

Answers to Selected Textbook Questions

Chapter 1

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

REVIEW QUESTIONS

- 1.1 PDT or photodynamic therapy requires a photosensitizer, light and oxygen.
- 1.3 The tumour must be located in a place that can be subjected to light.
- 1.5 Toxicology is the study of the ill effects (toxicity) of substances on the body. Before introducing a porphyrin into the body for PDT, it must be established that the porphyrin, by itself, is non-toxic.
- 1.7 Chemotherapy is the use in medicine of substances that are selectively toxic to malignant cells or to a disease-causing virus or bacterium. As such, a vaccine would not be considered chemotherapy. The use of garlic to treat gangrene, on the other hand, is an example of chemotherapy. Garlic is a mild antiseptic which kills bacteria infecting tissue leading to gangrene.
- 1.9 Yes, arsenic is generally considered to be toxic. However, Sec. 6.1 discusses how the toxicity of arsenic varies dramatically depending on the species containing the arsenic atoms. For example, whereas elemental arsenic is toxic, the arsenic containing species in lobster are not.
- 1.11 Both Vitamin B12 and Visudyne are porphyrin-based.
- 1.13 A natural product is a compound produced by a living organism.
- 1.15 (a) The Haber process combines hydrogen and nitrogen to make ammonia. Ammonia is used to make fertilizer.
(b) In the Bohr model, a hydrogen atom consists of an electron in a circular orbit about a proton.
(c) A conical flask used in chemistry labs to carry out reactions.
(d) van der Waals equation is a relation between the pressure, temperature and volume of a gas that accounts for the non-zero size of the gas molecules and the attractive forces between them.
(e) Gibbs free energy, $G = H - TS$, combines enthalpy and entropy to give a quantity which must decrease for any processes that actually happens.
(f) Lewisite is a chlorinate alkyl arsenic compound which was produced as a chemical weapon causing blisters and lung irritation.
(g) A Lewis base has a lone pair of electrons that it can donate to an electron pair acceptor – a Lewis acid.
(h) Schrodinger's equation determines the wave function that describes the state of an atom.

- 1.17 An organic compound consists of molecules made from carbon, hydrogen and oxygen atoms. There can be other atoms – for example, nitrogen, sulfur.
- 1.19
1. Acetylsalicylic acid, the common mild pain reliever, is a derivative of the natural product, salicin, obtained from willow bark.
 2. Morphine, obtained from poppies, is a powerful pain reliever.
 3. Cocaine, obtained from the coca plant, is also a pain reliever – still used for topical pain relief.
 4. Quinine, an anti-malaria agent, was isolated from the bark of cinchona trees.
 5. Menthol, isolated from mint leaves, is a topical pain reliever which also relieves itching.
- 1.21 The chemical structure of the synthetic drugs is identical to those extracted from plants. It is the impurities associated with the synthetic procedure, in the case of synthetic drugs, and those associated with the biological source and the means of extraction, in the case of natural products, that are different.
- 1.23 Mycotoxins are toxins produced by fungi such as poisonous mushrooms. Penicillin is a mycotoxin that is toxic to bacteria, making it the original antibiotic. It is a natural product and an organic compound.

SUMMARY AND CONCEPTUAL QUESTIONS

- 1.25 Due to their sensitivity, porphyria sufferers would avoid sunlight like the vampires of legend.
- 1.27 Infrared light excites bends and vibrations of molecular bonds. Infrared spectra are used to determine the types of bonds present in a molecule.

Chapter 2

2.1

<i>Pure</i>	<i>Mixture</i>	
<i>Compounds</i> (h) testosterone (f) sodium chloride	<i>Solutions</i> (b) air (c) vinegar (g) athlete's urine sample	(a) mud (e) milk
<i>Elements</i> (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 CH₄, the C to H atom ratio is 1:4.
(c) In C₂H₂, the C to H atom ratio is 1:1.
(d) In C₆H₁₂O₆, 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}Ga : 31 protons, 38 neutrons
 ^{71}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) 1.90×10^{24} atoms
- 2.20 0.97 g

REVIEW QUESTIONS

- 2.27 The piece of table salt is the macroscopic view. The representation of its internal structure is the particulate view. The macroscopic view arises when the number of particles is very large – vast.
- 2.29 (a) physical property
(b) chemical property
(c) chemical property
(d) physical property
(e) physical property
(f) physical property
- 2.31 (a) “colourless” is a physical property; “burns in air” is a chemical property
(b) “shiny” and “metal” are physical properties of aluminium; “orange” and “liquid” are physical properties of bromine; “aluminium reacts readily with ... bromine” is a chemical property of aluminium and bromine.
- 2.33 (a) 27
(b) 48
(c) 62
- 2.35 $^{57}_{27}\text{Co}$, $^{58}_{27}\text{Co}$, $^{60}_{27}\text{Co}$
- 2.37 ^{205}Tl
- 2.39 50%.
- 2.41
- | | | | | |
|---|------------------|------------------|-------------------|------------------|
| Symbol | ^{65}Cu | ^{86}Kr | ^{195}Pt | ^{81}Br |
| Number of protons | 29 | 36 | 78 | 35 |
| Number of neutrons | 36 | 50 | 117 | 46 |
| Number of electrons in the neutral atom | 29 | 36 | 78 | 35 |
| Name of element | copper | krypton | platinum | bromine |
- 2.43 2
- 2.45 1
- 2.47 134.9 g
- 2.49 Two periods have 8 elements, two periods have 18 elements, and two periods have 32 elements.

- 2.51 (a) Bk
 (b) Br
 (c) B
 (d) Ba
 (e) Bi
- 2.53 (a) Si is a metalloid, while P is a non-metal
 (b) Si has some electrical conductivity, while P does not
 (c) Both Si and P are solids at 25°C

SUMMARY AND CONCEPTUAL QUESTIONS

- 2.55 (a) anything from beryllium, Be, to radium, Ra
 (b) anything from sodium, Na, to argon, Ar
 (c) carbon, C
 (d) sulphur, S
 (e) iodine, I
 (f) magnesium, Mg
 (g) krypton, Kr
 (h) germanium, Ge, or arsenic, As.
- 2.57 Boron
- 2.59 9.42×10^{-5} mol
 5.67×10^{19} atoms
- 2.61 (a) $A_r(^1\text{H}) = 1$, $A_r(^{11}\text{B}) = 10.9241$, $A_r(^{24}\text{Mg}) = 23.7994$, and $A_r(^{63}\text{Cu}) = 62.4525$
 (b) $A_r(^1\text{H}) = 1.0088$, $A_r(^{11}\text{B}) = 11.0199$, $A_r(^{24}\text{Mg}) = 24.0080$, and $A_r(^{63}\text{Cu}) = 63$
 (c) $A_r(^1\text{H}) = 1.0084$, $A_r(^{11}\text{B}) = 11.0162$, $A_r(^{24}\text{Mg}) = 24$, and $A_r(^{63}\text{Cu}) = 62.9790$
- 2.63 $\delta^{13}\text{C} = -28.90$ is consistent with a thermogenic sample
- 2.65 We need the density of iron, (d), in order to determine the mass of 1 cm^3 of iron. Dividing this mass by the molar mass of iron, (b), determines the number of moles in 1 cm^3 of iron. Multiplying that number by Avogadro's constant, (c), provides the final answer – the number of atoms in 1 cm^3 of iron.
- 2.67 You could count how many jelly beans it takes to fill a smaller container – fewer jelly beans, easier to count – then multiply by the ratio of the volume of jar to that of the smaller container. If you only have the picture, you could count the number of jelly beans half way around the perimeter of the cylindrical jar, and from bottom to top of the jar. You have determined $\pi \times$ radius of jar and the height of the jar in jelly bean length units. Squaring the first quantity, then dividing by π and multiplying by the second quantity provides an estimate of the number of jelly beans in the jar.

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 g mol^{-1}
(b) 53.5 g mol^{-1}
(c) 213 g mol^{-1}
(d) 120.3 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 C_8H_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

REVIEW QUESTIONS

- 3.27 (a) molecular
(b) covalent network
(c) molecular
(d) ionic (with some covalent character)
- 3.29 (a) Se^{2-}
(b) F^-
(c) Fe^{2+} and Fe^{3+}
(d) N^{3-}
- 3.31 (a) ammonium, NH_4^+ , has one more proton than electron - hence the +1 charge.
(b) phosphate, PO_4^{3-} , has three more electrons than protons - hence the -3 charge.
(c) dihydrogen phosphate, H_2PO_4^- , has one more electron than protons - hence the -1 charge.
- 3.33 Na_2CO_3 sodium carbonate
 BaCO_3 barium carbonate
 NaI sodium iodide
 BaI_2 barium iodide

- 3.35 (a) chlorine trifluoride
 (b) nitrogen trichloride
 (c) strontium sulphate (ionic)
 (d) calcium nitrate (ionic)
 (e) xenon tetrafluoride
 (f) oxygen difluoride
 (g) potassium iodide (ionic)
 (h) aluminium sulphide (ionic with some covalent character)
 (i) phosphorus trichloride
 (j) potassium phosphate (ionic)
- 3.36 (a) NaOCl (ionic)
- 3.37 (iii) electrons are set free within a lattice of positive ions
- 3.39 A chemical reaction of oxygen requires breaking the oxygen-oxygen double bond, and generally forming other bonds. As such, the propensity of oxygen to react depends on the strength of the O=O bond, as well as the strength of bonds formed in the reaction. The boiling point of oxygen depends only on the strength of the weak intermolecular bonds between neighbouring oxygen molecules.
- 3.41 Only the calculated molecular mass, 28.03132, of C₂H₄ comes really close to this value. If the data were from a low resolution spectrometer, we could not rule out H₂CN (molecular mass = 28.01873), N₂ (molecular mass = 28.00614) and CO (molecular mass = 27.99491).
- 3.43 Infrared spectroscopy and structure
- (a) absorption frequencies in cm⁻¹:
- | | |
|----------------------------------|---|
| 2850-2980 | due to alkyl C-H stretches |
| 3000-3100 | due to aromatic C-H stretches |
| 2700-2850 | due to aldehyde C-H stretch |
| 1720-1740 | due to aldehyde C=O stretch |
| 1700-1725 | due to carboxylic C=O stretch |
| 675-900, 1400-1500 and 1585-1600 | due to aromatic C-C bends and stretches |
- (b)
- | | |
|-----------|-----------------------------|
| 3020-3100 | due to alkene C-H stretches |
| 2850-2980 | due to alkyl C-H stretches |
| 1730-1750 | due to ester C=O stretch |
| 1640-1670 | due to C=C stretch |
| 1000-1300 | due to ester C-O stretch |
- (c)
- | | |
|-----------|----------------------------|
| 3200-3550 | due to alcohol O-H stretch |
| 2850-2980 | due to alkyl C-H stretches |
| 1705-1725 | due to ketone C=O stretch |
| 1000-1260 | due to alcohol C-O stretch |

- 3.45 (a) carboxylic acid and aromatic ring
absorption wavenumbers in cm^{-1} :
(b) ester and aromatic ring
(c) alcohol, nitrile, and aromatic ring
3200-3550 broad peak due to alcohol (phenol) O-H stretch
2210-2260 due to nitrile $\text{C}\equiv\text{N}$ stretch
(d) ketone and alkene
3020-3100 due to alkene C-H stretches
2850-2980 due to alkane C-H stretches
1705-1725 due to ketone C=O stretch
(e) ketone and ester
3020-3100 due to alkene C-H stretches
2850-2980 due to alkane C-H stretches
1705-1725 due to ketone C=O stretch
1700-1725 due to ester C=O stretch (would probably overlap with the ketone stretch)
1000-1300 due to ester C-O stretch
- 3.47 (a) $159.688 \text{ g mol}^{-1}$
(b) $117.170 \text{ g mol}^{-1}$
(c) $176.1241 \text{ g mol}^{-1}$
- 3.49 21 million kMol
- 3.51 CaS (c)
- 3.53 (a) $305.4119 \text{ g mol}^{-1}$
(b) $1.8 \times 10^{-4} \text{ mol}$
(c) 39 mg
- 3.55 (a) 0.0130 mol
(b) NiF_2
(c) Nickel (II) fluoride

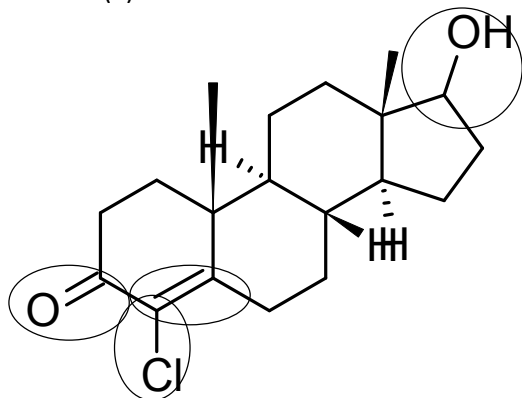
SUMMARY AND CONCEPTUAL QUESTIONS

- 3.57 Sodium chloride is ionic. Its solid is held together by the strong attraction between oppositely charged ions. Chlorine is a molecular substance – it consists of Cl_2 molecules. In the solid state, the molecules are held together by weak intermolecular forces.
- 3.59 (a) silicon dioxide is a covalent network solid which melts at very high temperature
carbon dioxide is a molecular substance which melts (sublimes at 1 atm pressure) at very low temperature
(b) sodium sulfide is an ionic substance melting at high temperature
hydrogen sulfide is a molecular substance which melts at very low temperature

- 3.61 (a) calcium and chloride ions are in a 1:2 ratio in CaCl_2
 (b) calcium, carbon and oxygen atoms are in a 1:1:3 ratio in CaCO_3
 (c) nitrogen and hydrogen atoms are in a 1:3 ratio in NH_3
 (d) silicon and carbon atoms are in a 1:1 ratio in SiC
 (e) hydrogen and chlorine atoms are in a 1:1 ratio in HCl
- 3.63 Al^{3+} is most attracted to water because it has the largest magnitude charge.

3.65

(a)



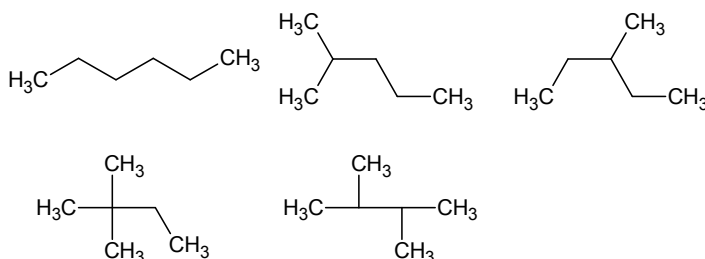
Clostebol has alkyl groups, an alkene, a ketone, a chloride and an alcohol group – the last four groups are circled.

- (b) The testosterone molecular ion peak is at 288, whereas the clostebol molecular ion peak is at 322. There are peaks at both these positions, though the peak at 322 is smaller. It would appear that this mass spectrum does not rule out clostebol. However, chlorinated compounds generally show peaks associated with loss of a chlorine atom from the molecular ion. We therefore would expect to see a peak at 287. No such peak is seen. The peak at 322 must be due to some other compound. The data is consistent with the expert analysis.
- 3.67 absorption frequencies in cm^{-1}
 2850-2980 due to alkyl C-H stretches
 2210-2260 due to nitrile $\text{C}\equiv\text{N}$ stretch – not given in Table 3.5
 1705-1725 due to ketone $\text{C}=\text{O}$ stretch
 1640-1670 due to $\text{C}=\text{C}$ stretch
- 3.69 (a) Look for the N-H stretch of $\text{CH}_3\text{CH}_2\text{NHCH}_3$ – a peak around $3250\text{-}3400\text{ cm}^{-1}$ not seen for $(\text{CH}_3)_3\text{N}$.
 (b) Look for the ketone $\text{C}=\text{O}$ stretch of CH_3COCH_3 – a peak around $1705\text{-}1725\text{ cm}^{-1}$ – or the OH stretch – a broad peak around $2500\text{-}3300\text{ cm}^{-1}$.
 (c) Look for the aldehyde C-H peaks (2 of them) of $\text{CH}_3\text{CH}_2\text{CHO}$, around $2700\text{-}2850\text{ cm}^{-1}$.

Chapter 4

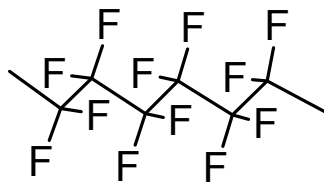
- 4.1 Covalent forces hold the carbon and hydrogen atoms together within a methane molecule.
- 4.2 Weak dispersion forces – a type of intermolecular or non-bonding force – hold neighboring methane molecules together
- 4.3 The CFCs do not have H atoms bonded to C. Such H atoms readily react with hydroxyl 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 8.4×10^{17} 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



REVIEW QUESTIONS

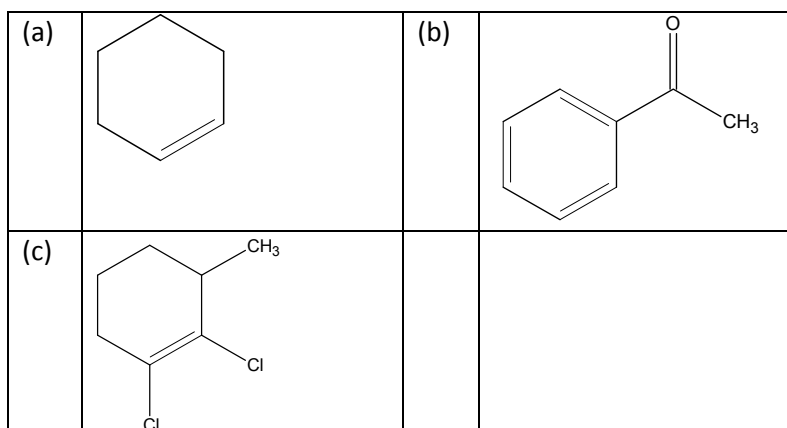
- 4.13 (a) Covalent bonds hold the nitrogen atoms together in the N_2 molecules, inside the clathrate hydrate.
(b) Dispersion forces attract the N_2 and H_2O molecules within the clathrate hydrate cage.
(c) Hydrogen bonding holds neighboring H_2O together molecules to make the clathrate hydrate cage.
(d) Dispersion forces attract the N_2 and O_2 molecules within the clathrate hydrate cage.
- 4.15 A greenhouse prevents convection of heat – a key component of the heat flow from the earth's surface out into the atmosphere. Greenhouse gases do not prevent convection. However, like the greenhouse walls and roof, they reflect some of the radiation emitted by the earth back down again. This occurs because much of the absorbed energy is re-emitted (a random process) back towards the earth, or spread to surrounding molecules by collisional de-excitation.
- 4.17 $CH_3CH_3(g)$; ozone, $O_3(g)$; and chloroform, $CHCl_3$
- 4.19 1750 is the beginning of the industrial revolution. Radiative forcing of our climate was subject only to natural fluctuations before that time.
- 4.21 Clouds cause cooling by reflecting incoming sunlight back out into space.
- 4.23 Increasing levels of tropospheric ozone has a positive radiative forcing effect.
- 4.24 Stratospheric ozone has a negative radiative forcing effect. It absorbs UV light preventing it from reaching the earth's surface. The stratosphere is heated, but the surface cools.
- 4.25 In the troposphere.
- 4.27 The radiative forcing and global warming potential of methane are both enhanced by methane's strong absorption of IR. However, the global warming potential also depends upon how long methane stays in the atmosphere before being eliminated by oxidation and subsequently returning to the surface in rain. The global warming potential of methane is an estimate of how much a given mass of methane will contribute to global warming relative to the same mass of carbon dioxide.
- 4.29 Consulting the ranking of levels of scientific uncertainty in Figure 2.20 of the 2007 IPCC summary report:
tropospheric carbon dioxide > tropospheric nitrous oxide > stratospheric ozone > jet contrails (we understand that its effect is very small) > solar irradiance

- 4.31 The advantages of using biofuels are as follows:
- (1) They are renewable – we get a new crop each year.
 - (2) There is no net addition to atmospheric carbon dioxide. Atmospheric CO₂ is consumed as the plant grows. It is returned to the atmosphere when the fuel is combusted.
 - (3) Biofuel can be produced in most places – provided a suitable crop can be found. Fossil fuels are found only in certain places.

The disadvantages of the biofuel strategy, in practice, are as follows:

- (1) Energy is needed to produce the crop and manufacture the biofuel. These energy demands must be minimized to make biofuel production worth the effort.
 - (2) Only a small portion of corn, for example, can be used to produce biofuels. The cellulosic part of the plant (its bulk), is simply plowed back into the field. This significantly reduces the viability of biofuel as an alternative energy strategy, as currently produced in North America.
 - (3) Biofuel production takes land away from food production. This has driven up food prices in North America in recent years.
- 4.33 The principal difference between the data sets is the size of the annual oscillation in CO₂ level. The CO₂ level drops in the spring in summer months due to the growth of vegetation on the land masses of the northern hemisphere. It rises again when this growth stops. The antarctic data is less sensitive to this oscillation since it is so far away from the northern hemisphere.

4.35



- 4.37
- (a) alkane
 - (b) alkene and alkane
 - (c) alkene, alkane and alcohol
 - (d) Benzaldehyde has aromatic and aldehyde functional groups

SUMMARY AND CONCEPTUAL QUESTIONS

- 4.45 Table 7.3 shows the bond energies of C-H, C-F and C-Cl bonds to be 413, 485 and 339 kJ mol⁻¹, respectively. When a hydroxyl radical reacts it breaks the C-X bond and forms an O-X bond. The bond energies of the bonds with O are 463 for O-H and 218 for O-Cl. There is no energy given for the O-F bond. Here, we see that the most favorable reaction is that which breaks the C-H bond to form the stronger O-H bond.
- 4.47 SF₆ has more bonds than CO₂ and consequently more vibrational modes – and more associated IR absorption peaks. This and its long life in the atmosphere increase its global warming potential.
- 4.49 Perhaps we should look for oxygen, water and carbon dioxide – at least if the importance of these molecules to life on earth is a guide. Plants use light and carbon dioxide to drive their life processes. Animals react fuels (food) with oxygen to drive their processes. Water is the medium in which the chemistry primarily takes place.
- 4.51 2×10⁶ g. (Based on the assumptions that my car consumes about 10 L of gasoline per 100 km travelled, and I travel about 10 000 km per year. Density of gasoline = 0.7 g/mL)
- 4.53 Fossil fuels are more valuable as feedstocks for the production of polymers. This should be the most important use.
- 4.55 No, we should not be concerned about human breathing as a source of atmospheric carbon dioxide. The main point of concerns about global warming is the impact on human life (yes, other species are also affected). Flooding of coastal areas, associated with global warming, is a concern because of the negative impact on humans living in these areas. Human breathing has to be an acceptable variable, as there is no alternative.

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 O₂(g)
3.0 mol of Al₂O₃(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 $\text{Ca}^{2+}(\text{aq})$ ions and $\text{CO}_3^{2-}(\text{aq})$ both at a concentration of $6 \times 10^{-5} \text{ mol L}^{-1}$.
 (c) A mixture containing solid calcium carbonate and $\text{Ca}^{2+}(\text{aq})$ ions and $\text{CO}_3^{2-}(\text{aq})$ 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_3OH produced
 (c) 14 g of H_2 remain
- 5.12 (a) Fe_2O_3 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 %
- 5.20 (a) For the production of maleic anhydride by oxidation of benzene
 (i) the C atom efficiency = 66.7%
 the O atom efficiency = 33.3%
 the H atom efficiency = 33.3%
 (ii) the overall atom efficiency = 44.1%
 (iii) the E-factor = 1.27
- (b) For the production of maleic anhydride by oxidation of butene
 (i) the C atom efficiency = 100.0%
 the O atom efficiency = 50.0%
 the H atom efficiency = 25.0%
 (ii) the overall atom efficiency = 64.5%
 (iii) the E-factor = 0.55

REVIEW QUESTIONS

- 5.21 (a) balanced for electrical charge and for all relevant atoms
 (b) balanced for electrical charge and for all relevant atoms
 (c) balanced for electrical charge and for all relevant atoms
- 5.23 (a) $\text{H}_2\text{O}(\text{g}) \longrightarrow \text{H}_2\text{O}(\text{l})$ is the spontaneous direction of reaction
 (b) Water vapour at 1 bar pressure has a higher chemical potential than liquid water at 25°C.

- 5.25 (a) A mixture containing a piece of copper in a 1 mol L^{-1} aqueous silver nitrate solution has a higher chemical potential than a mixture containing some solid silver in an aqueous solution in which the concentration of $\text{Cu}^{2+}(\text{aq})$ ions is about 0.5 mol L^{-1} and the concentration of $\text{Ag}^+(\text{aq})$ ions is about $1 \times 10^{-10} \text{ mol L}^{-1}$.
 (b) A mixture containing some solid silver in an aqueous solution in which the concentration of $\text{Cu}^{2+}(\text{aq})$ ions is about 0.5 mol L^{-1} and the concentration of $\text{Ag}^+(\text{aq})$ ions is about $1 \times 10^{-10} \text{ mol L}^{-1}$ is more stable than a mixture containing a piece of copper in a 1 mol L^{-1} aqueous silver nitrate solution.
- 5.27 theoretical yield of $\text{CO}_2 = 36.6 \text{ g}$
- 5.29 mass of arginine required = 275 mg
 mass of ornithine produced = 210 mg
- 5.31 The total mass of the beakers and solutions after reaction is the same as it was before reaction (167.170 g)
- 5.33 (a) 1.76 kg
 (b) 1.19 kg
- 5.35 617 kg
- 5.37 $\text{TiO}_{1.5}$ or Ti_2O_3
 5.39 11.2%
- 5.41 66.7 kg
- 5.43 weight percent CuS in ore = 30 %
 weight percent Cu_2S in ore = 70 %

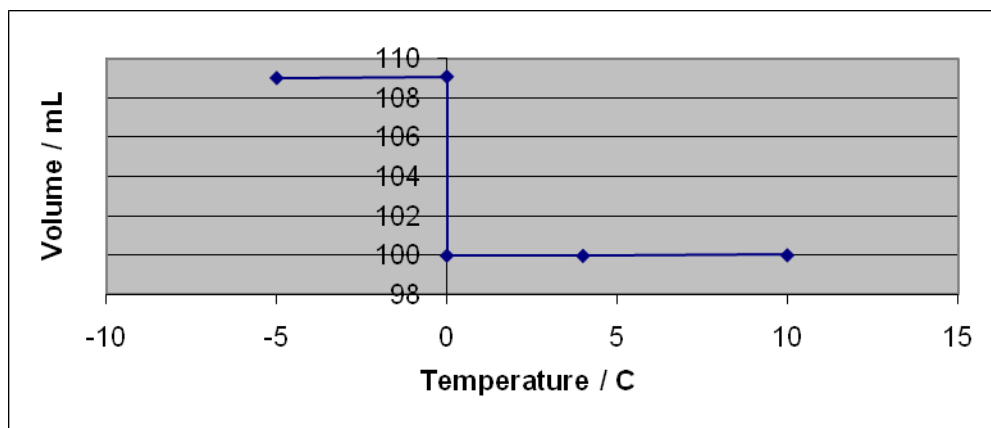
SUMMARY AND CONCEPTUAL QUESTIONS

- 5.45 (a) 8.8 g.
 (b) 1.5
 (c) FeBr_3
 (d) $2 \text{ Fe}(\text{s}) + 3 \text{ Br}_2(\ell) \rightarrow 2 \text{ FeBr}_3$
 (e) iron (III) bromide
 (f) (i) **TRUE**
 (ii) **FALSE**
 (iii) **FALSE**
 (iv) **FALSE**

- 5.47 (a) 65.0% Pt by weight.
9.3% N by weight.
23.6% Cl by weight.
(b) mass of ammonia required = 1.31 g.
mass of $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$ produced = 11.6 g.
- 5.49 (1) There is more than enough zinc. In this case, HCl is the limiting reactant – all of it reacts, producing enough H_2 to inflate the balloon. $0.107 - 0.050 \text{ mol} = 0.057 \text{ mol}$ of zinc remains.
(2) In this case, there is just enough zinc to consume all of the HCl. The same amount of H_2 is produced as in part (1) – i.e. enough to inflate the balloon. No zinc remains.
(3) In this case, there is not enough zinc to consume all of the HCl. Zinc is the limiting reactant. Only 40% as much H_2 is produced as in part (1) – i.e. not enough to inflate the balloon. No zinc remains.

Chapter 6

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

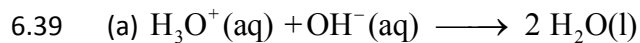


- 6.2 35 s
- 6.3 (a) $1.10 \times 10^3 \text{ kJ}$
(b) 727 kJ
- 6.4 diethyl ether > carbon disulfide > acetone > bromine > hexane > ethanol > water
- 6.5 The order of normal boiling points is the same as the order of enthalpy changes of vaporization. This is what we expect because both boiling point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

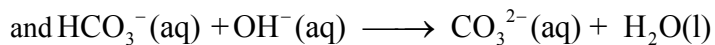
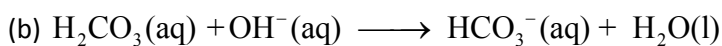
- 6.6 The surface tension is that which pulls the drop into a spherical shape – minimizing surface area. Since this force is smaller for diethyl ether we expect its drops to be even more distorted by gravity than those of water.
- 6.7 (a) The intermolecular force of attraction between water molecules 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) $H \rightarrow F$ is more polar than $H \rightarrow I$
 (b) $B \rightarrow C$ is less polar than $B \rightarrow F$
 (c) $C \leftarrow Si$ is more polar than $C \rightarrow S$
- 6.10 (a) The $C=O$ and $C-H$ bonds are polar, while $C-C$ and $C=C$ are non-polar.
 (b) The $C=O$ bond is the most polar, with O at the negative end.
- 6.12 CS_2 and CO_2 are non-polar because of their linear shape. SO_2 and H_2O are polar because of their bent shape. The two bond dipole vectors only partially cancel out, leaving a NET dipole moment.
- 6.13 (a) $BFC l_2$ 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 BCl_3 , then the bond dipoles would cancel.
 (b) NH_2Cl is trigonal pyramidal. It has a NET dipole because it is asymmetrical and has one bond different from the other two – $N-Cl$ vs. $N-H$.
 (c) SCl_2 is bent like water. It has a NET dipole because the $S-Cl$ bond dipoles only partially cancel out.
- 6.15 (a) Bent SO_2 has a net dipole. So, there are dipole-dipole forces between neighboring molecules.
 (b) Linear CO_2 has no net dipole. There are no dipole-dipole forces between these molecules – only dispersion forces.
 (c) HCl has just one polar bond, and so has a dipole moment. There are dipole-dipole forces between neighboring molecules.

- 6.17 $\text{CH}_3\text{-O}\cdots\text{O-H}$
 $\quad\quad\quad |$
 $\quad\quad\quad \text{CH}_3\text{CH}_3$
 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 I_2 . This interaction is weaker than the dispersion force between I_2 molecules.
 (d) Octane, $\text{C}_8\text{H}_{18}(\ell)$ 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.

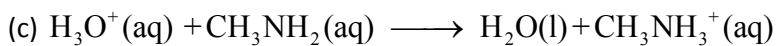
- 6.30 (a) Benzene, $C_6H_6(\ell)$, is non-polar and soluble in non-polar octane. Dispersion forces are all that are at play in the pure substances and mixtures. The entropy of mixing is sufficient to drive dissolution.
 (b) Water is polar and insoluble in non-polar octane. It turns out that reason for 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, $CH_3CH_2CH_2CH_2OH(\ell)$, should be more soluble in hexane than butan-2,4-diol, $HOCH_2CH_2CH_2CH_2OH(\ell)$. 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.
- 6.32 (a) $HBr(g) + H_2O(l) \longrightarrow H_3O^+(aq) + Br^-(aq)$
 (b) $HF(aq) + H_2O(l) \xrightleftharpoons{\text{only some ionised}} H_3O^+(aq) + F^-(aq)$
 (c) $HCOOH(aq) + H_2O(l) \xrightleftharpoons{\text{only some ionised}} HCOO^-(aq) + H_3O^+(aq)$
 (d) $C_{12}H_{22}O_{11}(s) \xrightarrow{H_2O} C_{12}H_{22}O_{11}(aq)$
- 6.36 (a) $Cu^{2+}(s) + CO_3^{2-}(aq) \longrightarrow CuCO_3(s)$
 Na^+ and Cl^- are spectator ions
 (b) No precipitate forms
 (c) $Ni^{2+}(s) + 2 OH^-(aq) \longrightarrow Ni(OH)_2(s)$
 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.



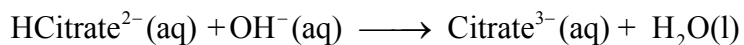
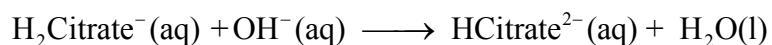
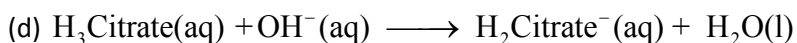
Li⁺ and Br⁻ are spectator ions



K⁺ is a spectator ion.



NO₃⁻ is a spectator ion



Na⁺ is a spectator ion

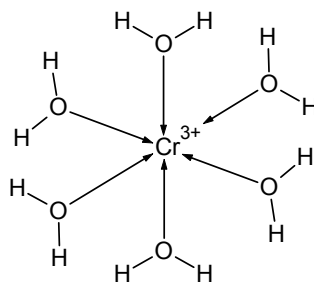
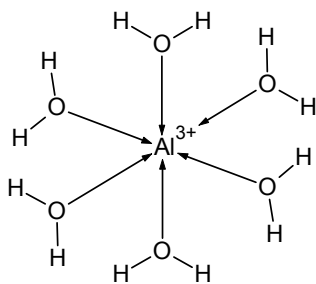
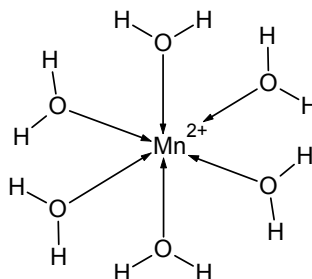
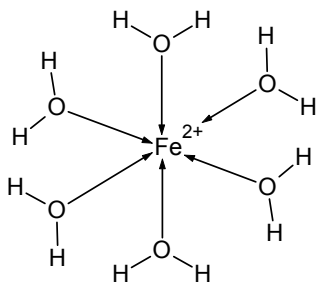
6.40 (a) Co²⁺ is the Lewis acid, while Cl⁻ is the Lewis base.

(b) Fe²⁺ is the Lewis acid, while CN⁻ is the Lewis base.

(c) Ni²⁺ is the Lewis acid, while CH₃NH₂ is the Lewis base.

(d) Cu²⁺ is the Lewis acid, while Cl⁻ and NH₃ are the Lewis bases.

6.41



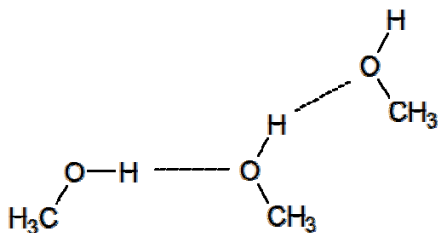
- 6.42 (a) $[\text{Co}(\text{H}_2\text{O})_6]^{2+}(\text{aq}) + 4 \text{Cl}^{-}(\text{aq}) \rightarrow [\text{CoCl}_4]^{2-}(\text{aq}) + 6 \text{H}_2\text{O}(\ell)$
Lewis base, Cl^{-} , competes successfully with the Lewis base, H_2O , to complex Co^{2+} .
- (b) $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}(\text{aq}) + 6 \text{CN}^{-}(\text{aq}) \rightarrow [\text{Fe}(\text{CN})_6]^{4-}(\text{aq}) + 6 \text{H}_2\text{O}(\ell)$
Lewis base, CN^{-} , competes successfully with the Lewis base, H_2O , to complex Fe^{2+} .
- (c) $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}(\text{aq}) + 2 \text{CH}_3\text{NH}_2(\text{aq}) \rightarrow [\text{Ni}(\text{CH}_3\text{NH}_2)_2]^{2+}(\text{aq}) + 6 \text{H}_2\text{O}(\ell)$
Lewis base, CH_3NH_2 , competes successfully with the Lewis base, H_2O , to complex Ni^{2+} .
- (d) $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}(\text{aq}) + 4 \text{Cl}^{-}(\text{aq}) + 2 \text{NH}_3(\text{aq}) \rightarrow [\text{Cu}(\text{NH}_3)_2\text{Cl}_4]^{2-}(\text{aq}) + 6 \text{H}_2\text{O}(\ell)$
Lewis bases, Cl^{-} and NH_3 , compete successfully with the Lewis base, H_2O , to complex Cu^{2+} .
- 6.43 0.478 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 $\text{NO}_3^{-}(\text{aq})$

REVIEW QUESTIONS

- 6.51 Water has a lower vapour pressure than hexane, 3.17 vs. 20.2 kPa at 25 °C. It takes a higher temperature to get 1 atm vapour from water, than it does from hexane – i.e. water has a higher boiling point.
- 6.53 (a) Intramolecular forces.
(b) Intermolecular forces.
(c) Intramolecular forces.
(d) Intermolecular forces.
- 6.55 (a) $\text{C} \rightarrow \text{O}$
(b) $\text{P} \rightarrow \text{Cl}$
(c) $\text{B} \rightarrow \text{O}$
(d) $\text{B} \rightarrow \text{F}$
- 6.57 $\text{HF} > \text{HCl} > \text{HBr} > \text{HI}$
- 6.59 (a) BeCl_2 is non-polar.
(b) HBF_2 is polar. The negative end is at the two F atoms.
(c) CH_3Cl is polar. The negative end is at the Cl atom.
(d) SO_3 is non-polar.
- 6.61 $\text{H}_2\text{S}(\text{g})$

- 6.63 (b) HCOOH
- 6.65 (Kr) It is bigger with more electrons
- 6.67 (a) dispersion forces
(b) metallic bonds
(c) dipole-dipole and dispersion forces
(d) H-bonds and dispersion forces
- 6.69 (a) < (b) < (c) < (d). (a), (b) and (c) are gases at 25°C and 1 atm.
- 6.71 (a) higher.
(b) higher.
(c) unchanged.
(d) higher.
(e) smaller.
(f) higher.
- 6.73 Propan-1-ol (CH₃CH₂CH₂OH) has a higher boiling point than methyl ethyl ether (CH₃CH₂OCH₃), a compound with the same empirical formula, because propan-1-ol molecules can form hydrogen bonds, whereas methyl ethyl ether cannot.
- 6.75 (a) O₂
(b) SO₂
(c) HF
(d) GeH₄

6.77



- 6.79 (a) Water has a higher viscosity than hexane, in spite of its smaller dispersion forces, because of its strong hydrogen bonds.
(b) Glycerol (propan-1,2,3-triol, HOCH₂CHOHCH₂OH) is even more viscous than water because it has three O-H groups and can form more hydrogen bonds than water.
- 6.81 The melting point of fumaric acid (287 °C) is much higher than that of maleic acid (131 °C) even though these substances are just *cis* and *trans* isomers.
Maleic acid makes a strong intramolecular hydrogen bond – this reduces opportunities for intermolecular hydrogen bonds, as an O and H are already hydrogen bonding. Strong intermolecular pairs of hydrogen bonds are formed between adjacent fumaric acid molecules.

- 6.83 (a) The O end (the negative end) of water points to Ca^{2+} .
 (b) The H end (the positive end) of water points to Br^- .
 (c) The H end (the positive end) of water points to $\text{Cr}_2\text{O}_7^{2-}$.
 (d) The O end (the negative end) of water points to $\text{NH}_4^+(\text{aq})$.
- 6.85 $\text{H}_2\text{O}(\ell)$, $\text{Ag}^+(\text{aq})$, $\text{NO}_3^-(\text{aq})$, $\text{K}^+(\text{aq})$ and $\text{Cl}^-(\text{aq})$.
- 6.87 Cooking oil is not miscible with water because its molecules are non-polar (or very weakly polar). They do not interact with water strongly enough for water to solvate them – water molecules prefer to interact with other water molecules. Cooking oil is soluble in hexane – a non-polar solvent.
- 6.89 The concentrations of hydronium ion and hydroxide ion equal in pure water because of the stoichiometry of the self-ionization reaction,

$$2 \text{H}_2\text{O}(\ell) \rightarrow \text{H}_3\text{O}^+(\text{aq}) + \text{OH}^-(\text{aq})$$
- 6.91 Since barium sulfate, $\text{BaSO}_4(\text{s})$, precipitates from water, whereas iron (II) sulfate does not, we conclude that $\text{BaSO}_4(\text{s})$ is insoluble in water (it has a very low solubility) whereas $\text{FeSO}_4(\text{s})$ is soluble.
- 6.93
- $$2 \text{Cr}_2\text{O}_7^{2-}(\text{aq}) + 28 \text{H}^+(\text{aq}) + 12 \text{e}^- \longrightarrow 4 \text{Cr}^{3+}(\text{aq}) + 14 \text{H}_2\text{O}(\ell)$$
- $$3 \text{C}_2\text{H}_5\text{OH}(\text{aq}) + 3 \text{H}_2\text{O}(\ell) \longrightarrow 3 \text{CH}_3\text{COOH}(\text{aq}) + 12 \text{H}^+(\text{aq}) + 12 \text{e}^-$$
- Here, ethanol, $\text{C}_2\text{H}_5\text{OH}$, is oxidized to acetic acid, CH_3COOH . Dichromate, $\text{Cr}_2\text{O}_7^{2-}$, is the oxidizing agent. $\text{Cr}_2\text{O}_7^{2-}$ is reduced to Cr^{3+} . Ethanol is the reducing agent.
- 6.95 When nitric acid dissolves in water, nitrate and hydronium ions are produced.
 When barium hydroxide dissolves in water, $\text{Ba}^{2+}(\text{aq})$ and $\text{OH}^-(\text{aq})$ are produced.
- 6.97 (a) $[\text{Fe}(\text{NH}_3)_6]^{2+}$
 (b) $[\text{Zn}(\text{CN})_4]^{2-}$
 (c) $[\text{MnF}_6]^{4-}$
 (d) $[\text{Fe}(\text{CN})_6]^{3-}$
 (e) $[\text{CoCl}_4]^{2-}$
 (f) $[\text{Ni}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+}$
- 6.99 To prepare the desired solution, carefully weigh 0.849 g of $\text{AgNO}_3(\text{s})$, add it to the volumetric flask, add ~150 mL of de-ionized water, stopper the flask and shake to dissolve the AgNO_3 and ensure a homogenous solution. After the AgNO_3 has dissolved, top up the volume to the 250 mL mark with de-ionized water – add the additional de-ionized water in steps, swirling between each step to ensure a homogeneous solution.
- 6.101 1250 mL of $0.060 \text{ mol L}^{-1} \text{Na}_2\text{CO}_3$ solution has the greater mass of solute.
- 6.103 0.494 g
- 6.105 5.08 L

6.107 3.38 g

6.109 concentration of $\text{Na}_2\text{CO}_3 = 0.254 \text{ molL}^{-1}$
concentration of $\text{Na}^+ = 0.508 \text{ molL}^{-1}$
concentration of $\text{CO}_3^{2-} = 0.254 \text{ molL}^{-1}$

SUMMARY AND CONCEPTUAL QUESTIONS

- 6.111 (a) Kinetic energy of the water molecules within and on the surface of the bubble prevents its collapse. These “hot” molecules smash into their neighbours pushing open the bubble.
(b) Bubbles form when the vapour pressure within the heated liquid slightly exceeds atmospheric pressure—enough to push open the bubble.
- 6.113 (a) Hydronium ions appear to diffuse very quickly through an aqueous solution—faster than they should be able to via diffusion—because the transfer of hydronium across a cluster of water molecules is achieved through successive H^+ ion transfers between adjacent water molecules.
(b) Each proton transfer involves one O atom of a hydronium ion taking the pair of electrons from an H atom bonded to it, and another O atom (on a water molecule on the other side of the H) donating a lone pair of electrons to the released proton—i.e., accepting the proton.
- 6.115 (a) Here, the electrostatic attraction of the Ag^+ and Cl^- ions overcomes the dipole-ion forces between solvating water molecules and the ions to cause growth of the ionic lattice.
(b) The lattice is an array of Ag^+ and Cl^- ions. It does not consist of distinct AgCl molecules.
- 6.117 (a) The electrons in the O–H bond of the CH_3COOH molecule go entirely to the O atom releasing a proton which attaches to a lone pair of electrons on a water molecule.
(b) A covalent bond is broken and a new one made.
- 6.119 (a) Ammonia is the Lewis base, donating lone pairs of electrons to the copper atom, in the form of a coordinate bond. Cu^{2+} is the Lewis acid.
(b) Ammonia molecules replace water molecules because the N in ammonia forms a stronger coordinate bond with copper than the O in water—ammonia is a better ligand.
- 6.121 (a) an acid-base reaction
(b) precipitation reaction
(c) acid-base, and complexation reaction
(d) oxidation-reduction reaction

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 °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 $\text{Br}_2(\ell)$.
(b) metallic liquid, $\text{Hg}(\ell)$.
(c) ionic solid $\text{Na}_2\text{SO}_4(\text{s})$.
(d) molecular liquid $\text{CH}_3\text{CH}_2\text{OH}(\ell)$.
(e) 1 mol L^{-1} concentration $\text{Cl}^-(\text{aq})$.

- 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 O₂(g) – both gases separately at 1 bar pressure – are combined in a vessel such that the total pressure is 1 bar (i.e. 1 ½ × the vessel containing the carbon monoxide), then reacted completely at fixed pressure to form 1 mol CO₂(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⁺(aq) at 1.00 mol L⁻¹ concentration react completely to form 1.00 mol of Mg²⁺(aq) at 1.00 mol L⁻¹ concentration and 1 mol H₂(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⁺(aq) and 1.00 mol of OH⁻(aq) both at 1.00 mol L⁻¹ concentration react completely to form 1.00 mol of H₂O(l).
- 7.19 (a) 1.9 kJ
- 7.20 116.8 kJ
- 7.21 (a) The standard molar enthalpy of formation of bromine, Br₂(l), is the standard enthalpy change of the following reaction:

$$\text{Br}_2(\ell) \rightarrow \text{Br}_2(\ell) \text{ at } 25 \text{ }^\circ\text{C}$$
- (b) The standard molar enthalpy of formation of solid iron (iii) chloride, FeCl₃(s), is the standard enthalpy change of the following reaction:

$$\text{Fe}(\text{s}) + \text{Cl}_2(\text{g}) \rightarrow \text{FeCl}_3(\text{s}) \text{ at } 25 \text{ }^\circ\text{C}$$
- (c) The standard molar enthalpy of formation of solid sucrose, C₁₂H₂₂O₁₁(s), is the standard enthalpy change of the following reaction:

$$12 \text{ C}(\text{graphite}) + 11 \text{ H}_2(\text{g}) + \frac{11}{2} \text{ O}_2(\text{g}) \rightarrow \text{C}_{12}\text{H}_{22}\text{O}_{11}(\text{s}) \text{ at } 25 \text{ }^\circ\text{C}$$
- 7.22 The standard molar enthalpy of formation of liquid methanol, CH₃OH(l), is the standard enthalpy change of the following reaction:

$$\text{C}(\text{graphite}) + 2 \text{ H}_2(\text{g}) + \frac{1}{2} \text{ O}_2(\text{g}) \rightarrow \text{CH}_3\text{OH}(\ell) \text{ at } 25 \text{ }^\circ\text{C}$$
- 7.26 -3267.4 KJ
- 7.27 -53 KJ
- 7.28 -694 KJ
- 7.31 (a) FALSE
 (b) TRUE
 (c) TRUE
 (d) TRUE

REVIEW QUESTIONS

7.33 The liquid water has more energy.

7.35 49.3 kJ

7.37 181 kJ

7.39 200 kJ

7.41 6190 kJ

7.43 23 kJ

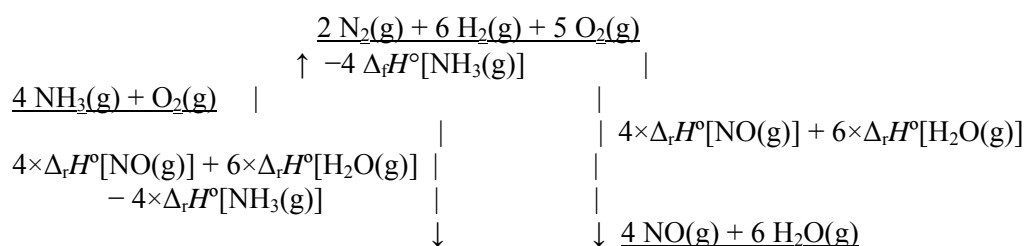
SUMMARY AND CONCEPTUAL QUESTIONS

7.45 (a) $\text{H}_2\text{O}(\ell)$
 (b) $\text{NaCl}(\text{s})$
 (c) $\text{Hg}(\ell)$
 (d) $\text{CH}_4(\text{g})$
 (e) 2.00 mol L^{-1} is the $\text{Na}^+(\text{aq})$ concentration

7.47 90.3 kJ

7.49 (a) $-601.24 \text{ kJ mol}^{-1}$
 (b) -1503.1 kJ

7.51 -905.47 kJ



7.53 -77.69 kJ

7.55 $\Delta_f H^\circ = -352.9 \text{ kJ}$. Mass of $\text{Mg}(\text{s}) = 7.24 \text{ mg}$.

7.57 Enthalpy change per g of hydrazine = -16.67 kJ g^{-1}
 Enthalpy change per g of 1,1-dimethylhydrazine = -30.00 kJ g^{-1}
 1,1-dimethylhydrazine evolves more heat on a per gram basis.

7.59 301 kJ

- 7.61 (a) -1070 kJ
(b) -1352.97 kJ
- 7.63 -1273 kJ
- 7.65 (a) An exothermic reaction releases energy which must be removed to return the system to its original temperature – heat leaves the system. An endothermic reaction absorbs energy which must be supplied for the system to stay at its original temperature – heat enters the system.
- (b) The system is the set of all substances of interest – e.g. the reactants and products of a reaction. The surroundings consist of everything else.
- (c) The specific heat capacity of substance is the amount of heat (usually expressed in J) required to raise the temperature of exactly 1 g of the substance $1 \text{ }^\circ\text{C}$ - assuming no phase transitions occur during heating.
- (d) A state function is anything that depends only on the “state” of a system. A state function is any property of the system such as temperature, pressure, volume or energy. A changed value of a state function indicates a change in the state of the system.
- (e) The standard state of a substance is the stable form of the substance at 1 atm and – unless specified otherwise – $25 \text{ }^\circ\text{C}$.
- (f) The enthalpy change of reaction, $\Delta_r H$, is the change in enthalpy when the extent of reaction is 1 mol (i.e. reactants form products with numbers of moles given by the stoichiometric coefficients), and the temperature of the products is returned to the initial temperature of reactants.
- (g) The standard enthalpy change of reaction, $\Delta_r H^\circ$, is the enthalpy change of reaction under standard conditions – all reactants and products are at 1 atm pressure, and solutes are at 1 mol L^{-1} concentration.
- (h) The standard molar enthalpy change of formation, $\Delta_f H^\circ$, is the standard enthalpy change of a formation reaction wherein 1 mol of a substance is formed.
- 7.67 A perpetual motion machine is impossible as soon as there is friction or other forms of energy dissipation. Because energy is constantly lost to friction, there must be a constant supply of incoming useful energy – here we invoke conservation of energy. For the machine to run forever, it must have an infinite supply of energy – impossible in a finite machine.
- 7.69 $\Delta_r H^\circ = -1433.5 \text{ kJ}$
- 7.71 A bond dissociation energy is the enthalpy change associated with breaking a single bond. All bond breaking processes are endothermic – the enthalpy change is positive. It always takes energy input to break a bond.
- 7.73 $-6.2 \times 10^{10} \text{ kJ}$

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, Br₂(g)
(b) Sodium, Na(s)
(c) Chlorine, Cl₂(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. Al³⁺ 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⁻
(b) Ba²⁺
(c) K
(d) Se²⁻
(e) Cl⁻
(f) Pb²⁺
- 8.14 (a) O⁻
(b) Cl⁻

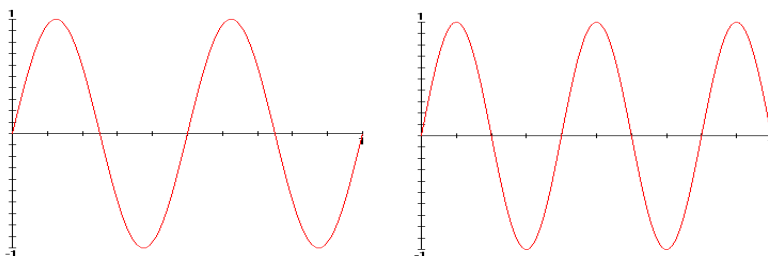
- 8.15 (a) $O < C < Si$
 (b) $Si < C < O$
 (c) $Si < C < O$

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

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

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

8.20

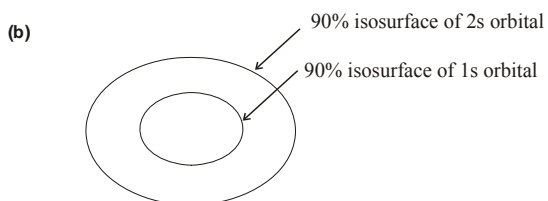
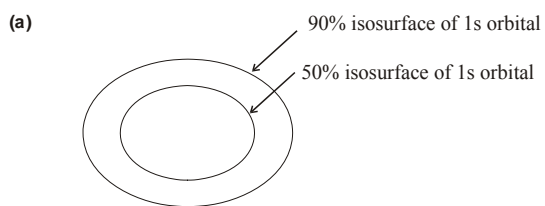


- 8.22 (a) valid
 (b) not valid
 (c) not valid

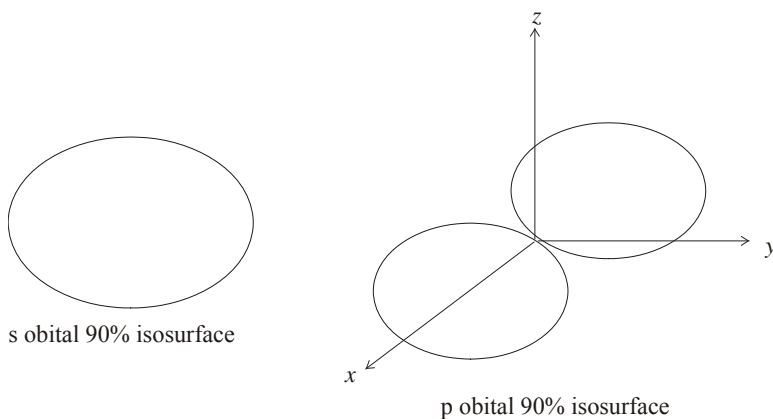
- 8.24 (a) 0 or 1
 (b) $-1, 0$ or 1 p subshell
 (c) d subshell
 (d) l is 0 and m_l has the value 0
 (e) 3 orbitals
 (f) 7 values of m_l 7 orbitals

- 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 $n - 1$.

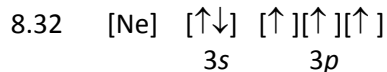
8.27



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 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 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.

REVIEW QUESTIONS

- 8.45 MgCl_2 is an ionic material—a compound of a metal and non-metal. It has a high melting point—i.e., $714\text{ }^\circ\text{C}$ —and it conducts electricity in its molten state but not its solid state.
 PCl_3 is a molecular substance—a compound of two non-metals. Its solid consists of molecules held together by intermolecular forces. It has a low melting point—i.e., $112\text{ }^\circ\text{C}$ —and it does not conduct electricity.
- 8.47 $\text{C} < \text{B} < \text{Al} < \text{Na} < \text{K}$
- 8.49 $\text{K} < \text{Ca} < \text{Si} < \text{P}$
- 8.51 (a) S^-
 (b) Cl^-
- 8.53 (a) $\text{C} < \text{B} < \text{Al}$
 (b) $\text{Al} < \text{B} < \text{C}$
 (c) carbon

- 8.55 (a) $S < O < F$
 (b) O
 (c) Cl
 (d) O^{2-}

8.59 $2.179 \times 10^{-18} \text{ J}$

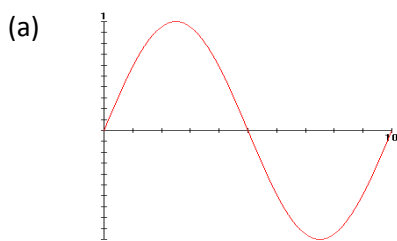
8.61 Blue; $n_{\text{initial}} = 6$.

- 8.63 (a) 10
 (b) $n = 5$ to a level with $n = 1$.
 (c) $n = 5$ to the level with $n = 4$.

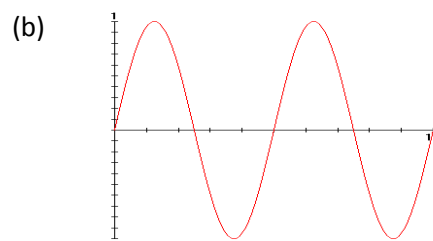
- 8.65 (a) $n = 4$ to $n = 2$
 (b) $n = 4$ to $n = 1$

8.67 0.145 nm

8.69

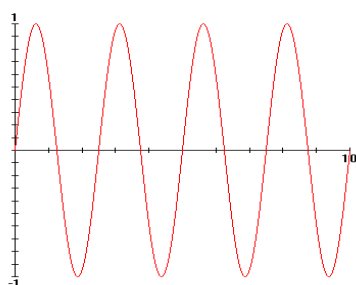


The wavelength of this wave is 10 cm.



The wavelength of this wave is 5 cm.

(c) Four waves fit in the interval if the wavelength of the standing wave is 2.5 cm. The number of nodes between the ends is $2 \times 4 - 1 = 7$.



8.71 $n = 4$, $l = 1$ and $m_l = -1, 0, 1$

- 8.73 (a) $n = 2$, $l = 2$, $m_l = 0$ is NOT allowed because l must be no greater than 1 when $n = 2$.
 (b) $n = 3$, $l = 0$, $m_l = -2$ is NOT allowed because m_l must equal 0 when $l = 0$.
 (c) $n = 6$, $l = 0$, $m_l = 1$ is NOT allowed because m_l must equal 0 when $l = 0$.

