

**Chapter 1**

There are no in-chapter answers necessary for this chapter.

**Chapter 2**

2.1

<i>Pure</i>	<i>Mixture</i>	
<i>Compounds</i>	<i>Solutions</i>	
(h) testosterone	(b) air	(a) mud
(f) sodium chloride	(c) vinegar	(e) milk
<i>Elements</i>	(g) athlete's urine sample	
(d) gold		
	<i>Homogeneous</i>	<i>Heterogeneous</i>

- 2.2 (a) symbolic,  
(b) observable  
(c) molecular

- 2.3 (a) Na, Cl and Cr are the symbols for sodium, chlorine and chromium, respectively.  
(b) Zn, Ni and K are the symbols for zinc, nickel and potassium.

- 2.4 Sucrose is a colorless molecular solid with a moderate melting temperature. Carbon is a black solid (graphite) or a hard crystalline material (diamond). Both are network solids. Hydrogen and oxygen are both colorless diatomic gases.

- 2.5 (a) In CO, there is one carbon atom for every oxygen atom (or the ratio of C to O atoms is 1:1).  
 (b) In CH<sub>4</sub>, the C to H atom ratio is 1:4.  
 (c) In C<sub>2</sub>H<sub>2</sub>, the C to H atom ratio is 1:1.  
 (d) In C<sub>6</sub>H<sub>12</sub>O<sub>6</sub>, C, H and O atoms are in proportion to 1:2:1.
- 2.6 Six carbon dioxide and six water molecules combine to form one glucose and six oxygen molecules.
- 2.7 Ozone and nitric oxide gases combine to form oxygen and nitrogen dioxide gases. The relative numbers of molecules of the four respective species are 1:1:1:1 – i.e. the stoichiometric coefficients.
- 2.8 The atom is bigger than the nucleus by the factor,  $100 \text{ pm}/0.001 \text{ pm} = 10^5$ . If the radius of the atom were 100 m, then the nucleus radius would be  $100 \text{ m}/10^5 = 0.001 \text{ m} = 1 \text{ mm}$ . Very small pebbles and small peas are this size.
- 2.9 (a) 56  
 (b) 30 protons, 34 neutrons, 30 electrons
- 2.12 (a)  $^{36}_{18}\text{Ar}$ ,  $^{38}_{18}\text{Ar}$ ,  $^{40}_{18}\text{Ar}$ . % abundance of  $^{40}_{18}\text{Ar} = 99.600 \%$   
 (b)  $^{69}\text{Ga}$ : 31 protons, 38 neutrons  
 $^{71}\text{Ga}$  (% abundance, 39.9 %): 31 protons, 40 neutrons
- 2.13 (a) 1.99875  
 (b) 2.16522  
 (c) 1.08329
- 2.14 Atomic weight of chlorine =  $\frac{75.77}{100} \times 34.96885 + \frac{24.23}{100} \times 36.96590 = 35.45$
- 2.18 10
- 2.19 (a) 59 g  
 (b)  $1.90 \times 10^{24}$  atoms
- 2.20 0.97 g

## Chapter 3

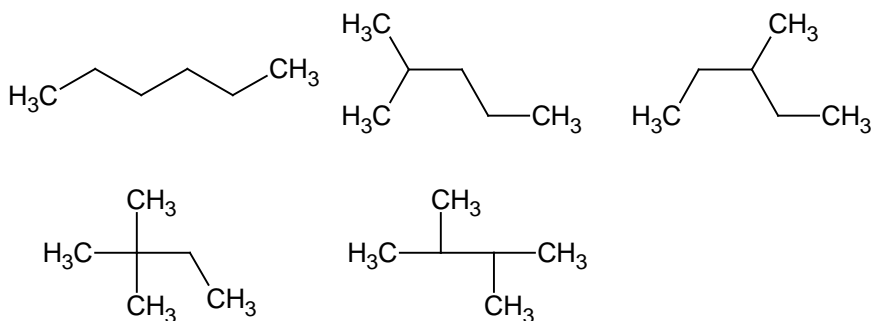
- 3.1 BN
- 3.2 Sodium chloride is held together in a lattice by strong ionic bonds – attraction between positively and negatively charged ions. Silicon carbide is a network solid. The atoms are similarly held together in a lattice, but in this case it is by covalent bonds. Covalent bonds are generally stronger than ionic bonds. Silicon carbide is expected to have the higher melting point. This is in fact the case – silicon carbide decomposes at 2730 °C, while sodium chloride melts at 800°C.
- 3.3 (a) S has 16 protons and 16 electrons.  $S^{2-}$  has 16 protons and 18 electrons.  
(b) Al has 13 protons and 13 electrons.  $Al^{3+}$  has 13 protons and 10 electrons.  
(c) H has 1 proton and 1 electron.  $H^+$  has 1 proton and no electrons.
- 3.4  $N^{3-}$ ,  $O^{2-}$ ,  $F^-$ ,  $Na^+$ ,  $Mg^{2+}$ , and  $Al^{3+}$  have 7, 8, 9, 11, 12 and 13 protons, respectively. All of these species have 10 electrons, the number of electrons in a neutral Ne atom (10 protons).
- 3.6 (a) equal amounts of  $Na^+$  and  $F^-$  in NaF; twice as much  $NO_3^-$  as  $Cu^{2+}$  in  $Cu(NO_3)_2$ ;  
equal amounts of  $Na^+$  and  $CH_3CO_2^-$  in  $NaCO_2CH_3$   
(b)  $FeCl_2$  and  $FeCl_3$  are the compounds formed by  $Fe^{2+}$  and  $Fe^{3+}$ , respectively  
(c)  $Na_2S$ ,  $Na_3PO_4$ ,  $BaS$  and  $Ba_3(PO_4)_2$
- 3.10 (a)  $119.0 \text{ g mol}^{-1}$   
(b)  $53.5 \text{ g mol}^{-1}$   
(c)  $213 \text{ g mol}^{-1}$   
(d)  $120.3 \text{ g mol}^{-1}$
- 3.11 (a) 0.0250 mol  
(b)  $6.95 \times 10^{-5} \text{ mol}$   
(c)  $5 \times 10^3 \text{ mol}$
- 3.14 (a) electrons  
(b) electrons and to a lesser extent  $Mg^{2+}$  ions (they are less mobile)  
(c)  $Mg^{2+}$  and  $Cl^-$  ions  
(d)  $Mg^{2+}$  and  $Cl^-$  ions
- 3.15 (b), (d) and (e) are molecular substances.
- 3.16 Silicon has a much higher melting point because it is a network solid. It does not consist of discrete molecules. Covalent bonding extends throughout a lattice giving the material exceptional strength. Sulfur consists of discrete  $S_8$  molecules which are, in turn, held in a lattice by weaker intermolecular bonds.
- 3.17  $^{12}C$ ,  $^{16}O$  and  $^1H$  are the most common isotopes of carbon, oxygen and hydrogen. The molar mass of the most abundant isotopologue,  $^{12}C_2^1H_6^{16}O$ , is  $46.04189 \text{ g mol}^{-1}$ . This is not in exact agreement with the experimental value.

- 3.18 (a)  $16.043 \text{ g mol}^{-1}$   
(b)  $58.080 \text{ g mol}^{-1}$   
(c)  $93.129 \text{ g mol}^{-1}$
- 3.19 (a) 1.53 g  
(b) 4.60 g  
(c) 4.59 g
- 3.23 A single chlorine atom  
 $\text{C}_6\text{H}_5\text{Cl}$   
112.008002; 114.005052
- 3.24  $\text{C}_6\text{H}_5\text{CHCH}_2$  or  $\text{C}_8\text{H}_8$
- 3.25 (a) C=O stretch - ketone, aldehyde or carboxylic acid  
(b) C-N-H bend of an amine  
(c)  $\text{C}\equiv\text{N}$  stretch of a nitrile  
(d) C=O and O-H stretches of a carboxylic acid  
(e) N-H and C=O stretches of an amide

## Chapter 4

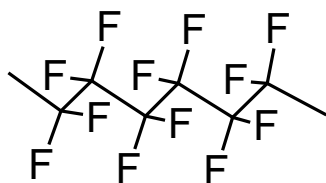
- 4.1 Covalent forces hold the carbon and hydrogen atoms together within a methane molecule.
- 4.2 Weak dispersion forces – a type of intermolecular or non-bonding force – hold neighboring methane molecules together
- 4.3 The CFCs do not have H atoms bonded to C. Such H atoms readily react with hydroxyl radicals.
- 4.4 Most greenhouse gas absorption takes place in troposphere. This is where most of the IR absorbing compounds are found. IR absorbing molecules are generally heavier than most air molecules, and are found within the lowest layer of the atmosphere.
- 4.5 Nitrous oxide absorbs strongly in regions of the IR spectrum emitted by the earth that carbon dioxide and water do not absorb.
- 4.6  $8.4 \times 10^{17} \text{ g}$
- 4.7 Today, I drank from a plastic cup. The plastic material was polymerized from monomers obtained from fractionation and cracking, etc., of petroleum extracted from fossil deposits. I am using a number of plastic products today – for example, the keyboard keys I am typing on, and the computer monitor I am viewing. Another fraction of the same petroleum was used to drive my car. Natural gas – from fossil deposits of mostly methane – is used to heat my house.

4.8



4.11 4

4.12



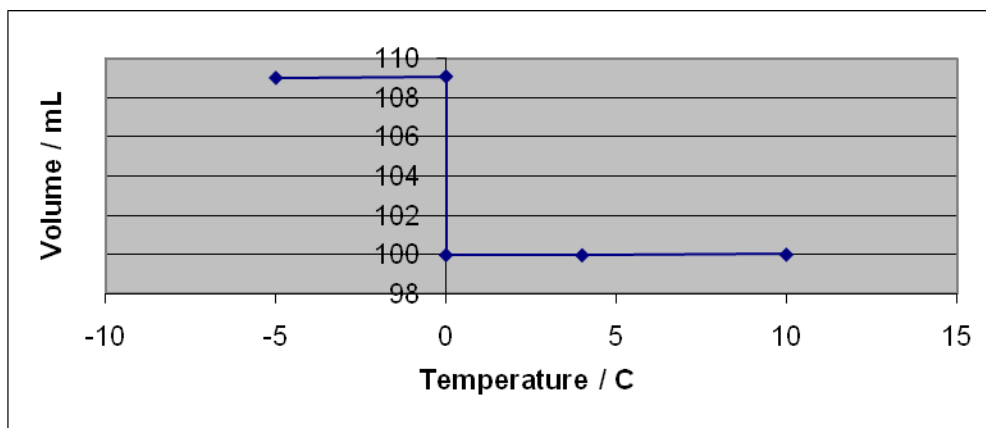
## Chapter 5

- 5.2 (a) balanced for electrical charge and for all relevant atoms  
(b) balanced for electrical charge and for all relevant atoms  
(c) NOT balanced for electrical charge; balanced for Ca and C, but NOT for O atoms
- 5.4 4.5 mol of  $O_2(g)$   
3.0 mol of  $Al_2O_3(s)$
- 5.5 (a) A small amount of solid sodium chloride in water has a higher chemical potential than a dilute solution of sodium chloride.  
(b) A dilute solution of sodium chloride is more stable than a small amount of solid sodium chloride in water.
- 5.6 (a) Neither. Chemical potential on both sides of these reactions are equal.  
(b) A mixture of solid calcium carbonate in pure water has a higher chemical potential than a mixture containing solid calcium carbonate and  $Ca^{2+}(aq)$  ions and  $CO_3^{2-}(aq)$  both at a concentration of  $6 \times 10^{-5} \text{ mol L}^{-1}$ .  
(c) A mixture containing solid calcium carbonate and  $Ca^{2+}(aq)$  ions and  $CO_3^{2-}(aq)$  both at a concentration of  $6 \times 10^{-5} \text{ mol L}^{-1}$  is more stable than a mixture of solid calcium carbonate in pure water.
- 5.7 26.7 g of oxygen reacts with 25.0 g of glucose. 36.7 g of  $CO_2$  and 15.0 g of  $H_2O$  are formed.

- 5.11 (a) CO is the limiting reactant  
 (b) 407 g of CH<sub>3</sub>OH produced  
 (c) 14 g of H<sub>2</sub> remain
- 5.12 (a) Fe<sub>2</sub>O<sub>3</sub> is the limiting reactant  
 (b) 35.0 g of Fe
- 5.17 Theoretical yield of hydrogen = 15.7 g  
 Percent yield of hydrogen = 86.6 %
- 5.19 Mass percent of NiS = 13.8 %

## Chapter 6

- 6.1 (a) 108.99 mL  
 (b) 109.06 mL  
 (c) 100.01 mL  
 (d) 100.00 mL  
 (e) 100.03 mL



- 6.2 35 s
- 6.3 (a)  $1.10 \times 10^3$  kJ  
 (b) 727 kJ
- 6.4 diethyl ether > carbon disulfide > acetone > bromine > hexane > ethanol > water
- 6.5 The order of normal boiling points is the same as the order of enthalpy changes of vaporization. This is what we expect because both boiling point and enthalpy change of vaporization increase with increasing strength of intermolecular forces.

- 6.6 The surface tension is that which pulls the drop into a spherical shape – minimizing surface area. Since this force is smaller for diethyl ether we expect its drops to be even more distorted by gravity than those of water.
- 6.7 (a) The intermolecular force of attraction between water molecules and other water molecules or the molecules on the surface of the blade of grass is sufficient to allow water molecules to stick together on the blade of grass.  
 (b) When a piece of paper burns, carbon-carbon and carbon-hydrogen bonds are broken while new bonds with oxygen are formed. Intramolecular forces are the losing (in the breaking reactant bonds) and winning forces (in the making of bonds) at work when paper burns.  
 (c) Intermolecular forces holding water molecules together, and next to clothes fiber molecules, are overcome when wet clothes are hung out to dry.  
 (d) Intermolecular forces cause water molecules to arrange themselves into a lattice of lowest potential energy. The freezer takes away the kinetic energy thereby liberated, leaving water in its crystalline, solid form – ice.
- 6.9 (a)  $\text{H} \rightarrow \text{F}$  is more polar than  $\text{H} \rightarrow \text{I}$   
 (b)  $\text{B} \rightarrow \text{C}$  is less polar than  $\text{B} \rightarrow \text{F}$   
 (c)  $\text{C} \leftarrow \text{Si}$  is more polar than  $\text{C} \rightarrow \text{S}$
- 6.10 (a) The  $\text{C}=\text{O}$  and  $\text{C}-\text{H}$  bonds are polar, while  $\text{C}-\text{C}$  and  $\text{C}=\text{C}$  are non-polar.  
 (b) The  $\text{C}=\text{O}$  bond is the most polar, with O at the negative end.
- 6.12  $\text{CS}_2$  and  $\text{CO}_2$  are non-polar because of their linear shape.  $\text{SO}_2$  and  $\text{H}_2\text{O}$  are polar because of their bent shape. The two bond dipole vectors only partially cancel out, leaving a NET dipole moment.
- 6.13 (a)  $\text{BFCl}_2$  is trigonal planar. It has a NET dipole because one of the three bonds is different – more polar – than the other two. If the three substituents on B were the same, as in  $\text{BCl}_3$ , then the bond dipoles would cancel.  
 (b)  $\text{NH}_2\text{Cl}$  is trigonal pyramidal. It has a NET dipole because it is asymmetrical and has one bond different from the other two –  $\text{N}-\text{Cl}$  vs.  $\text{N}-\text{H}$ .  
 (c)  $\text{SCl}_2$  is bent like water. It has a NET dipole because the  $\text{S}-\text{Cl}$  bond dipoles only partially cancel out.
- 6.15 (a) Bent  $\text{SO}_2$  has a net dipole. So, there are dipole-dipole forces between neighboring molecules.  
 (b) Linear  $\text{CO}_2$  has no net dipole. There are no dipole-dipole forces between these molecules – only dispersion forces.  
 (c)  $\text{HCl}$  has just one polar bond, and so has a dipole moment. There are dipole-dipole forces between neighboring molecules.

- 6.17  $\text{CH}_3\text{-O}\cdots\text{O-H}$   
 $\begin{array}{c} | \\ \text{CH}_3\text{CH}_3 \end{array}$   
 shows the hydrogen bonding between neighbouring methanol molecules as they move past each other.
- 6.19 (a) bromine  
 (b) butane
- 6.23 (a) ICl  
 (b) Krypton  
 (c) ethanol
- 6.24 (a) dispersion forces  
 (b) hydrogen bonds and dispersion forces  
 (c) dispersion forces
- 6.27  $\text{Mg}^{2+}(\text{aq})$  and  $\text{Br}^{-}(\text{aq})$  are the main species present in solution when some magnesium bromide,  $\text{MgBr}_2(\text{s})$ , is dissolved in water.
- 6.28 (a) soluble  

$$\text{LiNO}_3(\text{s}) \xrightarrow{\text{H}_2\text{O}} \text{Li}^{+}(\text{aq}) + \text{NO}_3^{-}(\text{aq})$$
 (b) soluble  

$$\text{CaCl}_2(\text{s}) \xrightarrow{\text{H}_2\text{O}} \text{Ca}^{2+}(\text{aq}) + 2 \text{Cl}^{-}(\text{aq})$$
 (c) insoluble  
 (d) soluble  

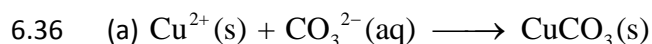
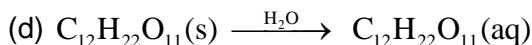
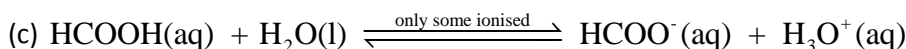
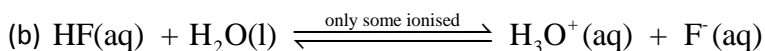
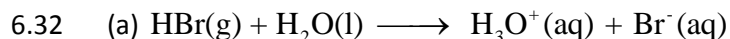
$$\text{NaCH}_3\text{COO}(\text{s}) \xrightarrow{\text{H}_2\text{O}} \text{Na}^{+}(\text{aq}) + \text{CH}_3\text{COO}^{-}(\text{aq})$$
- 6.29 (a) Ammonia,  $\text{NH}_3(\text{g})$ , is soluble in water because water molecules can make strong hydrogen bonds with ammonia molecules – O-H and H-N.  
 (b) Hydrogen chloride,  $\text{HCl}(\text{g})$ , is soluble in water because water molecules can make strong hydrogen bonds with HCl molecules – O-H only.  
 (c) Iodine,  $\text{I}_2(\text{s})$ , is non-polar and insoluble in water. Only dispersion-like forces can be made between water and  $\text{I}_2$ . This interaction is weaker than the dispersion force between  $\text{I}_2$  molecules.  
 (d) Octane,  $\text{C}_8\text{H}_{18}(\text{l})$  is non-polar and insoluble in water. Only dispersion-like forces can be made between water and octane. This interaction is weaker than the dispersion force between octane molecules.
- 6.30 (a) Benzene,  $\text{C}_6\text{H}_6(\text{l})$ , is non-polar and soluble in non-polar octane. Dispersion forces are all that are at play in the pure substances and mixtures. The entropy of mixing is sufficient to drive dissolution.



(b) Water is polar and insoluble in non-polar octane. It turns out that reason for this is more subtle than appears. Dissolving octane in water decreases the entropy of neighboring water molecules. This effect overwhelms the entropy of mixing, and dissolution is not spontaneous.

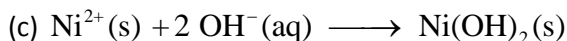
(c) Iodine,  $I_2(s)$ , is non-polar and soluble in non-polar octane. Dispersion forces are all that are at play in the pure substances and mixtures. The entropy of mixing is sufficient to drive dissolution.

6.31 Butan-1-ol,  $CH_3CH_2CH_2CH_2OH(l)$ , should be more soluble in hexane than butan-2,4-diol,  $HOCH_2CH_2CH_2CH_2OH(l)$ . The latter compound has two hydroxyl ( $-OH$ ) groups vs. only one for the former. Like the  $-O-H$  of water, these hydroxyls do not spontaneously mix with hexane – that is, not without the help of the favorable dispersion interactions of the alkyl chains.



$Na^+$  and  $Cl^-$  are spectator ions

(b) No precipitate forms



$K^+$  and  $Cl^-$  are spectator ions

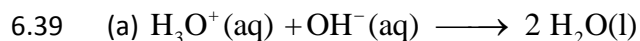
6.37  $Fe^{2+}$  is oxidized to  $Fe^{3+}$ . The oxidizing agent is  $MnO_4^-$ .  $MnO_4^-$  is reduced to  $Mn^{2+}$ .  $Fe^{2+}$  is the reducing agent.

6.38 (a)  $HCOOH$  is the acid reactant, while  $OH^-$  is the base reactant.

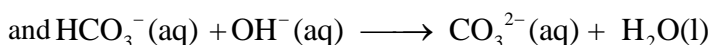
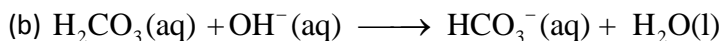
(b)  $H_2CO_3$  is the acid reactant, while  $NH_3$  is the base reactant.

(c)  $H_2C_4H_4O_6$  is the acid reactant, while  $HCO_3^-$  is the base reactant.

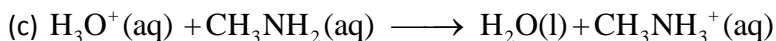
(d)  $H_3O^+$  is the acid reactant, while  $CH_3NH_2$  is the base reactant.



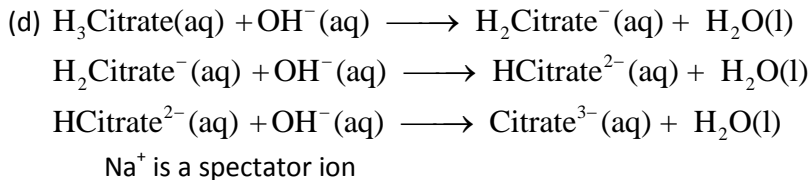
$Li^+$  and  $Br^-$  are spectator ions



$K^+$  is a spectator ion.

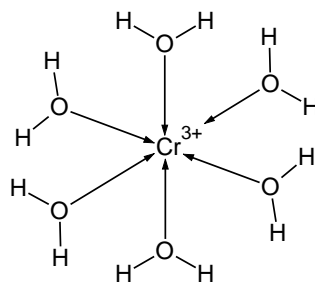
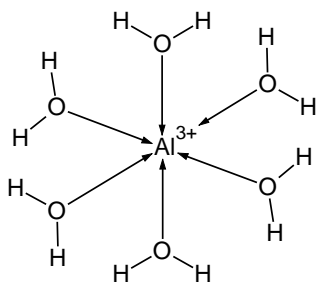
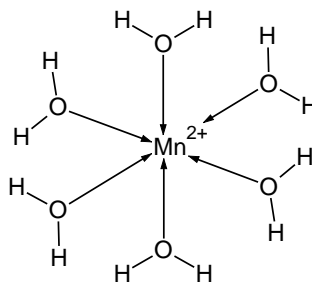
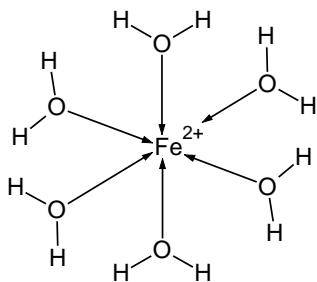


$NO_3^-$  is a spectator ion



- 6.40 (a)  $\text{Co}^{2+}$  is the Lewis acid, while  $\text{Cl}^-$  is the Lewis base.  
 (b)  $\text{Fe}^{2+}$  is the Lewis acid, while  $\text{CN}^-$  is the Lewis base.  
 (c)  $\text{Ni}^{2+}$  is the Lewis acid, while  $\text{CH}_3\text{NH}_2$  is the Lewis base.  
 (d)  $\text{Cu}^{2+}$  is the Lewis acid, while  $\text{Cl}^-$  and  $\text{NH}_3$  are the Lewis bases.

6.41



- 6.42 (a)  $[\text{Co}(\text{H}_2\text{O})_6]^{2+}(\text{aq}) + 4 \text{Cl}^-(\text{aq}) \rightarrow [\text{CoCl}_4]^{2-}(\text{aq}) + 6 \text{H}_2\text{O}(\text{l})$   
 Lewis base,  $\text{Cl}^-$ , competes successfully with the Lewis base,  $\text{H}_2\text{O}$ , to complex  $\text{Co}^{2+}$ .  
 (b)  $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}(\text{aq}) + 6 \text{CN}^-(\text{aq}) \rightarrow [\text{Fe}(\text{CN})_6]^{4-}(\text{aq}) + 6 \text{H}_2\text{O}(\text{l})$   
 Lewis base,  $\text{CN}^-$ , competes successfully with the Lewis base,  $\text{H}_2\text{O}$ , to complex  $\text{Fe}^{2+}$ .  
 (c)  $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}(\text{aq}) + 2 \text{CH}_3\text{NH}_2(\text{aq}) \rightarrow [\text{Ni}(\text{CH}_3\text{NH}_2)_2]^{2+}(\text{aq}) + 6 \text{H}_2\text{O}(\text{l})$   
 Lewis base,  $\text{CH}_3\text{NH}_2$ , competes successfully with the Lewis base,  $\text{H}_2\text{O}$ , to complex  $\text{Ni}^{2+}$ .  
 (d)  $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}(\text{aq}) + 4 \text{Cl}^-(\text{aq}) + 2 \text{NH}_3(\text{aq}) \rightarrow [\text{Cu}(\text{NH}_3)_2\text{Cl}_4]^{2-}(\text{aq}) + 6 \text{H}_2\text{O}(\text{l})$   
 Lewis bases,  $\text{Cl}^-$  and  $\text{NH}_3$ , compete successfully with the Lewis base,  $\text{H}_2\text{O}$ , to complex  $\text{Cu}^{2+}$ .

