cancel{\text{s}}}$$

$$= \frac{9.65 \times 10^4 \frac{\text{C}}{\text{mol}}}{\text{mol}}$$

$$n_{\text{e}^-} = 0.00311 \text{ mol}$$

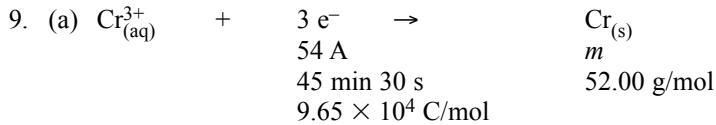
$$n_{\text{Zn}} = 0.00311 \cancel{\text{mol e}^-} \times \frac{1 \text{ mol Zn}}{2 \cancel{\text{mol e}^-}}$$

$$n_{\text{Zn}} = 0.00155 \text{ mol}$$

$$m_{\text{Zn}} = 0.00155 \cancel{\text{mol}} \times 65.38 \frac{\text{g}}{\cancel{\text{mol}}}$$

$$m_{\text{Zn}} = 0.102 \text{ g}$$

The mass of zinc oxidized is 0.102 g.



$$I = 54 \text{ A} = 54 \text{ C/s}$$

$$t = 45 \cancel{\text{min}} \times \frac{60 \text{ s}}{1 \cancel{\text{min}}} + 30 \text{ s}$$

$$= 2700 \text{ s} + 30 \text{ s}$$

$$t = 2730 \text{ s}$$

Note: Because time was measured to a precision of seconds, this time value (2730 s) has a certainty of 4 significant digits.

$$n_{\text{e}^-} = \frac{q}{F}$$

$$= \frac{It}{F}$$

$$= \frac{54 \frac{\text{C}}{\text{s}} \times 2730 \cancel{\text{s}}}{\cancel{\text{s}}}$$

$$= \frac{9.65 \times 10^4 \frac{\text{C}}{\text{mol}}}{\text{mol}}$$

$$n_{\text{e}^-} = 1.5 \text{ mol}$$

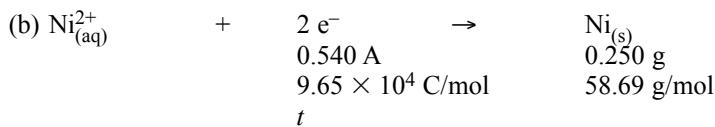
$$n_{\text{Cr}} = 1.5 \cancel{\text{mol e}^-} \times \frac{1 \text{ mol Cr}}{3 \cancel{\text{mol e}^-}}$$

$$n_{\text{Cr}} = 0.51 \text{ mol}$$

$$m_{\text{Cr}} = 0.51 \text{ mol} \times 52.00 \frac{\text{g}}{\text{mol}}$$

$$m_{\text{Cr}} = 26 \text{ g}$$

The mass of chromium produced is 26 g.



$$I = 0.540 \text{ A} = 0.540 \text{ C/s}$$

$$n_{\text{Ni}} = 0.250 \text{ g} \times \frac{1 \text{ mol}}{58.69 \text{ g}}$$

$$n_{\text{Ni}} = 0.00426 \text{ mol}$$

$$n_{\text{e}^-} = 0.00426 \text{ mol Ni} \times \frac{2 \text{ mol e}^-}{1 \text{ mol Ni}}$$

$$n_{\text{e}^-} = 0.00852 \text{ mol}$$

$$n_{\text{e}^-} = \frac{q}{F}$$

$$n_{\text{e}^-} = \frac{It}{F}$$

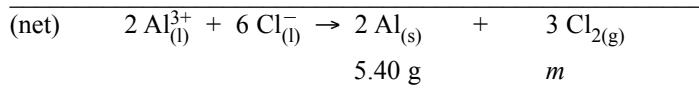
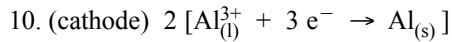
$$t = \frac{n_{\text{e}^-} F}{I}$$

$$= \frac{0.00852 \text{ mol} \times 9.65 \times 10^4 \frac{\text{C}}{\text{mol}}}{0.540 \frac{\text{C}}{\text{s}}}$$

$$t = 1.52 \times 10^3 \text{ s} \times \frac{1 \text{ min}}{60 \text{ s}}$$

$$t = 25.4 \text{ min}$$

The time to plate the nickel is 25.4 min.

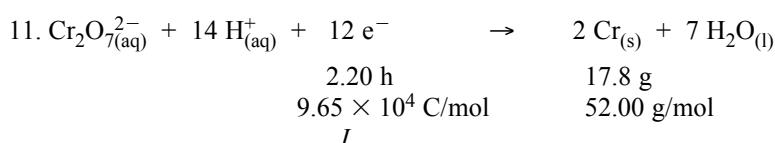


$$n_{\text{Al}} = 5.40 \text{ g} \times \frac{1 \text{ mol}}{26.98 \text{ g}} = 0.200 \text{ mol}$$

$$n_{\text{Cl}_2} = 0.200 \text{ mol Al} \times \frac{3 \text{ mol Cl}_2}{2 \text{ mol Al}} = 0.300 \text{ mol}$$

$$m_{\text{Cl}_2} = 0.300 \text{ mol} \times 70.90 \frac{\text{g}}{\text{mol}} = 21.3 \text{ g}$$

The mass of chlorine gas produced at the anode is 21.3 g.



$$t = 2.20 \text{ h} \times \frac{3600 \text{ s}}{1 \text{ h}}$$

$$t = 7.92 \times 10^3 \text{ s}$$

$$n_{\text{Cr}} = 17.8 \text{ g} \times \frac{1 \text{ mol}}{52.00 \text{ g}}$$

$$n_{\text{Cr}} = 0.342 \text{ mol}$$

$$n_{\text{e}^-} = 0.342 \text{ mol Cr} \times \frac{12 \text{ mol e}^-}{2 \text{ mol Cr}}$$

$$n_{\text{e}^-} = 2.05 \text{ mol}$$

$$n_{\text{e}^-} = \frac{q}{F}$$

$$n_{\text{e}^-} = \frac{It}{F}$$

$$I = \frac{n_{\text{e}^-} F}{t}$$

$$= \frac{2.05 \text{ mol} \times 9.65 \times 10^4 \frac{\text{C}}{\text{mol}}}{7.92 \times 10^3 \text{ s}}$$

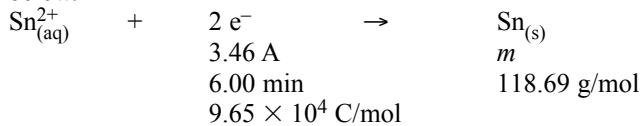
$$I = 25.0 \text{ C/s} = 25.0 \text{ A}$$

The current required is 25.0 A.

Applying Inquiry Skills

Prediction

12. (a) According to the stoichiometry of the known half-reaction and Faraday's law, 0.766 g of tin should form as shown below.



$$I = 3.46 \text{ A} = 3.46 \text{ C/s}$$

$$t = 6.00 \text{ min} \times \frac{60 \text{ s}}{1 \text{ min}} = 360 \text{ s}$$

$$n_{\text{e}^-} = \frac{q}{F}$$

$$n_{\text{e}^-} = \frac{It}{F}$$

$$= \frac{3.46 \frac{\text{C}}{\text{s}} \times 360 \text{ s}}{9.65 \times 10^4 \frac{\text{C}}{\text{mol}}}$$

$$n_{\text{e}^-} = 0.0129 \text{ mol}$$

$$n_{\text{Sn}} = 0.0129 \text{ mol e}^- \times \frac{1 \text{ mol Sn}}{2 \text{ mol e}^-}$$

$$n_{\text{Sn}} = 0.00645 \text{ mol}$$

$$m_{\text{Sn}} = 0.00645 \text{ mol} \times 118.69 \frac{\text{g}}{\text{mol}}$$

$$m_{\text{Sn}} = 0.766 \text{ g}$$

Analysis

- (b) The mass of tin produced is $(118.05 - 117.34) \text{ g} = 0.71 \text{ g}$.

Evaluation

$$(c) \text{ % difference} = \frac{|\text{experimental value} - \text{predicted value}|}{\text{predicted value}} \times 100\%$$

$$= \frac{|0.71 \text{ g} - 0.766 \text{ g}|}{0.766 \text{ g}} \times 100\%$$

$$= \frac{0.06 \text{ g}}{0.766 \text{ g}} \times 100\%$$

% difference = 7%

The percentage difference in this experimental result is 7%.

(The percentage difference is properly obtained by not rounding any numbers in any of the calculations. If rounded values from previous steps are used, a slightly different percentage will be obtained. Note that the subtraction of two very close values in the % difference produces only one significant digit in the answer.)

- (d) The prediction is judged to be verified because its value agrees fairly well with the experimental value; and the difference can be accounted for by typical experimental errors or uncertainties. The stoichiometric method based on the tin half-reaction is judged acceptable because the prediction was verified.

Making Connections

13. (a) A car battery ampere-hour rating tells you how much total charge the battery can deliver, which is proportional to the quantity of energy the battery can provide.

$$I = 125 \text{ A} = 125 \text{ C/s}$$

$$t = 1 \text{ h} = 3600 \text{ s}$$

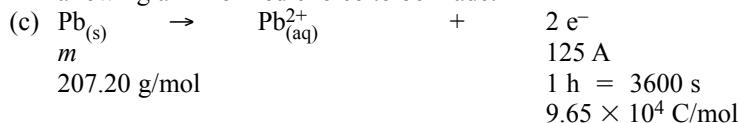
$$q = It$$

$$= 125 \frac{\text{C}}{\text{s}} \times 3600 \text{ s}$$

$$q = 4.50 \times 10^5 \text{ C}$$

The maximum charge that can be transferred by this battery is $4.50 \times 10^5 \text{ C}$.

- (b) This is a useful way to rate batteries because cost can then be compared to how much energy a battery will supply, allowing an informed choice to be made.



$$I = 125 \text{ A} = 125 \text{ C/s}$$

$$n_{\text{e}^-} = \frac{q}{F}$$

$$n_{\text{e}^-} = \frac{It}{F}$$

$$= \frac{125 \frac{\text{C}}{\text{s}} \times 3600 \text{ s}}{9.65 \times 10^4 \frac{\text{C}}{\text{mol}}}$$

$$n_{\text{e}^-} = 4.66 \text{ mol}$$

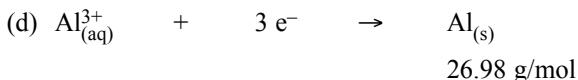
$$n_{\text{Pb}} = 4.66 \cancel{\text{mol e}^-} \times \frac{1 \text{ mol Pb}}{2 \cancel{\text{mol e}^-}}$$

$$n_{\text{Pb}} = 2.33 \text{ mol}$$

$$m_{\text{Pb}} = 2.33 \cancel{\text{mol}} \times 207.20 \frac{\text{g}}{\cancel{\text{mol}}}$$

$$m_{\text{Pb}} = 483 \text{ g}$$

The mass of lead oxidized as the battery discharges is 483 g.



$$n_{\text{e}^-} = 4.66 \text{ mol}$$

$$n_{\text{Al}} = 4.66 \cancel{\text{mol e}^-} \times \frac{1 \text{ mol Al}}{3 \cancel{\text{mol e}^-}}$$

$$n_{\text{Al}} = 1.55 \text{ mol}$$

$$m_{\text{Al}} = 1.55 \cancel{\text{mol}} \times 26.98 \frac{\text{g}}{\cancel{\text{mol}}}$$

$$m_{\text{Al}} = 41.9 \text{ g}$$

The mass of aluminum oxidized would be 41.9 g.

- (e) Obviously, there would be a huge weight advantage to using an aluminum–oxygen fuel cell; the mass of metal required for discharge is less than 9% as much, if the charge delivered is equal.

SECTION 10.3 QUESTIONS

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Understanding Concepts

1. $I = 0.300 \text{ A} = 0.300 \text{ C/s}$

$$t = 15.0 \cancel{\text{min}} \times \frac{60 \text{ s}}{1 \cancel{\text{min}}} = 900 \text{ s}$$

$$F = 9.65 \times 10^4 \text{ C/mol}$$

$$n_{\text{e}^-} = \frac{q}{F}$$

$$= \frac{It}{F}$$

$$= \frac{0.300 \frac{\text{C}}{\text{s}} \times 900 \text{ s}}{9.65 \times 10^4 \frac{\text{C}}{\text{mol}}}$$

$$= \frac{2.70}{9.65 \times 10^4} \frac{\text{mol}}{\text{mol}}$$

$$n_{\text{e}^-} = 0.00280 \text{ mol} = 2.80 \text{ mmol}$$

The amount of electrons transferred is 2.80 mmol.

2. $2 \text{Cl}_{(\text{aq})}^- \rightarrow \text{Cl}_{2(\text{g})} + 2 \text{e}^-$

$$m \quad \quad \quad 55 \text{ kA}$$

$$70.90 \text{ g/mol} \quad \quad \quad 8.0 \text{ h}$$

$$9.65 \times 10^4 \text{ C/mol}$$

$$I = 55 \text{ kA} = 5.5 \times 10^4 \text{ C/s}$$

$$t = 8.0 \cancel{\text{h}} \times \frac{3600 \text{ s}}{1 \cancel{\text{h}}} = 2.9 \times 10^4 \text{ s}$$

$$n_{\text{e}^-} = \frac{q}{F}$$

$$= \frac{It}{F}$$

$$= \frac{5.5 \times 10^4 \frac{\text{C}}{\text{s}} \times 2.9 \times 10^4 \text{ s}}{9.65 \times 10^4 \frac{\text{C}}{\text{mol}}}$$

$$= \frac{1.6 \times 10^4 \text{ mol}}{9.65 \times 10^4 \frac{\text{C}}{\text{mol}}}$$

$$n_{\text{e}^-} = 1.6 \times 10^4 \text{ mol}$$

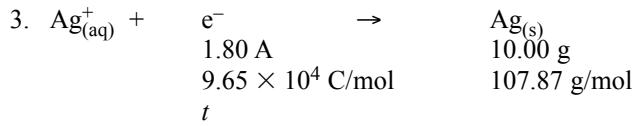
$$n_{\text{Cl}_2} = 1.6 \times 10^4 \cancel{\text{mol e}^-} \times \frac{1 \text{ mol Cl}_2}{2 \cancel{\text{mol e}^-}}$$

$$n_{\text{Cl}_2} = 8.2 \times 10^3 \text{ mol}$$

$$m_{\text{Cl}_2} = 8.2 \times 10^3 \text{ mol} \times 70.90 \frac{\text{g}}{\text{mol}}$$

$$m_{\text{Cl}_2} = 5.8 \times 10^5 \text{ g} = 0.58 \text{ Mg}$$

The mass of chlorine produced is 0.58 Mg or 0.58 t.



$$I = 1.80 \text{ A} = 1.80 \text{ C/s}$$

$$n_{\text{Ag}} = 10.00 \text{ g} \times \frac{1 \text{ mol}}{107.87 \text{ g}}$$

$$n_{\text{Ag}} = 0.0927 \text{ mol}$$

$$n_{\text{e}^-} = 0.0927 \text{ mol Ag} \times \frac{1 \text{ mol e}^-}{1 \text{ mol Ag}}$$

$$= 0.0927 \text{ mol}$$

$$n_{\text{e}^-} = \frac{q}{F}$$

$$n_{\text{e}^-} = \frac{It}{F}$$

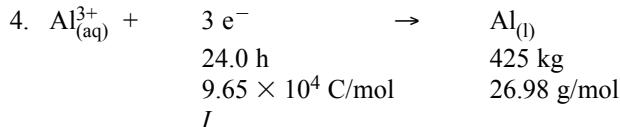
$$t = \frac{n_{\text{e}^-} F}{I}$$

$$t = \frac{0.0927 \text{ mol} \times 9.65 \times 10^4 \frac{\text{C}}{\text{mol}}}{1.80 \frac{\text{C}}{\text{s}}}$$

$$t = 4.97 \times 10^3 \text{ s} \times \frac{1 \text{ min}}{60 \text{ s}}$$

$$t = 82.8 \text{ min}$$

The time to silverplate the teapot is 82.8 min.