8.77 4

- 8.81 (a) The n and l values for $6s$, $4p$, $5d$, and $4f$ are as follows:
 $6s$ means $n = 6, l = 0$
 $4p$ means $n = 4, l = 1$
 $5d$ means $n = 5, l = 2$
 $4f$ means $n = 4, l = 3$
- (b) For a $4p$ orbital there are $n - 1 = 3$ radial nodes (spherical in shape) and $l = 1$ nodal planes. $3 + 1 = 4$ altogether
 For a $6d$ orbital there are $n - 1 = 5$ radial nodes (spherical in shape) and $l = 2$ nodal planes (or cones). $5 + 2 = 7$ altogether
- 8.83 (a) energy
 (b) quantum number l
 (c) more
 (d) 7
 (e) 1
 (f) 0, 1, 2, 3 and 4
 (g) $1 + 3 + 5 + 7 = 16$
- 8.87 (a) $1s^2 2s^2 2p^6 3s^2 3p^4$
 (b) $1s^2 2s^2 2p^6 3s^2 3p^1$
- 8.89 (a) $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^3$ or $[\text{Ar}]4s^2 3d^{10} 4p^3$
 (b) $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6$ or $[\text{Ar}]4s^2 3d^{10} 4p^6 = [\text{Kr}]$
- 8.93 (i) $Z^*(\text{Mg}) = +2.85$
 (ii) $Z^*(\text{Mg}^+) = +3.2$
 (iii) $Z^*(\text{Mg}^{2+}) = +7.85$
 The increasing effective nuclear charge for these three species correlates with their sizes: $\text{Mg} > \text{Mg}^+ > \text{Mg}^{2+}$. Note, especially the jump from Mg^+ to Mg^{2+} .
- 8.95 $Z^*(\text{N}^{3-}) = +2.85; Z^*(\text{O}^{2-}) = +3.85; Z^*(\text{F}^-) = +4.85$
 These effective nuclear charges correlate with the relative sizes of the ions: $\text{F}^- < \text{O}^{2-} < \text{N}^{3-}$

SUMMARY AND CONCEPTUAL QUESTIONS

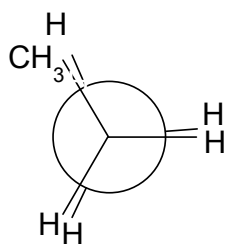
- 8.97 (c) Electrons are moving from a given energy level to one of lower n .
- 8.99 Electrons and other subatomic “particles” are found to exhibit properties of both waves and particles. We can measure the position of the “particles” – a particle property. However, the results of such measurements can show interference patterns characteristic of a wave.

- 8.101 Li^+ ions are so much smaller than Li atoms because Li has a lone valence electron in the $n = 2$ shell, whereas $\text{Li}^{\square+}$ just has the two $n = 1$ electrons. In any case, with a net positive charge, cations hold on to their electrons more tightly, and are correspondingly much smaller. F^- ions are so much larger than F atoms, because they are anions. Anions, with a net negative charge hold on to their electrons more loosely, and are much larger than associated neutral atoms.
- 8.103 The ionization energy of atoms increases from left to right across the periodic table, and decreases going down a group. The decrease going down a group is attributable to the valence electrons being further from the nucleus. The effective nuclear charge is the same (or similar) because the elements are in the same group. What changes is the distance from the nucleus. Electrons further from the nucleus are more easily removed.

Chapter 9

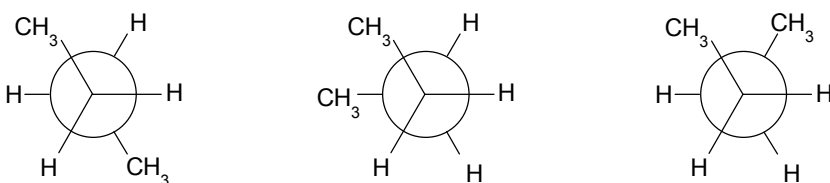
- 9.1 The spectra on the left and right are those of diethyl ether and butan-1-ol, respectively.
- 9.2 One could distinguish butan-1-ol and diethyl ether by looking for the distinctive O-H stretch peak (broad peak around $3200\text{-}3550\text{ cm}^{-1}$) of butan-1-ol in the IR spectra.
- 9.3 The spectra 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

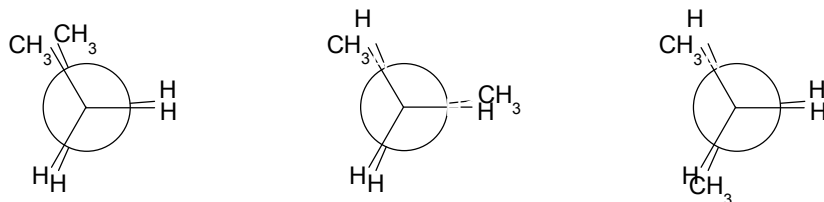


This is the eclipsed conformation – it is the least stable.

9.7

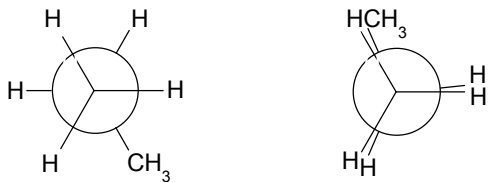


These are the Newman projections of the three staggered conformations. The conformation on the left has the lowest energy. The other two have the same energy.

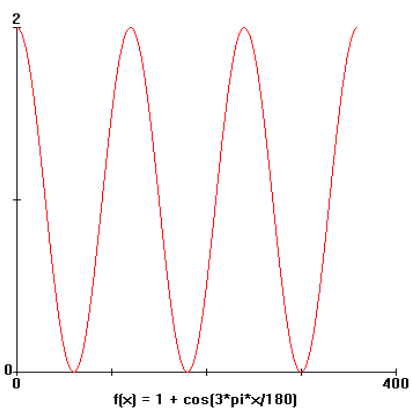


These are the Newman projections of the three eclipsed conformations. The conformation on the left has the highest energy. The other two have the same energy.

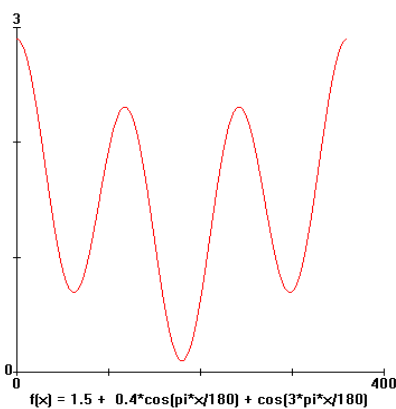
9.8 There is only one staggered and one eclipsed conformation of propane.



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



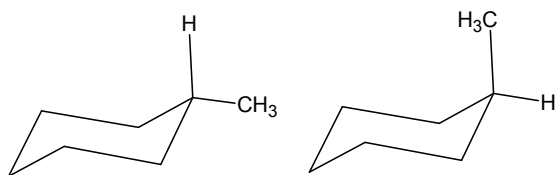
energy vs. angle for ethane



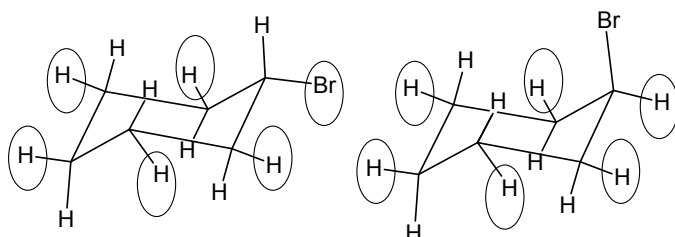
energy vs. angle for butane

- 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



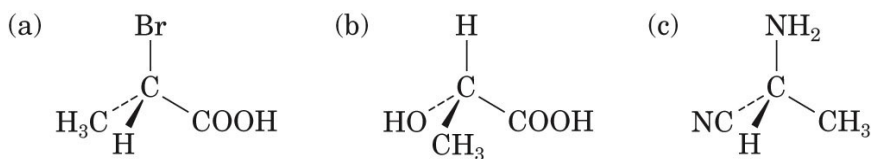
Here are the equatorial (on the left) bromine and axial bromine conformations of bromocyclohexane. The equatorial positions are circled.

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

9.18 16.1°

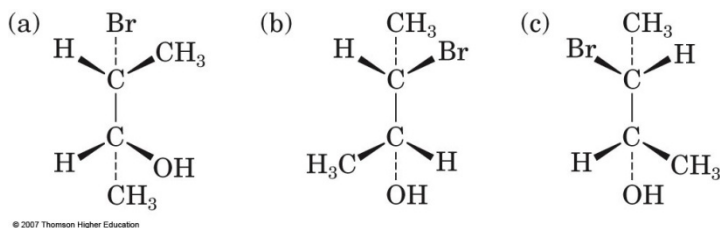
- 9.21 (a) $-Br > -CH_2CH_2OH > -CH_2CH_3 > -H$
 (b) $-OH > -CO_2CH_3 > -CO_2H > -CH_2OH$
 (c) $-Br > -Cl > -CH_2Br > -CH_2Cl$

9.22



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

9.23



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

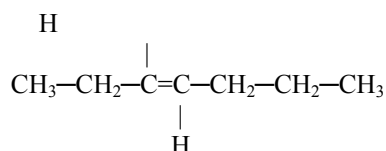
9.26 (a) and (c) are meso molecules – they are *R, S*.
(b) is an *R, R* enantiomer.

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

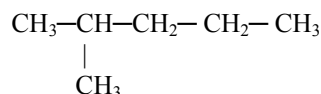
9.28 Darvon is the *2R, 3S* (+) enantiomer of propoxyphene.
Novrad is the *2S, 3R* (-) enantiomer.

REVIEW QUESTIONS

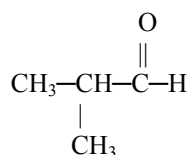
9.29 (a)



(b)



(c)

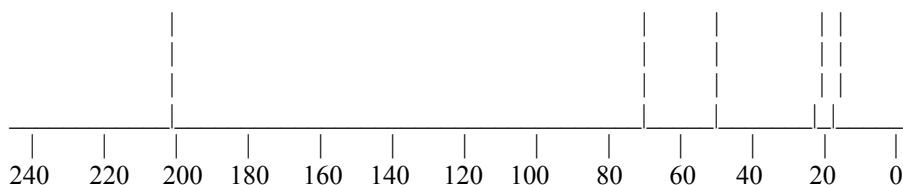


9.31 NMR uses photons with lower energy than those used in IR spectroscopy. 400 MHz is a much lower frequency than the 10-100 THz range of IR spectroscopy. NMR causes transitions between spin energy levels that are very close. IR causes vibrational energy transitions that are much higher in energy.

9.33 Reasonable values for the carbon atom chemical shifts are as follows:

- carbonyl carbon at 200 ppm
- two methyl carbons at around 20 ppm – two distinct peaks
- two methyl carbons at around 20 ppm – two distinct peaks
- C-O methylene carbon at 70 ppm
- C-Cl methine carbon at 50 ppm

The carbon-13 spectrum might look something like



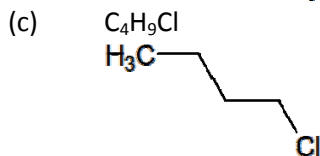
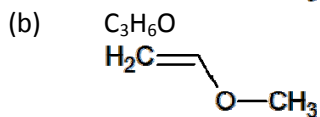
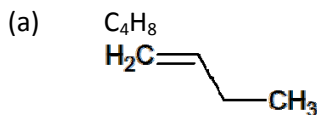
9.35 (a) 77.23 ppm downfield from TMS

(b) 46338 Hz downfield from TMS

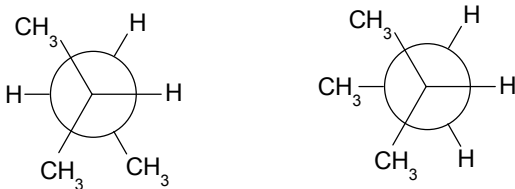
(c) 77.23 δ

9.37 $\text{CH}_4 < \text{CH}_2\text{Cl}_2 < \text{HC}\equiv\text{CH} < \text{benzene} < \text{HC(O)C(O)H}$ (two carbonyls bonded together)

9.39 Possible skeletal structures:



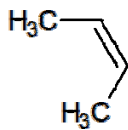
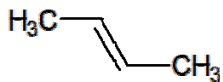
9.41



The staggered conformation on the left is expected to have the lower energy because the methyl substituent on the back carbon is close to both of the methyl substituents on the front carbon in the right conformation, but only one in the left conformation.

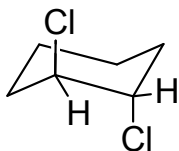
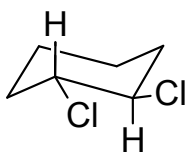
9.43 7.4 kJ mol^{-1}

9.45



cis and *trans* 2-butene

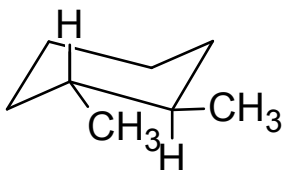
9.47



Either both Cl atoms are equatorial (top conformation) or axial (bottom conformation) because on adjacent carbon atoms the two axial positions are on opposite sides of the ring – the two equatorial are necessarily also on opposite sides of the ring.

9.49 In the ring-flipped form, the blue and red substituents are axial whereas the yellow is equatorial.

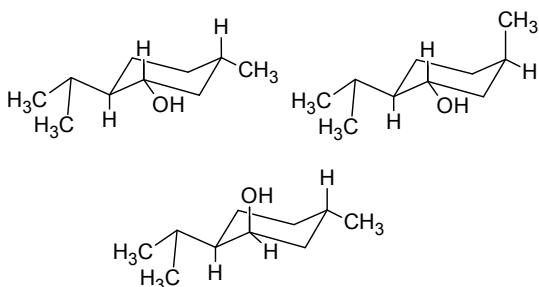
9.51



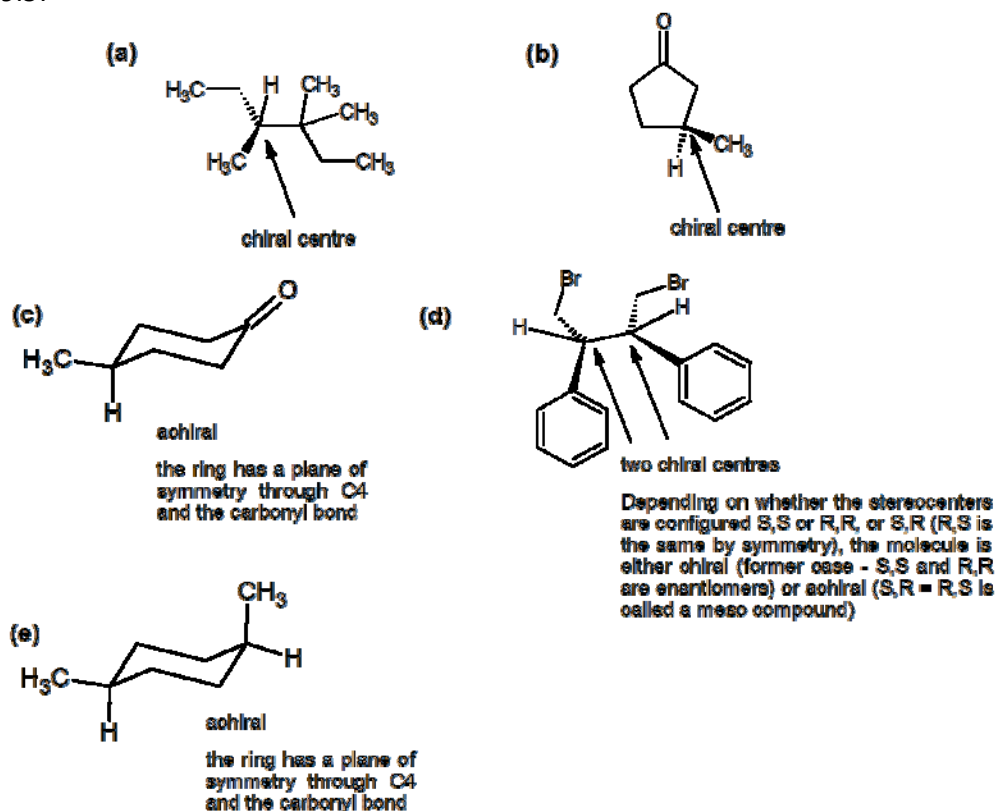
The methyl groups are in equatorial positions.

9.53 The methyl substituent has greater steric requirements than the electron lone pair – the former is in the more accommodating equatorial position.

9.55

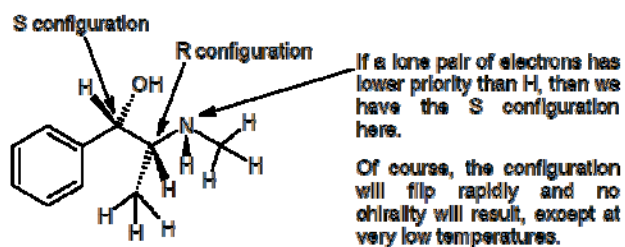


9.57

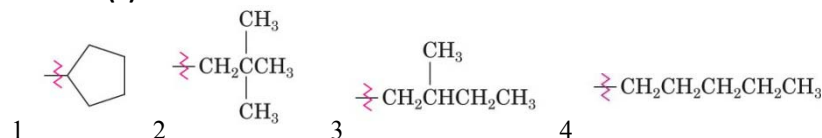


9.59 37.0°

9.61



9.63 (a)



(b) 1 -SO₃H 2 -SH 3 -OCH₂CH₂OH 4 -NH₂

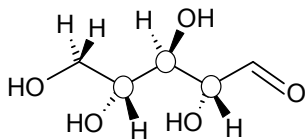
9.65 The configurations at the chiral centers are:

(a) S (b) S (c) S

9.67 The specific rotations of (2*R*,3*R*)-dihydroxypentane and (2*S*,3*S*)-dihydroxypentane are the same (not equal to zero) except for the sign. These species are enantiomers. The specific rotation of (2*R*,3*R*)-dihydroxypentane is zero – it is a meso compound.

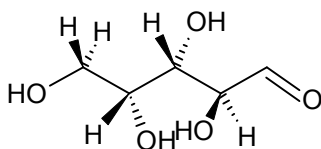
9.69 The stereochemical configurations of the two diastereomers of (2*S*,4*R*)-dibromooctane are (2*R*,4*R*) and (2*S*,4*S*).

9.71

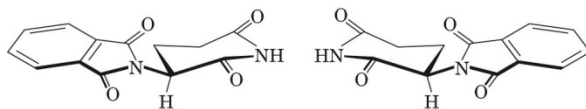


Ribose – three stereocenters indicated with circles. There are $2^3 = 8$ stereoisomers of ribose.

9.73



9.75

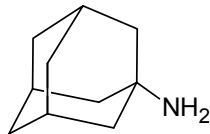


Thalidomide

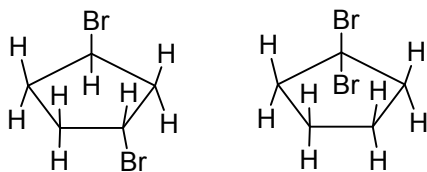
- (a) The lone stereocenter is the C atom bonded to the N atom of the bicyclic substituent.
 (b) The structure on the right is the *S* enantiomer - the *R* enantiomer is the structure on the left.

SUMMARY AND CONCEPTUAL QUESTIONS

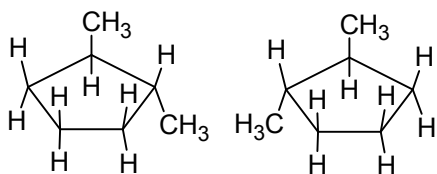
9.77



9.79

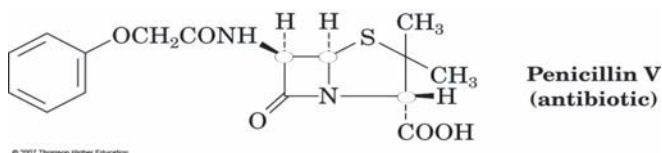


9.81



The two enantiomers of *trans*-1,2-dimethylcyclopentane – they are the non-superimposable mirror images of each other.

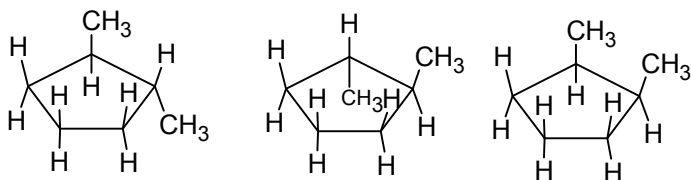
9.83



The stereocenters are denoted by solid white circles.

9.85 +6.83°

9.87



The stereoisomers of 1,2-dimethylcyclopentane. From left to right, the stereocenters are configured as (*R,R*), (*S,S*) and (*R,S*).

The two on the left (the *trans* isomers) are enantiomers. The structure of the right (the *cis* isomer) is a meso molecule.

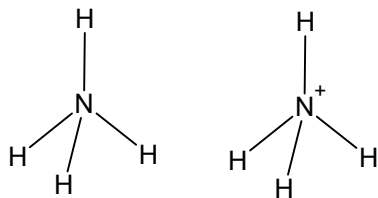
- 9.89 (a) The chiral carbon here has the *S* configuration.
(b) Both of the chiral carbons here have the *S* configurations.

- 9.91 (a) (*S*)-5-Chloro-2-hexene and chlorocyclohexane are structural or constitutional isomers. Specifically, they are skeletal isomers.
(b) (*2R,3R*)-Dibromopentane and (*2S,3R*)-dibromopentane are diastereomers.

- 9.93 The stereocenter (the top carbon in the projection) is in the *S* configuration.

Chapter 10

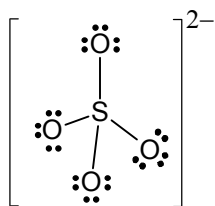
10.3 NH_4^+



CO

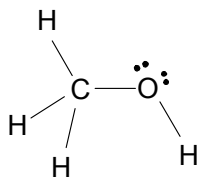


SO_4^{2-}

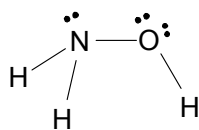


10.4

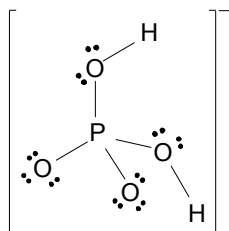
CH_3OH



NH_2OH

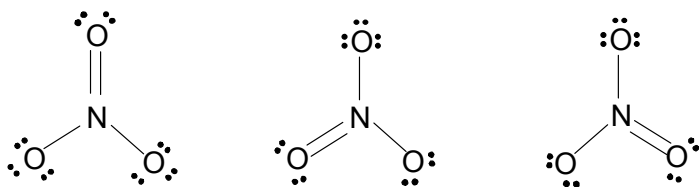


10.5

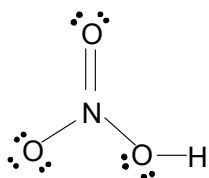


- 10.6 (a) Acetylide ion, C_2^{2-} , is isoelectronic with N_2 .
(b) SO_2
(c) OH^-

10.9

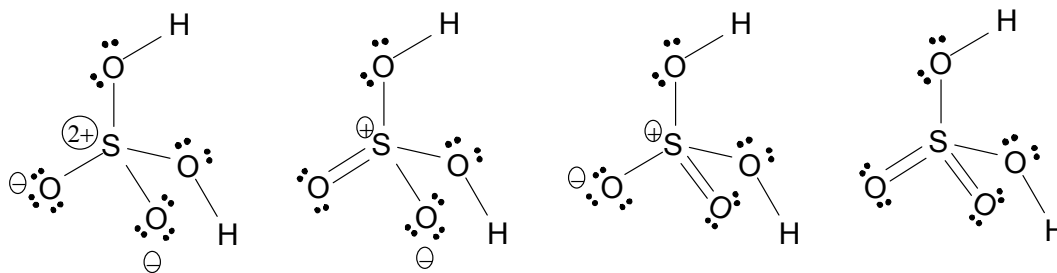


The three resonance structures of nitrate, NO_3^- .



A structure for nitric acid, HNO_3

10.11



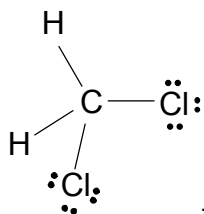
The structure on the right, with no formal charges, is the preferred Lewis structure.

10.12



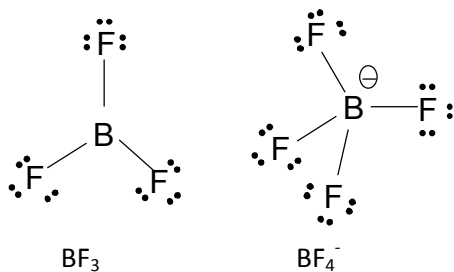
Equivalent resonance structures that together best describe the charge distribution within ozone.

10.13



Tetrahedral shape. The $\text{Cl}-\text{C}-\text{Cl}$ bond angle is predicted to be 109.5°

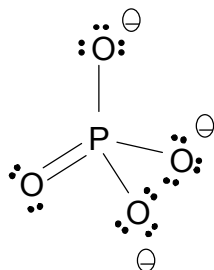
10.16



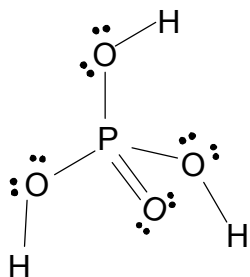
BF_3 is trigonal planar. BF_4^- is tetrahedral.

10.17

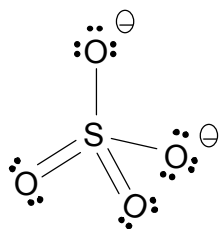
(a) phosphate ion, PO_4^{3-} , is tetrahedral



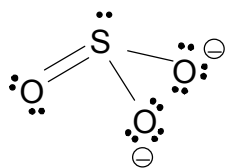
(b) phosphoric acid molecule, H_3PO_4 , is tetrahedral at the P



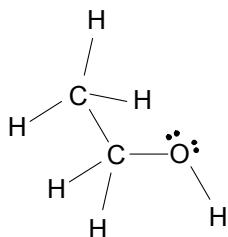
(c) sulfate ion, SO_4^{2-} , is tetrahedral



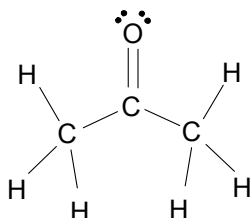
(d) sulfite ion, SO_3^{2-} , is trigonal pyramidal



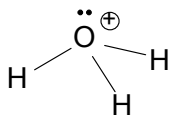
(e) ethanol is tetrahedral at the carbons and bent at the oxygen



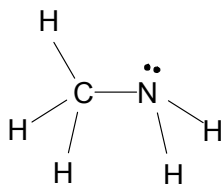
(f) Acetone, $\text{CH}_3\text{C}(\text{O})\text{CH}_3$, is trigonal planar at the carbonyl carbon and tetrahedral at the methyl carbons.



10.18



(a)



(b)

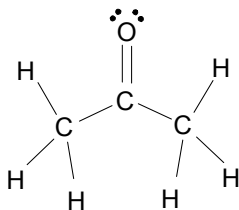
Lewis structures of (a) hydronium ion, and (b) methyl amine

(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



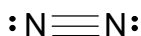
The methyl C atoms have the tetrahedral distribution of electron regions. This means sp^3 hybridization at the methyl carbon atoms. Three of the sp^3 orbitals overlap with s orbitals on H atoms to form the C-H bonds, while the fourth makes a bond with the carbonyl C atom.

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 σ 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 σ 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 π bond.

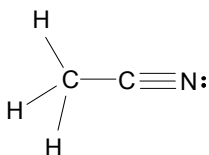
10.20



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 σ 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 π bonds. Specifically, the p_x orbitals overlap to form the π_x bond, while the p_y orbitals overlap to form the π_y bond.

10.21



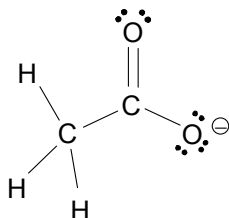
The H-C-H, H-C-C, and C-C-N bond angles are estimated to be 109.5° , 109.5° and 180° , respectively.

The methyl C atom has the tetrahedral distribution of electron regions - sp^3 hybridization at the methyl carbon atoms.

The nitrile C and N atoms have a linear arrangement of two electron regions.

The two remaining p orbitals on the nitrile C and N atoms overlap in pairs to form the two C-N π bonds.

10.22



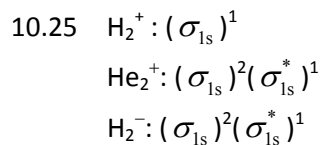
The methyl C atom has the tetrahedral distribution of electron regions - sp^3 hybridization at the methyl carbon atoms. Three of the sp^3 orbitals overlap with s orbitals on H atoms to form the C-H bonds, while the fourth makes a bond with the carbonate C atom.

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 σ 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 σ 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.

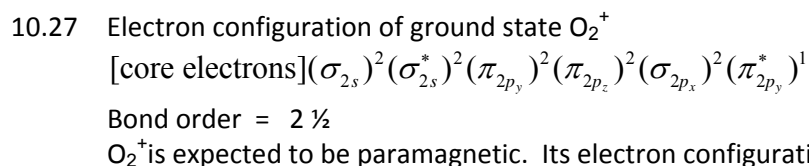
What remains are a p orbital on each of the O atoms and the unhybridized p orbital on the carbonate carbon atom – three orbitals in all. Two electron pairs also remain. In a valence bond description, a π bond is formed using the p orbital on C and one of the O atom p orbitals. The other O-atom p orbital 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 π 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 π bond with carbon, the other accommodates the remaining lone pair of electrons.



H_2^+ has a bond order of $\frac{1}{2}$. It should exist. But, it is weakly bound. He_2^+ and H_2^- have the same bond order.

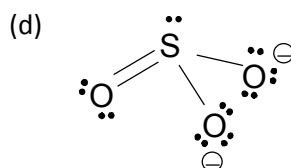
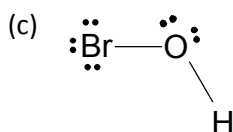
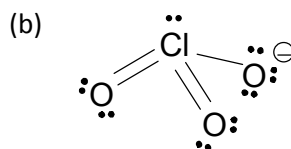
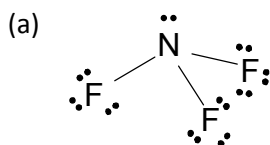
10.26 Li_2^- anion should exist. It is weakly bound with bond order, $\frac{1}{2}$.



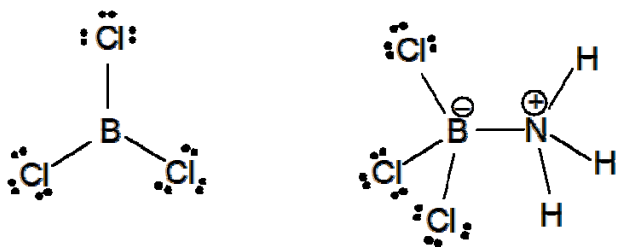
REVIEW QUESTIONS

10.31 4

10.33

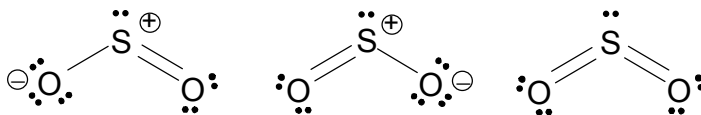


10.35

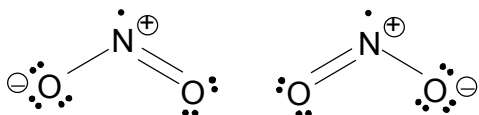


10.37

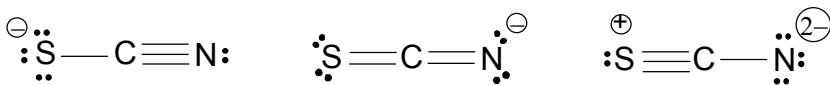
(a) SO_2



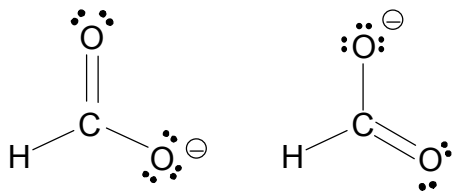
(b) NO_2



(c) SCN^-



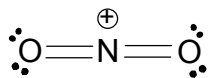
10.39



Average C-O bond order = $3/2$

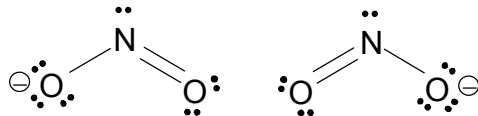
10.41

(a)



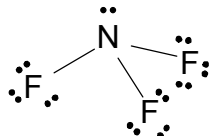
Formal charges are zero on O's and +1 on N.

(b)



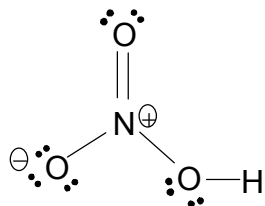
The N has a formal charge of zero. The formal charges on the two equivalent O's are zero and -1.

(c)



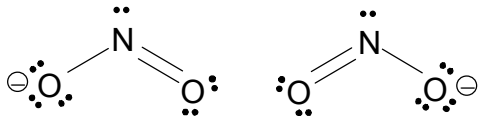
All atoms have zero formal charge.

(d)



Formal charges are as shown.

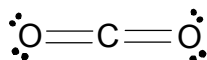
10.43



If H^+ attaches to NO_2^- (to form the acid HNO_2), it attaches to an O atom – not N.

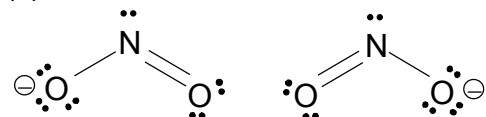
10.45

(a)



There are two electron regions about the carbon atom. The electron geometry and the molecular geometry are linear.

(b)



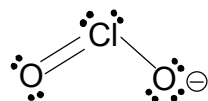
There are three electron regions about the nitrogen atom. The electron geometry is trigonal planar, while the molecular geometry is bent – there is one lone pair on the central atom.

(c)



There are three electron regions about the oxygen atom. The electron geometry is trigonal planar, while the molecular geometry is bent – there is one lone pair on the central atom. This molecule is isoelectronic with NO_2^- . They have the same shape and Lewis structure – aside from the formal charge on the central atom.

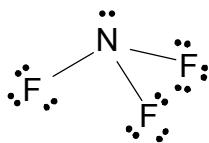
(d)



There are four electron regions about the oxygen atom. The electron geometry is tetrahedral, while the molecular geometry is bent – there are two lone pairs on the central atom. This molecule is likely more bent than O_3 or NO_2^- , because there are two lone pairs on the central atom in this case.

- 10.47
- (1) 120°
 - (2) 109.5°
 - (3) 120°
 - (4) 109.5° (actually the value is 107° - the angle is smaller due to greater repulsion of the lone pairs)
 - (5) 109.5° (actually slightly less)

10.49



The molecular geometry is trigonal pyramidal – there is a lone pair – while the electron geometry about the N atom is tetrahedral.

A tetrahedral distribution of electron regions means sp^3 hybridization at nitrogen. Three of the sp^3 orbitals overlap with sp orbitals on F atoms – we assume the F atoms to be sp hybridized (in contrast to the Lewis structure depiction which implies sp^3 hybridization). The remaining nitrogen sp^3 orbital accommodates the lone pair on N. The remaining one sp and two p orbitals on each F accommodates the fluorine lone pairs – three on each atom.

10.51 (a) The carbon atoms in dimethyl ether, H_3COCH_3 use sp^3 hybridized orbitals to form σ bonds with H atoms, and with the O atom. The oxygen atom in dimethyl ether, H_3COCH_3 uses two sp^3 hybridized orbitals to form σ bonds with C atoms.

The remaining two sp^3 orbitals on O accommodate the two lone pairs.

10.53

(a) SO_2

The O-S-O bond angle is about 120° .

The sulfur atom uses sp^2 orbitals to form two σ bonds – one with each O atom.

The other sp^2 orbital accommodates a lone pair. We can describe the Lewis structure with only one double S-O bond with the remaining unhybridized p orbital. It forms a π bond with just one of the O atoms.

However, the structure with two S-O double bonds minimizes formal charges and, as such, is preferred. To describe the bonding in this case requires the use of a 1 d orbital on S – since in this structure, S accommodates 10 electrons in its valence shell. Two pd orbitals on S form two π bonds - one with each of the O atoms.

(b) SO_3

The O-S-O bond angle is 120° .

The sulfur atom uses sp^2 orbitals to form three σ bonds – one with each O atom.

In accord with the formal charge minimized structure, we use three pd^2 orbitals on S to form three π bonds - one with each of the O atoms. Otherwise, if we use just the p orbital, then S can form only one S-O π bond.

(c) SO_3^{2-}

The O-S-O bond angle is 109.5° .

The sulfur atom uses sp^3 orbitals to form three σ bonds – one with each O atom.

The other sp^3 orbital accommodates a lone pair on S.

In accord with the formal charge minimized structure, we use two pd orbitals on S to form two π bonds - one with each of two O atoms.

(d) SO_4^{2-}

The O-S-O bond angle is 109.5° .

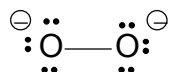
The sulfur atom uses sp^3 orbitals to form four σ bonds – one with each O atom. In accord with the formal charge minimized structure, we use two pd orbitals on S to form two π bonds - one with each of two O atoms.

10.55 In linear CO_2 the carbon atom uses two sp orbitals to form σ bonds with each O atom. Each of the two unhybridized p orbitals forms a π bond with an O atom. In CO_3^{2-} , there are two single C-O bonds and one double C-O bond, giving rise to three equivalent resonance structures. The carbon atom uses three sp^2 orbitals to form σ bonds with each of the three O atoms. The unhybridized p orbital forms a π bond with just one O atom. Since it can be any one of the three, we get three equivalent resonance structures.

10.57 (a) The angles A , B , C , and D are about 120° , 109.5° (actually 104°), 109.5° and 120° , respectively.
 (b) According to the valence bond model, carbon atoms 1, 2, and 3 are sp^2 , sp^2 and sp^3 hybridized, respectively.

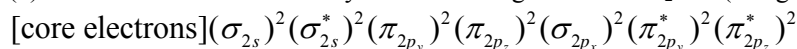
10.59

(a)



The bond order in O_2^{2-} is 1.

(b) The molecular orbital theory electron configuration for O_2^{2-} is (using unhybridized orbitals)

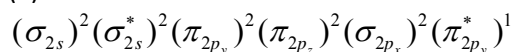


$$\text{bond order} = \frac{1}{2} \times (2 + 2 + 2 + 2 - 2 - 2 - 2) = 1$$

(c) For O_2^{2-} , the valence bond description and the molecular orbital description predict the same bond order and the same magnetic behaviour (i.e. diamagnetic – NOT paramagnetic – there are no unpaired electrons in either description).

10.61 Molecular orbital; theory electron configurations (core electrons omitted):

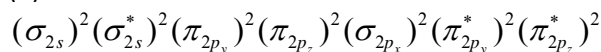
(a) NO



an unpaired electron \rightarrow paramagnetic

HOMO = $\pi_{2p_y}^*$ or $\pi_{2p_z}^*$ \leftarrow same energy (by symmetry)

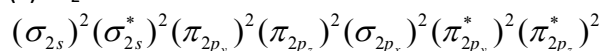
(b) OF^-



no unpaired electrons \rightarrow NOT paramagnetic – i.e. diamagnetic

HOMO = $\pi_{2p_y}^*$ or $\pi_{2p_z}^*$ \leftarrow same energy (by symmetry)

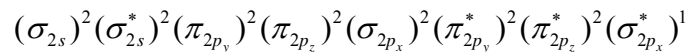
(c) O_2^{2-}



no unpaired electrons \rightarrow NOT paramagnetic – i.e. diamagnetic

HOMO = $\pi_{2p_y}^*$ or $\pi_{2p_z}^*$ ← same energy (by symmetry)

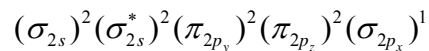
(d) Ne_2^+



an unpaired electron → paramagnetic

HOMO = $\sigma_{2p_x}^*$

(e) CN

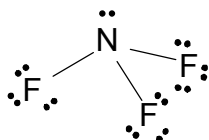


an unpaired electron → paramagnetic

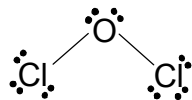
HOMO = σ_{2p_x}

SUMMARY AND CONCEPTUAL QUESTIONS

10.63



NF_3 has four electron pairs about the central atom, and a trigonal pyramidal shape.



OCl_2 has four electron pairs about the central atom, and a bent shape.

10.65 The average C-O bond order in formate (HCO_2^-) is 1.5 – there are two equivalent C-O bonds represented as a single and a double bond in the two resonance structures.

In methanol (CH_3OH), the C-O bond is just a single bond – there is just one structure.

In carbonate (CO_3^{2-}), there are three equivalent C-O bonds. One is a double bond, while the other two are single bonds. The average bond order is $4/3 = 1.3333$.

Formate has the strongest C-O bond, which is expected to be the shortest.

Methanol has the weakest C-O bond, which is expected to be the longest.

10.67 NO_2^+ is linear. Its O-N-O bond angle is 180° .

NO_2^- is bent. Its O-N-O bond angle is less than 120° .

10.69 (a) Angles 1, 2, and 3 equal about 120° , 180° and 120° , respectively.

(b) The carbon-carbon double bond is shorter.

(c) The carbon-carbon double bond is stronger.

(d) The C-N triple bond is the most polar – largest difference in electronegativity.

- 10.71 (a) Bond angles 1, 2 and 3 are about 120° , 109.5° (actually 104°) and 120° , respectively.
 (b) The shortest carbon–oxygen bond is the carbonyl C=O double bond at the top of the structure.
 (c) The most polar bond in the molecule is the O-H bond at the bottom of the structure.
- 10.73 (a) The geometry about the boron atom in $\text{H}_3\text{N}\rightarrow\text{BF}_3$ is tetrahedral.
 (b) In BF_3 , the valence orbitals of boron are sp^2 hybridized.
 In $\text{H}_3\text{N}\rightarrow\text{BF}_3$, the valence orbitals of boron are sp^3 hybridized.
 (c) We expect the hybridization of boron to change when this coordinate bond forms.

Chapter 11

- 11.4 $32 \times 10^4 \text{ L}$
- 11.5 650 balloons
- 11.6 136 kPa
- 11.10 121 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 gmol^{-1}
- 11.23 (a) the dispersion forces in liquid O_2 < (c) the dipole induced dipole interactions of O_2 dissolved in H_2O < (b) the hydrogen bonding forces in liquid CH_3OH
- 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 CO_2 is less than that of solid CO_2 .
(b) gas phase
(c) No.

11.29 $T(80 \text{ km}) < T(25 \text{ km}) < T(110 \text{ km}) < T(5 \text{ km})$

REVIEW QUESTIONS

11.29 $T(80 \text{ km}) < T(25 \text{ km}) < T(110 \text{ km}) < T(5 \text{ km})$

- 11.31 The temperature stops decreasing, and starts increasing, as we move from the troposphere into the stratosphere. Absorption of UV light by oxygen produces oxygen atoms which, in turn, produce ozone (together with other oxygen molecules). The ozone produces additional UV light. The energy absorbed increases the local temperature. The density of the atmosphere at the top of the stratosphere and bottom of mesosphere is sufficient to absorb enough UV light to increase the temperature. As we descend into the stratosphere and below, the intensity of incoming UV radiation is diminished due to absorption at higher altitudes. At 1 km above earth's surface in the troposphere there is too little UV radiation to cause significant absorption by oxygen to produce O atoms, and ozone etc.

- 11.33 (a) $c(\text{CO}_2)$ was lower at 30,000 years ago compared to 125,000 years ago, then was lower again at 260,000 years ago.
(b) Temperature was lower at 30,000 years ago compared to 125,000 years ago, then was lower again at 260,000 years ago.

11.35 $0.276 \text{ atm} = 30.0 \text{ kPa} = 0.300 \text{ bar}$

11.37 0.117 L

11.39 9.7 atm

- 11.41 Molar volume (at 448.15 K and 1.00 bar) of H_2 , CO_2 and SF_6 are 37.277, 37.218 and 37.157 L mol^{-1} , respectively. The three gases are more alike – in terms of molar volume – at 448.15 K than 298.15 K.

11.43 565 kPa

11.45 57.5 g mol^{-1}

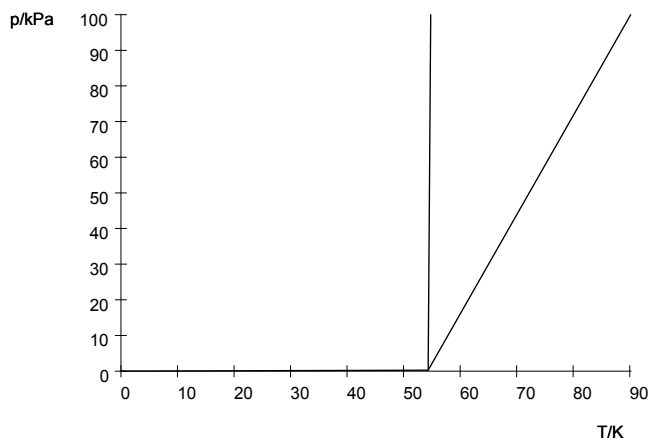
- 11.47 $1.22 \times 10^7 \text{ L}$. Though the pressure dropped by almost 20%, the decrease in temperature compensates and the change in volume is not very big. Nevertheless, there would have to be allowance for expansion of the balloon at higher altitudes.

11.49 33.97 g mol^{-1}

11.51 173 g

- 11.53 171 kPa
- 11.55 $P_{\text{Total}} = 580 \text{ kPa}$
 $P(\text{H}_2) = 412 \text{ kPa}$
 $P(\text{Ar}) = 168 \text{ kPa}$
- 11.61 $3.65041 \text{ cm s}^{-1}$
- 11.63 4.58 cm s^{-1}
1.194
- 11.67 36 g mol^{-1}
- 11.69 Using ideal gas law, $p = 4990 \text{ kPa}$. Using van der Waals equation, $p = 2991 \text{ kPa}$.
- 11.71 When solid I_2 dissolves in methanol, CH_3OH , dispersion forces holding I_2 molecules in their lattice positions must be overcome. Hydrogen bonding forces between methanol molecules are disrupted when methanol solvates iodine. The solvation forces between methanol and iodine are dipole induced dipole interactions.
- 11.75 (a) 18.7 kPa
(b) At about $75 \text{ }^\circ\text{C}$
(c) The equilibrium vapour pressure of ethanol is higher than that of water at $70 \text{ }^\circ\text{C}$.
- 11.77 About 80 kPa. 1.0 g of diethyl ether is more than enough to achieve this partial pressure. 0.24 g of diethyl ether evaporates, while 0.76 g remains in the liquid phase – the two phases are in equilibrium. If the flask is placed in an ice bath, the temperature lowers causing the vapour pressure to lower. The gas becomes supersaturated and liquid diethyl ether condenses out of the vapour.

11.81



This phase diagram is constructed by (1) connecting ($T = 0 \text{ K}$, $p = 0 \text{ kPa}$) to the triple point, ($T = 54.34 \text{ K}$, $p = 0.267 \text{ kPa}$), to get the solid-gas coexistence curve, (2) connecting the triple point to the normal melting point, ($T = 54.8 \text{ K}$, $p = 100 \text{ kPa}$), to get the solid-liquid coexistence curve, and (3) connecting the triple point to the normal boiling point, ($T = 90.18 \text{ K}$, $p = 100 \text{ kPa}$), to get the liquid-gas coexistence curve.

At $T = -196 \text{ }^\circ\text{C}$ (i.e. $T = 77 \text{ K}$), $p = 76.5 \text{ kPa}$

11.83 1.624 kJ

11.87 CH_3Cl can be liquefied at or above room temperature, up to 416 K (143 $^\circ\text{C}$) the critical temperature. Above the critical temperature, chloromethane cannot be liquified – it can only be compressed into a supercritical fluid. Below the triple point temperature, 175.4 K ($-97.8 \text{ }^\circ\text{C}$), chloromethane cannot be liquified – it solidifies upon compression. However, room temperature is between these limits on liquification.

11.89 Ice V only exists over the range of temperatures and pressures shown in the phase diagram. The lowest pressure at which Ice V is stable is about 3 Mbar – i.e. about 3 million atmospheres.

SUMMARY AND CONCEPTUAL QUESTIONS

11.91 306 K

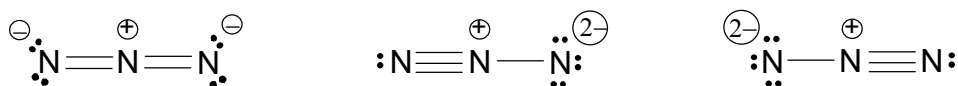
11.93 (a) A 1.0-L flask containing 10.0 g each of O_2 and CO_2 at 25 $^\circ\text{C}$ has greater partial pressure of O_2 than CO_2 . The partial pressures depend on the numbers of moles – 10.0 g of the lower molar mass O_2 has more moles than 10.0 g of CO_2 .

(b) The lighter O_2 molecules have greater average speed – average speed is proportional to $M^{-1/2}$.

- 11.95 (a) This is NOT a gas. An ideal gas would expand 100 fold if its pressure were changed from 100 bar to 1 bar (atmospheric pressure). Only a liquid or solid is so incompressible as to expand only 10% when relieved of such a large pressure.
 (b) This is NOT a gas. A density of $8.2 \text{ g mL}^{-1} = 8200 \text{ g L}^{-1}$ is way too high for such a gas.
 (c) There is insufficient information. Chlorine is a transparent and pale green gas. But, there are also many transparent and pale green liquids and solids.
 (d) A material that contains as many molecules in 1.0 m^3 as the same volume of air, at the same temperature and pressure, is definitely a gas (assuming the temperature and pressure are not unusual).

11.97 (a) 46.0 g

(b)



The structure on the left is the most reasonable.

(c) The azide ion is linear.

11.99 0.61 kPa corresponds to essentially zero pressure in the given phase diagram. To solidify carbon dioxide requires a temperature no greater than $-90 \text{ }^\circ\text{C}$.

11.101 (a) $\text{O}_2 < \text{B}_2\text{H}_6 < \text{H}_2\text{O}$ - i.e. in descending order according to molar mass
 (b) 102.3 kPa

11.103 64 g

11.105 (a) 28.7 g mol^{-1}
 (b) $x(\text{O}_2) = 0.17$; $x(\text{N}_2) = 0.83$

11.107 21.7 kPa

11.109 (a) 7.76 mg L^{-1}
 (b) 4.61 mg L^{-1}

The mass density of water vapour is higher at $20 \text{ }^\circ\text{C}$ with 45% humidity than $0 \text{ }^\circ\text{C}$ with 95% humidity.

11.111 $5.49 \times 10^{19} \text{ atoms/m}^3$

11.113 The molecules of cooking oil do not form hydrogen bonds with water, and do not have strong dipoles to form significant dipole-dipole interactions.

11.115

(a) 27 °C

(b) At 25 °C, there is net evaporation of liquid CCl₂F₂ until the dichlorodifluoromethane partial pressure inside the steel cylinder equals about 6.5 atm, the vapour pressure of CCl₂F₂ at 25 °C. Here we assume that the cylinder is not so big that 25 kg of CCl₂F₂ is not enough to fill the cylinder to this pressure – i.e. no bigger than about 780 L.

(c) The CCl₂F₂ vapour rushes out of the cylinder quickly at first because of the large pressure imbalance.

The flow slows as the inside pressure approaches 1 atm.

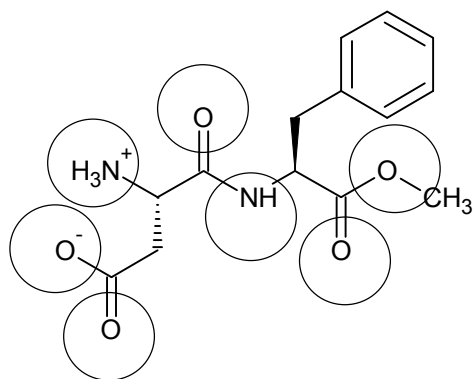
The outside of the cylinder becomes icy because when the gas expands, intermolecular forces are overcome – the energy required is drawn from the thermal energy of the gas and cylinder. Expansion of a gas can cause significant cooling. This expansion is driven by the increase in entropy, and the resulting cooling is inexorable.

- (d)
- (1) Turning the cylinder upside down, and opening the valve, would produce a dangerous situation. The cylinder would behave like a rocket. It would empty quickly though.
 - (2) Cooling the cylinder to –78 °C in dry ice, then opening the valve would allow the cylinder to be emptied safely. It would not happen quickly though – the vapour pressure of CCl₂F₂ at –78 °C (not shown in the figure) is quite small.
 - (3) Knocking the top off the cylinder, valve and all, with a sledge hammer would provide rapid and relatively safe discharge of the cylinder. The flow velocity would be smaller because of the large cross-sectional area of the open top of the cylinder.

11.117 90.1 kJ

11.119

(a)



(b) Aspartame is capable of hydrogen bonding. Sites of hydrogen bonding are circled on the structure.

Chapter 12

- 12.2 (a) The lattice enthalpy of LiCl(s) is larger than that of KCl(s) because the Li^+ ion is smaller than K^+ and so gets closer to Cl^- . The electrostatic potential energy is lower – it takes more energy to break the ionic bonds.
(b) The enthalpy of aquation of Li^+ and Cl^- is larger in magnitude than that of K^+ and Cl^- (they are both negative) because the Li^+ ion is smaller than K^+ . The interaction of water molecules with Li^+ is stronger than with 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 Li_2SO_4 in water decreases slightly as we increase the temperature from 10°C . The amount of solid Li_2SO_4 in the second beaker will increase a little.

The solubility of LiCl in water increases slightly as we increase the temperature from 10°C . The amount of solid LiCl in the first beaker will decrease.
- 12.7 mole fraction = 0.00210
molality = 0.117 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°C . The added ethylene glycol is not enough to prevent freezing at -25°C .
- 12.14 472 g mol^{-1}
- 12.16 -2.81°C
- 12.18 $1.40 \times 10^5 \text{ g mol}^{-1}$
- 12.19 754 kPa
- 12.20 (a) volume = $4.19 \times 10^6 \text{ nm}^3$
Surface area = $1.26 \times 10^5 \text{ nm}^2$
(b) 2.4×10^{14} spheres; surface area = 30 m^2

REVIEW QUESTIONS

- 12.21 (a) $6.20 \times 10^{-6} \text{ mol L}^{-1} \text{ kPa}^{-1}$.
Because O_2 is a gas, it is less soluble in water at higher temperatures – dissolution is an exothermic process.
- 12.23 For a saturated NaCl solution at 25°C with no solid in the beaker, the amount of dissolved NaCl in the solution is increased by
(c) Raising the temperature of the solution and adding some NaCl.
The solubility of NaCl in water increases with temperature - not a lot, but some.
(a) Adding more solid NaCl does not increase NaCl in solution because the solution is saturated.
(b) Raising the temperature of the solution does not increase NaCl in solution because there is no extra solid NaCl in the beaker to dissolve.
(d) Lowering the temperature of the solution and adding some NaCl decreases the amount of NaCl in solution because the solubility goes down.
- 12.25 mole fraction = 0.000780
molality = $0.0434 \text{ mol kg}^{-1}$
mass percent = 0.509%
- 12.27 2.65 g
- 12.29 5.65 mol kg^{-1}
- 12.31 (a) 16.2 mol kg^{-1}
(b) 37.1%
- 12.35 The $0.15 \text{ mol kg}^{-1} \text{ Na}_2\text{SO}_4$ solution has the higher equilibrium vapour pressure of water.
- 12.37 (a) 8.60 mol kg^{-1}
(b) 28.4%
- 12.41 In order of decreasing freezing point, we have
(a) 0.20 mol kg^{-1} ethylene glycol solution
(d) 0.12 mol kg^{-1} KBr solution $\rightarrow 0.24 \text{ mol kg}^{-1}$ ions
(c) 0.10 mol kg^{-1} MgCl_2 solution $\rightarrow 0.30 \text{ mol kg}^{-1}$ ions
(b) 0.12 mol kg^{-1} K_2SO_4 solution $\rightarrow 0.36 \text{ mol kg}^{-1}$ ions
i.e. in order of increasing concentration of aquated species
- 12.43 510 g
- 12.45 52.9 kPa

SUMMARY AND CONCEPTUAL QUESTIONS

There are no summary and conceptual answers necessary for this chapter.

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

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

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

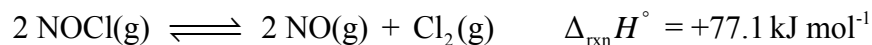
13.15 [butane] = 0.77 mol L^{-1}

[isobutane] = 1.93 mol L^{-1}

13.16 (a) When extra H_2 is added to an equilibrium mixture, the mixture is shifted out of equilibrium by the increase in H_2 concentration. There is net forward reaction until a new equilibrium is attained. Some, but not all, of the additional H_2 is consumed. The concentration of N_2 decreases, since it is a reactant, while the concentration of product NH_3 increases. When extra 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.

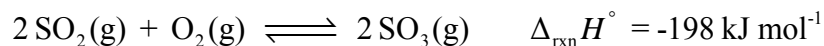
(b) When the volume of the system is increased, all concentrations are decreased by the same factor. Since there are a different number of moles of reactant and product gases, this will change the value of the reaction quotient, shifting it away from its equilibrium value. In this case, there are more 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_3 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.

REVIEW QUESTIONS

- 13.19 Because $Q (1.4 \times 10^{-4}) < K (4.0 \times 10^{-4})$, the reaction proceeds in the forward direction
- 13.21 $K = 1.2$
- 13.25 $K = 9.3 \times 10^{-5}$
- 13.29 (a) $K = 1.6$
(b) The new equilibrium concentrations of H_2O and CO are both 0.014 mol L^{-1}
- 13.31 0.0002 g
- 13.33 $[\text{NH}_3]_{\text{eqm}} = 0.66 \text{ mol L}^{-1}$
 $[\text{N}_2]_{\text{eqm}} = 0.57 \text{ mol L}^{-1}$
 $[\text{H}_2]_{\text{eqm}} = 1.71 \text{ mol L}^{-1}$
 $p = 17.7 \text{ MPa}$
- 13.35 4.44×10^{25}
- 13.37 (a) $K = 0.041$
(b) $K = 590$
- 13.39 (a) [butane] = 1.1 mol L^{-1}
[isobutane] = 2.9 mol L^{-1}
(b) same as in part (a)
- 13.41 (a) All three gases increase in concentration.
(b) All three gases increase in concentration.
(c) A net decrease in all gas concentrations.
(d) Product gases decrease in concentration, while reactant gases increase in concentration.
- 13.43 (a) (i) no net reaction
(b) (ii) net reaction to form more $\text{BaCO}_3(\text{s})$
(c) (i) no net reaction
(d) (iii) net reaction to form more $\text{BaO}(\text{s})$ and $\text{CO}_2(\text{g})$.
(e) (iii) net reaction to form more $\text{BaO}(\text{s})$ and $\text{CO}_2(\text{g})$.
- 13.45 $[\text{PCl}_5]_{\text{eqm}} = 0.0198 \text{ mol L}^{-1}$
 $[\text{PCl}_3]_{\text{eqm}} = 0.0232 \text{ mol L}^{-1}$
 $[\text{Cl}_2]_{\text{eqm}} = 0.0404 \text{ mol L}^{-1}$

SUMMARY AND CONCEPTUAL QUESTIONS

- 13.47 (a) 81%
(b) There will be net reaction in the reverse direction
- 13.49 (a) 0.60
(b) 0.50
(c) The fractions of $\text{SO}_2\text{Cl}_2(\text{g})$ dissociated in part (b) is less than that in part (a), in agreement with Le Chatelier's principle. There was net reaction in the reverse direction to counter the increase in chlorine gas concentration.