6.43  $0.478 \text{ mol L}^{-1}$

- 6.47 (a) (A)  
 (b) (A)  
 (c) (B)

- (d) (A)  
(e) (A) and (B) have the same concentration – (B) is just a sample of (A).
- 6.49 (a)  $0.50 \text{ mol L}^{-1} \text{ NH}_4^+(\text{aq})$  and  $0.25 \text{ mol L}^{-1} \text{ SO}_4^{2-}(\text{aq})$   
(b)  $0.246 \text{ mol L}^{-1} \text{ Na}^+(\text{aq})$  and  $0.123 \text{ mol L}^{-1} \text{ CO}_3^{2-}(\text{aq})$   
(c)  $0.056 \text{ mol L}^{-1} \text{ H}_3\text{O}^+(\text{aq})$  and  $\text{NO}_3^-(\text{aq})$

## Chapter 7

- 7.1 (a) 1 mol each of  $\text{H}^+(\text{aq})$  ions and  $\text{OH}^-(\text{aq})$  ions, that have not reacted, have more energy than 1 mol of water.  
(b) Your fingers would feel hot. This is because the negative energy change requires removal of excess energy.
- 7.3 The chemical potential energy stored in a battery can be converted to the mechanical energy of sound waves – from your mp3 player – the electrical and magnetic energy of an image taken by your digital camera, or the light energy emitted by a flashlight – to name a few possibilities.
- 7.4 Heat always flows from higher temperature (water) to lower temperature (air).
- 7.5 (a) The system is the contents of the combustion chamber of the gas furnace – a mixture of air and methane. The surroundings are the furnace and everything around it.  
(b) The system is the water drops plus the air around you. The surroundings consist of your body and the sun – they provide the heat that evaporates the water drops.  
(c) The water, initially at  $25^\circ\text{C}$ , is the system. The container and the rest of the freezer contents – including the air – are the surroundings.  
(d) The aluminum and  $\text{Fe}_2\text{O}_3(\text{s})$  mixture is the system (initially – later it consists of  $\text{Al}_2\text{O}_3(\text{s})$  and iron). The flask and the laboratory bench are the surroundings.
- 7.6 (a) The volume of a balloon is a state function.  
(b) The time it takes to drive from your home to your college or university is NOT a state function  
(c) The temperature of the water in a coffee cup is a state function.  
(d) The potential energy of a ball held in your hand is a state function.
- 7.7 333 kJ
- 7.10 32.1 kJ
- 7.11 0.16 kJ
- 7.12 heat evolved = 2.38 kJ
- 7.15 -56.3 kJ

- 7.16 (a) molecular liquid Br<sub>2</sub>(l).  
 (b) metallic liquid, Hg(l).  
 (c) ionic solid Na<sub>2</sub>SO<sub>4</sub>(s).  
 (d) molecular liquid CH<sub>3</sub>CH<sub>2</sub>OH(l).  
 (e) 1 mol L<sup>-1</sup> concentration Cl<sup>-</sup>(aq).
- 7.17 (a) The standard enthalpy change of this reaction,  $\Delta_r H^\circ$ , is the heat absorbed (hence a negative number when is evolved) at a constant temperature of 25 °C, when exactly 1.00 mol of CO(g) and 0.500 mol of O<sub>2</sub>(g) – both gases separately at 1 bar pressure – are combined in a vessel such that the total pressure is 1 bar (i.e. 1/2 × the vessel containing the carbon monoxide), then reacted completely at fixed pressure to form 1 mol CO<sub>2</sub>(g) at 1 bar.  
 (b) The standard enthalpy change of this reaction,  $\Delta_r H^\circ$ , is the heat absorbed under constant pressure conditions of 1 bar, and constant temperature at 25 °C, when exactly 1.00 mol of Mg(s) and 2.00 mol of H<sup>+</sup>(aq) at 1.00 mol L<sup>-1</sup> concentration react completely to form 1.00 mol of Mg<sup>2+</sup>(aq) at 1.00 mol L<sup>-1</sup> concentration and 1 mol H<sub>2</sub>(g) at 1 bar partial pressure.  
 (c) The standard enthalpy change of this reaction,  $\Delta_r H^\circ$ , is the heat absorbed under constant pressure conditions of 1 bar, and constant temperature at 25 °C, when exactly 1.00 mol of H<sup>+</sup>(aq) and 1.00 mol of OH<sup>-</sup>(aq) both at 1.00 mol L<sup>-1</sup> concentration react completely to form 1.00 mol of H<sub>2</sub>O(l).
- 7.19 (a) 1.9 kJ
- 7.20 116.8 kJ
- 7.21 (a) The standard molar enthalpy of formation of bromine, Br<sub>2</sub>(l), is the standard enthalpy change of the following reaction:  
 Br<sub>2</sub>(l) → Br<sub>2</sub>(l) at 25 °C
- (b) The standard molar enthalpy of formation of solid iron (III) chloride, FeCl<sub>3</sub>(s), is the standard enthalpy change of the following reaction:  
 Fe(s) + Cl<sub>2</sub>(g) → FeCl<sub>3</sub>(s) at 25 °C
- (c) The standard molar enthalpy of formation of solid sucrose, C<sub>12</sub>H<sub>22</sub>O<sub>11</sub>(s), is the standard enthalpy change of the following reaction:
- $$12 \text{ C(graphite)} + 11 \text{ H}_2(\text{g}) + \frac{11}{2} \text{ O}_2(\text{g}) \rightarrow \text{C}_{12}\text{H}_{22}\text{O}_{11}(\text{s}) \text{ at } 25 \text{ }^\circ\text{C}$$
- 7.22 The standard molar enthalpy of formation of liquid methanol, CH<sub>3</sub>OH(l), is the standard enthalpy change of the following reaction:
- $$\text{C(graphite)} + 2 \text{ H}_2(\text{g}) + \frac{1}{2} \text{ O}_2(\text{g}) \rightarrow \text{CH}_3\text{OH}(\text{l}) \text{ at } 25 \text{ }^\circ\text{C}$$
- 7.26 -3267.4 KJ
- 7.27 -53 KJ
- 7.28 -694 KJ

- 7.31 (a) FALSE  
(b) TRUE  
(c) TRUE  
(d) TRUE

## Chapter 8

- 8.1 (a) Element with atomic number 8 greater than F – i.e. atomic number = 17 – is Cl.  
Element with atomic number 18 greater than Cl – i.e. atomic number = 35 – is Br.  
Element with atomic number 18 greater than Br – i.e. atomic number = 53 – is I.  
Element with atomic number 32 greater than I – i.e. atomic number = 85 – is At.  
These are all halogens.  
(b) The atomic numbers of the group 15 elements, N, P, As, Sb & Bi, are  
7, 15, 33, 51 and 83  
Differences between successive atomic numbers =  
8, 18, 18 and 32.
- 8.2 (a) Strontium, Sr(s)  
(b) Calcium, Ca(s)  
(c) Rubidium, Rb(s)
- 8.3 (a) Bromine, Br<sub>2</sub>(g)  
(b) Sodium, Na(s)  
(c) Chlorine, Cl<sub>2</sub>(g)  
(d) The elements with atomic numbers 34, 35, 36, 37, and 38 are Se, Br, Kr and Rb. Rubidium, Rb, is the most powerful reducing agent.
- 8.5 C < Si < Al
- 8.7 (c) Li < Si < C < Ne
- 8.8 (a) The fourth ionization energy of Al is much larger than the third – more so than successive ionization energies usually increase. After removing three electrons from an aluminum atom – the result of the first three ionization steps – the atom (now an ion) is left with the electron configuration of Ne, a noble gas. Al<sup>3+</sup> has filled n=1 and n=2 shells. The next electron to be removed is a tightly held member of the second shell. The first three electrons came from the third shell.  
(b) Mg
- 8.9 (a) +2  
(b) -2
- 8.13 (a) Cl<sup>-</sup>  
(b) Ba<sup>2+</sup>  
(c) K  
(d) Se<sup>2-</sup>

- (e)  $\text{Cl}^-$   
 (f)  $\text{Pb}^{2+}$

- 8.14 (a)  $\text{O}^-$   
 (b)  $\text{Cl}^-$

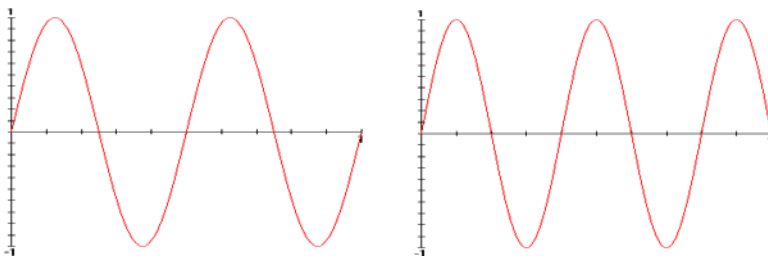
- 8.15 (a)  $\text{O} < \text{C} < \text{Si}$   
 (b)  $\text{Si} < \text{C} < \text{O}$   
 (c)  $\text{Si} < \text{C} < \text{O}$

- 8.16 (a)  $-1.46 \times 10^5 \text{ Jmol}^{-1} = -146 \text{ kJmol}^{-1}$   
 (b)  $182 \text{ KJmol}^{-1}$

- 8.18  $2.043 \times 10^{-18} \text{ J}$ ; 308.3 THz; 97.24 nm

- 8.19  $2.2 \times 10^{-25} \text{ nm}$

8.20

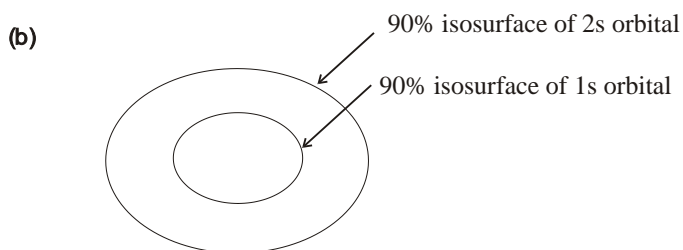
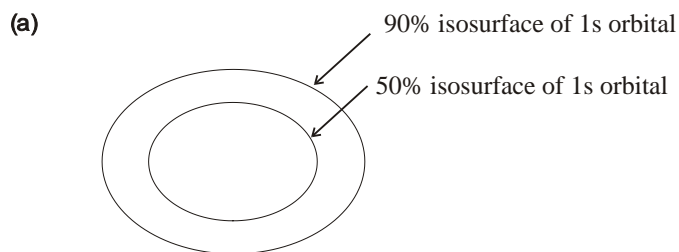


- 8.22 (a) valid  
 (b) not valid  
 (c) not valid

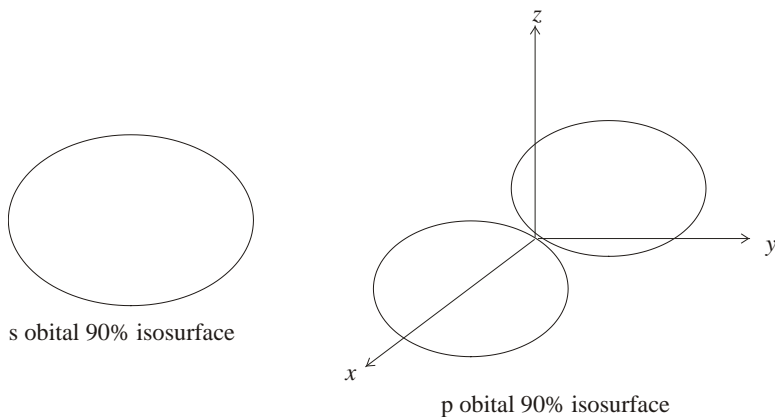
- 8.24 (a) 0 or 1  
 (b) -1, 0 or 1                      p subshell  
 (c) d subshell  
 (d)  $l$  is 0 and  $m_l$  has the value 0  
 (e) 3 orbitals  
 (f) 7 values of  $m_l$                       7 orbitals

- 8.25 (a)  $n = 4, l = 2, m_l = 0, m_s = 0$  is not valid because  $m_s$  is always  $\pm \frac{1}{2}$  because  $s = \frac{1}{2}$  for an electron.  $m_s$  is never equal to zero.  
 (b)  $n = 3, l = 1, m_l = -3, m_s = -\frac{1}{2}$  is not valid because  $m_l = -3$  does not go with  $l = 1$ .  $m_l = -1, 0,$  or  $1$  in this case.  
 (c)  $n = 3, l = 3, m_l = -1, m_s = +\frac{1}{2}$  is not valid because  $l$  must be less than or equal to  $n - 1$ .

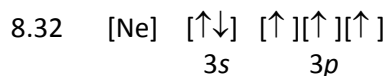
8.27



8.28



- 8.30 (a) 18  
(b) 10  
(c) 1  
(d) none



The last five electrons correspond to the quantum numbers,  
 $n = 3$ ,  
 $l = 0$  and  $m_l = 0$ , and  $m_s = -\frac{1}{2}$  or  $+\frac{1}{2}$  2 electron states  
 $l = 1$  and  $m_l = -1, 0$  or  $1$  and  $m_s = +\frac{1}{2}$  3 electron states

- 8.34  $Z^*(_{12}\text{Mg}) = +2.85$ ;  $Z^*(_{15}\text{P}) = +4.8$ ;  $Z^*(_{18}\text{Ar}) = +6.75$
- 8.35  $Z^*(_{8}\text{O}) = +4.55$ ;  $Z^*(_{8}\text{O}^{2-}) = +3.85$
- 8.36 Although  $_{84}\text{Po}$  has a lot more electrons than  $_{11}\text{Na}$ , the electrons of Po are held so much more tightly that it is smaller. The effective nuclear charges, +5.45 and +2.2, show that even the valence electrons of Po are held more tightly than the valence electrons of Na. The valence electrons determine the size of the atom.
- 8.39  $Z^*(\text{Na}) = +2.2$ ;  $Z^*(\text{Si}) = +4.15$ ;  $Z^*(\text{Ar}) = +6.75$
- 8.40  $Z^*(\text{N}^{3-}) = +2.85$ ;  $Z^*(\text{S}^{3-}) = -0.8$   
 N can form a 3- ion because the valence electrons are still held by an effective nuclear charge of +2.85. S cannot form such an ion because its valence electrons would be repelled by a net negative effective nuclear charge. Adding an electron to  $\text{S}^{2-}$  requires putting the electron in a new shell which is well-shielded by the filled shells.
- 8.41  $Z^*(\text{Na}^+) = +6.85$ ;  $Z^*(\text{Mg}^{2+}) = +7.85$ ;  $Z^*(\text{Al}^{3+}) = +8.85$   
 The valence electrons of these three ions are increasingly tightly held. This is consistent with the trend in sizes – the ions decrease in size.
- 8.42  $Z^*(\text{Mg}^-) = +2.5$ ;  $Z^*(\text{Cl}^-) = +5.75$   
 The larger effective nuclear charge in  $\text{Cl}^-$  shows that chlorine has a greater attraction for an additional electron. This is consistent with chlorine having a larger electronegativity.
- 8.43  $Z^*(\text{Ar}^-) = +1.2$   
 We see that Ar will hold an extra electron even less tightly than Mg. Argon, being inert, has no electronegativity. Its electronegativity cannot be defined since it forms no chemical bonds.

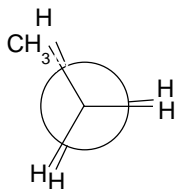
## Chapter 9

- 9.1 The spectra on the left and right are those of diethyl ether and butan-1-ol, respectively.
- 9.2 One could distinguish butan-1-ol and diethyl ether by looking for the distinctive O-H stretch peak (broad peak around  $3200\text{-}3550\text{ cm}^{-1}$ ) of butan-1-ol in the IR spectra.
- 9.3 The spectra on the right and left are those of propan-2-amine and propan-1-amine, respectively.
- 9.4 (a) 1  
 (b) 4  
 (c) 3  
 (d) 7
- 9.5 (a) 1 peak in both carbon-13 and proton spectra  
 (b) 1 peak in both carbon-13 and proton spectra  
 (c) 2 peaks in both carbon-13 and proton spectra  
 (d) 1 peak in both carbon-13 and proton spectra



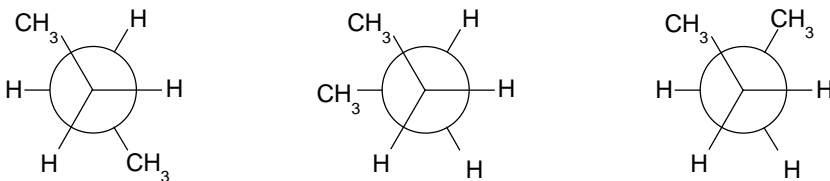
- (e) 1 peak in both carbon-13 and proton spectra
- (f) 1 peak in both carbon-13 and proton spectra
- (g) 2 peaks in both carbon-13 and proton spectra
- (h) 2 peaks in both carbon-13 and proton spectra
- (i) 2 peaks in carbon-13 spectrum and 1 peak in proton spectrum

9.6

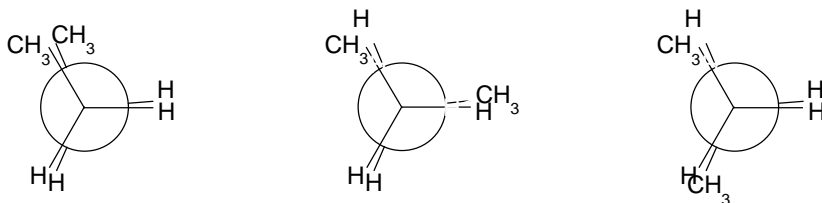


This is the eclipsed conformation – it is the least stable.

9.7

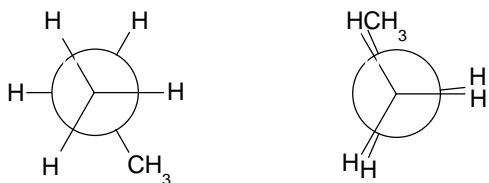


These are the Newman projections of the three staggered conformations. The conformation on the left has the lowest energy. The other two have the same energy.

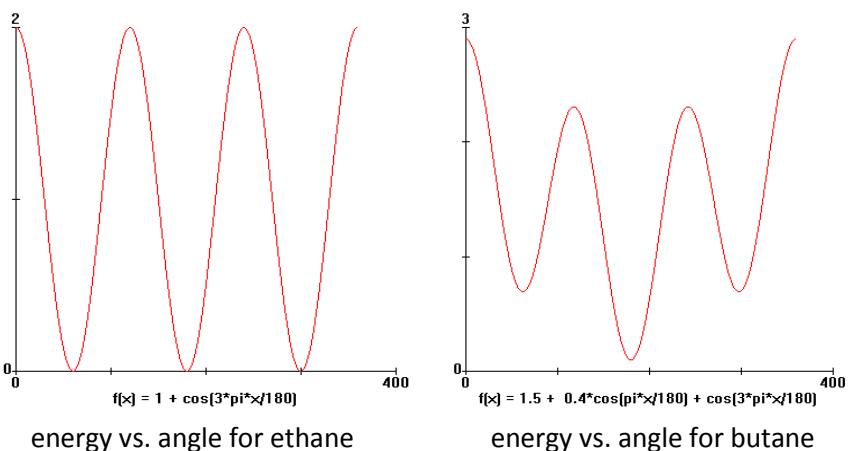


These are the Newman projections of the three eclipsed conformations. The conformation on the left has the highest energy. The other two have the same energy.

9.8 There is only one staggered and one eclipsed conformation of propane.

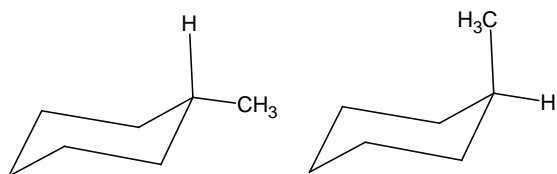


For ethane and butane, the energy as a function of angle of rotation about the C-C bond (the 2-3 bond in butane) looks like

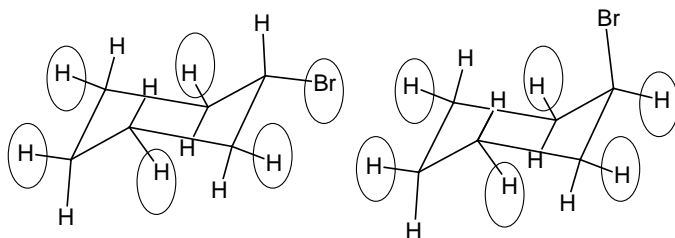


- 9.10 (a)  $C_5H_5N$ : one H atom is bonded to each C atom  
 (b)  $C_6H_{12}O$ : two H atoms are bonded to each C atom, except the C=O carbon  
 (c)  $C_8H_6NH$ : one H atom is bonded to each C atom, except the two C atoms belonging to both rings

9.14



9.15



Here are the equatorial (on the left) bromine and axial bromine conformations of bromocyclohexane. The equatorial positions are circled.

9.17 Since  $[\alpha]_D = 16^\circ$  is positive for cocaine, cocaine is termed dextrorotatory.

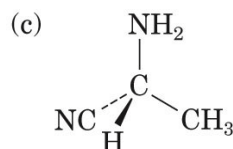
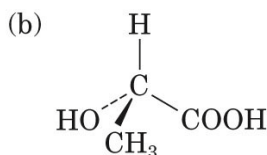
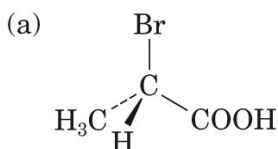
9.18  $16.1^\circ$

9.21 (a)  $-\text{Br} > -\text{CH}_2\text{CH}_2\text{OH} > -\text{CH}_2\text{CH}_3 > -\text{H}$

(b)  $-\text{OH} > -\text{CO}_2\text{CH}_3 > -\text{CO}_2\text{H} > -\text{CH}_2\text{OH}$

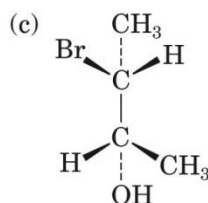
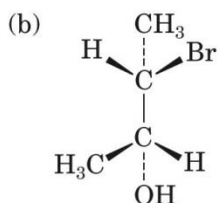
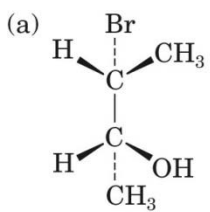
(c)  $-\text{Br} > -\text{Cl} > -\text{CH}_2\text{Br} > -\text{CH}_2\text{Cl}$

9.22



At the carbon stereocenter, the configurations are **(a) S**, **(b) S** and **(c) R**

9.23



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At the top and bottom (respectively) carbon stereocenter, the configurations are **(a) R** and **R**, **(b) S** and **R**, and **(c) R** and **S**

9.24 At the top and bottom (respectively) carbon stereocenter, the configurations are **R** and **R**

9.25 (a) is a meso compound

(b) is a meso compound

9.26 (a) and (c) are meso molecules – they are *R, S*. (b) is an *R, R* enantiomer.

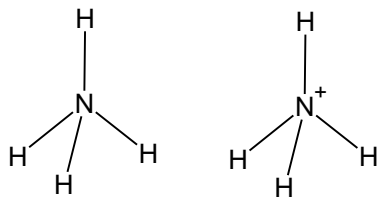
9.27 Nandrolone has 6 stereocenters. There could in principle be as many as  $2^6 = 64$  different stereoisomers.

9.28 Darvon is the *2R,3S*(+) enantiomer of propoxyphene.

Novrad is the *2S,3R* (-) enantiomer.

## Chapter 10

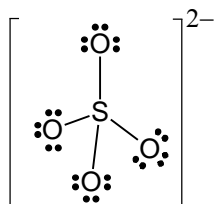
### 10.3 $\text{NH}_4^+$



### CO

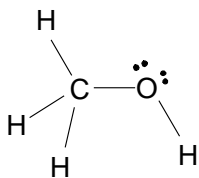


### $\text{SO}_4^{2-}$

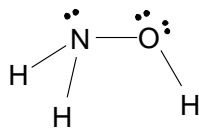


### 10.4

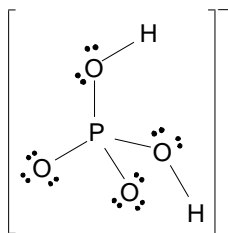
#### $\text{CH}_3\text{OH}$



#### $\text{NH}_2\text{OH}$

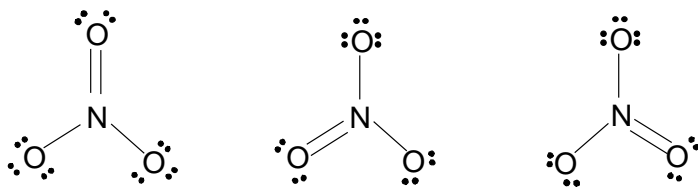


10.5

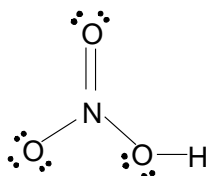


- 10.6 (a) Acetylide ion,  $C_2^{2-}$ , is isoelectronic with  $N_2$ .  
(b)  $SO_2$   
(c)  $OH^-$

10.9

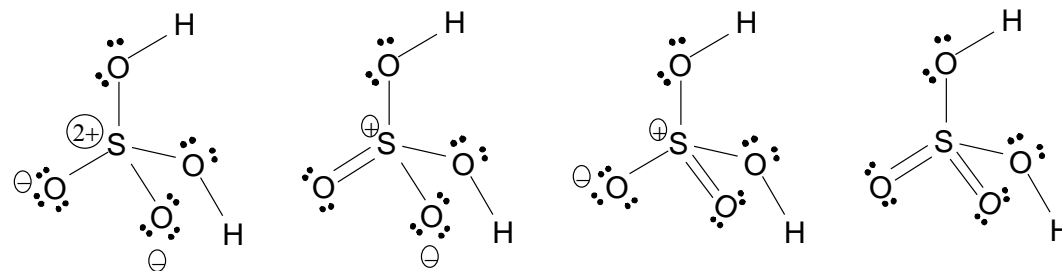


The three resonance structures of nitrate,  $NO_3^-$ .



A structure for nitric acid,  $HNO_3$

10.11



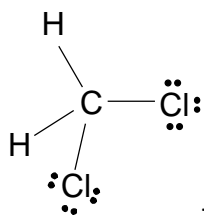
The structure on the right, with no formal charges, is the preferred Lewis structure.

10.12



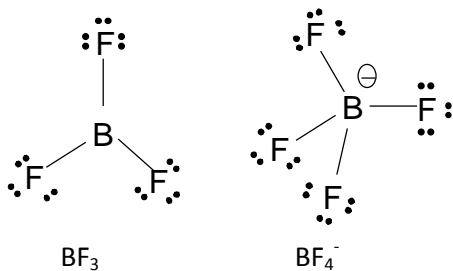
Equivalent resonance structures that together best describe the charge distribution within ozone.

10.13



Tetrahedral shape. The Cl—C—Cl bond angle is predicted to be  $109.5^\circ$

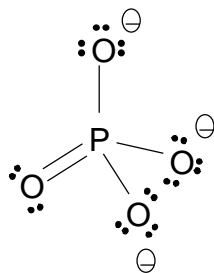
10.16



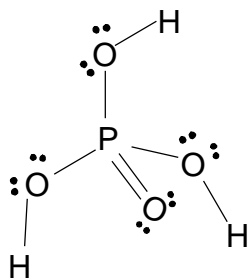
$\text{BF}_3$  is trigonal planar.  $\text{BF}_4^-$  is tetrahedral.

10.17

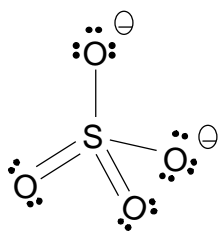
(a) phosphate ion,  $\text{PO}_4^{3-}$ , is tetrahedral



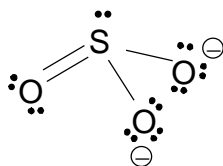
(b) phosphoric acid molecule,  $\text{H}_3\text{PO}_4$ , is tetrahedral at the P



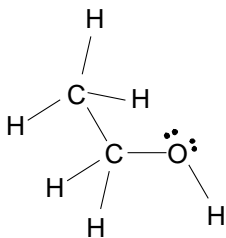
(c) sulfate ion,  $\text{SO}_4^{2-}$ , is tetrahedral



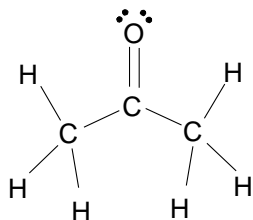
(d) sulfite ion,  $\text{SO}_3^{2-}$ , is trigonal pyramidal



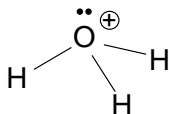
(e) ethanol is tetrahedral at the carbons and bent at the oxygen



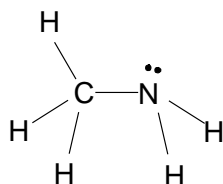
(f) Acetone,  $\text{CH}_3\text{C}(\text{O})\text{CH}_3$ , is trigonal planar at the carbonyl carbon and tetrahedral at the methyl carbons.



10.18



(a)



(b)

Lewis structures of (a) hydronium ion, and (b) methyl amine

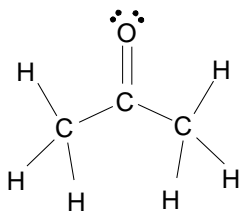
(a) The O atom of hydronium has four electron regions - distributed tetrahedrally. This means  $sp^3$  hybridization at O. Three of the  $sp^3$  orbitals overlap with s orbitals on H atoms to form the O-H bonds, while the fourth accommodates the lone pair on O.

(b) The C atom has four electron regions - distributed tetrahedrally. This means  $sp^3$  hybridization at C. Three of the  $sp^3$  orbitals overlap with s orbitals on H atoms to form the C-H bonds, while the fourth makes a bond with the N atom.

The N atom has four electron regions - distributed tetrahedrally. Consequently, we have  $sp^3$  hybridization at N. Two of the  $sp^3$  orbitals overlap with s orbitals on H atoms to form the N-H bonds, one of them forms the bond with carbon, while the fourth accommodates the lone pair on N.



10.19



The methyl C atoms have the tetrahedral distribution of electron regions. This means  $sp^3$  hybridization at the methyl carbon atoms. Three of the  $sp^3$  orbitals overlap with s orbitals on H atoms to form the C-H bonds, while the fourth makes a bond with the carbonyl C atom.

The carbonyl C atom has a trigonal-planar arrangement of electron regions - consequently, we use  $sp^2$  hybridization here. The C-C bonds are formed from carbonyl-carbon  $sp^2$  orbitals, and methyl-carbon  $sp^3$  orbitals. The remaining  $sp^2$  orbital forms the  $\sigma$  bond to oxygen.

The oxygen atom has three electron regions – the trigonal-planar arrangement – as depicted above. This O atom uses one  $sp^2$  orbital to make the  $\sigma$  bond to C. The remaining two  $sp^2$  orbitals accommodate lone pairs.

The C=O double bond is formed from the unhybridized  $p$  orbitals on each atom – both atoms are  $sp^2$  hybridized with one unhybridized  $p$  orbital. This  $p$ - $p$  bond is the C-O  $\pi$  bond.

10.20



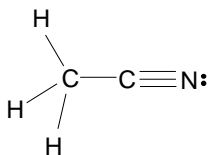
The N atoms have a linear arrangement of two electron regions. This means  $sp$  hybridization.

An  $sp$  orbital from each N atom is used to make the N-N  $\sigma$  bond. The remaining  $sp$  orbitals accommodate the lone pairs – one on each atom.

The two remaining  $p$  orbitals on each atom overlap in pairs to form the two N-N  $\pi$  bonds.

Specifically, the  $p_x$  orbitals overlap to form the  $\pi_x$  bond, while the  $p_y$  orbitals overlap to form the  $\pi_y$  bond.

## 10.21



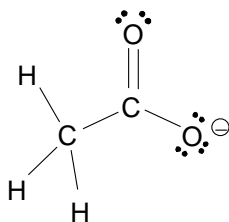
The H-C-H, H-C-C, and C-C-N bond angles are estimated to be  $109.5^\circ$ ,  $109.5^\circ$  and  $180^\circ$ , respectively.