$$t = 24.0 \text{ h} \times \frac{3600 \text{ s}}{1 \text{ h}}$$

$$= 8.64 \times 10^4 \text{ s}$$

$$n_{\text{Al}} = 425 \text{ kg} \times \frac{1 \text{ mol}}{26.98 \text{ g}}$$

$$n_{\text{Al}} = 15.8 \text{ kmol}$$

$$n_{\text{e}^-} = 15.8 \text{ kmol Al} \times \frac{3 \text{ mol e}^-}{1 \text{ mol Al}}$$

$$n_{\text{e}^-} = 47.3 \text{ kmol}$$

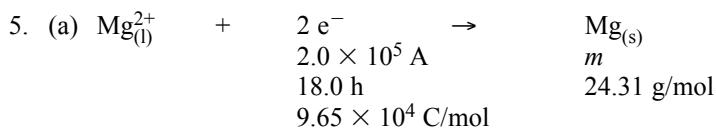
$$n_{\text{e}^-} = \frac{q}{F}$$

$$n_{\text{e}^-} = \frac{It}{F}$$

$$I = \frac{n_{\text{e}^-} F}{t}$$

$$I = \frac{47.3 \text{ kJ/mol} \times 9.65 \times 10^4 \frac{\text{C}}{\text{mol}}}{8.64 \times 10^4 \text{ s}}$$

$I = 52.8 \text{ kC/s} = 52.8 \text{ kA}$
The average current required is 52.8 kA.



$$I = 2.0 \times 10^5 \text{ A} = 2.0 \times 10^5 \text{ C/s}$$

$$t = 18.0 \text{ h} \times \frac{3600 \text{ s}}{1 \text{ h}} = 6.48 \times 10^4 \text{ s}$$

$$n_{\text{e}^-} = \frac{q}{F}$$

$$n_{\text{e}^-} = \frac{It}{F}$$

$$= \frac{2.0 \times 10^5 \frac{\text{C}}{\text{s}} \times 6.48 \times 10^4 \text{ s}}{9.65 \times 10^4 \frac{\text{C}}{\text{mol}}}$$

$$n_{\text{e}^-} = 134 \text{ kmol}$$

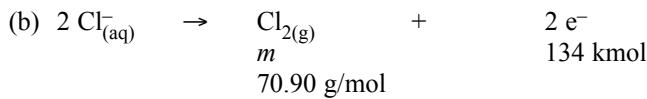
$$n_{\text{Mg}} = 134 \text{ kmol e}^- \times \frac{1 \text{ mol Mg}}{2 \text{ mol e}^-}$$

$$n_{\text{Mg}} = 67.2 \text{ kmol}$$

$$m_{\text{Mg}} = 67.2 \text{ kmol} \times 24.31 \frac{\text{g}}{\text{mol}}$$

$$m_{\text{Mg}} = 1.63 \times 10^3 \text{ kg} = 1.63 \text{ Mg}$$

The mass of magnesium produced is 1.63 Mg or 1.63 t.



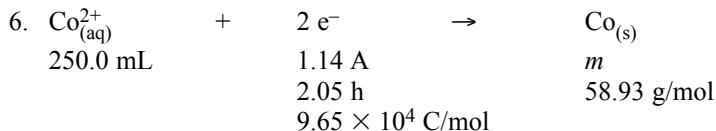
$$n_{\text{Cl}_2} = 134 \text{ kmol e}^- \times \frac{1 \text{ mol Cl}_2}{2 \text{ mol e}^-}$$

$$n_{\text{Cl}_2} = 67.2 \text{ kmol}$$

$$m_{\text{Cl}_2} = 67.2 \text{ kmol} \times 70.90 \frac{\text{g}}{\text{mol}}$$

$$m_{\text{Cl}_2} = 4.76 \times 10^3 \text{ kg} = 4.76 \text{ Mg}$$

The mass of chlorine produced is 4.76 Mg or 4.76 t.



$$I = 1.14 \text{ A} = 1.14 \text{ C/s}$$

$$t = 2.05 \text{ h} \times \frac{3600 \text{ s}}{1 \text{ h}} = 7.38 \times 10^3 \text{ s}$$

$$n_{\text{e}^-} = \frac{q}{F}$$

$$n_{e^-} = \frac{It}{F}$$

$$= \frac{1.14 \frac{\text{C}}{\text{s}} \times 7.38 \times 10^3 \text{ s}}{9.65 \times 10^4 \frac{\text{C}}{\text{mol}}}$$

$$n_{e^-} = 0.0872 \text{ mol}$$

$$n_{\text{Co}^{2+}} = 0.0872 \frac{\text{mol e}^-}{2 \text{ mol e}^-} \times \frac{1 \text{ mol Co}^{2+}}{1 \text{ mol e}^-}$$

$$n_{\text{Co}^{2+}} = 0.0436 \text{ mol}$$

$$n_{\text{CoSO}_4} = 0.0436 \frac{\text{mol Co}^{2+}}{1 \text{ mol Co}^{2+}} \times \frac{1 \text{ mol CoSO}_4}{1 \text{ mol Co}^{2+}}$$

$$n_{\text{CoSO}_4} = 0.0436 \text{ mol}$$

$$C_{\text{CoSO}_4} = \frac{0.0436 \text{ mol}}{0.2500 \text{ L}}$$

$$C_{\text{CoSO}_4} = 0.174 \text{ mol/L}$$

The minimum molar concentration of cobalt(II) sulfate required is 0.174 mol/L.

7. $\text{Cu}_{(\text{s})} \rightarrow \text{Cu}_{(\text{aq})}^{2+} + 2 \text{ e}^-$
- $m_i = 25.72 \text{ g}$ 0.876 A
 m_f 75.0 min
 63.55 g/mol $9.65 \times 10^4 \text{ C/mol}$
 $I = 0.876 \text{ A} = 0.876 \text{ C/s}$
 $t = 75.0 \text{ min} \times \frac{60 \text{ s}}{1 \text{ min}} = 4.50 \times 10^3 \text{ s}$

$$n_{e^-} = \frac{q}{F}$$

$$n_{e^-} = \frac{It}{F}$$

$$= \frac{0.876 \frac{\text{C}}{\text{s}} \times 4.50 \times 10^3 \text{ s}}{9.65 \times 10^4 \frac{\text{C}}{\text{mol}}}$$

$$n_{e^-} = 0.0408 \text{ mol}$$

$$n_{\text{Cu}} = 0.0408 \frac{\text{mol e}^-}{2 \text{ mol e}^-} \times \frac{1 \text{ mol Cu}}{1 \text{ mol e}^-}$$

$$n_{\text{Cu}} = 0.0204 \text{ mol}$$

$$m_{\text{Cu}} = 0.0204 \frac{\text{mol}}{\text{mol}} \times 63.55 \frac{\text{g}}{\text{mol}}$$

$$m_{\text{Cu}} = 1.30 \text{ g} \quad (\text{mass loss at the anode})$$

The final mass of the copper anode will be $(25.72 - 1.30) \text{ g} = 24.42 \text{ g}$.

Making Connections

8. In a chlor-alkali cell, Faraday's law is critical to the process design because the quantities of electrical current required must be determined by the desired production of chemical products. The cost of power, size of conductors, and time of operation are all matters of concern to industrial processes. Process control just involves varying the quantity of charge through the cell, which will proportionally vary the amount of product.
9. (a) Chemical technicians prepare solutions; order inventory; maintain and clean equipment; set up bays/areas for experimentation; perform many kinds of analyses with all types of equipment; and maintain records of lab stocks, policies, and procedures.
(b) Chemical technician education requirements vary, but usually include certification in a two- or three-year instruction program at a technical school or college.
(c) (Educational facilities listed may be local facilities or those farther afield.)
(d) (Job listings will, of course, vary with the newspaper selected and the date.)

CHAPTER 10 LAB ACTIVITIES

INVESTIGATION 10.1.1 A POTASSIUM IODIDE ELECTROLYTIC CELL

(Page 754)

Evidence

(a)

Before the cell was connected,

the solution was completely colourless and both litmus and halogen tests gave negative results.

After the cell was connected and in operation for a few minutes,

at the black (negative) electrode and nearby solution:

- many colourless gas bubbles were continuously produced,
- red litmus turned blue,
- the hexane layer remained colourless.

at the red (positive) electrode and nearby solution:

- a yellow-brown colour of solution and some black precipitate formed and settled to the bottom of the tube,
- litmus did not change in colour,
- the hexane layer was purple.

Analysis

- (b) According to the evidence collected, a colourless gas and hydroxide ions were likely produced at the negative electrode. The observations strongly suggest the formation of iodine at the positive electrode.

Evaluation

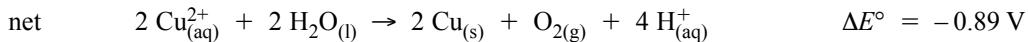
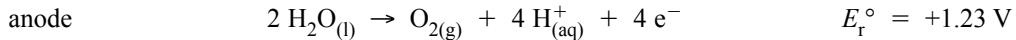
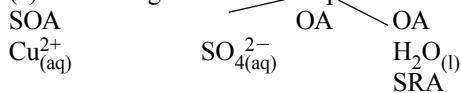
- (c) The design was mostly adequate to answer the question, except for the identification of the gas. An improvement would be to collect and test the gas produced. The presence of hydroxide ions could be further confirmed by an additional test such as a precipitation. The control tests were quite adequate to show changes.
- (d) It was not possible to identify the gas produced because it could not be collected in the apparatus used.
- (e) A Hoffmann apparatus could be used to conduct the electrolysis and collect the gas. (Alternatively, a test tube filled with solution and inverted over the electrode in a large beaker could be used.) A splint and matches should be provided to conduct the hydrogen and oxygen tests.
- (f) The electrodes should not touch because this would short-circuit the cell. The electricity would flow directly from one electrode to the other without being forced through the solution and little or no reaction would occur. (This may also be dangerous because the current in the circuit may become high enough to melt some components or blow a fuse.)
- (g) Iodine is formed at the positive electrode. Iodine solution and solid are more dense than water and therefore sink to the bottom of the tube.
- (h) The quality of evidence is quite good, except for the identification of the gas. The litmus and halogen tests, compared with the control, clearly showed that a basic solution and iodine were formed as a result of the reaction.

INVESTIGATION 10.1.2 INVESTIGATING SEVERAL ELECTROLYTIC CELLS

(Page 755)

Prediction

- (a) According to redox concepts and the table of half-reactions,



minimum potential difference = +0.89 V

CHAPTER 10 LAB ACTIVITIES

INVESTIGATION 10.1.1 A POTASSIUM IODIDE ELECTROLYtic CELL

(Page 754)

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- the hexane layer was purple.

Analysis

- (b) According to the evidence collected, a colourless gas and hydroxide ions were likely produced at the negative electrode. The observations strongly suggest the formation of iodine at the positive electrode.

Evaluation

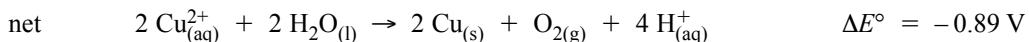
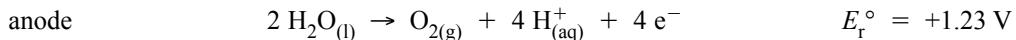
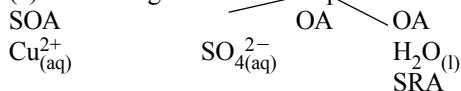
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- (g) Iodine is formed at the positive electrode. Iodine solution and solid are more dense than water and therefore sink to the bottom of the tube.
- (h) The quality of evidence is quite good, except for the identification of the gas. The litmus and halogen tests, compared with the control, clearly showed that a basic solution and iodine were formed as a result of the reaction.

INVESTIGATION 10.1.2 INVESTIGATING SEVERAL ELECTROLYtic CELLS

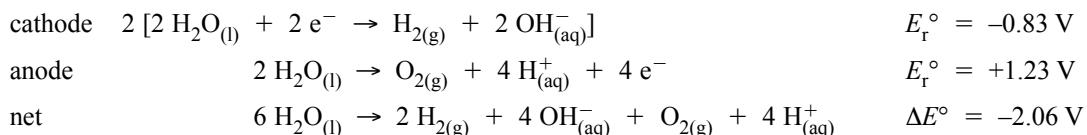
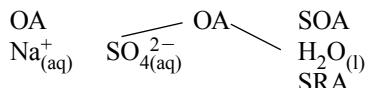
(Page 755)

Prediction

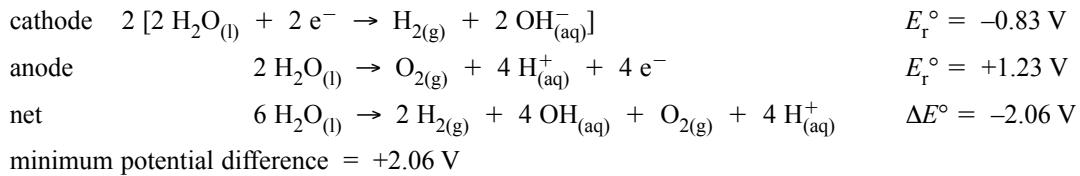
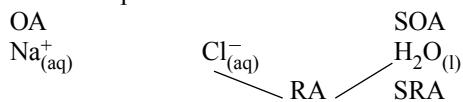
- (a) According to redox concepts and the table of half-reactions,



minimum potential difference = +0.89 V



minimum potential difference = +2.06 V



minimum potential difference = +2.06 V

Evidence

(b)

Cell	Cathode	Anode
$\text{C}_{(\text{s})} \text{CuSO}_4_{(\text{aq})} \text{C}_{(\text{s})}$ applied voltage 6 V	<ul style="list-style-type: none"> blue litmus turned red before and after the cell operated red-brown solid formed on $\text{C}_{(\text{s})}$ 	<ul style="list-style-type: none"> blue litmus turned red before and after the cell operated gas bubbles formed on $\text{C}_{(\text{s})}$
$\text{Pt}_{(\text{s})} \text{Na}_2\text{SO}_4_{(\text{aq})} \text{Pt}_{(\text{s})}$ applied voltage 6 V	<ul style="list-style-type: none"> no change in litmus before the cell operated red litmus turned blue in final solution about 31 mL of gas collected a loud, squeaky sound heard when gas sample was ignited 	<ul style="list-style-type: none"> no change in litmus before the cell operated blue litmus turned red in final solution about 16 mL of gas collected a glowing splint burst into flame in gas sample
$\text{Pt}_{(\text{s})} \text{NaCl}_{(\text{aq})} \text{Pt}_{(\text{s})}$ applied voltage 6 V	<ul style="list-style-type: none"> no change in litmus before the cell operated red litmus turned blue in final solution about 31 mL of gas collected a loud, squeaky sound heard when gas sample was ignited 	<ul style="list-style-type: none"> no change in litmus before the cell operated both red and blue litmus turned white in final solution a strong odour of bleach detected yellow-brown colour appeared on addition of $\text{NaI}_{(\text{aq})}$ to a sample of the solution purple colour of hexane layer observed

Analysis

(c) According to the evidence collected, the products of the electrolytic cells are:

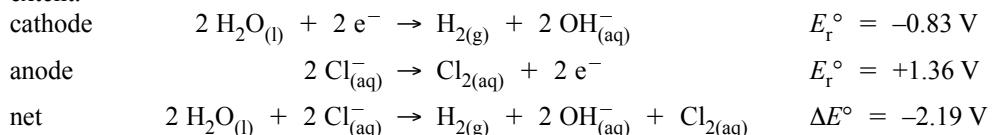
Cell	Cathode products	Anode products
$\text{CuSO}_4_{(\text{aq})}$	$\text{Cu}_{(\text{s})}$	colourless gas
$\text{Na}_2\text{SO}_4_{(\text{aq})}$	$\text{H}_{2(\text{g})}, \text{OH}_{(\text{aq})}^-$	$\text{O}_{2(\text{g})}, \text{H}_{(\text{aq})}^+$
$\text{NaCl}_{(\text{aq})}$	$\text{H}_{2(\text{g})}, \text{OH}_{(\text{aq})}^-$	$\text{Cl}_{2(\text{aq})}$

Evaluation

- (d) The experimental design is judged to be adequate with no obvious flaws. The problem was answered with reasonable certainty and the controls for the litmus test were adequate. There are two ways to improve the electrolysis of aqueous copper(II) sulfate. One is to use an apparatus so that the gas can be collected and identified. The other is to use pH paper or a pH meter instead of litmus paper. These changes would increase the certainty of the results.
- (e) The overall quality of the evidence is good. There is some uncertainty about the results for the litmus test on the copper(II) sulfate solution. This could be solved by using pH paper or a pH meter. Overall, I am quite certain because the majority of the products were clearly identified with the diagnostic tests.
- (f) The predictions for the cathode product of copper(II) sulfate and the cathode and anode products of the sodium sulfate solution were verified because the predicted products clearly agree with the experimental results. The prediction of the anode product for copper(II) sulfate could not be judged with sufficient certainty. The prediction for the cathode products of sodium chloride was also verified but the prediction for the anode products was falsified by the evidence obtained.
- (g) The redox concepts and table remain acceptable until further results are obtained. Most of the predictions were verified except for the anode product of the sodium chloride electrolysis. It is necessary to determine how unique the result for sodium chloride is. It may be necessary to restrict or revise the concepts or procedure used to predict the products.