Chapter 14

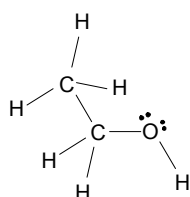
- 14.1 (a) $\text{HCOOH}(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{HCOO}^-(\text{aq}) + \text{H}_3\text{O}^+(\text{aq})$
acid base conj. base conj. Acid
- (b) $\text{NH}_3(\text{aq}) + \text{H}_2\text{S}(\text{aq}) \rightleftharpoons \text{NH}_4^+(\text{aq}) + \text{HS}^-(\text{aq})$
base acid conj. acid conj. Base
- (c) $\text{HSO}_4^-(\text{aq}) + \text{OH}^-(\text{aq}) \rightleftharpoons \text{SO}_4^{2-}(\text{aq}) + \text{H}_2\text{O}(\text{l})$
acid base conj. base conj. acid
- 14.3 $\text{HC}_2\text{O}_4^-(\text{aq})$ acting as a Brønsted-Lowry acid:
 $\text{HC}_2\text{O}_4^-(\text{aq}) + \text{OH}^-(\text{aq}) \rightleftharpoons \text{C}_2\text{O}_4^{2-}(\text{aq}) + \text{H}_2\text{O}(\text{l})$
- $\text{HC}_2\text{O}_4^-(\text{aq})$ acting as a Brønsted-Lowry base:
 $\text{HC}_2\text{O}_4^-(\text{aq}) + \text{H}_3\text{O}^+(\text{aq}) \rightleftharpoons \text{H}_2\text{C}_2\text{O}_4(\text{aq}) + \text{H}_2\text{O}(\text{l})$
- 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) $\text{pOH} = 2.9$; $\text{pH} = 11.1$
(b) $[\text{H}_3\text{O}^+] = 4.79 \times 10^{-5} \text{ mol L}^{-1}$; $[\text{OH}^-] = 2.09 \times 10^{-10} \text{ mol L}^{-1}$
(c) $\text{pOH} = 3.54$; $[\text{OH}^-] = 2.88 \times 10^{-4} \text{ mol L}^{-1}$
- 14.9 (a) $\text{pK}_a = 4.2$
(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)



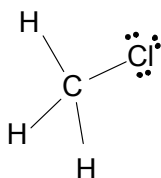
Lewis Base

(c)



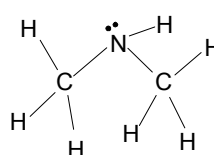
Lewis Base

(e)



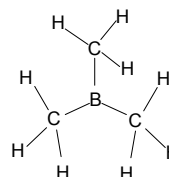
Lewis base, through Cl atoms

(b)



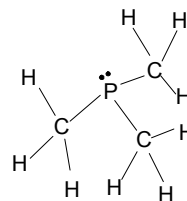
Lewis Base

(d)



Lewis Acid

(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.

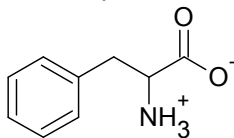
- 14.27 (a) 0.30 mol L^{-1} aqueous solution of formic acid
 $\text{pH} = 2.14$; % ionisation = 2.4 %
- 0.10 mol L^{-1} aqueous solution of formic acid
 $\text{pH} = 3.27$; % ionisation = 0.18 %
- (b) 0.18%
- 14.28 $[\text{HOCl}] = [\text{OH}^-] = 6.6 \times 10^{-6} \text{ mol L}^{-1}$
 $\text{pH} = 8.82$
- 14.30 $[\text{oxalate}^-] = [\text{H}_3\text{O}^+] = 0.053 \text{ mol L}^{-1}$
 $\text{pH} = 1.28$
- 14.31 (a) According to increasing acidity (i.e. decreasing pH) we have
 $\text{C} < \text{A} < \text{B}$
- (b) according to amount of NaOH that can be consumed, we have
 $\text{B} (0.001 \text{ mol L}^{-1}) < \text{A} (0.005 \text{ mol L}^{-1}) < \text{C} (0.006 \text{ mol L}^{-1})$
- 14.34 (a) 2.88×10^3
 (b) 2.88
 (c) 2.88×10^{-3}
- 14.35 (a) At pH 6.0
 (i) 1.33×10^{-4}
 (ii) 16
 (iii) 2.78×10^6
 At pH = 6.0, the dominant species is H_2PO_4^-
- (b) At pH = 9.0
 (i) 1.33×10^{-7}
 (ii) 1.6×10^{-2}
 (iii) 2.78×10^3
 At pH = 9.0, the dominant species is 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.



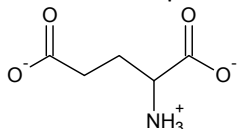
(b) glutamic acid

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

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

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

The dominant species at pH = 7.40 is HGlu⁻



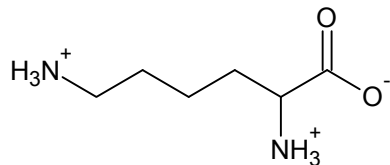
(c) lysine

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

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

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

The dominant species at pH = 7.40 is H₂Lys⁺



- 14.40 pH = 4.13
- 14.42 (b) NH_3 and NH_4Cl 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 mol L^{-1}
mass of acetic acid in vinegar sample = 1.62 g
- 14.49 0.119 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 $1.049 \times 10^{-7} \text{ mol L}^{-1}$

REVIEW QUESTIONS

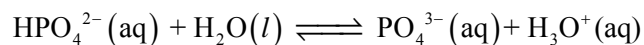
- 14.55 pH = 2.12
 $[\text{OH}^-] = 1.3 \times 10^{-12} \text{ mol L}^{-1}$
- 14.56 $K_b = 6.31 \times 10^{-5}$
- 14.57 $[\text{H}_3\text{O}^+] = 10^{-\text{pH}} = 10^{-3.75} = 1.78 \times 10^{-4} \text{ mol L}^{-1}$
The solution is acidic (pH < 7).

14.59

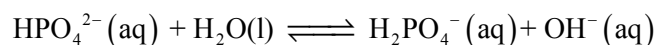
$$\begin{aligned}
 K_b \left((\text{CH}_3)_3 \text{N}(\text{aq}) \right) &= \frac{[(\text{CH}_3)_3 \text{NH}^+][\text{OH}^-]}{[(\text{CH}_3)_3 \text{N}]} = \left(\frac{[(\text{CH}_3)_3 \text{N}][\text{H}_3\text{O}^+]}{[(\text{CH}_3)_3 \text{NH}^+][\text{H}_3\text{O}^+][\text{OH}^-]} \right)^{-1} \\
 &= \left(K_a \left((\text{CH}_3)_3 \text{NH}^+ \right) \frac{1}{K_w} \right)^{-1} = \frac{K_w}{K_a \left((\text{CH}_3)_3 \text{NH}^+ \right)} \\
 &= \frac{10^{-14}}{10^{-pK_a}} = \frac{10^{-14}}{10^{-9.80}} = 10^{-4.20} = 6.31 \times 10^{-5}
 \end{aligned}$$

14.61

$\text{HPO}_4^{2-}(\text{aq})$ ions acting as an acid:



$\text{HPO}_4^{2-}(\text{aq})$ ions acting as a base:



14.63 (b) $\text{ClC}_6\text{H}_4\text{COOH}$ ($pK_a = 2.88$) is the stronger acid, stronger than benzoic acid ($pK_a = 4.20$). The acid with the lowest pK_a value is the strongest.

14.65 (a) $\text{HCOOH}(\text{aq})$ (formic acid) is the strongest acid.

$\text{C}_6\text{H}_5\text{OH}(\text{aq})$ (phenol) is the weakest acid.

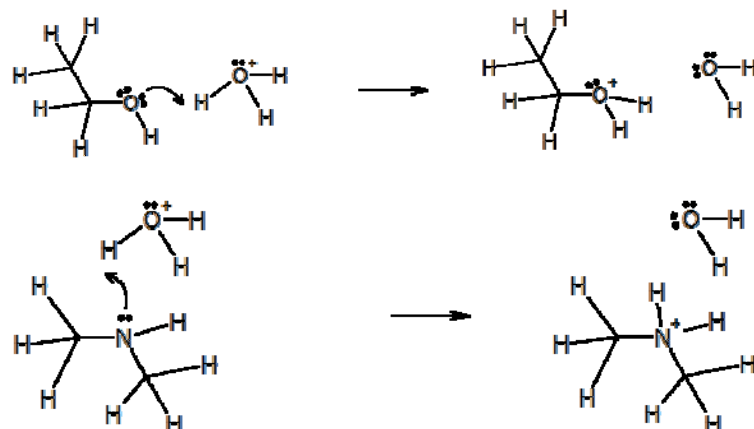
(b) $\text{HCOOH}(\text{aq})$ (formic acid) has the weakest conjugate base.

(c) $\text{C}_6\text{H}_5\text{OH}(\text{aq})$ (phenol) has the strongest conjugate base.

14.69 The 0.10 mol L^{-1} solution of (a) $\text{Na}_2\text{S}(\text{s})$ has the highest pH.
The 0.10 mol L^{-1} solution of (f) $\text{AlCl}_3(\text{s})$ has the lowest pH.

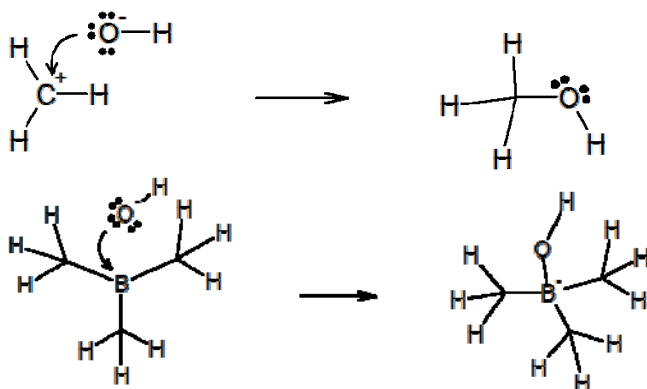
14.71

(a)



trimethyl phosphine, $(\text{CH}_3)_3\text{P}$, plus H_3O^+ is similar to dimethyl amine, $(\text{CH}_3)_2\text{NH}$, plus H_3O^+

(b)



Br^- does not behave as a Lewis acid

14.73 $[\text{H}_3\text{O}^+] = 1.58 \times 10^{-4} \text{ mol L}^{-1}$

(b) $K_a = 1.1 \times 10^{-5}$ (moderately weak acid)

14.75 (a) decreases pH

(b) increases pH

(c) No effect on the pH

14.77 $[\text{NH}_4^+] = [\text{OH}^-] = 1.6 \times 10^{-3} \text{ mol L}^{-1}$

$[\text{NH}_3] = 0.015 \text{ mol L}^{-1}$

$[\text{H}_3\text{O}^+] = 6.25 \times 10^{-12} \text{ mol L}^{-1}$

pH = 11.20

% NH_3 ionized = 1.1 %

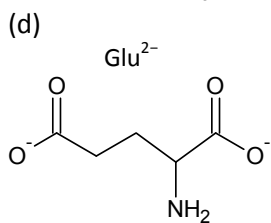
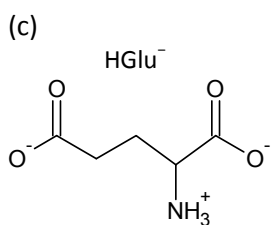
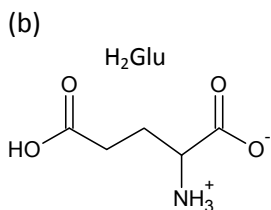
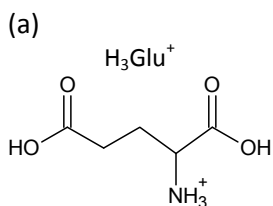
11.79 (i) 0.054 %

(ii) 0.17 %

(iii) 5.4 %

- 14.81 (a) $[\text{OH}^-] = 9.2 \times 10^{-5} \text{ mol L}^{-1}$
 $[\text{N}_2\text{H}_5^+] = 9.2 \times 10^{-5} \text{ mol L}^{-1}$
 $[\text{N}_2\text{H}_6^{2+}] = 9.0 \times 10^{-16} \text{ mol L}^{-1}$
- (b) $\text{pH} = 9.96$
- 14.83 At $\text{pH} = 3.00$, $[\text{CH}_3\text{NH}_2]/[\text{CH}_3\text{NH}_3^+] = 0.42$
 At $\text{pH} = 7.00$, $[\text{CH}_3\text{NH}_2]/[\text{CH}_3\text{NH}_3^+] = 4200$
 At $\text{pH} = 11.00$, $[\text{CH}_3\text{NH}_2]/[\text{CH}_3\text{NH}_3^+] = 4.2 \times 10^7$
 When $\text{pH} = \text{pK}_a = 3.38$, $[\text{CH}_3\text{NH}_2] = [\text{CH}_3\text{NH}_3^+]$
- 14.85 (a) At
 (i) $\text{pH} = 6$, $\text{H}_2\text{A}(\text{aq})$ has the highest concentration
 (ii) $\text{pH} = 8$, $\text{HA}^-(\text{aq})$ has the highest concentration
 (iii) $\text{pH} = 10$, $\text{HA}^-(\text{aq})$ still has the highest concentration – but not by as wide a margin
- (b) pK_{a1} and pK_{a2} can be seen in the plot.
 $[\text{H}_2\text{A}(\text{aq})] = [\text{HA}^-(\text{aq})]$ when $\text{pH} = \text{pK}_{a1}$
 So, $\text{pK}_{a1} = \text{about } 6.4$
 $[\text{HA}^-(\text{aq})] = [\text{A}^{2-}(\text{aq})]$ when $\text{pH} = \text{pK}_{a2}$
 So, $\text{pK}_{a2} = \text{about } 10.3$
- (c) Since $\text{pK}_{a1} = 6.38$ and $\text{pK}_{a2} = 10.32$ for carbonic acid, the acid is very likely carbonic acid.

14.87



14.89 3.89

14.91 (a) 3.59
(b) 2.24

14.93 The buffer solution is prepared by adding 0.479 mol of Na_2CO_3 for every 1.000 mol of NaHCO_3 added to water to give a not-too-dilute concentration (so we have a buffer with some capacity).

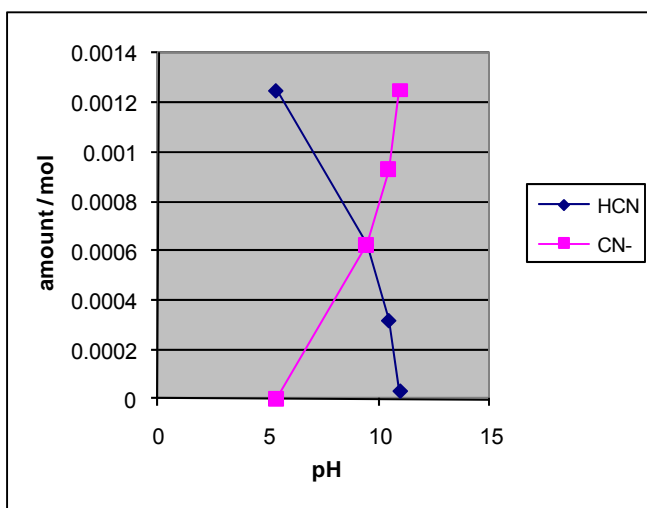
14.95 (a) 4.95
(b) 5.05

14.99 0.167 mol L^{-1}

14.101 (a) 7.46
(b) 7.28

14.103 (a) 0.180 mol L^{-1}
(b) $[\text{H}_3\text{O}^+] = 2.1 \times 10^{-3} \text{ mol L}^{-1}$
 $[\text{C}_6\text{H}_5\text{NH}_3^{\oplus}] = 0.178 \text{ mol L}^{-1}$
 $[\text{OH}^-] = 6.76 \times 10^{-12} \text{ mol L}^{-1}$
(c) 2.68

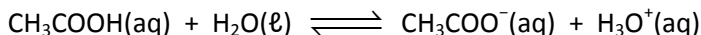
- 14.105 (a) 5.35
 (b) 9.40
 (c) 10.12
 (d) 16.7 mL
 (e) 10.93
 (f) We need an indicator with pK_a near the equivalence point pH – i.e. $pK_a \approx 10.93$. Indicators which change colour in the neighborhood of pH = 11 include alizarine yellow R.



SUMMARY AND CONCEPTUAL QUESTIONS

- 14.107 (a) 10 H_3O^+ ions.
 (b) 1 H_3O^+ ion
 (c) If the pH were 4, then there would likely not be any hydronium ions in the cube. To visualize pH = 4, you would have to imagine the cube as a snapshot taken from a larger quantity of water. If many such snapshots were considered, then about 1 in 10 of them would have a single hydronium ion.
 (d) If the H_3O^+ ion to water molecule ratio is 100:55000 = 1:550 when pH = 1.0, then this ratio is 1:55000000 when pH = 6.0 (i.e. a hydronium concentration 10^5 times smaller).
- 14.109 A buffer solution contains a not-too-dilute solution of both a weak acid and a weak base. When a strong base is added, the weak acid reacts with it and consumes most of it. In the case of a carbonate/hydrogencarbonate buffer, the hydrogencarbonate reacts with the added base.
 $HCO_3^-(aq) + OH^-(aq) \rightarrow CO_3^{2-}(aq) + H_2O(l)$

14.111 (a) The fraction of acetic acid declines and that of acetate ion increases as the pH increases, in accord with the buffer equation (see the 14.107 above). We can understand this using Le Chatelier's principle.



Increasing pH means decreasing H_3O^+ which, according to Le Chatelier's principle, causes a shift in the equilibrium to the right – i.e. depleted acetic acid and increased acetate.

(b) From the buffer equation,

$$[\text{H}_3\text{O}^+] = \frac{[\text{CH}_3\text{COOH}]}{[\text{CH}_3\text{COO}^-]} \times 1.8 \times 10^{-5} = 10^{-4}$$

at pH = 4. Here, we see that $[\text{CH}_3\text{COOH}] / [\text{CH}_3\text{COO}^-]$ must be greater than 1 – i.e. acetic acid predominates.

At pH = 6, the right side of the above equation is 10^{-6} and $[\text{CH}_3\text{COOH}] / [\text{CH}_3\text{COO}^-]$ must be less than 1 – i.e. acetate predominates.

(c) From the buffer equation, we see that $[\text{H}_3\text{O}^+] = K_a = 1.8 \times 10^{-5}$, when the acetic acid and acetate concentrations are equal – i.e. $\text{pH} = -\log_{10}(1.8 \times 10^{-5}) = 4.74$.

14.113 (a) 0.00135

(b) 12.0 %

(c) pH at halfway = 2.86

pH at equivalence point = 7.32

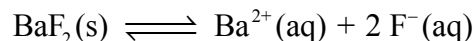
Chapter 15

15.1 (a)



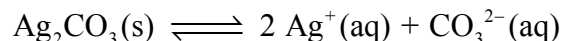
$$Q = [\text{Ag}^+][\text{I}^-] = K_{\text{sp}} = 1.5 \times 10^{-16} \text{ at equilibrium}$$

(b)



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

(c)



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

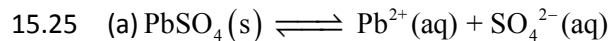
15.4 $K_{\text{sp}} = 1.9 \times 10^{-7}$

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

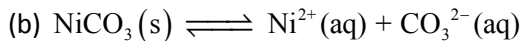
(b) $9.6 \times 10^{-1} \text{ g L}^{-1}$

- 15.8 (a) AgCl
(b) Ca(OH)₂
(c) Ca(OH)₂
- 15.10 The solubility of Ag₃PO₄ is larger than that predicted using K_{sp} of the salt because the phosphate ion, PO₄⁻³, reacts with water to form HPO₄⁻² (H₂PO₄⁻ and H₃PO₄ upon further reaction with water). The concentration of PO₄⁻³ is consequently significantly reduced, and the reaction quotient for dissolution of Ag₃PO₄ remains less than the solubility product for larger initial concentrations of Ag₃PO₄ than predicted using K_{sp}.
- 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) Ag₂CO₃(s)
(c) Al(OH)₃(s)
- 15.16 $Q = 5.3 \times 10^{-9} < K_{sp} = 9.8 \times 10^{-9}$
The solution is not saturated. More PbI₂ can dissolve.
- 15.19 $Q = 6.3 \times 10^{-8} < K_{sp} = 3.4 \times 10^{-7}$
The mixture is not saturated. SrSO₄(s) will not precipitate.
- 15.20 $[I^-] = 4.4 \times 10^{-9} \text{ mol L}^{-1}$
 $[Pb^{2+}] = 4.4 \times 10^{-3} \text{ mol L}^{-1}$
- 15.22 $[OH^-] = 5.3 \times 10^{-6} \text{ mol L}^{-1}$
- 15.24 $K_{net} = 1.1 \times 10^{-6}$
- 15.25 At pH = 1, the cyanide appears only as hydrogen cyanide, HCN(aq). Silver appears only as Ag⁺(aq). As pH increases past pK_a = -log₁₀(3.5 × 10⁻⁴) = 3.5, the cyanide ion, CN⁻, concentration increases. Depending on the relative amounts of cyanide and silver, some or all of the cyanide complexes silver – the Ag⁺(aq) concentration decreases and the [Ag(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.

REVIEW QUESTIONS

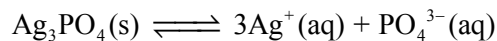


$$Q = [\text{Pb}^{2+}][\text{SO}_4^{2-}] = K_{\text{sp}} = 1.8 \times 10^{-8} \text{ at equilibrium.}$$

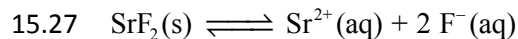


$$Q = [\text{Ni}^{2+}][\text{CO}_3^{2-}] = K_{\text{sp}} = 1.4 \times 10^{-7} \text{ at equilibrium.}$$

(c)

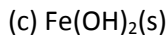
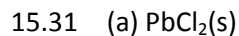


$$Q = [\text{Ag}^+]^3[\text{PO}_4^{3-}] = K_{\text{sp}} = 1.3 \times 10^{-20} \text{ at equilibrium.}$$



$$K_{\text{sp}} = 4.0 \times 10^{-9}$$

15.29 51 mg of PbSO_4 remains undissolved



15.33 $Q = 1.1 \times 10^{-6} > K_{\text{sp}} = 1.8 \times 10^{-8}$

AgCl will precipitate out of solution

15.35 (a) $Q = 2.4 \times 10^{-9} < K_{\text{sp}} = 6.6 \times 10^{-9}$

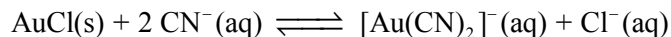
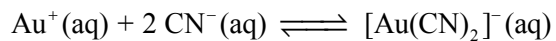
NiCO_3 will not precipitate

(b) $Q = 2.4 \times 10^{-7} > K_{\text{sp}} = 6.6 \times 10^{-9}$

NiCO_3 will precipitate

15.37 $\text{Fe}(\text{OH})_3(\text{s})$ precipitates first, followed by $\text{Al}(\text{OH})_3(\text{s})$. $\text{Pb}(\text{OH})_2(\text{s})$ is last to precipitate

15.39



$$K_{\text{net}} = 4.0 \times 10^{25}$$

SUMMARY AND CONCEPTUAL QUESTIONS

15.41 5.51×10^{-5}

15.43 $1.4 \times 10^{-4} \text{ mol L}^{-1}$

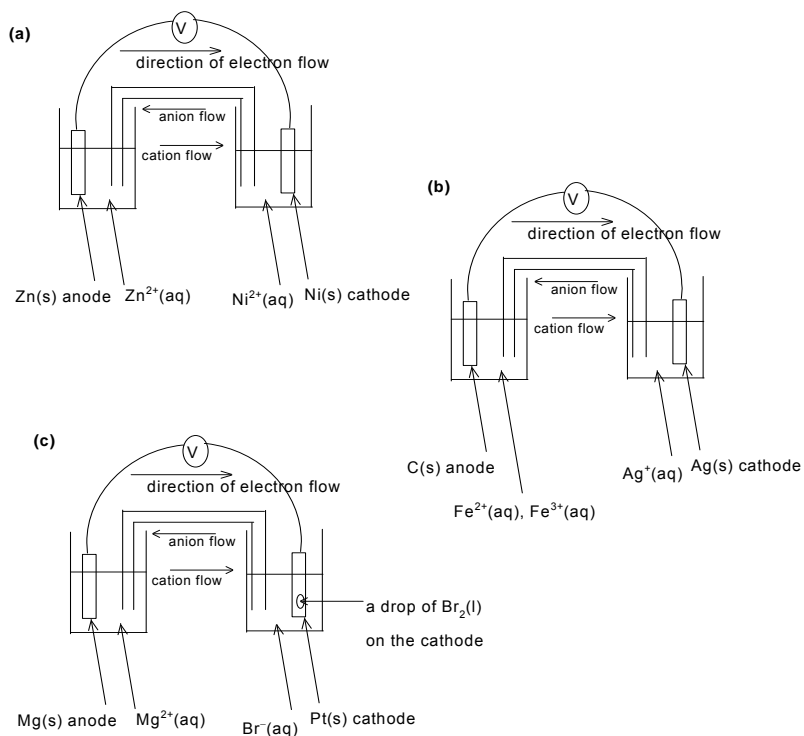
Chapter 16

- 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 AgNO_3 provides the cathode. A nickel electrode immersed in an 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 $\text{Ag}(\text{s})$. NO_3^- in the salt bridge flows towards the anode compartment and Na^+ in the salt bridge flows toward the cathode compartment.

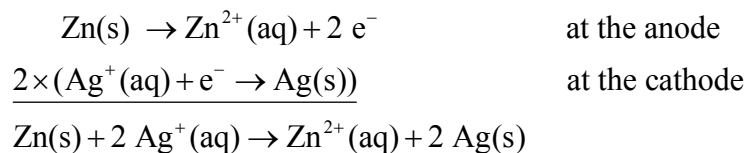
16.7



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

- 16.27 $2 \text{H}_2\text{O}(\text{l}) + 2 \text{e}^- \longrightarrow \text{H}_2(\text{g}) + 2 \text{OH}^-(\text{aq})$ (Cathode reaction)
 $4 \text{OH}^-(\text{aq}) \longrightarrow \text{O}_2(\text{g}) + 2 \text{H}_2\text{O}(\text{l}) + 4 \text{e}^-$ (Anode reaction)
 $E^\circ_{\text{cell}} = -1.23 \text{ V}$

- 16.28 The brass fittings provide cathodes where oxygen is reduced to water. The steel provides the anode where iron is oxidized to 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 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.

REVIEW QUESTIONS

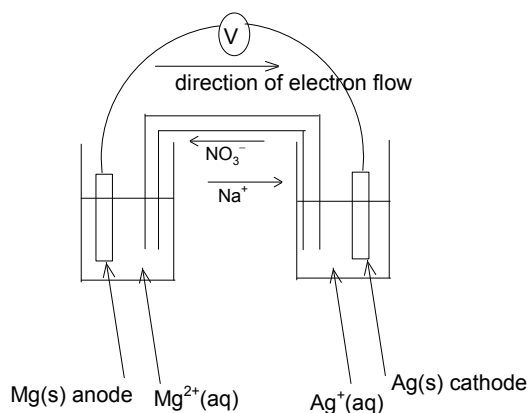
- 16.31 (a) $OS(\text{f}) = -1$ $OS(\text{P}) = +5$
 (b) $OS(\text{h}) = +1$ & $OS(\text{O}) = -2$ $OS(\text{As}) = +5$
 (c) $OS(\text{O}) = -2$ $OS(\text{U}) = +4$
 (d) $OS(\text{O}) = -2$ $OS(\text{N}) = +5$
 (e) $OS(\text{Cl}) = -1$ & $OS(\text{O}) = -2$ $OS(\text{P}) = +5$
 (f) $OS(\text{O}) = -2$ $OS(\text{Xe}) = +6$
- 16.33 (a) is not an oxidation-reduction reaction
 (b) is an oxidation-reduction reaction
 (c) is not an oxidation-reduction reaction
 (d) is an oxidation-reduction reaction

- 16.35 (a) $\text{Sn(s)} + 2\text{H}^+(\text{aq}) \longrightarrow \text{Sn}^{2+}(\text{aq}) + \text{H}_2(\text{g})$
 (b) $\text{Cr}_2\text{O}_7^{2-}(\text{aq}) + 6\text{Fe}^{2+}(\text{aq}) + 14\text{H}^+(\text{aq}) \longrightarrow 2\text{Cr}^{3+}(\text{aq}) + 6\text{Fe}^{3+}(\text{aq}) + 7\text{H}_2\text{O(l)}$
 (c) $\text{MnO}_2(\text{s}) + 2\text{Cl}^-(\text{aq}) + 4\text{H}^+(\text{aq}) \longrightarrow \text{Mn}^{2+}(\text{aq}) + \text{Cl}_2(\text{g}) + 2\text{H}_2\text{O(l)}$
 (d) $\text{HCHO(aq)} + 2\text{Ag}^+(\text{aq}) + \text{H}_2\text{O(l)} \longrightarrow \text{HCOOH(aq)} + 2\text{Ag(s)} + 2\text{H}^+(\text{aq})$

16.37 Electrons in the external circuit flow from the chromium electrode (the anode) to the iron electrode (the cathode). Negative ions move in the salt bridge from the Fe^{2+}/Fe half-cell (the reduction half-cell) to the Cr/Cr^{3+} half-cell (the oxidation half-cell). The half-reaction at the anode is $\text{Cr(s)} \rightarrow \text{Cr}^{3+}(\text{aq}) + 3\text{e}^-$ and that at the cathode is $\text{Fe}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Fe(s)}$.

16.39

(a) + (c)



- (b) $\text{Mg(s)} \longrightarrow \text{Mg}^{2+}(\text{aq}) + 2\text{e}^-$ (oxidation half-reaction that occurs at the anode).
 $\text{Ag}^+(\text{aq}) + \text{e}^- \longrightarrow \text{Ag(s)}$ (reduction half-reaction that occurs at the cathode)
 $\text{Mg(s)} + 2\text{Ag}^+(\text{aq}) \rightarrow \text{Mg}^{2+}(\text{aq}) + 2\text{Ag(s)}$ (net reaction in the cell)

- 16.41 (a) + 0.78 V
 (b) = -0.32 V

16.43 (a) when

$$Q = \frac{p(\text{NO})}{[\text{NO}_3^-][\text{H}^+]^4} = 1.00$$

(b) $E^\circ[\text{NO}_3^-(\text{aq})|\text{NO}(\text{g})] = 0.96\text{ V}$

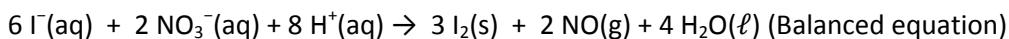
- 16.45 (a) To make a cell with potential close to 1.1 V, using the $\text{Zn}^{2+}(\text{aq})|\text{Zn(s)}$ half-cell, we could use the $\text{Cu}^{2+}(\text{aq})|\text{Cu(s)}$ half-cell as the cathode and the $\text{Zn}^{2+}(\text{aq})|\text{Zn(s)}$ half-cell as the anode.
 $E^\circ_{\text{cell}} = E^\circ[\text{Cu}^{2+}(\text{aq})|\text{Cu(s)}] - E^\circ[\text{Zn}^{2+}(\text{aq})|\text{Zn(s)}] = 0.337\text{ V} - (-0.763\text{ V}) = 1.10\text{ V}$
- (b) To make a cell with potential close to 0.5 V, using the $\text{Zn}^{2+}(\text{aq})|\text{Zn(s)}$ half-cell, we could use the $\text{Ni}^{2+}(\text{aq})|\text{Ni(s)}$ half-cell as the cathode and the $\text{Zn}^{2+}(\text{aq})|\text{Zn(s)}$ half-cell as the anode.
 $E^\circ_{\text{cell}} = E^\circ[\text{Ni}^{2+}(\text{aq})|\text{Ni(s)}] - E^\circ[\text{Zn}^{2+}(\text{aq})|\text{Zn(s)}] = -0.25\text{ V} - (-0.763\text{ V}) = 0.51\text{ V}$

- 16.47 (a) Se(s)
 (b) F⁻(aq)
 (c) F₂(g), Cl₂(g)
 (d) F₂(g), Cl₂(g), Br₂(ℓ), I₂(s), O₂(g)
 (e) Yes
 (f) No
 (g) No
 (h) Yes

- 16.49 (a) is NOT the direction of spontaneous reaction
 (b) is the direction of spontaneous reaction
 (c) is NOT the direction of spontaneous reaction
 (d) is the direction of spontaneous reaction

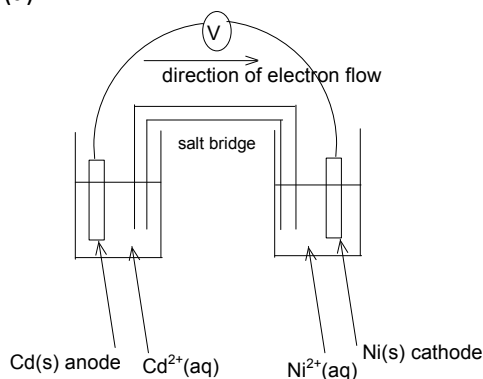
- 16.53 (a) is the direction of spontaneous reaction
 (b) is NOT the direction of spontaneous reaction
 (c) is NOT the direction of spontaneous reaction
 (d) is the direction of spontaneous reaction

16.55 Adding a KI solution to a standard acidic solution of Cu(NO₃)₂ causes a brown colour and a precipitate to form because the nitrate ion oxidizes iodide under these conditions. The I₂ that is formed first reacts with iodide to form the brown I₃⁻(aq) ion. As iodide gets consumed the excess insoluble iodine precipitates. A similar response is not observed when KCl or KBr solutions are added because nitrate cannot oxidize chloride or bromide under standard conditions – there is no reaction.

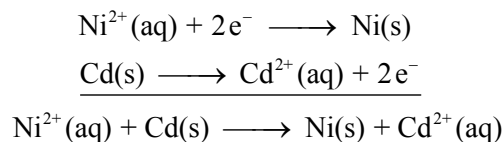


16.57 $E_{\text{cell}} = + 1.585 \text{ V}$

- 16.59 (a)



- (b)



(c) The Ni(s) electrode is the cathode – it is labeled +. The cadmium anode is labeled –.

(d) $E^\circ_{\text{cell}} = +0.15 \text{ V}$

(e) from anode to cathode

(f) The $\text{Na}^+(\text{aq})$ ions in the salt bridge move from the anode compartment to the cathode compartment. The $\text{NO}_3^-(\text{aq})$ ions move from the cathode compartment to the anode compartment.

(g) $K = 1.2 \times 10^5$

(h) $E_{\text{cell}} = +0.21 \text{ V}$

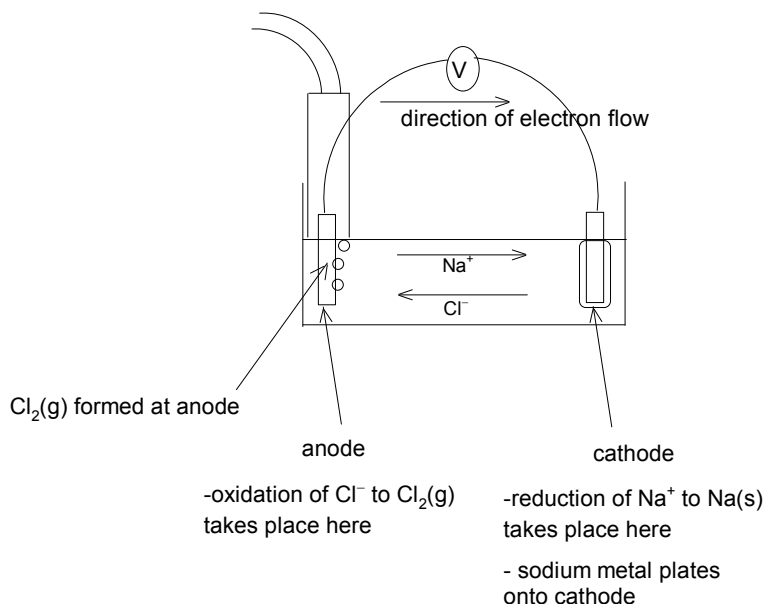
Since E_{cell} is still positive, the net reaction is in the same direction given in part (b).

16.61 (a) $E^\circ_{\text{cell}} = +0.236 \text{ V}$, $K = 9.5 \times 10^7$

(b) $E^\circ_{\text{cell}} = -0.531 \text{ V}$, $K = 1.1 \times 10^{-18}$

16.65 $K_f = 2.3 \times 10^{25}$

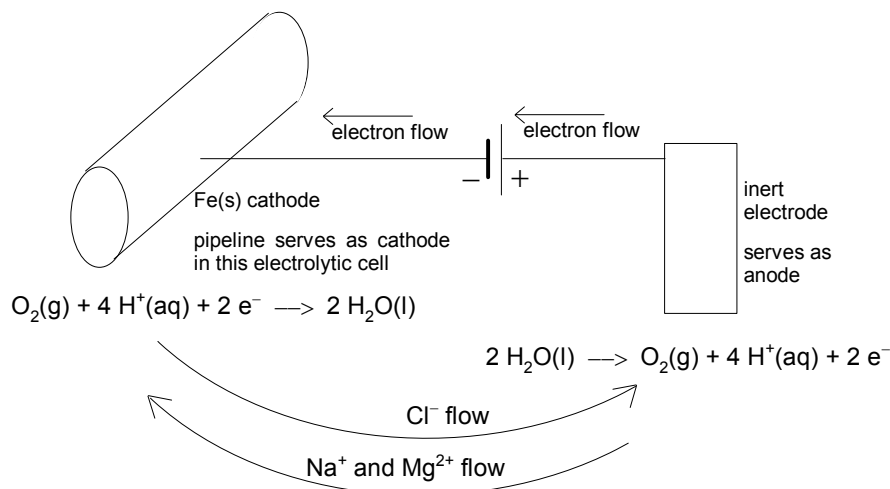
16.67



16.69 Fluorine has the largest reduction potential of all species. Oxygen gas will form at the anode in the electrolysis of an aqueous KF solution.

16.71 The bumper on an off-road vehicle is likely to get scratched. The chrome plated steel will corrode at the scratch faster than it would without the plating. This is because chromium is a (slightly) more noble metal than iron. The galvanized steel stays protected, even with scratches, until all of the zinc plating is oxidized by corrosion. Note that corrosion of zinc is slower than that for iron because zinc oxide coats the zinc protecting it from atmospheric oxygen. When iron oxidizes, its oxide does not coat the metal. This is the trouble with iron – it is vulnerable to corrosion.

16.73



By keeping the pipeline at a higher potential than the inert electrode, the pipeline behaves like a metal even more noble - it does not corrode.

SUMMARY AND CONCEPTUAL QUESTIONS

- 16.75 (a) In this case, the iron screws in contact with the more noble copper alloy corrode rapidly. They crumble, leaving holes in the copper alloy sheets where water leaks in.
 (b) In this case, the iron wrench is the more noble metal. It accelerates the corrosion of the aluminum in contact with it by polarizing the aluminum, making it slightly positive. The aluminum corrodes rapidly leaving a wrench-shaped hole in the hull.
- 16.77 If the emf is applied in the wrong direction, the corrosion of the pipeline will be accelerated. The potential of the pipeline is lowered – it is charged positively – and the oxidation (of Fe(s)) half reaction is made more favourable.

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 O₃(g)
 (b) 1 mol of SnCl₄(g)
 (c) 3 mol of O₂(g)
- 17.8 (a) +160.59 JK⁻¹
 (b) -198.76 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) $3 \text{ C}(\text{s}) + 3 \text{ H}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow \text{CH}_3\text{CH}_2\text{COOH}(\ell)$
 (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 kJ
- 17.27 +147 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) 1.43×10^{-25}
(c) 6.67×10^{-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 kJ

REVIEW QUESTIONS

17.33 $22.0 \text{ J K}^{-1} \text{ mol}^{-1}$

- 17.35 (a) NaCl(g)
(b) $\text{H}_2\text{S(g)}$
(c) $\text{C}_2\text{H}_4\text{(g)}$
(d) $\text{H}_2\text{SO}_4\text{(l)}$

17.37

$$\begin{aligned}\Delta_r S^\circ &= 1 \times S^\circ(\text{C}_2\text{H}_6, \text{g}) - [2 \times S^\circ(\text{C, graphite}) + 3 \times S^\circ(\text{H}_2, \text{g})] \\ &= 229.60 \text{ J K}^{-1} \text{ mol}^{-1} - [2 \times 5.740 \text{ J K}^{-1} \text{ mol}^{-1} + 3 \times 130.684 \text{ J K}^{-1} \text{ mol}^{-1}] \\ &= -173.93 \text{ J K}^{-1} \text{ mol}^{-1}\end{aligned}$$

17.41 1. $\text{C(s)} = \text{C(graphite)}$

$$\begin{aligned}\Delta_r S_1^\circ &= S^\circ[\text{CH}_4\text{(g)}] - (S^\circ[\text{C(s)}] + 2 S^\circ[\text{H}_2\text{(g)}]) \\ &= 186.3 \text{ J K}^{-1} \text{ mol}^{-1} - (5.74 \text{ J K}^{-1} \text{ mol}^{-1} + 2 \times 130.7 \text{ J K}^{-1} \text{ mol}^{-1}) = -80.8 \text{ J K}^{-1} \text{ mol}^{-1}\end{aligned}$$

$$\begin{aligned}2. \Delta_r S_2^\circ &= S^\circ[\text{CH}_3\text{OH(l)}] - (S^\circ[\text{CH}_4\text{(g)}] + \frac{1}{2} S^\circ[\text{O}_2\text{(g)}]) \\ &= 126.8 \text{ J K}^{-1} \text{ mol}^{-1} - (186.3 \text{ J K}^{-1} \text{ mol}^{-1} + \frac{1}{2} \times 205.1 \text{ J K}^{-1} \text{ mol}^{-1}) = -162.1 \text{ J K}^{-1} \text{ mol}^{-1}\end{aligned}$$

$$\begin{aligned}3. \Delta_r S_3^\circ &= S^\circ[\text{CH}_3\text{OH(l)}] - (S^\circ[\text{C(s)}] + 2 S^\circ[\text{H}_2\text{(g)}] + \frac{1}{2} S^\circ[\text{O}_2\text{(g)}]) \\ &= 126.8 \text{ J K}^{-1} \text{ mol}^{-1} - (5.74 \text{ J K}^{-1} \text{ mol}^{-1} + 2 \times 130.7 \text{ J K}^{-1} \text{ mol}^{-1} + \frac{1}{2} \times 205.1 \text{ J K}^{-1} \text{ mol}^{-1}) \\ &= -242.9 \text{ J K}^{-1} \text{ mol}^{-1}\end{aligned}$$

Just as reactions 1 & 2 add to give reaction 3, the $\Delta_r S^\circ$ values add in the same fashion.

$$\Delta_r S_1^\circ + \Delta_r S_2^\circ = -80.8 \text{ J K}^{-1} \text{ mol}^{-1} - 162.1 \text{ J K}^{-1} \text{ mol}^{-1} = -242.9 \text{ J K}^{-1} \text{ mol}^{-1} = \Delta_r S_3^\circ$$

This is an example of Hess's Law applied to entropy, which can only be the case if S is a state function.

17.43

$$\begin{aligned}\Delta S^{\circ}_{\text{univ}} &= \Delta S^{\circ}_{\text{sys}} + \Delta S^{\circ}_{\text{surr}} = 20.0 \text{ JK}^{-1} \text{ mol}^{-1} + 619.5 \text{ JK}^{-1} \text{ mol}^{-1} \\ &= +639.5 \text{ JK}^{-1} \text{ mol}^{-1}\end{aligned}$$

This reaction is spontaneous in the forward direction, under the reaction mixture conditions specified.

17.45 $\text{H}_2\text{O}(\text{l}) \longrightarrow \text{H}_2(\text{g}) + \frac{1}{2} \text{O}_2(\text{g})$

$$\begin{aligned}\Delta S^{\circ}_{\text{sys}} &= (S^{\circ}[\text{H}_2(\text{g})] + \frac{1}{2} S^{\circ}[\text{O}_2(\text{g})]) - S^{\circ}[\text{H}_2\text{O}(\text{l})] \\ &= (130.7 \text{ J K}^{-1} \text{ mol}^{-1} + \frac{1}{2} \times 205.1 \text{ J K}^{-1} \text{ mol}^{-1}) - 69.91 \text{ J K}^{-1} \text{ mol}^{-1} = 163.3 \text{ J K}^{-1} \text{ mol}^{-1}\end{aligned}$$

$$\begin{aligned}\Delta H^{\circ}_{\text{sys}} &= (\Delta_f H^{\circ}[\text{H}_2(\text{g})] + \frac{1}{2} \Delta_f H^{\circ}[\text{O}_2(\text{g})]) - \Delta_f H^{\circ}[\text{H}_2\text{O}(\text{l})] \\ &= -285.8 \text{ kJ mol}^{-1} - 0 - 0 = -285.8 \text{ kJ mol}^{-1}\end{aligned}$$

$$\Delta S^{\circ}_{\text{surr}} = -\frac{\Delta H^{\circ}_{\text{sys}}}{T} = -\frac{-285.8 \times 10^3 \text{ J mol}^{-1}}{298 \text{ K}} = 959.1 \text{ JK}^{-1} \text{ mol}^{-1}$$

$$\begin{aligned}\Delta S^{\circ}_{\text{univ}} &= \Delta S^{\circ}_{\text{sys}} + \Delta S^{\circ}_{\text{surr}} = 163.3 \text{ JK}^{-1} \text{ mol}^{-1} - 959.1 \text{ JK}^{-1} \text{ mol}^{-1} \\ &= -795.8 \text{ JK}^{-1} \text{ mol}^{-1}\end{aligned}$$

This reaction is NOT spontaneous. There is no danger of water spontaneously decomposing into its elements. On the contrary, reaction in the opposite direction is spontaneous (but very slow) if in the reaction mixture at 25 °C, $p(\text{H}_2) = p(\text{O}_2) = 1 \text{ bar}$.

17.47 At sufficiently high T , the system change in entropy will be the dominant term and the reaction will be spontaneous.17.49 (a) = $-1258.1 \text{ kJ mol}^{-1}$

This reaction is spontaneous. It is enthalpy driven.

(b) = $124.6 \text{ kJ mol}^{-1}$

This reaction is NOT spontaneous. Both enthalpy and entropy terms disfavour this process.

17.51 This problem is answered using thermochemical data from the NIST webbook (webbook.nist.gov).

This value agrees with the tabulated free energy of formation ($\Delta_f G^{\circ}$) for acetic acid, as long as the same database is used—to be consistent (these data are not always accurately determined, or tabulated). This should not be surprising because the reaction of interest is the one for which $\Delta_r G^{\circ} = \Delta_f G^{\circ}$, by definition.

17.53 = $-1139.2 \text{ kJ mol}^{-1}$ 17.55 = $106 \text{ }^{\circ}\text{C}$.17.57 = $-1441.61 \text{ kJ mol}^{-1}$ This is in accord with experience.17.59 K is very small, in accord with a positive standard free energy change—the forward reaction is NOT favoured in a reaction mixture at 25 °C and all reactants and products in their standard states (i.e., the conditions that apply for specification of the standard free energy change of reaction).17.61 = 4.73 kJ mol^{-1} 17.63 = $-166.27 \text{ kJ mol}^{-1}$

$$17.65 = 92.4 \text{ }^\circ\text{C}$$

SUMMARY AND CONCEPTUAL QUESTIONS

$$17.67 \quad (a) \quad \Delta_r S^\circ = 2 S^\circ[\text{Hg}(\ell)] + S^\circ[\text{O}_2(\text{g})] - 2 S^\circ[\text{HgO}(\text{s})]$$

$$= 2 \times 76.02 \text{ J K}^{-1} \text{ mol}^{-1} + 205.138 \text{ J K}^{-1} \text{ mol}^{-1} - 2 \times 70.29 \text{ J K}^{-1} \text{ mol}^{-1} =$$

$$216.60 \text{ J K}^{-1} \text{ mol}^{-1} \quad \checkmark$$

$$\Delta_r H^\circ = 0 + 0 - 2 \times \Delta_f H^\circ[\text{HgO}(\text{s})] = -2 \times (-90.83 \text{ kJ mol}^{-1}) = 181.66 \text{ kJ mol}^{-1}$$

$$\checkmark$$

A positive $\Delta_r H^\circ$ corresponds to a negative $\Delta H^\circ_{\text{surr}}$ and a negative $\Delta S^\circ_{\text{surr}}$. \checkmark

$$\Delta_r G^\circ = \Delta_{\text{vap}} H^\circ - T \Delta_{\text{vap}} S^\circ$$

$$= 181.66 \text{ kJ mol}^{-1} - 298.15 \text{ K} \times 216.60 \text{ J K}^{-1} \text{ mol}^{-1} / (1000 \text{ J/kJ}) = 117 \text{ kJ mol}^{-1} \quad \checkmark \quad \checkmark$$

We have $\Delta_r G^\circ$ at 25 °C, so we can calculate K at 25 °C (298 K) from $\Delta_r G^\circ = -RT \ln K$

$$117 \text{ 000 J mol}^{-1} = (-8.314 \text{ J K}^{-1} \text{ mol}^{-1})(298 \text{ K}) \ln K$$

$$\ln K = (117 \text{ 000 J mol}^{-1}) / (-8.314 \text{ J K}^{-1} \text{ mol}^{-1})(298 \text{ K}) = -47.22$$

$$K \text{ at } 298 \text{ K} = 3.1 \times 10^{-21}$$

$$17.69 \quad (a) \quad \Delta_r S^\circ = 128.133 \text{ J K}^{-1} \text{ mol}^{-1}$$

(b) The reaction is NOT spontaneous at 25 °C and under standard conditions.

$$(c) \quad \Delta_r H^\circ = \Delta_r G^\circ + T \Delta_r S^\circ$$

$$= 115.55 \text{ kJ mol}^{-1} - 298 \text{ K} \times 128.133 \text{ J K}^{-1} \text{ mol}^{-1} / (1000 \text{ J/kJ}) = 77.37 \text{ kJ mol}^{-1}$$

The minimum temperature at which the reaction becomes spontaneous is such that

$$\Delta_r G^\circ = \Delta_r H^\circ - T_{\text{spont}} \Delta_r S^\circ = 0 \quad (\text{above } T_{\text{spont}}, \Delta_r G^\circ < 0)$$

$$T_{\text{spont}} = \Delta_r H^\circ / \Delta_r S^\circ = 77.37 \times 10^3 \text{ J mol}^{-1} / 128.133 \text{ J K}^{-1} \text{ mol}^{-1} = 604 \text{ K}$$

$$17.71 \quad (a) \quad = 0.141 \text{ kJ mol}^{-1}$$

The rhombic form of S_8 solid is more stable than the monoclinic form at 80 °C.

$$\Delta_r G^\circ = \Delta_r H^\circ - T \Delta_r S^\circ = 3.213 \text{ kJ mol}^{-1} - 383.15 \text{ K} \times (8.7 \text{ J K}^{-1} \text{ mol}^{-1}) / (1000 \text{ J/kJ}) =$$

$$-0.120 \text{ kJ mol}^{-1}$$

The monoclinic form of S_8 solid is more stable than the rhombic form at 110 °C.

$$(b) \quad \Delta_r G^\circ = \Delta_r H^\circ - T_{\text{trans}} \Delta_r S^\circ = 0$$

at temperature, T_{trans} , the temperature at which rhombic sulfur transforms to monoclinic sulfur.

$$T_{\text{trans}} = \Delta_r H^\circ / \Delta_r S^\circ = 3.213 \times 10^3 \text{ J mol}^{-1} / (8.7 \text{ J K}^{-1} \text{ mol}^{-1}) = 369 \text{ K} = 96 \text{ }^\circ\text{C}.$$

$$17.73 \quad (a) \quad \Delta_r H^\circ = -62.10 \text{ kJ mol}^{-1}$$

$$\Delta_r S^\circ = -132.738 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\Delta_r G^\circ = -22.524 \text{ kJ mol}^{-1}$$

$$(b) \quad = 1.13 \times 10^{-4} \text{ bar}$$

$$(c) \quad \Delta_r G^\circ = \Delta_r H^\circ - T \Delta_r S^\circ = 0$$

$$\text{at } T = \Delta_r H^\circ / \Delta_r S^\circ = -62.10 \times 10^3 \text{ J mol}^{-1} / (-132.738 \text{ J K}^{-1} \text{ mol}^{-1}) = 468 \text{ K}$$

At this temperature, the vapour pressure of oxygen is 1.00 bar.

17.75 $\text{Hg}(\ell) \rightarrow \text{Hg}(\text{g})$
 $\Delta_r H^\circ = \Delta_f H^\circ[\text{Hg}(\text{g})] = 61.38 \text{ kJ mol}^{-1}$
 $\Delta_r S^\circ = S^\circ[\text{Hg}(\text{g})] - S^\circ[\text{Hg}(\ell)] = 174.97 \text{ J K}^{-1} \text{ mol}^{-1} - 76.02 \text{ J K}^{-1} \text{ mol}^{-1}$
 $= 98.95 \text{ J K}^{-1} \text{ mol}^{-1}$
 $\Delta_r G^\circ = \Delta_r H^\circ - T \Delta_r S^\circ = 61.38 \text{ kJ mol}^{-1} - 298.15 \text{ K} \times (98.95 \text{ J K}^{-1} \text{ mol}^{-1}) / (1000 \text{ J/kJ}) =$
 $31.88 \text{ kJ mol}^{-1}$

(a) $p(\text{Hg}) = 1.00 \text{ bar}$
 $K = 1.00$

$\Delta_r G^\circ = -RT \ln(K) = 0$
 $= \Delta_r H^\circ - T \Delta_r S^\circ$

So,

$T = \Delta_r H^\circ / \Delta_r S^\circ = 61.38 \times 10^3 \text{ J mol}^{-1} / 98.95 \text{ J K}^{-1} \text{ mol}^{-1} = 620 \text{ K}$

(b) $p(\text{Hg}) = 1.33 \times 10^{-3} \text{ bar}$
 $K = 1.33 \times 10^{-3}$

$\Delta_r G^\circ = -RT \ln(K) = \Delta_r H^\circ - T \Delta_r S^\circ$

Solve for T .

$T = \Delta_r H^\circ / (\Delta_r S^\circ - R \ln(K))$
 $= 61.38 \times 10^3 \text{ J mol}^{-1} / (98.95 \text{ J K}^{-1} \text{ mol}^{-1} - 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \ln(1.33 \times 10^{-3})) = 399 \text{ K}$

17.77 (a) Entropy *of the system* decreases in some spontaneous reactions. These reactions occur because of the increase in the entropy of the surroundings caused by the heat liberated—they are enthalpy driven reactions. However it is correct that the entropy *of the universe* increases with every spontaneous reaction.

(b) Reactions with a negative free energy change ($\Delta_r G^\circ < 0$) are product-favoured. However, these reactions sometimes occur very slowly. $\Delta_r G^\circ$ tells us how far a reaction will go to attain a condition of equilibrium, but does not tell us the speed of the reaction.

(c) Some spontaneous processes are endothermic. These reactions occur because the system entropy increases sufficiently to exceed the entropy lost by surroundings due to heat absorbed by the system—they are entropy driven reactions.

(d) Endothermic processes are sometimes spontaneous—see answer to (c).

17.79 $\Delta_r S^\circ$ is usually positive for the dissolution of condensed substances. Dissolved species have more freedom as a solute than as a pure condensed phase. There is a positive component to the entropy of dissolution simply due to the disorder of having a mixture of two species. In this typical case of positive entropy of dissolution, if $\Delta_r H^\circ = 0$

$$\Delta_r G^\circ = \Delta_r H^\circ - T \Delta_r S^\circ < 0$$

and the dissolution is spontaneous. Such dissolutions are driven by entropy.

Some condensed substances—e.g., liquid hydrocarbons—actually have negative entropy of dissolution in water. The hydrophobic effect is actually attributable to the negative change in entropy associated with the water molecules solvating the hydrophobic molecule.

- 17.81 $\text{C}_6\text{H}_6(\text{s}) \rightarrow \text{C}_6\text{H}_6(\text{l})$
 (a) $\Delta_r H^\circ > 0$
 It takes energy (enthalpy) to break the intermolecular bonds holding the benzene molecules rigidly in their lattice positions.
 (b) $\Delta_r S^\circ > 0$
 A liquid has more disorder—more entropy—than the corresponding solid.
 (c) $\Delta_r G^\circ = 0$ at 5.5°C , the melting point, where the solid and liquid co-exist.
 (d) $\Delta_r G^\circ > 0$ at $0.0^\circ\text{C} <$ the melting point, where the solid is the more stable phase.
 (e) $\Delta_r G^\circ < 0$ at $25.0^\circ\text{C} >$ the melting point, where the liquid is the more stable phase.
- 17.83 $\Delta_r G^\circ < 0$
 This process is spontaneous—iodine dissolves readily in CCl_4 .
 $\Delta_r S^\circ = (\Delta_r H^\circ - \Delta_r G^\circ) / T > 0$ since $\Delta_r H^\circ = 0$
 This dissolution is an entropy-driven process.
- 17.85 (a) $\text{N}_2\text{H}_4(\text{l}) + \text{O}_2(\text{g}) \rightarrow \text{N}_2(\text{g}) + 2 \text{H}_2\text{O}(\text{l})$
 This is an oxidation-reduction reaction—oxygen is the oxidizing agent and hydrazine is the reducing agent.
- (b) $\Delta_r H^\circ = -622.29 \text{ kJ mol}^{-1}$
 $\Delta_r S^\circ = 5.08 \text{ J K}^{-1} \text{ mol}^{-1}$
 $\Delta_r G^\circ = -623.80 \text{ kJ mol}^{-1}$

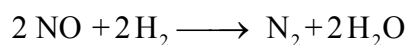
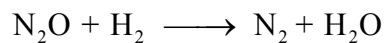
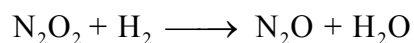
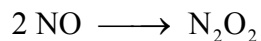
Chapter 18

- 18.2 For every 2 moles of NOCl consumed, there are 2 moles of NO and one mole of Cl_2 produced. The relative rate of appearance of Cl_2 is $\frac{1}{2}$ the rate of appearance of NO which equals the rate of disappearance of NOCl .
- 18.3 In the first two hours: $0.0085 \text{ mol L}^{-1} \text{ h}^{-1}$
 In the last two hours: $0.002 \text{ mol L}^{-1} \text{ h}^{-1}$
 The instantaneous rate of decay at $t = 4.0 \text{ h}$: $0.0044 \text{ mol L}^{-1} \text{ h}^{-1}$
- 18.4 (a) $\text{Rate} = k [\text{NO}_2][\text{O}_3]$
 (b) The rate triples.
 (c) The rate is halved.
- 18.7 $\text{Rate} = k [\text{NO}]^2[\text{O}_2]$
 $k = 7100 \text{ mol}^{-2} \text{ L}^2 \text{ s}^{-1}$
- 18.9 $0.0035 \text{ mol L}^{-1}$
- 18.11 $0.00217 \text{ mol L}^{-1}$
- 18.13 The plot of $\ln([\text{N}_2\text{O}_5])$ versus time gives a straight line. The reaction is first order.

- 18.15 (a) $t_{1/2}$ of $^{241}\text{Am} = 430$ years
 $t_{1/2}$ of $^{125}\text{I} = 63$ years
 (b) ^{125}I
 (c) 1.57×10^{15} atoms

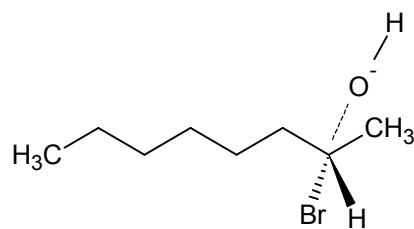
18.17 57.2 kJmol^{-1}

- 18.19 All three of these processes are bimolecular.
 The rate equation for the third step: $\text{Rate} = k [\text{N}_2\text{O}] [\text{H}_2]$



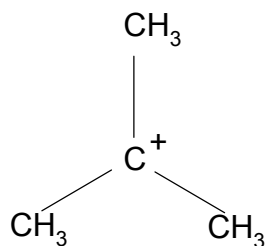
- 18.21 (a) $2\text{NH}_3(\text{aq}) + \text{OCl}^-(\text{aq}) \rightarrow \text{N}_2\text{H}_4(\text{aq}) + \text{H}_2\text{O}(\ell) + \text{Cl}^-(\text{aq})$
 (b) step 2
 (c) $\text{Rate} = k [\text{NH}_2\text{Cl}] [\text{NH}_3]$
 (d) NH_2Cl , N_2H_5^+ and OH^-

- 18.22 (a) $\text{Rate} = k [\text{CH}_3(\text{CH}_2)_5\text{CHBrCH}_3] [\text{OH}^-]$
 (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 S_N2 mechanism is negligible because the rate of the S_N1 mechanism is enhanced by the relatively stable carbocation intermediate, and because the rate of the S_N2 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 S_N2 reaction. The S_N1 mechanism presents no such obstacle – the iodide reacts with a reactive planar intermediate.