The methyl C atom has the tetrahedral distribution of electron regions -  $sp^3$  hybridization at the methyl carbon atoms. Three of the  $sp^3$  orbitals overlap with s orbitals on H atoms to form the C-H bonds, while the fourth makes a bond with the nitrile C atom.

The nitrile C and N atoms have a linear arrangement of two electron regions. This means  $sp$  hybridization. One  $sp$  orbital from each atom are used to make the C-N  $\sigma$  bond. The remaining  $sp$  orbital on the nitrile C atom forms the bond with the methyl C atom, while the remaining  $sp$  orbital on the N atom accommodate the lone pair.

The two remaining  $p$  orbitals on the nitrile C and N atoms overlap in pairs to form the two C-N  $\pi$  bonds. Specifically, the  $p_x$  orbitals overlap to form the  $\pi_x$  bond, while the  $p_y$  orbitals overlap to form the  $\pi_y$  bond.

## 10.22



The methyl C atom has the tetrahedral distribution of electron regions -  $sp^3$  hybridization at the methyl carbon atoms. Three of the  $sp^3$  orbitals overlap with s orbitals on H atoms to form the C-H bonds, while the fourth makes a bond with the carbonate C atom.

The carbonate C atom has a trigonal-planar arrangement of electron regions -  $sp^2$  hybridization here. The C-C bond is formed from one of these  $sp^2$  orbitals, and a methyl-carbon  $sp^3$  orbital.

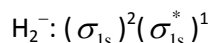
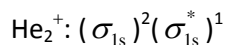
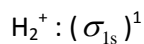
The remaining two  $sp^2$  orbitals form  $\sigma$  bonds to oxygen atoms.

The oxygen atoms can be described as  $sp$  or  $sp^2$  hybridized. Because of symmetry, we should to use the same description for both atoms – in contrast to the Lewis structure which implies that one of the O atoms is  $sp^3$  hybridized. We will assume  $sp$  hybridized O atoms. Each O atom uses one  $sp$  orbital to make a  $\sigma$  bond to C. The other  $sp$  orbital on each atom accommodates a lone pair. The other lone pair, on each O atom, occupies one of the two unhybridized  $p$  orbitals.

What remains are a  $p$  orbital on each of the O atoms and the unhybridized  $p$  orbital on the carbonate carbon atom – three orbitals in all. Two electron pairs also remain. In a valence bond description, a  $\pi$  bond is formed using the  $p$  orbital on C and one of the O atom  $p$  orbitals. The other O-atom  $p$  orbital accommodates the remaining lone pair of electrons. This can be written in one of two equivalent ways – the resonance structures of carbonate. However, because of

symmetry it is more accurate to think of the  $p$  orbital on C and both of the O atom  $p$  orbitals forming a delocalized  $\pi$  bond, though this goes beyond valence bond theory. We must think of the two O atom  $p$  orbitals being combined to form two delocalized (over the two O atoms) orbitals – analogous to orbital hybridization except that the orbitals are on different atoms (these are molecular orbitals). One of the delocalized orbitals forms a symmetric  $\pi$  bond with carbon, the other accommodates the remaining lone pair of electrons.

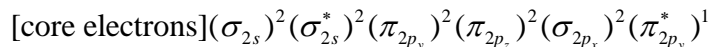
10.25



$\text{H}_2^+$  has a bond order of  $\frac{1}{2}$ . It should exist. But, it is weakly bound.  $\text{He}_2^+$  and  $\text{H}_2^-$  have the same bond order.

10.26  $\text{Li}_2^-$  anion should exist. It is weakly bound with bond order,  $\frac{1}{2}$ .

10.27 Electron configuration of ground state  $\text{O}_2^+$



Bond order =  $2\frac{1}{2}$

$\text{O}_2^+$  is expected to be paramagnetic. Its electron configuration shows an unpaired electron.

## Chapter 11

11.4  $32 \times 10^4 \text{ L}$

11.5 650 balloons

11.6 136 kPa

11.10  $121 \text{ gmol}^{-1}$

11.13  $p(\text{C}_2\text{HBrClF}_3) = 37.7 \text{ kPa}$   
 $P(\text{O}_2) = 364 \text{ kPa}$

11.16 0.798

11.17 Taking He as the reference,  $\frac{\text{Rate of effusion of SF}_6}{\text{Rate of effusion of He}} = 0.166$

and  $\frac{\text{Rate of effusion of N}_2}{\text{Rate of effusion of He}} = 0.378$

- 11.19  $160 \text{ gmol}^{-1}$
- 11.23 **(a)** the dispersion forces in liquid  $\text{O}_2$  < **(c)** the dipole induced dipole interactions of  $\text{O}_2$  dissolved in  $\text{H}_2\text{O}$  < **(b)** the hydrogen bonding forces in liquid  $\text{CH}_3\text{OH}$
- 11.25 (a) 167 mmHg  
(b) the vapour and liquid are NOT at equilibrium – the vapour is supersaturated and vapour condenses to form more liquid.
- 11.26 0.50 g of water is not enough to achieve a partial pressure of 19.3 kPa. Instead, we achieve only 15 kPa.  
With 2.0 g of water, the partial pressure of water would be 19.3 kPa.
- 11.27 (a) The density of liquid  $\text{CO}_2$  is less than that of solid  $\text{CO}_2$ .  
(b) gas phase  
(c) No.

## Chapter 12

- 12.2 **(i)** The lattice enthalpy of  $\text{LiCl(s)}$  is larger than that of  $\text{KCl(s)}$  because the  $\text{Li}^+$  ion is smaller than  $\text{K}^+$  and so gets closer to  $\text{Cl}^-$ . The electrostatic potential energy is lower – it takes more energy to break the ionic bonds.  
**(ii)** The enthalpy of hydration of  $\text{Li}^+$  and  $\text{Cl}^-$  is larger in magnitude than that of  $\text{K}^+$  and  $\text{Cl}^-$  (they are both negative) because the  $\text{Li}^+$  ion is smaller than  $\text{K}^+$ . The interaction of water molecules with  $\text{Li}^+$  is stronger than with  $\text{K}^+$  because they get closer to the smaller lithium ions.
- 12.4  $1.12 \times 10^{-2} \text{ molL}^{-1}$
- 12.5 The solubility of  $\text{Li}_2\text{SO}_4$  in water decreases slightly as we increase the temperature from  $10^\circ\text{C}$ . The amount of solid  $\text{Li}_2\text{SO}_4$  in the second beaker will increase a little.  
The solubility of  $\text{LiCl}$  in water increases slightly as we increase the temperature from  $10^\circ\text{C}$ . The amount of solid  $\text{LiCl}$  in the first beaker will decrease.
- 12.7 mole fraction = 0.00210  
molality =  $0.117 \text{ molkg}^{-1}$   
mass percent = 3.85 %
- 12.8 19.85 kPa
- 12.10 4.66 kPa
- 12.12 The freezing point of the solution is  $-5.25^\circ\text{C}$ . The added ethylene glycol is not enough to prevent freezing at  $-25^\circ\text{C}$ .
- 12.14  $472 \text{ g mol}^{-1}$

12.16  $-2.81\text{ }^{\circ}\text{C}$

12.18  $1.40 \times 10^5\text{ g mol}^{-1}$

12.19  $754\text{ kPa}$

12.20 (a) volume =  $4.19 \times 10^6\text{ nm}^3$   
Surface area =  $1.26 \times 10^5\text{ nm}^2$

(b)  $2.4 \times 10^{14}$  spheres; surface area =  $30\text{ m}^2$

## Chapter 13

13.3 (a)  $Q = \frac{[\text{PCl}_3][\text{Cl}_2]}{[\text{PCl}_5]}$

(b)  $Q = \frac{[\text{CO}]^2}{[\text{CO}_2]}$

(c)  $Q = \frac{[\text{Cu}^{2+}][\text{NH}_3]^4}{[\text{Cu}(\text{NH}_3)_4^{2+}]}$

(d)  $Q = \frac{[\text{CH}_3\text{COO}^-][\text{H}_3\text{O}^+]}{[\text{CH}_3\text{COOH}]}$

13.5 (a)  $Q_c = 2.25$ . NOT at equilibrium. Because  $Q_c < K_c$ , the reaction proceeds in the forward direction.  
(b)  $Q_c = 3.47$ . NOT at equilibrium. Because  $Q_c > K_c$ , the reaction proceeds in the reverse direction

13.6 (a)  $[\text{NH}_3] = 6.2 \times 10^{-4}\text{ mol L}^{-1}$

(b)  $[\text{NH}_3] = 1.8 \times 10^{-2}\text{ mol L}^{-1}$

The cadmium solution has a higher ammonia concentration

13.7 (a)  $[\text{C}_6\text{H}_{10}\text{l}_2] = 0.015\text{ mol L}^{-1}$

$[\text{C}_6\text{H}_{10}] = 0.035\text{ mol L}^{-1}$

(b)  $K = 0.082$

13.10  $[\text{H}_2] = [\text{I}_2] = 1.54 \times 10^{-3}\text{ mol L}^{-1}$

$[\text{HI}] = 8.92 \times 10^{-3}\text{ mol L}^{-1}$

13.11 (b)  $K_2 = K_1^2$

13.13 (a)  $K_2 = (K_1)^2 = (2.5 \times 10^{-29})^2 = 6.3 \times 10^{-58}$

(b)  $K_3 = (K_2)^{-1} = (6.3 \times 10^{-58})^{-1} = 1.6 \times 10^{57}$

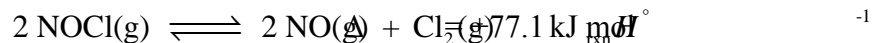
13.14  $K_3 = K_1 \times (K_2)^{-2} = 8.12 \times (0.771)^{-2} = 13.7$

13.15 [butane] =  $0.77 \text{ mol L}^{-1}$   
[isobutane] =  $0.93 \text{ mol L}^{-1}$

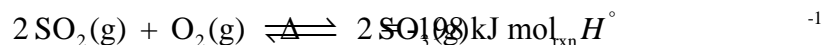
13.16 (a) When extra  $\text{H}_2$  is added to an equilibrium mixture, the mixture is shifted out of equilibrium by the increase in  $\text{H}_2$  concentration. There is net forward reaction until a new equilibrium is attained. Some, but not all, of the additional  $\text{H}_2$  is consumed. The concentration of  $\text{N}_2$  decreases, since it is a reactant, while the concentration of product  $\text{NH}_3$  increases. When extra  $\text{NH}_3$  is added, net reverse reaction follows consuming some – but not all – of the added ammonia. The final equilibrium mixture has a higher concentration of both hydrogen and nitrogen (reactants) and a higher concentration of ammonia than the original equilibrium mixture.

(b) When the volume of the system is increased, all concentrations are decreased by the same factor. Since there are a different number of moles of reactant and product gases, this will change the value of the reaction quotient, shifting it away from its equilibrium value. In this case, there are more reactant gases than product gases, and the reaction quotient gets bigger. This causes the reaction to proceed in the reverse direction (the reaction quotient must decrease to revert to its equilibrium value), generating a net increase in moles of gas. The reaction proceeds in the direction which counters the decrease in total gas concentration caused by the change in volume.

- 13.17 (a) The equilibrium concentration of NOCl decreases if the temperature of the system is increased.



- (i) Initially, the mixture is at equilibrium. So,  $Q = K$ . When temperature increases, the equilibrium constant generally changes. For an endothermic reaction such as this, the equilibrium constant increases. Now,  $Q < K'$  where  $K'$  is the new equilibrium constant.  $Q$  has not changed – at least at first. However, because  $Q$  is less than  $K'$ , the reaction must proceed in the forward direction to return to equilibrium – i.e. increasing  $Q$  up to  $K'$ . This direction consumes reactant – i.e. the concentration of NOCl decreases.
- (ii) The reaction proceeds in the forward – endothermic – direction after the temperature is increased. The endothermic direction is the direction that consumes heat and lowers temperature – i.e. countering the increase in temperature in accord with Le Chatelier's principle.
- (b) The equilibrium concentration of SO<sub>3</sub> decreases if the temperature is increased?

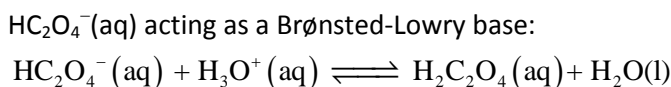


- (i) Initially, the mixture is at equilibrium. So,  $Q = K$ . For an exothermic reaction such as this, the equilibrium constant decreases. Now,  $Q > K'$  where  $K'$  is the new equilibrium constant. To return to equilibrium,  $Q$  must decrease – i.e. the reaction proceeds in the reverse direction to return to equilibrium – i.e. decreasing  $Q$  down to  $K'$ .
- (ii) The reaction proceeds in the reverse – endothermic – direction after the temperature is increased. The endothermic direction is the direction that consumes heat and lowers temperature – i.e. countering the increase in temperature in accord with Le Chatelier's principle.

## Chapter 14

- 14.1 (a)  $\text{HCOOH(aq)} + \text{H}_2\text{O(l)} \rightleftharpoons \text{HCOO}^-\text{(aq)} + \text{H}_3\text{O}^+\text{(aq)}$   
           acid                  base                  conj. base      conj. acid
- (b)  $\text{NH}_3\text{(aq)} + \text{H}_2\text{S(aq)} \rightleftharpoons \text{NH}_4^+\text{(aq)} + \text{HS}^-\text{(aq)}$   
           base          acid                  conj. acid      conj. base
- (c)  $\text{HSO}_4^-\text{(aq)} + \text{OH}^-\text{(aq)} \rightleftharpoons \text{SO}_4^{2-}\text{(aq)} + \text{H}_2\text{O(l)}$   
           acid                  base                  conj. base      conj. acid

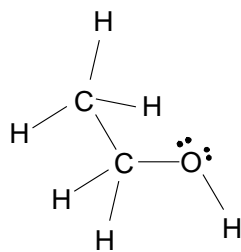
- 14.3  $\text{HC}_2\text{O}_4^-\text{(aq)}$  acting as a Brønsted-Lowry acid:  
 $\text{HC}_2\text{O}_4^-\text{(aq)} + \text{OH}^-\text{(aq)} \rightleftharpoons \text{C}_2\text{O}_4^{2-}\text{(aq)} + \text{H}_2\text{O(l)}$



- 14.5  $[\text{H}_3\text{O}^+] = 4.0 \times 10^{-3} \text{ mol L}^{-1}$   
 $[\text{OH}^-] = 2.5 \times 10^{-12} \text{ mol L}^{-1}$

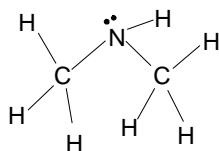
- 14.7 (a)  $pOH = 2.9$ ;  $pH = 11.1$   
 (b)  $[H_3O^+] = 4.79 \times 10^{-5} \text{ mol L}^{-1}$ ;  $[OH^-] = 2.09 \times 10^{-10} \text{ mol L}^{-1}$   
 (c)  $pOH = 3.54$ ;  $[OH^-] = 2.88 \times 10^{-4} \text{ mol L}^{-1}$
- 14.9 (a)  $pK_a = 4.2$   
 (b) aquated chloroacetic acid is a stronger acid than aquated benzoic acid
- 14.10 It fits between benzoic and acetic acids in Table 14.5.
- 14.12  $K_b = 7.1 \times 10^{-11}$   
 It fits between dihydrogenphosphate and fluoride in Table 14.5.
- 14.13 (a) An aqueous solution of KBr has a pH of 7.  
 (b) An aqueous solution of  $NH_4NO_3$  has a  $pH < 7$   
 (c) An aqueous solution of  $AlCl_3$  has a  $pH < 7$   
 (d) An aqueous solution of  $Na_2HPO_4$  has  $pH > 7$
- 14.15 (a) The H attached to N has the greatest concentration of positive charge. As such, this is the most acidic hydrogen atom.  
 (b) The unprotonated ring nitrogen has the greatest concentration of negative charge. It is the most basic nitrogen atom in imidazole.
- 14.16 CO a Lewis base.

14.17 (a)



Lewis Base

(b)



Lewis Base

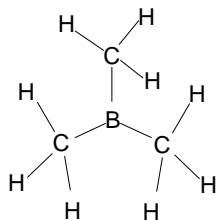


(c)



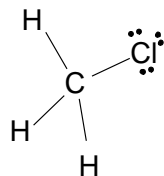
Lewis Base

(d)



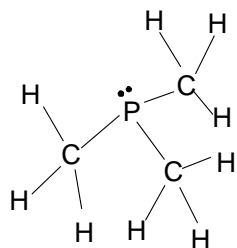
Lewis Acid

(e)



Lewis base, through Cl atoms

(f)



Lewis Base

14.19  $K_a = 6.87 \times 10^{-5}$

14.22  $[\text{CH}_3\text{COO}^-] = [\text{H}_3\text{O}^+] = 0.0013 \text{ mol L}^{-1}$   
 $[\text{CH}_3\text{COOH}] = 0.0987 \text{ mol L}^{-1}$   
pH = 2.89  
% acetic acid ionized = 1.3 %

14.24 The results shown in Table 14.7 are correct.

14.25 The results shown in Table 14.8 are correct.

14.27 (a)  $0.30 \text{ mol L}^{-1}$  aqueous solution of formic acid  
pH = 2.14; % ionisation = 2.4 %

$0.10 \text{ mol L}^{-1}$  aqueous solution of formic acid  
pH = 3.27; % ionisation = 0.18 %

(b) 0.18%

14.28  $[\text{HOCl}] = [\text{OH}^-] = 6.6 \times 10^{-6} \text{ mol L}^{-1}$   
pH = 8.82

14.30  $[\text{oxalate}^-] = [\text{H}_3\text{O}^+] = 0.053 \text{ mol L}^{-1}$   
pH = 1.28

14.31 (a) According to increasing acidity (i.e. decreasing pH) we have  
 $C < A < B$   
(b) according to amount of NaOH that can be consumed, we have  
 $B (0.001 \text{ mol L}^{-1}) < A (0.005 \text{ mol L}^{-1}) < C (0.006 \text{ mol L}^{-1})$

14.34 (a)  $2.88 \times 10^3$   
(b) 2.88  
(c)  $2.88 \times 10^{-3}$

14.35 (a) At pH 6.0  
(i)  $1.33 \times 10^{-4}$   
(ii) 16  
(iii)  $2.78 \times 10^6$   
At pH = 6.0, the dominant species is  $\text{H}_2\text{PO}_4^-$

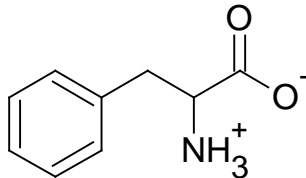
(b) At pH = 9.0  
(i)  $1.33 \times 10^{-7}$   
(ii)  $1.6 \times 10^{-2}$   
(iii)  $2.78 \times 10^3$   
At pH = 9.0, the dominant species is  $\text{HPO}_4^{2-}$

14.36 (a) phenylalanine

$$\frac{[\text{H}_2\text{Phe}^+]}{[\text{HPhe}]} = \frac{[\text{H}_3\text{O}^+]}{K_{a1}} = \frac{10^{-7.40}}{10^{-1.83}} = 10^{-5.57} = 2.7 \times 10^{-6}$$

$$\frac{[\text{HPhe}]}{[\text{Phe}^-]} = \frac{[\text{H}_3\text{O}^+]}{K_{a2}} = \frac{10^{-7.40}}{10^{-9.13}} = 10^{1.73} = 54$$

The dominant species at pH = 7.40 is HPhe.



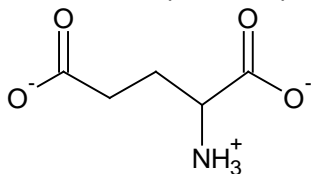
(b) glutamic acid

$$\frac{[\text{H}_3\text{Glu}^+]}{[\text{H}_2\text{Glu}]} = \frac{[\text{H}_3\text{O}^+]}{K_{a1}} = \frac{10^{-7.40}}{10^{-2.19}} = 10^{-5.21} = 6.2 \times 10^{-6}$$

$$\frac{[\text{H}_2\text{Glu}]}{[\text{HGlu}^-]} = \frac{[\text{H}_3\text{O}^+]}{K_{a2}} = \frac{10^{-7.40}}{10^{-4.25}} = 10^{-3.15} = 7.1 \times 10^{-4}$$

$$\frac{[\text{HGlu}^-]}{[\text{Glu}^{2-}]} = \frac{[\text{H}_3\text{O}^+]}{K_{a3}} = \frac{10^{-7.40}}{10^{-9.67}} = 10^{2.27} = 190$$

The dominant species at pH = 7.40 is HGlu<sup>-</sup>



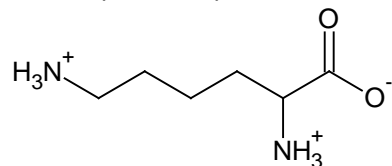
(c) lysine

$$\frac{[\text{H}_3\text{Lys}^{2+}]}{[\text{H}_2\text{Lys}^+]} = \frac{[\text{H}_3\text{O}^+]}{K_{a1}} = \frac{10^{-7.40}}{10^{-2.18}} = 10^{-5.22} = 6.0 \times 10^{-6}$$

$$\frac{[\text{H}_2\text{Lys}^+]}{[\text{HLys}]} = \frac{[\text{H}_3\text{O}^+]}{K_{a2}} = \frac{10^{-7.40}}{10^{-8.95}} = 10^{1.55} = 35$$

$$\frac{[\text{HLys}]}{[\text{Lys}^-]} = \frac{[\text{H}_3\text{O}^+]}{K_{a3}} = \frac{10^{-7.40}}{10^{-10.53}} = 10^{3.13} = 1350$$

The dominant species at pH = 7.40 is  $\text{H}_2\text{Lys}^+$



14.40 pH = 4.13

14.42 (b)  $\text{NH}_3$  and  $\text{NH}_4\text{Cl}$  would make a buffer solution near pH = 9

14.43 If we prepare a (not too dilute) solution with a 2.0 to 1 ratio (on a moles basis) of  $\text{Na}_2\text{HPO}_4(\text{s})$  to  $\text{NaH}_2\text{PO}_4(\text{s})$ , it will function as a buffer solution with pH = 7.5.

14.45 (a) pH = 3.89

(b) pH = 3.86

14.46 (a)(i) pH = 10.02

(ii)  $\Delta\text{pH} = 10.26 - 10.02 = 0.24$

(b) (i) 11.02

(ii)  $\Delta\text{pH} = 11.30 - 11.02 = 0.28$

14.47 concentration of the acetic acid in vinegar sample =  $1.08 \text{ mol L}^{-1}$   
mass of acetic acid in vinegar sample = 1.62 g

14.49  $0.119 \text{ mol L}^{-1}$

14.51 (a) 4.47

(b) 8.72

14.52 (a) 4.19

(b) 6.38

(c) 9.19

(d) 10.32

(e) 11.13

14.53 8.77

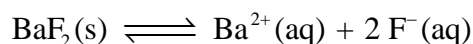
## Chapter 15

15.1 (a)



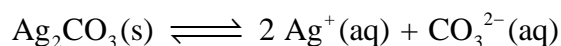
$$Q = [\text{Ag}^+][\text{I}^-] = K_{\text{sp}} = 1.5 \times 10^{-16} \text{ at equilibrium}$$

(b)



$$Q = [\text{Ba}^{2+}][\text{F}^-]^2 = K_{\text{sp}} = 1.7 \times 10^{-6} \text{ at equilibrium}$$

(c)



$$Q = [\text{Ag}^+]^2[\text{CO}_3^{2-}] = K_{\text{sp}} = 8.1 \times 10^{-12} \text{ at equilibrium}$$

15.4  $K_{\text{sp}} = 1.9 \times 10^{-7}$

- 15.6 (a)  $1.3 \times 10^{-2} \text{ mol L}^{-1}$   
(b)  $9.6 \times 10^{-1} \text{ g L}^{-1}$

- 15.8 (a) AgCl  
(b) Ca(OH)<sub>2</sub>  
(c) Ca(OH)<sub>2</sub>

15.10 The solubility of Ag<sub>3</sub>PO<sub>4</sub> is larger than that predicted using K<sub>sp</sub> of the salt because the phosphate ion, PO<sub>4</sub><sup>3-</sup>, reacts with water to form HPO<sub>4</sub><sup>2-</sup> (H<sub>2</sub>PO<sub>4</sub><sup>-</sup> and H<sub>3</sub>PO<sub>4</sub> upon further reaction with water). The concentration of PO<sub>4</sub><sup>3-</sup> is consequently significantly reduced, and the reaction quotient for dissolution of Ag<sub>3</sub>PO<sub>4</sub> remains less than the solubility product for larger initial concentrations of Ag<sub>3</sub>PO<sub>4</sub> than predicted using K<sub>sp</sub>.

- 15.13 (a)  $1.0 \times 10^{-5} \text{ mol L}^{-1}$   
(b)  $1.1 \times 10^{-8} \text{ mol L}^{-1}$

- 15.15 (a) PbS(s)  
(b) Ag<sub>2</sub>CO<sub>3</sub>(s)  
(c) Al(OH)<sub>3</sub>(s)

15.16  $Q = 5.3 \times 10^{-9} < K_{\text{sp}} = 9.8 \times 10^{-9}$   
The solution is not saturated. More PbI<sub>2</sub> can dissolve.

15.19  $Q = 6.3 \times 10^{-8} < K_{\text{sp}} = 3.4 \times 10^{-7}$   
The mixture is not saturated. SrSO<sub>4</sub>(s) will not precipitate.

15.20  $[\text{I}^-] = 4.4 \times 10^{-9} \text{ mol L}^{-1}$   
 $[\text{Pb}^{2+}] = 4.4 \times 10^{-3} \text{ mol L}^{-1}$

15.22  $[\text{OH}^-] = 5.3 \times 10^{-6} \text{ mol L}^{-1}$

15.24  $K_{\text{net}} = 1.1 \times 10^{-6}$

15.25 At pH = 1, the cyanide appears only as hydrogen cyanide, HCN(aq). Silver appears only as  $\text{Ag}^+(\text{aq})$ . As pH increases past  $\text{p}K_{\text{a}} = -\log_{10}(3.5 \times 10^{-4}) = 3.5$ , the cyanide ion,  $\text{CN}^-$ , concentration increases. Depending on the relative amounts of cyanide and silver, some or all of the cyanide complexes silver – the  $\text{Ag}^+(\text{aq})$  concentration decreases and the  $[\text{Ag}(\text{CN})_2]^-$  increases. The concentrations remain constant for pH from about 5 (i.e. when very little hydrogen cyanide remains) all the way to 13.

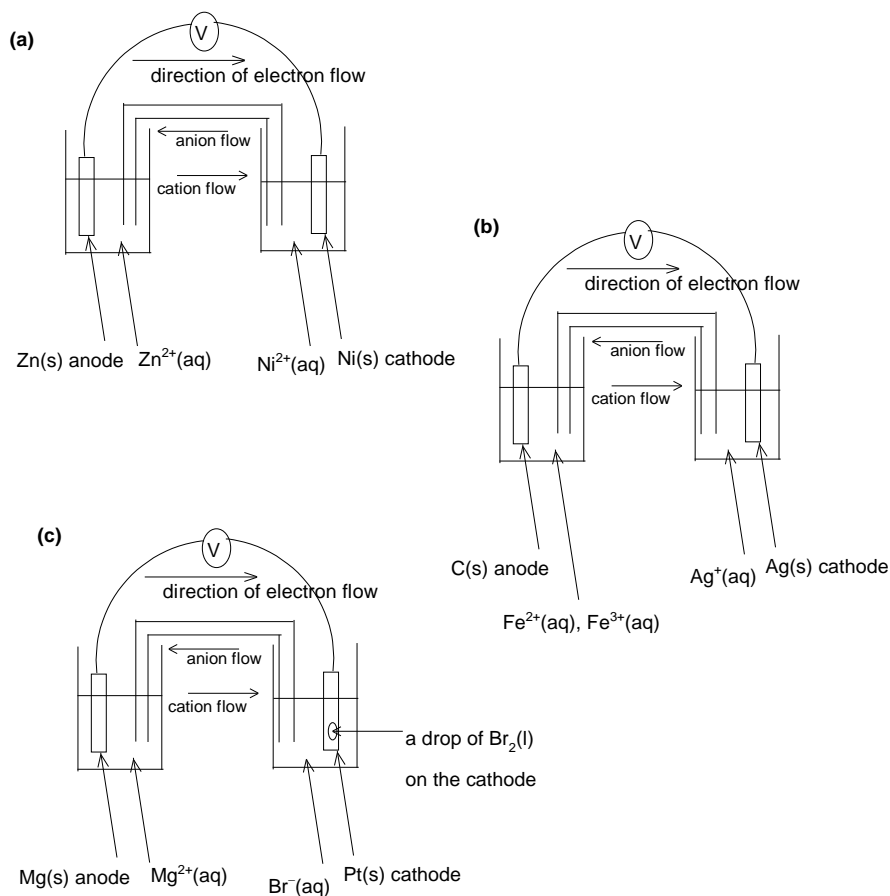
## Chapter 16

- 16.2 (a) +3  
(b) +6  
(c) +4  
(d) +5

16.4  $\text{CH}_3\text{CH}_2\text{OH}$  is oxidized.  $\text{CH}_3\text{CH}_2\text{OH}$  is the reducing agent.  $\text{Cr}_2\text{O}_7^{2-}$  is reduced.  $\text{Cr}_2\text{O}_7^{2-}$  is the oxidizing agent.