Synthesis

- (h) The oxidation of water at the anode of the sodium chloride cell did not seem to occur, or occurred to a very limited extent.



The minimum potential difference is +2.19 V.

- (i) The minimum potential difference for oxygen as a product is 2.06 V and for chlorine as a product is 2.19 V. There is only 0.13 V difference between the two.
- (j) The applied voltage in the electrolysis was 6 V, which is considerably higher than both minimum potential differences. Based on this fact and the fact that the minimum potential differences are so close, it is possible that the production of chlorine is much faster than that of oxygen. This could explain the larger quantity of chlorine produced.
- (k) The rules should be retained until additional electrolyses of chloride solutions are conducted. If the same results appear, then the rules should be revised to account for this new information.

INVESTIGATION 10.3.1 INVESTIGATING AN ELECTROLYTIC CELL

(Page 756)

Prediction

- (a) According to a modern reference, the value of the Faraday, F , is $9.65 \times 10^4 \text{ C/mol}$.

Evidence

Electrode	Masses of copper electrodes	
	Initial mass (g)	Final mass (g)
labelled A	2.88	2.35
labelled C	2.74	3.28

- electric current decreased slightly near the start and was adjusted to a relatively constant 0.75 A
- elapsed time = 35 min 4 s
- cathode developed some dark brown crystals particularly at the edges
- some very thin, darker-coloured flakes fell off the anode when dipped in distilled water and acetone
- the final masses did not change when remeasured after a few minutes

Analysis

(b) for the cathode:
$$\begin{aligned}\Delta m &= 3.28 \text{ g} - 2.74 \text{ g} \\ &= 0.54 \text{ g}\end{aligned}$$

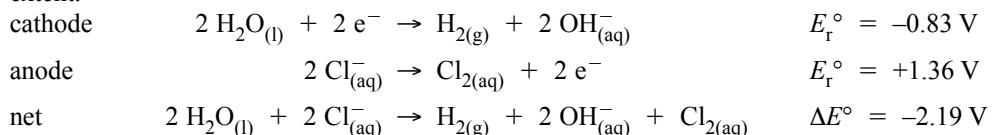
for the anode:
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Evaluation

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Synthesis

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INVESTIGATION 10.3.1 INVESTIGATING AN ELECTROLYTIC CELL

(Page 756)

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- the final masses did not change when remeasured after a few minutes

Analysis

(b) for the cathode:
$$\begin{aligned}\Delta m &= 3.28 \text{ g} - 2.74 \text{ g} \\ &= 0.54 \text{ g}\end{aligned}$$

for the anode:
$$\begin{aligned}\Delta m &= 2.88 \text{ g} - 2.35 \text{ g} \\ &= 0.53 \text{ g}\end{aligned}$$

$$(c) \text{ average } \Delta m = (0.54 \text{ g} + 0.53 \text{ g})/2$$

$$= 0.535 \text{ g}$$



$$n \quad \frac{0.535 \text{ g}}{63.55 \text{ g/mol}}$$

$$n_{\text{Cu}} = 0.535 \text{ g} \times \frac{1 \text{ mol}}{63.55 \text{ g}}$$

$$n_{\text{Cu}} = 0.0084 \text{ mol}$$

$$n_{\text{e}^-} = 0.0084 \text{ mol} \times \frac{2}{1}$$

$$n_{\text{e}^-} = 0.017 \text{ mol}$$

$$(d) q = It$$

$$= 0.75 \frac{\text{C}}{\text{s}} \times 2104 \text{ s}$$

$$q = 1.6 \times 10^3 \text{ C}$$

$$(e) F = \frac{1.6 \times 10^3 \text{ C}}{0.017 \text{ mol}}$$

$$F = 9.4 \times 10^4 \text{ C/mol}$$

According to evidence collected and the copper(II) half-reaction, the value of the Faraday is $9.4 \times 10^4 \text{ C/mol}$.

Evaluation

(f) The experimental design appears quite adequate to answer the question with no obvious flaws. It was important to control the electric current because it tended to change slightly during the electrolysis. The procedure was clear and produced sufficient evidence to answer the question. With the particular power supply used, it was not possible to get a current between one and two amperes. However, this is not a significant problem as long the current is known and controlled. A slight quantity of material was lost from the anode when removing the electrodes and rinsing. This could suggest that the copper foil used was not completely pure and some other substance was present but not oxidized. One improvement that could be made is to use a better quality of copper metal for the electrodes. Another improvement would be to run the cell for a longer period of time and/or at a higher current to obtain three significant digits for the change in mass. A more precise ammeter would also be required to improve the precision of the result.

(g) Considering the design, materials, and procedure used, I am fairly certain that the overall quality of the evidence is quite adequate. There do not appear to be any significant problems or sources of error other than the usual measurement uncertainties and the loss of a small amount of some material from the anode.

$$(h) \text{ % difference} = \frac{|9.4 \times 10^4 \text{ C/mol} - 9.65 \times 10^4 \text{ C/mol}|}{9.65 \times 10^4 \text{ C/mol}} \times 100\%$$

$$\text{ % difference} = 2.9\%$$

(i) The evidence suggests that copper is both oxidized and reduced in this cell.



The change in masses of the electrodes is virtually identical and the small percent difference can easily be explained by experimental uncertainties. There is some evidence to suggest that the copper was not completely pure but this seems to be a minor problem.

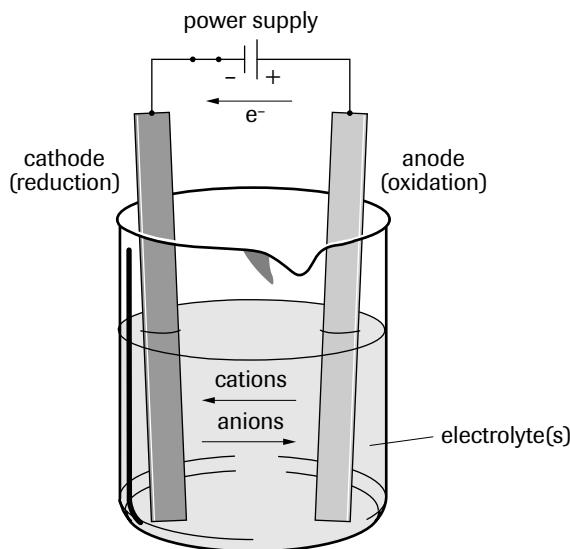
Synthesis

(j) This type of cell is used in the electrorefining of copper to convert impure copper to copper of much higher purity.

CHAPTER 10 SUMMARY

MAKE A SUMMARY

(Page 758)



- The minimum electrolytic cell potential is determined by subtracting the E_r° (reduction potential) of the strongest reducing agent present from the E_r° (reduction potential) of the strongest oxidizing agent present, using a standard table of reduction potentials.

Note: These tabulated values are established for standard half-cells, using aqueous electrolytes, at SATP. Any variation from these conditions will make the predicted value less accurate; and most electrolytic cells are not operated under these conditions. For electrolytic cells using molten electrolytes, these tabled values are essentially meaningless.

Category	Description	Examples
rechargeable batteries	reversing a secondary cell to charge it	batteries for phones and laptop computers
element production	producing elements from naturally occurring compounds	aluminum from aluminum oxide to make aluminum cans
metal refining	producing pure metals from impure metals	copper for electrical wiring
electroplating	covering an object with a layer of metal	chromium plating of faucets

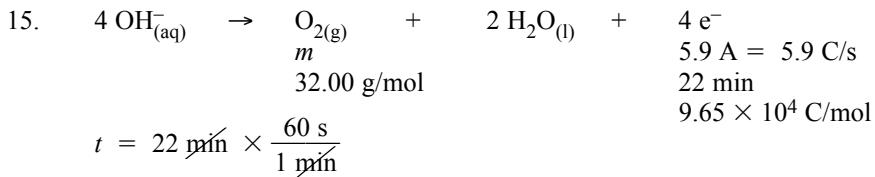
CHAPTER 10 SELF-QUIZ

(Page 759)

1. True
2. False: Reduction occurs at the ~~anode~~ cathode and oxidation occurs at the ~~cathode~~ anode in an electrolytic cell.
3. False: Electrolytic cells generally have a single electrolyte ~~so they are really half cells with the power supply serving as the other half cell~~ but they have oxidation and reduction processes occurring at two electrodes so they are complete cells. The power supply creates a potential difference to drive the reaction.
4. True
5. True
6. True
7. False: If you want to deposit twice a given mass of silver in an electrolytic cell, then you must either use twice the current ~~for~~ or double the time.
8. (c)
9. (a)
10. (b)
11. (d)
12. (b)
13. (c)
14. (c)
15. (a)
16. (d)

Worked Solutions:

11. $[-0.76] - (+1.07) \text{ V} = -1.83 \text{ V}$ (d)



$$t = 1.3 \times 10^3 \text{ s}$$

$$n_{\text{e}^-} = \frac{q}{F}$$

$$n_{\text{e}^-} = \frac{It}{F}$$

$$= \frac{5.9 \frac{\text{C}}{\text{s}} \times 1.3 \times 10^3 \text{ s}}{9.65 \times 10^4 \frac{\text{C}}{\text{mol}}}$$

$$n_{\text{e}^-} = 0.081 \text{ mol}$$

$$n_{\text{O}_2} = 0.081 \text{ mol e}^- \times \frac{1 \text{ mol O}_2}{4 \text{ mol e}^-}$$

$$n_{\text{O}_2} = 0.020 \text{ mol}$$

$$m_{\text{O}_2} = 0.020 \text{ mol} \times 32.00 \frac{\text{g}}{\text{mol}}$$

$$m_{\text{O}_2} = 0.65 \text{ g}$$
 (a)

CHAPTER 10 REVIEW

(Page 760)

Understanding Concepts

1. (a) Electrolysis is the forcing of a possible but nonspontaneous oxidation-reduction reaction by the application of a potential difference from an outside power source.
(b) Oxidation (electron loss) occurs at the anode; reduction (electron gain) occurs at the cathode.
(c) In electrolysis of molten compounds, water is not present and there are fewer oxidizing agents and reducing agents present (often only one of each). The temperature is usually very high, making container and electrode selection more difficult because they must be able to withstand the temperature conditions. In all other aspects, the process is similar to electrolysis with aqueous electrolytes.
2. In both types of cells, the strongest oxidizing agent present undergoes a reduction at the cathode and the strongest reducing agent present undergoes an oxidation at the anode. Both the electrons and ions move in the same direction in electrolytic and galvanic cells.

The major difference between galvanic cells and electrolytic cells is that the most likely redox reaction in electrolytic cells is not spontaneous; thus, the reaction must be driven by the application of potential difference (voltage) from an outside power supply. Electrolytic cells have a negative cell potential and galvanic cells have a positive cell potential. By convention, the positive/negative designation of the electrodes differs as well; in electrolytic cells, the cathode is designated negative and the anode positive. In galvanic cells, the cathode is designated positive and the anode negative.

3. (a) Nonspontaneous reaction — external voltage required.
(b) Spontaneous reaction — no external voltage required.
(c) Spontaneous reaction — no external voltage required.
(d) Nonspontaneous reaction — external voltage required.
4. $\Delta E^\circ = E_r^\circ \text{ (cathode)} - E_r^\circ \text{ (anode)}$

(a) $\Delta E^\circ = [(-0.45) - (+0.77)] \text{ V} = -1.22 \text{ V}$

The minimum potential difference that must be applied to cause a reaction is 1.22 V.

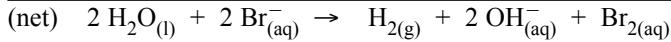
(b) $\Delta E^\circ = [(0.00) - (+0.80)] \text{ V} = -0.80 \text{ V}$

The minimum potential difference that must be applied to cause a reaction is 0.80 V.

(c) $\Delta E^\circ = [(-0.14) - (-0.14)] \text{ V} = 0.00 \text{ V}$

Any potential difference applied will cause tin to dissolve at the anode and to plate out at the cathode, but there is no net chemical reaction. $\Delta E^\circ = 0.00 \text{ V}$ for this cell.

5. (a) (cathode) $2 \text{H}_2\text{O}_{(l)} + 2 \text{e}^- \rightarrow \text{H}_{2(g)} + 2 \text{OH}_{(aq)}^-$ $E_r^\circ = -0.83 \text{ V}$
(anode) $2 \text{Br}_{(aq)}^- \rightarrow \text{Br}_{2(aq)} + 2 \text{e}^-$ $E_r^\circ = +1.07 \text{ V}$



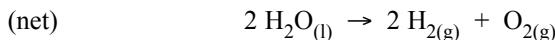
$$\Delta E^\circ = E_r^\circ \text{ (cathode)} - E_r^\circ \text{ (anode)}$$

$$= -0.83 \text{ V} - (+1.07 \text{ V})$$

$$\Delta E^\circ = -1.90 \text{ V}$$

The minimum applied potential difference required to produce a chemical change is 1.90 V.

- (b) (cathode) $2[2 \text{H}_2\text{O}_{(l)} + 2 \text{e}^- \rightarrow \text{H}_{2(g)} + 2 \text{OH}_{(aq)}^-]$ $E_r^\circ = -0.83 \text{ V}$
(anode) $4 \text{OH}_{(aq)}^- \rightarrow \text{O}_{2(g)} + 2 \text{H}_2\text{O}_{(l)} + 4 \text{e}^-$ $E_r^\circ = +0.40 \text{ V}$
-

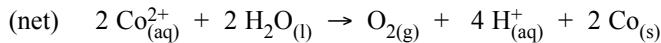
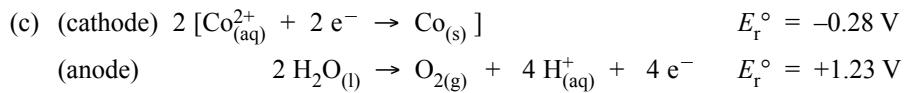


$$\Delta E^\circ = E_r^\circ \text{ (cathode)} - E_r^\circ \text{ (anode)}$$

$$= -0.83 \text{ V} - (+0.40 \text{ V})$$

$$\Delta E^\circ = -1.23 \text{ V}$$

The minimum applied potential difference required to produce a chemical change is 1.23 V.