REVIEW QUESTIONS

- 18.25 $3.0 \times 10^{-4} \text{ mol L}^{-1} \text{ min}^{-1}$
- 18.27 The reaction is second order in A and first order in B. The total order of the reaction is three.
- 18.29 $1.8 \times 10^{-3} \text{ mol L}^{-1} \text{ h}^{-1}$. The rate of reaction is the rate of change of Cl^- , for this reaction.
- 18.31 (a) second order in NO and first order in O_2
 (b) $\text{Rate} = k [\text{NO}]^2 [\text{O}_2]$
 (c) $25 \text{ mol}^{-2} \text{ L}^2 \text{ s}^{-1}$
 (d) $2.8 \times 10^{-5} \text{ mol L}^{-1} \text{ s}^{-1}$
 (e) O_2 (g) reacts at rate = $5.0 \times 10^{-5} \text{ mol L}^{-1} \text{ s}^{-1}$; i.e. one half the rate of NO. NO_2 (g) forms at the same rate as NO, $1.0 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$.
- 18.33 (a) The reaction is second order in NO and first order in H_2
 (b) $\text{Rate} = k [\text{NO}]^2 [\text{H}_2]$
 (c) $6.32 \text{ mol}^{-2} \text{ L}^2 \text{ s}^{-1}$
 (d) $0.159 \text{ mol L}^{-1} \text{ s}^{-1}$
- 18.35 (a) $\text{Rate} = k [\text{CO}]^2 [\text{O}_2]$
 (b) second order in [CO] and first order in $[\text{O}_2]$
 (c) $4.6 \text{ mol}^{-2} \text{ L}^2 \text{ min}^{-1}$

18.37 (a) 0.58
(b) 1280 s

18.39 495 min⁻¹

18.43 105 min

18.45 The ln[phenyl acetate] data is best fit by a straight line. The hydrolysis of phenyl acetate is a first reaction.
 $k = 0.021 \text{ s}^{-1}$

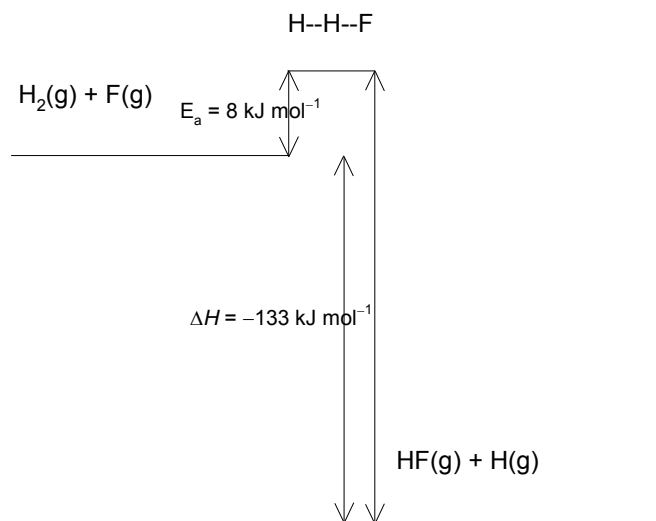
18.47 Rate = $k [\text{NO}_2]^2$
 $k = 1.1 \text{ L mol}^{-1} \text{ s}^{-1}$

18.49 (a) 23 min
(b) 77 min

18.51 36 s

18.53 84.9 kJmol⁻¹

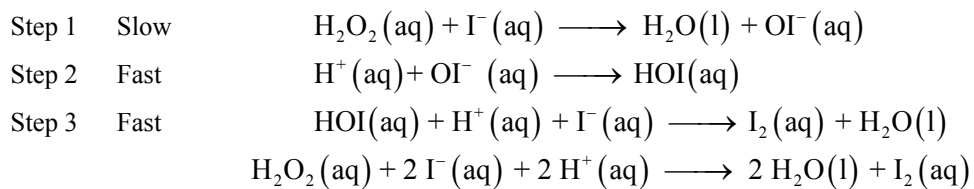
18.55



18.57 (a) Rate = $k [\text{Cl}][\text{ICl}]$
(b) Rate = $k [\text{O}][\text{O}_3]$
(c) Rate = $k [\text{NO}_2]^2$

18.59 (a) Step 2
(b) Rate = $k_2 [\text{O}_3] [\text{O}]$

18.61 (a)



(b) The first two steps are bimolecular, while the last is ternary.

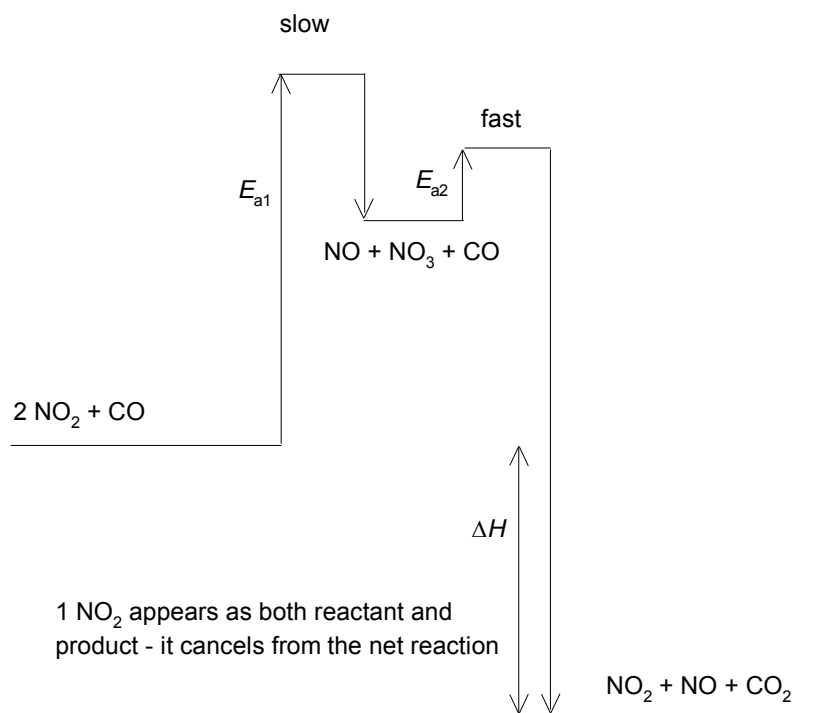
(c) Rate = $k_2 [\text{H}_2\text{O}_2] [\text{I}^-]$

18.63 (a) $\text{NO}_2(\text{g})$ and $\text{CO}(\text{g})$ are reactants.

$\text{NO}_3(\text{g})$ is an intermediate.

$\text{CO}_2(\text{g})$ and $\text{NO}(\text{g})$ are products.

(b)



SUMMARY AND CONCEPTUAL QUESTIONS

18.65 No answer provided. They will be derived from exploration of this activity.

18.67 (a) False

While the observed rate law is consistent with a single step process, there may be other multi-step mechanisms also consistent with the observed rate law.

(b) True

(c) False

Increasing temperature means more frequent and more energetic collisions (that are more frequently successful) – i.e. the rate increases with temperature.

(d) False

The activation energy is fixed by the reaction. It does not vary with temperature.

(e) False

The rate will increase fourfold if both concentrations are doubled.

(f) True

18.69 (a) True

(b) True

(c) False

The rate generally varies with time – e.g. in first and second order reactions. Only for zero order reactions does the rate remain constant. Zero order reactions arise when there is a limited amount of a catalyst and the reactants are present in abundance. In any case, reactions are only zero order for a time. Eventually, reactants deplete sufficiently that the amount of catalyst is no longer rate limiting, and the reaction is no longer zero order.

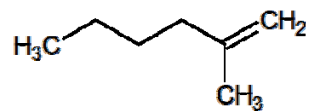
(d) False

It is possible that the reaction proceeds via a single ternary process. Ternary processes are infrequent, but they can play important roles.

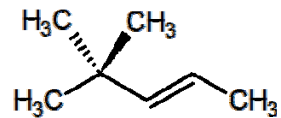
Chapter 19

19.2

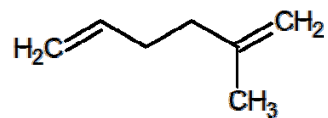
(a)



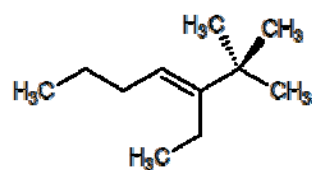
(b)



(c)



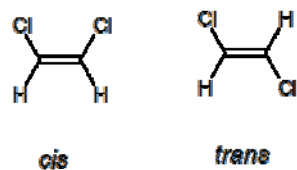
(d)



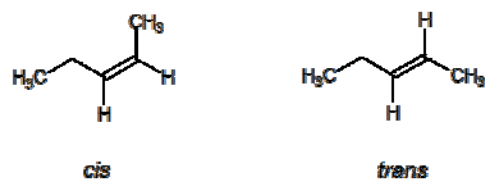
19.4 (a) $\text{CH}_3\text{CH}=\text{CH}_2$
No *cis-trans* isomers.

(b) $(\text{CH}_3)_2\text{C}=\text{CHCH}_3$
No *cis-trans* isomers.

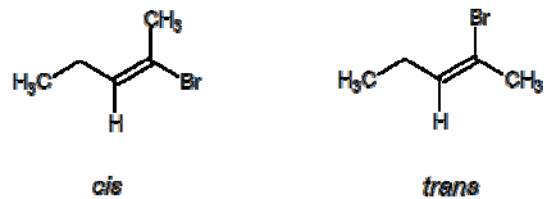
(c)



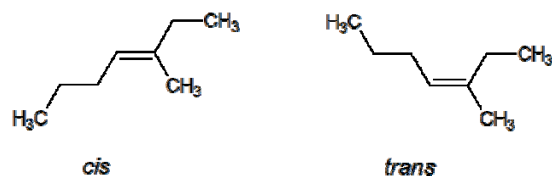
(d)



(e)

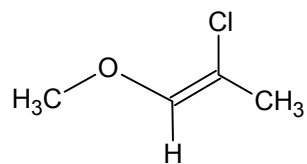


(f)



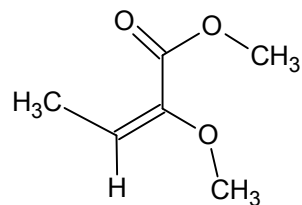
19.6 (a) $-\text{Br}$
(b) $-\text{Br}$
(c) $-\text{CH}_2\text{CH}_3$
(d) $-\text{OH}$
(e) $-\text{CH}_2\text{OH}$
(f) $-\text{CH}=\text{O}$

19.7 (a)



Z

(b)

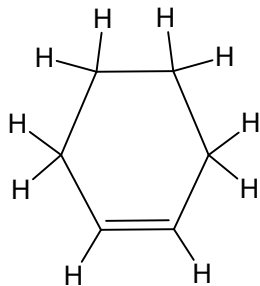


E

19.8 This is the Z isomer.

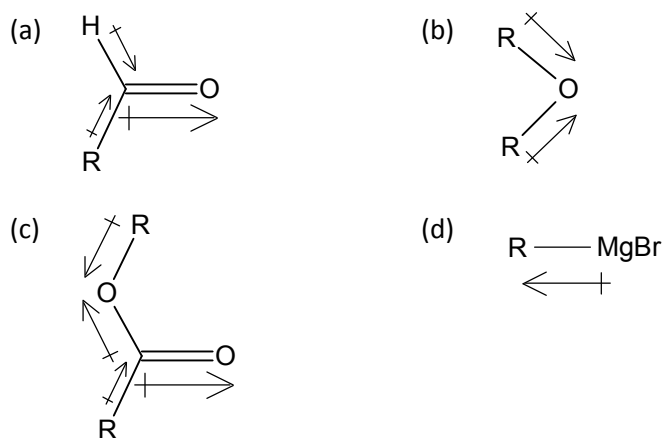
19.9 The two downfield lines, at about 139 and 113 ppm, are the two alkene carbon peaks.

19.10



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

19.13



19.14 (a) 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) 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) Br^-

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

(d) CH_3NH_2

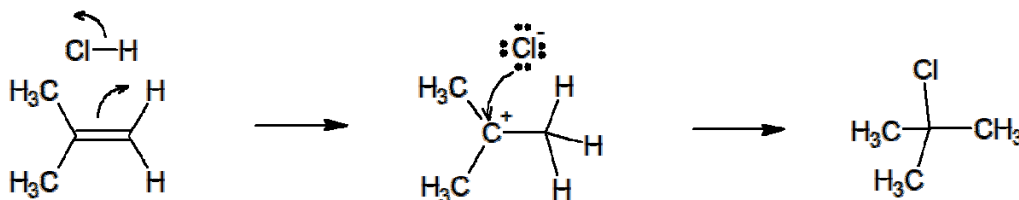
The amine N atom is a nucleophile. It is attracted to concentrations of positive charge (i.e. regions of depleted electron density).

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

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

19.15 BF_3 is electron deficient at the low-electronegativity boron atom. In the Lewis structure of BF_3 , the boron atom has only 6 electrons in its valence shell. BF_3 is electrophilic at the boron center.

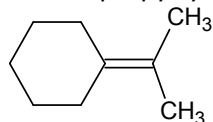
19.16



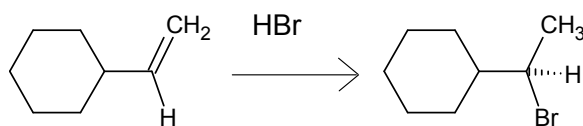
- 19.17 (a) $\text{CH}_3\text{CH}_2\text{CHClCH}_3$
 (b) $(\text{CH}_3)_2\text{ClCH}_2\text{CH}_2\text{CH}_3$
 (c) chlorocyclohexane



- 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,

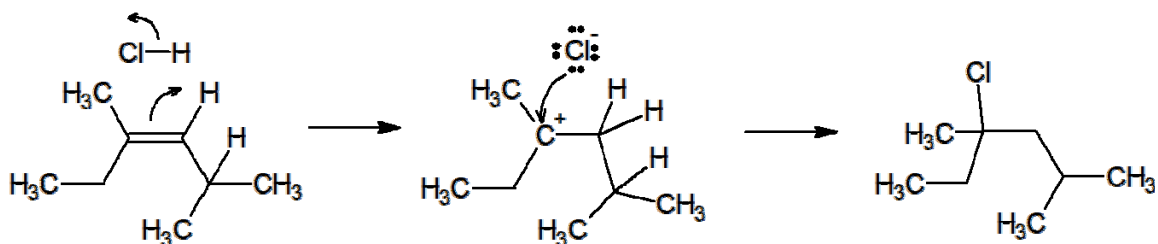


(d)

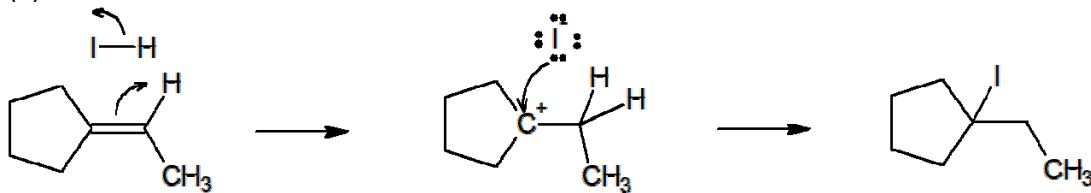


19.19

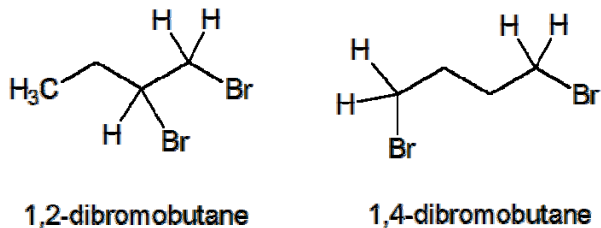
(a)



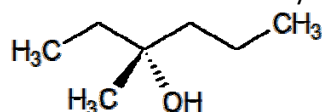
(b)



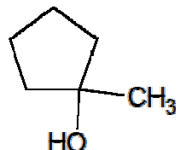
19.20



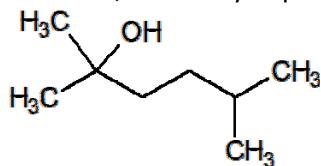
19.21 (a) Addition of water to 3-methylhex-3-ene gives 3-methylhexan-3-ol,



(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

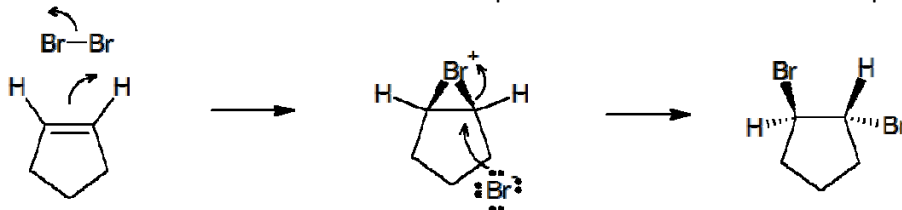


19.22 (a) Butan-2-ol can be made by addition of water to but-1-ene or but-2-ene.

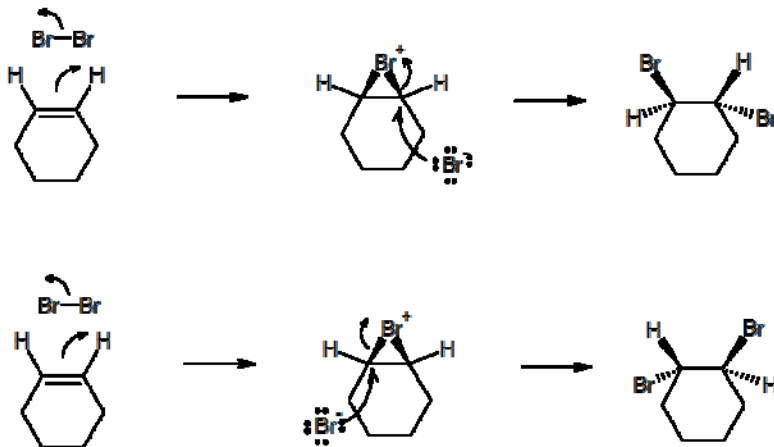
(b) 3-Methylpentan-3-ol can be made by addition of water to 3-methylpent-2-ene or 2-ethylbut-1-ene.

(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

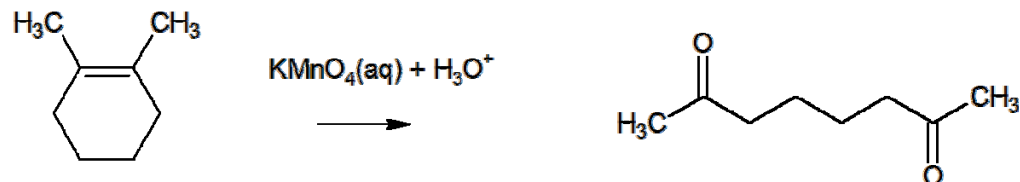


The two enantiomers of 1,2-dibromo-1,2-dimethylcyclohexane are expected upon bromination of 1,2-dimethylcyclohexene.

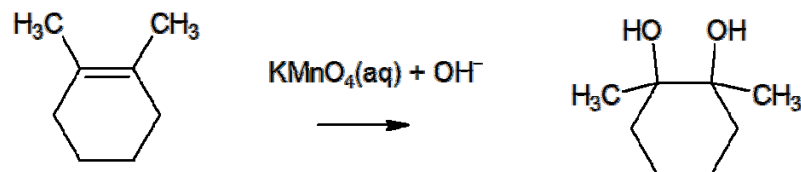
19.25 See Exercise 19.24 above

- 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 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 KMnO_4 .

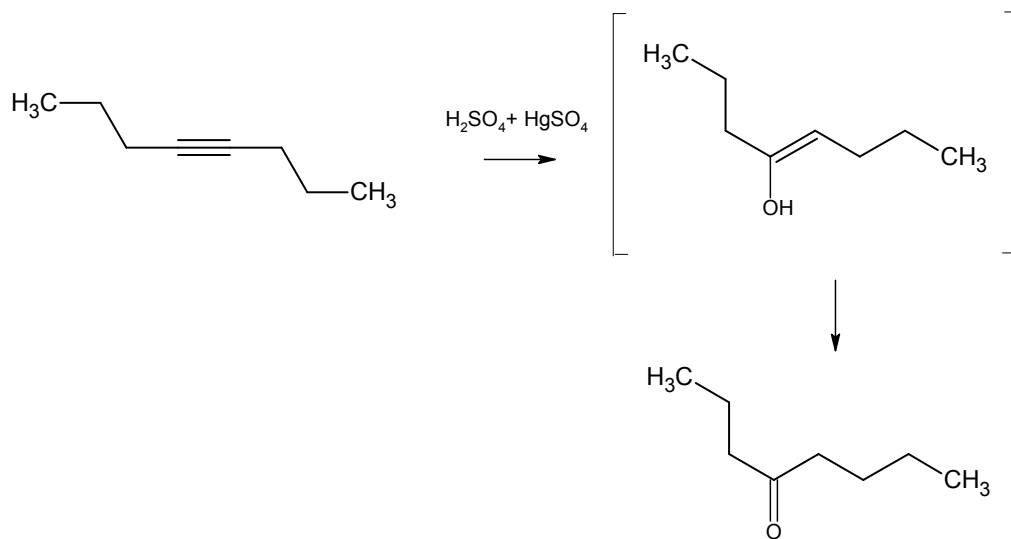
- 19.29 (a) 6-methylhept-3-yne
(b) 3,3-dimethylbut-1-yne
(c) 5-methylhex-2-yne
(d) hept-2-en-5-yne

19.30 The peak just above 3300 cm^{-1} looks like an alkyne C–H stretch, while the peak just above 2100 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 cm^{-1} . The compound likely has alkyl H's in addition to the alkynyl H.

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

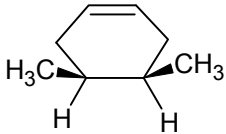
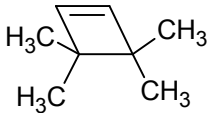
19.32 The unknown compound is either $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{C}\equiv\text{CH}$ or $(\text{CH}_3\text{CH}_2)_3\text{CHC}\equiv\text{CH}$.

19.33



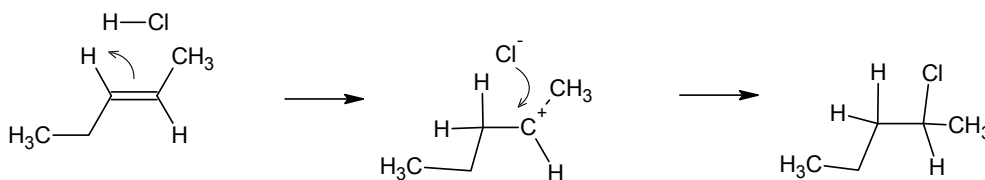
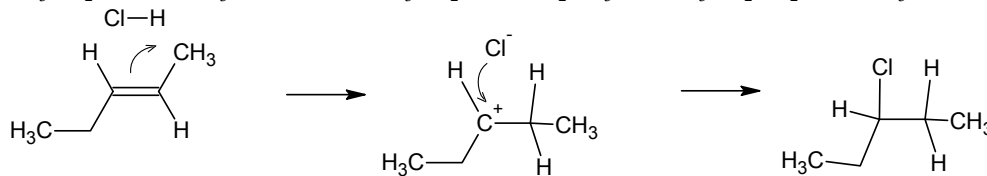
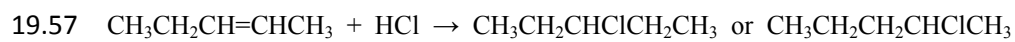
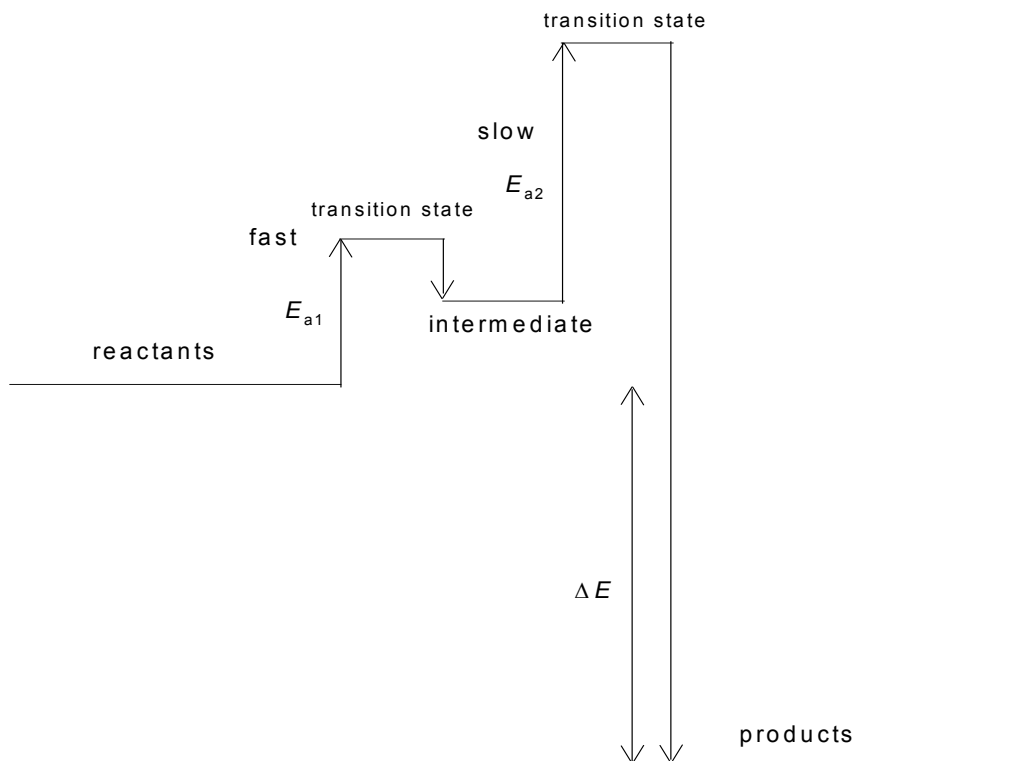
- 19.34 (a) To make 2-pentanone you could hydrate 1-pentyne, $\text{CH}_3\text{CH}_2\text{CH}_2\text{C}\equiv\text{CH}$.
 (b) To make 3-hexanone you could hydrate 2-hexyne, $\text{CH}_3\text{CH}_2\text{CH}_2\text{C}\equiv\text{CCH}_3$.
- 19.35 (a) To make 5-methylhex-1-yne, $(\text{CH}_3)_2\text{CHCH}_2\text{CH}_2\text{C}\equiv\text{CH}$ you could start with ethyne (acetylene), $\text{HC}\equiv\text{CH}$, treat it with 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 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 NaNH_2 to make sodium pentynylide add to methylbromide, CH_3Br
 (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 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 NaNH_2 to make sodium 3-methylbutynylide add to methylbromide, CH_3Br

REVIEW QUESTIONS

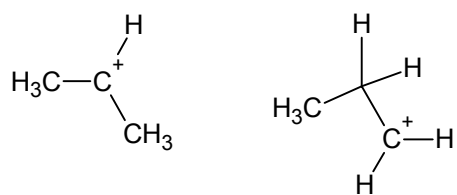
- 19.37 β -carotene is added to commercial food for ornamental fish to make the colour of the fish (specifically the red-orange component of the colour) brighter and richer. β -carotene is a red-orange pigment, used in nature along with other pigments to make colours.
- 19.39 (a) Alkyl and nitrile (or cyano) groups are present in propanenitrile (a.k.a. cyanoethane).
(b) Alkyl and ether groups are present in cyclopentyl methyl ether.
(c) Alkyl, ketone and ester groups are present in methyl 3-ketobutanoate (a.k.a. methyl ethanoylethanoate or methyl acetylacetate).
(d) Alkene and ketone groups are present in 1,4-benzoquinone.
(e) Alkene and amide groups are present in 2-butenamide.
(f) Phenyl and carboxyl groups are present in benzoic acid.
- 19.41 The double bonds within the rings at the ends of β -carotene are between carbon 1 (the carbon connected to the chain) and carbon 2, whereas the ring double bonds in α -carotene are between carbon 2 and carbon 3. Otherwise, the two molecules are identical. The HOMO-LUMO gap for α -carotene is larger than that for lycopene. Whereas α -carotene absorbs blue light and appears orange, lycopene absorbs green light (lower frequency and lower energy than blue light) and appears red.
- 19.43
- (a)
- 
- The diagram shows the skeletal structure of cis-2-butene. It consists of a central carbon-carbon double bond. Each carbon of the double bond is also bonded to a hydrogen atom (H) and a methyl group (H₃C). The two methyl groups are on the same side of the double bond, and the two hydrogen atoms are on the opposite side.
- (b)
- 
- The diagram shows the skeletal structure of trans-2-butene. It consists of a central carbon-carbon double bond. Each carbon of the double bond is also bonded to a methyl group (H₃C) and another methyl group (CH₃). The two methyl groups are on opposite sides of the double bond.
- 19.45 (a) 4-methylpent-1-ene
(b) 3-heptene
(c) 1,5-heptadiene
(d) 2-methylhex-3-ene
- 19.47 (a+b+c) All three of these molecules have cis-trans isomers.
- 19.49 Methylcarboxylate, $-\text{COOCH}_3$, has higher priority than carboxyl, $-\text{COOH}$.
- 19.51 (a) *Z*
(b) *Z*

- 19.53 (a) substitution
 (b) elimination
 (c) addition
 (d) substitution

19.55

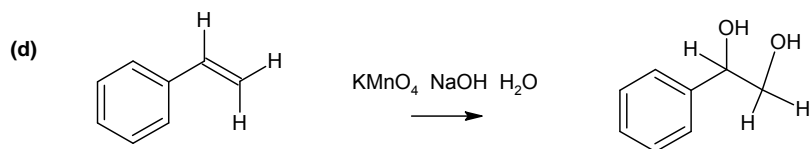
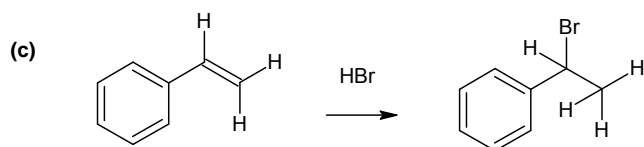
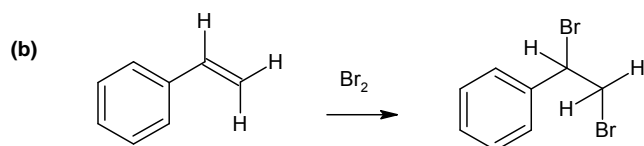
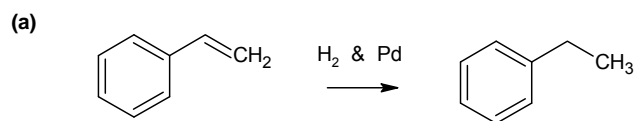


19.59



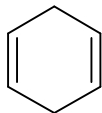
The carbocation on the left is the more stable.

19.61

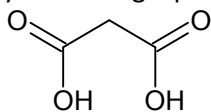


19.63

Oxidative cleavage of

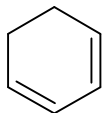


yields a single product,

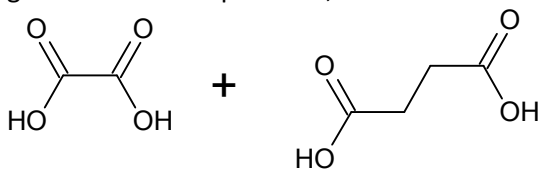


because of symmetry.

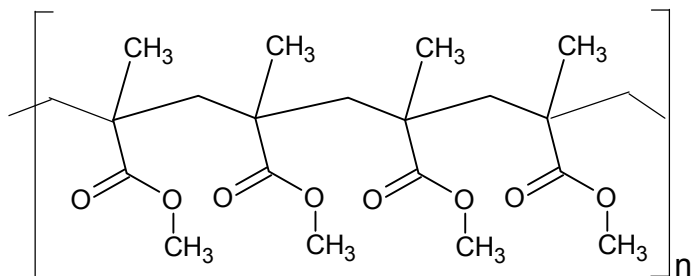
Oxidative cleavage of



gives two distinct products,



19.65

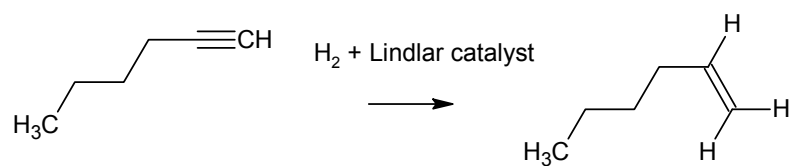
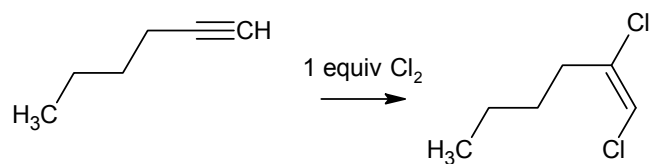
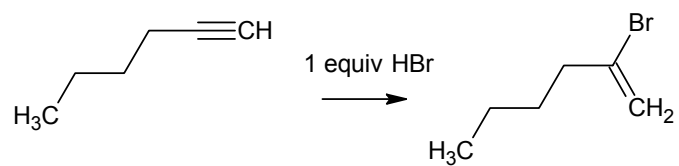


19.67 (a) 6

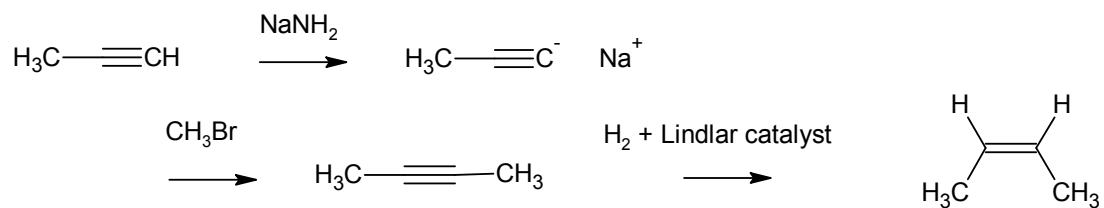
(b) 6

(c) 3

19.69

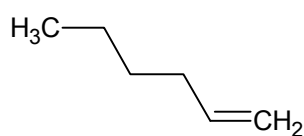


19.71

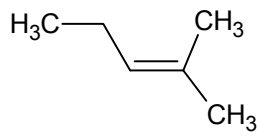


SUMMARY AND CONCEPTUAL QUESTIONS

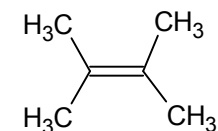
19.73 (a)



1-hexene,

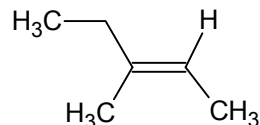


2-methylpent-2-ene

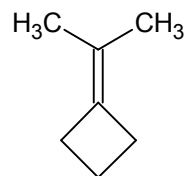


2,3-dimethylbut-2-ene

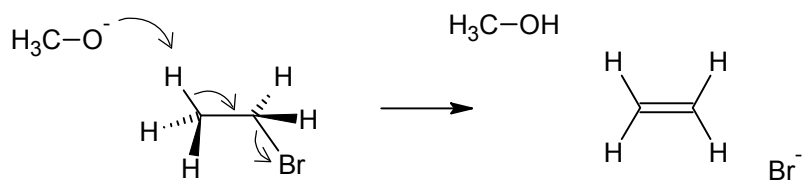
(b)



(c)

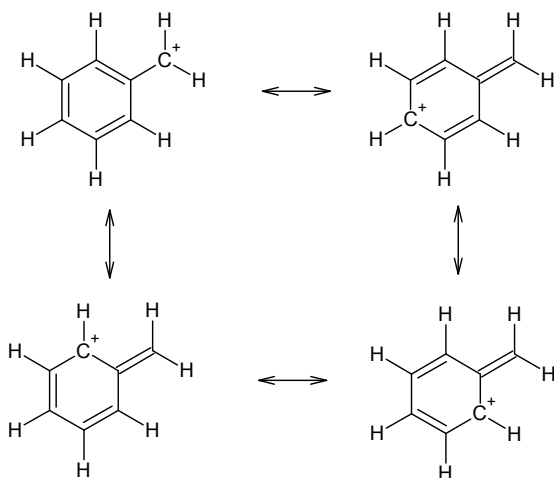


19.75



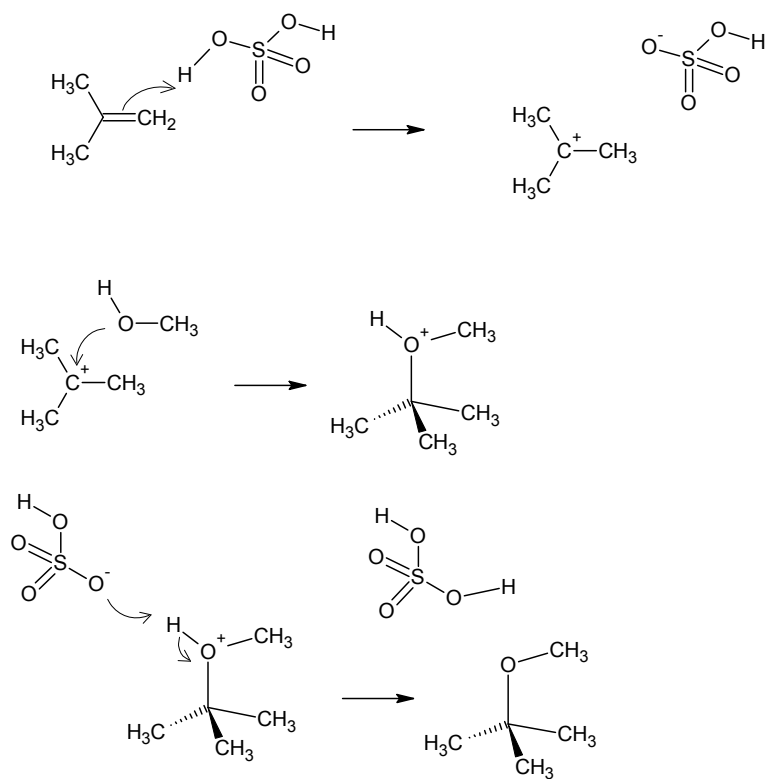
An O-H bond is formed, a C-H bond is broken, a C-C bond is formed (to make a double bond) and a C-Br bond is broken.

19.77

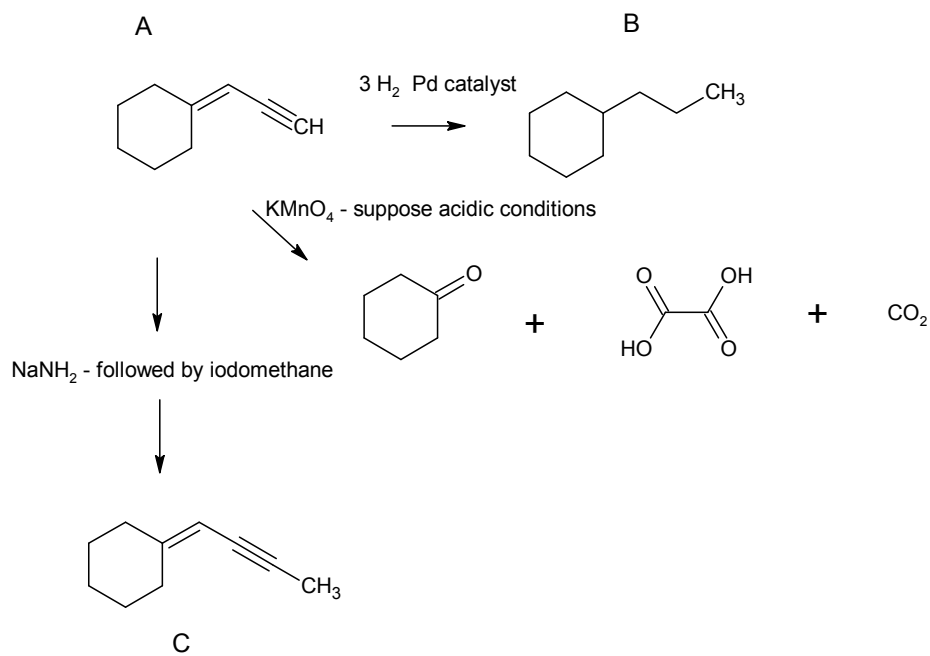


Because of these three additional resonance structures, the + charge of the carbocation is spread out – delocalized – over four carbon atoms. This makes the benzyl carbocation especially stable – for a carbocation.

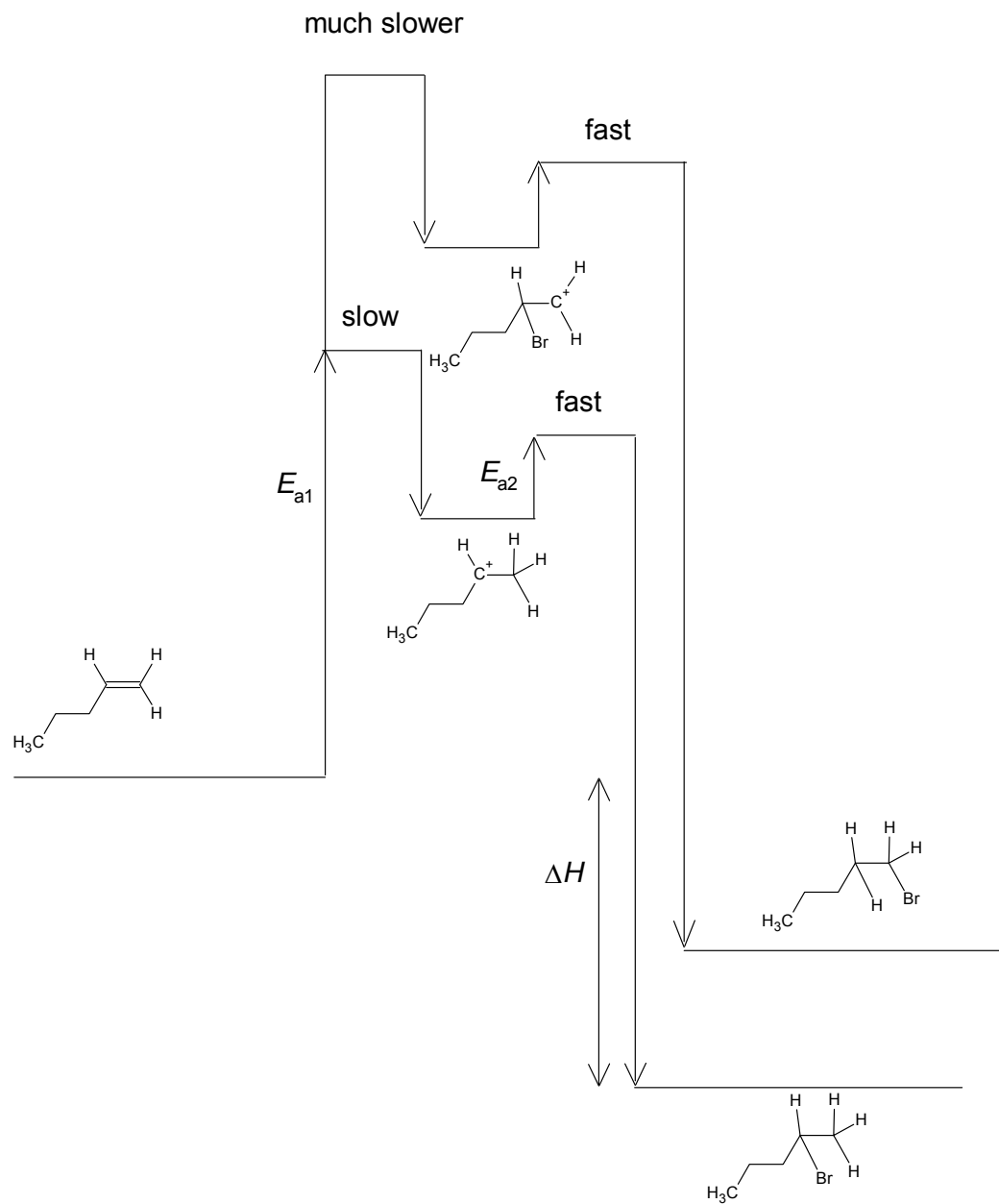
19.79



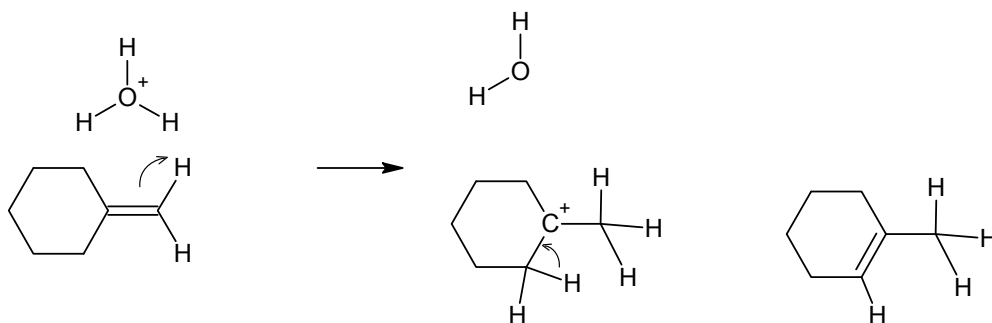
19.81



19.83 Treat acetylene with NaNH_2 to get acetylide, $\text{HC}\equiv\text{C}^-$. Add to 1-bromotridecane, $\text{CH}_3(\text{CH}_2)_{12}\text{Br}$ to get $\text{CH}_3(\text{CH}_2)_{12}\text{C}\equiv\text{CH}$. Treat with NaNH_2 to get pentadecynylide. Add to 1-bromooctane, $\text{CH}_3(\text{CH}_2)_7\text{Br}$ to get $\text{CH}_3(\text{CH}_2)_{12}\text{C}\equiv\text{C}(\text{CH}_2)_7\text{CH}_3$.



19.87



Chapter 20

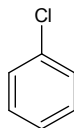
20.1 -236 kJ/mol

- 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.

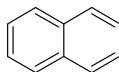
20.3 (a) Benzene has just one ^{13}C NMR absorption peak.



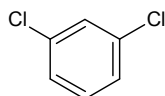
(b) Chlorobenzene has four ^{13}C NMR absorption peaks.



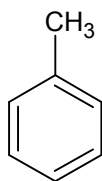
(c) Naphthalene has three ^{13}C NMR absorption peaks.



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



20.4



- (a) There is an aryl C-H stretching band with three peaks at 3100, 3070 and 3030 cm^{-1} . The alkyl C-H stretching band with principal peaks at 2925 and 2850 cm^{-1} .
(b) The out-of-plane C-H bending vibrations give rise to two peaks at 740 and 700 cm^{-1} .
(c) The in-plane C-H bending vibrations produce peaks at 1090 and 1030 cm^{-1} . The aryl C-C stretches produce a band with principal peaks at 1610, 1510 and 1470 cm^{-1} .

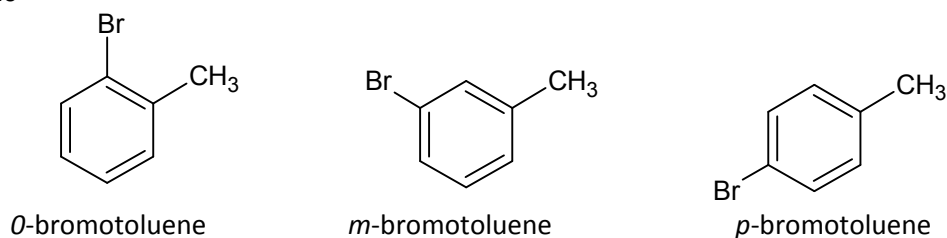
20.5 Furan has 6 electrons in its π system. It is aromatic, with ^1H NMR shifts are at 6.4 and 7.4 ppm.

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

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

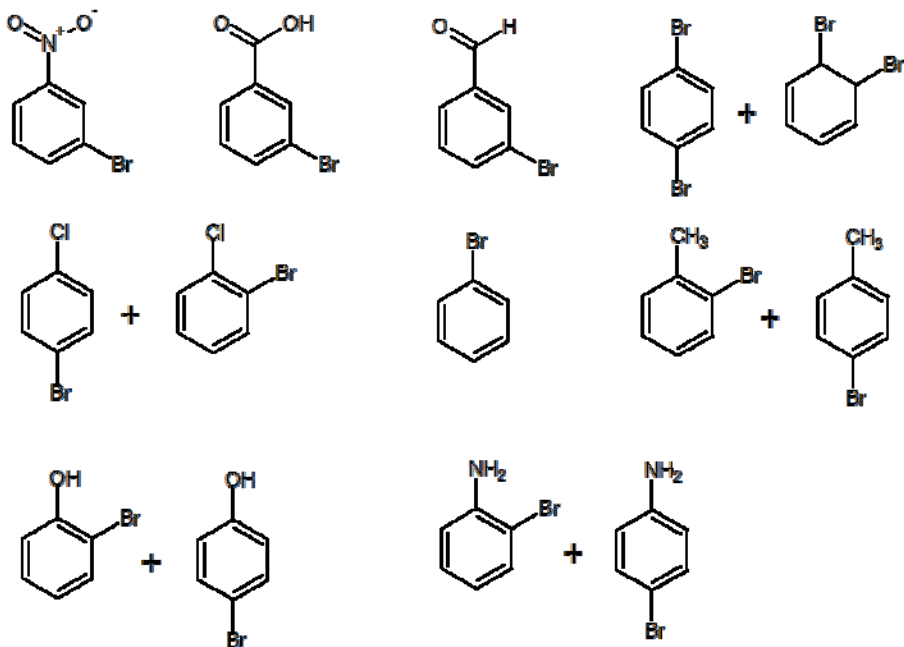
- 20.9 (a) 1-bromo-3-chlorobenzene, or m-bromochlorobenzene
(b) 2-methylpropylbenzene, or 2-methyl-1-phenylpropane
(c) 1-amino-4-bromobenzene, or p-aminobromobenzene or p-bromoaniline

20.10

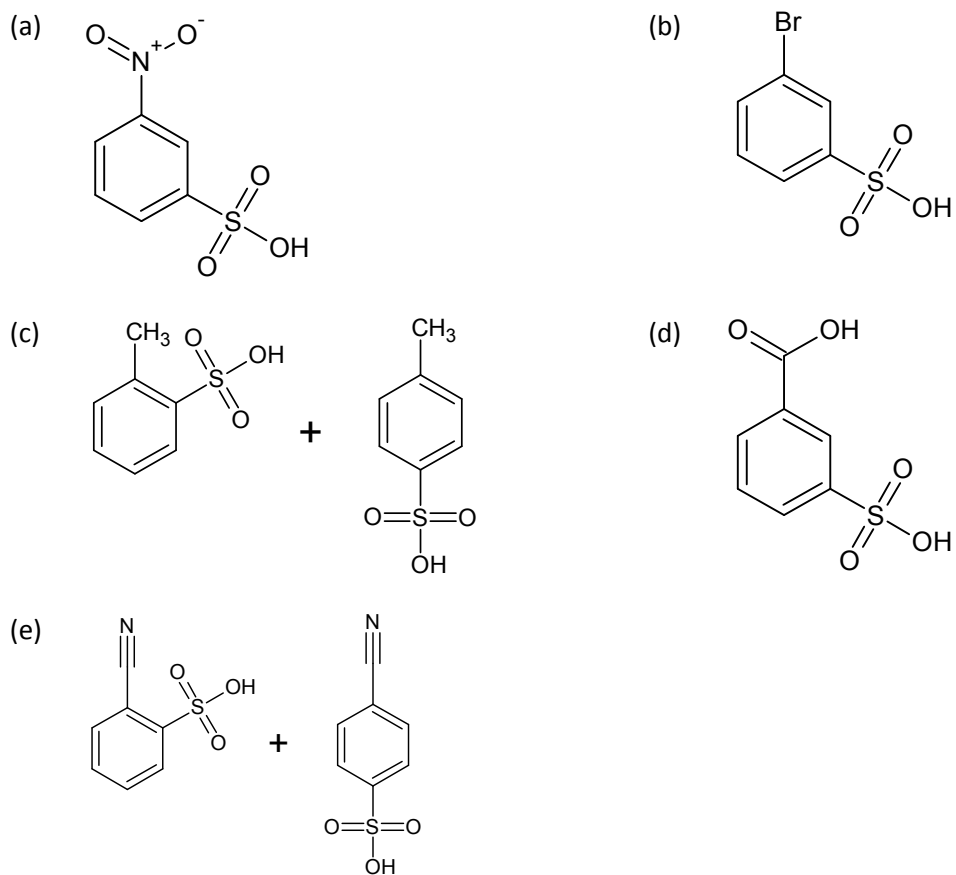


- 20.11 D_2SO_4 sulfonates the benzene ring reversibly. On sulfonation, an H^+ is lost to the solvent (D_2SO_4). On de-sulfonation, D^+ adds to the ring. Since the solvent far outnumbers the benzene, the H 's are lost in a sea of D 's. The benzene ends up with all H 's replaced by D 's.
- 20.12 (a) Nitrobenzene < toluene < phenol (hydroxybenzene)
(b) Benzoic acid < chlorobenzene < benzene < phenol
(c) Benzaldehyde < bromobenzene < benzene < aniline (aminobenzene)

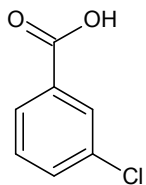
20.13 The products of electrophilic bromination of nitrobenzene, benzoic acid, benzaldehyde, bromobenzene, chlorobenzene, benzene, toluene, phenol and aniline, respectively, are



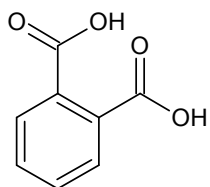
20.14



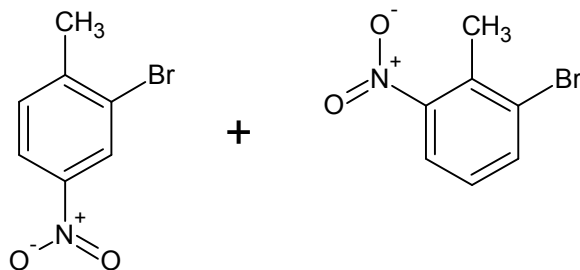
20.15 Oxidizing *m*-chloroethylbenzene with KMnO_4 produces *m*-chlorobenzoic acid,



Oxidizing tetralin with 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 $-\text{NO}_2$

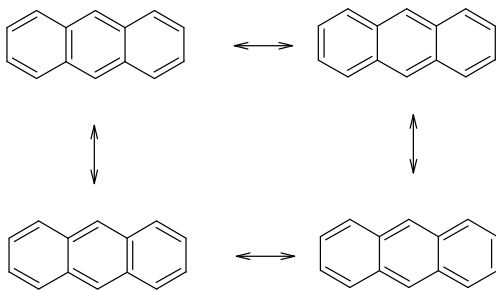
Reduce the nitrobenzene product using hydrogen to get aniline

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

REVIEW QUESTIONS

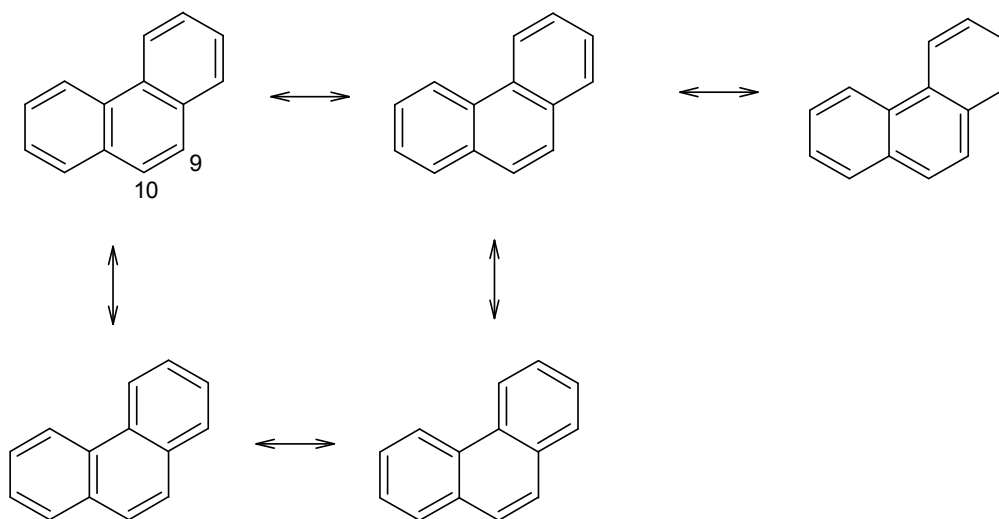
- 20.17 Many skilled Huguenot silk weavers and dyers emigrated from France to Germany following the revocation of the Edict of Nantes. Coal tar was available, at the time, as a source of starting materials. The Rhine River provided the water needed to do the chemistry.
- 20.19 Nitrates are needed to make trinitrotoluene (TNT), an important explosive, from toluene. They are also used to make other explosives (e.g. nitroglycerin) and as fertilizers. During the lead up to World War II, the British controlled the world's supply of naturally occurring nitrates – in massive guano deposits in Chile. The Germans needed a synthetic supply of nitrates. Fritz Haber and Carl Bosch developed an effective means of producing ammonia from nitrogen (from the air) and hydrogen. The ammonia could then be oxidized to produce the desired nitrate.
- 20.21 The planar arrangement of 1,3,5,7-tetramethylcyclooctatetraene produces an anti-aromatic π electron configuration. It is destabilized with respect to simply having four localized double bonds, as it does in the tub conformation. The tub conformation, therefore, provides the observed lowest energy conformation.

20.23



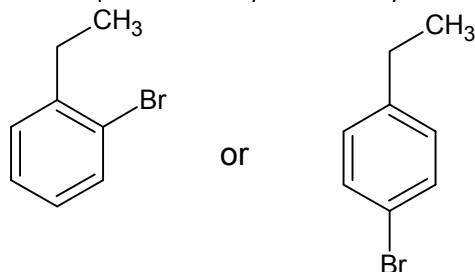
- 20.25 There are three non-equivalent H's in anthracene – the central vertical pair, and two pairs (related via reflection through the vertical axis) of vertical pairs of H's. The chemical shifts are expected to be in the 6.5 to 8 ppm range typical of aromatics.
- 20.27 Phenanthrene has $14 = 4 \times 3 + 2$ π electrons. Although it is not monocyclic, it certainly qualifies as aromatic. The outer ring of atoms provides the principal path over which $4 \times 3 + 2$ electrons are delocalized in accord with Hückel's rule.