16.6 A silver electrode immersed in an aqueous solution of  $\text{AgNO}_3$  provides the cathode. A nickel electrode immersed in an  $\text{Ni}^{2+}$  solution provides the anode.  
The overall cell reaction is :  $2\text{Ag}^+(\text{aq}) + \text{Ni}(\text{s}) \rightarrow 2\text{Ag}(\text{s}) + \text{Ni}^{2+}(\text{aq})$   
Electrons flow from the  $\text{Ni}(\text{s})$  to the  $\text{Ag}(\text{s})$ .  $\text{NO}_3^-$  in the salt bridge flows towards the anode compartment and  $\text{Na}^+$  in the salt bridge flows toward the cathode compartment.

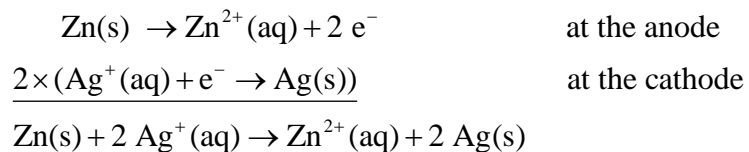
16.7



- 16.8 (a)  $E^\circ[\text{Ni}^{2+}(\text{aq})|\text{Ni}(\text{s})] = -0.25 \text{ V}$   
 (b)  $E^\circ[\text{Cl}_2(\text{g})|\text{Cl}^-(\text{aq})|\text{Pt}(\text{s})] = 1.36 \text{ V}$

16.9 See above – Exercise 16.8(b).

16.13



$$E^\circ_{\text{cell}} = 1.56 \text{ V}$$

- 16.14 (a)  $E^\circ_{\text{cell}} = -1.298 \text{ V}$  (cell reaction is not written in the spontaneous direction)  
 (b)  $E^\circ_{\text{cell}} = -0.51 \text{ V}$  (cell reaction is not written in the spontaneous direction)  
 (c)  $E^\circ_{\text{cell}} = -1.023 \text{ V}$  (cell reaction is not written in the spontaneous direction)  
 (d)  $E^\circ_{\text{cell}} = 0.028 \text{ V}$  (cell reaction is written in the spontaneous direction)

16.17 (a) Aluminum

(b) Aluminum and zinc

(c)  $\text{Fe}^{2+}(\text{aq}) + \text{Sn}(\text{s}) \rightarrow \text{Fe}(\text{s}) + \text{Sn}^{2+}(\text{aq})$ . This is NOT the direction of spontaneous reaction.

(d)  $\text{Zn}^{2+}(\text{aq}) + \text{Sn}(\text{s}) \rightarrow \text{Zn}(\text{s}) + \text{Sn}^{2+}(\text{aq})$ . This is NOT the direction of spontaneous reaction.

16.20  $E^\circ_{\text{cell}} = +1.24 \text{ V}$

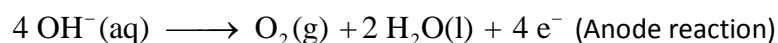
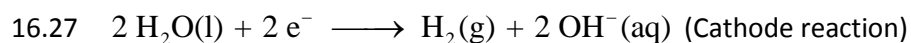
16.22  $0.041 \text{ mol L}^{-1}$

16.23 (a) At  $\text{pH} = 0$ ,  $E_{\text{cell}} = +1.51 \text{ V}$

(b) At  $\text{pH} = 5.0$ ,  $E_{\text{cell}} = +1.04 \text{ V}$

The cell potential is greater at  $\text{pH} = 0$ . This means permanganate is a stronger oxidizing agent under acidic conditions.

16.25  $K = 1.2 \times 10^{-19}$



$E^\circ_{\text{cell}} = -1.23 \text{ V}$

16.28 The brass fittings provide cathodes where oxygen is reduced to water. The steel provides the anode where iron is oxidized to  $\text{Fe}^{2+}$ . Of course, the steel can provide its own cathode and can corrode without brass fittings. However, because copper (the principal component of brass) is a more noble metal than iron, when it is in contact with iron there is a slight polarization at the junction, with iron becoming slightly positively charged. This makes the oxidation process at the surface of iron more favorable. At the same time, the slight negative charge on the brass makes the reduction of oxygen more favorable.

The rate of corrosion varies from city to city because it depends upon the ionic strength – the total concentration of ions – of the city water. Ions in the water carry current from the anode to cathode – to complete the circuit. The conductivity of the water increases with ion concentration.

16.29 The corrosion of iron requires water to carry the current that completes the circuit and to provide the aqueous environment of the product  $\text{Fe}^{2+}$  ions. It also requires oxygen from the air – the reactant at the cathode. These requirements are met best at the air – water - pier interface. Corrosion below the surface can take place due to dissolved oxygen, but the concentration is less than the oxygen concentration in air. Corrosion above the surface occurs when the steel gets wet, through water splashing onto it or when it rains. This water is not always available.



- 16.30 (i) Tin impedes corrosion of iron by coating it, preventing oxygen from contacting the iron. If the tin coating gets scratched, the iron will corrode quickly at the scratch because the more noble metal tin provides a preferred cathode for reduction of oxygen.
- (ii) Zinc impedes corrosion of iron by providing a “sacrificial anode”. Because zinc is a less noble metal, it provides a preferred anode. The zinc is oxidized, consuming the oxygen, in preference to the oxidation of iron. Scratching the zinc coating will not impact its ability to protect the iron.
- (iii) Paint impedes corrosion simply by providing a coating, keeping the oxygen away from the iron. If it is scratched, the iron will corrode at the scratch, but only at its normal rate of corrosion. The non-conducting paint does not provide an electrode for corrosion.

## Chapter 17

- 17.1 The change in entropy for a reversible process (i.e. add the heat very slowly) is just heat flow into the system divided by temperature. Therefore, the entropy of the water and hexane change by the same amount – it depends only on the temperature of the system and the amount of heat added.

$$\Delta S = q / T = 10^6 \text{ J} / 323.15 \text{ K} = 3095 \text{ J/K, for both the water and hexane.}$$

- 17.3 121 J/K

- 17.5 (a) 1 mol of  $\text{O}_3(\text{g})$   
 (b) 1 mol of  $\text{SnCl}_4(\text{g})$   
 (c) 3 mol of  $\text{O}_2(\text{g})$

- 17.8 (a)  $+160.59 \text{ JK}^{-1}$   
 (b)  $-198.76 \text{ JK}^{-1}$

- 17.10  $\Delta S_{\text{sys}}^{\circ} = -134.23 \text{ JK}^{-1}$   
 $\Delta H_{\text{sys}}^{\circ} = -657.01 \text{ kJ}$   
 $\Delta S_{\text{univ}}^{\circ} = +2071 \text{ JK}^{-1}$

Since the change in entropy for the universe upon forward reaction is positive, the reaction is spontaneous.

- 17.12 (a) Type 2  
 (b) Type 3  
 (c) Type 1  
 (d) Type 2

- 17.14  $\Delta_r S^{\circ} = -198.76 \text{ JK}^{-1}$   
 $\Delta_r H^{\circ} = -91.8 \text{ kJ}$   
 $\Delta_r G^{\circ} = -32.6 \text{ kJ}$

- 17.15 (a)  $\frac{1}{2} \text{N}_2(\text{g}) + \frac{3}{2} \text{H}_2(\text{g}) \rightarrow \text{NH}_3(\text{g})$   
(b)  $2 \text{Fe}(\text{s}) + \frac{3}{2} \text{O}_2(\text{g}) \rightarrow \text{Fe}_2\text{O}_3(\text{s})$   
(c)  $3 \text{C}(\text{s}) + 3 \text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow \text{CH}_3\text{CH}_2\text{COOH}(\text{l})$   
(d) Ni(s) is the element in its standard state. Its  $\Delta_r G^\circ = 0$ .

17.17  $\Delta_r G^\circ = -70.87 \text{ kJ}$

- 17.18  $\Delta_r G^\circ = -142.12 \text{ kJ}$   
The reaction is spontaneous in the forward direction

17.19  $T = 838.7 \text{ K}$

- 17.21 (a)  $\Delta_r S^\circ < 0$ .  $\Delta_r G^\circ$  increases with increasing  $T$ .  
(b)  $\Delta_r S^\circ > 0$ .  $\Delta_r G^\circ$  decreases with increasing  $T$ .  
(c)  $\Delta_r S^\circ < 0$ .  $\Delta_r G^\circ$  increases with increasing  $T$ .  
(d)  $\Delta_r S^\circ > 0$ .  $\Delta_r G^\circ$  decreases with increasing  $T$ .

17.22  $\Delta_r G^\circ = -1.13 \text{ kJ}$

17.25  $\Delta_r G^\circ = +120.023 \text{ kJ}$   
 $K = 9.18 \times 10^{-22}$

17.26  $-41 \text{ kJ}$

- 17.27  $+147 \text{ kJ}$ . The reverse reaction is spontaneous.

17.28 (a)  $E^\circ = 0.236 \text{ V}$   
 $\Delta_r G^\circ = -45.5 \text{ kJ}$   
 $K = 9.46 \times 10^7$

(b)  $E^\circ = -0.531 \text{ V}$   
 $\Delta_r G^\circ = -102 \text{ kJ}$   
 $K = 7.58 \times 10^{17}$

17.30 (a)  $\Delta_r G^\circ = 141.73 \text{ kJ}$   
(b)  $1.43 \times 10^{-25}$   
(c)  $6.67 \times 10^{-5}$

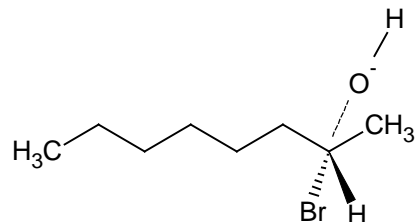
17.32 (a)  $p_{40^\circ\text{C}} = 1.37 \times 10^{-3} \text{ bar}$   
(b)  $p_{100^\circ\text{C}} = 6.20 \times 10^{-2} \text{ bar}$   
(c)  $62.5 \text{ kJ}$

## Chapter 18

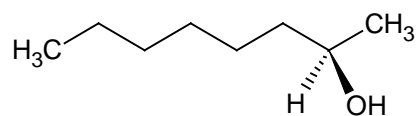
- 18.2 For every 2 moles of NOCl consumed, there are 2 moles of NO and one mole of Cl<sub>2</sub> produced.  
The relative rate of appearance of Cl<sub>2</sub> is ½ the rate of appearance of NO which equals the rate of disappearance of NOCl.
- 18.3 In the first two hours: 0.0085 mol L<sup>-1</sup> h<sup>-1</sup>  
In the last two hours: 0.002 mol L<sup>-1</sup> h<sup>-1</sup>  
The instantaneous rate of decay at t = 4.0 h: 0.0044 mol L<sup>-1</sup> h<sup>-1</sup>
- 18.4 (a) Rate = k [NO<sub>2</sub>][O<sub>3</sub>]  
(b) The rate triples.  
(c) The rate is halved.
- 18.7 Rate = k [NO]<sup>2</sup>[O<sub>2</sub>]  
k = 7100 mol<sup>-2</sup> L<sup>2</sup> s<sup>-1</sup>
- 18.9 0.0035 mol L<sup>-1</sup>
- 18.11 0.00217 mol L<sup>-1</sup>
- 18.13 The plot of ln([N<sub>2</sub>O<sub>5</sub>]) versus time gives a straight line. The reaction is first order.
- 18.15 (a) t<sub>1/2</sub> of <sup>241</sup>Am = 430 years  
t<sub>1/2</sub> of <sup>125</sup>I = 63 years  
(b) <sup>125</sup>I  
(c) 1.57 × 10<sup>15</sup> atoms
- 18.17 57.2 kJmol<sup>-1</sup>
- 18.19 All three of these processes are bimolecular.  
The rate equation for the third step: Rate = k [N<sub>2</sub>O] [H<sub>2</sub>]
- $$2 \text{ NO} \longrightarrow \text{N}_2\text{O}_2$$
- $$\text{N}_2\text{O}_2 + \text{H}_2 \longrightarrow \text{N}_2\text{O} + \text{H}_2\text{O}$$
- $$\text{N}_2\text{O} + \text{H}_2 \longrightarrow \text{N}_2 + \text{H}_2\text{O}$$
- 
- $$2 \text{ NO} + 2 \text{ H}_2 \longrightarrow \text{N}_2 + 2 \text{ H}_2\text{O}$$
- 18.21 (a) 2NH<sub>3</sub>(aq) + OCl<sup>-</sup>(aq) → N<sub>2</sub>H<sub>4</sub>(aq) + H<sub>2</sub>O(l) + Cl<sup>-</sup>(aq)  
(b) step 2  
(c) Rate = k [NH<sub>2</sub>Cl] [NH<sub>3</sub>]  
(d) NH<sub>2</sub>Cl, N<sub>2</sub>H<sub>5</sub><sup>+</sup> and OH<sup>-</sup>

- 18.22 (a) Rate =  $k [\text{CH}_3(\text{CH}_2)_5\text{CHBrCH}_3] [\text{OH}^-]$   
 (b) The rate of reaction will double.  
 (c) The rate of reaction will double.

(d)

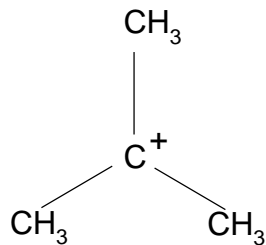


(e) (*R*)-octan-2-ol



- 18.23 (a) The rate of substitution will double  
 (b) The rate of substitution will not change

(c)

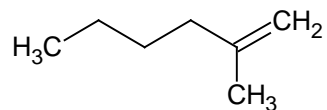


- (d) Whether or not inversion takes place is irrelevant here because the product is the same in both cases – due to symmetry.  
 (e) The proportion of this reaction that proceeds by the  $\text{S}_{\text{N}}2$  mechanism is negligible because the rate of the  $\text{S}_{\text{N}}1$  mechanism is enhanced by the relatively stable carbocation intermediate, and because the rate of the  $\text{S}_{\text{N}}2$  mechanism is reduced by the presence of the three methyl groups about the carbon center. The portion of collisions between iodide and *tert*-butyl chloride which can lead to reaction is much smaller than the value for methyl chloride (for example). The three methyl groups present an obstacle limiting the rate of the  $\text{S}_{\text{N}}2$  reaction. The  $\text{S}_{\text{N}}1$  mechanism presents no such obstacle – the iodide reacts with a reactive planar intermediate.

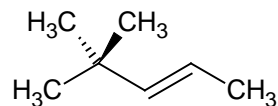
## Chapter 19

19.2

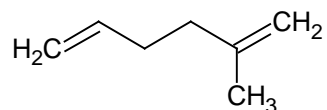
(a)



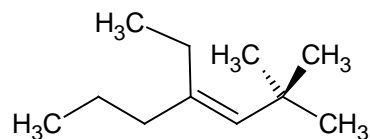
(b)



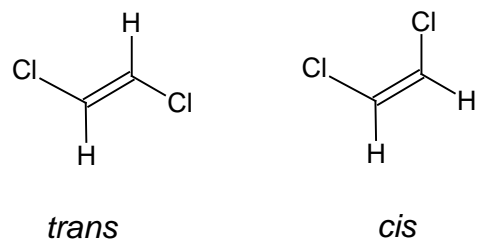
(c)



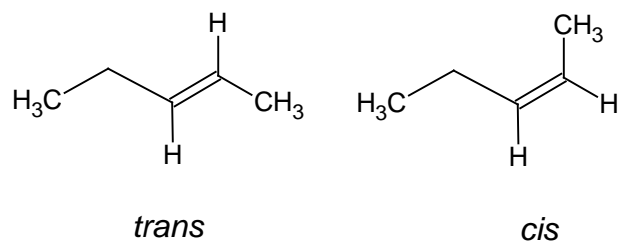
(d)



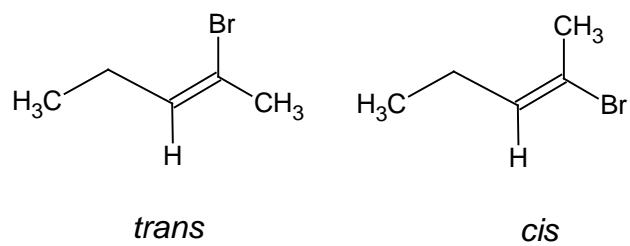
19.4 (c)



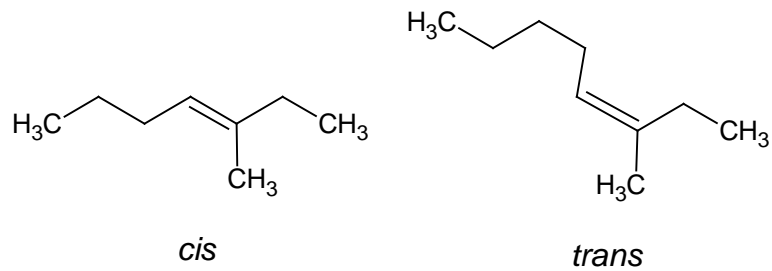
(d)



(e)

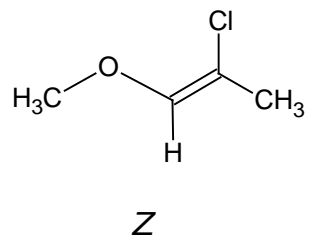


(f)

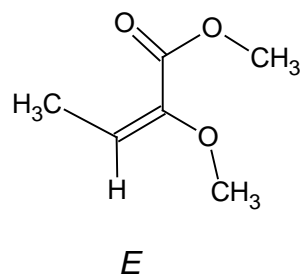


- 19.6 (a) -Br  
(b) -Br  
(c) -CH<sub>2</sub>CH<sub>3</sub>  
(d) -OH  
(e) -CH<sub>2</sub>OH  
(f) -CH=O

19.7 (a)



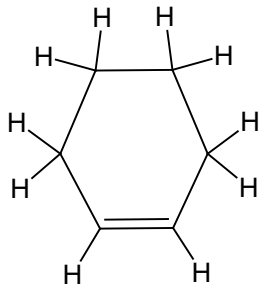
(b)



19.8 This is the Z isomer.

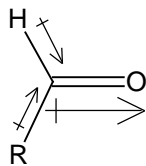
19.9 The two downfield lines, at about 139 and 113 ppm, are the two alkene carbon peaks.

19.10

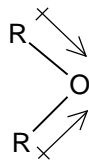


19.11 (a) substitution  
(b) elimination  
(c) addition

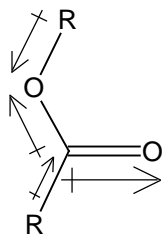
19.13 (a)



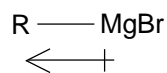
(b)



(c)



(d)



19.14 (a)  $\text{NH}_4^+$

Ammonium is an electrophile. It is attracted to concentrations of negative charge, and will donate a proton to proton acceptors – i.e. nucleophiles.

(b)

$\text{CN}^-$

Cyanide is a nucleophile. It is attracted to concentrations of positive charge (i.e. regions of depleted electron density) such as acidic protons and carbonyl carbons.

(c)  $\text{Br}^-$

Bromide is a nucleophile. It is attracted to concentrations of positive charge (i.e. regions of depleted electron density).

(d)  $\text{CH}_3\text{NH}_2$

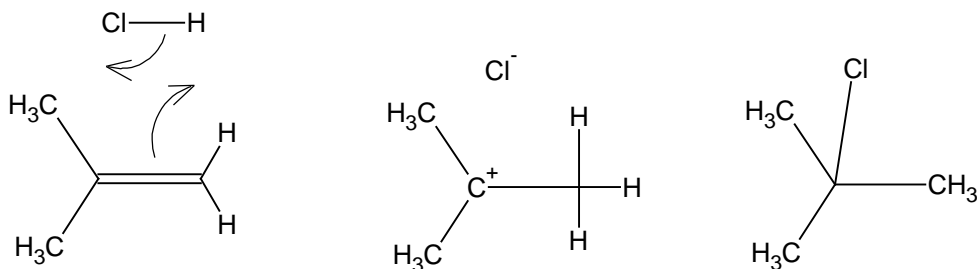
The amine N atom is a nucleophile. It is attracted to concentrations of positive charge (i.e. regions of depleted electron density).

(e)  $\text{H}-\text{C}\equiv\text{C}-\text{H}$

Acetylene is a nucleophile. It has a relatively loosely held cloud of  $\pi$  electrons which electrophiles are attracted to – and vice versa.

19.15  $\text{BF}_3$  is electron deficient at the low-electronegativity boron atom. In the Lewis structure of  $\text{BF}_3$ , the boron atom has only 6 electrons in its valence shell.  $\text{BF}_3$  is electrophilic at the boron center.

19.16



19.17 (a)  $\text{CH}_3\text{CH}_2\text{CHClCH}_3$

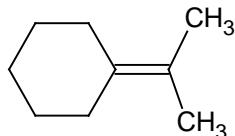
(b)  $(\text{CH}_3)_2\text{CICH}_2\text{CH}_2\text{CH}_3$

(c) chlorocyclohexane

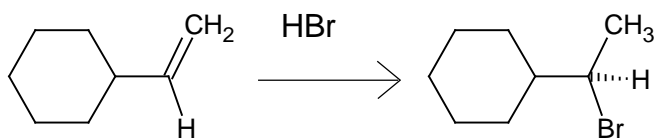




- 19.18 (a) Bromocyclopentane can be prepared from cyclopentene and HBr.  
 (b) 3-Bromohexane can be prepared from hex-2-ene and HBr.  
 (c) 1-Iodo-1-isopropylcyclohexane can be prepared from dimethylmethylenecyclohexane,

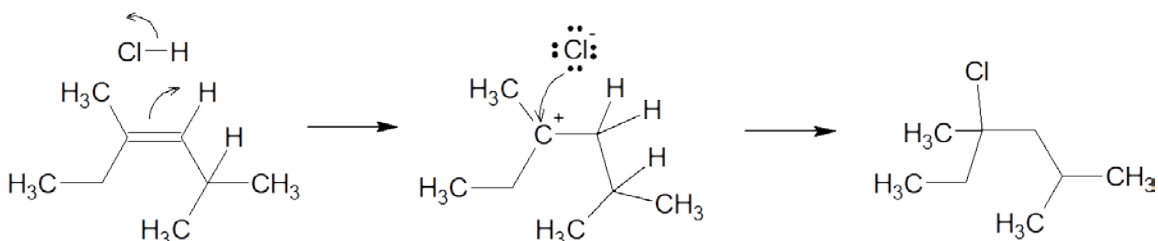


(d)

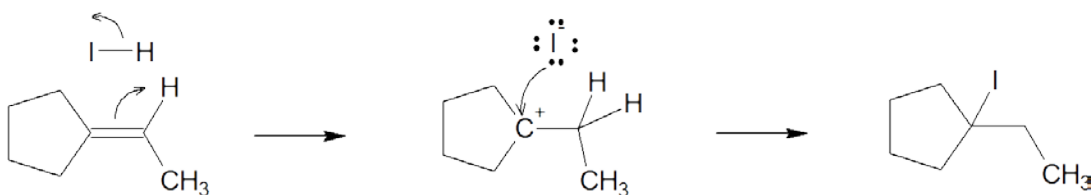


19.19

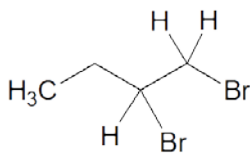
(a)



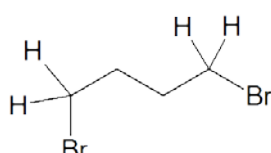
(b)



19.20

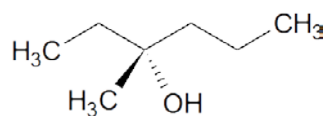


1,2-dibromobutane

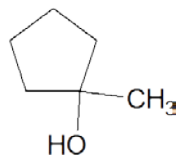


1,4-dibromobutane

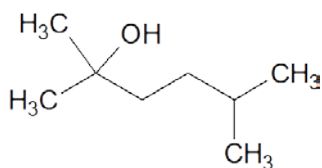
19.21 (a) Addition of water to 3-methylhex-3-ene gives 3-methylhexan-3-ol,



(b) Addition of water to 1-methylcyclopentene gives 1-methylcyclopentanol



(c) Addition of water to 2,5-dimethylhept-2-ene gives 2,5-dimethylheptan-2-ol

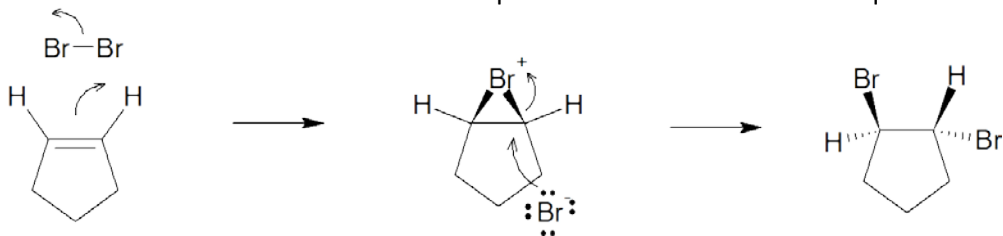


19.22 (a) Butan-2-ol can be made by addition of water to but-1-ene or but-2-ene.

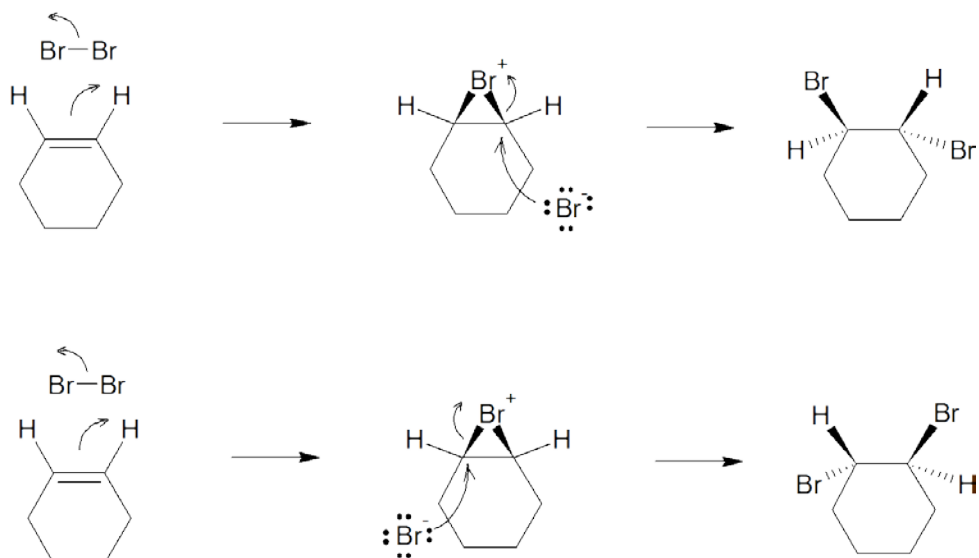
(b) 3-Methylpentan-3-ol can be made by addition of water to 3-methylpent-2-ene or 2-ethylbut-1-ene.

(c) 1,2-Dimethylcyclohexanol can be made by addition of water to 1,2-dimethylcyclohexene or 1,6-dimethylcyclohexene.

19.23 If the second bromine added to the other carbon – the one on the left, then the enantiomeric product would be formed. By symmetry, this pathway is just as likely as the one shown in Figure 19.30 of the text. The two enantiomeric products would be formed in equal amounts.



19.24

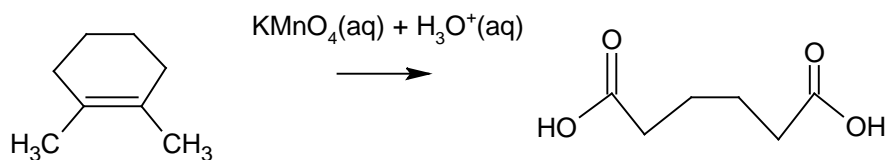


The two enantiomers of 1,2-dibromo-1,2-dimethylcyclohexane are expected upon bromination of 1,2-dimethylcyclohexene.

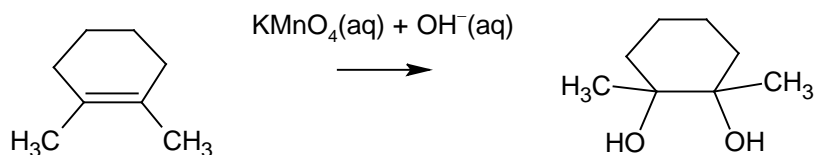
19.25 See Exercise 19.24 above

- 19.26 (a) Catalytic hydrogenation of  $(\text{CH}_3)_2\text{C}=\text{CHCH}_2\text{CH}_3$  produces  $(\text{CH}_3)_2\text{CHCH}_2\text{CH}_2\text{CH}_3$ .  
 (b) Catalytic hydrogenation of 3,3-dimethylcyclopentene gives 3,3-dimethylcyclopentane.