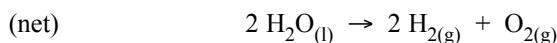
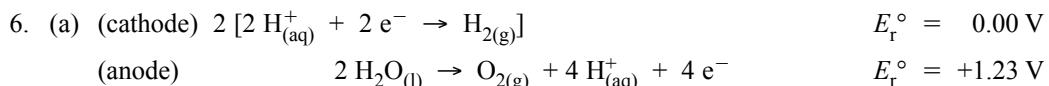


$$\Delta E^\circ = E_r^\circ (\text{cathode}) - E_r^\circ (\text{anode}) \\ = -0.28 \text{ V} - (+1.23 \text{ V})$$

$$\Delta E^\circ = -1.51 \text{ V}$$

Note: If the voltage is slightly higher (1.64 V), the anode product will be predominantly chlorine, because the Cl^- ion oxidation is *very* much faster than that of H_2O molecules.

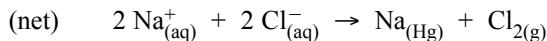
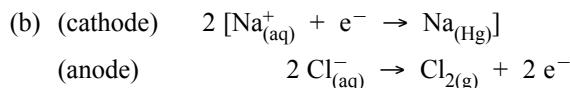
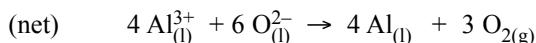
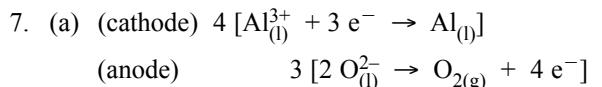
The minimum applied potential difference required to produce a chemical change is 1.51 V.



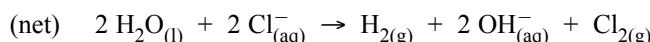
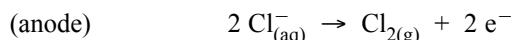
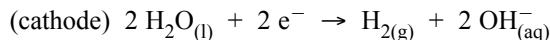
$$(b) \Delta E^\circ = E_r^\circ (\text{cathode}) - E_r^\circ (\text{anode}) \\ = 0.00 \text{ V} - (+1.23 \text{ V})$$

$$\Delta E^\circ = -1.23 \text{ V}$$

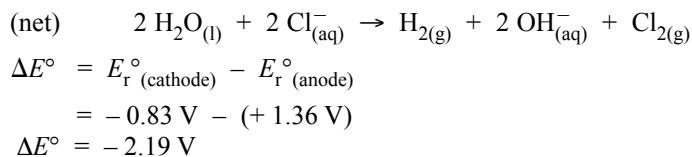
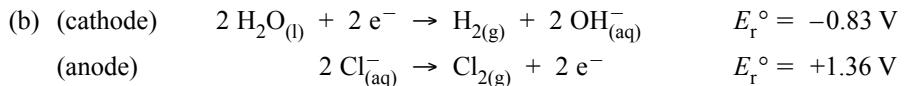
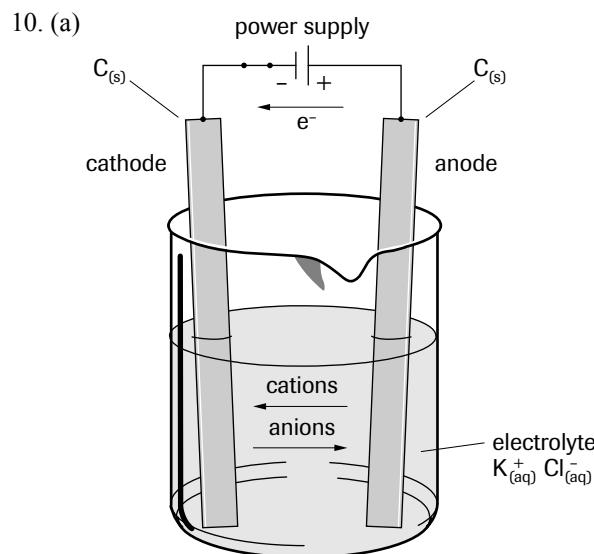
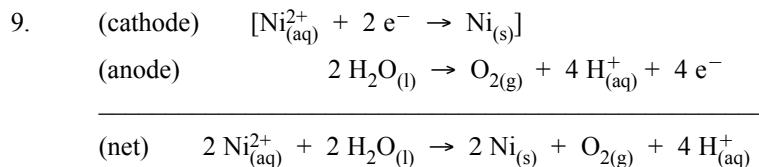
The minimum applied potential difference required to produce a chemical change is 1.23 V.



Note: The cathode half-reaction given is for the original chlor-alkali process, which uses a mercury cathode. The sodium metal produced is reacted with fresh water to produce hydrogen gas and sodium hydroxide. In newer diaphragm and ion-exchange membrane cells, water reacts at the cathode instead of sodium ions as shown below.



8. (a) In the electrorefining of copper, the anode is impure copper, the cathode is highly pure copper, and the solution contains copper (II) ions.
 (b) In the electrorefining of copper, the silver, gold, and platinum impurities are not oxidized at the anode, and so fall to the bottom of the cell as tiny particles of solid metal, forming a sludge. Iron and zinc impurities are oxidized to ions at the anode, but are not reduced at the cathode because copper(II) ions are a stronger oxidizing agent. This means that unless the voltage applied is too high, the iron and zinc ions will remain in solution.
 (c) High-purity copper is especially important in electronics as an efficient conductor of electric current.



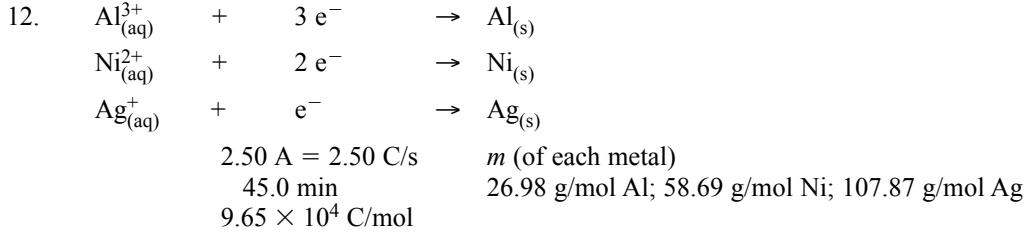
Note: The electrolysis of aqueous potassium chloride should be very similar to that of aqueous sodium chloride. Therefore, chloride ions will be predominantly oxidized over water at the anode, because the $Cl_{(aq)}^-$ ion oxidation is much faster than that of H_2O molecules.

The minimum applied potential difference is 2.19 V (versus 2.06 V for water oxidation).

11. (a) The bolt must be attached at the cathode because that is where the copper(II) ions will be reduced to copper metal.
 (b) The anode half-reaction is: $2 H_2O_{(l)} \rightarrow O_{2(g)} + 4 H_{(aq)}^+ + 4 e^-$
 Oxygen gas and hydrogen ions are the anode products.
 (c) $Cu_{(aq)}^{2+} + 2 e^- \rightarrow Cu_{(s)}$
 $1.5 \text{ A} = 1.5 \text{ C/s}$
 $30 \text{ min} \quad m$
 $9.65 \times 10^4 \text{ C/mol}$
- $$t = 30 \cancel{\text{min}} \times \frac{60 \text{ s}}{1 \cancel{\text{min}}}$$
- $$t = 1.8 \times 10^3 \text{ s}$$
- $$n_{e^-} = \frac{q}{F}$$

$$\begin{aligned}
 n_{e^-} &= \frac{It}{F} \\
 &= \frac{1.5 \frac{\text{C}}{\text{s}} \times 1.8 \times 10^3 \text{s}}{9.65 \times 10^4 \frac{\text{C}}{\text{mol}}} \\
 n_{e^-} &= 0.0280 \text{ mol} \\
 n_{\text{Cu}} &= 0.0280 \frac{\text{mol}}{\text{mol e}^-} \times \frac{1 \text{ mol Cu}}{2 \text{ mol e}^-} \\
 n_{\text{Cu}} &= 0.0140 \text{ mol} \\
 m_{\text{Cu}} &= 0.0140 \frac{\text{mol}}{\text{mol}} \times 63.55 \frac{\text{g}}{\text{mol}} \\
 m_{\text{Cu}} &= 0.889 \text{ g}
 \end{aligned}$$

The mass of copper plated out is 0.889 g.

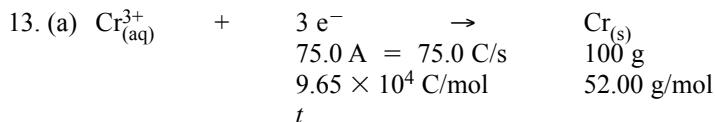


$$\begin{aligned}
 t &= 45.0 \frac{\text{min}}{\text{min}} \times \frac{60 \text{ s}}{1 \frac{\text{min}}{\text{min}}} \\
 t &= 2.7 \times 10^3 \text{ s} \\
 n_{e^-} &= \frac{q}{F} \\
 n_{e^-} &= \frac{It}{F} \\
 &= \frac{2.50 \frac{\text{C}}{\text{s}} \times 2.7 \times 10^3 \text{s}}{9.65 \times 10^4 \frac{\text{C}}{\text{mol}}}
 \end{aligned}$$

$$\begin{aligned}
 n_{e^-} &= 0.0699 \text{ mol} \\
 n_{\text{Al}} &= 0.0699 \frac{\text{mol}}{\text{mol e}^-} \times \frac{1 \text{ mol Al}}{3 \frac{\text{mol}}{\text{mol e}^-}} \\
 n_{\text{Al}} &= 0.0233 \text{ mol} \\
 m_{\text{Al}} &= 0.0233 \frac{\text{mol}}{\text{mol}} \times 26.98 \frac{\text{g}}{\text{mol}} \\
 m_{\text{Al}} &= 0.629 \text{ g}
 \end{aligned}$$

$$\begin{aligned}
 n_{\text{Ni}} &= 0.0699 \frac{\text{mol}}{\text{mol e}^-} \times \frac{1 \text{ mol Ni}}{2 \frac{\text{mol}}{\text{mol e}^-}} \\
 n_{\text{Ni}} &= 0.0350 \text{ mol} \\
 m_{\text{Ni}} &= 0.0350 \frac{\text{mol}}{\text{mol}} \times 58.69 \frac{\text{g}}{\text{mol}} \\
 m_{\text{Ni}} &= 2.05 \text{ g} \\
 n_{\text{Ag}} &= 0.0699 \frac{\text{mol}}{\text{mol e}^-} \times \frac{1 \text{ mol Ag}}{1 \frac{\text{mol}}{\text{mol e}^-}} \\
 n_{\text{Ag}} &= 0.0699 \text{ mol} \\
 m_{\text{Ag}} &= 0.0699 \frac{\text{mol}}{\text{mol}} \times 107.87 \frac{\text{g}}{\text{mol}} \\
 m_{\text{Ag}} &= 7.54 \text{ g}
 \end{aligned}$$

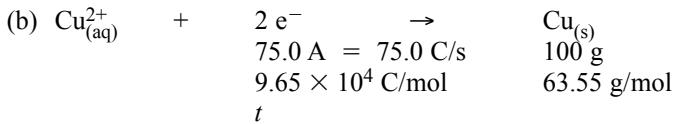
Given exactly the same current flow in each cell connected in series, the mass of aluminum plated out is 0.629 g, the mass of nickel plated out is 2.05 g, and the mass of silver plated out is 7.54 g.



$$\begin{aligned} n_{\text{Cr}} &= 100 \text{ g} \times \frac{1 \text{ mol}}{52.00 \text{ g}} \\ n_{\text{Cr}} &= 1.92 \text{ mol} \\ n_{\text{e}^-} &= 1.92 \text{ mol Cr} \times \frac{3 \text{ mol e}^-}{1 \text{ mol Cr}} \\ n_{\text{e}^-} &= 5.77 \text{ mol} \\ n_{\text{e}^-} &= \frac{q}{F} = \frac{It}{F} \\ t &= \frac{n_{\text{e}^-} F}{I} \\ &= \frac{5.77 \text{ mol} \times 9.65 \times 10^4 \frac{\text{C}}{\text{mol}}}{75.0 \frac{\text{C}}{\text{s}}} \end{aligned}$$

$$t = 7.42 \times 10^3 \text{ s}$$

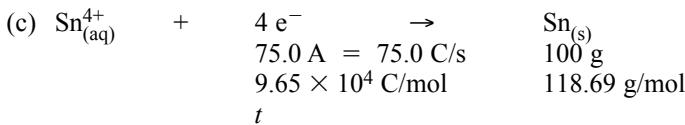
The time to plate 100 g of chromium is 7.42×10^3 s (or 2.06 h).



$$\begin{aligned} n_{\text{Cu}} &= 100 \text{ g} \times \frac{1 \text{ mol}}{63.55 \text{ g}} \\ n_{\text{Cu}} &= 1.57 \text{ mol} \\ n_{\text{e}^-} &= 1.57 \text{ mol Cu} \times \frac{2 \text{ mol e}^-}{1 \text{ mol Cu}} \\ &= 3.15 \text{ mol} \\ n_{\text{e}^-} &= \frac{q}{F} \\ n_{\text{e}^-} &= \frac{It}{F} \\ t &= \frac{n_{\text{e}^-} F}{I} \\ &= \frac{3.15 \text{ mol} \times 9.65 \times 10^4 \frac{\text{C}}{\text{mol}}}{75.0 \frac{\text{C}}{\text{s}}} \end{aligned}$$

$$t = 4.05 \times 10^3 \text{ s}$$

The time to plate 100 g of copper is 4.05×10^3 s (or 1.12 h).



$$\begin{aligned} n_{\text{Sn}} &= 100 \text{ g} \times \frac{1 \text{ mol}}{118.69 \text{ g}} \\ n_{\text{Sn}} &= 0.843 \text{ mol} \end{aligned}$$

$$n_{e^-} = 0.843 \text{ mol Sn} \times \frac{4 \text{ mol e}^-}{1 \text{ mol Sn}}$$

$$n_{e^-} = 3.37 \text{ mol}$$

$$n_{e^-} = \frac{q}{F}$$

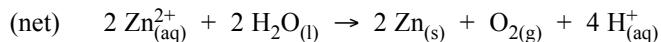
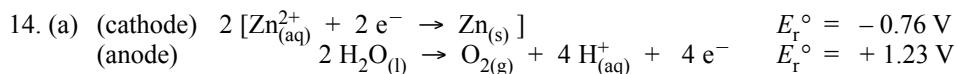
$$n_{e^-} = \frac{It}{F}$$

$$t = \frac{n_e F}{I}$$

$$= \frac{3.37 \text{ mol} \times 9.65 \times 10^4 \frac{\text{C}}{\text{mol}}}{75.0 \frac{\text{C}}{\text{s}}}$$

$$t = 4.34 \times 10^3 \text{ s}$$

The time to plate 100 g of tin is 4.34×10^3 s (or 1.20 h).