20.29



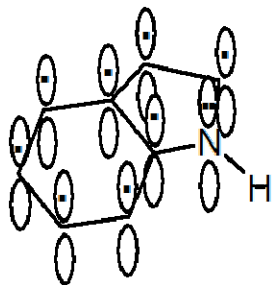
The shortest bonds have the highest order – look for the bonds which are double more often than the others. The shortest C–C bond is the C9-C10 bond (labeled in the first structure). It is a double bond in 4 of the 5 structures. Its bond order is $1\frac{4}{5}$.

20.31 C_8H_9Br has 4 degrees of unsaturation, consistent with a single phenyl ring (a ring and 3 double bonds). The compound is *o*- or *p*- bromoethylbenzene,



20.33 The 1,3,5,7-tetramethylcyclooctatetraene dianion should be planar, as Hückel's rule is satisfied and the planar structure should have a special stability.

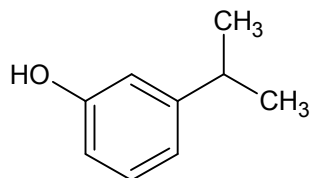
20.35



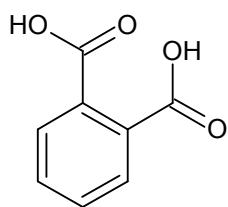
Indole has $10 = 4 \times 2 + 2$ π electrons. It is aromatic.

20.37 1,3,5,7-cyclononatetraene is expected to be unusually acidic because of the stabilization of the anion. It can be converted to a salt by treatment with a strong base such as NaNH_2 . The sodium salt of the aromatic cation would be formed.

20.39

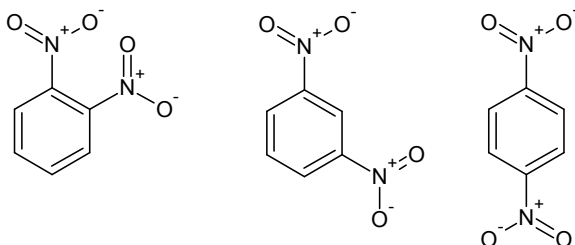


2-(3-hydroxyphenyl)propane or *m*-(1-methylethyl)phenol a.k.a. *m*-isopropylphenol

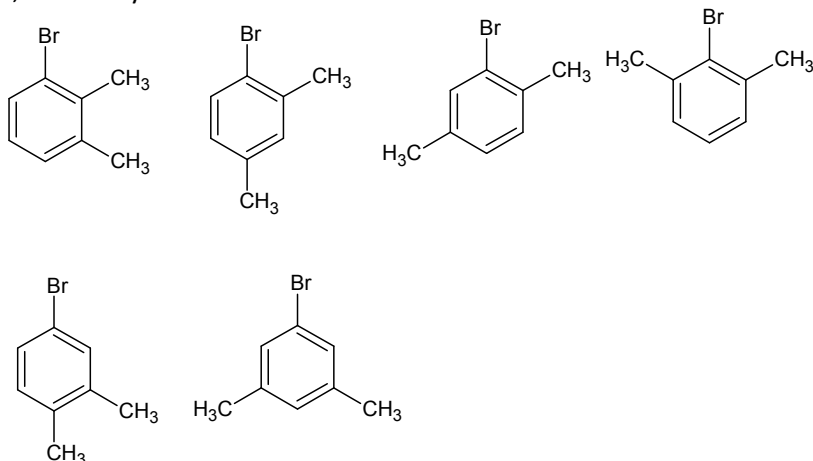


1,2-benzenedicarboxylic acid a.k.a phthalic acid

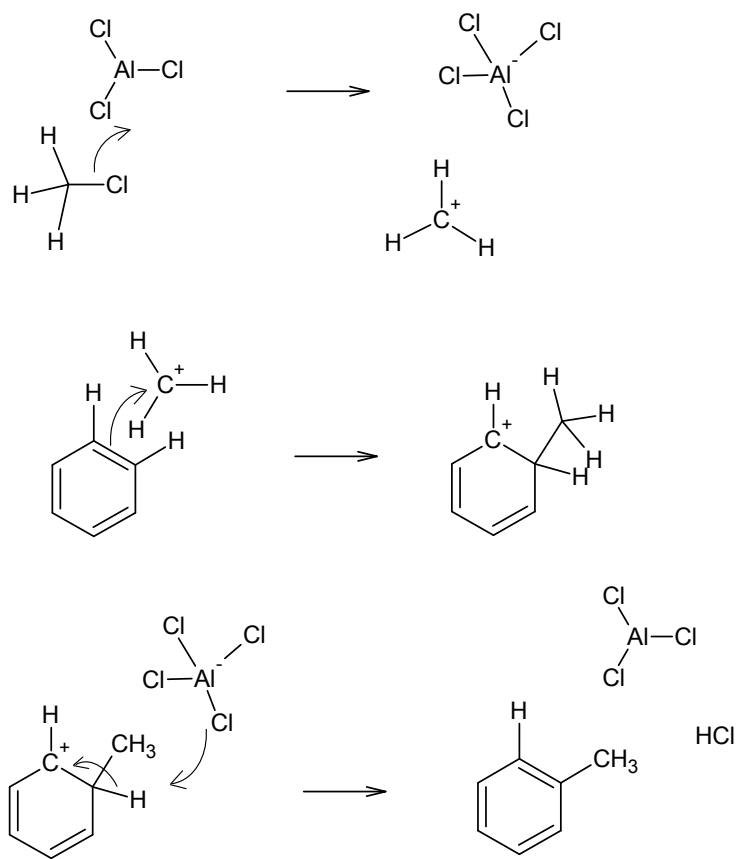
20.41 (a) *o*-dinitrobenzene, *m*-dinitrobenzene and *p*-dinitrobenzene



(b) 1-bromo-2,3-dimethylbenzene, 1-bromo-2,4-dimethylbenzene, 1-bromo-2,5-dimethylbenzene, 1-bromo-2,6-dimethylbenzene, 1-bromo-3,4-dimethylbenzene and 1-bromo-3,5-dimethylbenzene

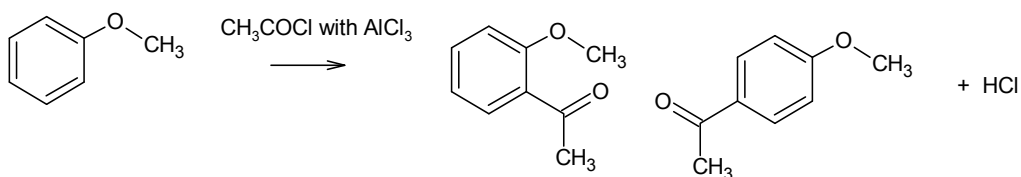
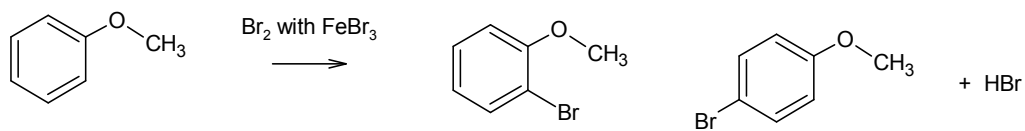


20.43



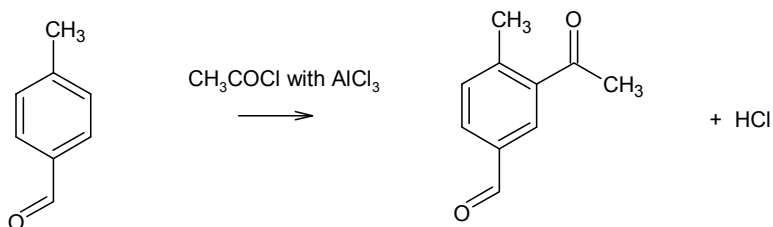
20.47

(a)



The products of bromination are *o*-bromomethoxybenzene and *p*-bromomethoxybenzene. The products of acylation are *o*-acetylmethoxybenzene and *p*-acetylmethoxybenzene.

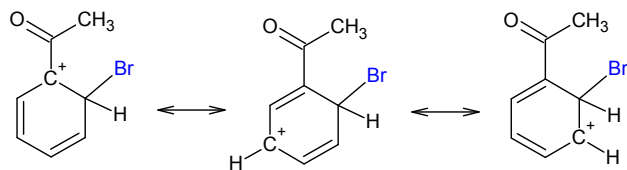
(b)



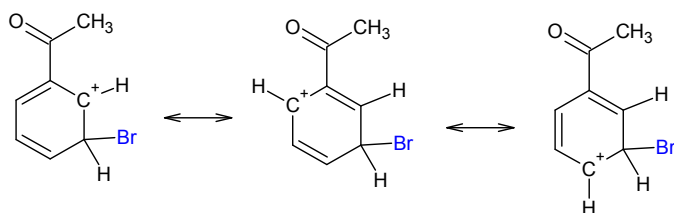
The product of bromination is 4-acyl-2-bromotoluene. While the methyl substituent is *o,p*-directing, the acyl substituent is *m*-directing - only one product is formed. The product of acylation is 2-acetyl-4-methylbenzaldehyde.

20.49

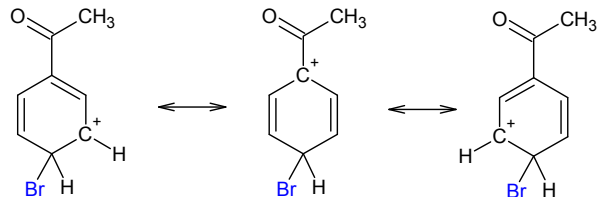
ortho addition



meta addition

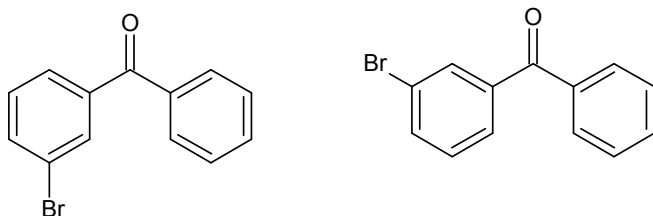


para addition



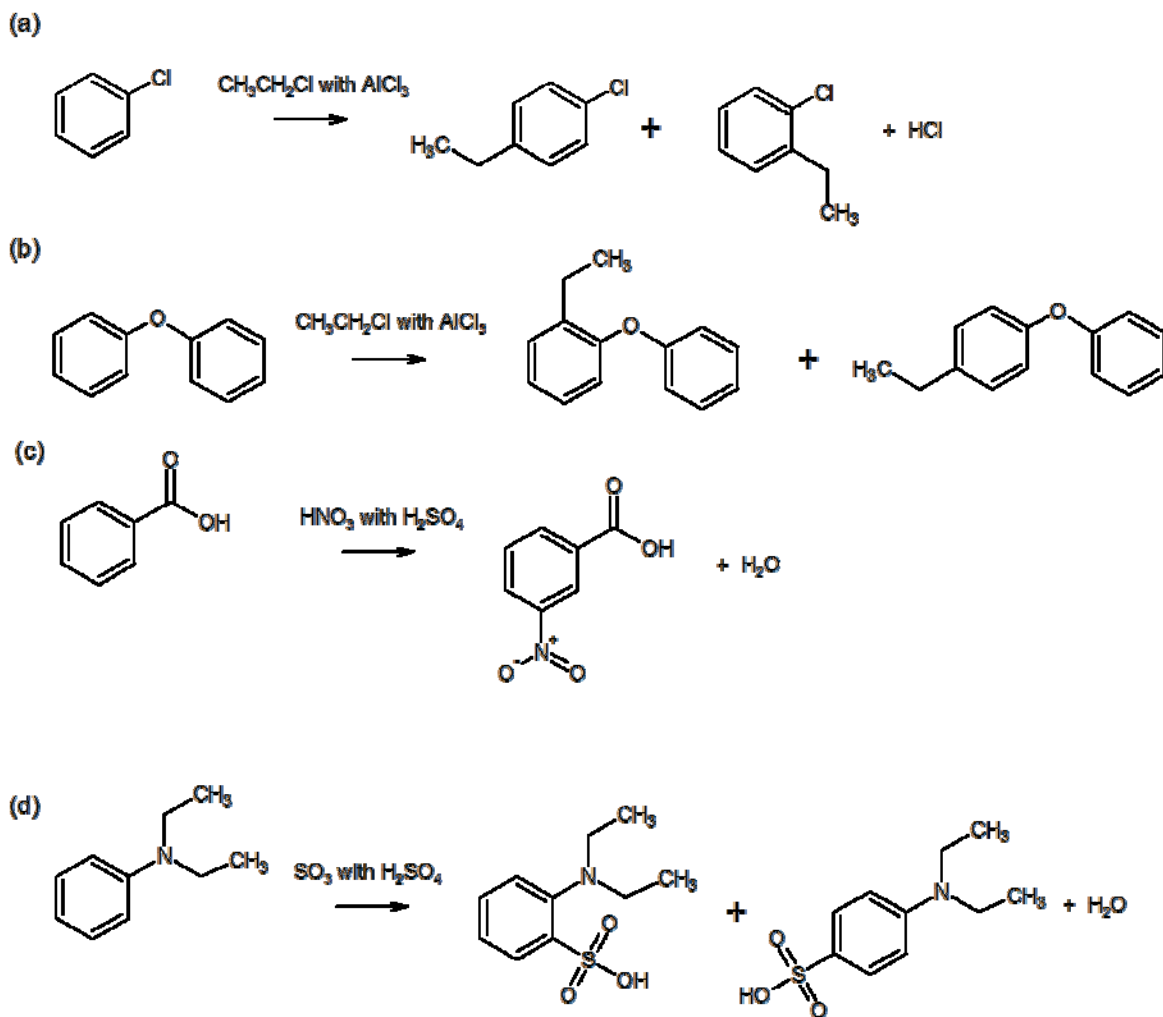
In the case of the ortho and para addition intermediates, one of the resonance structures has the positive charge on a carbon atom bonded to the electron-withdrawing acetyl group. This resonance structure is disfavored, making the carbocation intermediates less stable in the case of ortho and para addition. Meta addition is the favored pathway, by default.

20.51



The carbonyl is electron withdrawing. It leads to the meta bromination. However, because of the rigid relative orientation of the two phenyl rings, this corresponds to two products.

20.53



20.55 Diphenyl ether and diethylphenylamine react faster than benzene, while chlorobenzene and benzoic acid react slower.

20.57 (a) *o*-Bromotoluene can be synthesized from benzene via a Friedel-Crafts methylation (i.e. treat with 1 equivalent CH_3Cl and AlCl_3) to make toluene, followed by bromination (treat toluene with 1 equivalent Br_2 and FeBr_3) and separation of the ortho and para products. This separation might be achieved by distillation.

(b) 2-Bromo-1,4-dimethylbenzene is obtained if we apply another Friedel-Crafts methylation to the product, *o*-bromotoluene, from part (a). Because the first methyl is an activating ortho-para directing, whereas bromine is a deactivating ortho-para directing, the 1,4-dimethyl and 1,6-dimethyl products are obtained. A final separation step is required to obtain the desired compound.

20.59 Methylate benzene using CH_3Cl and AlCl_3 . Nitrate using HNO_3 and H_2SO_4 to get *o*- and *p*-nitrobenzene. Separate the para product. Oxidize it using KMnO_4 to obtain the desired *p*-nitrobenzoic acid.

20.61 (a) Methylate benzene using CH_3Cl and AlCl_3 .
Nitrate the toluene product using HNO_3 and H_2SO_4 . Separate the ortho product.
Oxidize using KMnO_4 to convert the methyl group to carboxylic acid.

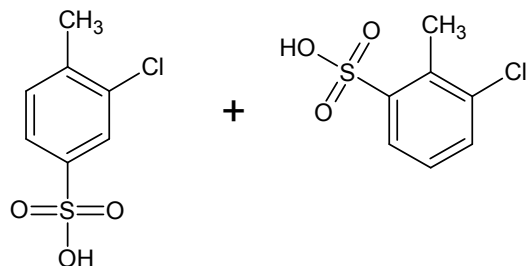
(b) Methylate benzene using two equivalents of CH_3Cl and AlCl_3 . Separate the *o*-dimethylbenzene from the para product.

SUMMARY AND CONCEPTUAL QUESTIONS

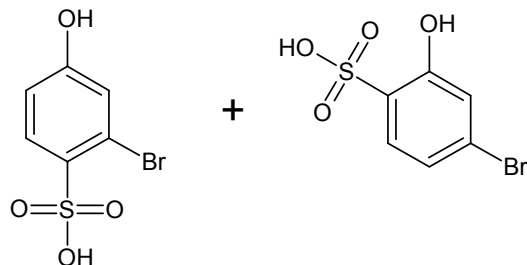
20.63 Trimethylammonium is a deactivating substituent. Unlike the amine substituent, ammonium has no lone pair of electrons to participate in the π system, and provide an additional resonance structure stabilizing the carbocation intermediates associated with ortho and para substitution. Nitrogen, being more electronegative than carbon, is otherwise somewhat electron withdrawing. More importantly, the positive charge on the ammonium substituent destabilizes the carbocation intermediate.

20.65

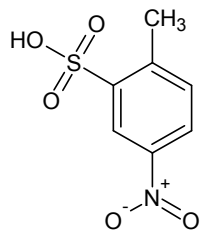
(a)



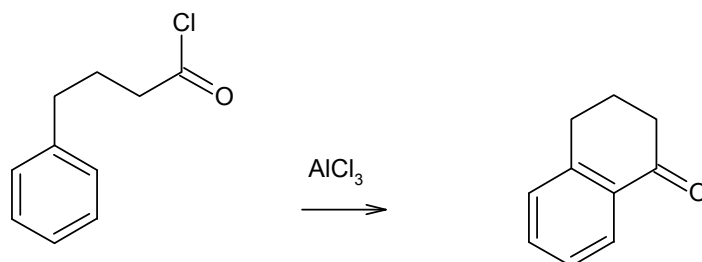
(b)



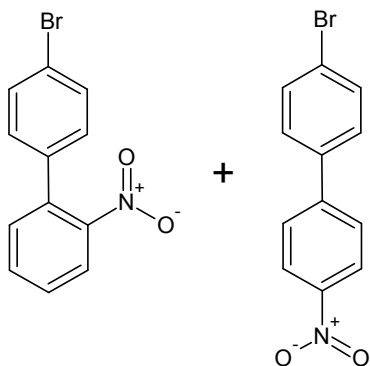
(c)



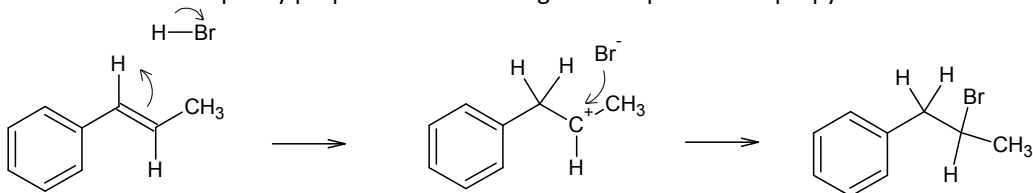
20.67



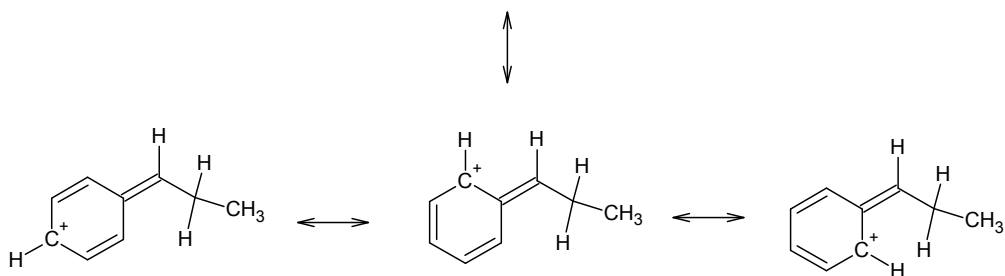
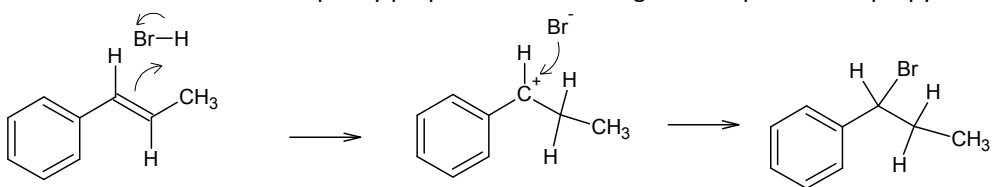
20.69



20.71 Addition of HBr to 1-phenylpropene with Br adding to the 2 position on propyl



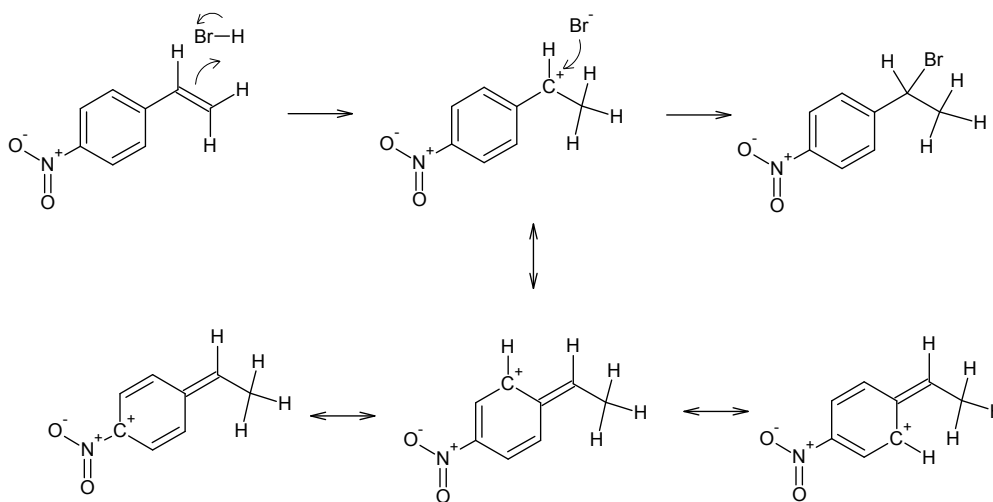
Addition of HBr to 1-phenylpropene with Br adding to the 1 position on propyl



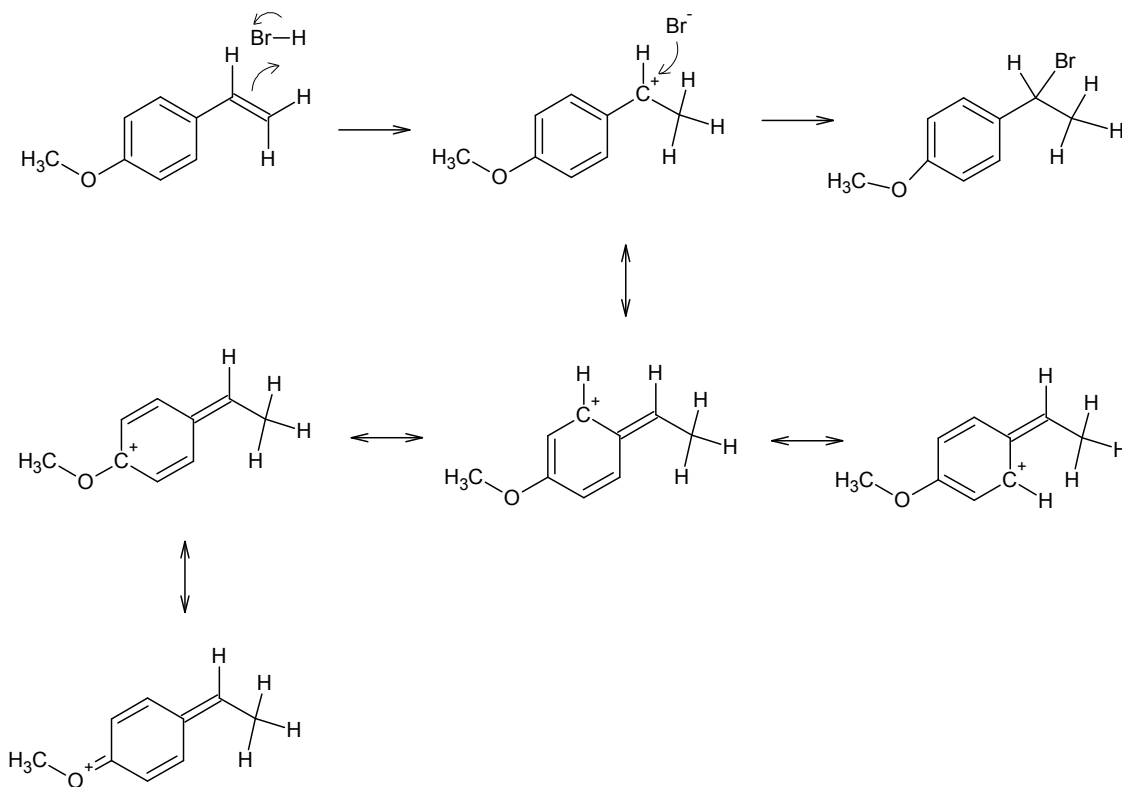
The extra resonance structures associated with the carbocation intermediate, in the case of addition of Br to the 1 position, stabilize the intermediate, enhancing the rate of the associated pathway, making the 1-bromopropyl product the exclusive product.

- 20.73 (a) In the first step, toluene is chlorinated at the meta position.
 (b) In the second step, *tert*-butyl is oxidized to make carboxylic acid.

20.75

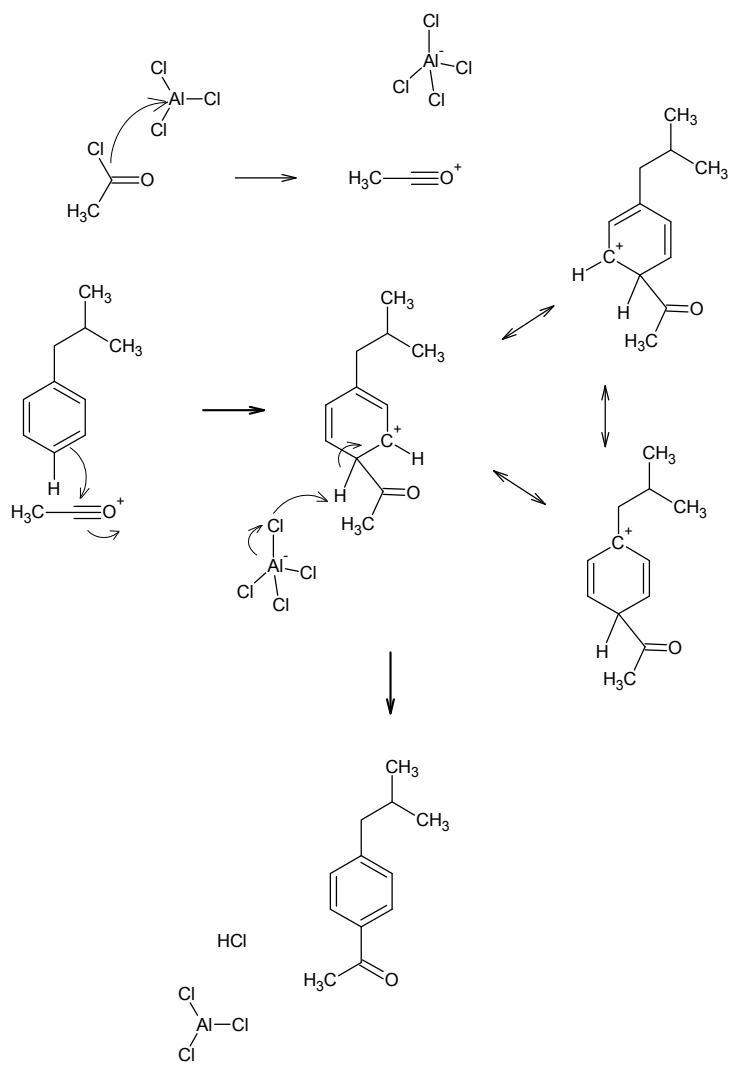


The carbocation intermediate is destabilized by the electron-withdrawing nitro group. The resonance structure with the + charge next to the formally + charged nitro N atom is especially destabilized.



The carbocation intermediate is stabilized by an extra resonance structure. Addition of HBr to the methoxy compound is much faster than addition to the nitro compound.

20.77

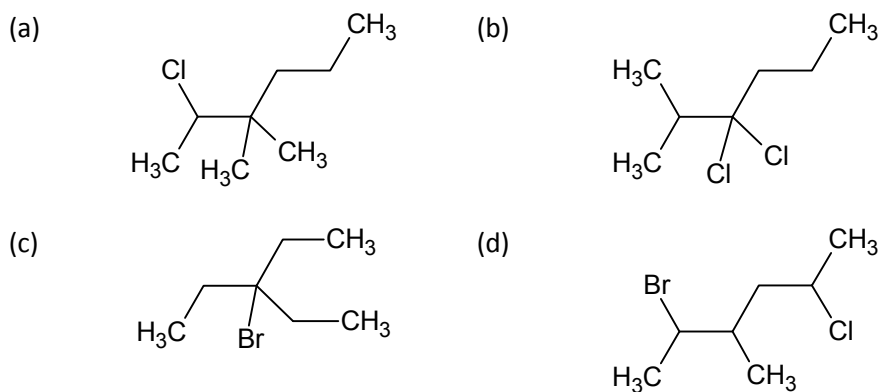


The para is the predominant product

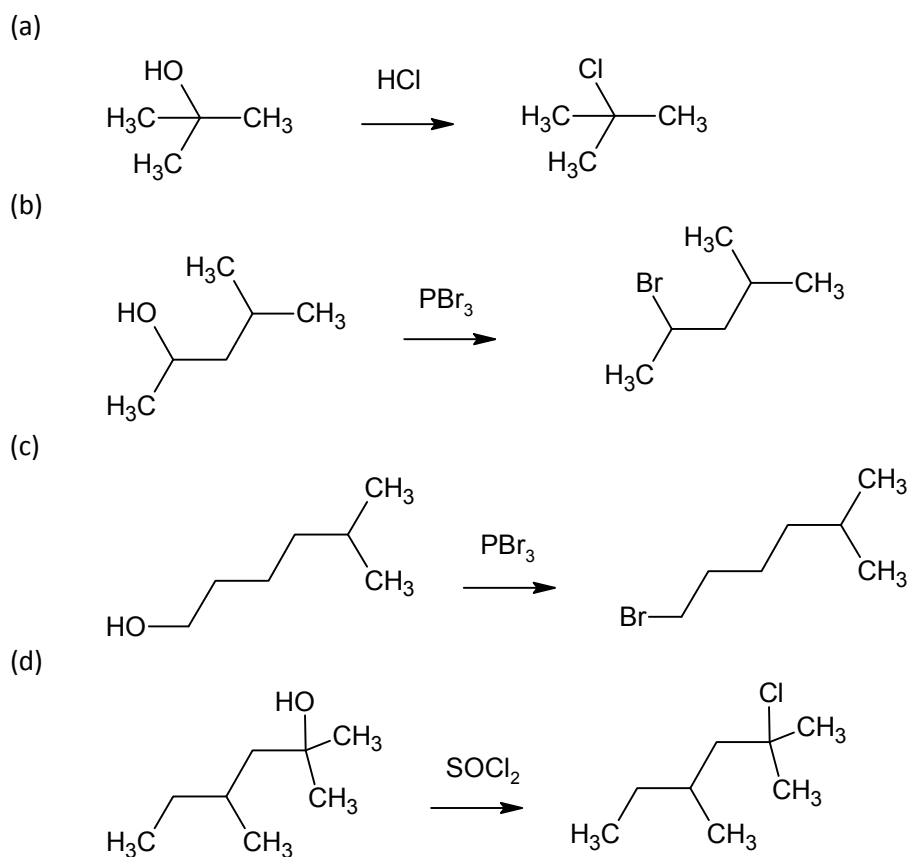
Chapter 21

- 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

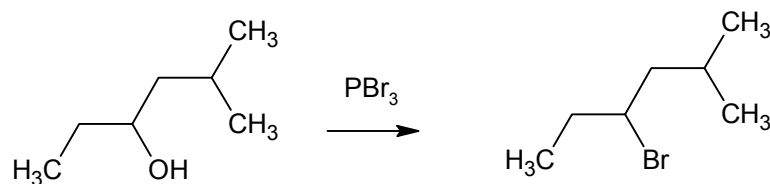


21.5

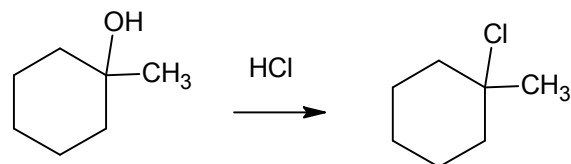


21.6

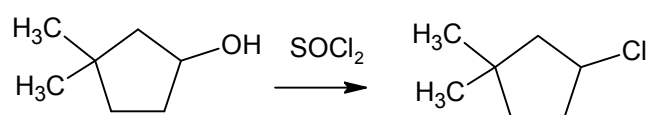
(a)



(b)

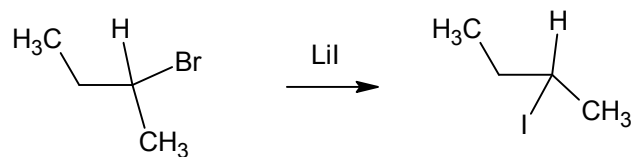


(c)

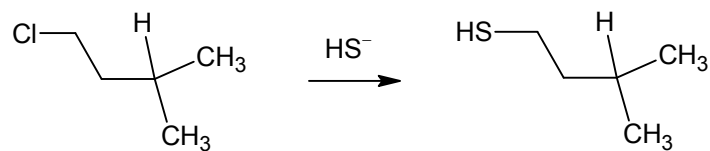


21.8

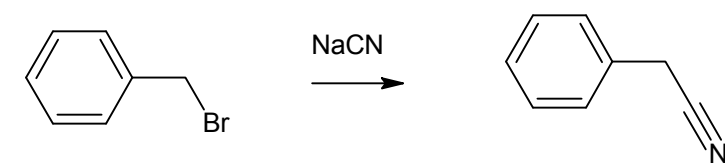
(a)



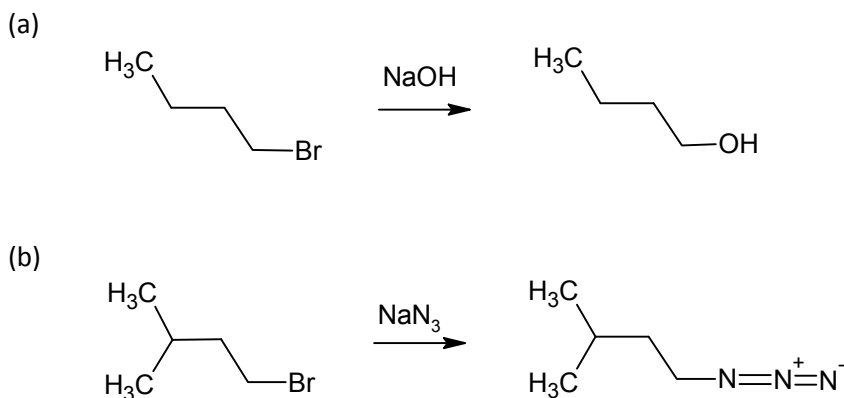
(b)



(c)

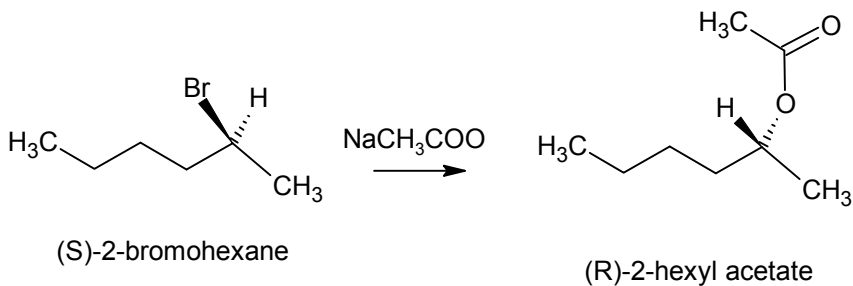


21.9

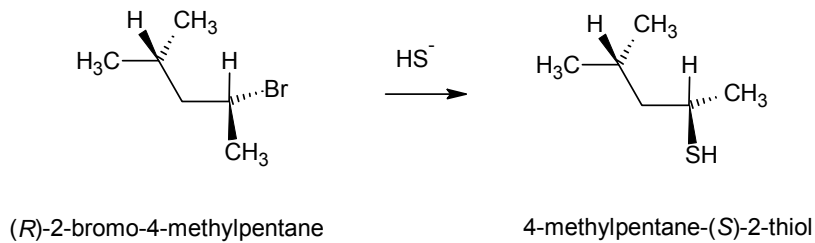


- 21.10 (a) The rate triples.
 (b) The rate increases by a factor of 4.

21.11



21.12

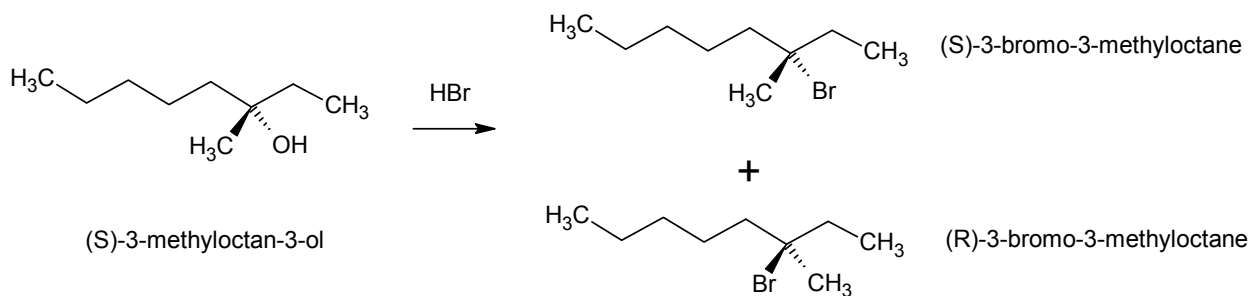


- 21.14 (a) CN^- (cyanide ion) reacts faster with $\text{CH}_3\text{CH}_2\text{CH}_2\text{Br}$
 (b) Reaction of I^- with $(\text{CH}_3)_2\text{CHCH}_2\text{Cl}$ is faster.

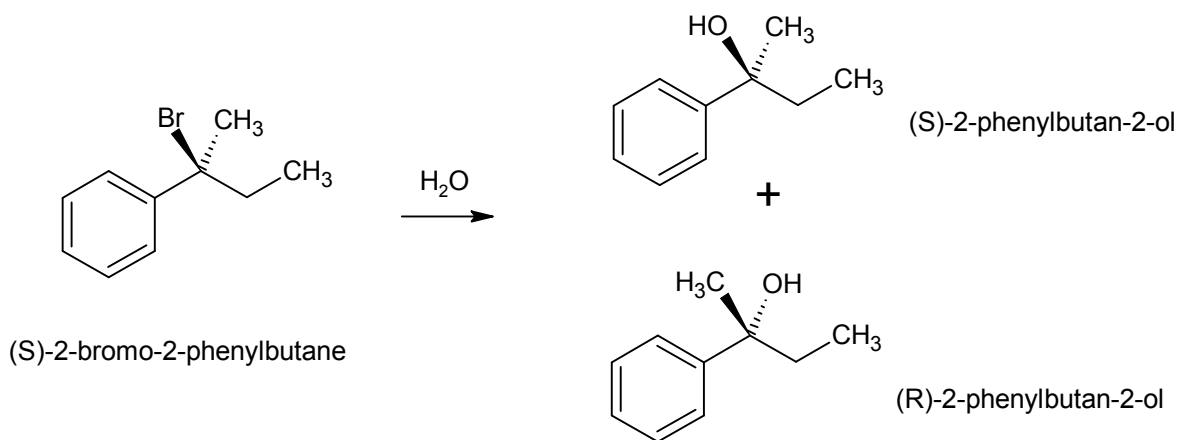
21.15 $\text{CH}_3\text{I} > \text{CH}_3\text{Br} > \text{CH}_3\text{F}$

- 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

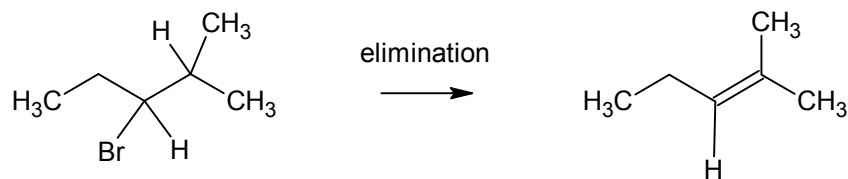


21.18

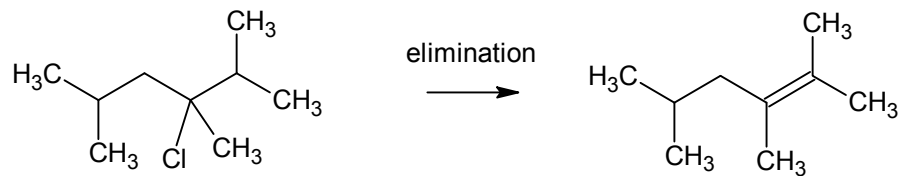


21.19

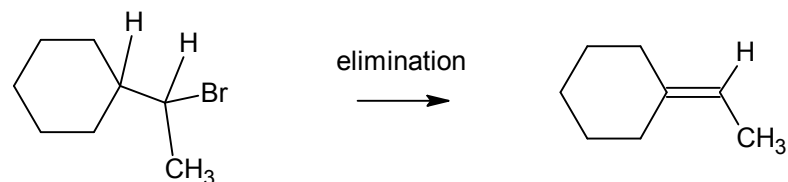
(a)



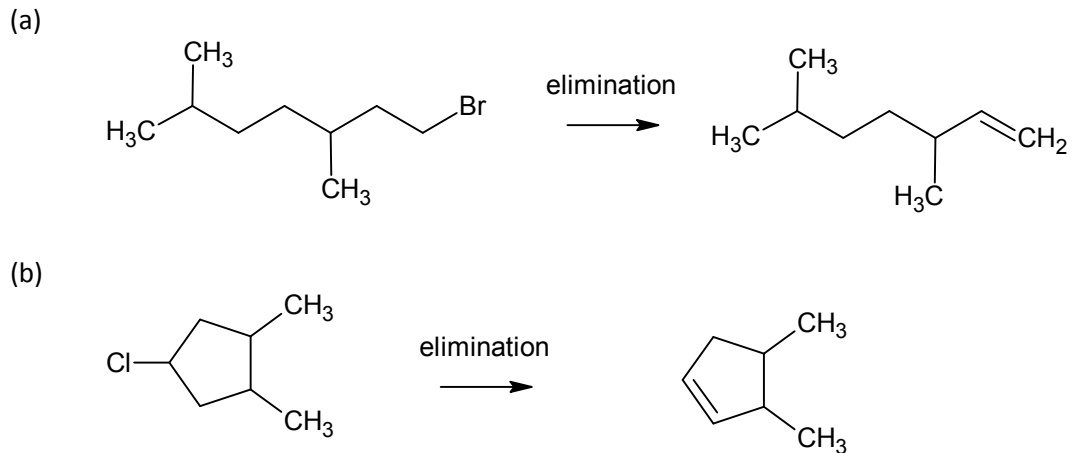
(b)



(c)



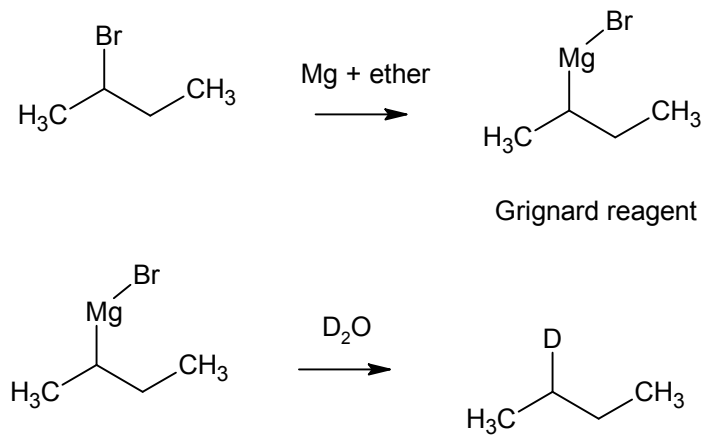
21.20



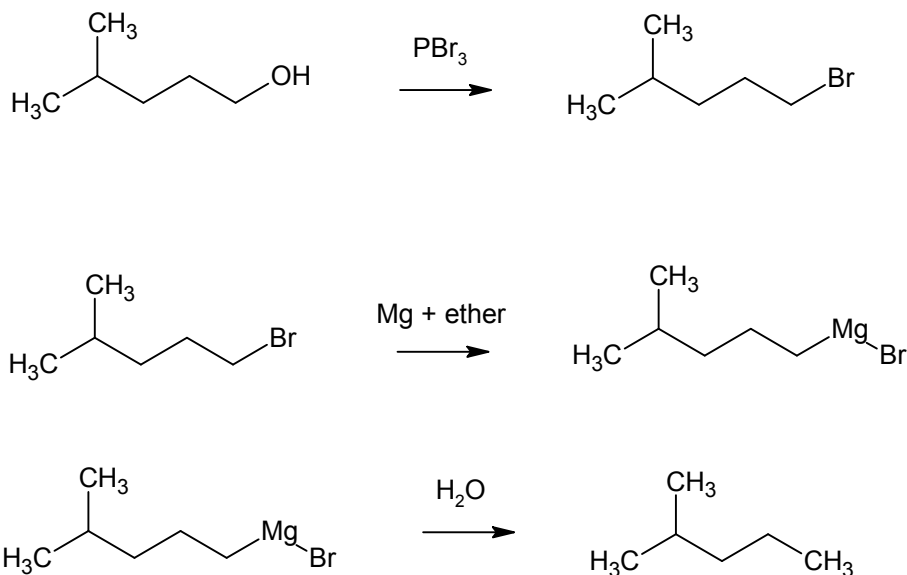
21.21 Rate of the elimination reaction triples.

- 21.22 (a) S_N2
(b) E2
(c) S_N1

21.23



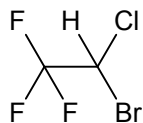
21.24



REVIEW QUESTIONS

21.25 Methyl bromide is manufactured from bromide salts recovered from seawater and methane – the principal component of natural gas. It is also naturally occurring - in the oceans, plants and soil. Methyl bromide has been used as a pesticide, or fumigant, in the agricultural industry. Because it is a potent ozone depleting substance, its use has been phased out. A large number of alternative pesticides are in use, or are being developed. For example, phosphine is used to fumigate food storage, transportation and processing facilities. Sulfuryl fluoride and 1,3-dichloropropene are two other alternative fumigants used to treat foods and forest seedlings.

21.27



2-bromo-2-chloro-1,1,1-trifluoroethane

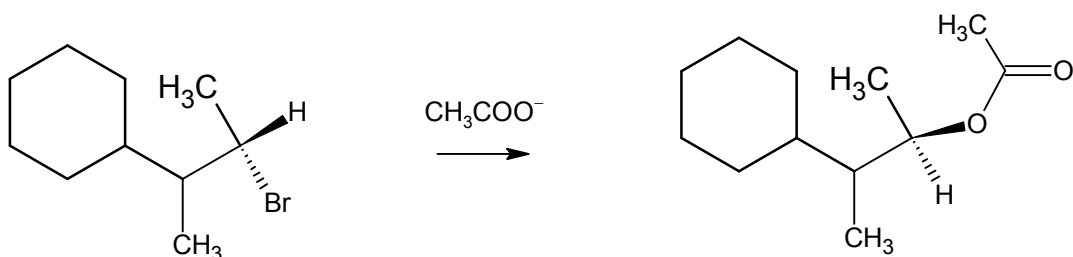
Halothane has alkyl and alkyl fluoride, chloride and bromide functionality.

21.29 More than 3800 different organohalogen compounds produced naturally by living organisms or by forest fires, volcanoes or other geothermal processes. The single largest biogenic source of these compounds is the oceans.

- 21.31 (a) Substrate structure plays an important role in determining whether an S_N1 or S_N2 substitution reaction will occur. S_N2 reactions are inhibited by bulky substituents – completely so in the case of attack at a tertiary carbon atom. This is because of the steric hindrance caused by the substituents. The S_N2 pathway is most favoured in the case of primary carbons. S_N1 reactions are favoured by substituents (unless they are electron-withdrawing) because they stabilize the carbocation intermediate of this mechanism.
- (b) A better leaving group increases the rate of both S_N1 and S_N2 reactions.

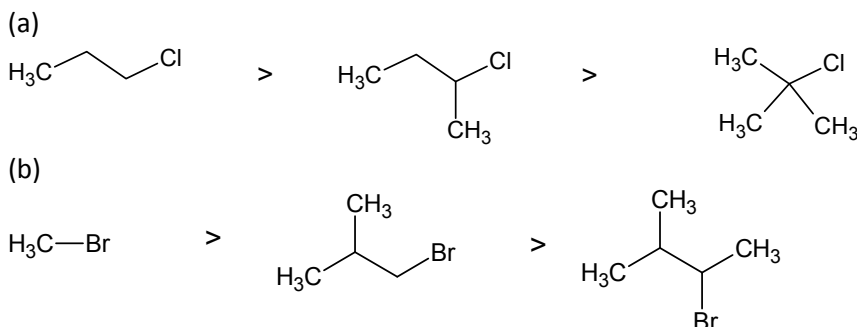
- 21.33 (a) Br^-
 (b) Cl^-
 (c) I^-

21.35



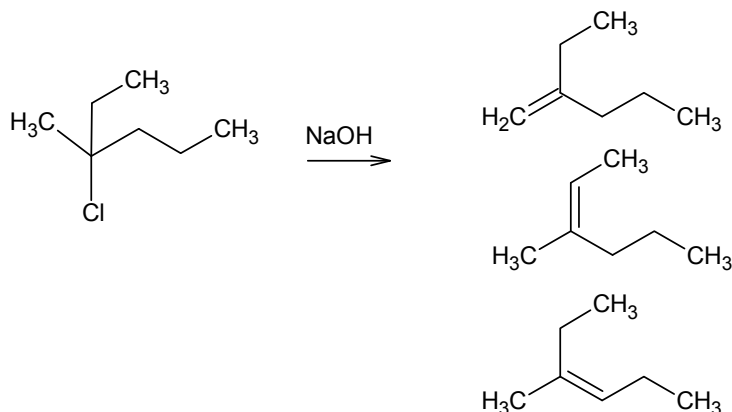
- 21.37 (a) The rate increases by the factor $3/2$.
 (b) The rate increases by the factor $3/2$.
 (c) The rate increases by the factor 6.
 (d) The rate increases
 (e) The concentration of all species is halved. The rate of reaction decreases 4 fold.

21.39



- 21.41 (a) This is an S_N2 reaction at a tertiary carbon atom. It is strongly hindered and would simply be too slow.
- (b) This is an S_N2 reaction at a primary carbon – this is good. The only trouble is that hydroxide is a bad leaving group.
- (c) This is an elimination reaction at a tertiary carbon – this is good. However, because HBr is the acid used to dehydrate the alcohol, the alkene product is subject to addition of HBr.

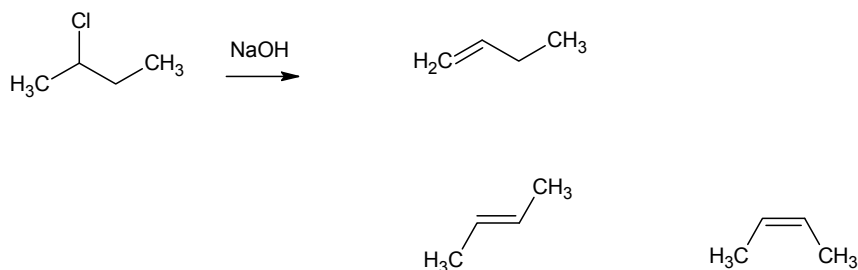
21.43



- 21.45 (a) The rate stays the same.
(b) The rate increases by a factor of 9.

- 21.47 (a) E2
(b) S_N1

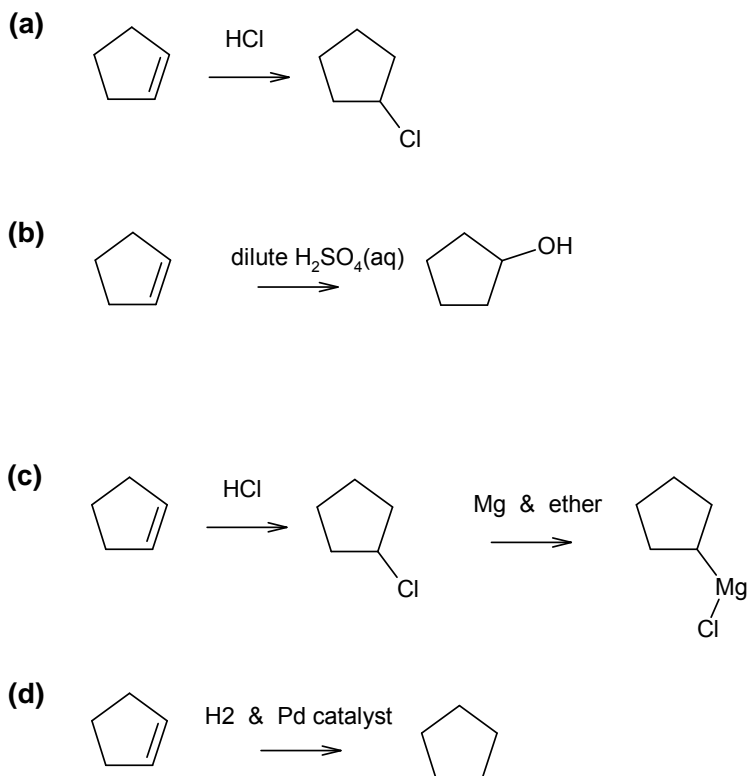
21.49



SUMMARY AND CONCEPTUAL QUESTIONS

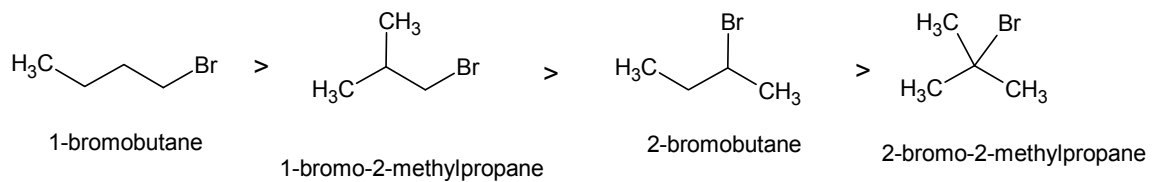
- 21.51 The oceans have high concentrations of halide ions. The oceans are also the likely origin of all life, and are still now brimming with life. It is natural that organohalogen compounds would be formed there, and formed there first. Moreover – and this is likely why the oceans have been so crucial to life – the oceans provide a solvent supporting vastly more chemistry than is possible of the land surface.

21.53

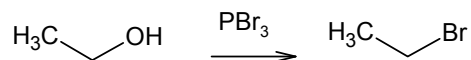
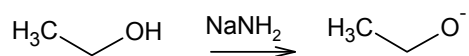


- 21.55 (a) 1-iodopropane
 (b) butanenitrile
 (c) 1-propanol
 (d) Upon reaction with Mg in ether, we get propylmagnesium bromide. Subsequent reaction with water produces propane.
 (e) methyl propyl ether

21.57



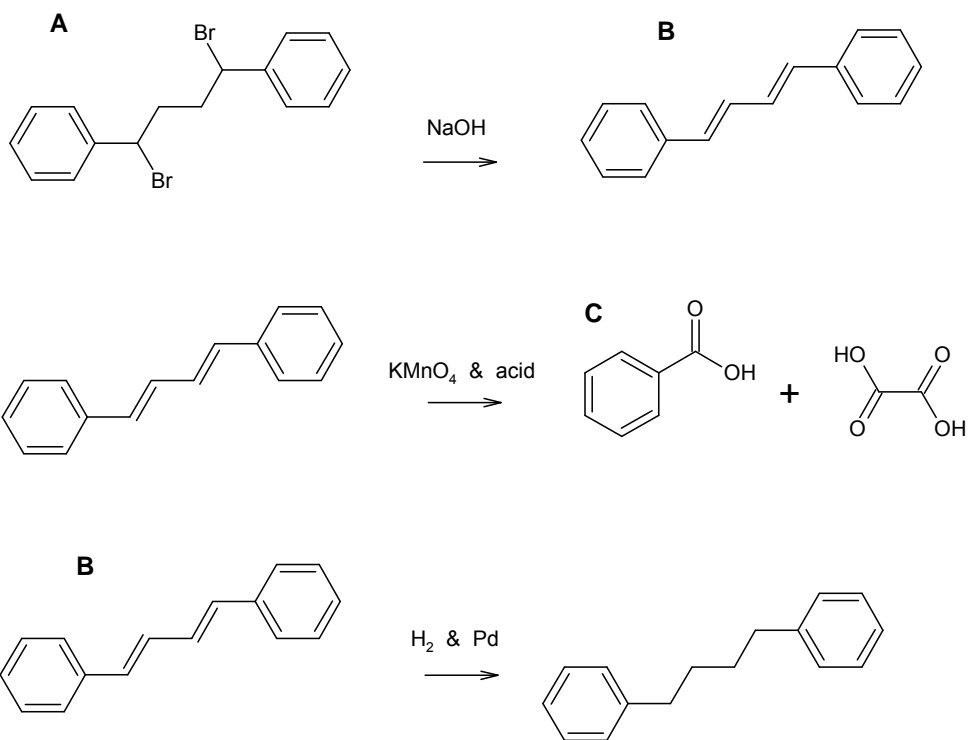
21.59



21.61 E2 elimination reactions yield non-Zaitsev products because elimination is favoured at the least hindered proton vicinal to bromine (on the carbon next to the bromo carbon). E2 elimination follows a concerted mechanism requiring a base to abstract the proton as the bromide leaves.

21.63 Reaction of HBr with (*R*)-3-methylhexan-3-ol yields (\pm)-3-bromo-3-methylhexane, because it is an $\text{S}_{\text{N}}1$ substitution. Once the carbocation is formed, the stereochemistry of the starting material is lost. The (*R*) and (*S*) products are equally likely.