19.27 (a)



(b)



- 19.28 (a)  $(\text{CH}_3)_2\text{C}=\text{O} + \text{CO}_2$  is the product upon treating  $(\text{CH}_3)_2\text{C}=\text{CH}_2$  with acidic  $\text{KMnO}_4$ .  
 (b) 2 equiv  $\text{CH}_3\text{CH}_2\text{CO}_2\text{H}$  is the product upon treating one equivalent of  $\text{CH}_3\text{CH}_2\text{CH}=\text{CHCH}_2\text{CH}_3$  with acidic  $\text{KMnO}_4$ .

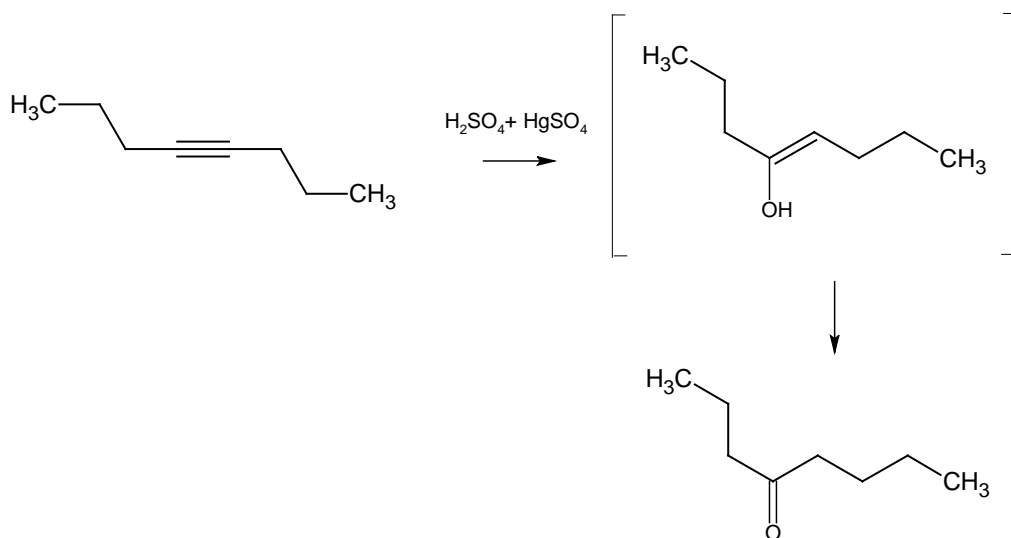
- 19.29 (a) 6-methylhept-3-yne  
 (b) 3,3-dimethylbut-1-yne  
 (c) 5-methylhex-2-yne  
 (d) hept-2-en-5-yne

19.30 The peak just above  $3300\text{ cm}^{-1}$  looks like an alkyne C–H stretch, while the peak just above  $2100\text{ cm}^{-1}$  looks like an asymmetric alkyne  $\text{C}\equiv\text{C}$  stretch. There also appear to be alkyl C–H stretch peaks just below  $3000\text{ cm}^{-1}$ . The compound likely has alkyl H's in addition to the alkynyl H.

19.31 The two downfield peaks,  $\sim 68$  and  $\sim 85$  ppm, are characteristic of an alkyne. Alkene  $^{13}\text{C}$  chemical shifts occur further downfield.

19.32 The unknown compound is either  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{C}\equiv\text{CH}$  or  $(\text{CH}_3\text{CH}_2)_3\text{CHC}\equiv\text{CH}$ .

19.33

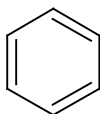


- 19.34 (a) To make 2-pentanone you could hydrate 1-pentyne,  $\text{CH}_3\text{CH}_2\text{CH}_2\text{C}\equiv\text{CH}$ .  
 (b) To make 3-hexanone you could hydrate 2-hexyne,  $\text{CH}_3\text{CH}_2\text{CH}_2\text{C}\equiv\text{CCH}_3$ .

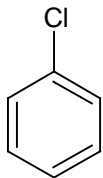
- 19.35 (a) To make 5-methylhex-1-yne,  $(\text{CH}_3)_2\text{CHCH}_2\text{CH}_2\text{C}\equiv\text{CH}$  you could start with ethyne (acetylene),  $\text{HC}\equiv\text{CH}$ , treat it with  $\text{NaNH}_2$  to make sodium acetylide add to 3-methylbutylbromide,  $(\text{CH}_3)_2\text{CHCH}_2\text{CH}_2\text{Br}$
- (b) To make 2-hexyne,  $\text{CH}_3\text{CH}_2\text{CH}_2\text{C}\equiv\text{CCH}_3$  you could start with propyne,  $\text{HC}\equiv\text{CCH}_3$ , treat it with  $\text{NaNH}_2$  to make sodium propynylide add to propylbromide,  $\text{CH}_3\text{CH}_2\text{CH}_2\text{Br}$
- Alternatively, you could treat pentyne,  $\text{CH}_3\text{CH}_2\text{CH}_2\text{C}\equiv\text{CH}$ , with  $\text{NaNH}_2$  to make sodium pentynylide add to methylbromide,  $\text{CH}_3\text{Br}$
- (c) To make 4-methylpent-2-yne,  $(\text{CH}_3)_2\text{CHC}\equiv\text{CCH}_3$  you could start with propyne,  $\text{HC}\equiv\text{CCH}_3$ , treat it with  $\text{NaNH}_2$  to make sodium propynylide add to isopropylbromide,  $(\text{CH}_3)_2\text{CHBr}$
- Alternatively, you could treat 3-methylbut-1-yne,  $(\text{CH}_3)_2\text{CHC}\equiv\text{CH}$ , with  $\text{NaNH}_2$  to make sodium 3-methylbutynylide add to methylbromide,  $\text{CH}_3\text{Br}$

## Chapter 20

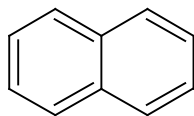
- 20.1  $-236 \text{ kJ/mol}$
- 20.2 (a) Cyclobutadiene is monocyclic, planar and fully conjugated. Cyclobutadiene is anti-aromatic.  
 (b) Cyclohepta-1,3,5-triene is monocyclic and planar, but not fully conjugated.  
 (c) Cyclopenta-1,3-diene is monocyclic and planar, but not fully conjugated.  
 (d) Cyclooctatetraene is monocyclic, planar and fully conjugated. Cyclobutadiene is anti-aromatic.
- 20.3 (a) Benzene has just one  $^{13}\text{C}$  NMR absorption peak.



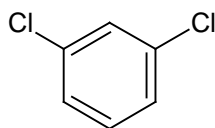
- (b) Chlorobenzene has four  $^{13}\text{C}$  NMR absorption peaks.



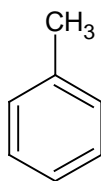
(c) Naphthalene has three  $^{13}\text{C}$  NMR absorption peaks.



(d) 1,3-dichlorobenzene has four  $^{13}\text{C}$  NMR absorption peaks.



20.4



(a) There is an aryl C-H stretching band with three peaks at  $3100$ ,  $3070$  and  $3030\text{ cm}^{-1}$ . The alkyl C-H stretching band with principal peaks at  $2925$  and  $2850\text{ cm}^{-1}$ .

(b) The out-of-plane C-H bending vibrations give rise to two peaks at  $740$  and  $700\text{ cm}^{-1}$ .

(c) The in-plane C-H bending vibrations produce peaks at  $1090$  and  $1030\text{ cm}^{-1}$ . The aryl C-C stretches produce a band with principal peaks at  $1610$ ,  $1510$  and  $1470\text{ cm}^{-1}$ .

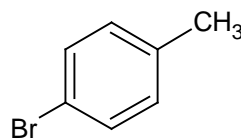
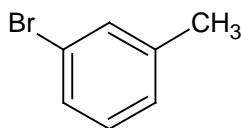
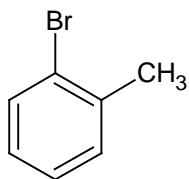
20.5 Furan has 6 electrons in its  $\pi$  system. It is aromatic, with  $^1\text{H}$  NMR shifts are at 6.4 and 7.4 ppm.

- 20.6 (a) Aromatic  
(b) Anti-aromatic  
(c) Aromatic

- 20.8 (a) meta  
(b) para  
(c) ortho

- 20.9 (a) 1-bromo-3-chlorobenzene, or m-bromochlorobenzene  
(b) 2-methylpropylbenzene, or 2-methyl-1-phenylpropane  
(c) 1-amino-4-bromobenzene, or p-aminobromobenzene or p-bromoaniline

20.10



*o*-bromotoluene

*m*-bromotoluene

*p*-bromotoluene

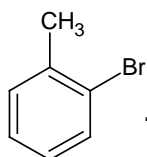
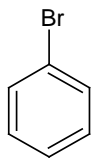
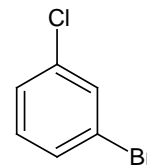
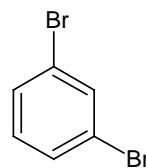
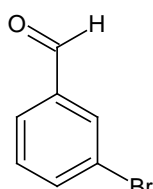
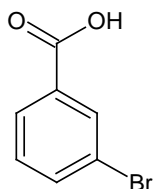
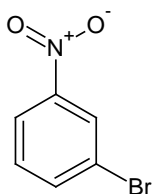
20.11  $D_2SO_4$  sulfonates the benzene ring reversibly. On sulfonation, an  $H^+$  is lost to the solvent ( $D_2SO_4$ ). On de-sulfonation,  $D^+$  adds to the ring. Since the solvent far outnumbers the benzene, the  $H$ 's are lost in a sea of  $D$ 's. The benzene ends up with all  $H$ 's replaced by  $D$ 's.

20.12 (a) Nitrobenzene < toluene < phenol (hydroxybenzene)

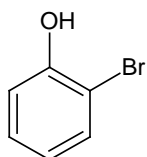
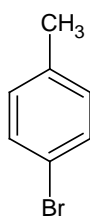
(b) Benzoic acid < chlorobenzene < benzene < phenol

(c) Benzaldehyde < bromobenzene < benzene < aniline (aminobenzene)

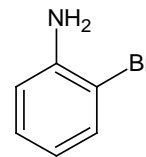
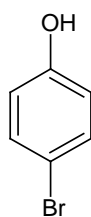
20.13 The products of electrophilic bromination of nitrobenzene, benzoic acid, benzaldehyde, bromobenzene, chlorobenzene, benzene, toluene, phenol and aniline, respectively, are



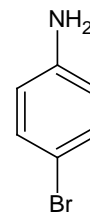
+



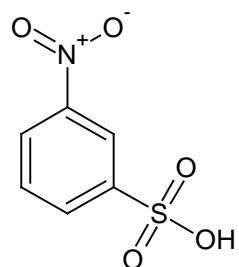
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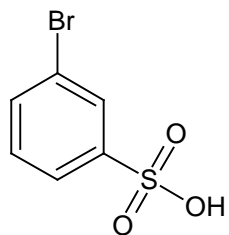
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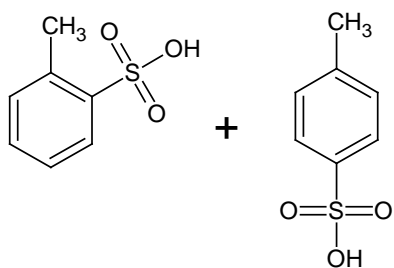
20.14 (a)



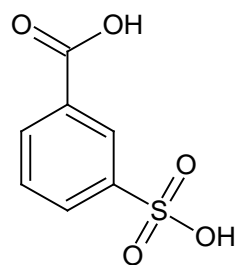
(b)



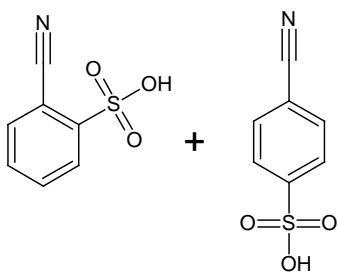
(c)



(d)

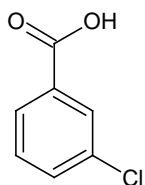


(e)

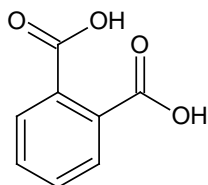




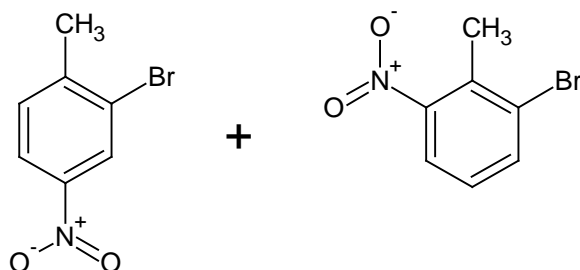
20.15 Oxidizing *m*-chloroethylbenzene with  $\text{KMnO}_4$  produces *m*-chlorobenzoic acid,



Oxidizing tetralin with  $\text{KMnO}_4$  produces 1,2-benzenedicarboxylic acid a.k.a. phthalic acid,



20.16 (a) Brominate toluene using  $\text{Br}_2 + \text{FeBr}_3$   
Separate the ortho product, 2-bromo-toluene  
Nitrate using nitric and sulfuric acids to obtain the 2-bromo-4-nitro and 2-bromo-6-nitro products:



Separate the desired 2-bromo-4-nitro product – e.g. using distillation or chromatography, or maybe even a molecular sieve.

(b) Nitrate benzene with 3 equivalents of  $-\text{NO}_2$ .

(c) First make aniline from benzene.

Nitrate benzene using nitric and sulfuric acids – with 1 equivalent of  $-\text{NO}_2$

Reduce the nitrobenzene product using hydrogen to get aniline

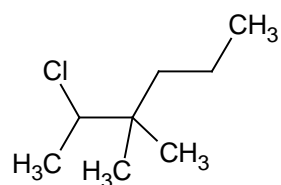
Brominate the aniline with 3 equivalents of bromine to get the fully brominated product, 2,4,6-tribromoaniline

## Chapter 21

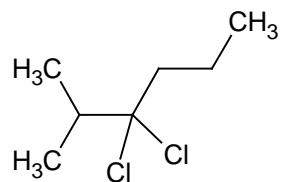
- 21.1 (a) 2-bromobutane  
(b) 3-chloro-2-methylpentane  
(c) 1-chloro-3-methylbutane  
(d) 1,3-dichloro-3-methylbutane  
(e) 1-bromo-4-chlorobutane  
(f) 4-bromo-1-chloropentane

21.3

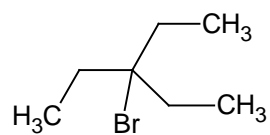
(a)



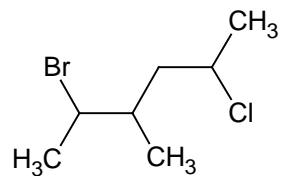
(b)



(c)

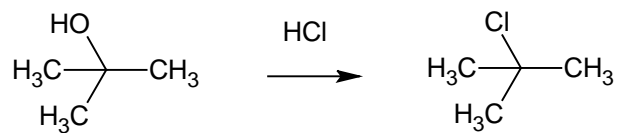


(d)

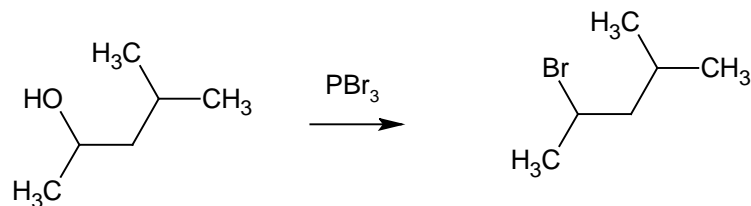


21.5

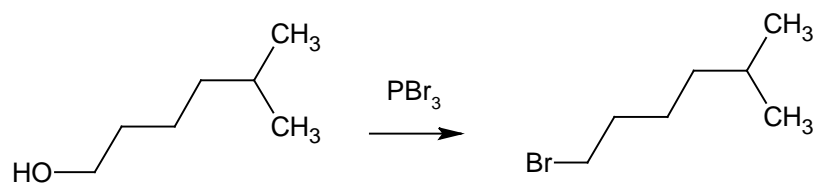
(a)



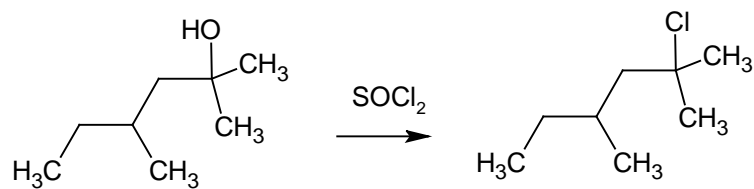
(b)



(c)

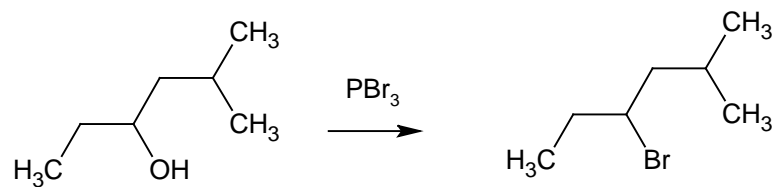


(d)

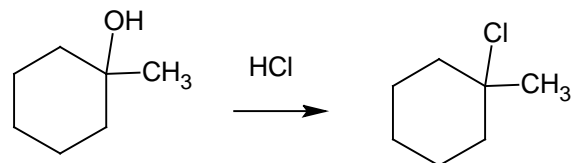


21.6

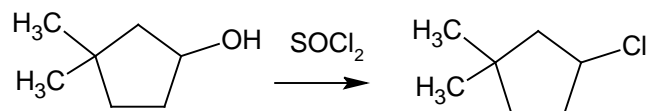
(a)



(b)

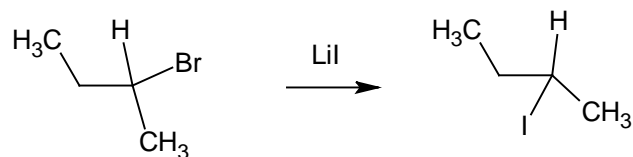


(c)

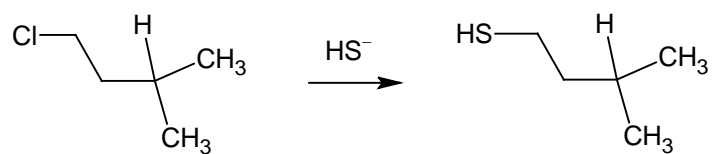


21.8

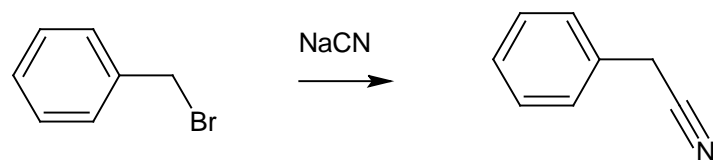
(a)



(b)

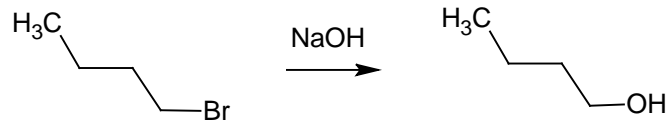


(c)

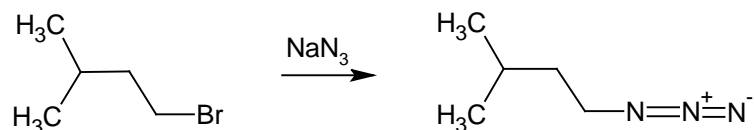


21.9

(a)



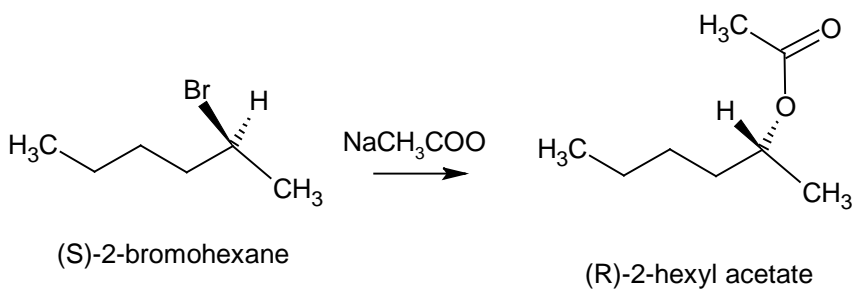
(b)



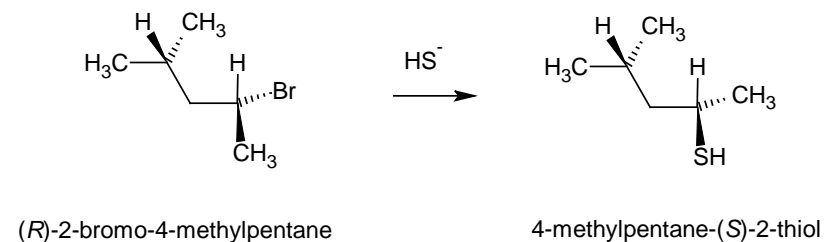
21.10 (a) The rate triples.

(b) The rate increases by a factor of 4.

21.11



21.12



21.14 (a)  $\text{CN}^-$  (cyanide ion) reacts faster with  $\text{CH}_3\text{CH}_2\text{CH}_2\text{Br}$

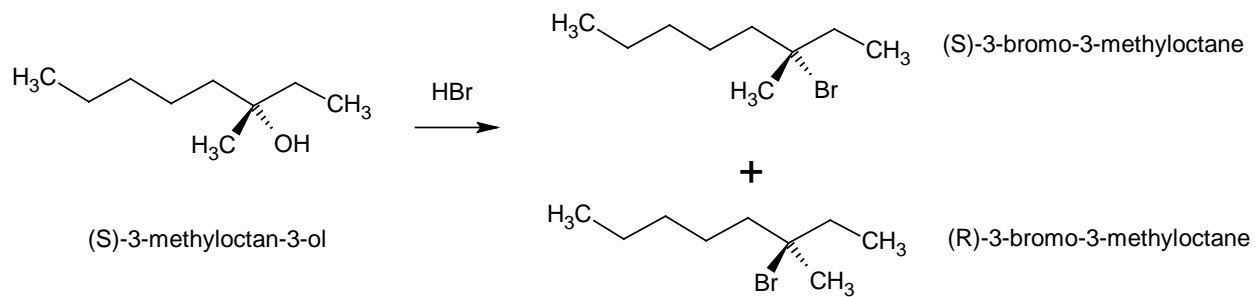
(b) Reaction of  $\text{I}^-$  with  $(\text{CH}_3)_2\text{CHCH}_2\text{Cl}$  is faster.

21.15  $\text{CH}_3\text{I} > \text{CH}_3\text{Br} > \text{CH}_3\text{F}$

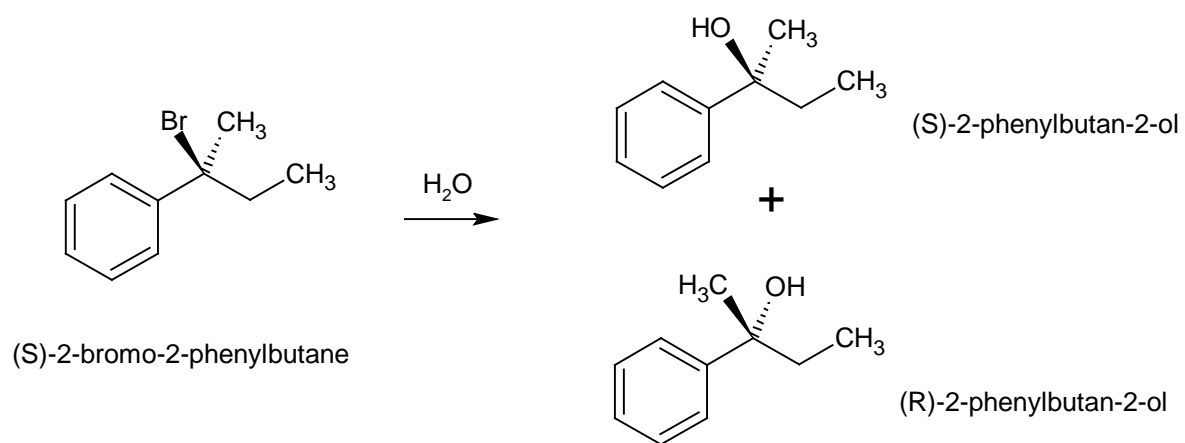
21.16 (a) No effect

(b) Halving the HBr concentration has no effect. However, doubling the *tert*-butyl alcohol concentration doubles the rate of reaction.

21.17

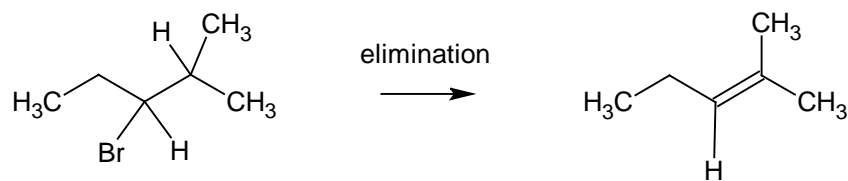


21.18

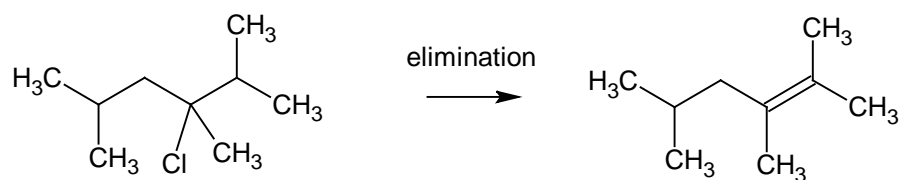


21.19

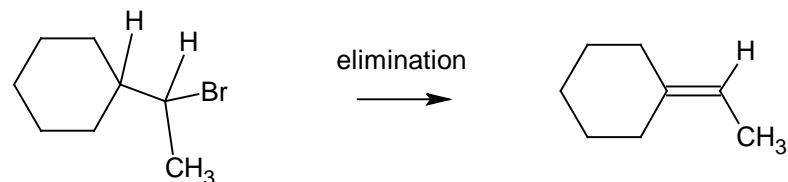
(a)



(b)

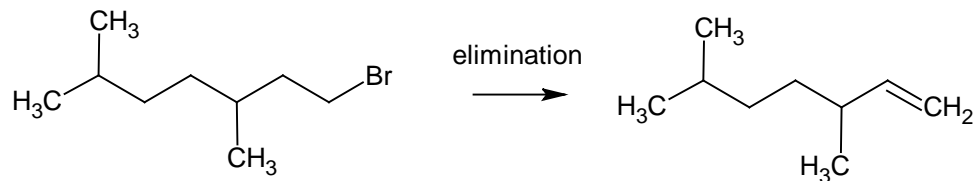


(c)

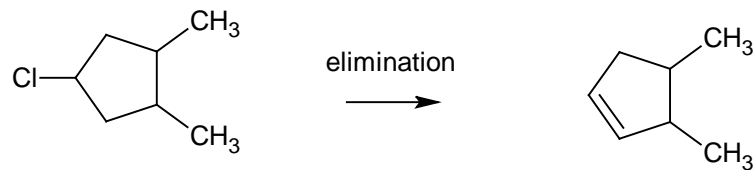


21.20

(a)



(b)



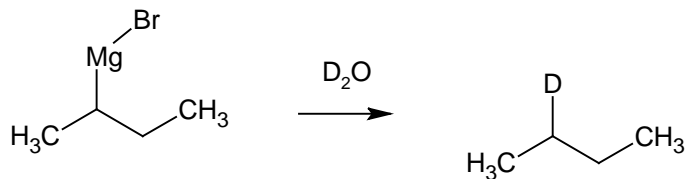
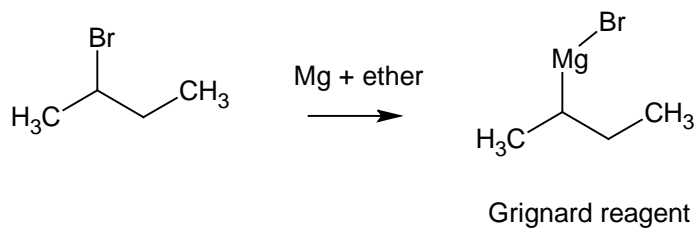
21.21 Rate of the elimination reaction triples.