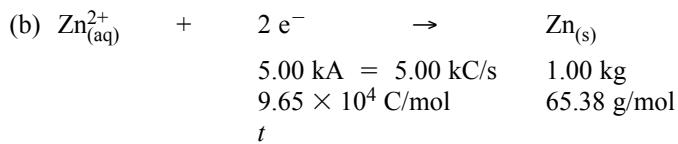


$$\Delta E^\circ = E_r^\circ \text{ (cathode)} - E_r^\circ \text{ (anode)}$$

$$= -0.76 \text{ V} - (+1.23 \text{ V})$$

$$\Delta E^\circ = -1.99 \text{ V}$$

The minimum applied potential difference required for the electrolysis is 1.99 V.



$$n_{\text{Zn}} = 1.00 \text{ kg} \times \frac{1 \text{ mol}}{65.38 \text{ g}}$$

$$n_{\text{Zn}} = 0.0153 \text{ kmol} = 15.3 \text{ mol}$$

$$n_{e^-} = 15.3 \text{ mol Zn} \times \frac{2 \text{ mol e}^-}{1 \text{ mol Zn}}$$

$$n_{e^-} = 30.6 \text{ mol}$$

$$n_{e^-} = \frac{q}{F}$$

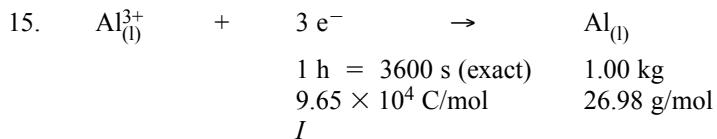
$$n_{e^-} = \frac{It}{F}$$

$$t = \frac{n_e F}{I}$$

$$= \frac{30.6 \text{ mol} \times 9.65 \times 10^4 \frac{\text{C}}{\text{mol}}}{5.00 \times 10^3 \frac{\text{C}}{\text{s}}}$$

$$t = 590 \text{ s}$$

The time to plate 1.00 kg of zinc is 590 s (or 9.84 min).



$$n_{\text{Al}} = 1.00 \text{ kg} \times \frac{1 \text{ mol}}{26.98 \text{ g}}$$

$$n_{\text{Al}} = 0.0371 \text{ kmol} = 37.1 \text{ mol}$$

$$n_{\text{e}^-} = 37.1 \text{ mol Al} \times \frac{3 \text{ mol e}^-}{1 \text{ mol Al}}$$

$$= 111 \text{ mol}$$

$$n_{\text{e}^-} = \frac{q}{F}$$

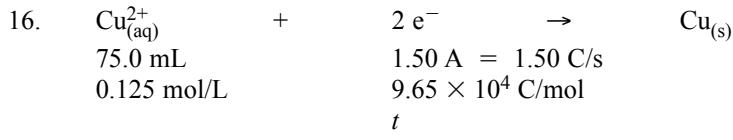
$$n_{\text{e}^-} = \frac{It}{F}$$

$$I = \frac{n_{\text{e}^-} F}{t}$$

$$= \frac{111 \text{ mol} \times 9.65 \times 10^4 \frac{\text{C}}{\text{mol}}}{3600 \text{ s}}$$

$$I = 2.98 \times 10^3 \text{ C/s} = 2.98 \text{ kA}$$

The current required to produce 1.00 kg of aluminum per hour is 2.98 kA.



$$n_{\text{Cu}^{2+}} = Cv$$

$$= 0.125 \frac{\text{mol}}{\text{L}} \times 0.0750 \text{ L}$$

$$n_{\text{Cu}^{2+}} = 0.00938 \text{ mol}$$

$$n_{\text{e}^-} = 0.00938 \text{ mol Cu}^{2+} \times \frac{2 \text{ mol e}^-}{1 \text{ mol Cu}^{2+}}$$

$$n_{\text{e}^-} = 0.0188 \text{ mol}$$

$$n_{\text{e}^-} = \frac{q}{F}$$

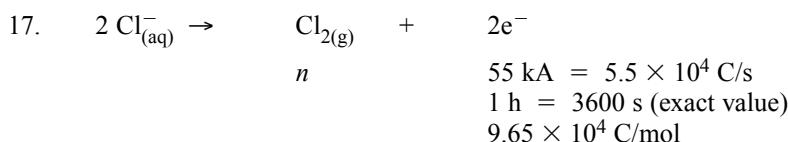
$$n_{\text{e}^-} = \frac{It}{F}$$

$$t = \frac{n_{\text{e}^-} F}{I}$$

$$= \frac{0.0188 \text{ mol} \times 9.65 \times 10^4 \frac{\text{C}}{\text{mol}}}{1.50 \frac{\text{C}}{\text{s}}}$$

$$t = 1.21 \times 10^3 \text{ s} \times \frac{1 \text{ min}}{60 \text{ s}} = 20.1 \text{ min}$$

The time for the copper to plate from solution is 20.1 min.



$$n_{e^-} = \frac{q}{F}$$

$$n_{e^-} = \frac{It}{F}$$

$$n_{e^-} = \frac{5.5 \times 10^4 \frac{\text{C}}{\text{s}} \times 3600 \text{ s}}{9.65 \times 10^4 \frac{\text{C}}{\text{mol}}}$$

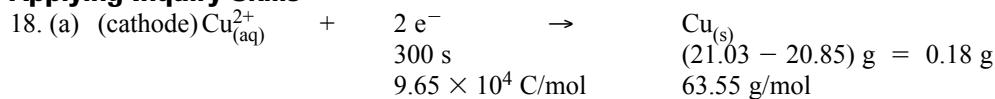
$$n_{e^-} = 2.1 \times 10^3 \text{ mol} = 2.1 \text{ kmol}$$

$$n_{\text{Cl}_2} = 2.1 \text{ kmol} \times \frac{1 \text{ mol Cl}_2}{2 \text{ mol e}^-}$$

$$n_{\text{Cl}_2} = 1.0 \text{ kmol}$$

The chlorine gas is produced at a rate of 1.0 kmol/h.

Applying Inquiry Skills



$$I \\ n_{\text{Cu}} = 0.18 \text{ g} \times \frac{1 \text{ mol}}{63.55 \text{ g}}$$

$$n_{\text{Cu}} = 0.00283 \text{ mol}$$

$$n_{\text{e}^-} = 0.00283 \text{ mol Cu} \times \frac{2 \text{ mol e}^-}{1 \text{ mol Cu}}$$

$$= 0.00566 \text{ mol}$$

$$n_{\text{e}^-} = \frac{q}{F}$$

$$n_{\text{e}^-} = \frac{It}{F}$$

$$I = \frac{n_{\text{e}^-} F}{t}$$

$$= \frac{0.00566 \text{ mol} \times 9.65 \times 10^4 \frac{\text{C}}{\text{mol}}}{300 \text{ s}}$$

$$I = 1.8 \text{ C/s} = 1.8 \text{ A}$$

The average current required to reduce 0.18 g of copper at the cathode is 1.8 A.

Note: The mass loss at the anode is the same value as the mass gain at the cathode, and the half-reaction ratios are the same; so the same value for average current will be obtained, if calculated from the anode mass change.



$$(53.14 - 52.96) \text{ g} = 0.18 \text{ g}$$

The average current required to oxidize 0.18 g of copper at the anode is 1.8 A.

- (b) The primary source of experimental error in this case is the precision of the balance, which limits the mass value used to only two significant digits. One could also say that the size of the mass change is too small because doing the experiment for ten times as long would give mass changes of three significant digits. Another likely source of error is the usual variation in the current flow over time as the cell operates, which requires constant adjustment of the current used by the experimenter.

$$(c) \% \text{ difference} = \frac{|\text{experimental value} - \text{predicted value}|}{\text{predicted value}} \times 100\%$$

$$= \frac{|1.8 \text{ A} - 1.85 \text{ A}|}{1.85 \text{ A}} \times 100\%$$

% difference = 2%

The ammeter accuracy appears reasonably good. However, this is a tentative conclusion because the precision of the experiment is poor.

Making Connections

19. (a) The plastic is made conductive by a chemical dipping of the cleaned/treated plastic to make an adhering layer of copper or nickel/palladium.
 - (b) The surface must be thoroughly cleaned and etched by removing some surface plastic molecules. In one process for ABS plastic, the initial layer is catalytic palladium, which is then covered with a layer of nickel. In other processes, copper is deposited first. In all cases, several other layers of metal are then added, usually by electrolysis, to produce the final plated product.
 - (c) An important limitation is the ability to create molecular-size pits in the plastic surface to adhere the initial metal layer. Metal plating plastics makes them less flexible and the plating may crack. As a general rule, if the object has to bend, then it should not be plated. Selective plating may be used with some objects.
20. Chromium from electroplating waste solutions can be removed by first reducing the chromium from the +6 oxidation state to the +3 state using a reducing agent such as sodium bisulfite. The chromium(III) ions are then precipitated as a nontoxic chromium(III) hydroxide.

UNIT 5 PERFORMANCE TASK: ELECTROPLATING

(Page 762)

Purpose

The purpose is to create a process for plating copper onto a metal object.

Question

What design produces a smooth layer of copper metal that adheres to a metal object?

Prediction

- (a) According to the redox concepts in this unit and some Internet research, a metal object can be plated at the cathode of a copper(II) sulfate electrolytic cell. The key independent variable is the electric current. The best plating should occur at relatively low currents because this produces a relatively low rate of plating. The assumption is that the quality of the copper plating will be better if it forms more slowly.

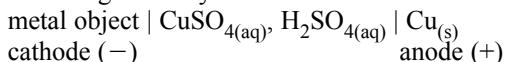


The amount of copper formed depends directly on the amount of electrons transferred. The amount of electrons per unit of time depends directly on the current.

Experimental Design

A small metal object is carefully cleaned and plated with copper. The dependent variable is the quality of the copper plating as determined by its thickness, appearance, and adherence to the object.

- (b) The following electrolytic cell is constructed.



Based on other copper-plating cells, copper(II) sulfate is acidified with a sulfuric cell.

- (c) The independent variable used is the electric current. Other potential variables that are held constant are: surface area of the metal in the solution; cleaning of the metal surface; distance between the electrodes; charge transferred ($q = It$); and the composition, concentration, and temperature of the electrolyte.

$$(c) \% \text{ difference} = \frac{|\text{experimental value} - \text{predicted value}|}{\text{predicted value}} \times 100\%$$

$$= \frac{|1.8 \text{ A} - 1.85 \text{ A}|}{1.85 \text{ A}} \times 100\%$$

$$\% \text{ difference} = 2\%$$

The ammeter accuracy appears reasonably good. However, this is a tentative conclusion because the precision of the experiment is poor.

Making Connections

19. (a) The plastic is made conductive by a chemical dipping of the cleaned/treated plastic to make an adhering layer of copper or nickel/palladium.
(b) The surface must be thoroughly cleaned and etched by removing some surface plastic molecules. In one process for ABS plastic, the initial layer is catalytic palladium, which is then covered with a layer of nickel. In other processes, copper is deposited first. In all cases, several other layers of metal are then added, usually by electrolysis, to produce the final plated product.
(c) An important limitation is the ability to create molecular-size pits in the plastic surface to adhere the initial metal layer. Metal plating plastics makes them less flexible and the plating may crack. As a general rule, if the object has to bend, then it should not be plated. Selective plating may be used with some objects.
20. Chromium from electroplating waste solutions can be removed by first reducing the chromium from the +6 oxidation state to the +3 state using a reducing agent such as sodium bisulfite. The chromium(III) ions are then precipitated as a nontoxic chromium(III) hydroxide.

UNIT 5 PERFORMANCE TASK: ELECTROPLATING

(Page 762)

Purpose

The purpose is to create a process for plating copper onto a metal object.

Question

What design produces a smooth layer of copper metal that adheres to a metal object?

Prediction

- (a) According to the redox concepts in this unit and some Internet research, a metal object can be plated at the cathode of a copper(II) sulfate electrolytic cell. The key independent variable is the electric current. The best plating should occur at relatively low currents because this produces a relatively low rate of plating. The assumption is that the quality of the copper plating will be better if it forms more slowly.

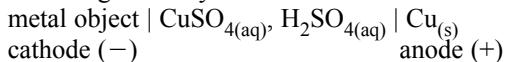


The amount of copper formed depends directly on the amount of electrons transferred. The amount of electrons per unit of time depends directly on the current.

Experimental Design

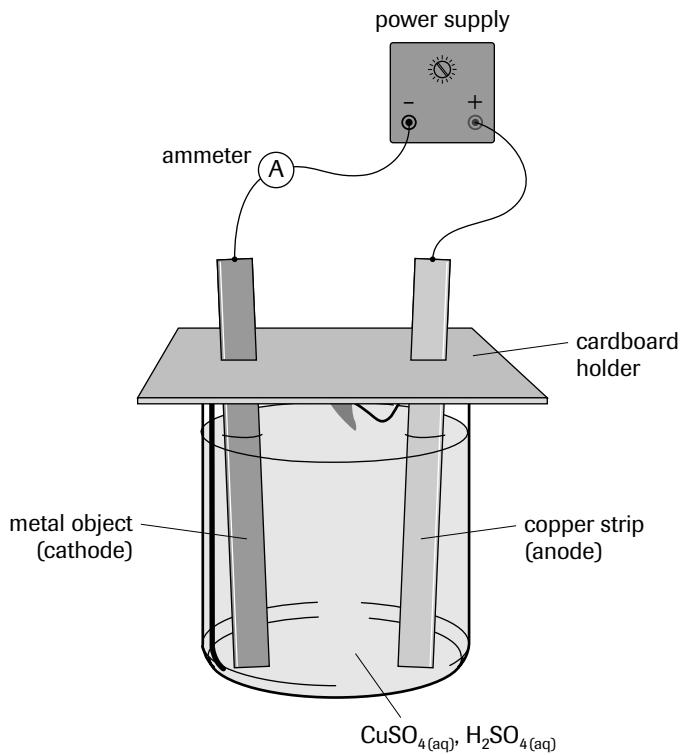
A small metal object is carefully cleaned and plated with copper. The dependent variable is the quality of the copper plating as determined by its thickness, appearance, and adherence to the object.

- (b) The following electrolytic cell is constructed.



Based on other copper-plating cells, copper(II) sulfate is acidified with a sulfuric cell.

- (c) The independent variable used is the electric current. Other potential variables that are held constant are: surface area of the metal in the solution; cleaning of the metal surface; distance between the electrodes; charge transferred ($q = It$); and the composition, concentration, and temperature of the electrolyte.



Materials

(d) lab apron

eye protection

150-mL beaker

three 250-mL beakers

cardboard holder

pure copper strip

4 stainless steel objects (e.g., lab scoopulas)

connecting wires

digital multimeter

variable power supply

steel wool

stirring rod

paper towel

bottle of distilled water

clock

acetone

0.50 mol/L $\text{CuSO}_4\text{(aq)}$

0.50 mol/L $\text{H}_2\text{SO}_4\text{(aq)}$ (corrosive, rinse with water on contact)

CAUTION:

Copper sulfate solution is toxic and an irritant. Sulfuric acid is corrosive. If either of them comes into contact with skin or clothing, rinse with lots of water.

Procedure

1. Set up three 250-mL beakers with about 200 mL each of distilled water, sulfuric acid, and acetone.
2. Carefully clean the stainless steel objects and the copper strip with steel wool. Rinse with distilled water.
3. Place the 4 steel objects and the copper for about 1 min into the 250-mL beaker of sulfuric acid, then the distilled water, and finally, the acetone.
4. Remove the metal strips and lay them out on a paper towel to dry. Be careful to handle the metals only by the end that will not be in the electrolyte.

5. Using the markings on the beaker, add 70 mL of $\text{CuSO}_4\text{(aq)}$ and 70 mL of $\text{H}_2\text{SO}_4\text{(aq)}$ to the 150-mL beaker and stir.
6. Insert the copper strip into a slit in the cardboard holder and one of the steel objects into the other slit. Arrange the metals so that they will reach the bottom of the beaker.
7. Connect the electrodes to the meter and power supply, making sure that the copper is the anode (+, red) and the steel object is the cathode (–, black).
8. Check all connections before plugging the power supply into the electrical outlet.
9. Turn on the power supply and note the time on the clock. Quickly adjust the power supply for a current of 0.050 A.
10. During the operation of the cell, make any small adjustments necessary to keep the current constant.
11. Shut off the power supply after 30.0 min and unplug.
12. Carefully remove the steel object, and dip it into the beaker of distilled water and then into the beaker of acetone. Set it on a paper towel to dry.
13. Dispose of the acidic electrolyte into the container labelled “Recycled acidic copper(II) sulfate.”
14. Repeat steps 5 to 13, using 0.150 A for 6.0 min, 0.500 A for 3.0 min, and 0.750 A for 2.0 min.
15. Clean and return all of the metals for reuse.