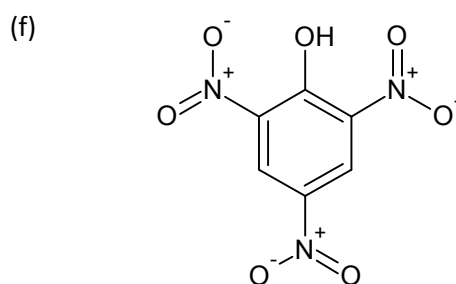
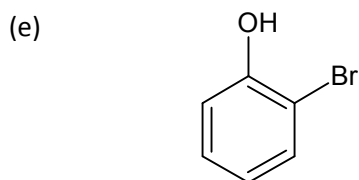
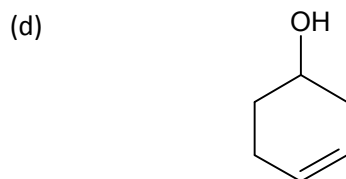
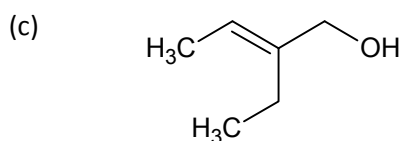
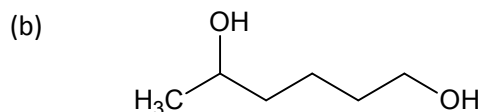
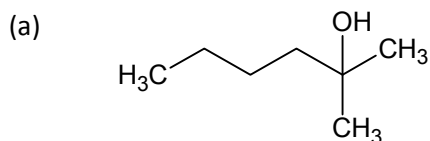
21.65



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

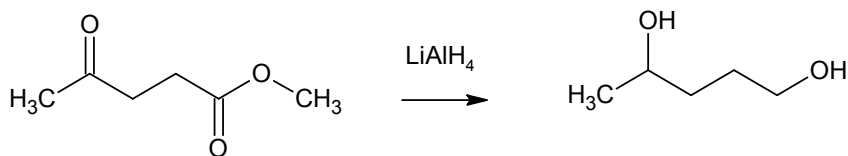
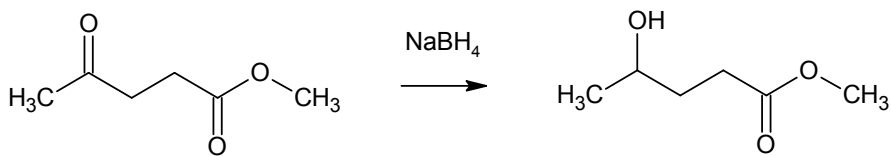


- 22.4 (a) di(2-propyl) ether a.k.a. diisopropyl ether
(b) cyclopentyl propyl ether
(c) 4-bromophenyl methyl ether
(d) ethyl 2-methyl-1-propyl ether

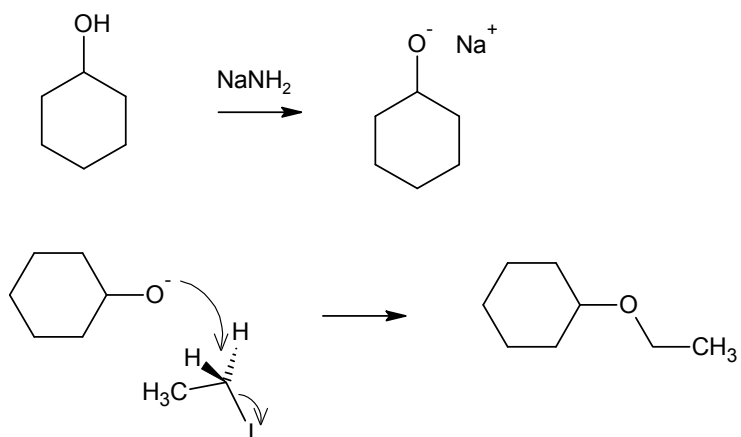
22.5 O–H stretch: 3320 cm^{-1} (strong, broad)
aromatic C–H stretches: $3090, 3070$ and 3010 cm^{-1} (sharp peaks).
alkyl C–H stretches: 2950 and 2890 cm^{-1} (broad).
C–O stretches: 1020 cm^{-1} (strong, somewhat broad).
C–C stretches of the benzene ring: 1500 to 1370 cm^{-1} (three sharp ones)
benzene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

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

22.7



22.8

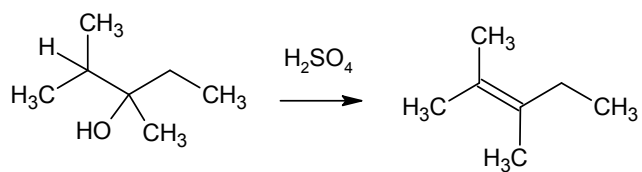


We cannot make cyclohexyl ethyl ether by first forming sodium ethoxide, then reacting it with cyclohexyl iodide.

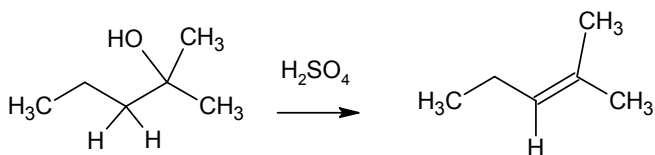
22.9 bromoethane > chloroethane > 2-bromopropane > 2-chloro-2-methylpropane

22.10

(a)

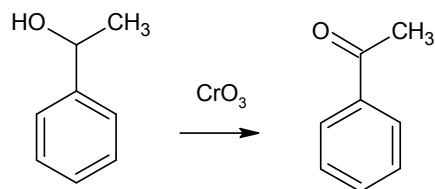


(b)

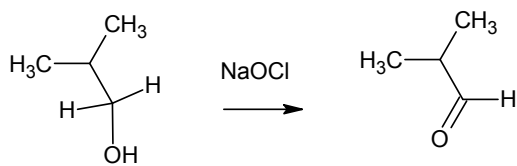


22.11

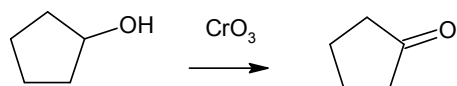
(a)



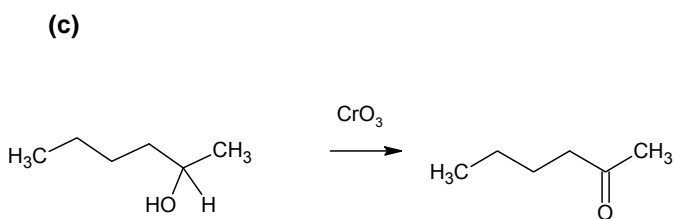
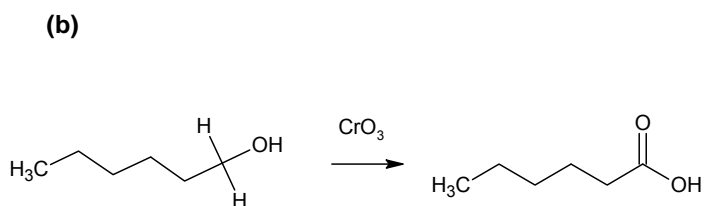
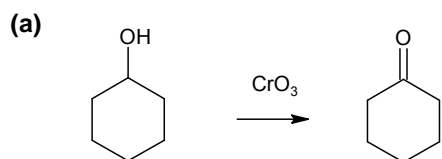
(b)



(c)

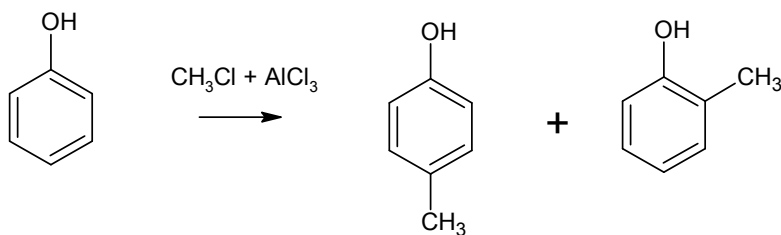
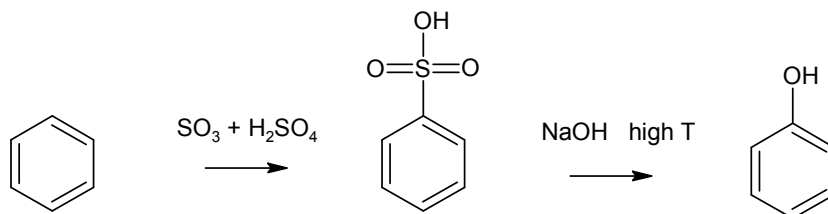


22.12

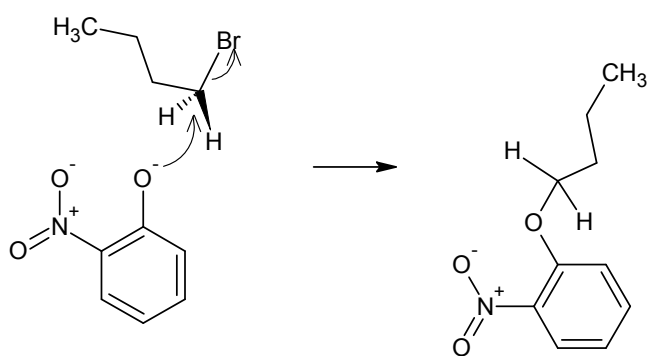
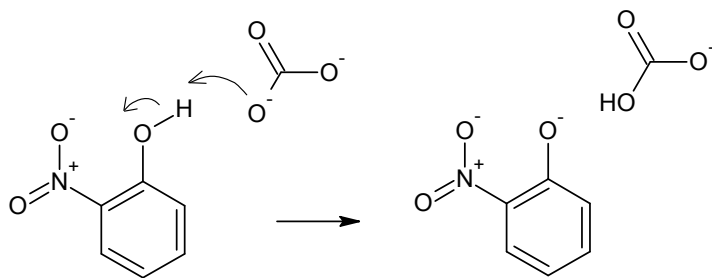


22.13 Oxidation of the alcohols in Exercise 22.12 with pyridinium chlorochromate (PCC) gives the same products in parts (a) and (b), and the aldehyde in part (b).

22.14



22.15

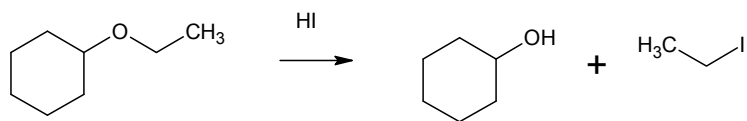


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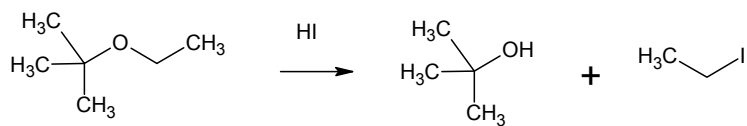
(a)



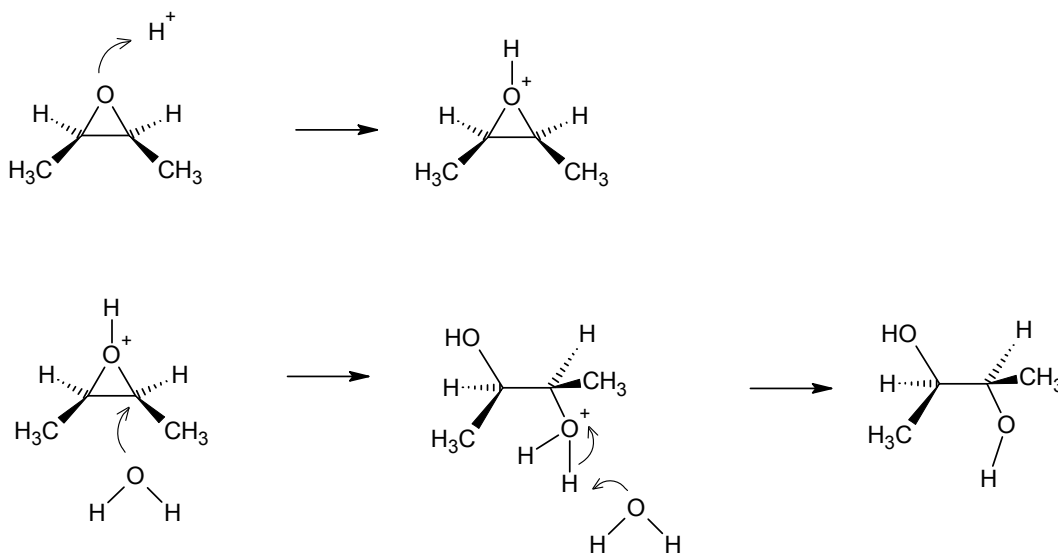
(b)



(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

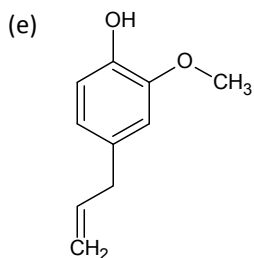
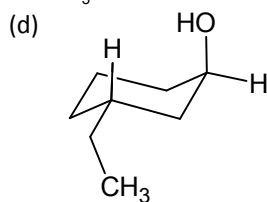
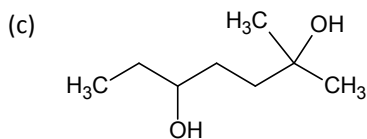
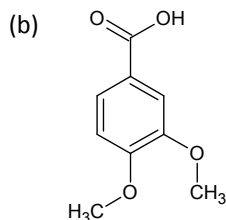
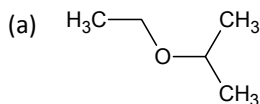
- 22.20 To make 2-butene-1-thiol from 2-butene-1-ol:
 You could treat 2-buten-1-ol with PBr_3 to make 1-bromobut-2-ene.
 1-bromobut-2-ene is then treated with NaSH to make 2-butene-1-thiol.

To make 2-butene-1-thiol from methyl but-2-enoate:
 First reduce methyl but-2-enoate with LiAlH_4 to get methanol and 2-butene-1-ol.
 2-butene-1-ol can then be processed as above.

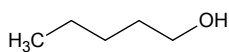
REVIEW QUESTIONS

- 22.21 The hydroxyl groups on the outside of cyclodextrins makes them soluble in water, allowing the drug encapsulated by the cyclodextrin to be delivered throughout the body.
- 22.23 The article describes the use of cyclodextrins to form aggregates and give rise to dispersed systems (i.e. not solutions) with more complex structures for dispersed drug delivery. Such dispersed structure include emulsions, micro and nano capsules and spheres, as well as liposomes and niosomes.
Sublingual literally means “under the tongue”, referring to the administration of a drug through dissolution and absorption of a tablet held under the tongue. In the context of this case study, sublingual might be used as a metaphor meaning “under the ability-to-detect (i.e. taste) by the tongue”.
- 22.25 Some types of wounds produce unpleasant odours. Cyclodextrins have been used to treat this problem by encapsulating odour molecules. This is in addition to their use in increasing bioavailability of antibiotics to the wound.

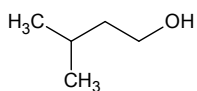
22.27



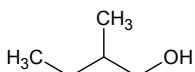
22.29



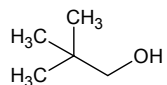
1-pentanol



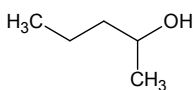
3-methyl-1-butanol
or 3-methylbutan-1-ol



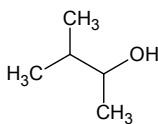
2-methyl-1-butanol
or 2-methylbutan-1-ol



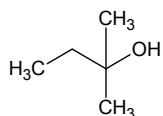
2,2-dimethyl-1-propanol
or 2,2-dimethylpropan-1-ol



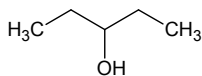
2-pentanol



3-methyl-2-butanol
or 3-methylbutan-2-ol

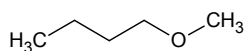


2-methyl-2-butanol
or 2-methylbutan-2-ol

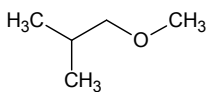


3-pentanol

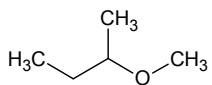
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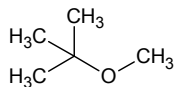
1-butyl methyl ether



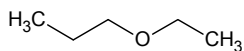
2-methylpropyl methyl ether



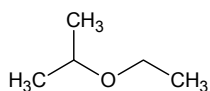
2-butyl methyl ether



tert-butyl methyl ether



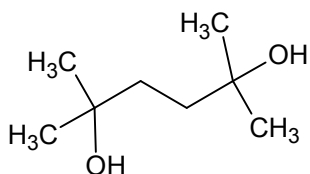
1-propyl ethyl ether



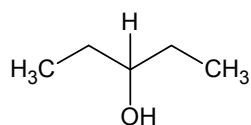
isopropyl ethyl ether

- 22.35 (a) singlet
 (b) doublet
 (c) triplet
 (d) doublet
 (e) doublet
 (f) singlet

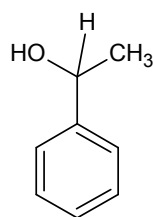
22.37



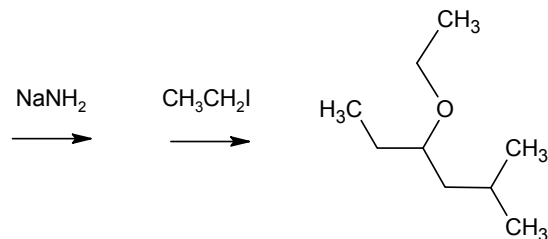
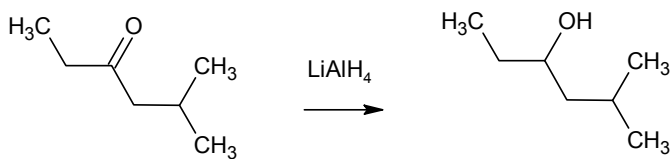
22.39 (a)



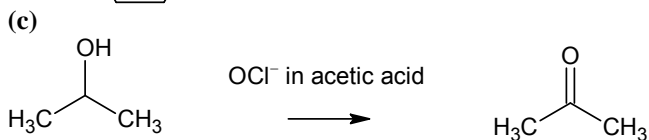
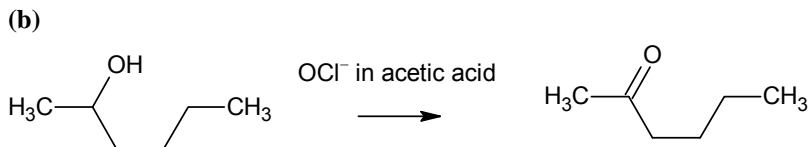
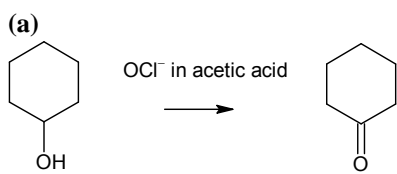
(b)



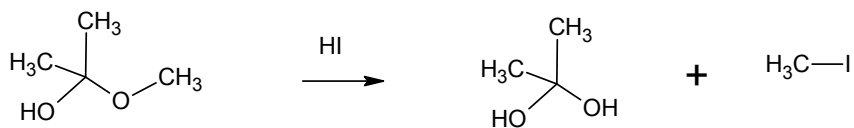
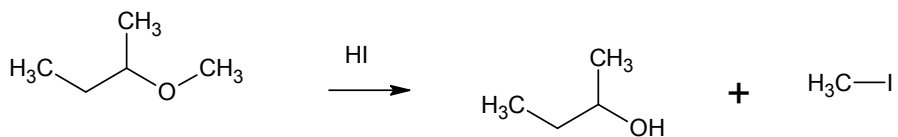
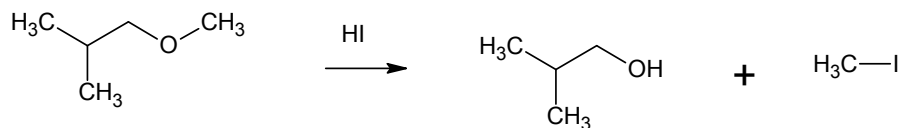
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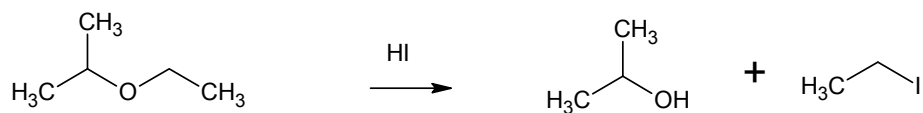
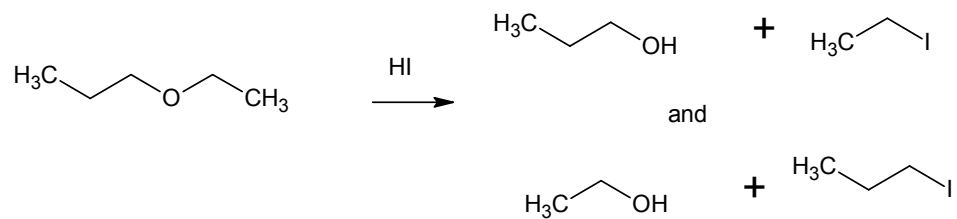


22.43

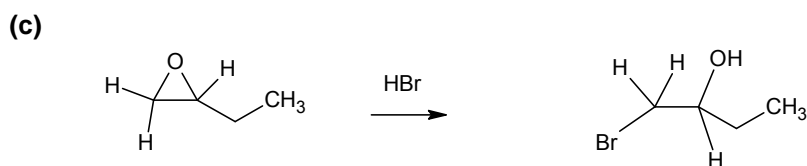
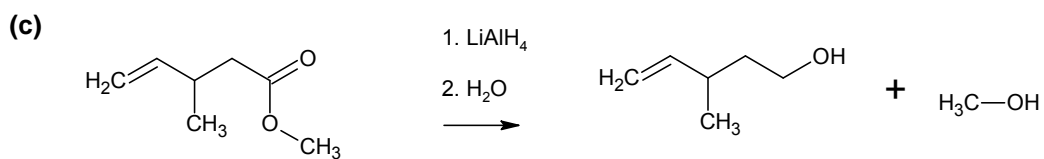
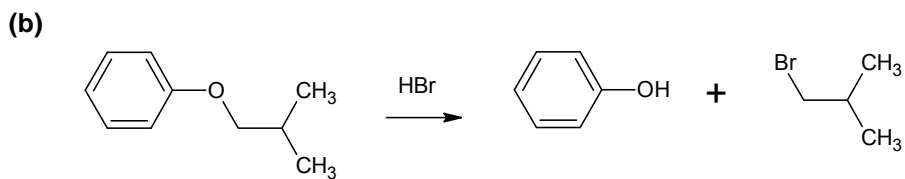
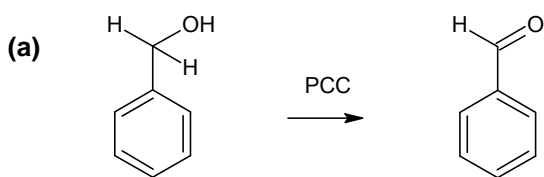


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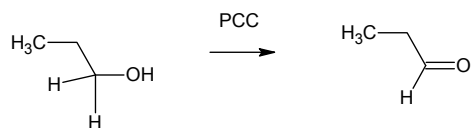


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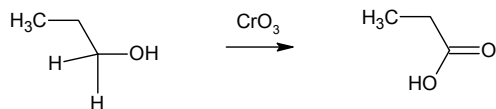


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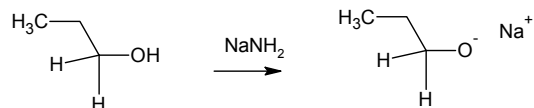
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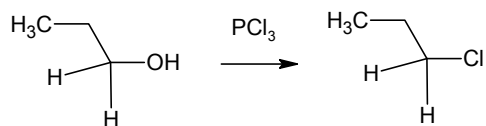
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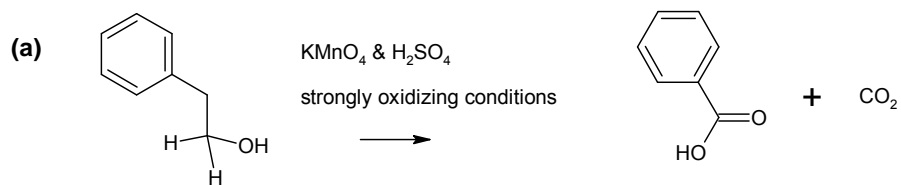
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(d)

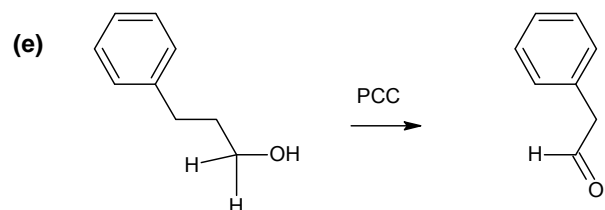
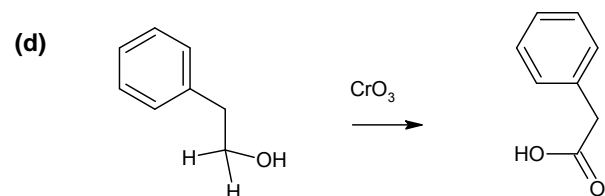
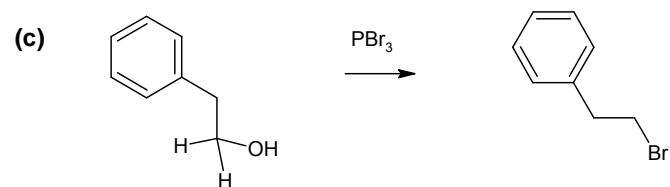
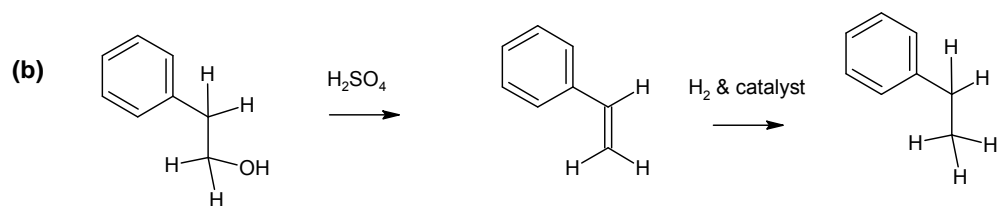


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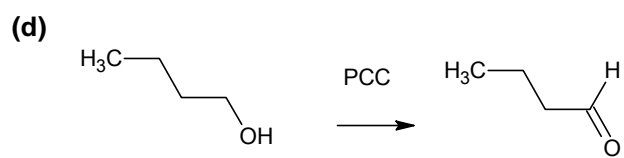
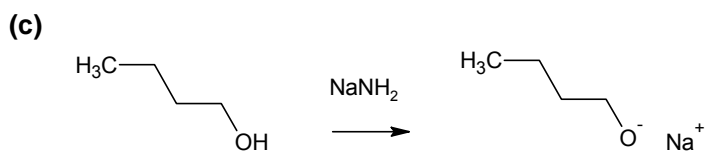
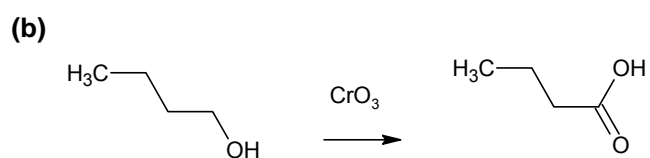
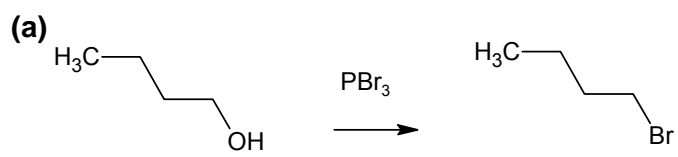


oxidation takes place at the benzylic position - in addition to the alcohol

intermediates are stabilized by the neighboring phenyl ring

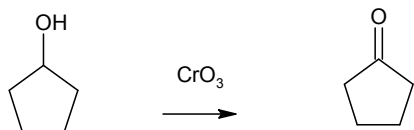


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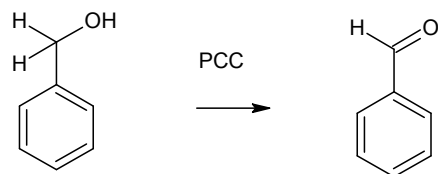


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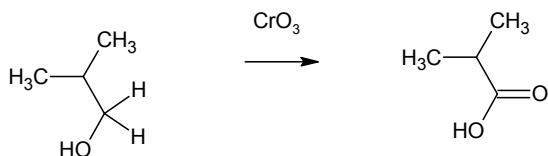
(a)



(b)

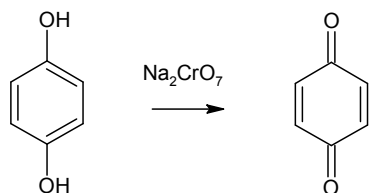


(c)

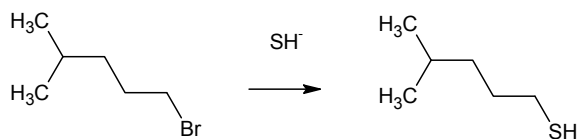


22.57

(a)



(b)



(c)



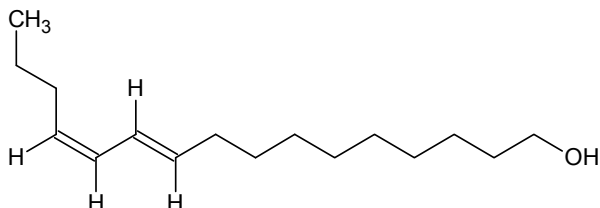
22.59 Acetic acid, pentane-2,4-dione and phenol will all react, essentially to completion, with NaOH.

22.61 Only acetic acid will react with NaHCO_3 .

- 22.63 The O atoms of the crown ether will coordinate a cation, holding it at one end of the molecule (the crown). To bind Cs^+ , one could prepare a larger crown ether by adding $-\text{OCH}_2\text{CH}_2\text{O}-$ units.

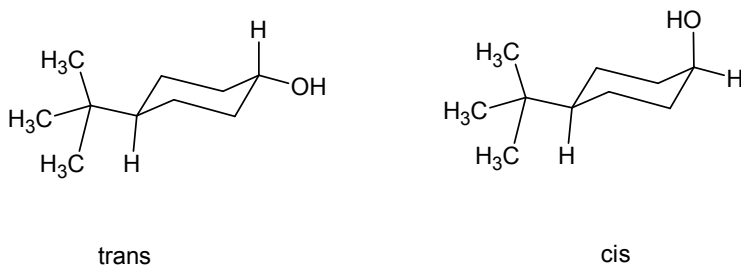
SUMMARY AND CONCEPTUAL QUESTIONS

22.65



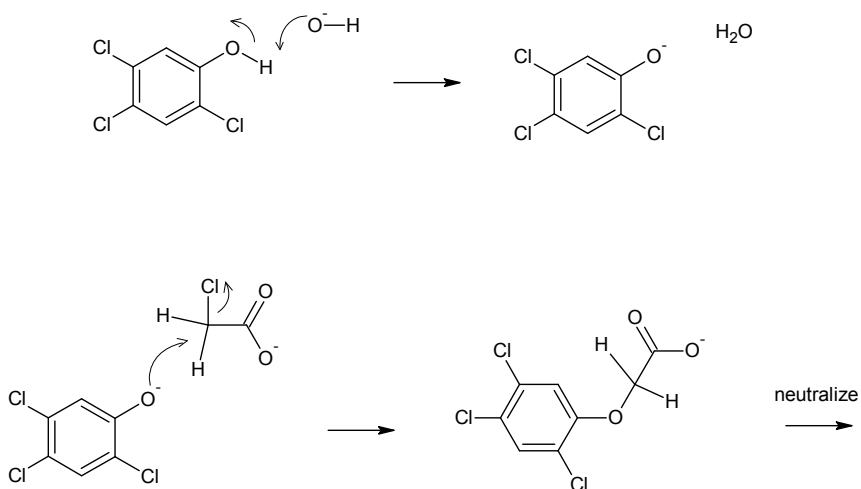
- 22.67 Williamson ether synthesis cannot be used to prepare diphenyl ether because one of the two reagents in Williamson ether synthesis is a halide which undergoes $\text{S}_{\text{N}}2$ substitution by (in this case) phenoxide. The trouble is that phenyl halides are not amenable to $\text{S}_{\text{N}}2$ substitution. Nucleophilic attack will not occur at an aromatic carbon atom.

22.69

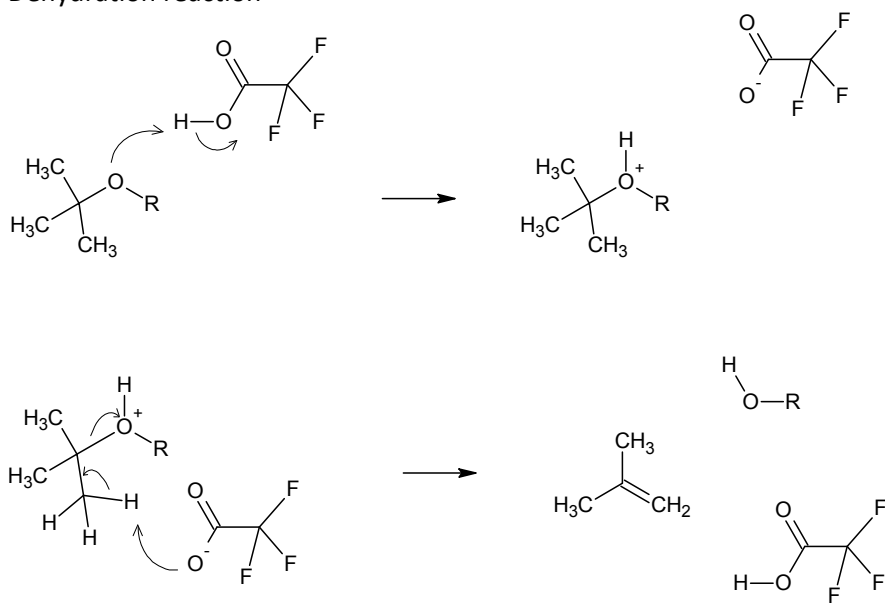


The *cis* isomer will oxidize faster with CrO_3 – the hydroxyl group is axial in this isomer.

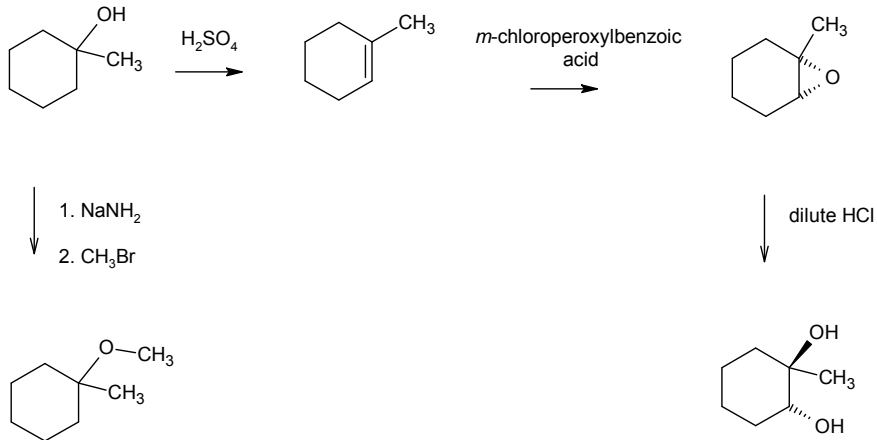
22.71



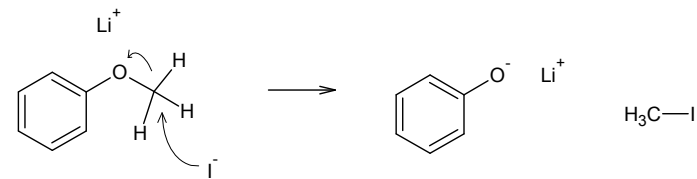
22.73 Dehydration reaction



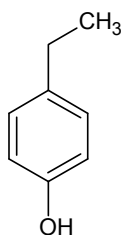
22.75



22.77



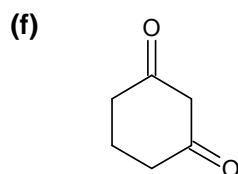
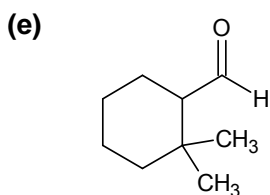
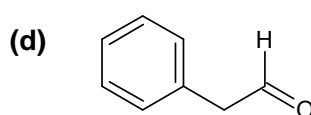
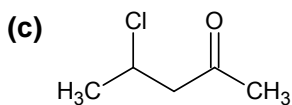
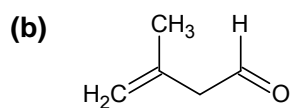
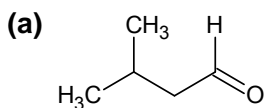
22.79



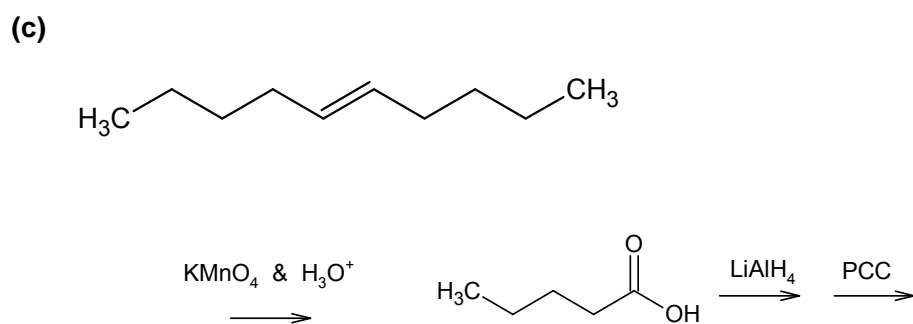
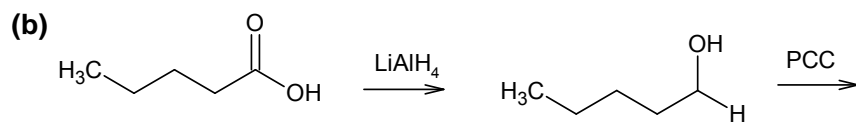
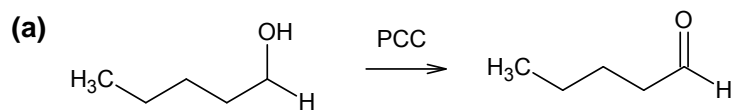
Chapter 23

- 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

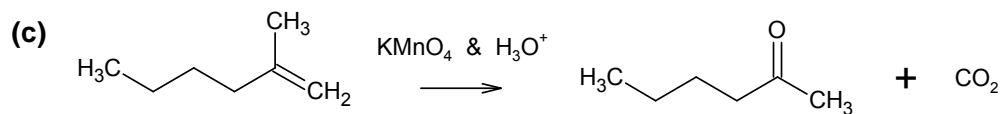
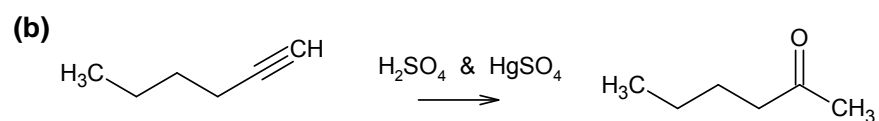
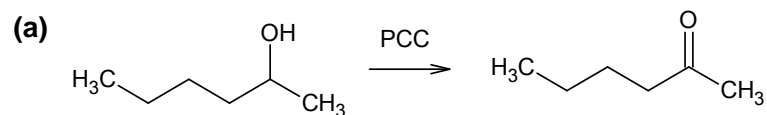
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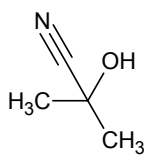
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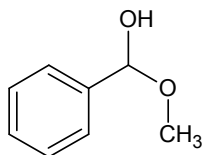
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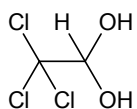
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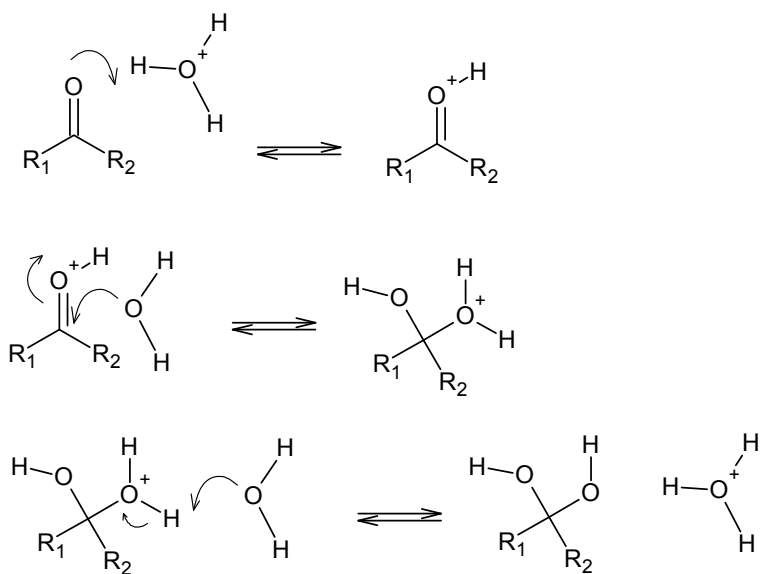
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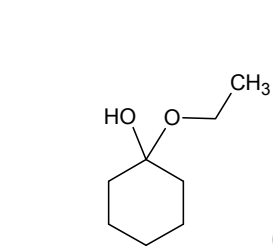
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23.9

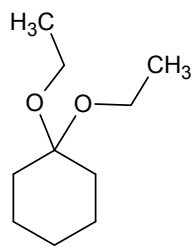


23.10



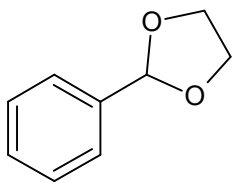
ethanol)

(1 equivalent of ethanol)



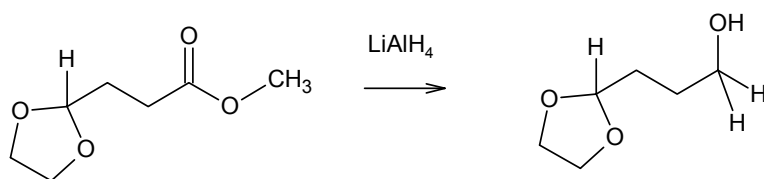
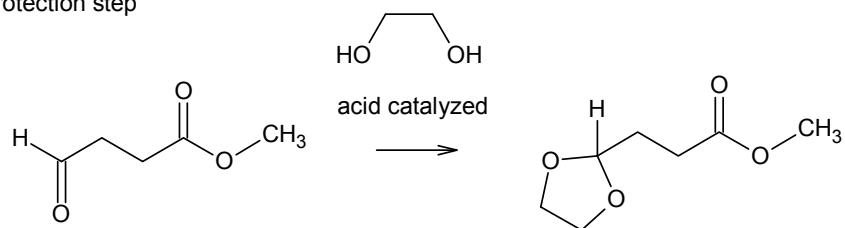
(2 equivalents of

23.11

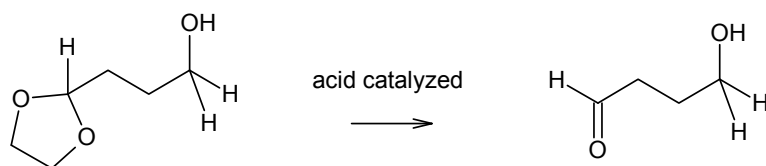


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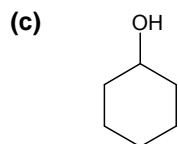
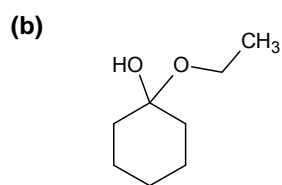
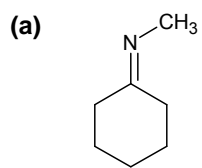
protection step



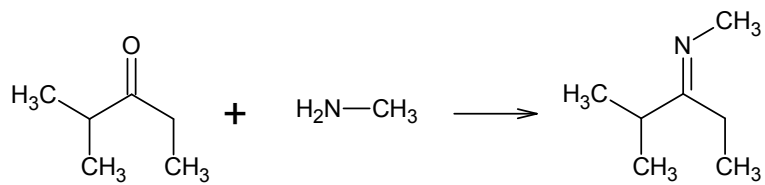
deprotection step



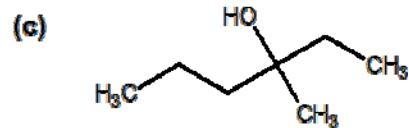
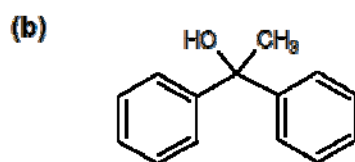
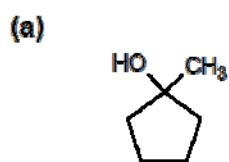
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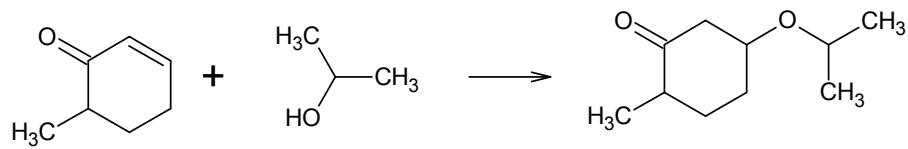
23.14



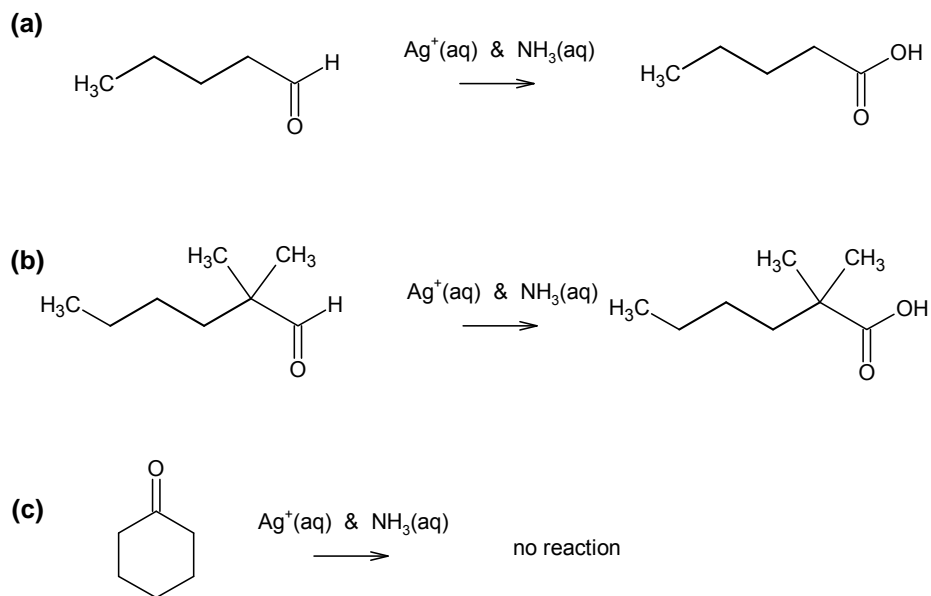
23.15



23.16



23.17

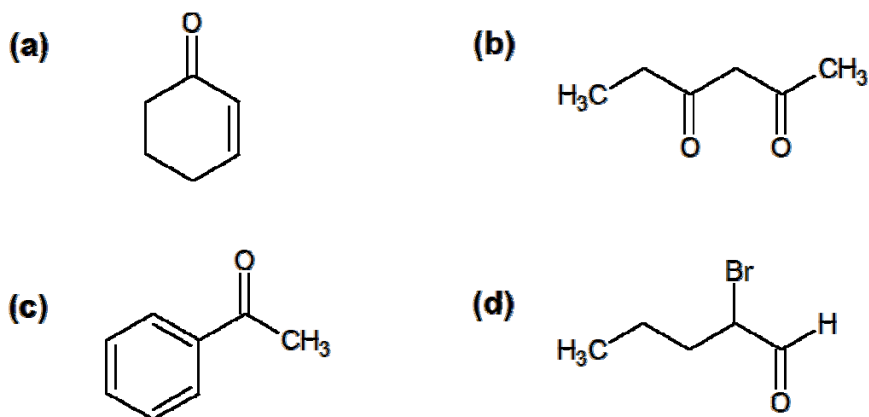


REVIEW QUESTIONS

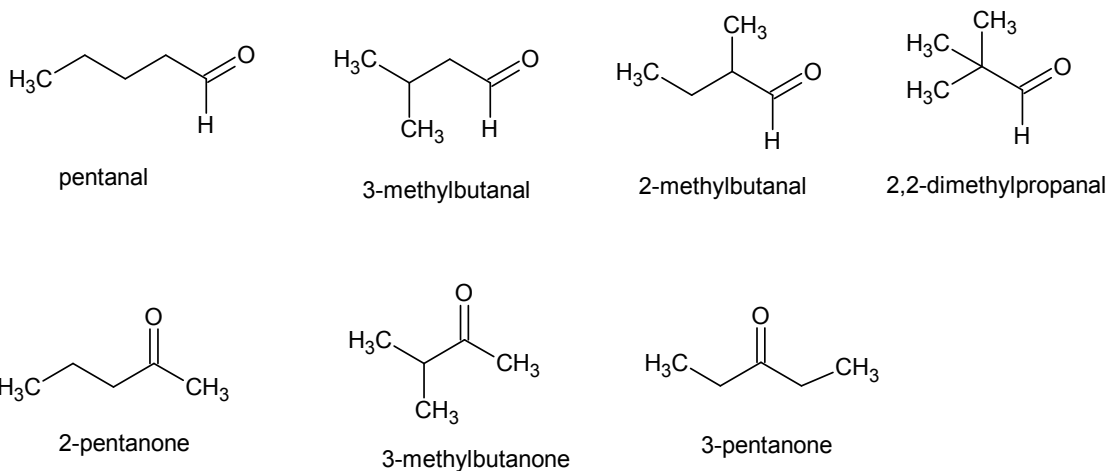
23.19 Functionalities exhibited by pheromones include alkyl chains and rings, alcohol, aldehyde, ester – especially acetate, alkene, ketone, and ether – especially epoxide – groups.

- 23.21 (a) alkyl & amide (specifically, acetamide)
 (b) alkyl & ester (specifically, acetate)
 (c) alkyl, aromatic, aldehyde & carboxylic acid

23.23

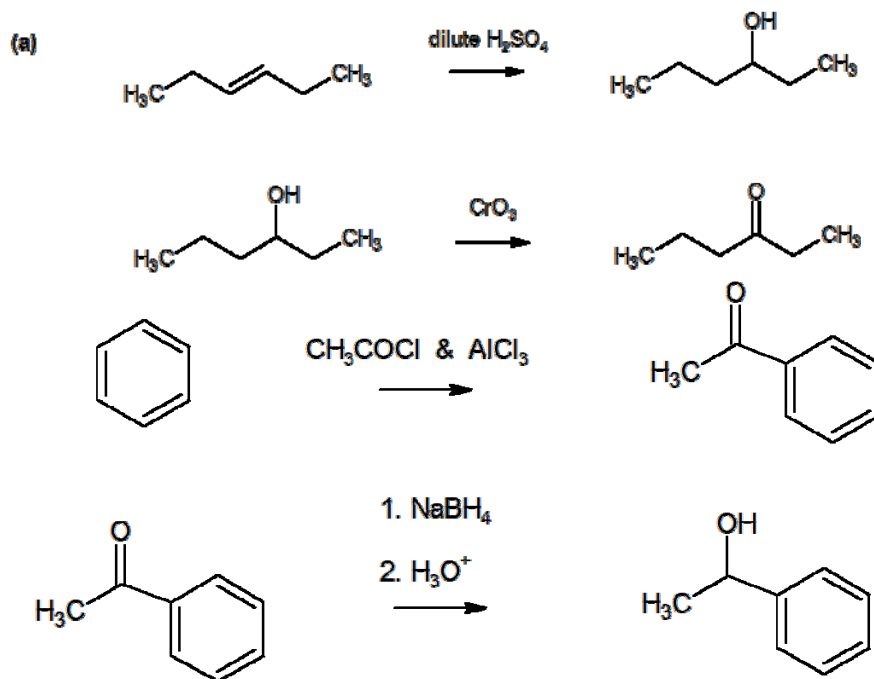


23.25

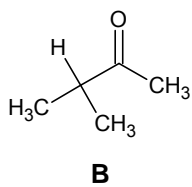


- 23.27 (a) 3-methylcyclohex-3-enone
 (b) 2,3-dihydroxypropanal
 (c) 5-isopropyl-2-methylcyclohex-2-enone
 (d) 2-methylpentan-3-one
 (e) 3-hydroxybutanal
 (f) 1,4-benzenedicarbaldehyde

23.29

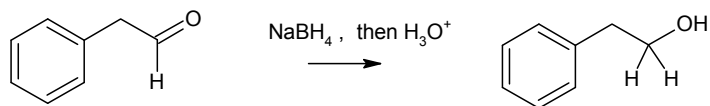


23.31

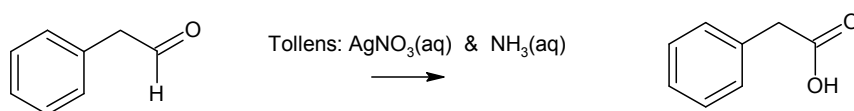


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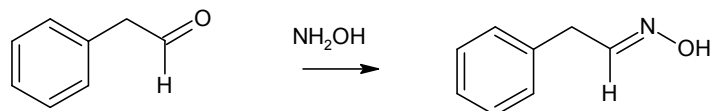
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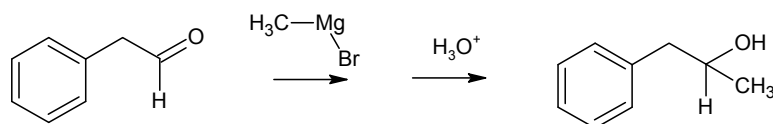
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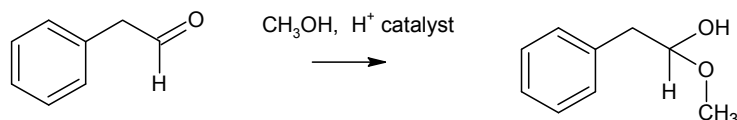
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(d)

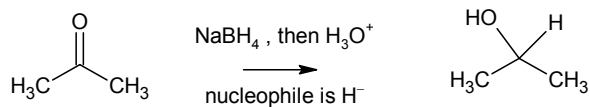


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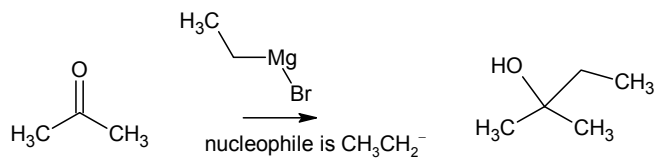


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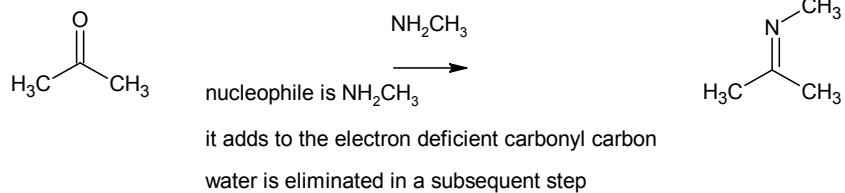
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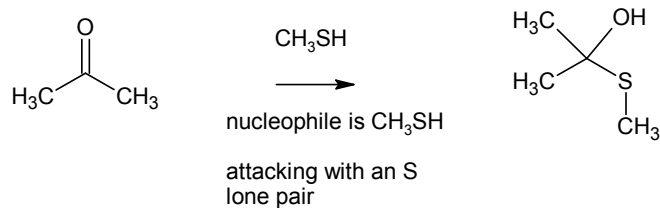
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(c)

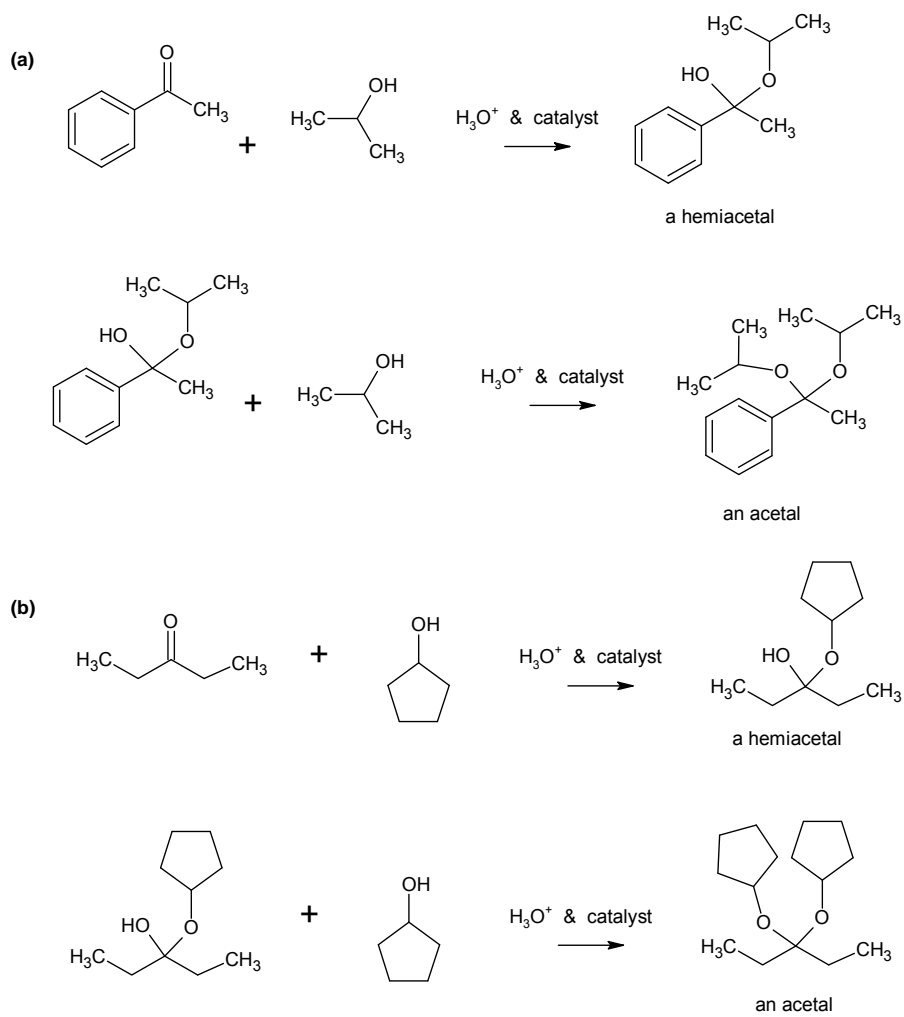


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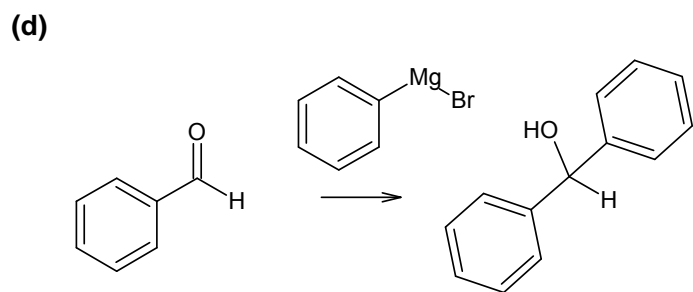
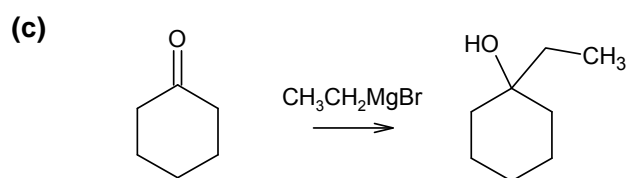
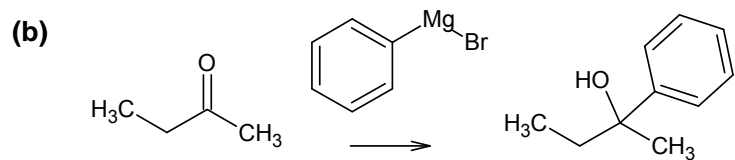
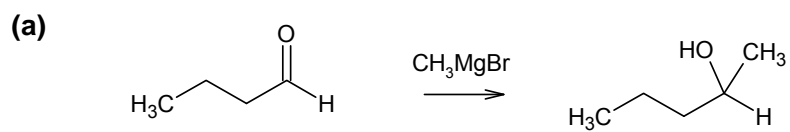