21.22 (a)  $S_N2$

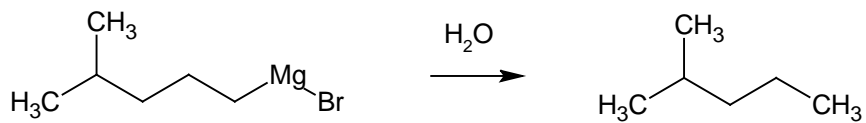
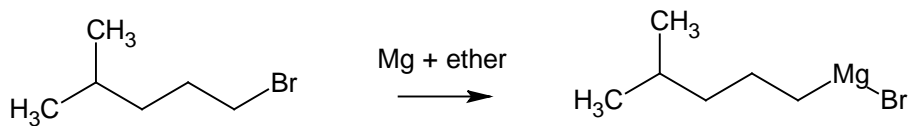
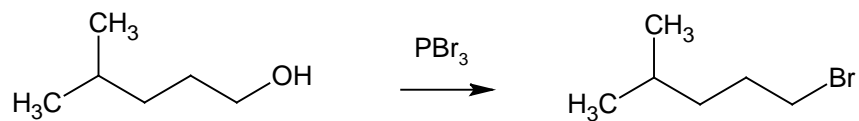
(b) E2

(c)  $S_N1$

21.23



21.24



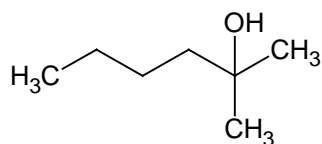


## Chapter 22

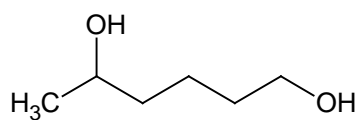
- 22.2 (a) tertiary alcohol.  
(b) contains primary and secondary alcohol functional groups.  
(c) primary alcohol.  
(d) secondary alcohol.  
(e) phenol  
(f) phenol

22.3

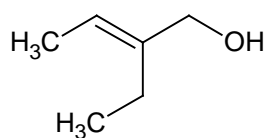
(a)



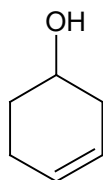
(b)



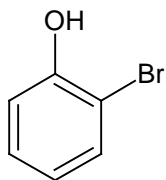
(c)



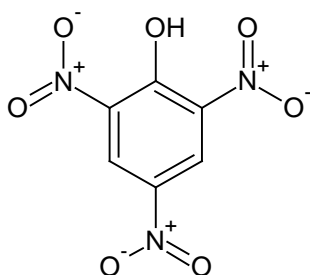
(d)



(e)



(f)

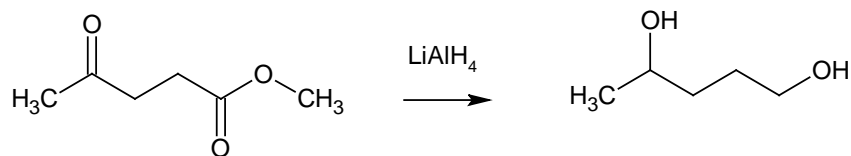
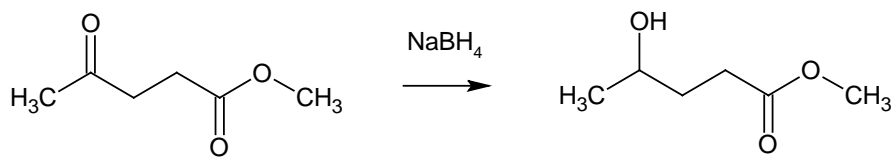


- 22.4 (a) di(2-propyl) ether a.k.a. diisopropyl ether  
(b) cyclopentyl propyl ether  
(c) 4-bromophenyl methyl ether  
(d) ethyl 2-methyl-1-propyl ether

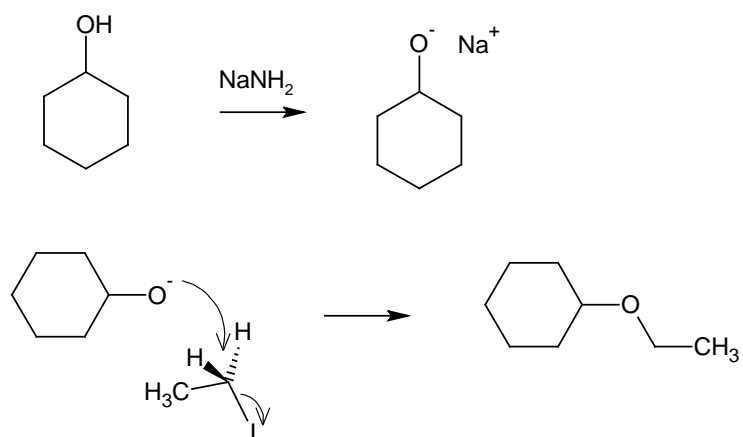
- 22.5 O–H stretch:  $3320\text{ cm}^{-1}$  (strong, broad)  
aromatic C–H stretches:  $3090$ ,  $3070$  and  $3010\text{ cm}^{-1}$  (sharp peaks).  
alkyl C–H stretches:  $2950$  and  $2890\text{ cm}^{-1}$  (broad).  
C–O stretches:  $1020\text{ cm}^{-1}$  (strong, somewhat broad).  
C–C stretches of the benzene ring:  $1500$  to  $1370\text{ cm}^{-1}$  (three sharp ones)  
benzene C–H in-plane: peaks at  $1080$  and  $1040\text{ cm}^{-1}$   
benzene C–H out-of-plane bends:  $730$  and  $700\text{ cm}^{-1}$

- 22.6 The IR spectrum of the product should not show the strong, broad alcohol O–H peak around  $3300\text{ cm}^{-1}$ , or the strong C–O peak near  $1000\text{ cm}^{-1}$ . Instead, it should show a strong C=O stretching peak near  $1750\text{ cm}^{-1}$ .

22.7



22.8

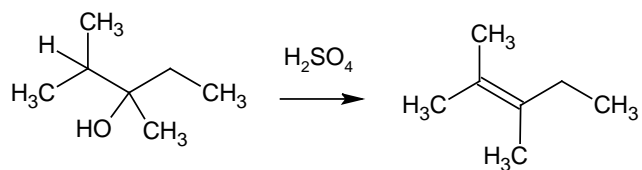


We cannot make cyclohexyl ethyl ether by first forming sodium ethoxide, then reacting it with cyclohexyl iodide.

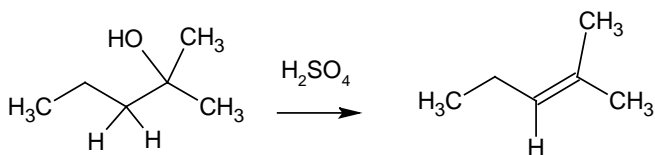
22.9 bromoethane &gt; chloroethane &gt; 2-bromopropane &gt; 2-chloro-2-methylpropane

22.10

(a)

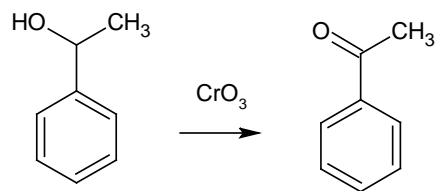


(b)

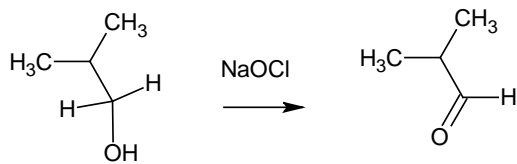


22.11

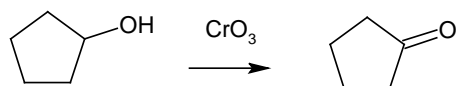
(a)



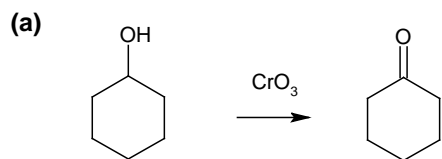
(b)



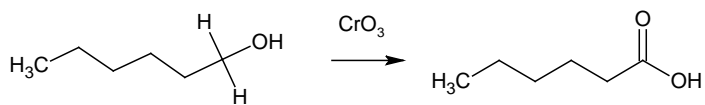
(c)



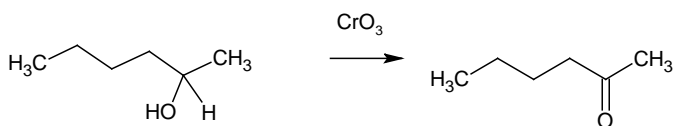
22.12



(b)

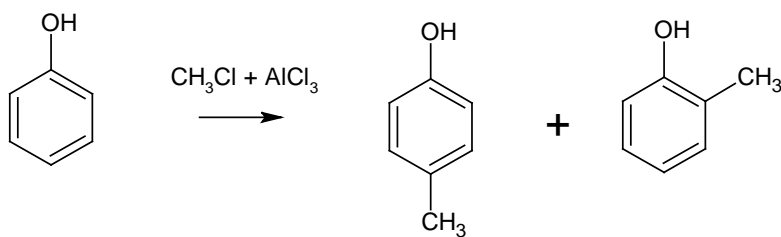
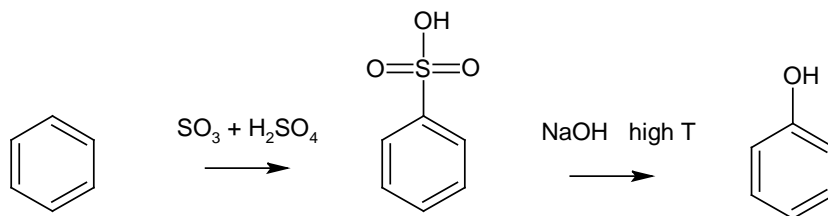


(c)

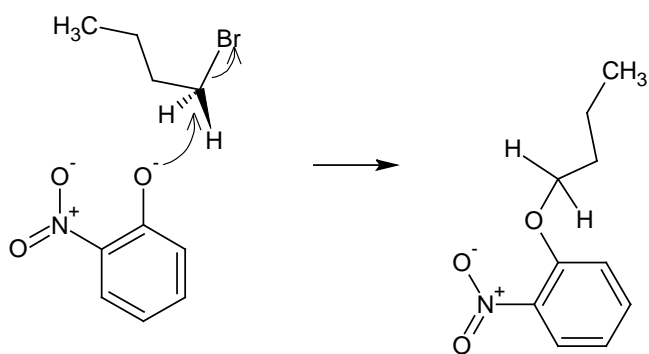
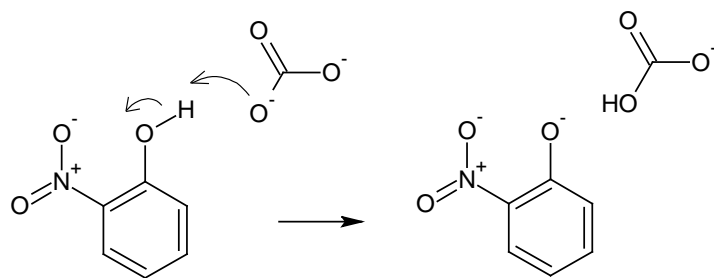


22.13 The same products are expected.

22.14



22.15

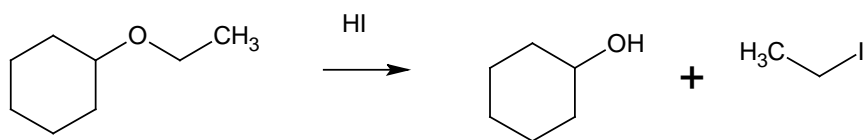


22.16

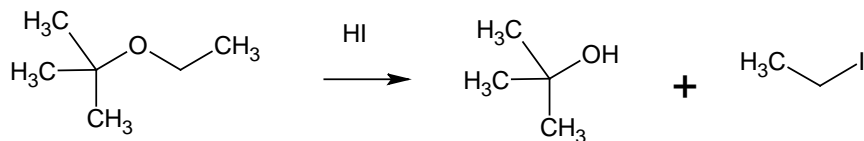
(a)



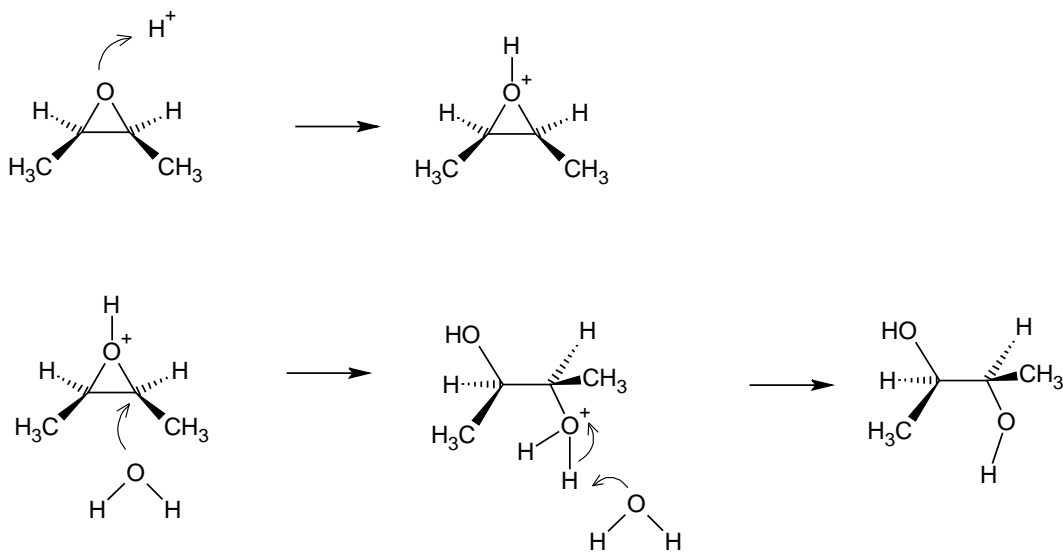
(b)



(c)



22.17



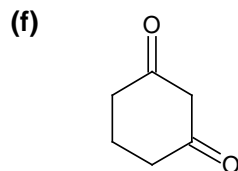
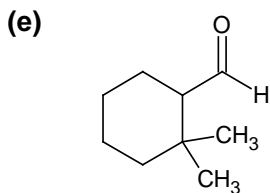
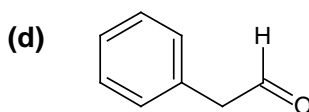
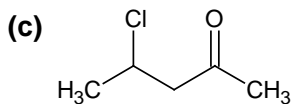
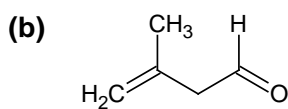
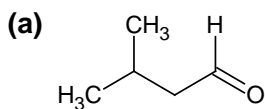
- 22.18 (a) 2-butanthiol  
 (b) 2,6,6-trimethylheptan-4-thiol  
 (c) 3-cyclopentenethiol
- 22.19 (a) ethyl methyl sulfide  
 (b) *tert*-butyl ethyl sulfide  
 (c) *o*-methylthiophenyl methyl sulfide
- 22.20 To make 2-butene-1-thiol from 2-butene-1-ol:  
 You could treat 2-buten-1-ol with  $\text{PBr}_3$  to make 1-bromobut-2-ene.  
 1-bromobut-2-ene is then treated with  $\text{NaSH}$  to make 2-butene-1-thiol.

To make 2-butene-1-thiol from methyl but-2-enoate:  
 First reduce methyl but-2-enoate with  $\text{LiAlH}_4$  to get methanol and 2-butene-1-ol.  
 2-butene-1-ol can then be processed as above.

## Chapter 23

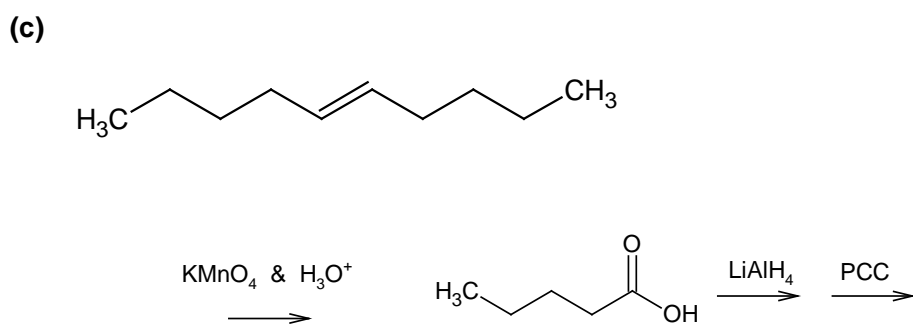
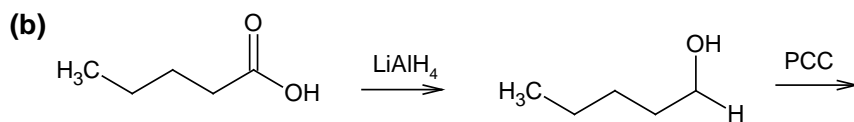
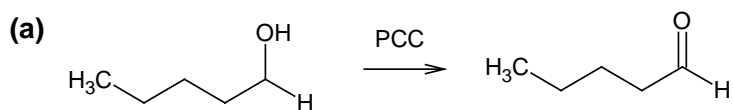
- 23.2 (a) 2-methylpentan-3-one  
 (b) 3-phenylpropanal  
 (c) 2,6-octandione  
 (d) *trans*-2-methylcyclohexanecarbaldehyde  
 (e) 1,5-pentanedial  
 (f) *cis*-2,5-dimethylcyclohexanone

23.3

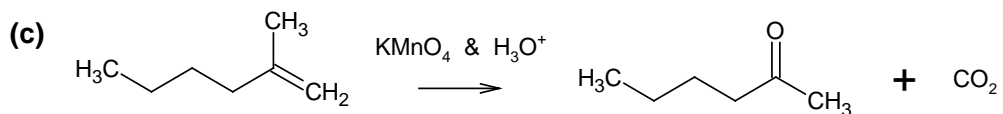
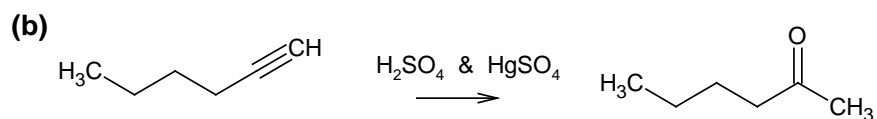
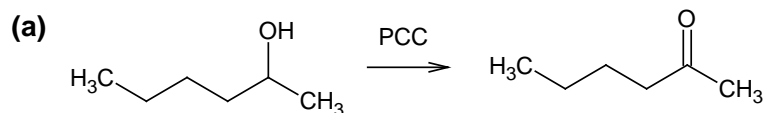




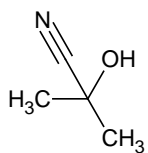
23.4



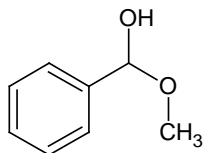
23.5



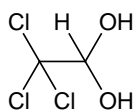
23.6



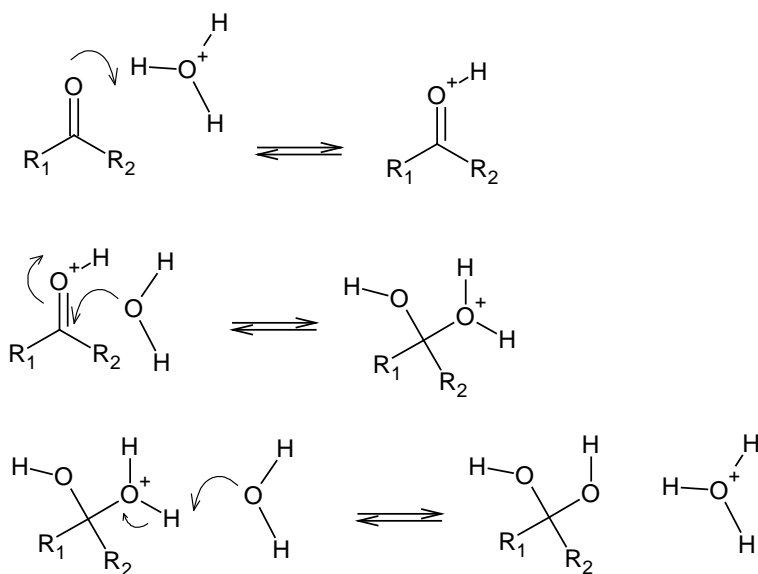
23.7



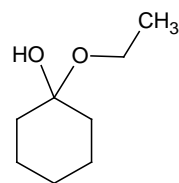
23.8



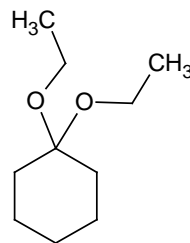
23.9



23.10

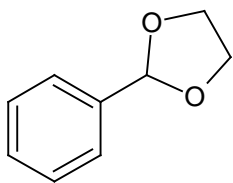


(1 equivalent of ethanol)



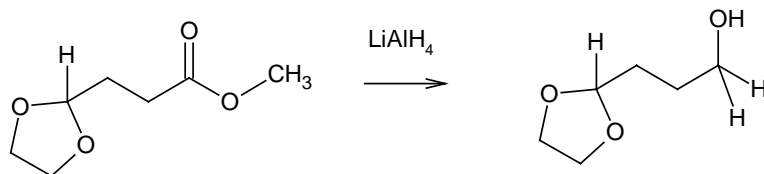
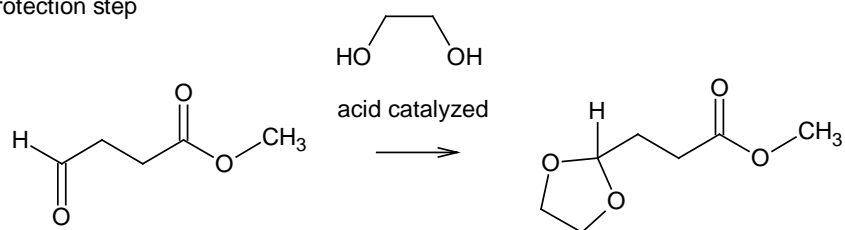
(2 equivalents of ethanol)

23.11

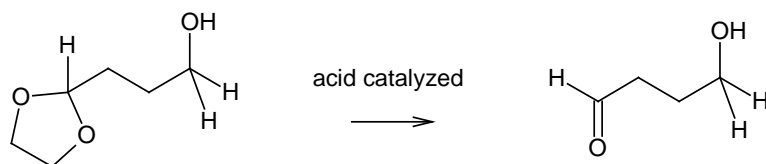


23.12

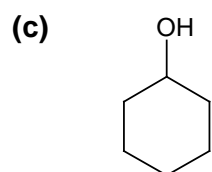
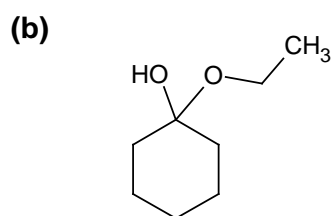
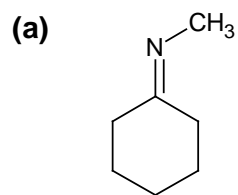
protection step



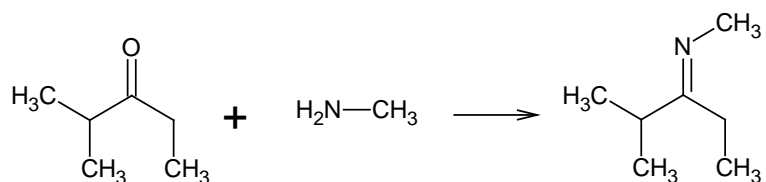
deprotection step



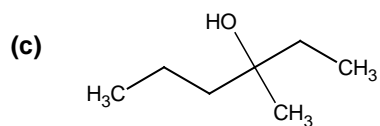
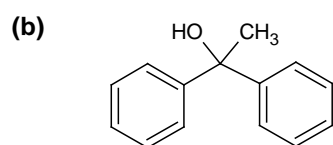
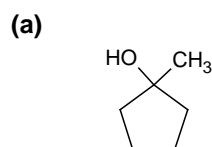
23.13



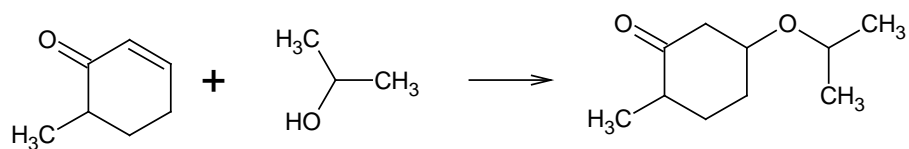
23.14



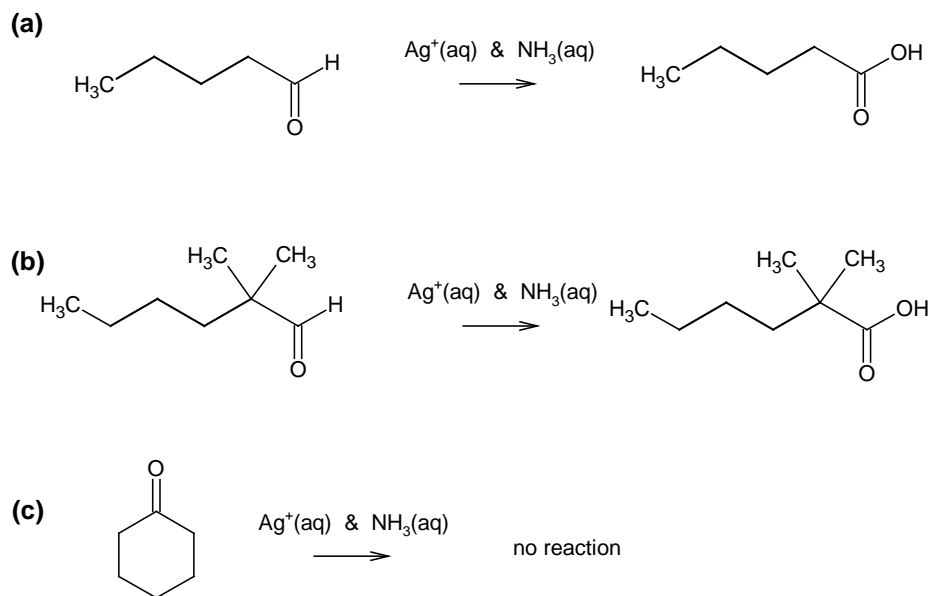
23.15



23.16

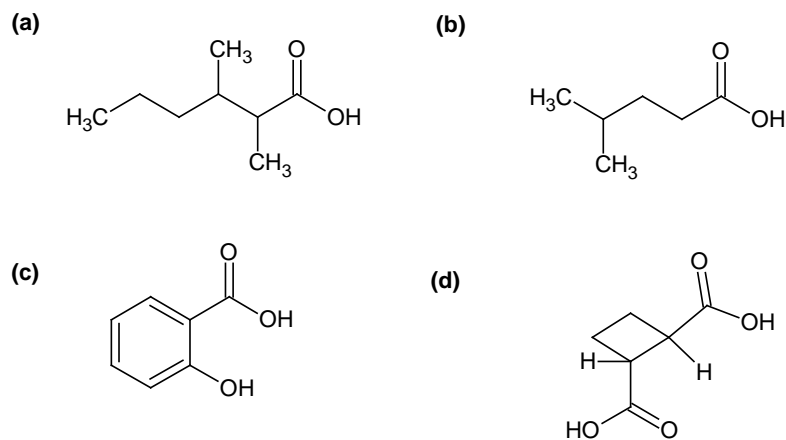


23.17

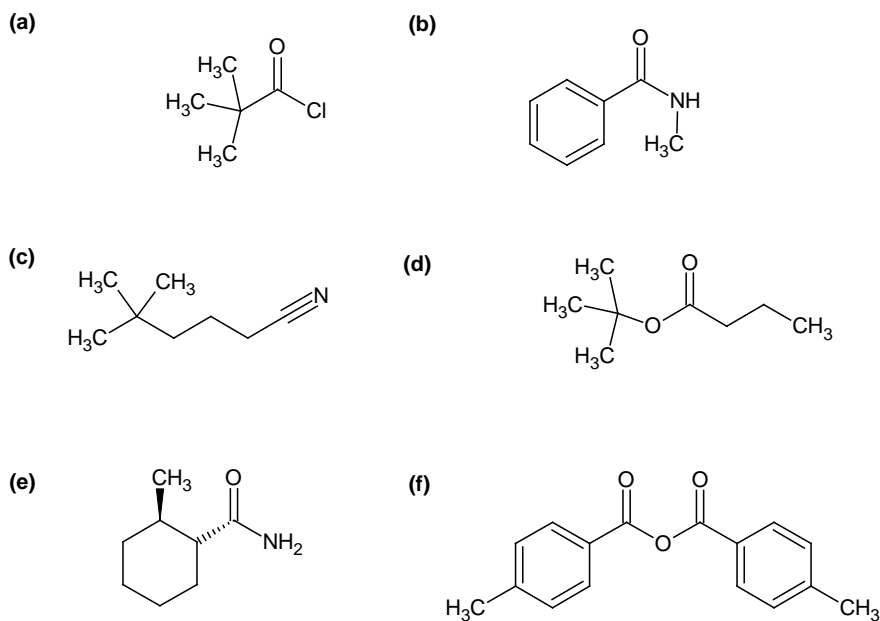


## Chapter 24

24.2

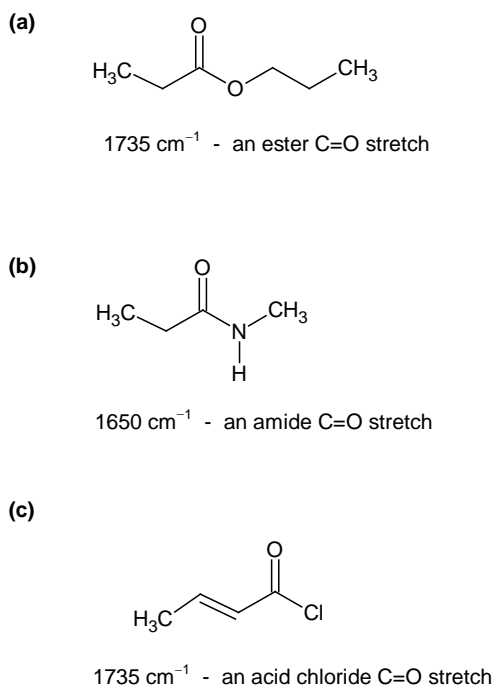


24.3



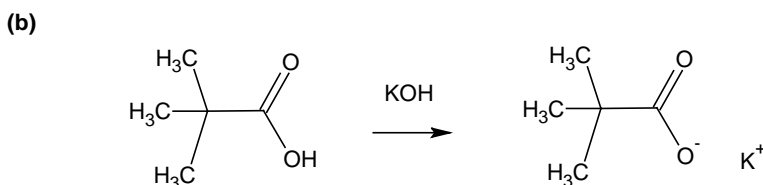
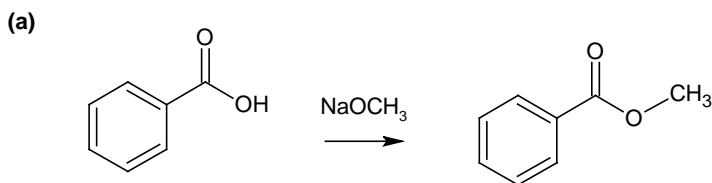
- 24.4 (a) a carbonyl stretch – most likely an ester or an aldehyde.  
(b) C=O stretching band (there are two) of an anhydride.  
(c) carboxylic acids.  
(d) a ketone (unless there is also a broad O–H stretch - 2400-3300 cm<sup>-1</sup>) C=O stretch.