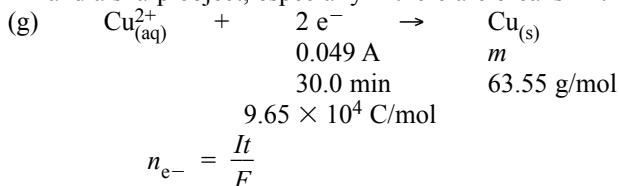
Evidence

Electroplating of Stainless Steel Objects				
Object	Initial appearance	Current (A)	Time (min)	Observations of final plating
1	shiny, silver	0.049	30.0	<ul style="list-style-type: none"> • somewhat shiny, light reddish-brown patches • does not rub off on paper or finger • comes off fairly easily with steel wool • very little plating on the back of the object
2	shiny, silver	0.249	6.0	<ul style="list-style-type: none"> • somewhat shiny, light reddish-brown in a smooth even layer • does not rub off with paper or finger • when rubbed lightly with steel wool, became more shiny and did not rub off • plating can be removed by scraping with a sharp object • some plating on the back of the object
3	shiny, silver	0.503	3.0	<ul style="list-style-type: none"> • darker, reddish-brown, fairly dull layer • rubs off easily with paper and finger • back of object is plated like the front of #2
4	shiny, silver	0.750	2.0	<ul style="list-style-type: none"> • darkest, red-brown layer with some light and dull, dark patches • appears thicker and quite granular • rubs off very easily with paper or finger • back of object is plated like the front of #2

- Each stainless steel object was about 1.5 cm wide, 15 cm long, and about 6 cm immersed in electrolyte.
- The distance between the electrodes was about 4 cm.

Analysis

(f) In general, the lower currents produce a thin layer of copper that is shiny and adheres reasonably well to the metal object. The larger currents produce a darker, duller, loose deposit that immediately wipes off to expose the original metal finish. The best copper plating appears to be at a current of about 0.250 A, although about 0.050 A may be as good if left longer to cover the whole surface of the object. Even the best plating can be removed with a little effort and a sharp object, especially if there are breaks in the surface.



$$= \frac{0.049 \text{ C/s} \times 30.0 \text{ min} \times 60 \text{ s/min}}{9.65 \times 10^4 \text{ C/mol}}$$

$$\begin{aligned}n_{e^-} &= 9.1 \times 10^{-4} \text{ mol} \\n_{\text{Cu}} &= 9.1 \times 10^{-4} \text{ mol e}^- \times \frac{1 \text{ mol Cu}}{2 \text{ mol e}^-} \\n_{\text{Cu}} &= 4.6 \times 10^{-4} \text{ mol} \\m_{\text{Cu}} &= 4.6 \times 10^{-4} \text{ mol} \times \frac{63.55 \text{ g}}{1 \text{ mol}} \\m_{\text{Cu}} &= 2.9 \times 10^{-4} \text{ g}\end{aligned}$$

The other masses of copper deposited were very similar because the charge was controlled. For objects 2, 3, and 4, the mass of copper deposited was $3.0 \times 10^{-2} \text{ g}$.

Evaluation

- (h) In general, the design appears adequate to answer the question because it appears that electric current is a significant variable that affects the plating process. The materials were adequate, although the power supply was a little difficult to control to a predetermined value of the current. However, this would not seem to be a major problem. I am uncertain about the purpose and effect of acidifying the copper(II) sulfate with sulfuric acid. The procedure seemed to work well and gave sufficient evidence to answer the question.
- (i) The design seems to be promising because the final results were relatively clear. However, even the best plating could be scratched off with a little effort. Either a better surface preparation or a protective layer (e.g., a varnish) may be needed to produce a better plated object. The object was plated mostly on the side facing the anode, which is not very good if you want all sides of the object to be plated. Some of the other controlled variables need to be investigated to see if some other combination of variables, along with a low current, can improve the plating.
- (j) Some minor adjustments include a better control of the power supply, and perhaps mixing the electrolyte during the process. Some major adjustments include rotating the object to plate it on all sides and creating a surface to which the copper might adhere better (perhaps a rougher or pitted surface).
- (k) Two things were learned. One is that plating is not as easy as it sounds in a textbook. Secondly, there are many possible variables that make the discovery of the right combination of them a very long trial-and-error process of experimentation.

UNIT 5 SELF-QUIZ

(Page 764)

1. True
2. False: Reduction is the gain of electrons and occurs at the *cathode anode* of any cell.
3. False: Oxidation is the ~~decrease increase~~ in oxidation number and reduction is the ~~decrease increase~~ in oxidation number.
4. True
5. False: Inert electrodes are required for *some all* electrolytic cells.
6. True
7. True
8. False: The cell potential is determined by *subtracting adding* the reduction potentials for the two half-cell reactions.
9. True
10. False: A standard hydrogen–cobalt cell has a cell potential of ~~-0.28~~ +0.28 V.
11. False: In a standard copper–lead cell, lead is the *anode cathode* and copper is the *cathode anode*.
12. True
13. False: The charge transferred by a 1.5-A current in a time of 2.0 min is 1.8×10^2 ~~3.0~~ C.
14. True
15. True
16. True
17. False: ~~Both tin and zinc plating work equally well in inhibiting the corrosion of iron. Zinc inhibits iron corrosion much better than tin, because its reduction potential is lower than that of iron.~~
18. False: Large *electrolytic galvanic* cells are used to refine metals and to produce nonmetals like chlorine.

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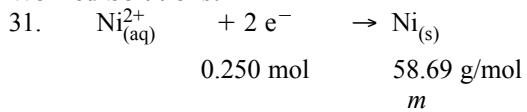
UNIT 5 SELF-QUIZ

(Page 764)

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18. False: Large *electrolytic galvanic* cells are used to refine metals and to produce nonmetals like chlorine.

19. (b)
 20. (d)
 21. (c)
 22. (c)
 23. (d)
 24. (a)
 25. (b)
 26. (d)
 27. (a)
 28. (d)
 29. (b)
 30. (b)
 31. (c)
 32. (a)
 33. (c)
 34. (d)
 35. (a)
 36. (b)

Worked Solutions:

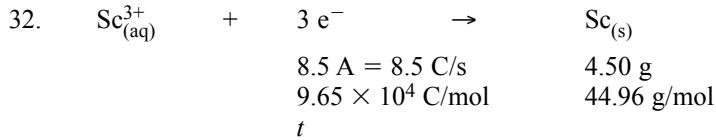


$$n_{\text{Ni}} = 0.250 \cancel{\text{mol e}^-} \times \frac{1 \text{ mol Ni}}{2 \cancel{\text{mol e}^-}}$$

$$n_{\text{Ni}} = 0.125 \text{ mol}$$

$$m_{\text{Ni}} = 0.125 \cancel{\text{mol}} \times 58.69 \frac{\text{g}}{\cancel{\text{mol}}}$$

$$m_{\text{Ni}} = 7.34 \text{ g} \quad (\text{c})$$



$$n_{\text{Sc}} = 4.50 \cancel{\text{g}} \times \frac{1 \text{ mol}}{44.96 \cancel{\text{g}}}$$

$$n_{\text{Sc}} = 0.100 \text{ mol}$$

$$n_{\text{e}^-} = 0.100 \cancel{\text{mol Sc}} \times \frac{3 \text{ mol e}^-}{1 \cancel{\text{mol Sc}}} \\ = 0.300 \text{ mol}$$

$$n_{\text{e}^-} = \frac{q}{F}$$

$$n_{\text{e}^-} = \frac{It}{F}$$

$$t = \frac{n_e F}{I}$$

$$= \frac{0.300 \cancel{\text{mol}} \times 9.65 \times 10^4 \frac{\text{C}}{\cancel{\text{mol}}}}{8.5 \frac{\text{C}}{\text{s}}}$$

$$t = 3.4 \times 10^3 \text{ s}$$

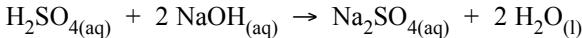
$$t = 3.4 \times 10^3 \cancel{\text{s}} \times \frac{1 \text{ min}}{60 \cancel{\text{s}}} = 57 \text{ min} \quad (\text{a})$$

UNIT 5 REVIEW

(Page 766)

Understanding Concepts

- Reduction is a process in which electrons are gained; and the oxidation number of an atom decreases.
 Oxidation is a process in which electrons are lost; and the oxidation number of an atom increases.
 A redox reaction is one involving the transfer of electrons from one particle to another.
- Some chemical reactions are not redox reactions. They can be recognized by the fact that no entity changes in oxidation number. Most examples are double displacement reactions, such as:



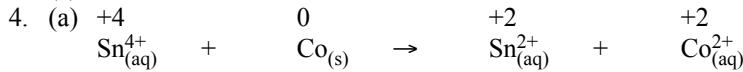
- (a) -2

(b) +4

(c) +6

(d) +4

(e) 0



Sn^{4+} is reduced; Co is oxidized.



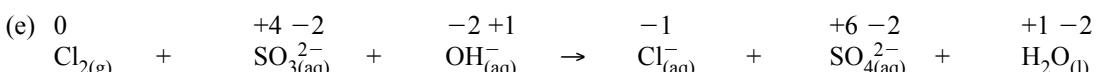
Fe^{3+} is reduced; Zn is oxidized.



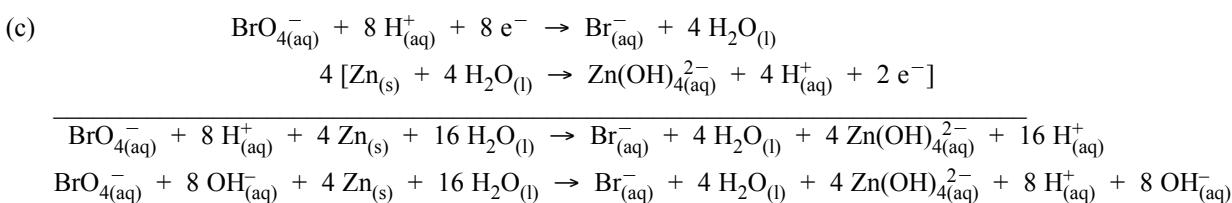
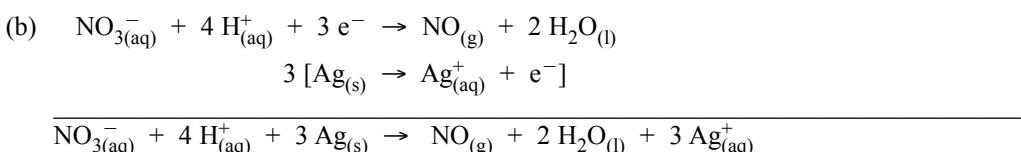
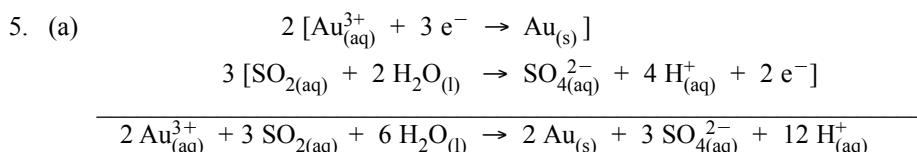
Cl is reduced; I^- is oxidized.

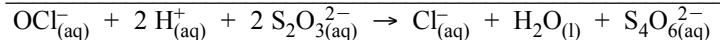
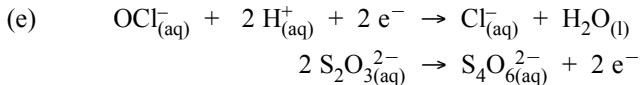
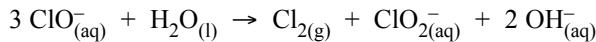
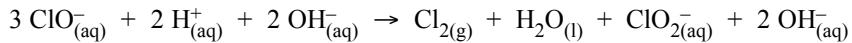
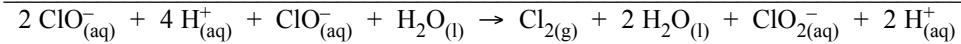
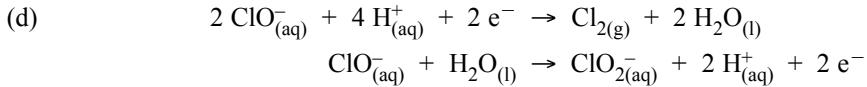
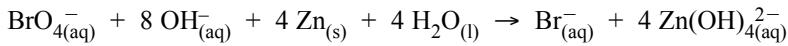


Mn is reduced; C is oxidized.



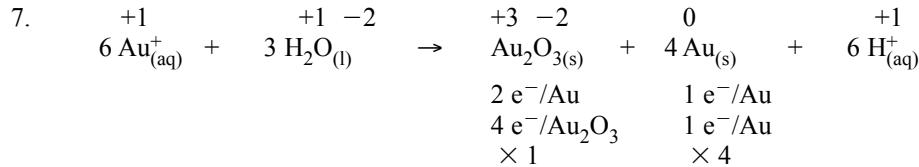
Cl is reduced; S is oxidized.





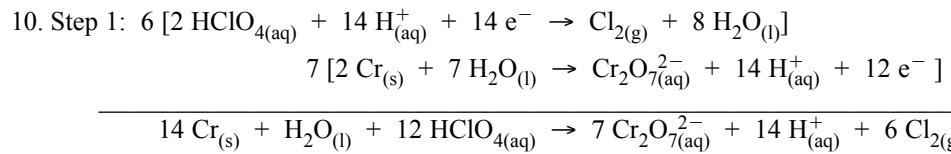
Note: Hypochlorite ion is commonly written both as ClO^- , and as OCl^- . It has been written in different ways in questions (d) and (e), to familiarize students with the use of both symbolisms.

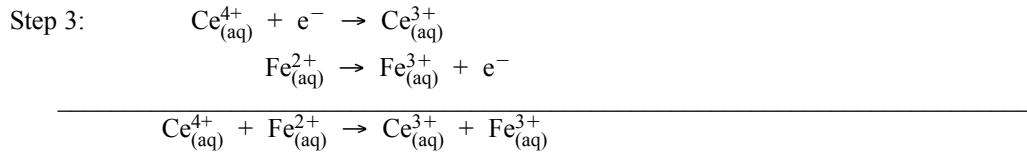
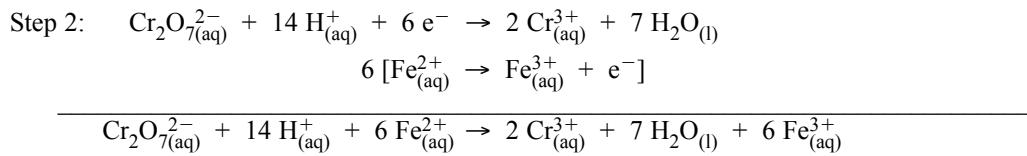
6. (a) Oxidation numbers: Cu^+ is +1, Cu is 0, and Cu^{2+} is +2
 (b) $\text{Cu}_{(\text{aq})}^+ \rightarrow \text{Cu}_{(\text{aq})}^{2+} + \text{e}^-$
 (c) $\text{Cu}_{(\text{aq})}^+ + \text{e}^- \rightarrow \text{Cu}_{(\text{s})}$
 (d) $2 \text{Cu}_{(\text{aq})}^+ \rightarrow \text{Cu}_{(\text{aq})}^{2+} + \text{Cu}_{(\text{s})}$
 (e) Three other ions that can behave as oxidizing or reducing agents are $\text{Sn}_{(\text{aq})}^+$, $\text{Cr}_{(\text{aq})}^{2+}$, and $\text{Fe}_{(\text{aq})}^{2+}$.



Note: When particles of a single reactant are both oxidized and reduced (auto-oxidation, or self-oxidation–reduction), then “bookkeeping” for electron gain and loss balancing can be done on the product side of the equation, as shown above.