23.37 The reaction of phenylmagnesium bromide with butan-2-one produces a racemic mixture of 2-phenylbutan-2-ol.

23.39

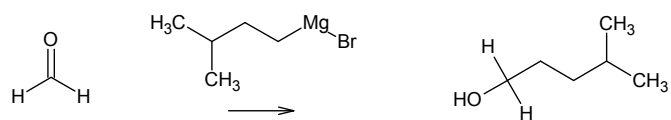


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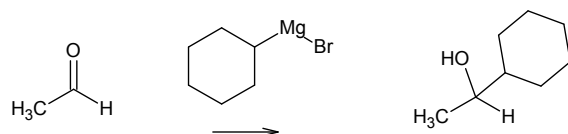
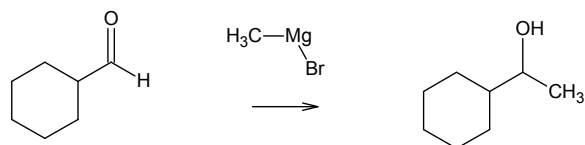


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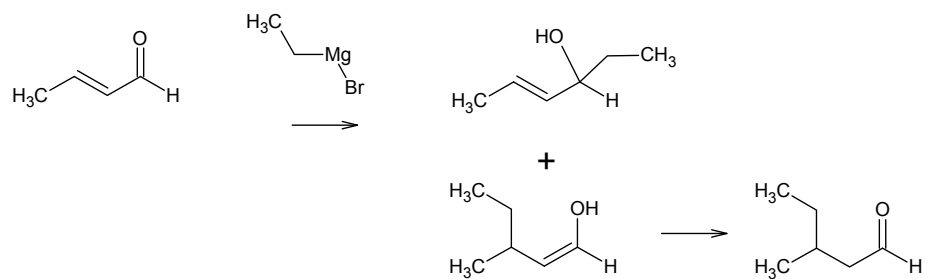
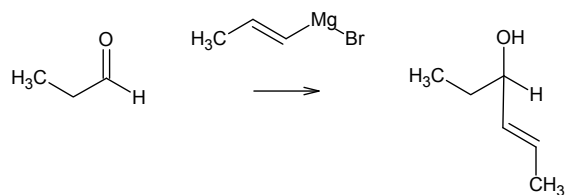
(a)



(b)



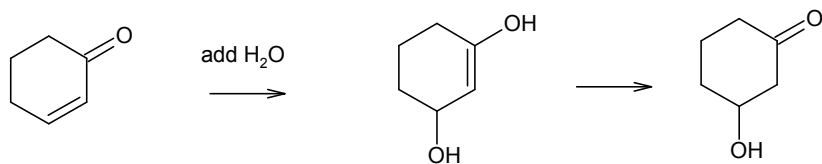
(c)



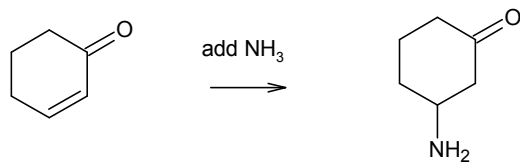
this choice leads to an additional aldehyde product which could then react with the Grignard reagent to form yet additional products

23.49

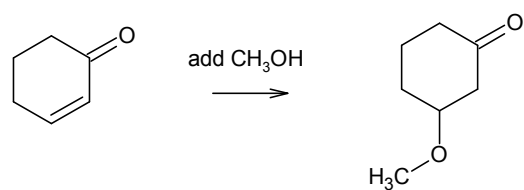
(a)



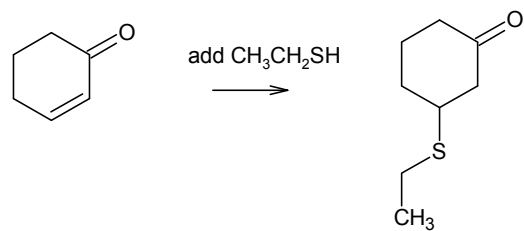
(b)



(c)



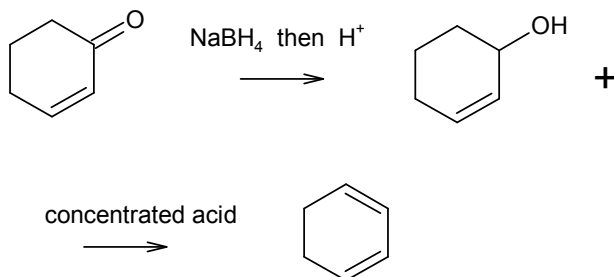
(d)



SUMMARY AND CONCEPTUAL QUESTIONS

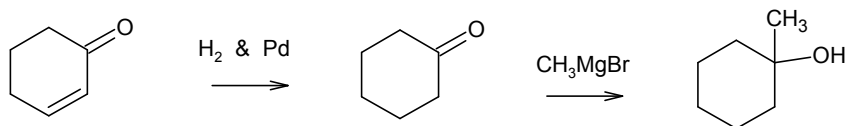
23.51

(a)

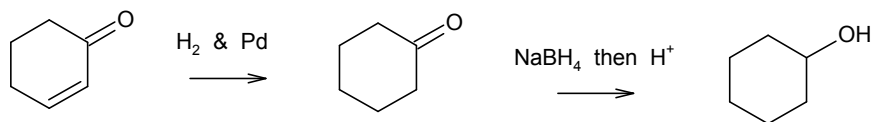


1,4 addition product
separation is necessary
chromatography is the likely choice
distillation would be difficult on
account of the similarity of the two
products

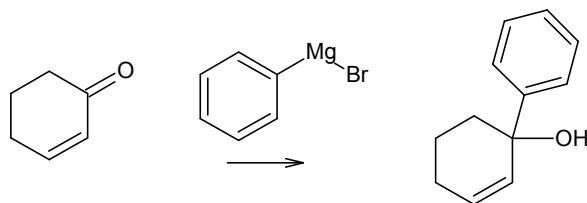
(b)



(c)



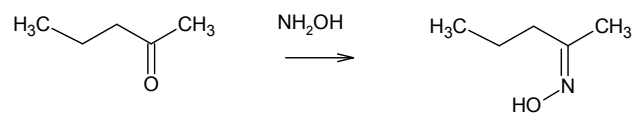
(d)



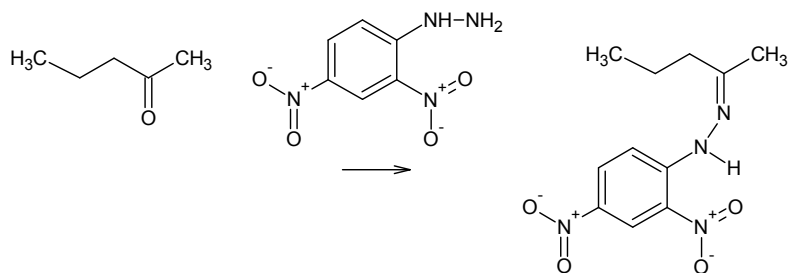
there may be a conjugate addition
product in addition to this one
the conjugate addition product can
add another equivalent of
phenylmagnesium bromide

23.53

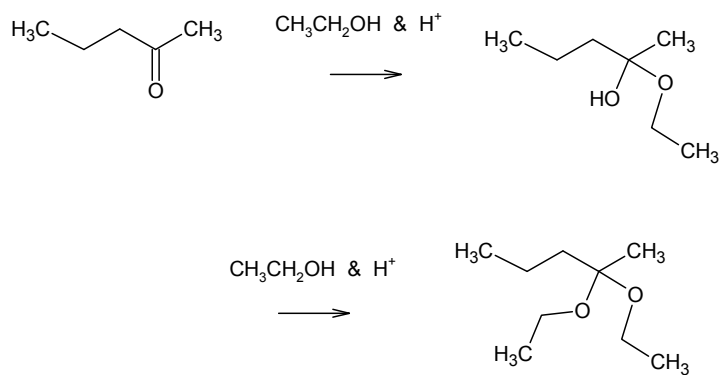
(a)



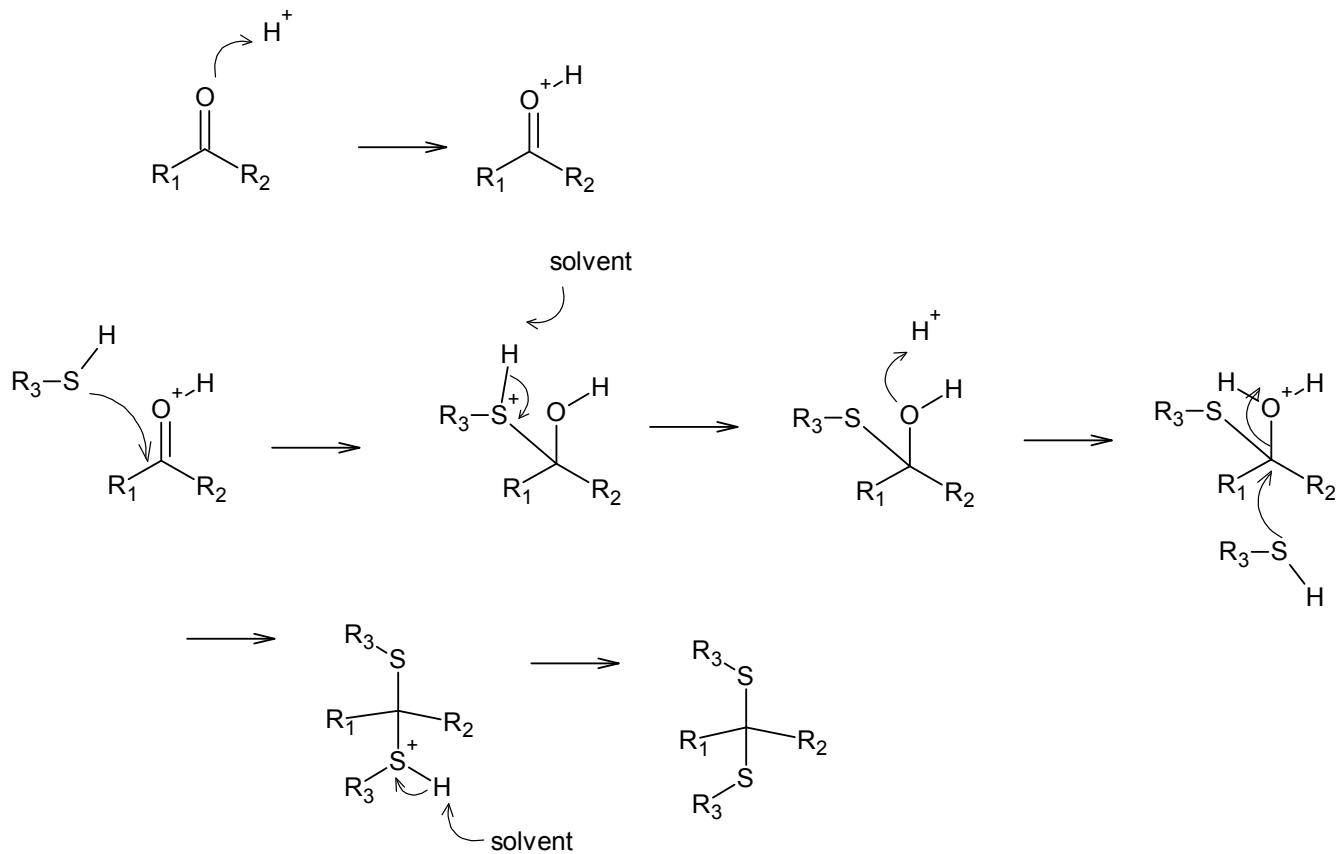
(b)



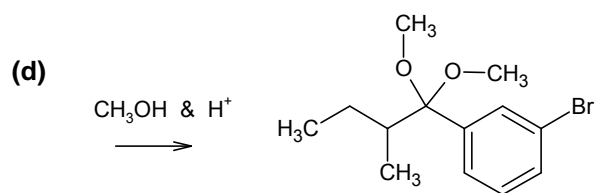
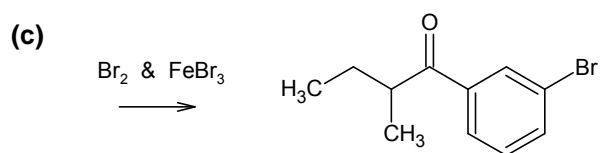
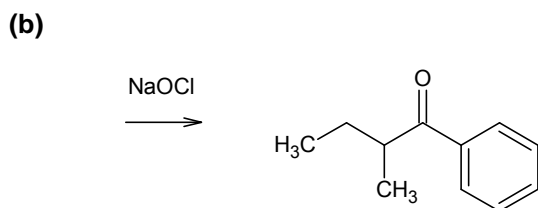
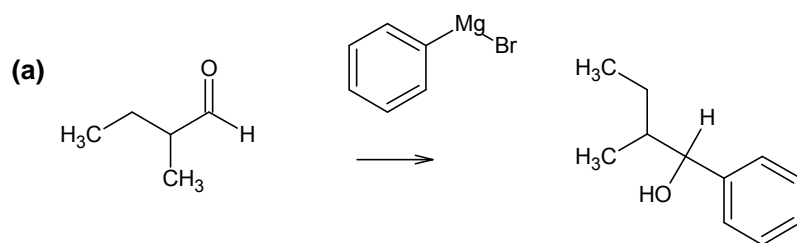
(c)



23.55 Thioacetal formation is analogous to acetal formation. In this case, it is thioals adding to a ketone rather than alcohols adding to a ketone.



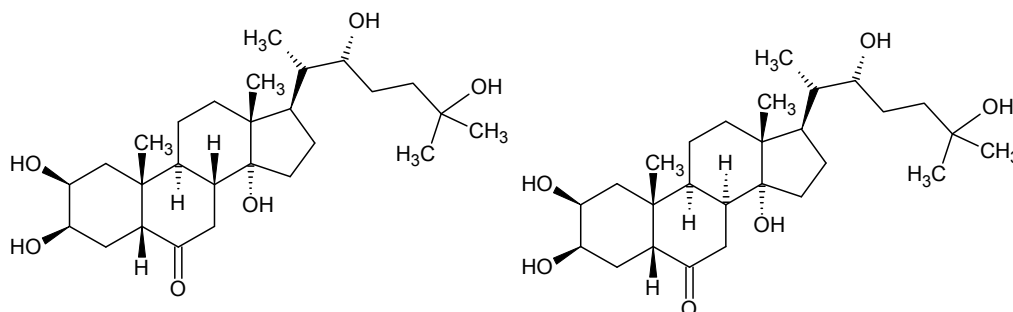
25.57



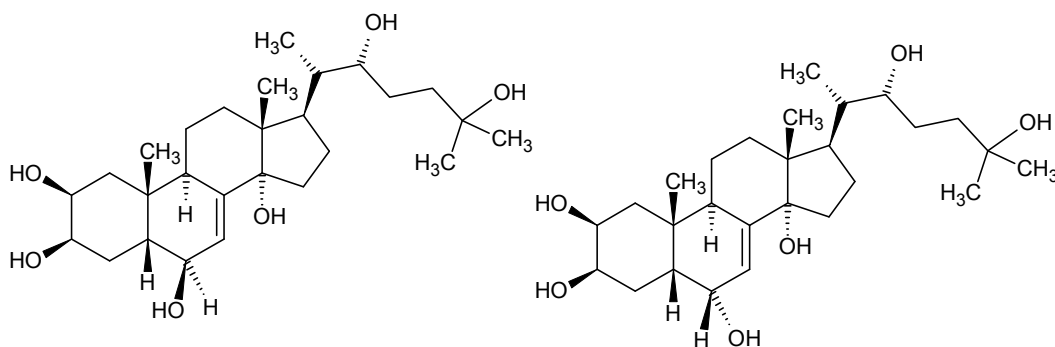
23.59

(a)

1,4 addition products



1,2 addition products



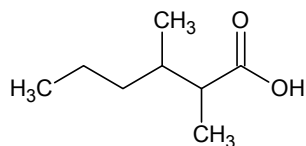
(b) The 1,4 addition products are enantiomers. The 1,2 addition products are a separate pair of enantiomers.

(c) I would not expect the 1,4 or 1,2 addition products to yield in equal amounts. Although the addition can take place from below or above the ring structure, the stereochemistry of the substrate at existing stereocenters can affect the rate of these two pathways. The 1,4 addition requires attack by hydride (carried by BH_4^-) at a carbon with two adjacent stereocenters. The enantiomeric excess is likely greater for the 1,4 addition products.

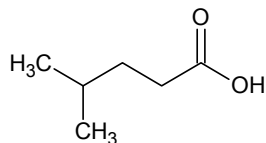
Chapter 24

24.2

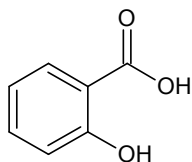
(a)



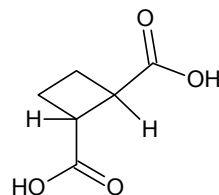
(b)



(c)

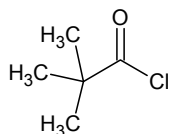


(d)

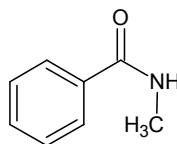


24.3

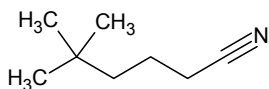
(a)



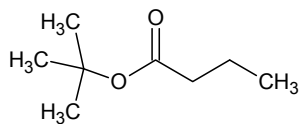
(b)



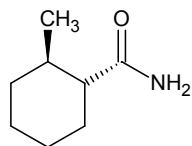
(c)



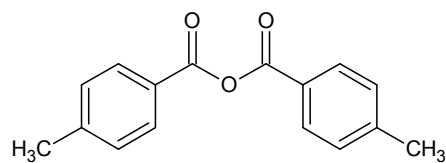
(d)



(e)



(f)

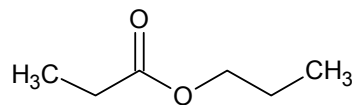


24.4

- (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^{-1}) C=O stretch.

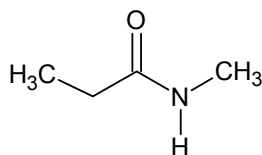
24.5

(a)



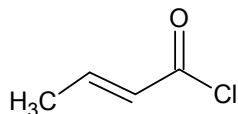
1735 cm^{-1} - an ester C=O stretch

(b)



1650 cm^{-1} - an amide C=O stretch

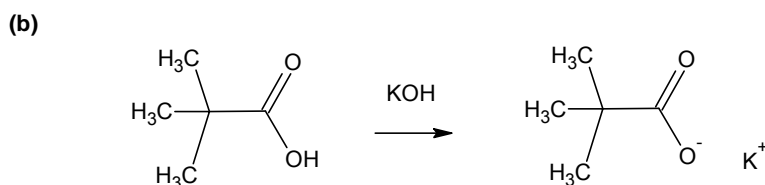
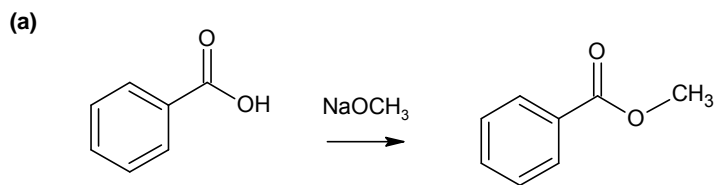
(c)



1735 cm^{-1} - an acid chloride C=O stretch

24.6 In ^{13}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 ^1H 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



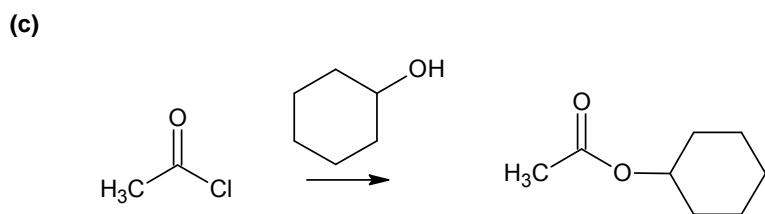
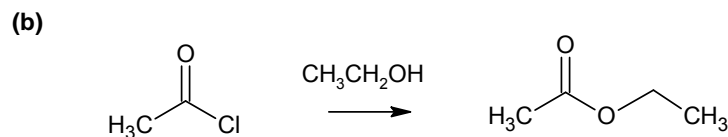
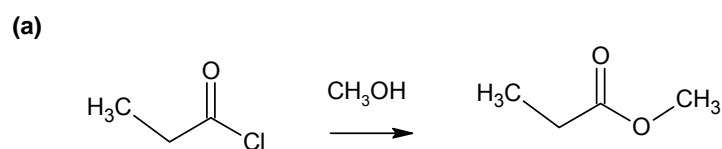
24.9 methanol < phenol < *p*-nitrophenol < acetic acid < sulfuric acid

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

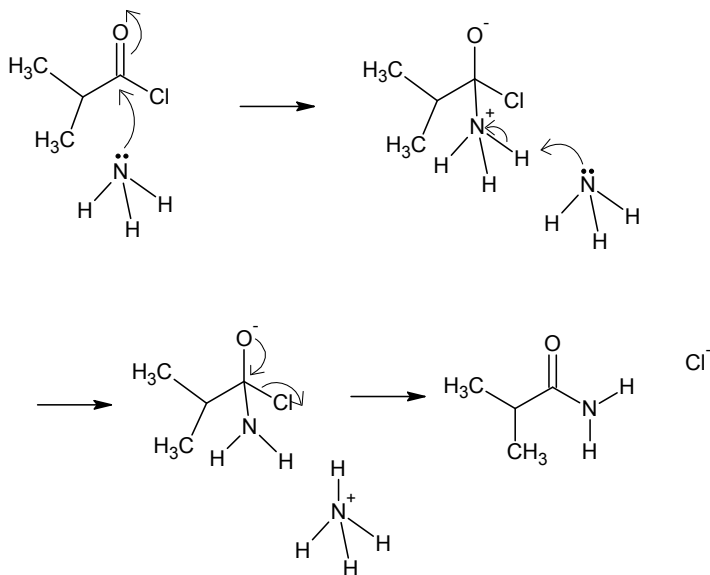
24.11 (a) CH_3COCl > $\text{CH}_3\text{CO}_2\text{CH}_3$ (b) $\text{CH}_3\text{CH}_2\text{CO}_2\text{CH}_3$ > $(\text{CH}_3)_2\text{CHCONH}_2$
(c) $\text{CH}_3\text{CO}_2\text{COCH}_3$ > $\text{CH}_3\text{CO}_2\text{CH}_3$ (d) $\text{CH}_3\text{CO}_2\text{CH}_3$ > CH_3CHO

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

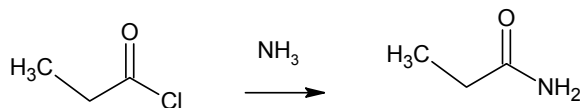


24.14

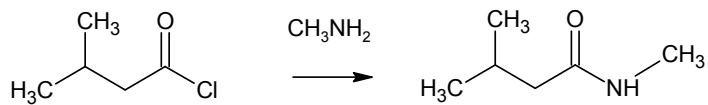


24.15

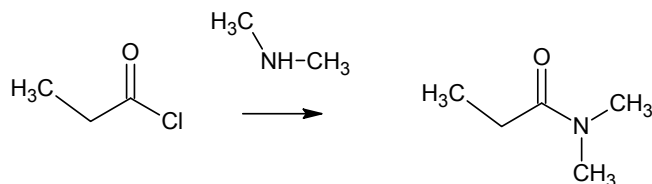
(a)



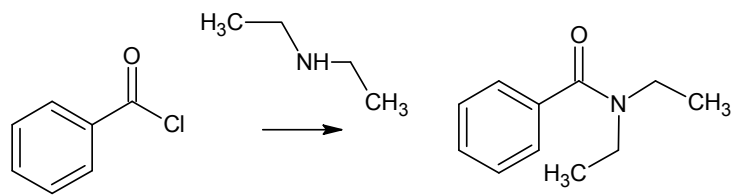
(b)



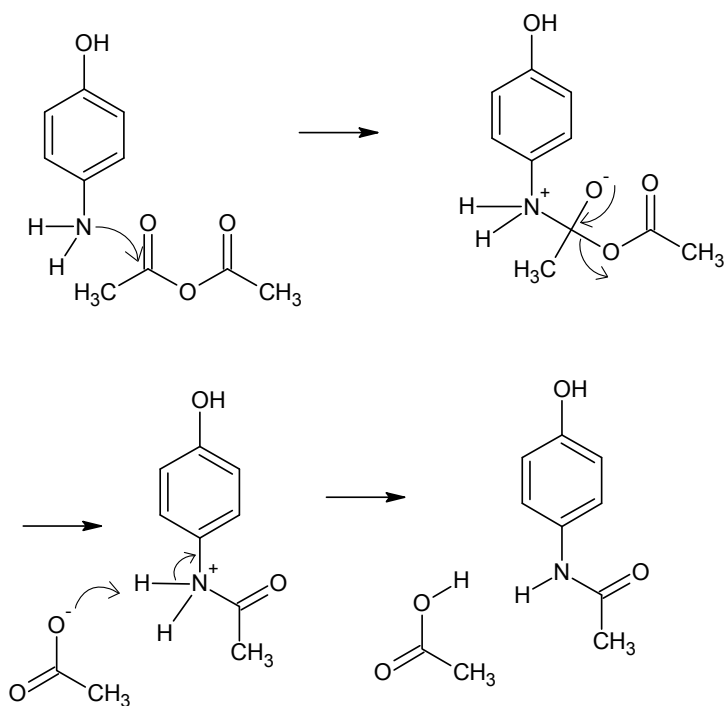
(c)



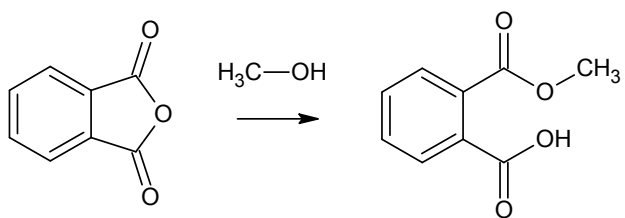
(d)



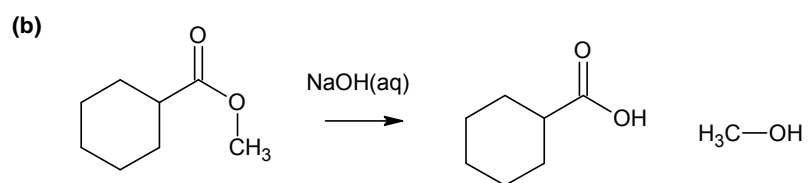
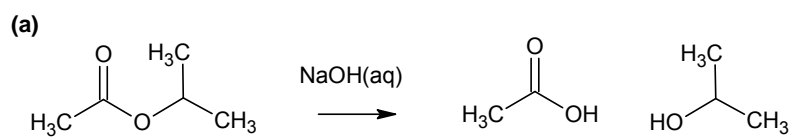
24.16



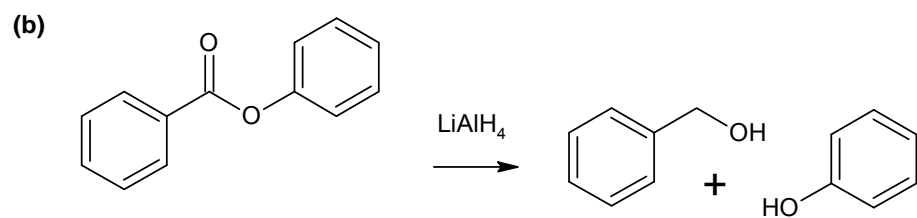
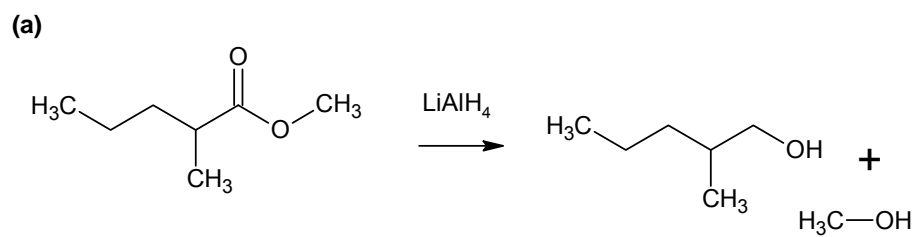
24.17



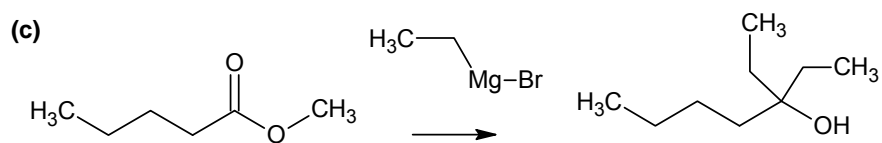
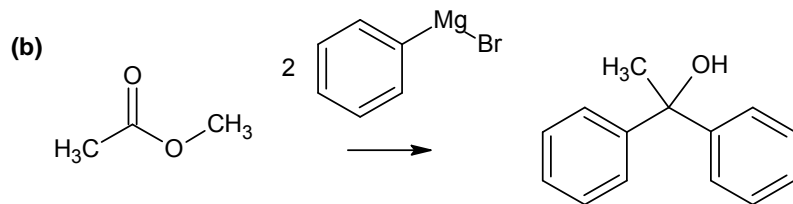
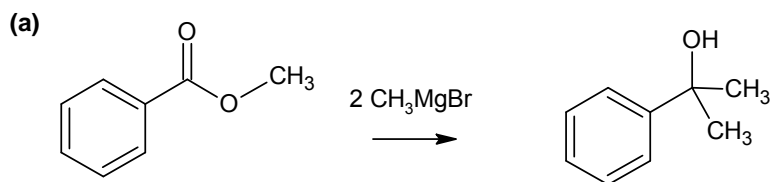
24.18



24.19

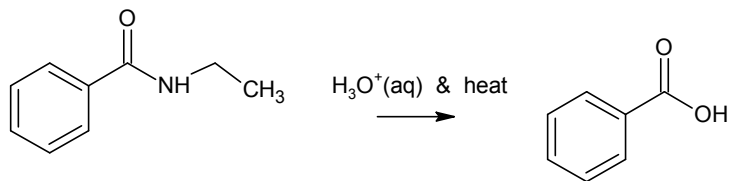


24.20

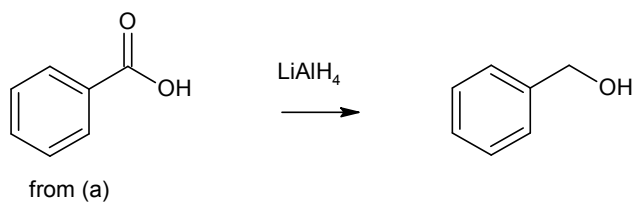


24.21

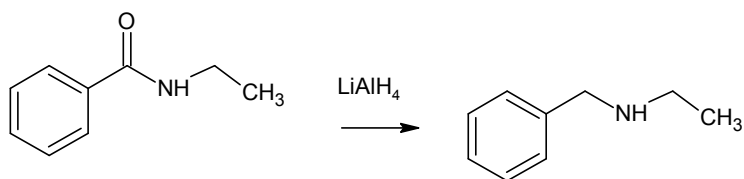
(a)



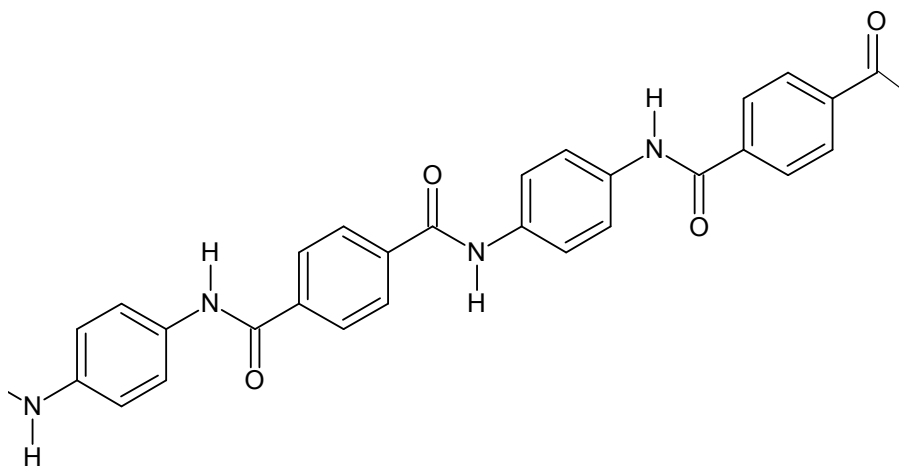
(b)



(c)



24.22



24.23 (a) $\text{CH}_3\text{CH}_2\text{CHO}$ has no acidic H's

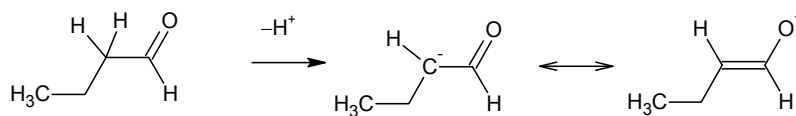
(b) $(\text{CH}_3)_3\text{CCOCH}_3$ is essentially non-acidic. However, the 3 H's on the methyl next to the carbonyl are slightly acidic.

(c) The H bonded to O is acidic in acetic acid, $\text{CH}_3\text{CO}_2\text{H}$.

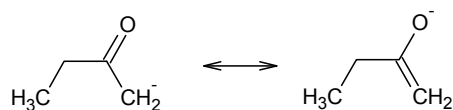
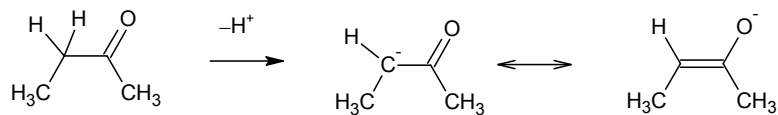
(d) The methylene H's between the two carbonyl C's are acidic in 1,3-Cyclohexanedione.

24.24

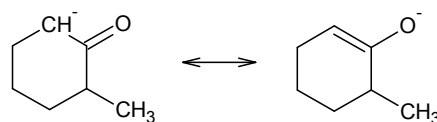
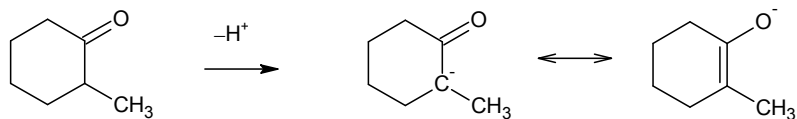
(a)



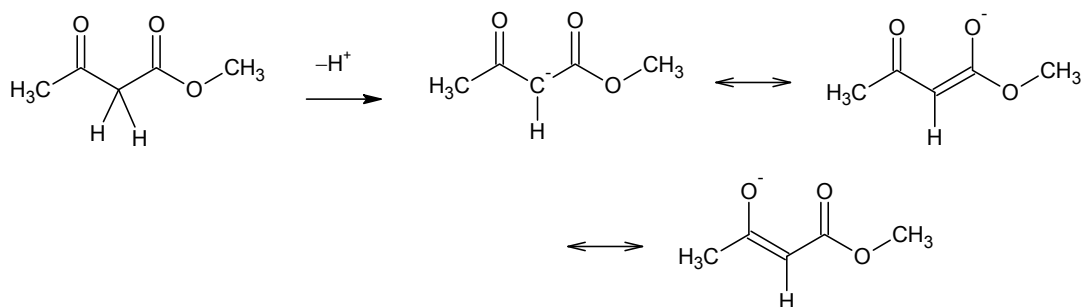
(b)



(c)

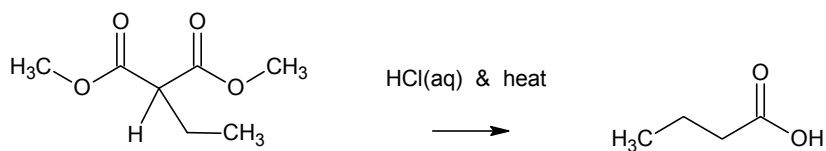
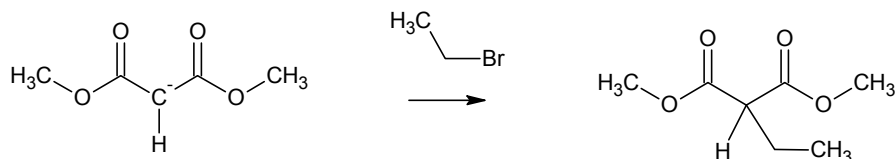
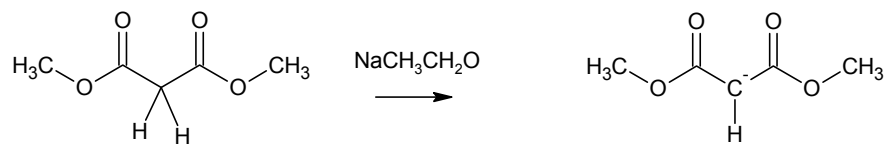


24.25

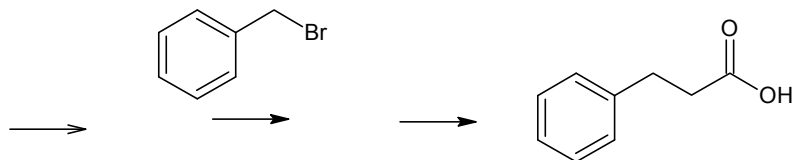


24.26

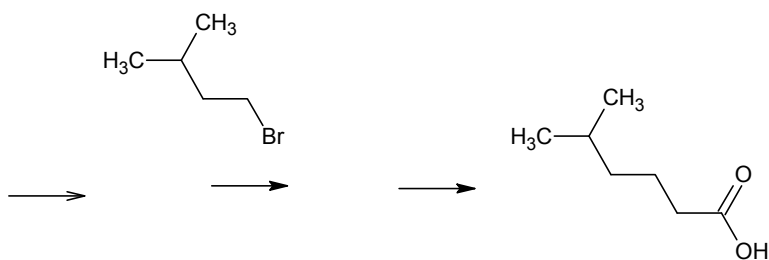
(a)



(b)

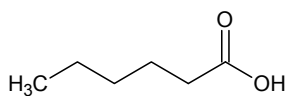


(c)

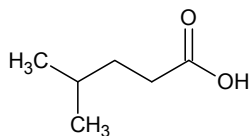


REVIEW QUESTIONS

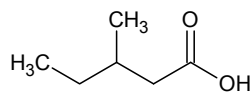
24.27



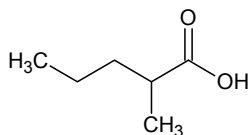
hexanoic acid



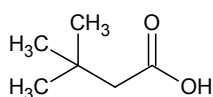
4-methylpentanoic acid



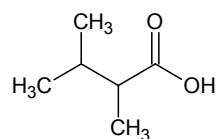
3-methylpentanoic acid
chiral at C3



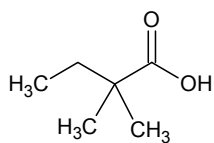
2-methylpentanoic acid
chiral at C2



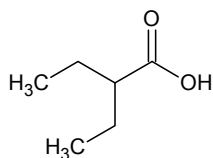
3,3-dimethylbutanoic acid



2,3-dimethylbutanoic acid
chiral at C2



2,2-dimethylbutanoic acid

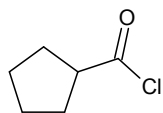


2-ethylbutanoic acid

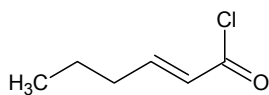
- 24.29 (a) p-methylbenzamide
(b) 4-ethylhex-2-enenitrile
(c) dimethyl butanedioate
(d) isopropyl 3-phenylpropanoate
(e) phenyl benzoate
(f) N-methyl 3-bromobutanamide
(g) 3,5-dibromobenzoyl chloride
(h) 1-cyanocyclopentene

24.31

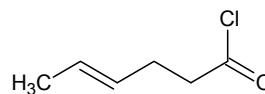
(a)



cyclopentanecarbonyl chloride

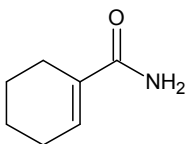


hex-2-enoyl chloride

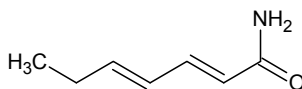


hex-4-enoyl chloride

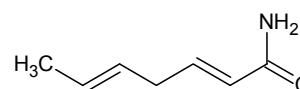
(b)



cyclohex-1-enecarboxamide

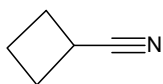


hept-2,4-dienamide

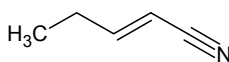


hept-2,5-dienamide

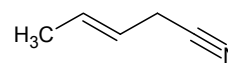
(c)



cyclopentanecarbonitrile

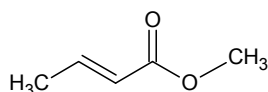


pent-2-enitrile

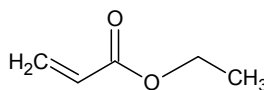


pent-3-enitrile

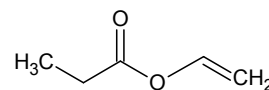
(d)



methyl but-2-enoate

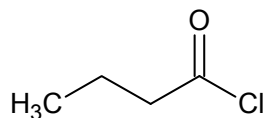


ethyl propenoate

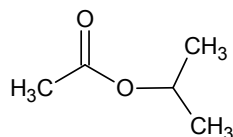


ethenyl propanoate

24.33 (a)

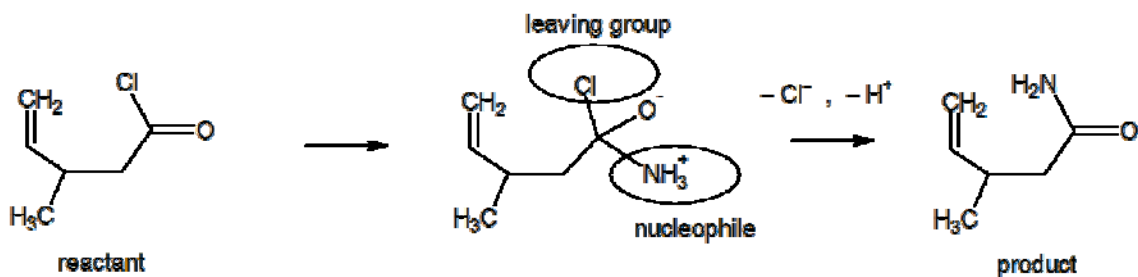


(b)



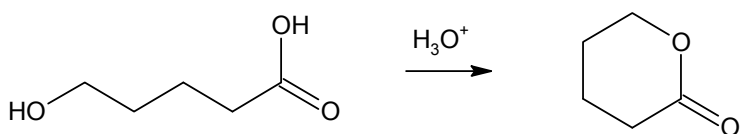
- 24.35 (a) acetic acid < chloroacetic acid < trifluoroacetic acid
 (b) benzoic acid < *p*-bromobenzoic acid < *p*-nitrobenzoic acid
 (c) cyclohexanol < phenol < acetic acid

24.37

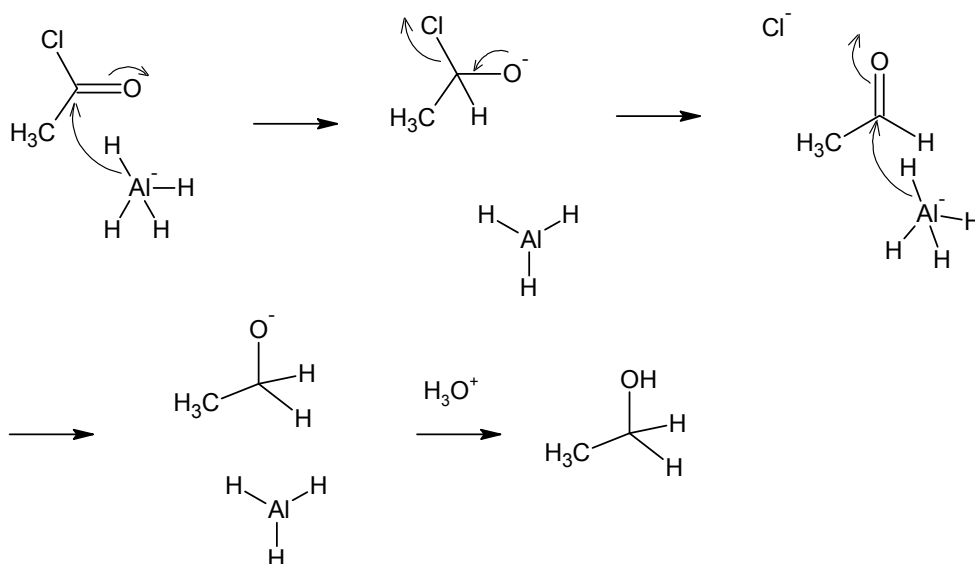


24.39 (c) $\text{CH}_3\text{CONH}_2 < \text{(a) } \text{CH}_3\text{CO}_2\text{CH}_3 < \text{(d) } \text{CH}_3\text{CO}_2\text{COCH}_3 < \text{(b) } \text{CH}_3\text{COCl}$

24.41

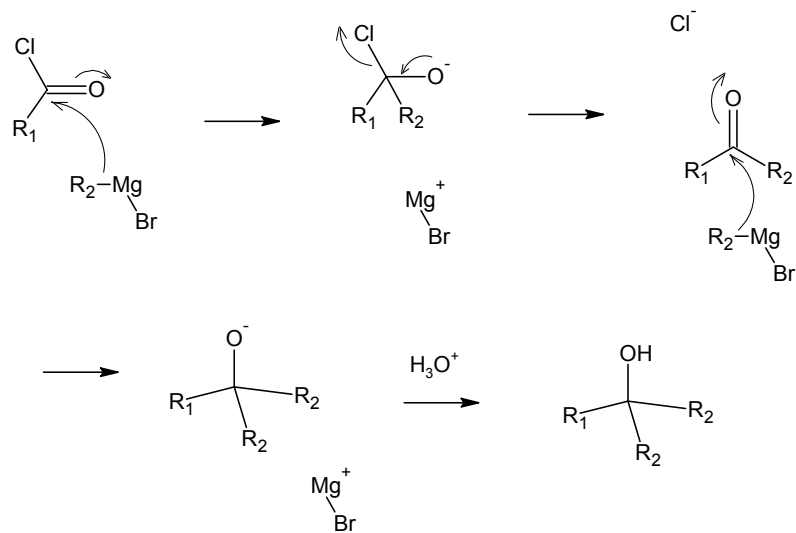


24.43



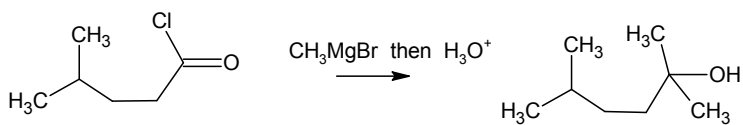
24.45

(a)

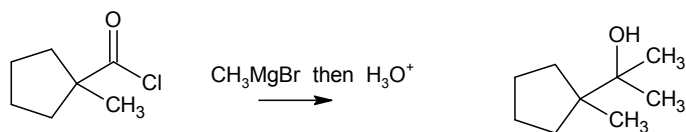


(b)

(a)

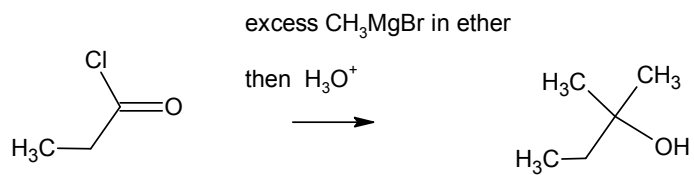


(b)

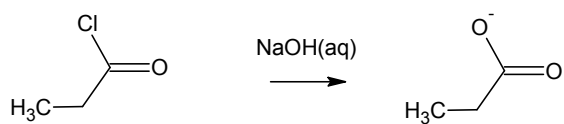


24.47

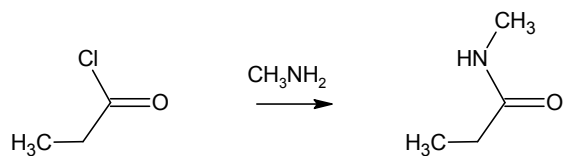
(a)



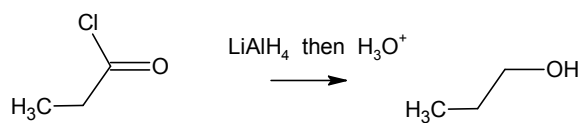
(b)



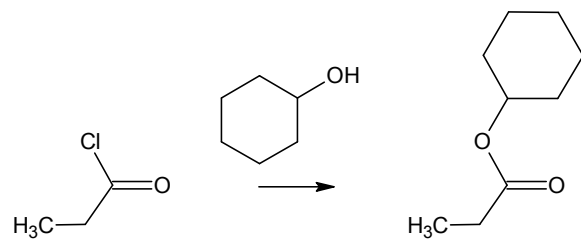
(c)



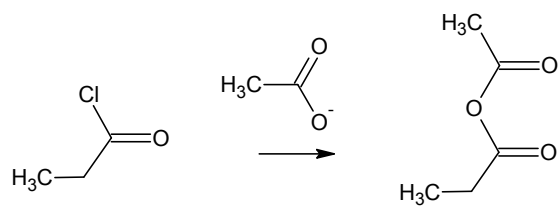
(d)



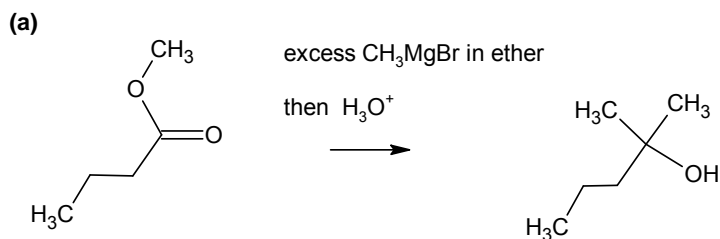
(e)



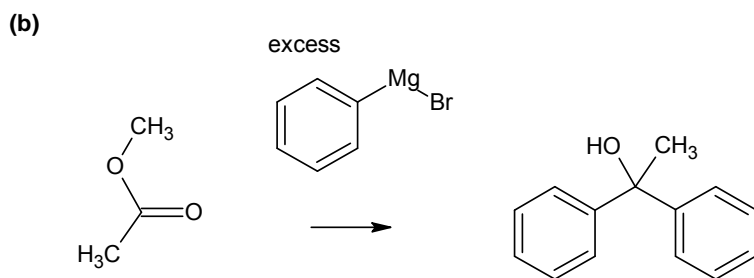
(f)



24.49

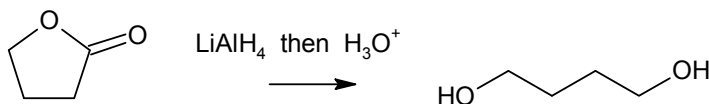


Alternatively, starting with methyl acetate, we could add 1 equivalent of propylmagnesium bromide, then 1 equivalent of methylmagnesium bromide.

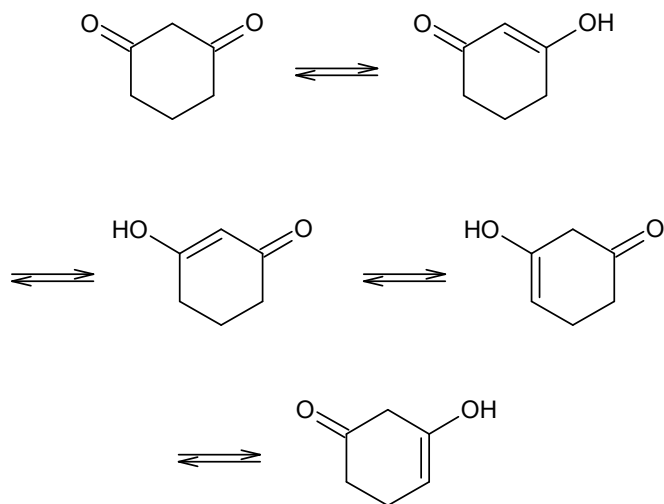


The alternative is to start with methyl benzoate and successively add 1 equivalent of phenylmagnesium bromide and 1 equivalent of methylmagnesium bromide.

24.51



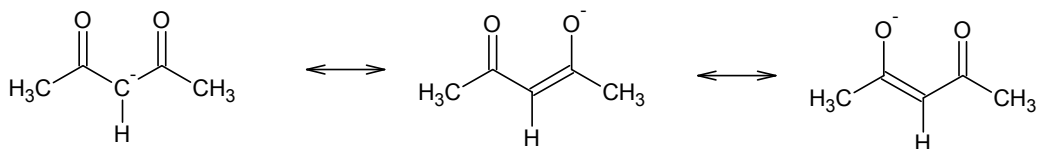
24.53



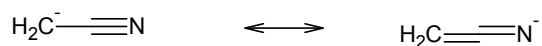
The first two enols shown are the most stable because the 2 carbon H's are more acidic – they are α to two carbonyls.

24.55

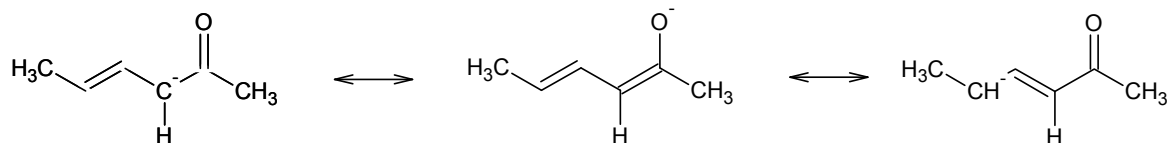
(a)



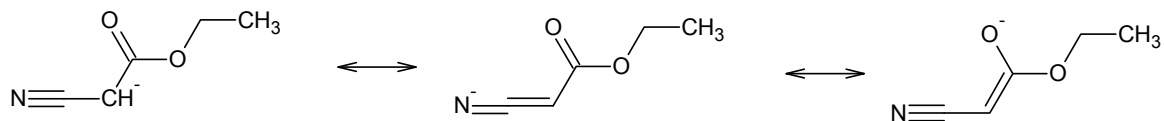
(b)



(c)

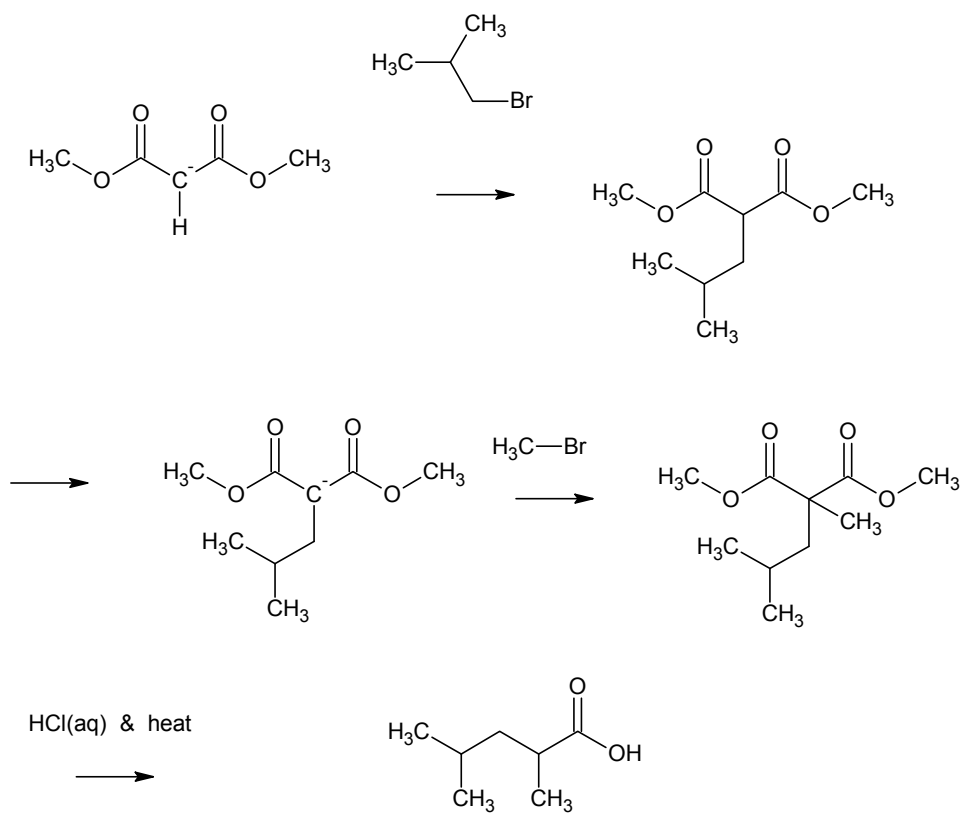


(d)



24.57 An enolate is a base or a nucleophile – it is a stabilized carbanion. It can react by donating a lone pair of electrons through the O atom or through the α carbon. It reacts with electrophiles. The neutral enol is the result of the enolate donating its electrons to a proton at the O atom. While it is an acid, when it donates its proton back to a base, it otherwise reacts the same way as the enolate – i.e. donating a lone pair of electrons through the O atom or the α carbon. Because it is neutral, when it reacts in this way, it typically acquires a positive charge. In contrast, the enolate is an anion typically reacting to form a neutral species. The reactions of the enolate are consequently more favourable (it is more favourable to form a neutral species from an ion, than an ion from a neutral species) – it is more reactive.