24.5



24.6 In  $^{13}\text{C}$  NMR spectroscopy, the carboxylic acid carbonyl carbon will absorb around 180-185 ppm and the ketone carbonyl range is from 180-220 ppm. Also, 4-hydroxycyclohexanone has a hydroxyl functionality and will have a C-O carbon absorption in the 50-90 ppm range. The other alkyl carbons will mostly absorb in the 10-30 ppm range – though the carbon next to the carbonyl (in both molecules) can be as far as 50 ppm downfield. In the  $^1\text{H}$  NMR spectra, the molecules are distinguished by possible splitting of the hydroxyl H peak in the case of 4-hydroxycyclohexanone, and (more importantly) by the extra downfield peak due to the methine H-C-O.

24.8



24.9 methanol < phenol < *p*-nitrophenol < acetic acid < sulfuric acid

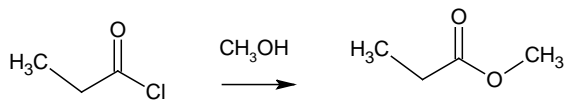
24.10 (a)  $\text{CH}_3\text{CH}_2\text{CO}_2\text{H}$  <  $\text{BrCH}_2\text{CH}_2\text{CO}_2\text{H}$  <  $\text{BrCH}_2\text{CO}_2\text{H}$   
 (b) ethanol < benzoic acid < *p*-cyanobenzoic acid

24.11 (a)  $\text{CH}_3\text{COCl}$  >  $\text{CH}_3\text{CO}_2\text{CH}_3$  (b)  $\text{CH}_3\text{CH}_2\text{CO}_2\text{CH}_3$  >  $(\text{CH}_3)_2\text{CHCONH}_2$   
 (c)  $\text{CH}_3\text{CO}_2\text{COCH}_3$  >  $\text{CH}_3\text{CO}_2\text{CH}_3$  (d)  $\text{CH}_3\text{CO}_2\text{CH}_3$  >  $\text{CH}_3\text{CHO}$

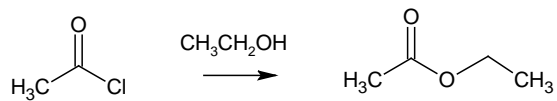
24.12 The fluorine substituents in  $\text{CF}_3\text{CO}_2\text{CH}_3$  are electron withdrawing, making the carbonyl carbon more electron deficient (attracting nucleophiles) and stabilizing the four coordinate intermediate which has additional electron density due to the bonded nucleophile.

24.13

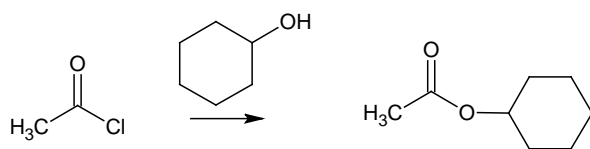
(a)



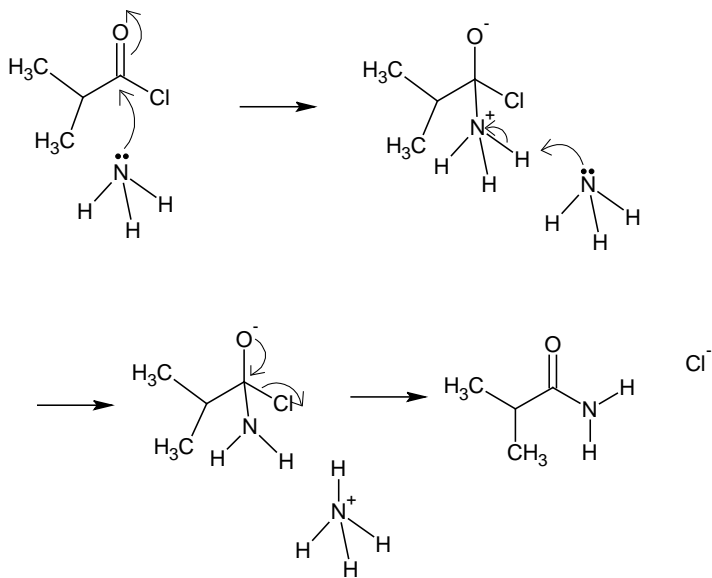
(b)



(c)



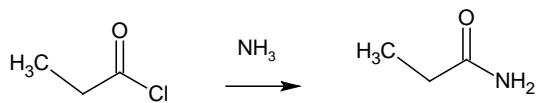
24.14



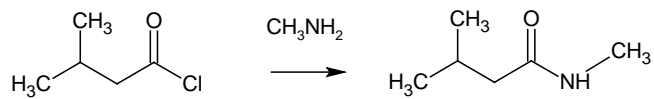


24.15

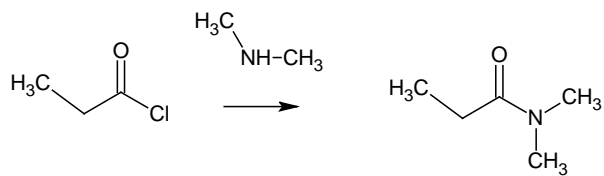
(a)



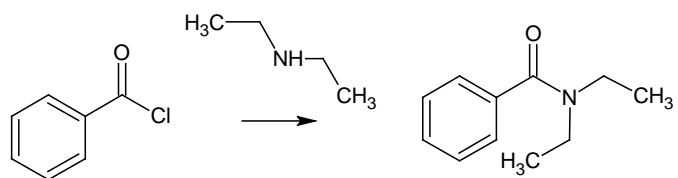
(b)



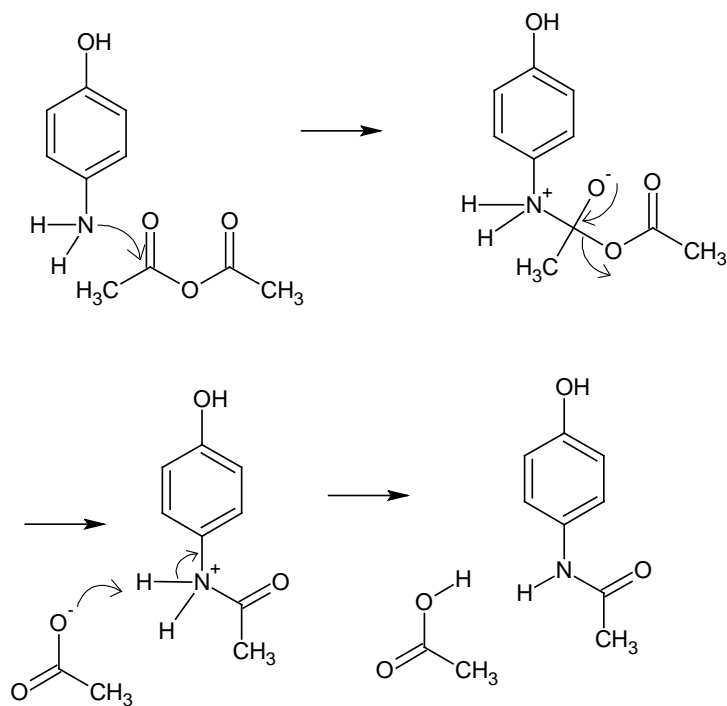
(c)



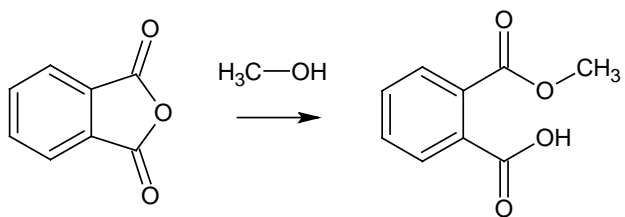
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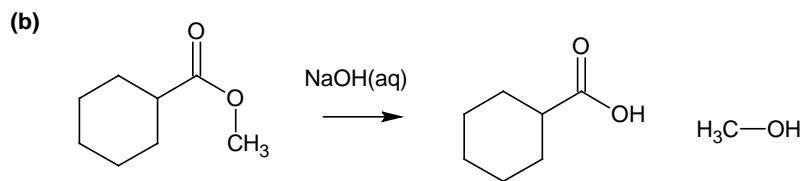
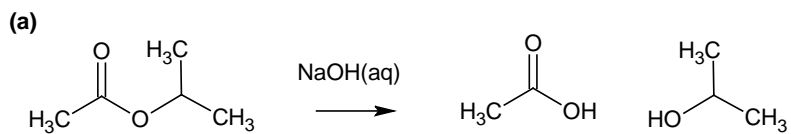
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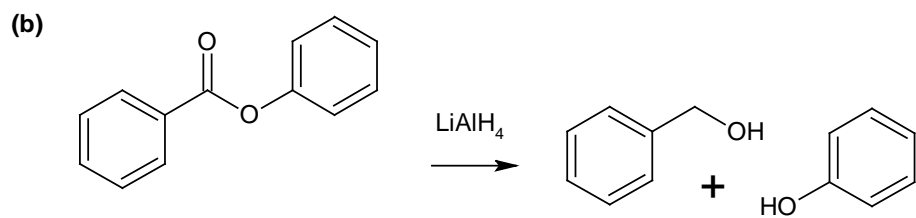
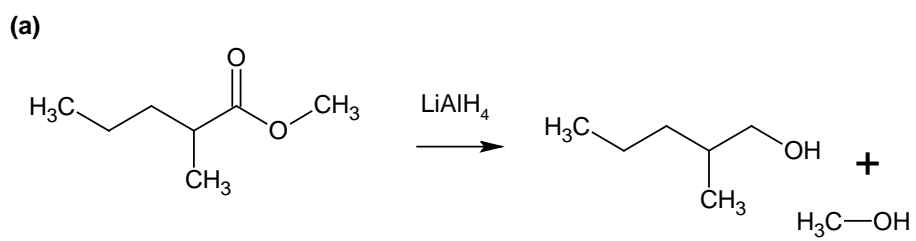
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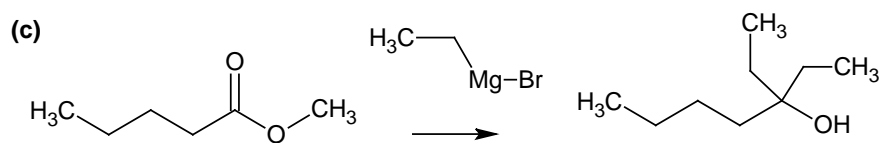
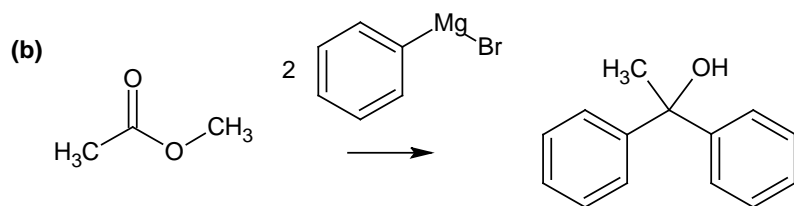
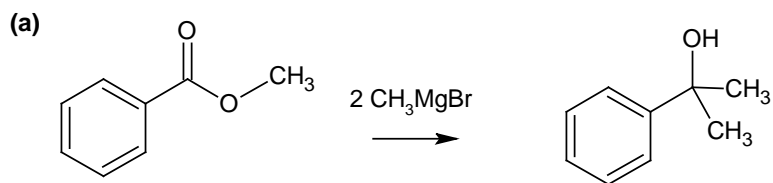
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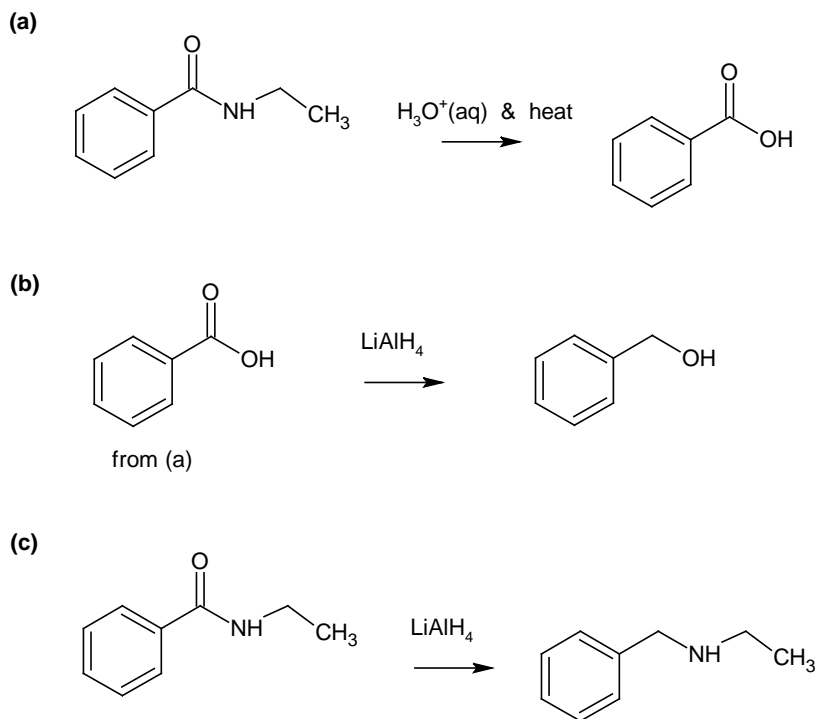
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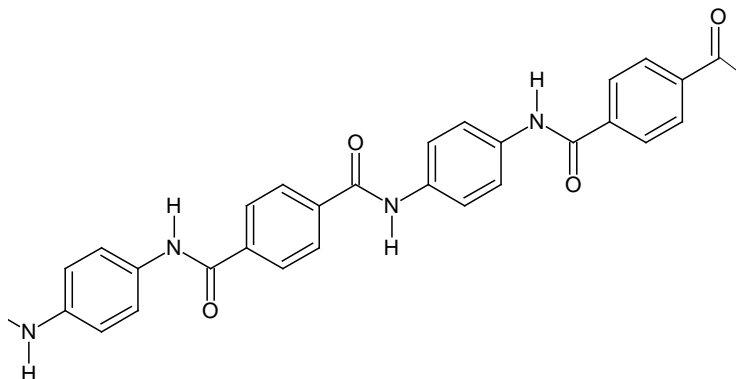
24.20



24.21



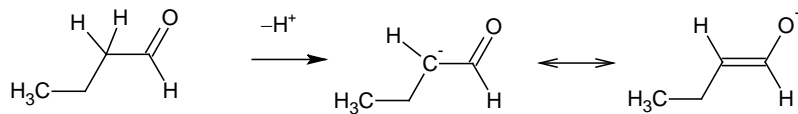
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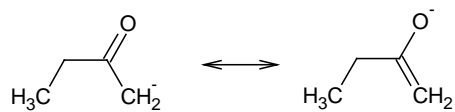
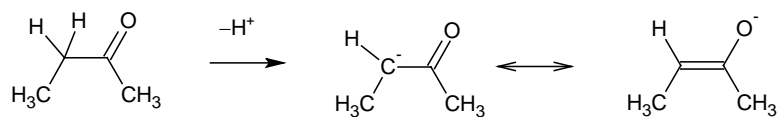
- 24.23 (a)  $\text{CH}_3\text{CH}_2\text{CHO}$  has no acidic H's  
(b)  $(\text{CH}_3)_3\text{CCOCH}_3$  is essentially non-acidic. However, the 3 H's on the methyl next to the carbonyl are slightly acidic.  
(c) The H bonded to O is acidic in acetic acid,  $\text{CH}_3\text{CO}_2\text{H}$ .  
(d) The methylene H's between the two carbonyl C's are acidic in 1,3-Cyclohexanedione.

24.24

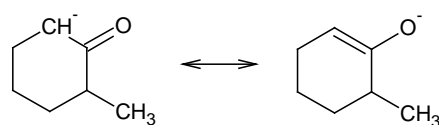
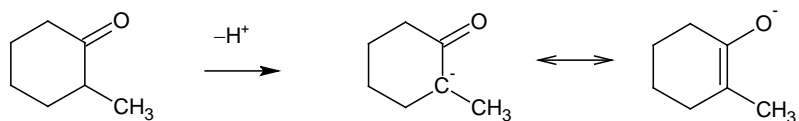
(a)



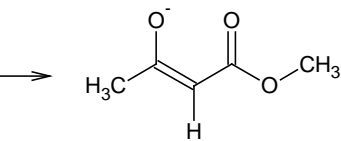
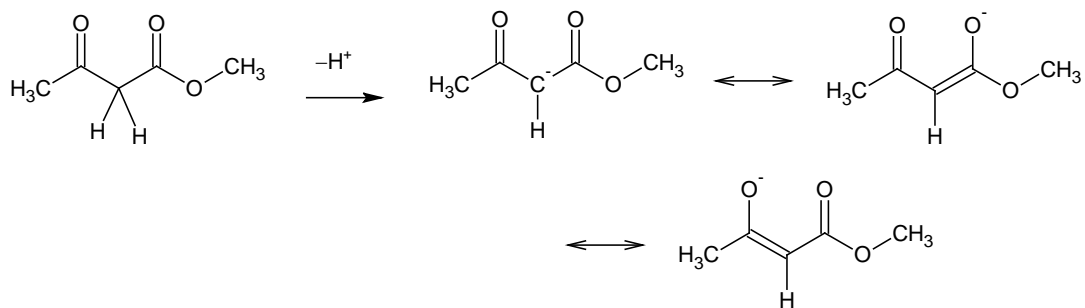
(b)



(c)

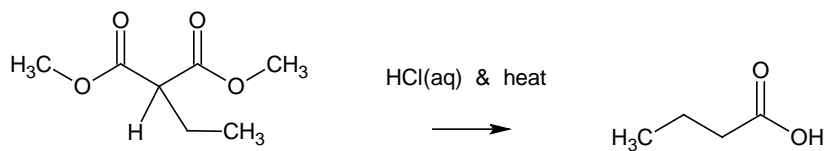
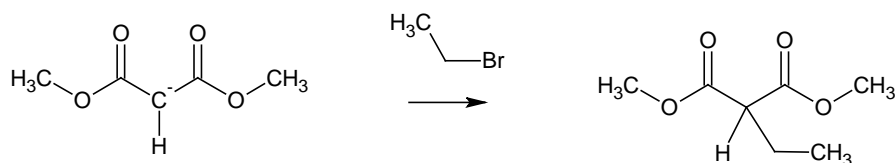
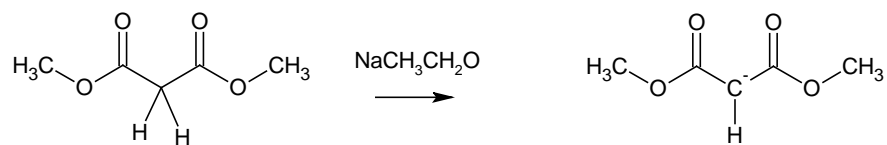


24.25

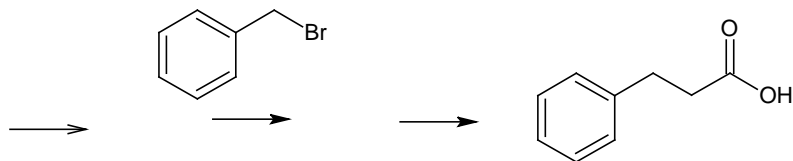


24.26

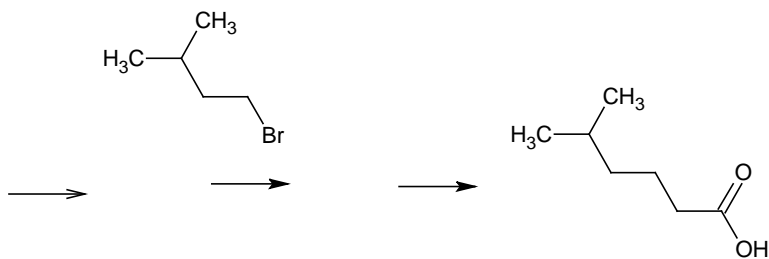
(a)



(b)



(c)



## Chapter 25

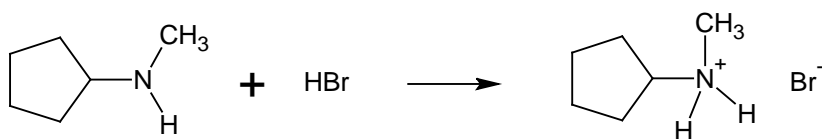
- 25.2 (a) primary amine  
(b) secondary amine  
(c) tertiary amine  
(d) quaternary ammonium salt

25.3 The integrals correspond to the H's coming in equivalent groups of 2, 2, 2, 2 and 3 – from downfield to upfield – accounting for the 11 H's in *p*-ethoxyaniline. The two downfield doublets at 6.7 and 6.6 ppm are consistent with phenyl H's. Moreover, the doublets “point” to each other – i.e. the peaks closest to the other doublet are larger – indicating that they are coupling to each other (coupled doublets well separated in chemical shift show two pairs of equal intensity peaks). This is consistent with the expected coupling of the C-2 and C-3 (C-1 is the amine carbon) phenyl H's and the equivalent C-6 and C-5 phenyl H's (to give integrals of 2, while splitting the neighboring peak into a doublet, rather than a triplet). As O is more electronegative than N, the furthest downfield doublet (i.e. at 6.7 ppm) likely corresponds to the C-3 and C-5 H's. The quartet at 3.9 ppm (integrating to 2) and the triplet at 1.3 ppm (integrating to 3) are consistent with the ethyl group – an alkyl methylene and methyl group, with the methylene H's downfield because their carbon is bonded to oxygen. The remaining broad peak, integrating to 2, corresponds to the amine H's. Their peak is broadened due to hydrogen bonding.

25.4 6 peaks. The methyl C peak (C bonded to another alkyl C) should appear in the 10-30 ppm range. The methylene C peak (C bonded to O) should appear in the 50-70 ppm. The phenyl C peaks will be in the 110-150 ppm range, with the C's bonded directly to O and N furthest downfield.

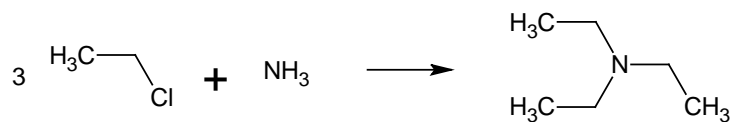
- 25.5 (a)  $\text{CH}_3\text{CH}_2\text{NH}_2$   
(b)  $\text{NaOH}$   
(c)  $\text{CH}_3\text{NHCH}_3$   
(d)  $(\text{CH}_3)_3\text{N}$

25.6

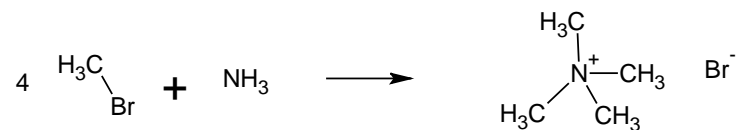


25.7

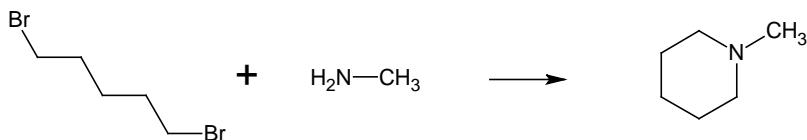
(a)



(b)

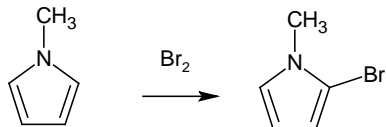


25.8

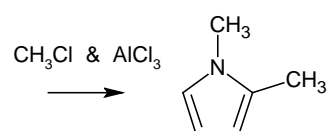


25.9

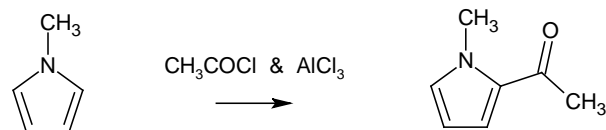
(a)



(b)

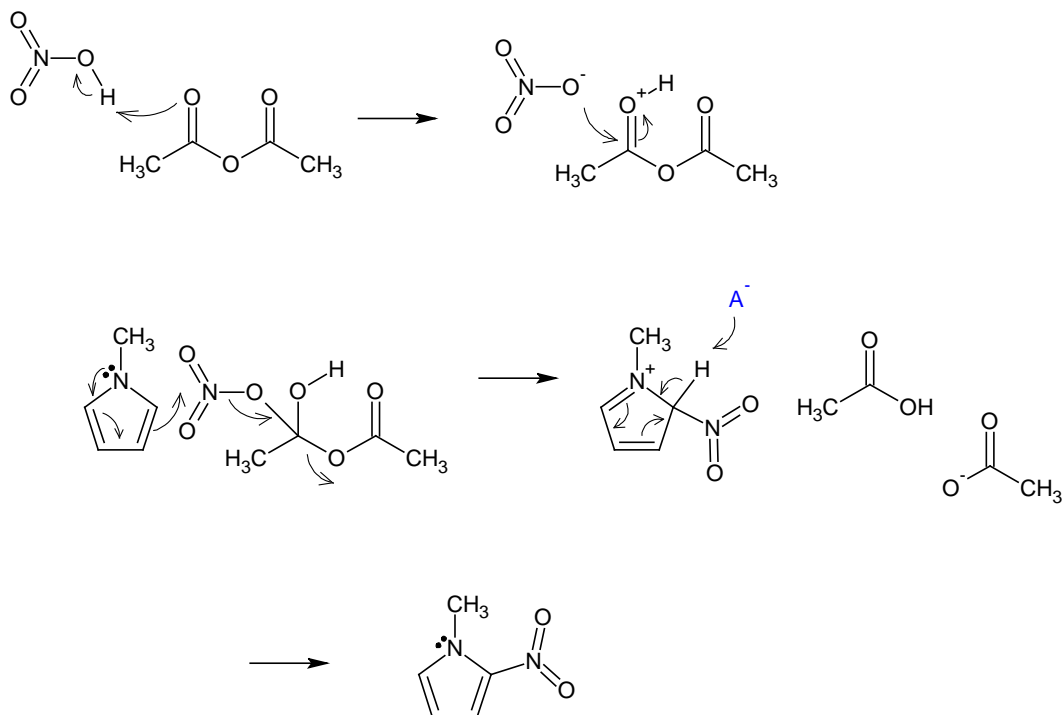


(c)

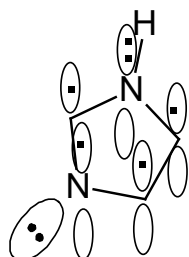




25.10



25.11



25.12 The pyridine-like N is more basic – we see the negative charge density appearing as a red patch in the electrostatic potential map.