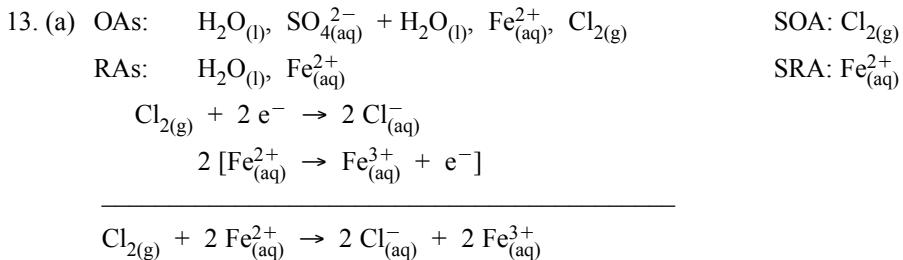
8. (a) $\text{I}_{(\text{aq})}^- + 3 \text{H}_2\text{O}_{(\text{l})} \rightarrow \text{IO}_{3(\text{aq})}^- + 6 \text{H}_{(\text{aq})}^+ + 6 \text{e}^-$
 (b) $\text{Cl}_{2(\text{aq})}^- + 2 \text{e}^- \rightarrow 2 \text{Cl}_{(\text{aq})}^-$ [$\times 3$, to balance electrons]
 (c) $\text{I}_{(\text{aq})}^- + 3 \text{H}_2\text{O}_{(\text{l})} + 3 \text{Cl}_{2(\text{aq})}^- \rightarrow \text{IO}_{3(\text{aq})}^- + 6 \text{H}_{(\text{aq})}^+ + 6 \text{Cl}_{(\text{aq})}^-$
 9. (a) $\text{Ni}_{(\text{s})} + 2 \text{H}_2\text{SO}_{4(\text{aq})} \rightarrow \text{NiSO}_{4(\text{aq})} + 2 \text{H}_2\text{O}_{(\text{l})} + \text{SO}_{2(\text{g})}$
 (b) $\text{I}_{2(\text{s})} + 10 \text{NO}_{3(\text{aq})}^- + 8 \text{H}_{(\text{aq})}^+ \rightarrow 2 \text{IO}_{3(\text{aq})}^- + 10 \text{NO}_{2(\text{s})} + 4 \text{H}_2\text{O}_{(\text{l})}$
 (c) $\text{Cr}_2\text{O}_{7(\text{aq})}^{2-} + 14 \text{H}_{(\text{aq})}^+ + 6 \text{Cl}_{(\text{aq})}^- \rightarrow 2 \text{Cr}_{(\text{aq})}^{3+} + 3 \text{Cl}_{2(\text{g})} + 7 \text{H}_2\text{O}_{(\text{l})}$
 (d) $4 \text{Zn}_{(\text{s})} + 5 \text{H}_2\text{SO}_{4(\text{aq})} \rightarrow 4 \text{ZnSO}_{4(\text{aq})} + \text{H}_2\text{S}_{(\text{g})} + 4 \text{H}_2\text{O}_{(\text{l})}$
 (e) $3 \text{I}_{2(\text{s})} + 6 \text{OH}_{(\text{aq})}^- \rightarrow 5 \text{I}_{(\text{aq})}^- + \text{IO}_{3(\text{aq})}^- + 3 \text{H}_2\text{O}_{(\text{l})}$



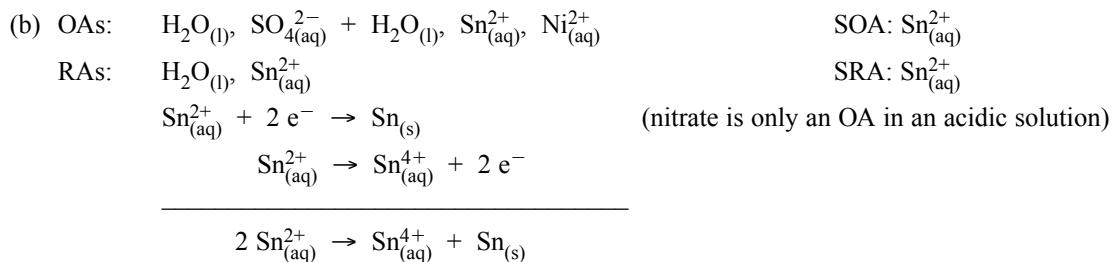


11. When a spontaneous redox reaction occurs, one might observe formation of a gas and/or solid, and/or a colour change, and/or an energy change.

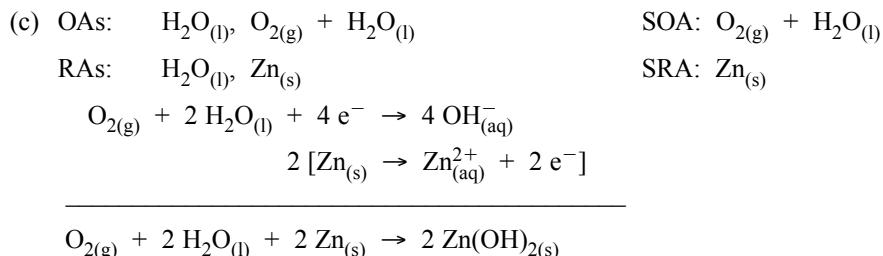
12. (a) nonspontaneous
 (b) spontaneous
 (c) nonspontaneous



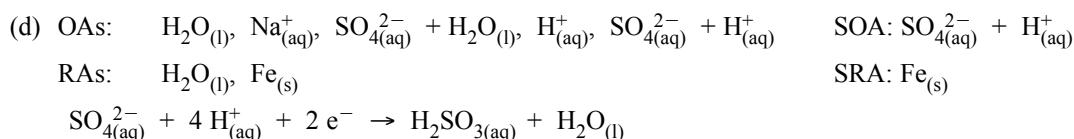
The strongest oxidizing agent present in the mixture is higher in the table of reduction potentials than is the strongest reducing agent, so the most probable oxidation-reduction reaction should be spontaneous.

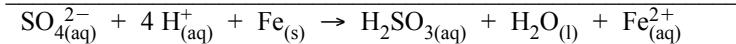
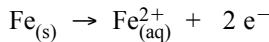


The strongest oxidizing agent present in the mixture is lower in the table of reduction potentials than is the strongest reducing agent, so the most probable oxidation-reduction reaction should be nonspontaneous.

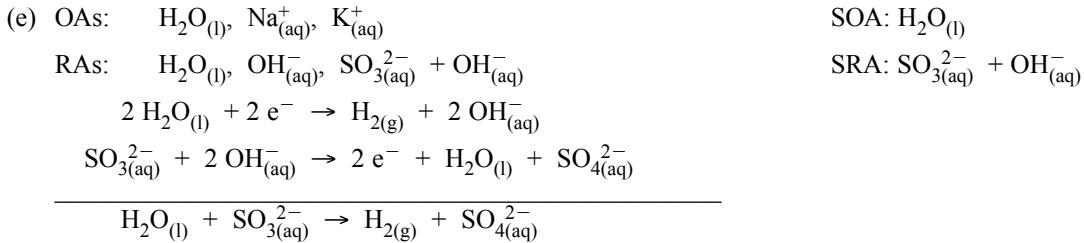


The strongest oxidizing agent present in the mixture is higher in the table of reduction potentials than is the strongest reducing agent, so the most probable oxidation-reduction reaction should be spontaneous.



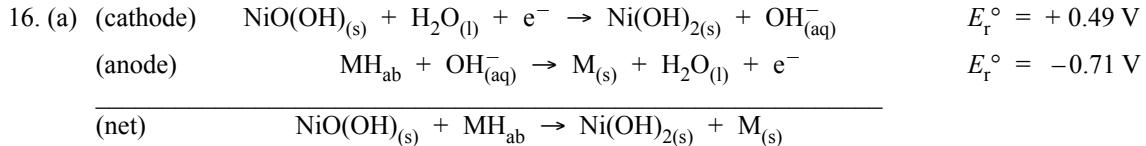


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The strongest oxidizing agent present is higher in the table of reduction potentials than is the strongest reducing agent, so the most probable oxidation-reduction reaction should be spontaneous.

14. Two technological solutions to the problem of batteries going “dead” are secondary (rechargeable) cells, and fuel cells.
15. Technology preceded scientific explanations in the areas of reduction of metals from ores, and in the oxidation of metals, and in the development of electric cells to supply electric current.

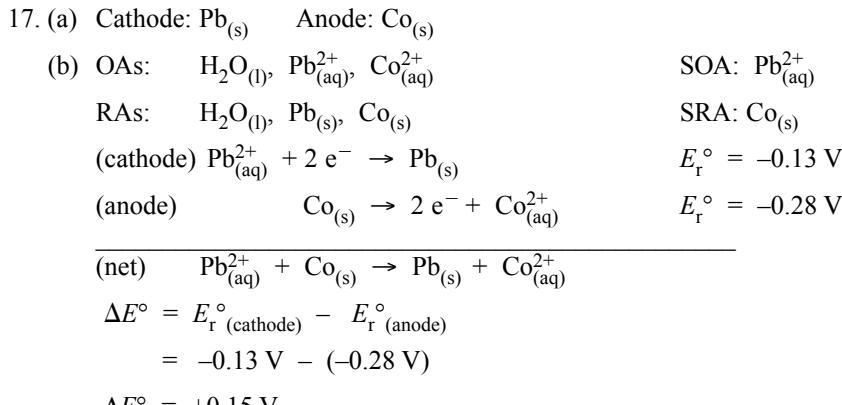


$$\begin{aligned} (\text{b}) \quad \Delta E^\circ &= E_r^\circ \text{ (cathode)} - E_r^\circ \text{ (anode)} \\ &= +0.49 \text{ V} - (-0.71 \text{ V}) \\ \Delta E^\circ &= +1.20 \text{ V} \end{aligned}$$

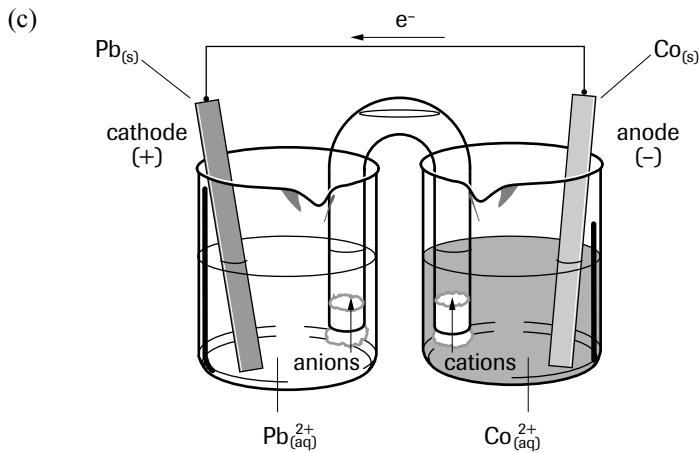
The cell potential of a NiMH battery is +1.20 V.

- (c) Considerations for evaluating the NiMH battery include:

- Economic: NiMH cells are considerably more expensive than alkaline cells or NiCd rechargeables.
- Technological: NiMH cells contain more energy than other rechargeables, and can be recharged many more times before failing, and can deliver higher current (more power) than other types.
- Ecological/environmental: NiMH cells contain no heavy metals and fewer toxic materials than other rechargeables, making them less dangerous and also easier to recycle.



The potential of a lead–cobalt standard cell is 0.15 V.



18. $\Delta E^\circ = E_r^\circ(\text{cathode}) - E_r^\circ(\text{anode})$

(a) $\Delta E^\circ = [-0.40 - (-0.91)] \text{ V}$
 $\Delta E^\circ = 0.51 \text{ V}$

(b) $\Delta E^\circ = [-0.13 - (-0.76)] \text{ V}$
 $\Delta E^\circ = 0.63 \text{ V}$

(c) $\Delta E^\circ = [+1.23 - (-0.28)] \text{ V}$
 $\Delta E^\circ = 1.51 \text{ V}$

19. (a) $\Delta E^\circ = E_r^\circ(\text{cathode}) - E_r^\circ(\text{anode})$

$$E_r^\circ(\text{anode}) = E_r^\circ(\text{cathode}) - \Delta E^\circ$$

$E_r^\circ(\text{anode}) = +0.34 \text{ V} - (+0.48 \text{ V})$ (Note that Cu²⁺ is reduced; therefore, Cu is the cathode.)

$$E_r^\circ(\text{anode}) = -0.14 \text{ V}$$

This answer matches the standard reduction potential of the $\text{Sn}_{(\text{aq})}^{2+} + 2 \text{ e}^- \rightarrow \text{Sn}_{(\text{s})}$ half-reaction. Therefore, X may be Sn.

- (b) The negative value obtained for this reduction potential means that tin(II) ions are weaker oxidizing agents than hydrogen ions, under standard conditions.

20. The cadmium/cadmium(II) reduction potential is -0.40 V and the cell potential is $+1.85 \text{ V}$. This means that the neodymium/neodymium(III) reduction potential must, therefore, either be 1.85 V higher, or lower, than -0.40 V .

If higher, neodymium is the cathode, and

$$\Delta E^\circ = E_r^\circ(\text{cathode}) - E_r^\circ(\text{anode})$$

$$E_r^\circ(\text{cathode}) = \Delta E^\circ + E_r^\circ(\text{anode})$$

$$E_r^\circ(\text{cathode}) = +1.85 \text{ V} + (-0.40 \text{ V})$$

$$E_r^\circ(\text{cathode}) = +1.45 \text{ V}$$

or if lower, neodymium is the anode, and

$$E_r^\circ(\text{anode}) = E_r^\circ(\text{cathode}) - \Delta E^\circ$$

$$E_r^\circ(\text{anode}) = -0.40 \text{ V} - (+1.85 \text{ V})$$

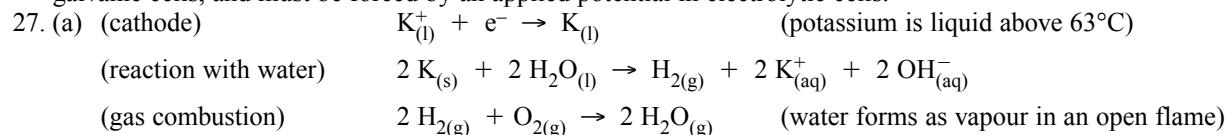
$$E_r^\circ(\text{anode}) = -2.25 \text{ V}$$

The standard reduction potential for the $\text{Nd}_{(\text{aq})}^{3+} | \text{Nd}_{(\text{s})}$ half-cell is either $+1.45 \text{ V}$, or -2.25 V .

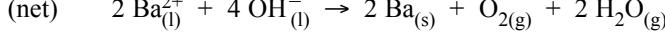
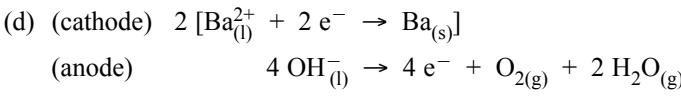
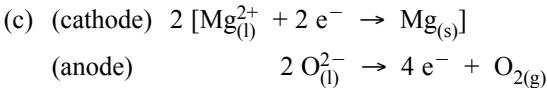
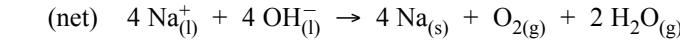
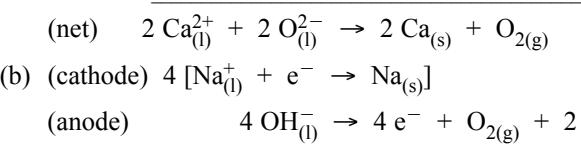
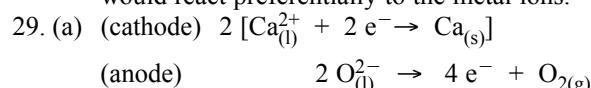
21. Gold, silver, and platinum are relatively unreactive as reducing agents, and thus resist corrosion.