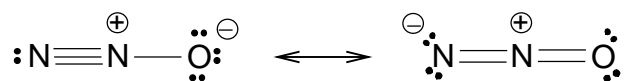
## Chapter 26

26.1  $\text{Be}^{2+}$  is more polarizing than  $\text{Ba}^{2+}$  because it is smaller.

26.2 (a) Chromium (VI) oxide has a very polarizing +6 charged metal cation, producing a chromium oxygen bonds with a strong covalent character.  
 (b) Because chromium (VI) is so strongly polarizing, it is acidic oxide, dissolving in water to produce chromic acid. The more weakly polarizing chromium (III) forms the insoluble oxide,  $\text{Cr}_2\text{O}_3$  which is amphoteric.

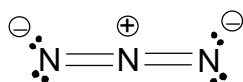
- 26.3  $2 \text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2 \text{H}_2\text{O}(\text{l})$   
 $\text{H}_2(\text{g}) + \text{Cl}_2(\text{g}) \rightarrow 2 \text{HCl}(\text{g})$   
 $3 \text{H}_2(\text{g}) + \text{N}_2(\text{g}) \rightarrow 2 \text{NH}_3(\text{g})$
- 26.4  $2 \text{K}(\text{s}) + \text{H}_2(\text{g}) \rightarrow 2 \text{KH}(\text{s})$   
 The product of this reaction is potassium hydride. It is an ionic solid (at room temperature). It is a very strong base – consisting of  $\text{K}^+$  and  $\text{H}^-$  ions. It is so strongly reactive that it is generally distributed as a slurry in mineral oil.
- 26.5  $2 \text{Na}(\text{s}) + \text{Cl}_2(\text{g}) \rightarrow 2 \text{NaCl}(\text{s})$  (exothermic reaction)  
 NaCl is a colourless ionic with high melting point. It is soluble in water.
- 26.6 (a)  $2 \text{Cl}^-(\text{aq}) \rightarrow \text{Cl}_2(\text{aq}) + 2 \text{e}^-$  (reaction at anode,  $\text{Cl}^-$  is oxidized)  
 $2 \text{H}_2\text{O}(\text{l}) + 2 \text{e}^- \rightarrow 2 \text{OH}^-(\text{aq}) + \text{H}_2(\text{g})$  (reaction at cathode,  $\text{H}_2\text{O}$  is reduced)
- (b)  $2 \text{I}^-(\text{aq}) \rightarrow \text{I}_2(\text{aq}) + 2 \text{e}^-$  (reaction at anode,  $\text{I}^-$  is oxidized)  
 Same reduction reaction as in part (a)
- 26.7  $2 \text{Ba}(\text{s}) + \text{O}_2(\text{g}) \rightarrow 2 \text{BaO}(\text{s})$  (exothermic reaction)  
 BaO is a colourless ionic solid with high melting point. It is somewhat soluble in water.
- 26.8 We would not expect to find calcium occurring naturally in the earth's crust as a free element because it is too electropositive – it too readily loses its valence electrons. It occurs only in the +2 oxidation state.
- 26.9 (a)  $\text{Ga}(\text{OH})_3(\text{s}) + 3 \text{HCl}(\text{aq}) \rightarrow \text{GaCl}_3(\text{aq}) + 3 \text{H}_2\text{O}(\text{l})$   
 $\text{Ga}(\text{OH})_3(\text{s}) + 3 \text{NaOH}(\text{aq}) \rightarrow \text{Na}_3\text{GaO}_3(\text{aq}) + 3 \text{H}_2\text{O}(\text{l})$
- (b)  $\text{Ga}^{3+}(\text{aq})$  is a stronger acid than  $\text{Al}^{3+}$   
 (c) 2.77 L
- 26.10  $\text{Al}(\text{s}) + 3 \text{HCl}(\text{aq}) \rightarrow \text{AlCl}_3(\text{aq}) + \frac{3}{2} \text{H}_2(\text{g})$   
 $\text{Al}(\text{s}) + \frac{3}{2} \text{Cl}_2(\text{g}) \rightarrow \text{AlCl}_3(\text{s})$   
 $\text{Al}(\text{s}) + \frac{3}{4} \text{O}_2(\text{g}) \rightarrow \frac{1}{2} \text{Al}_2\text{O}_3(\text{s})$
- 26.11 In  $\text{SiO}_2$ , silicon forms a network of single bonds with oxygen – i.e. we get a covalently bonded network solid. The melting point of  $\text{SiO}_2$  is therefore very high. The bonding in  $\text{CO}_2$  is also covalent, but  $\text{CO}_2$  is molecular. The intermolecular forces of attraction (dispersion forces) between  $\text{CO}_2$  molecules are weak and are easily broken. Carbon dioxide is gas at ordinary temperatures.
- 26.12  $\text{PbCl}_4$

26.13 (a)

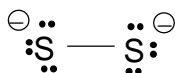


(b) exothermic

26.14



26.15



26.16 (a)  $\text{F}_2$  can oxidize  $\text{Cl}^-$  ( $X = \text{F}$ ,  $Y = \text{Cl}$ ) for example, whereas (b)  $\text{Cl}_2$  cannot oxidize  $\text{F}^-$  ( $X = \text{Cl}$ ,  $Y = \text{F}$ ).

26.17 (a)  $Z^*(\text{Ar}) = +6.75$ ;  $Z^*(\text{K}) = +2.2$ ;  $Z^*(\text{Cl}) = +6.1$

The valence electrons of Ar are held very tightly. In contrast, the valence electron of K experiences a much smaller effective nuclear charge. Although the valence electrons of neighbouring Cl are also held tightly, the effective nuclear charge in this case is not quite as large.

(b)  $Z^*(\text{Ar}^-) = +1.2$ ;  $Z^*(\text{K}^-) = +1.85$ ;  $Z^*(\text{Cl}^-) = +5.75$

The valence electron of  $\text{Ar}^-$  is held quite weakly. In contrast, the valence electrons of  $\text{Cl}^-$  experience a much larger effective nuclear charge. Even the  $\text{K}^-$  ion's valence electrons are held more tightly.

26.18 The ratio of the density of nitrogen to helium = 7.00.

26.19 While xenon and krypton have closed valence s and p subshells, they do have open d subshells in their valence shells. They can therefore expand their valence shells to form bonds. Nevertheless, there is a sizeable energy gap to the d subshells and such bonds are not very stable – but can be formed. In the case of neon, the valence shell has  $n = 2$ . To form bonds, neon would need to use  $n=3$  shell orbitals. There is a very large energy gap to such orbitals, and while one could envision such bonds they would be extremely unstable, and no such bonds have ever been formed.

## Chapter 27

27.1 (a) methyl amine,  $\text{CH}_3\text{NH}_2$ , (b) methyl nitrile,  $\text{CH}_3\text{CN}$ , (c) azide,  $\text{N}_3^-$  and (e) bromide,  $\text{Br}^-$  are monodentate ligands.  
(d) en - ethylenediamine,  $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$  and (f) phen - phenanthroline,  $\text{C}_{12}\text{H}_8\text{N}_2$  are bidentate (special case of polydentate) ligands

27.2  $\text{NH}_4^+$  has no lone pairs and does not serve as a ligand.

27.3 (a)  $[\text{Co}(\text{NH}_3)_3\text{Cl}_3]$   
(b) (i) oxidation number: +3. coordination number: 6  
(ii) oxidation number: +2. coordination number: 6

27.4 (a)  $2.0 \times 10^{-6} \text{ M}$   
(b)  $4.0 \times 10^{-6} \text{ M}$   
(c)  $5.0 \times 10^4$

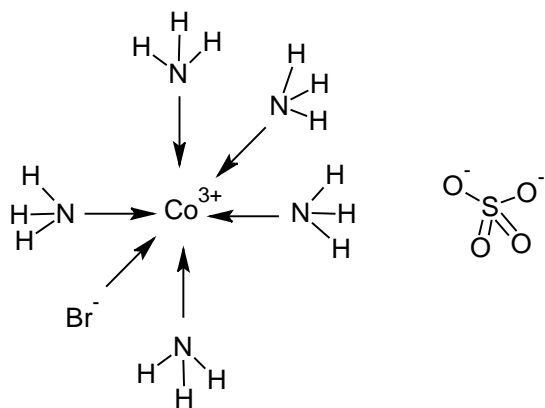
27.5 (i)  $\Delta_r G^\circ = -67.2 \text{ kJ mol}^{-1}$

The entropy term accounts for the better part of this negative change in free energy. The large positive entropy of this process results because 6 ligands are freed with only 3 bidentate ligands taking their place.

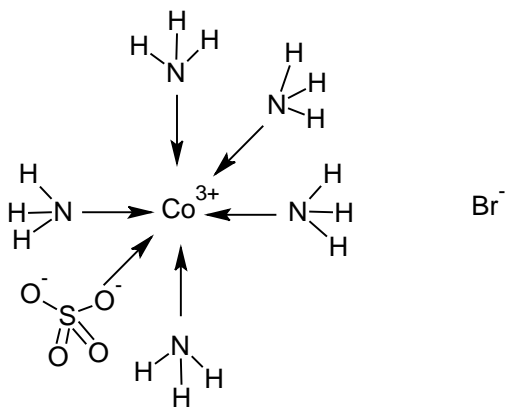
(ii)  $K = 6.02 \times 10^{11}$

27.6 Only 1.0 mol of  $\text{AgCl}(\text{s})$  will precipitate.

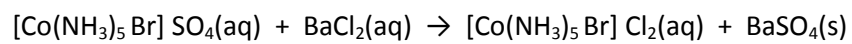
27.7



dark violet isomer (A)

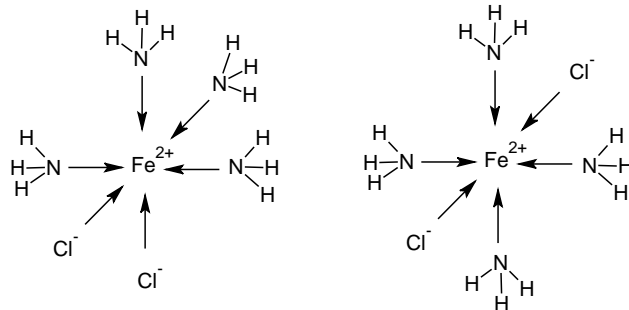


violet-red isomer (B)

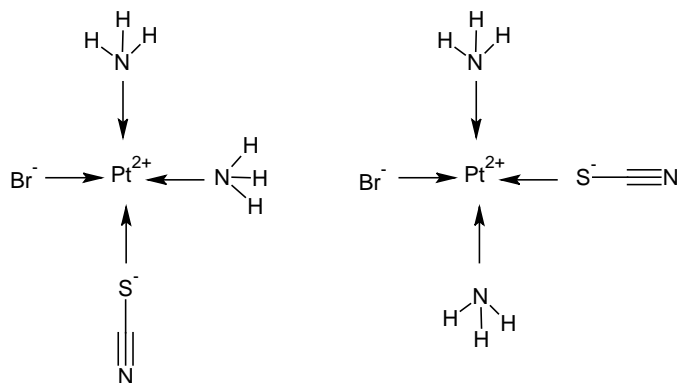


27.8

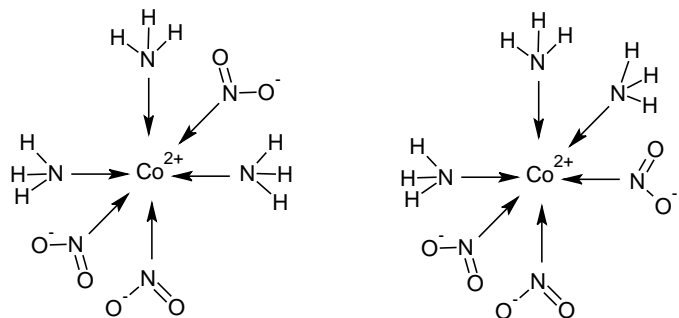
(a)



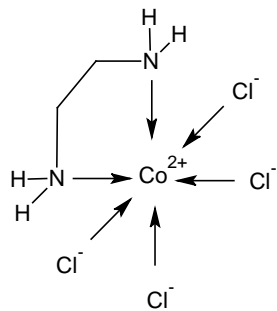
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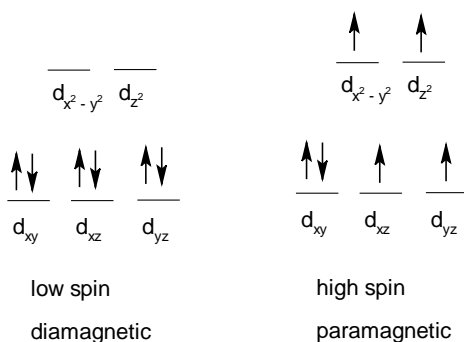
(c)



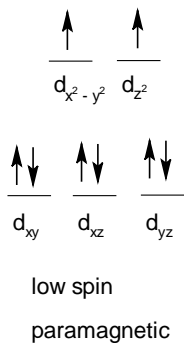
(d)



- 27.9 (a) *cis* and *trans* isomers  
 (b) no isomers  
 (c) no isomers  
 (d) two enantiomers  
 (e) no isomers  
 (f) no isomers
- 27.10 (a)  $[\text{Fe}(\text{en})_3]^{2+}$  has a stereocenter at  $\text{Fe}^{2+}$  giving rise to two enantiomers.  
 (b) The cobalt ion in *trans*- $[\text{Co}(\text{en})_2\text{Br}_2]^+$  is a stereocenter, giving rise to two isomers – the *cis* and *trans* species.  
 (c) The cobalt ion in *fac*- $[\text{Co}(\text{en})(\text{H}_2\text{O})\text{Cl}_3]$  is a stereocenter, giving rise to two isomers – the *fac* and *mer* species  
 (d) The platinum ion in  $[\text{Pt}(\text{NH}_3)(\text{H}_2\text{O})(\text{Cl})(\text{NO}_2)]$  is a stereocenter. For example, the  $\text{NH}_3$  ligand can be *trans* to any of the other three ligands.
- 27.11  $[\text{Ti}(\text{OH}_2)_6]^{3+} < [\text{Ti}(\text{NH}_3)_6]^{3+} < [\text{Ti}(\text{CN})_6]^{3-}$
- 27.12 (a) In  $[\text{Ru}(\text{H}_2\text{O})_6]^{2+}$ ,  $\text{Ru}^{2+}$  is in the +2 oxidation state.

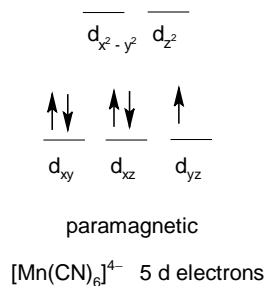


- (b) In  $[\text{Ni}(\text{NH}_3)_6]^{2+}$ ,  $\text{Ni}^{2+}$  is in the +2 oxidation state.

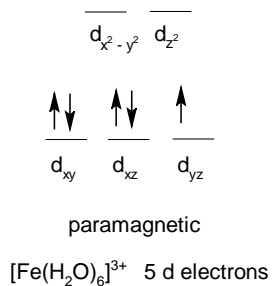


27.13

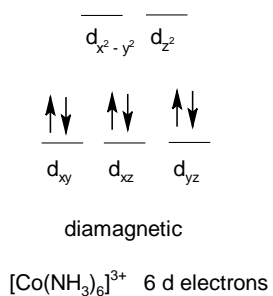
(a)



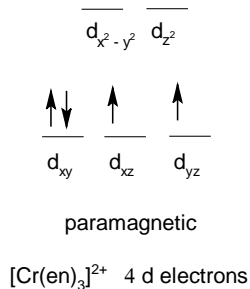
(c)



(b)



(d)



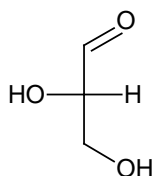
## Chapter 28

There are no in-chapter answers necessary for this chapter.

## Chapter 29

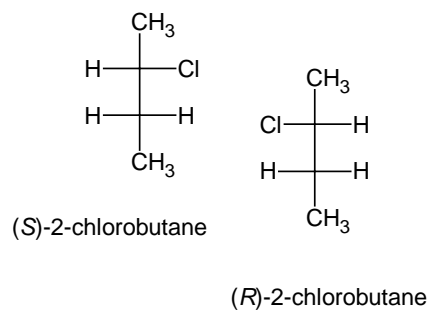
- 29.1
- (a) Threose is an aldobutose
  - (b) Ribulose is a ketopentose
  - (c) Tagatose is a ketohexose
  - (d) 2-deoxyribose is an aldopentose

29.2

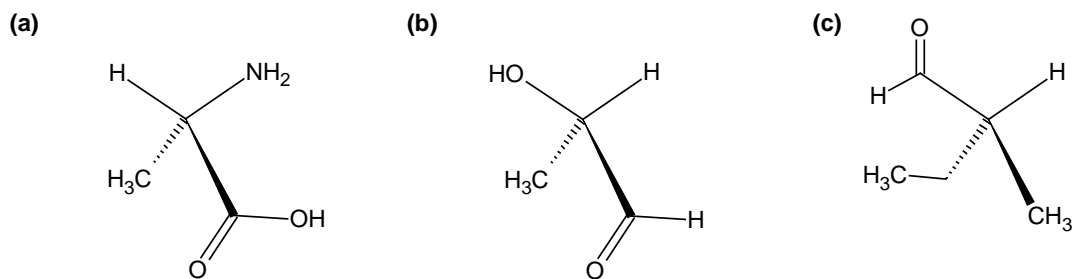




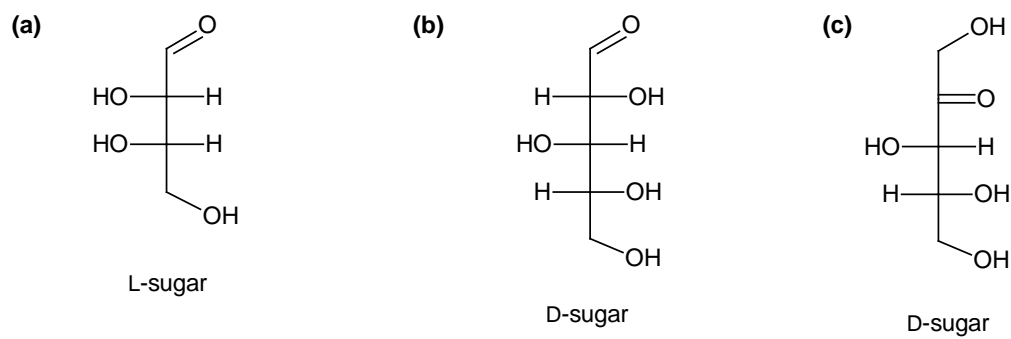
29.3



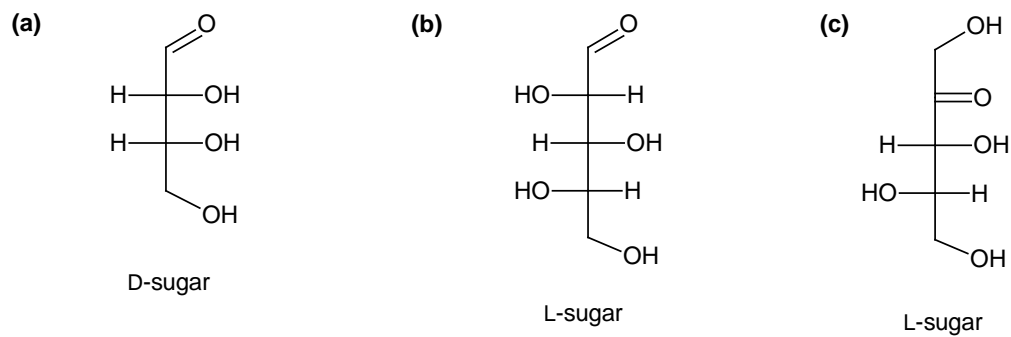
29.4



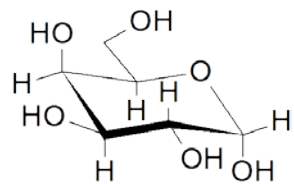
29.5



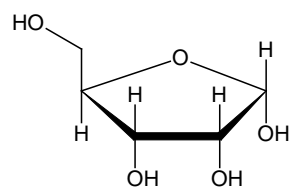
29.6



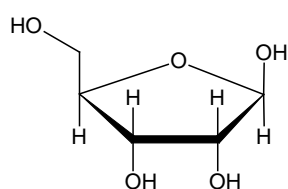
29.7



29.8

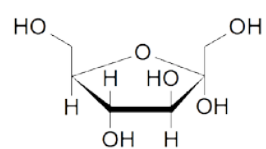


$\alpha$ -D-ribofuranose

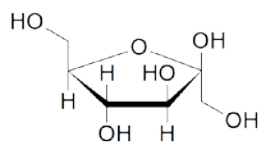


$\beta$ -D-ribofuranose

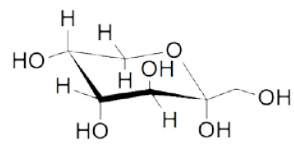
29.9



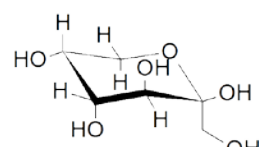
$\alpha$ -D-fructofuranose



$\beta$ -D-fructofuranose

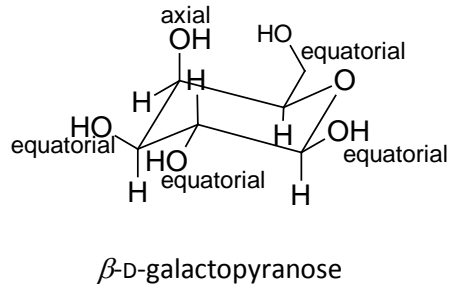
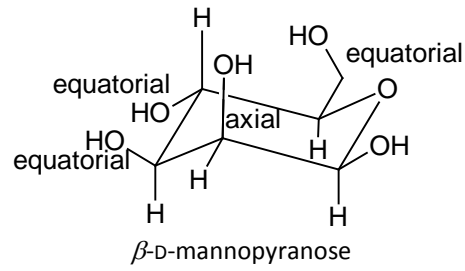


$\alpha$ -D-fructopyranose



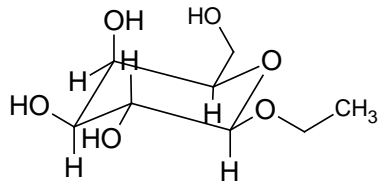
$\beta$ -D-fructopyranose

29.10



$\beta$ -D-mannopyranose and  $\beta$ -D-galactopyranose should be about equally stable

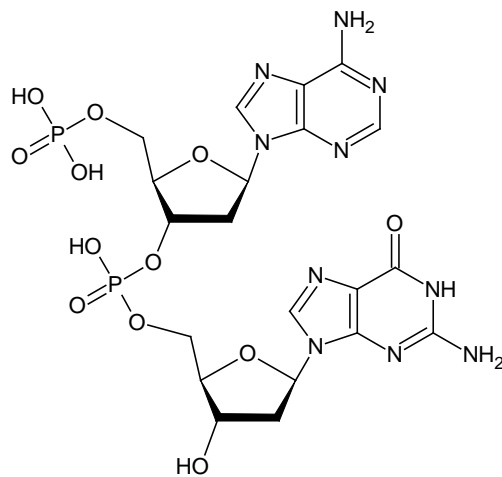
29.11



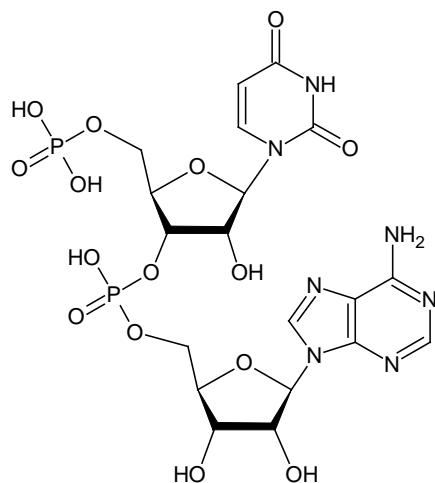
29.12 (a) Pyruvate decarboxylase and (c) alcohol dehydrogenase are are lyases.

chymotrypsin is a hydrolase.

29.13

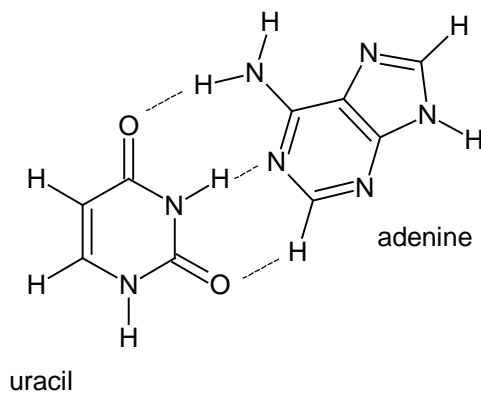


29.14



29.15 DNA sequence 3'-CCGATTAGGCA-5' is complementary to GGCTAATCCGT (by default this is 5' to 3'). Arranged 5' to 3', this sequence is ACGGATTAGCC.

29.16



29.17 RNA sequence 5'-CUAAUGGCAU-3' or UACGGUAAUC is complementary to DNA sequence 3' GATTACCGTA.

29.18 RNA sequence 5' UUCGCAGAGU 3' was transcribed from DNA sequence 3' ACTCTGCGAA.

- 29.19
- (a) Ala, alanine, is coded by GCU, GCC, GCA or GCG
  - (b) Phe, phenylalanine, is coded by UUU or UUC.
  - (c) Leu, leucine, is coded by UUA, UUG, CUU, CUC, CUA or CUG
  - (d) Tyr, tyrosine, is coded by UAU or UAC.

- 29.20 5' CUU-AUG-GCU-UGG-CCC-UAA codes for the polypeptide, Leu-Met-Ala-Trp-Pro-stop  
i.e. leucine, methionine, alanine, tryptophan and proline are linked together, in this order, then the chain is terminated at proline.
- 29.21 mRNA base sequence 5' CUU-AUG-GCU-UGG-CCC-UAA-3' gives rise to tRNA sequence 3' –GAA UAC CGA ACC GGG-5'.
- 29.22 mRNA base sequence 5' CUU-AUG-GCU-UGG-CCC-UAA 3' arose from transcription of DNA sequence, 3'-GAA TAC CGA ACC GGG ATT-5'.

## Chapter 30

- 30.1 (a)  ${}_{86}^{222}\text{Rn} \rightarrow {}_{84}^{218}\text{Po} + {}_2^4\text{He}$   
(b)  ${}_{84}^{218}\text{Po} \rightarrow {}_{85}^{218}\text{At} + {}_{-1}^0\text{e}$
- 30.2  $E_{\text{photon}} = 9.9 \times 10^{-14} \text{ J}$   
 $E = 60 \text{ GJ mol}^{-1}$
- 30.3 (a)  ${}_{90}^{232}\text{Th} \rightarrow {}_{82}^{208}\text{Pb} + 6 {}_2^4\text{He} + 4 {}_{-1}^0\text{e}$   
(b)  ${}_{90}^{232}\text{Th} \rightarrow {}_{88}^{228}\text{Ra} + {}_2^4\text{He}$   
 ${}_{88}^{228}\text{Ra} \rightarrow {}_{89}^{228}\text{Ac} + {}_{-1}^0\text{e}$   
 ${}_{89}^{228}\text{Ac} \rightarrow {}_{90}^{228}\text{Th} + {}_{-1}^0\text{e}$
- 30.4 (a)  ${}_{7}^{13}\text{N} \rightarrow {}_{6}^{13}\text{C} + {}_{-1}^0\beta$   
(b)  ${}_{20}^{41}\text{Ca} + {}_{-1}^0\beta \rightarrow {}_{19}^{41}\text{K}$   
(c)  ${}_{38}^{90}\text{Sr} \rightarrow {}_{39}^{90}\text{Y} + {}_{-1}^0\beta$   
(d)  ${}_{11}^{22}\text{Na} \rightarrow {}_{12}^{22}\text{Mg} + {}_{-1}^0\beta$
- 30.5 (a)  ${}_{14}^{32}\text{Si} \rightarrow {}_{15}^{32}\text{P} + {}_{-1}^0\beta$   
(b)  ${}_{22}^{45}\text{Ti} \rightarrow {}_{21}^{45}\text{Sc} + {}_{-1}^0\beta$   
(c)  ${}_{94}^{239}\text{Pu} \rightarrow {}_{92}^{235}\text{U} + {}_2^4\text{He}$   
(d)  ${}_{19}^{42}\text{K} \rightarrow {}_{20}^{42}\text{Ca} + {}_{-1}^0\beta$
- 30.6  $3.087 \times 10^9 \text{ kJ mol}^{-1}$   
 $5.145 \times 10^8 \text{ kJ mol}^{-1} \text{ nucleons}$

- 30.7 (a) 0.094 mg  
(b) 36.9 years  
(c) 81.7 years
- 30.8 26.9 days
- 30.9 6200 years
- 30.10 The sample is  $t = 3010$  years old.  
The ring data give the age of the tree to be  $2853 \pm 52$  years
- 30.11 150.0 mg