22. Sterling silver contains copper, which is a much stronger reducing agent than silver. In effect, the presence of the copper makes the alloy more reactive because the copper acts as a reducing agent in the presence of oxidizing agents such as oxygen.

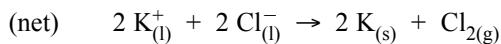
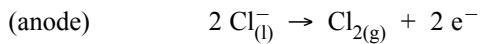
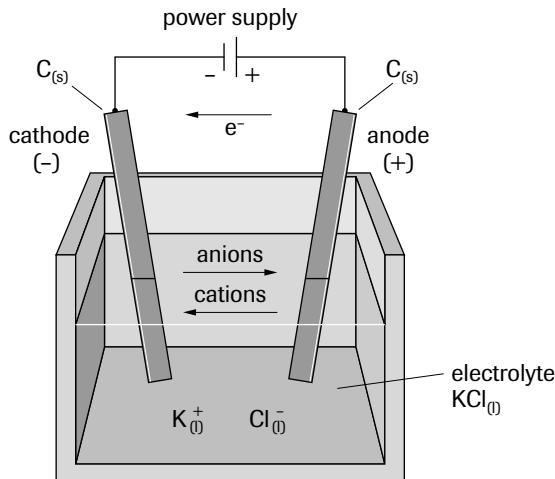
23. Chromium plating gives steel a very shiny surface. Zinc plating produces a mottled surface, and tin plating a fairly dull surface. All three metals are easily oxidized in air but the oxide layer on each metal is generally very thin and adheres tightly to the metal. Chromium and zinc are both stronger reducing agents than iron, meaning that if the plating is scratched, they will react in preference to the iron. If a tin plating surface is broken, a spontaneous reaction occurs between the iron and the tin ions on the tin's surface. This means that the presence of the tin will then actually accelerate any corrosion of the steel underneath.
24. An impressed current can be used to prevent the corrosion of a buried steel pipe by applying a voltage that forces the steel to act as a cathode, thus preventing oxidation of iron atoms.
25. Corrosion often occurs where two different metals join because any moisture connecting the two metals sets up a tiny galvanic cell (like Volta's cell). Two different metals have different electric potentials, which creates an electric current in the presence of an electrolyte.
26. The main differences between galvanic and electrolytic cells in terms of their purpose is that galvanic cells are designed to produce electrical energy, while electrolytic cells are designed to produce chemical substances using electrical energy. The types of half-reactions that occur are essentially the same, except that they are spontaneous only in galvanic cells, and must be forced by an applied potential in electrolytic cells.



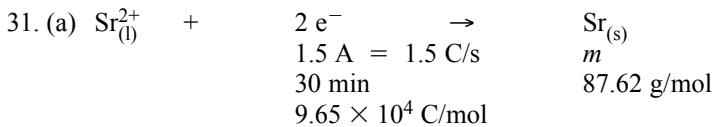
- (b) The gas burned with a violet flame because of the presence of traces of potassium ions.
28. (a) It was necessary to melt the compounds because only in molten state are the ions free to move to complete the charge transfer within the liquid.
- (b) Electrolyzing aqueous solutions of the compounds will not work because water is a stronger oxidizing agent and would react preferentially to the metal ions.



30. (a)



(c) Our redox table has reduction potentials only for standard conditions: 1 mol/L electrolytes and SATP. The conditions of molten salt electrolysis are very different. Therefore, the reduction potentials would be very different.



$$t = 30 \cancel{\text{min}} \times \frac{60 \text{ s}}{1 \cancel{\text{min}}} = 1.8 \times 10^3 \text{ s}$$

$$n_{e^-} = \frac{q}{F}$$

$$n_{e^-} = \frac{It}{F}$$

$$= \frac{1.5 \frac{C}{s} \times 1.8 \times 10^3 \cancel{s}}{9.65 \times 10^4 \frac{C}{mol}}$$

$$n_{e^-} = 0.0280 \text{ mol}$$

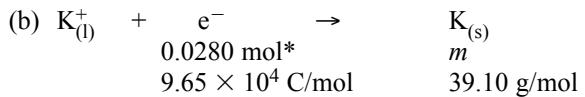
$$n_{Sr} = 0.0280 \cancel{mol e^-} \times \frac{1 \text{ mol Sr}}{2 \cancel{mol e^-}}$$

$$n_{Sr} = 0.0140 \text{ mol}$$

$$m_{Sr} = 0.0140 \cancel{mol} \times 87.62 \frac{g}{\cancel{mol}}$$

$$m_{Sr} = 1.23 \text{ g}$$

The mass of strontium produced is 1.23 g.



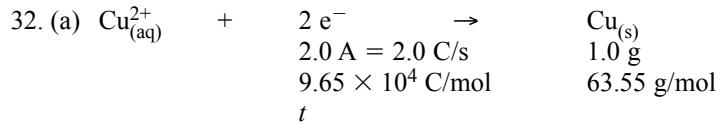
$n_{\text{K}} = 0.0280 \cancel{\text{mol}} \text{e}^- \times \frac{1 \text{ mol K}}{1 \cancel{\text{mol e}^-}}$ (* the amount of charge is identical to that in part (a))

$$n_{\text{K}} = 0.0280 \text{ mol}$$

$$m_{\text{K}} = 0.0280 \cancel{\text{mol}} \times 39.10 \frac{\text{g}}{\cancel{\text{mol}}}$$

$$m_{\text{K}} = 1.09 \text{ g}$$

The mass of potassium produced is 1.09 g.



t

$$n_{\text{Cu}} = 1.0 \cancel{\text{g}} \times \frac{1 \text{ mol}}{63.55 \cancel{\text{g}}}$$

$$n_{\text{Cu}} = 0.016 \text{ mol}$$

$$n_{\text{e}^-} = 0.016 \cancel{\text{mol Cu}} \times \frac{2 \text{ mol e}^-}{1 \cancel{\text{mol Cu}}}$$

$$n_{\text{e}^-} = 0.031 \text{ mol}$$

$$n_{\text{e}^-} = \frac{q}{F}$$

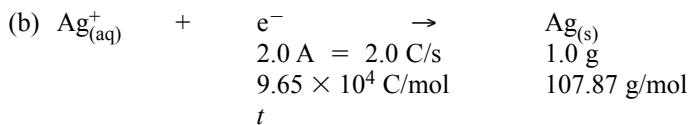
$$n_{\text{e}^-} = \frac{It}{F}$$

$$t = \frac{n_{\text{e}^-} F}{I}$$

$$= \frac{0.031 \cancel{\text{mol}} \times 9.65 \times 10^4 \frac{\text{C}}{\cancel{\text{mol}}}}{2.0 \frac{\text{C}}{\text{s}}}$$

$$t = 1.5 \times 10^3 \text{ s}$$

The time to plate 1.0 g of copper is 1.5×10^3 s (or 0.42 h).



t

$$n_{\text{Ag}} = 1.0 \cancel{\text{g}} \times \frac{1 \text{ mol}}{107.87 \cancel{\text{g}}}$$

$$n_{\text{Ag}} = 0.0093 \text{ mol}$$

$$n_{\text{e}^-} = 0.0093 \cancel{\text{mol Ag}} \times \frac{1 \text{ mol e}^-}{1 \cancel{\text{mol Ag}}}$$

$$n_{\text{e}^-} = 0.0093 \text{ mol}$$

$$n_{\text{e}^-} = \frac{q}{F}$$

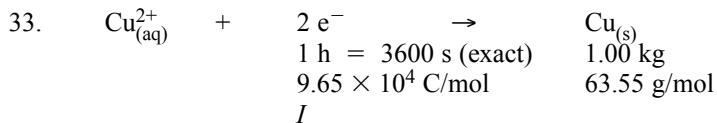
$$n_{\text{e}^-} = \frac{It}{F}$$

$$t = \frac{n_{\text{e}^-} F}{I}$$

$$= \frac{0.0093 \text{ mol} \times 9.65 \times 10^4 \frac{\text{C}}{\text{mol}}}{2.0 \frac{\text{C}}{\text{s}}}$$

$$t = 4.5 \times 10^2 \text{ s}$$

The time to plate 1.0 g of silver is 4.5×10^2 s (or 0.12 h).



$$n_{\text{Cu}} = 1.00 \text{ kg} \times \frac{1 \text{ mol}}{63.55 \text{ g}}$$

$$n_{\text{Cu}} = 0.0157 \text{ kmol} = 15.7 \text{ mol}$$

$$n_{\text{e}^-} = 15.7 \text{ mol Cu} \times \frac{2 \text{ mol e}^-}{1 \text{ mol Cu}}$$

$$n_{\text{e}^-} = 31.5 \text{ mol}$$

$$n_{\text{e}^-} = \frac{q}{F}$$

$$n_{\text{e}^-} = \frac{It}{F}$$

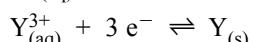
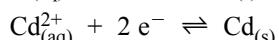
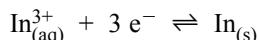
$$I = \frac{n_{\text{e}} F}{t}$$

$$= \frac{31.5 \text{ mol} \times 9.65 \times 10^4 \frac{\text{C}}{\text{mol}}}{3600 \text{ s}}$$

$$I = 844 \text{ A}$$

The average current needed to plate 1.00 kg of copper per hour is 844 A.

Applying Inquiry Skills

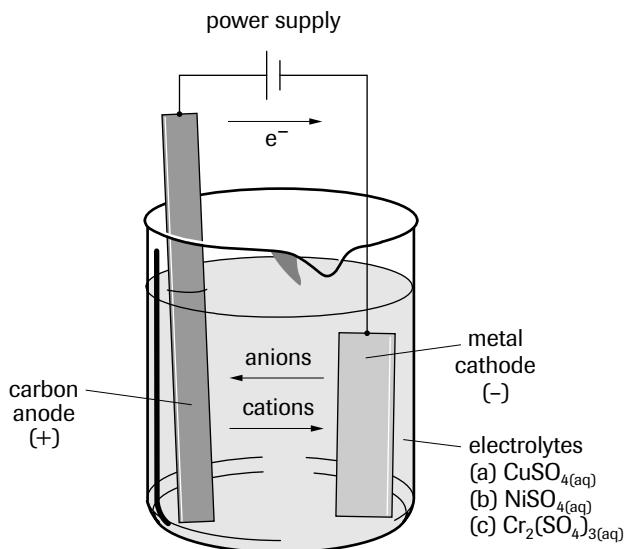


(b) A palladium(II) ion is the strongest oxidizing agent in the experiment because it attracts electrons better than any other metal ion.

(c) Yttrium metal is the strongest reducing agent in the experiment because it loses electrons more easily than any other metal atom present.

(d) $3 \text{Pd}_{(\text{aq})}^{2+} + 2 \text{Y}_{(\text{s})} \rightarrow 2 \text{Y}_{(\text{aq})}^{3+} + 3 \text{Pd}_{(\text{s})}$ This reaction should be spontaneous.

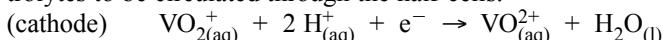
35. (a) A galvanized metal is made from the cathode of an electrolytic cell with a copper(II) sulfate electrolyte, and an inert carbon anode. After plating with copper, the electrolyte is replaced with nickel(II) sulfate. Finally, after plating with nickel, the electrolyte is replaced with chromium(III) sulfate.



- (b) The experimental variables include the current, the time of operation, and the volume and concentration of the electrolyte. Calculation begins with multiplying the surface area by thickness of plating to find the volume needed. The volume is then multiplied by density to find the mass of metal required. The mass is then divided by molar mass to find the amount (in moles) of metal required. The amount of metal is multiplied by the electron/atom mole ratio from the half-reaction equation to find the amount of electrons required. The amount of electrons is divided by the Faraday constant to find the charge that must be transferred. The transferred charge is related directly to both the current and the time.

Making Connections

36. A vanadium redox battery (cell) consists of graphite electrodes, aqueous vanadium ions in dilute sulfuric acid, a plastic membrane that allows hydrogen ions to transfer between half-cells, and external tanks that store half-cell electrolytes to be circulated through the half-cells.



The vanadium redox battery uses the unique chemistry of vanadium to store electrical energy as chemical energy. It is like a fuel cell but rechargeable. The cell can be instantly recharged by replacing the electrolyte or recharged using an external power source (e.g., solar cells) to reverse the reactions. Because the electrolyte circulates between a half-cell and its storage tank, the electrolyte also acts as a coolant. Some of the advantages include the indefinite life of the solutions; high rates of recharge; and low cost, availability, and environmental friendliness of vanadium. The vanadium redox battery has been proposed for use as an electric power source for remote areas and as an energy storage medium for photovoltaic and wind energy systems.

37. Copper is better than aluminum for interconnects because copper has a lower electrical resistance and has fewer problems with electromigration. There will likely be a cost advantage because the interconnects can be thinner than those of aluminum. Copper interconnects are created by electroplating copper from a copper(II) ion solution. This is the reduction of copper in an electrolytic cell. Copper interconnects can also be made by electroless plating. In this method, copper(II) ion complexes are reduced to copper metal using a reducing agent such as formaldehyde. This is a spontaneous redox reaction in solution.

38. Road salt is often sodium chloride but can also be calcium chloride, magnesium chloride, and other salts. Ontario uses more salt per year than any other province (about 40% of the total Canadian use of salt). Road salt is used to melt snow and ice to improve driving conditions. The main advantages are reduced accident rates, fewer and less severe injuries, and fewer travelling delays. However, the use of road salt causes severe corrosion problems of vehicles, bridges, etc. The salt dissolved in water is a very good electrolyte and greatly improves the charge transfer in electrochemical cells causing an accelerated rate of corrosion. Salt is also potentially harmful to aquatic organisms and may also contaminate ground water. There are several alternatives to the current practice of using large quantities of solid sodium chloride. One alternative is calcium magnesium acetate, which has less ability in promoting corrosion and is less harmful to aquatic organisms, but it is relatively expensive. One of the most promising alternatives is to

treat the roads with a brine solution before significant icing occurs. This uses a lot less salt but requires very good weather forecasting to predict likely trouble areas.

Extensions

39. To “boost” a dead car battery safely, the cables must be connected in a specific order.
- (1) The first connection is to clamp a positive (red) cable end to the positive terminal of the good battery.
 - (2) The second connection is to clamp the other end of the positive cable to the positive terminal of the dead battery.
 - (3) The third connection is to clamp a negative (black) cable end to the negative of the good battery — by connecting the cable clamp to any metal bracket or object that is part of the car body/frame structure, in a location well away from the battery location.
 - (4) The fourth and last connection is made by clamping the other negative end of the cable to the negative of the dead battery — again, by connecting the cable clamp to any metal bracket or object that is part of the car structure, well away from the battery location.

The final two connections to “ground” (negative terminal connections) are made at a distance from both batteries to reduce the risk of possible explosion of battery gases (hydrogen and oxygen). Such explosions can be caused by sparking as the last connection (and later, the first disconnection) is made, if one is foolish enough to make and break this connection directly to a negative battery terminal!

40. (a) Proton transfer reactions are usually thought of as equilibrium situations, where the extent of the reaction is quite variable and is the primary concern. Electron transfer reactions tend to occur either to a negligible extent, or to such an extent they are considered complete. Both types occur readily in aqueous solution. Most proton transfer reactions primarily involve molecular compounds or organic ions. Electron transfer reactions commonly involve either molecules or ions. Many oxidizing agents react subject to the activity of hydrogen ions, in situations that are really both types of reactions.
- (b) Neutralization reactions in solution release heat as water molecules from which is evidence for energy change during proton transfer from hydronium to hydroxide ions. Combustion reactions are electron transfer reactions, and commonly are very exothermic.
- (c) Nitric acid is the classic case of a material that is both a strong acid and a strong oxidizing agent. In a reaction with barium hydroxide solution, pH testing and a gas collection and a glowing splint test for oxygen could be done to establish which products predominate.