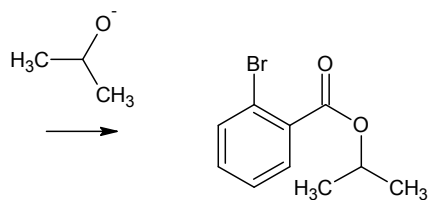
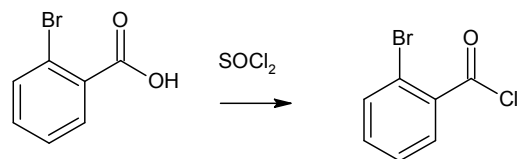
24.59



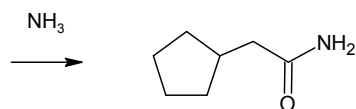
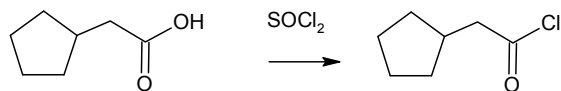
SUMMARY AND CONCEPTUAL QUESTIONS

24.61

(a)

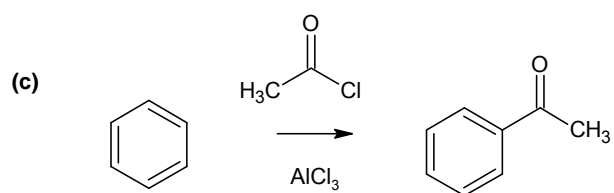
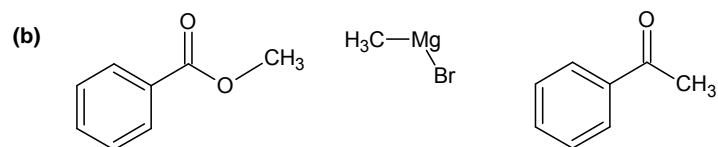
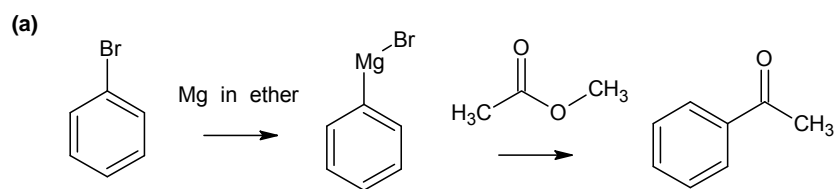


(b)

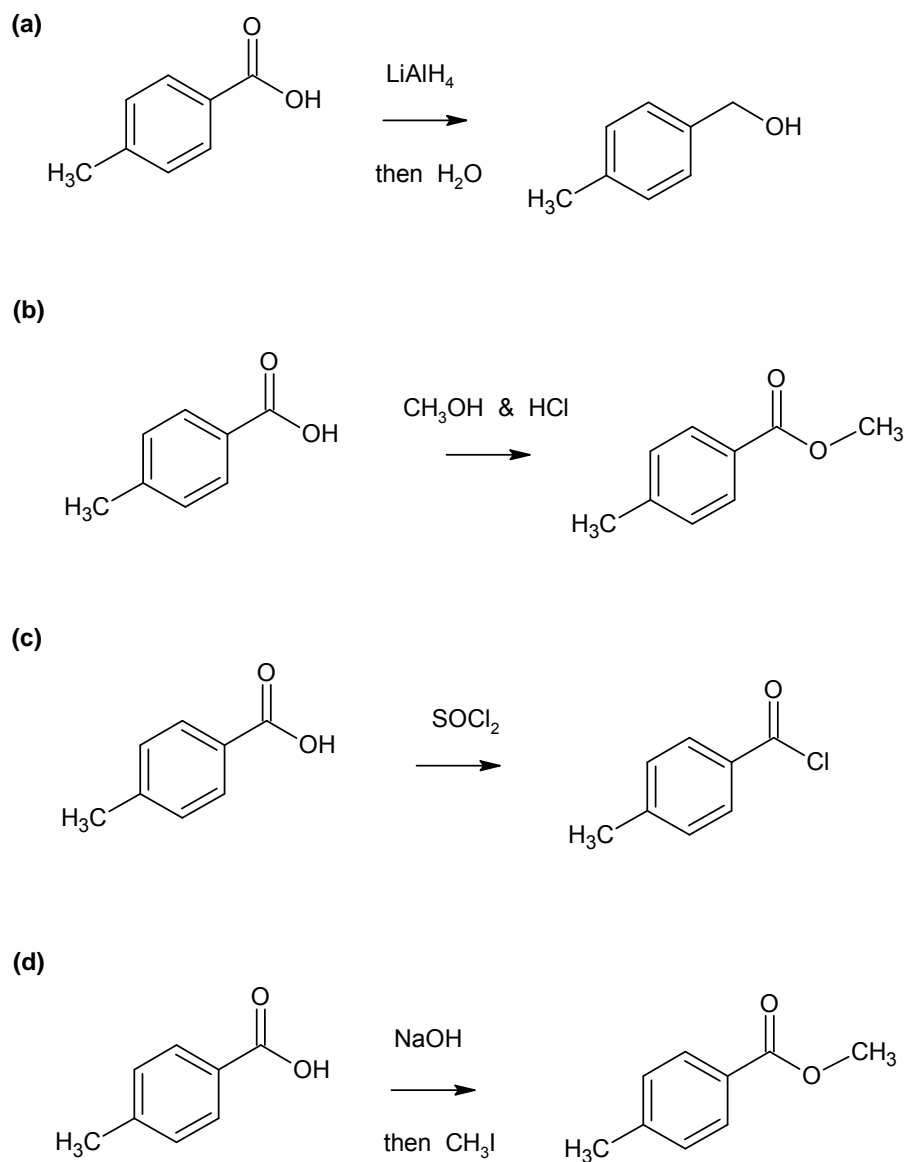


24.63 This order follows because of the increasing bulk of the alkoxide substituent at the carbonyl carbon. Hydroxide adds to the carbonyl carbon in the first step of saponification. A large alkoxide substituent reduces the accessibility of the electrophilic carbonyl carbon to hydroxide.

24.65

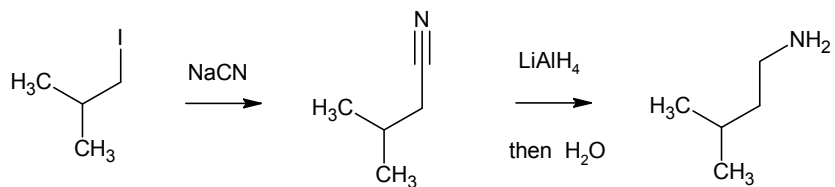


24.67

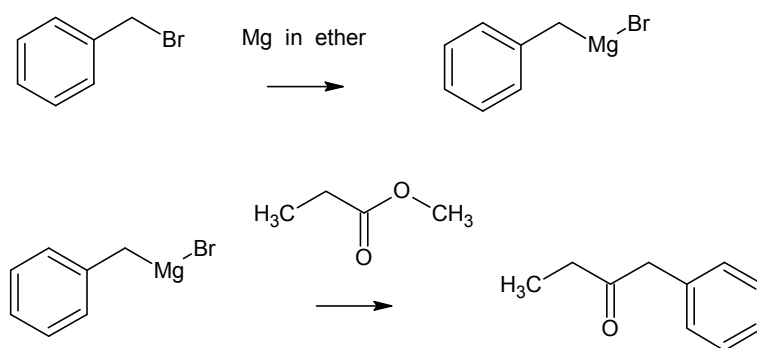


24.69

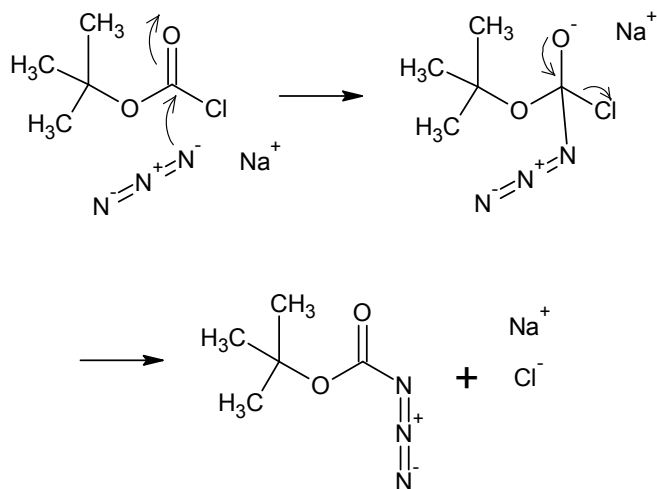
(a)



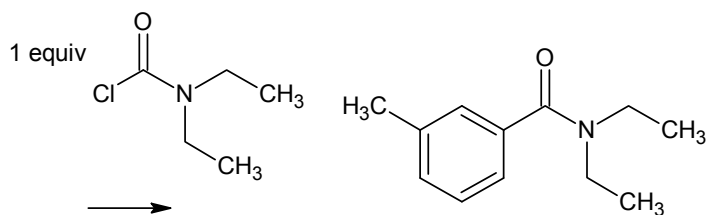
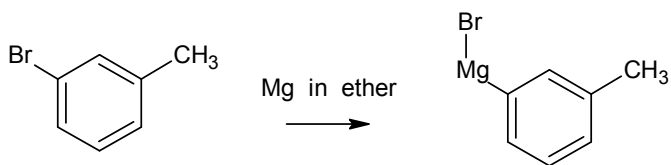
(b)



24.71

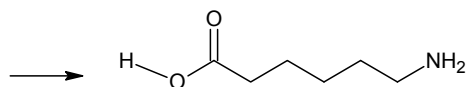
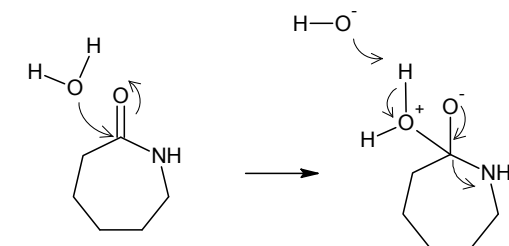


24.73

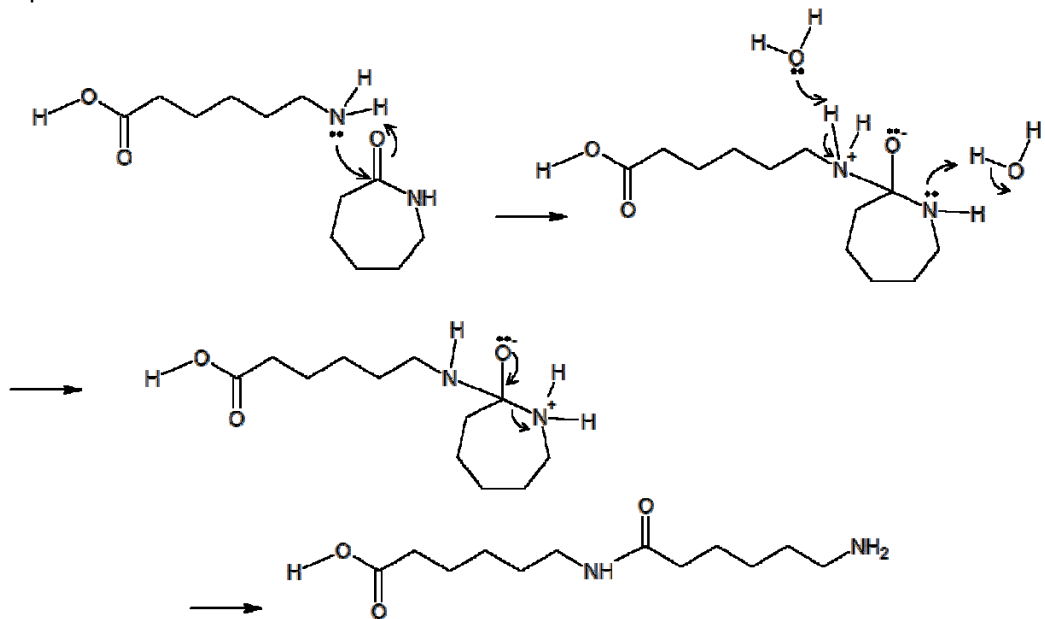


24.75

First step

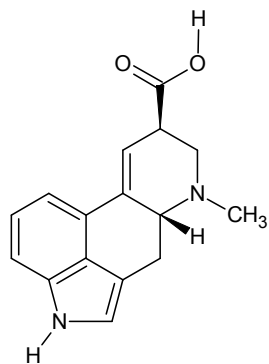


Polymerization step

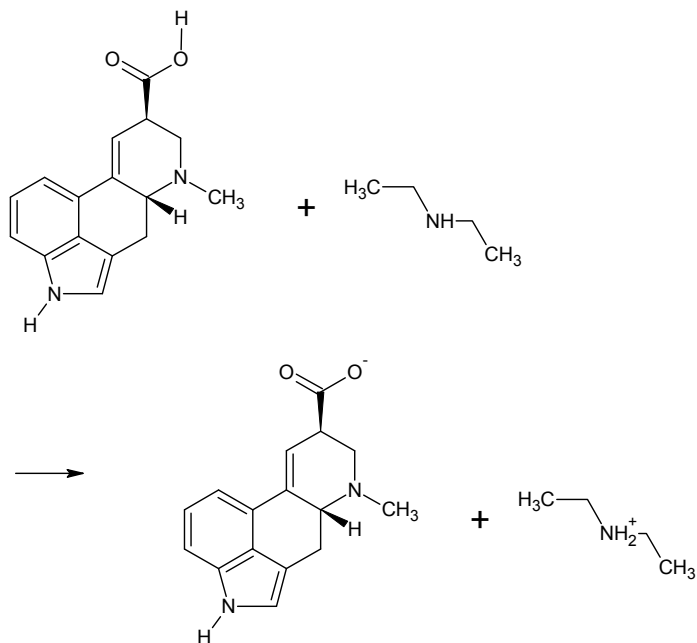


24.81

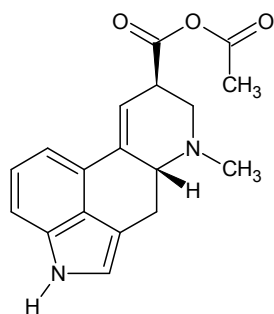
(a)



(b)



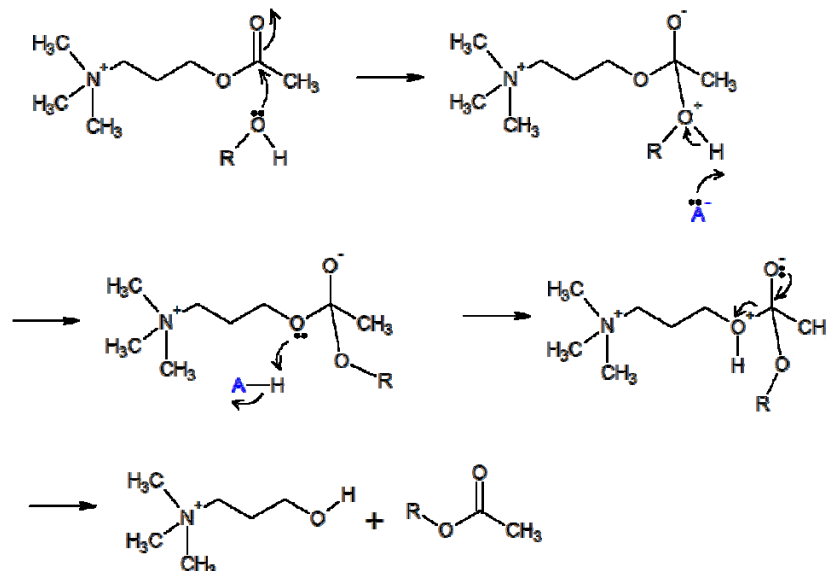
(c)



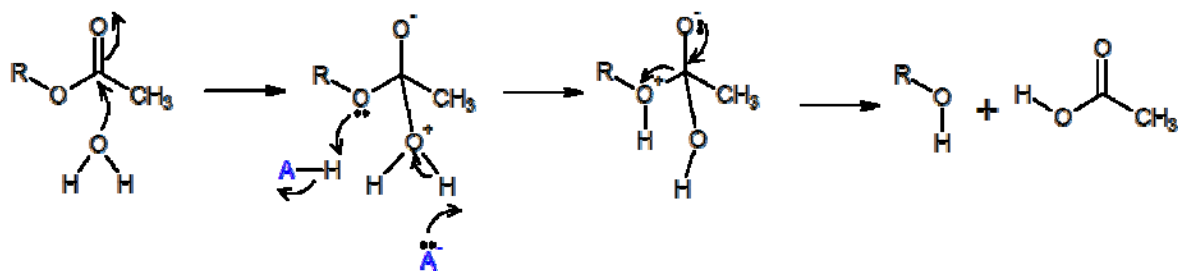
(d) A twofold excess of diethylamine is required because both LSD and diethyl acetamide are produced.

24.83

First step

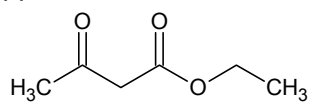


Hydrolysis of acetylated enzyme:

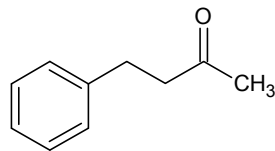


24.85

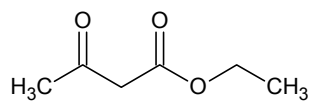
(a)



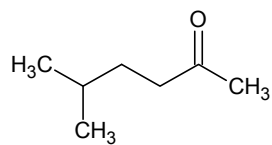
1. $\text{H}_3\text{C}-\text{CH}_2-\text{O}^-$
- 2.
3. H_3O^+



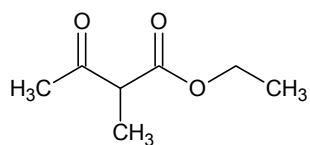
(b)



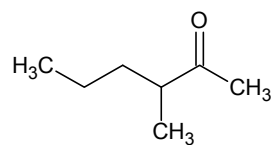
1. $\text{H}_3\text{C}-\text{CH}_2-\text{O}^-$
- 2.
3. H_3O^+



(c)



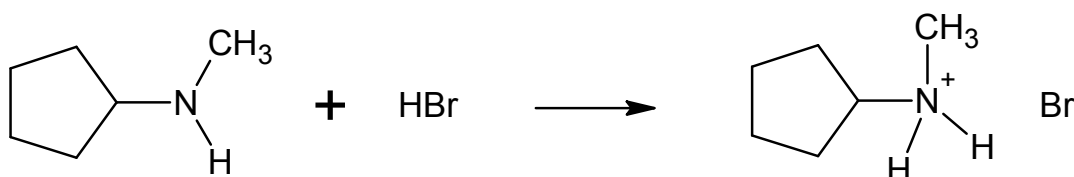
1. $\text{H}_3\text{C}-\text{CH}_2-\text{O}^-$
- 2.
3. H_3O^+



Chapter 25

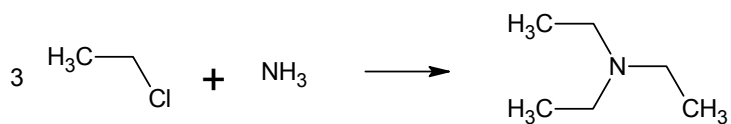
- 25.2 (a) primary amine
(b) secondary amine
(c) tertiary amine
(d) quaternary ammonium salt
- 25.3 The integrals correspond to the H's coming in equivalent groups of 2, 2, 2, 2 and 3 – from downfield to upfield – accounting for the 11 H's in *p*-ethoxyaniline. The two downfield doublets at 6.7 and 6.6 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) NaOH
(c) CH_3NHCH_3
(d) $(\text{CH}_3)_3\text{N}$

25.6

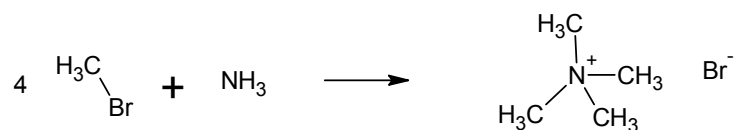


25.7

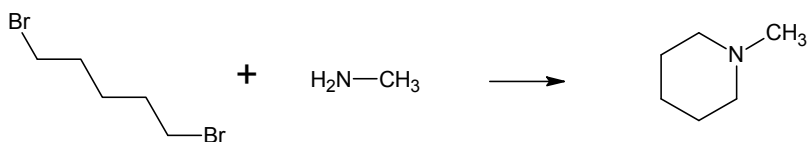
(a)



(b)

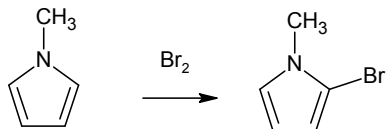


25.8

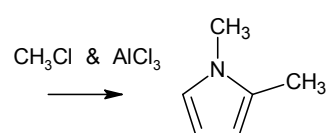


25.9

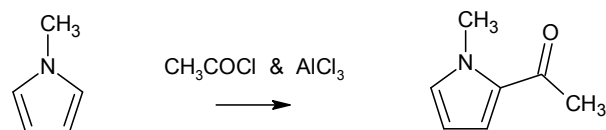
(a)



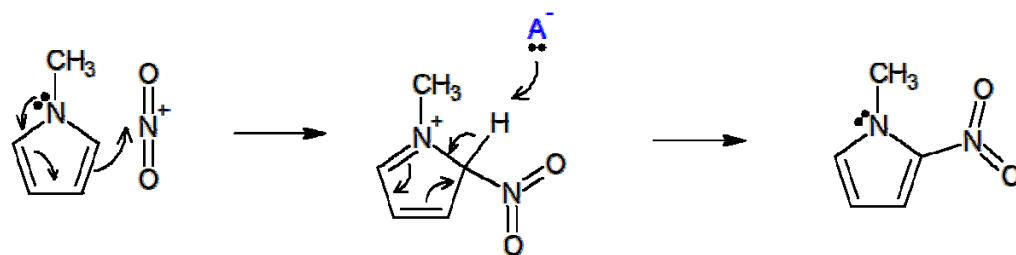
(b)



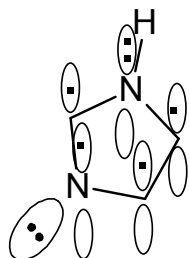
(c)



25.10



25.11



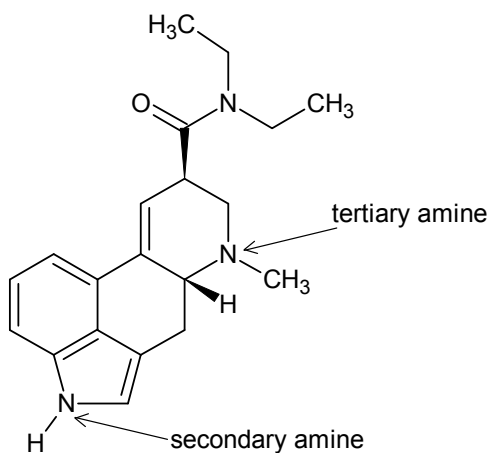
25.12 The pyridine-like N is more basic – we see the negative charge density appearing as a red patch in the electrostatic potential map.

REVIEW QUESTIONS

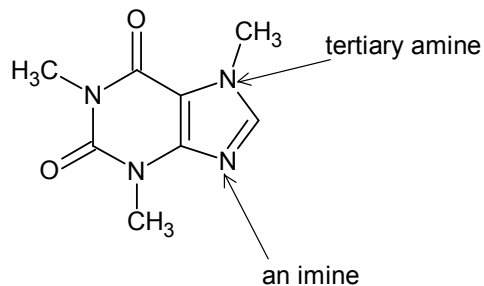
- 25.13 (a) *N*-methylisopropylamine – it is a secondary amine
(b) (2-methylcyclopentyl)amine – it is a primary amine
(c) *N*-isopropylaniline – it is a secondary amine

25.15

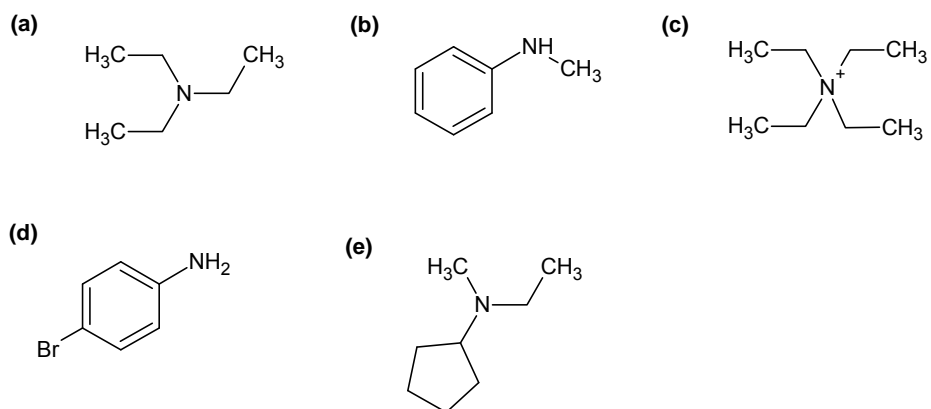
(a)



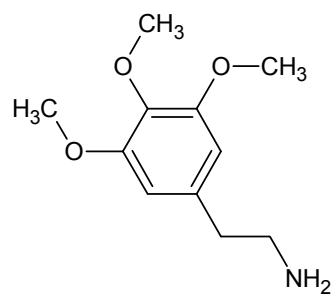
(b)



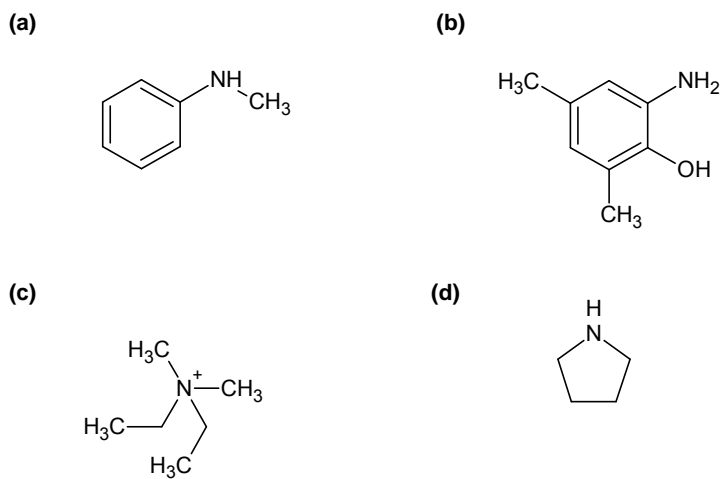
25.17



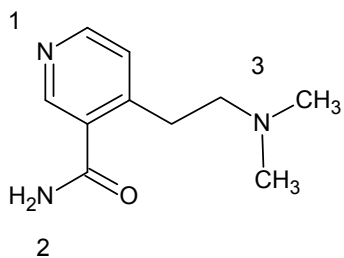
25.19



25.21



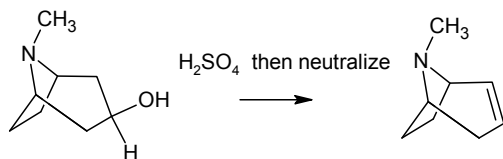
25.23



3 > 1 > 2

25.25 Trimethylamine has a lower boiling point than dimethylamine even though it has a higher molecular weight because it has no hydrogen bonding H's. Dimethylamine has one such H.

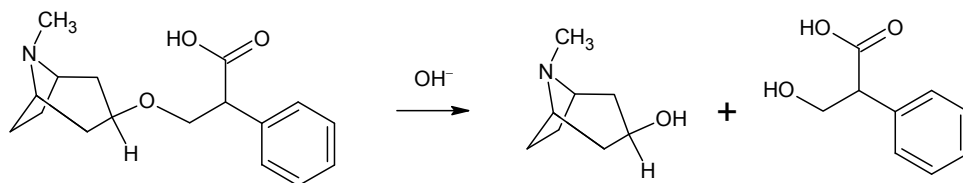
25.27



tropine

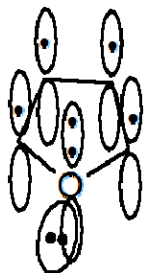
tropidine

note that the other position for the hydroxyl corresponds to an optically active alcohol

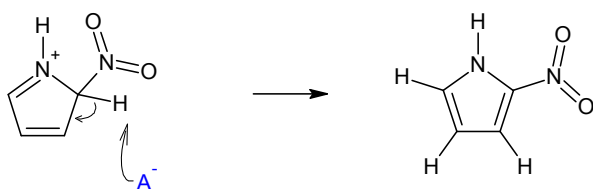
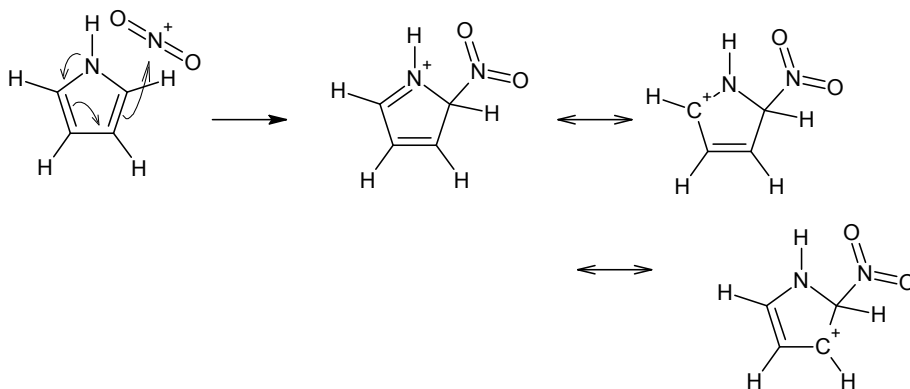


atropine

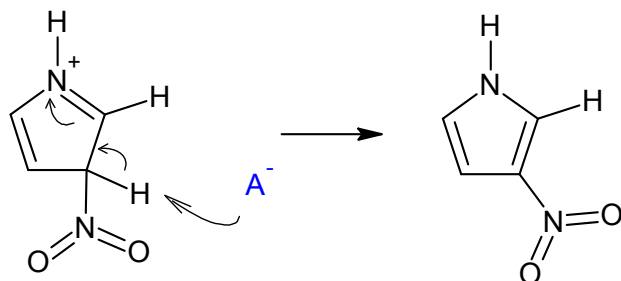
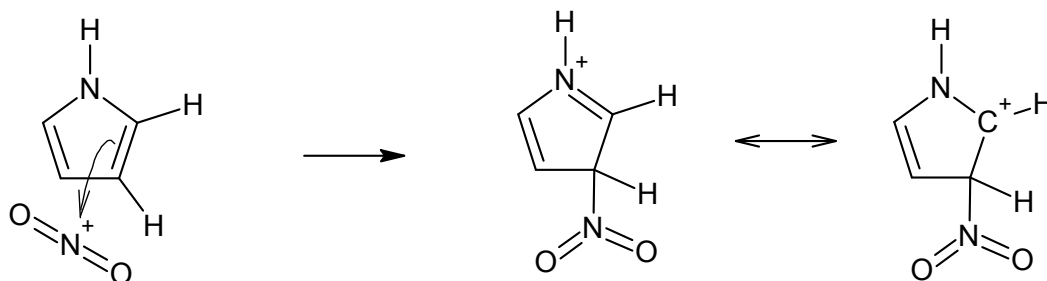
25.29



25.31 Nitration at the 2 position:



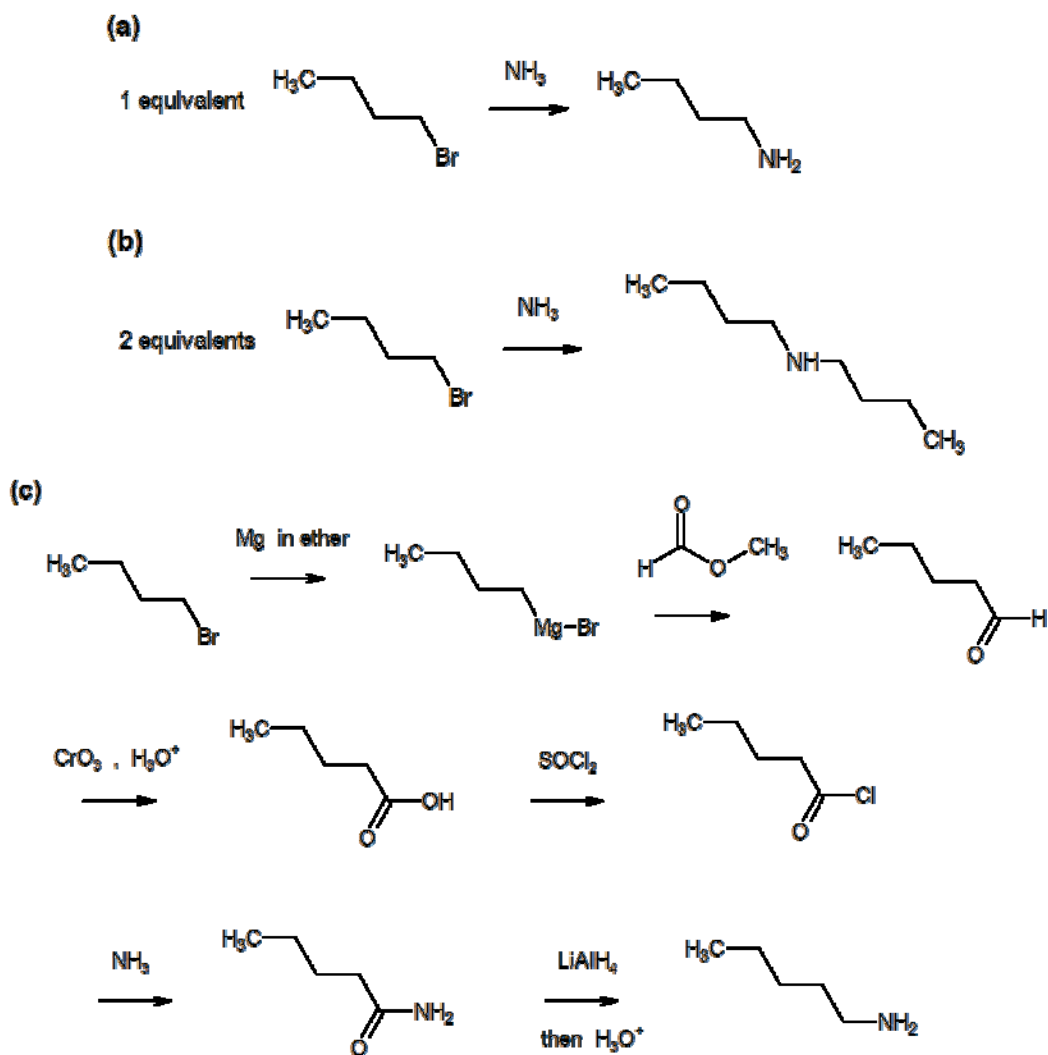
Nitration at the 3 position:



The carbocation intermediate in the case of substitution at the 2 position has three resonance structures. The carbocation more stable and the corresponding reaction pathway more favourable.

SUMMARY AND CONCEPTUAL QUESTIONS

25.33

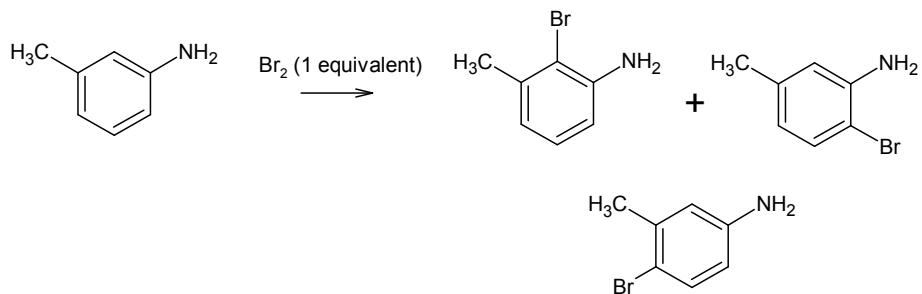


25.35 $\text{CH}_3\text{CH}_2\text{NH}_2$ is more basic than $\text{CF}_3\text{CH}_2\text{NH}_2$. The fluoro substituents are electron withdrawing – they reduce the availability of electrons at the nitrogen atom.

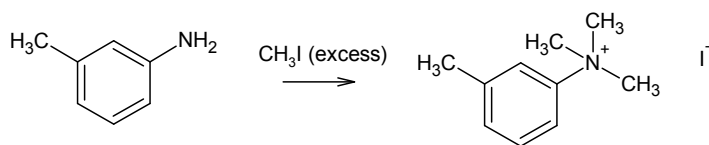
25.37 Triethylamine is more basic than aniline. The reaction does not go in the direction indicated.

25.39

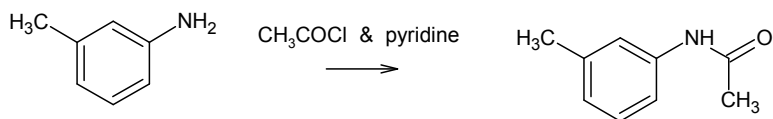
(a)



(b)



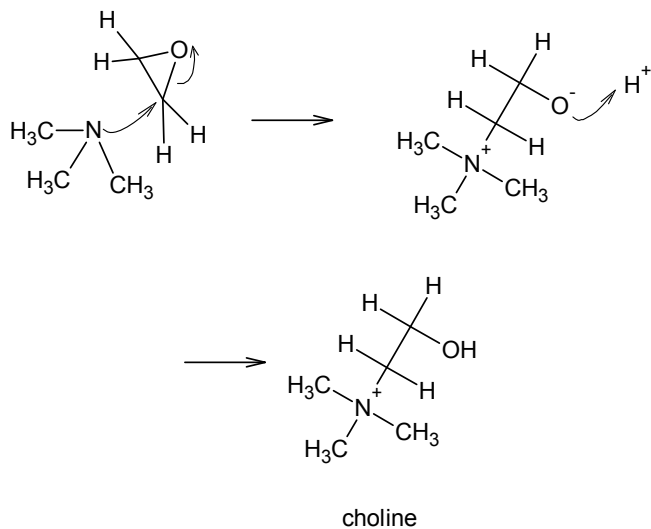
(c)



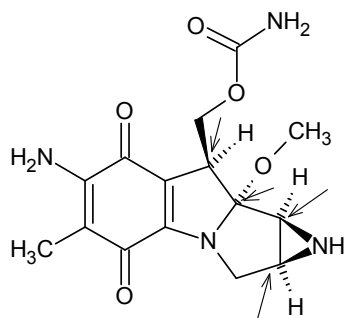
25.41 Diphenylamine is less basic than aniline because the nitrogen lone pair is partially delocalized over two benzene rings, rather than just one.

25.43 *p*-methoxyaniline is more basic than aniline because the methoxy group is electron donating.

25.45



25.47 Stereocenters are marked with arrows below. There are four stereocenters, and as such there are $2^4 = 16$ stereoisomers.



25.49 The aziridine group, like the epoxide group, is very reactive because the bonds are strained by the tight three-membered ring arrangement.

25.51 DEET is an amide that can be prepared by reaction of an amine, diethyl amine, with a carboxylic acid, m-methylbenzoic acid, liberating water in the process. In practice, this reaction is likely best carried out by first preparing the acid chloride from the carboxylic acid.

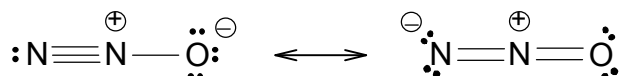
Chapter 26

- 26.1 Be^{2+} is more polarizing than 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, Cr_2O_3 which is amphoteric.
- 26.3 $2 \text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2 \text{H}_2\text{O}(\ell)$
 $\text{H}_2(\text{g}) + \text{Cl}_2(\text{g}) \rightarrow 2 \text{HCl}(\text{g})$
 $3 \text{H}_2(\text{g}) + \text{N}_2(\text{g}) \rightarrow 2 \text{NH}_3(\text{g})$
- 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 K^+ and H^- ions. It is so strongly reactive that 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, Cl^- is oxidized)
 $2 \text{H}_2\text{O}(\ell) + 2 \text{e}^- \rightarrow 2 \text{OH}^-(\text{aq}) + \text{H}_2(\text{g})$ (reaction at cathode, H_2O is reduced)
(b) $2 \text{I}^-(\text{aq}) \rightarrow \text{I}_2(\text{aq}) + 2 \text{e}^-$ (reaction at anode, 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) $\text{Ga}(\text{OH})_3(\text{s}) + 3 \text{HCl}(\text{aq}) \rightarrow \text{GaCl}_3(\text{aq}) + 3 \text{H}_2\text{O}(\ell)$
 $\text{Ga}(\text{OH})_3(\text{s}) + 3 \text{NaOH}(\text{aq}) \rightarrow \text{Na}_3\text{GaO}_3(\text{aq}) + 3 \text{H}_2\text{O}(\ell)$
(b) $\text{Ga}^{3+}(\text{aq})$ is a stronger acid than 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 SiO_2 , silicon forms a network of single bonds with oxygen – i.e. we get a covalently bonded network solid. The melting point of SiO_2 is therefore very high. The bonding in CO_2 is also covalent, but CO_2 is molecular. The intermolecular forces of attraction (dispersion forces) between CO_2 molecules are weak and are easily broken. Carbon dioxide is gas at ordinary temperatures.

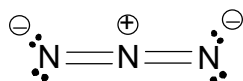
26.12 PbCl_4

26.13 (a)

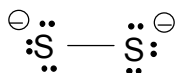


(b) exothermic

26.14



26.15



26.16 (a) F_2 can oxidize Cl^- ($X = \text{F}$, $Y = \text{Cl}$) for example, whereas (b) Cl_2 cannot oxidize 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 Ar^- is held quite weakly. In contrast, the valence electrons of Cl^- experience a much larger effective nuclear charge. Even the K^- ion's valence electrons are held more tightly.

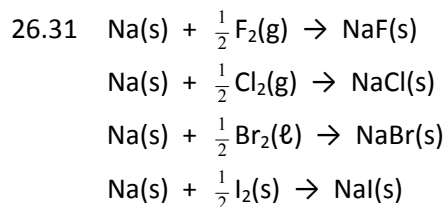
26.18 The ratio of the density of nitrogen to helium = 7.00.

- 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.

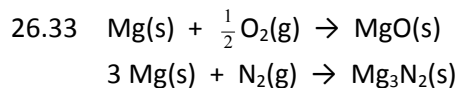
REVIEW QUESTIONS

- 26.21 (a) The properties of BeCl_2 , BCl_3 , AlCl_3 , TiCl_4 and FeCl_3 are typically covalent, because of the small size of and high charge of the cations which make them highly polarizing. In contrast, K^+ and Ag^+ , which are singly charged and not so small, are not nearly as polarizing. The chloride anion retains its independent anionic form next to these cations – the associated compounds are ionic.
- (b) Al^{3+} is highly polarizing, giving covalent character to bonds with halides. However, since the small fluoride ion is rather non-polarizable, AlF_3 is essentially an ionic compound – the bonding has very little covalent character. In contrast, chloride and especially bromide are much more polarizable. Bonds in AlCl_3 , and AlBr_3 have significantly more covalent character. These compounds more readily melt to form liquids of mobile AlCl_3 , and AlBr_3 molecules.
- (c) Singly charged cations, K^+ , Ag^+ and NH_4^+ , are not very polarizing. They do not attract water molecules strongly enough to hold them as coordinating ligands in the ionic crystal lattices of KCl , AgNO_3 and NH_4NO_3 . In contrast, the polarizing doubly and triply charged cations, Mg^{2+} , Fe^{3+} and Cr^{3+} , retain coordinated water ligands when their salts are precipitated from aqueous solution – i.e. they crystallize as hydrated compounds.
- (d) The smaller Li^+ ion is more polarizing than the larger Rb^+ ion. Consequently, Li^+ holds water ligands about it rather tightly, and its mobility in water is that of $[\text{Li}(\text{H}_2\text{O})_4]^+$ rather than that of free lithium ions. A rubidium ion is insufficiently polarizing to drag water molecules along with it. Its mobility is that of the free cation.
- 26.23 (a) The molar enthalpy change of hydration of Be^{2+} (2455 kJ mol⁻¹) is greater than that of Ba^{2+} (1275 kJ mol⁻¹) because the former is much smaller.
- (b) The molar enthalpy change of hydration of Fe^{3+} (4340 kJ mol⁻¹) is greater than that of Fe^{2+} (1890 kJ mol⁻¹) because the former has a greater charge – it is smaller too since there is one less electron to arrange around the iron nucleus.
- 26.25 Pb^{4+} polarizes the chlorides to such an extent that the bonds in lead (IV) chloride have significant covalent character and lead (IV) chloride can exist as individual neutral molecules in a non-polar solvent.
- 26.27 224 kJ.
The reaction is endothermic.

26.29 $\Delta_r H^\circ = 131.30 \text{ kJ}$
 $\Delta_r S^\circ = 134.0 \text{ J/K}$
 $\Delta_r G^\circ = 91.3 \text{ kJ}$



All alkali metal halides are ionic solids. They are crystalline, brittle, dissolve in water and are colourless (M^+ and X^- are closed shell species).



26.35 Limestone, CaCO_3 , is used in agriculture. It is added to fields to neutralize acidic soil, to provide a source of Ca^{2+} , an essential nutrient for plants (and animals). Since there is generally a magnesium impurity, it also provides a source of Mg^{2+} , another essential nutrient. Limestone is also used to make lime, CaO , which is used to make bricks and mortar.

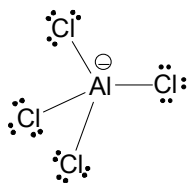
26.37 $1.3 \times 10^3 \text{ kg}$

26.39 Because the equilibrium constant for the above reaction is so large, $\sim 10^7$, it can be used to obtain magnesium hydroxide solid (wherein magnesium ions are concentrated in an ionic solid) from sea water with very small concentrations.

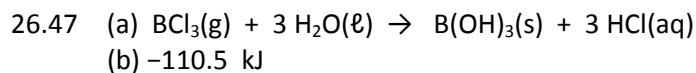
26.41 Beryllium and beryllium alloys are used in airplane (especially high speed planes), missile and spacecraft construction. It is also used in high energy physics experiments to make windows and filters. Because of its low density it is relatively transparent to X-rays, for example, yet has the high strength and stiffness of much heavier metals. Beryllium dust generated in manufacturing processes is very toxic. People breathing this dust over a period of time can develop berylliosis – an inflammatory disease of the lungs wherein sufferers experience coughing, shortness of breath, fever and weight loss.

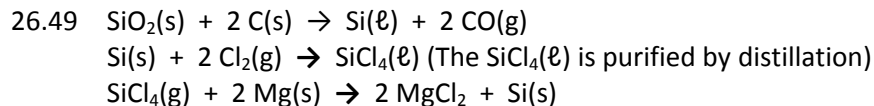
26.43 Iodine gets reduced and borohydride, BH_4^- , gets oxidized.

26.45

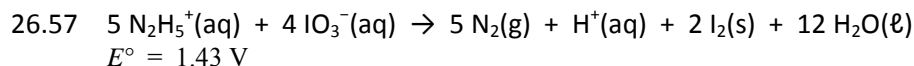
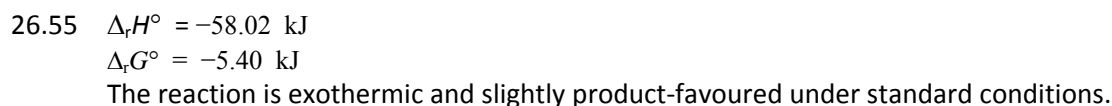
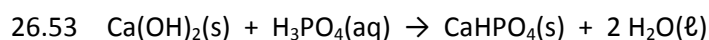
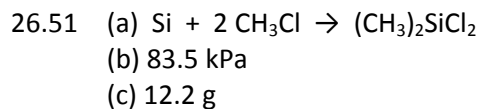


AlCl_4^- is tetrahedral

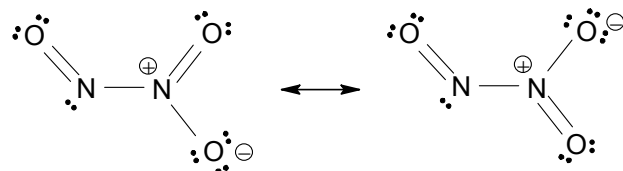




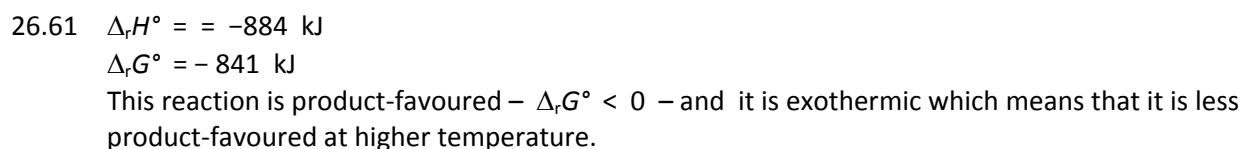
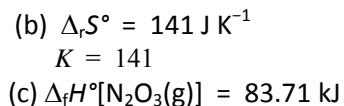
In the last step, the magnesium chloride by-product is washed away with water. The silicon left behind in this way is further purified by zone refining wherein a narrow cylinder of silicon is heated and melted in one segment along the cylinder. The heating slowly traverses the length of the cylinder. Impurities concentrate in the melted segment, leaving higher purity silicon behind.



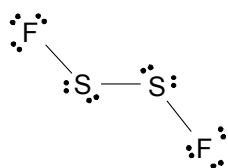
26.59 (a)



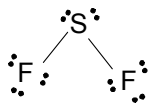
Two almost equivalent resonance structures can be drawn, giving the two N–O bonds on the right bond orders of about $1 \frac{1}{2}$. Resonance structures showing the N–O bond on the left as anything but a double bond are not at all dominant. This latter bond is thus more of a double bond. This is consistent with its observed shorter length.



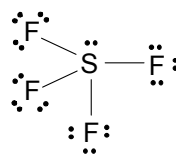
26.63



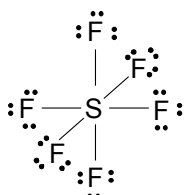
$$\text{ON}(\text{S}) = +1$$



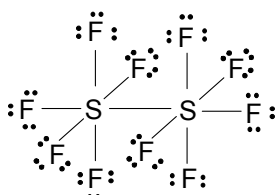
$$\text{ON}(\text{S}) = +2$$



$$\text{ON}(\text{S}) = +4$$

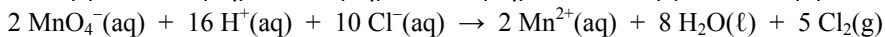
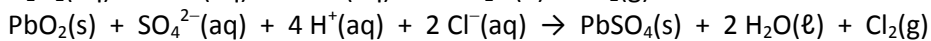
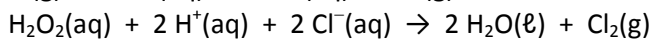
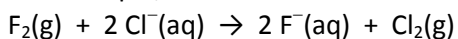


$$\text{ON}(\text{S}) = +6$$



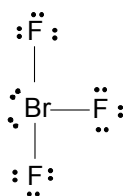
$$\text{ON}(\text{S}) = +5$$

26.65 Any species with reduction potential greater than that of chlorine (i.e. $> 1.36 \text{ V}$) can be used. For example,



26.67 The reduction potential of $\text{MnO}_4^-(\text{aq})$ is 1.51 V under standard conditions. Since this is greater than 1.44 V , it is NOT possible to oxidize $\text{Mn}^{2+}(\text{aq})$ with $\text{BrO}_3^-(\text{aq})$.

26.69



26.70 190 kJ

26.71 1.6 kg

SUMMARY AND CONCEPTUAL QUESTIONS

- 26.73 $\text{P}_4\text{O}_{10}(\text{s})$ and $\text{SO}_3(\text{g})$ are acidic oxides—potassium and sulfur are non-metals.
 $\text{P}_4(\text{s}) + 5 \text{O}_2(\text{g}) \rightarrow \text{P}_4\text{O}_{10}(\text{s})$
 $\text{S}_8(\text{s}) + 12 \text{O}_2(\text{g}) \rightarrow 8 \text{SO}_3(\text{g})$
The acidic oxides react with water to form acidic solutions:
 $\text{P}_4\text{O}_{10}(\text{s}) + 6 \text{H}_2\text{O}(\ell) \rightarrow 4 \text{H}_3\text{PO}_4(\text{aq})$ phosphoric acid, which ionizes in aqueous solution to form $\text{H}_3\text{O}^+(\text{aq})$.
 $\text{SO}_3(\text{g}) + \text{H}_2\text{O}(\ell) \rightarrow \text{HSO}_4^-(\text{aq})$ aquated hydrogensulfate ions, which ionize in aqueous solution to form $\text{H}_3\text{O}^+(\text{aq})$.
- 26.75 S^{2-} , Cl^- , K^+ and Ca^{2+} ions are monatomic ions with the same electron configuration as argon.
- 26.77 In order of increasing basicity, we have $\text{CO}_2 < \text{SiO}_2 < \text{SnO}_2$
- 26.79 (a) $2 \text{Na}(\text{s}) + \text{Br}_2(\ell) \rightarrow 2 \text{NaBr}(\text{s})$
(b) $2 \text{Mg}(\text{s}) + \text{O}_2(\text{g}) \rightarrow 2 \text{MgO}(\text{s})$
(c) $2 \text{Al}(\text{s}) + 3 \text{F}_2(\text{g}) \rightarrow 2 \text{AlF}_3(\text{s})$
(d) $\text{C}(\text{s}) + \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g})$
- 26.81 (a) Electrolysis of aqueous sodium chloride:
 $2 \text{Na}^+(\text{aq}) + 2 \text{Cl}^-(\text{aq}) + 2 \text{H}_2\text{O}(\ell) \rightarrow 2 \text{Na}^+(\text{aq}) + 2 \text{OH}^-(\text{aq}) + \text{Cl}_2(\text{g}) + \text{H}_2(\text{g})$
(b) Electrolysis of aqueous sodium chloride is not the only source of sodium hydroxide, or of hydrogen. It is, however, the principle source of chlorine.
- 26.83 (a) $\text{Li}(\text{s})$ and $\text{Be}(\text{s})$ are metals
 $\text{B}(\text{s})$ is a metalloid
 $\text{C}(\text{s})$, $\text{N}_2(\text{g})$, $\text{O}_2(\text{g})$, $\text{F}_2(\text{g})$ and $\text{Ne}(\text{g})$ are non-metallic substances.
(b) + (c) $\text{Li}(\text{s})$, $\text{Be}(\text{s})$ and $\text{B}(\text{s})$ are silver-white shiny, with metallic appearance. C is a black solid (graphite) or a lustrous transparent very hard crystalline material (diamond). $\text{N}_2(\text{g})$, $\text{O}_2(\text{g})$, $\text{F}_2(\text{g})$ and $\text{Ne}(\text{g})$ are all gases, colourless except for a yellow tinge in the case of fluorine.
- 26.85 (a) $2 \text{KClO}_3(\text{s}) + \text{heat} \rightarrow 2 \text{KCl} + 3 \text{O}_2(\text{g})$
(b) $2 \text{H}_2\text{S}(\text{g}) + 3 \text{O}_2(\text{g}) \rightarrow 2 \text{H}_2\text{O}(\ell) + 2 \text{SO}_2(\text{g})$
(c) $2 \text{Na}(\text{s}) + \text{O}_2(\text{g}) \rightarrow \text{Na}_2\text{O}_2(\text{s})$
(d) $\text{P}_4(\text{s}) + 3 \text{OH}^-(\text{aq}) + 3 \text{H}_2\text{O}(\ell) \rightarrow \text{PH}_3(\text{g}) + 3 \text{H}_2\text{PO}_4^-(\text{aq})$
(e) $2 \text{NH}_4\text{NO}_3(\text{s}) + \text{heat} \rightarrow \text{N}_2\text{O}(\text{g}) + 2 \text{H}_2\text{O}(\text{g})$
(f) $2 \text{In}(\text{s}) + 3 \text{Br}_2(\ell) \rightarrow 2 \text{InBr}_3(\text{s})$
(g) $\text{SnCl}_4(\ell) + 4 \text{H}_2\text{O}(\ell) \rightarrow \text{Sn}(\text{OH})_4(\text{aq}) + 4 \text{H}^+(\text{aq})$
- 26.87 Dry, inert powders are used to extinguish sodium fires. A class D fire extinguisher is required. The worst thing you can do is put water on the fire, as the sodium will react violently with water.

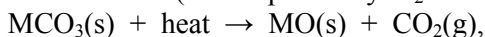
26.89 The amount of gas produced by heating 1.00 g A is

$$n(\text{gas}) = \frac{pV}{RT} = \frac{(27.86 \text{ kPa})(0.450 \text{ L})}{(8.314 \text{ L kPa K}^{-1} \text{ mol}^{-1})(298 \text{ K})} = 0.00506 \text{ mol}$$

Bubbling this gas through $\text{Ca}(\text{OH})_2(\text{aq})$ gives a white solid, C. This suggests the gas is carbon dioxide. Carbon dioxide reacts in aqueous calcium hydroxide to form insoluble calcium carbonate, $\text{CaCO}_3(\text{s})$. $\text{CO}_2(\text{g})$ is also a typical product in the thermal decomposition of carbonates, suggesting A is a carbonate. The other decomposition product, B, would then be an oxide. This is consistent with it forming a basic aqueous solution. If the gas were CO_2 , then the mass of 0.00506 mol would be

$$0.00506 \text{ mol} \times 44.01 \text{ g mol}^{-1} = 0.223 \text{ g}$$

This leaves $1.00 - 0.223 = 0.777 \text{ g}$ as the mass of the oxide. If we take the decomposition reaction to be (M is replaced by M_2 in case of a univalent metal, etc.)



then the molar mass of $\text{MO}(\text{s})$ is determined to be

$$0.777 \text{ g} / 0.00506 \text{ mol} = 154 \text{ g mol}^{-1}$$

Subtracting the molar mass of O leaves the molar mass of M,

$$154 \text{ g mol}^{-1} - 16 \text{ g mol}^{-1} = 138 \text{ g mol}^{-1}$$

This is pretty close to the molar mass of barium. This identification is verified by the green coloured flame, characteristic of barium. Also, the sulfate precipitate is characteristic of barium.



Chapter 27

- 27.1 (a) methyl amine, CH_3NH_2 , (b) methyl nitrile, CH_3CN , (c) azide, N_3^- and (e) bromide, 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 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) 5.0×10^4

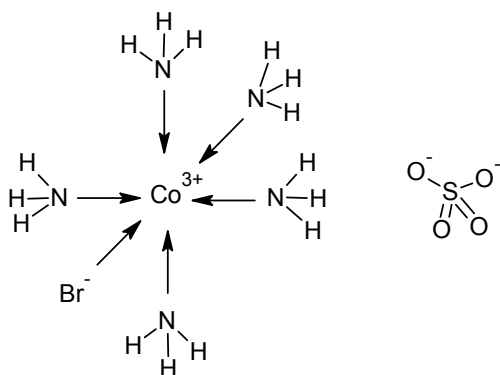
27.5 (i) $\Delta_r G^\circ = -67.2 \text{ kJ mol}^{-1}$

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.

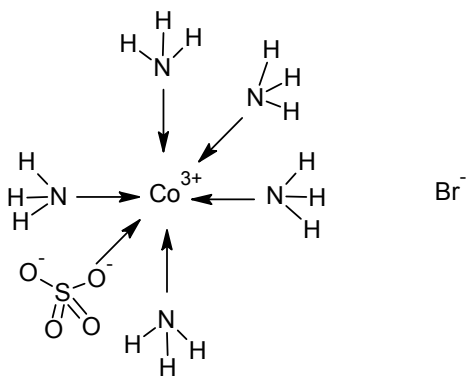
(ii) $K = 6.02 \times 10^{11}$

27.6 Only 1.0 mol of AgCl(s) will precipitate.

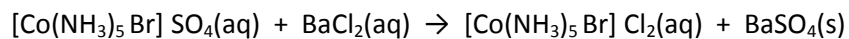
27.7



dark violet isomer (A)

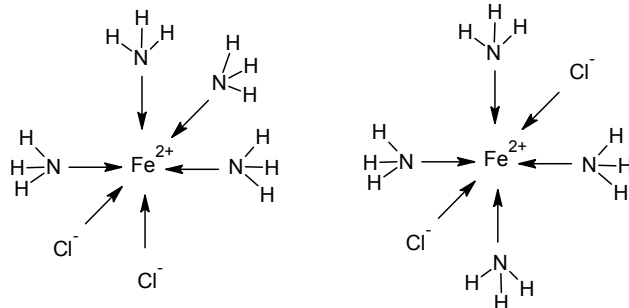


violet-red isomer (B)

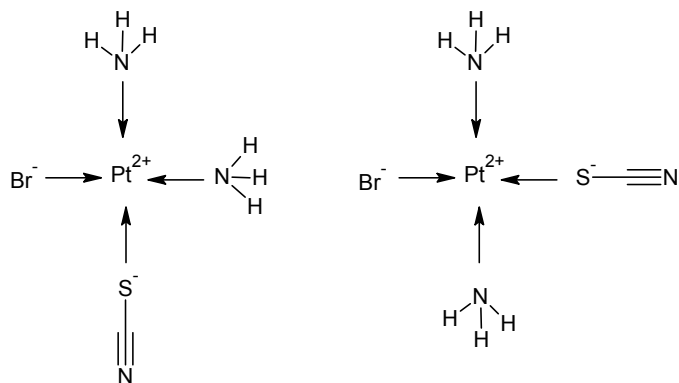


27.8

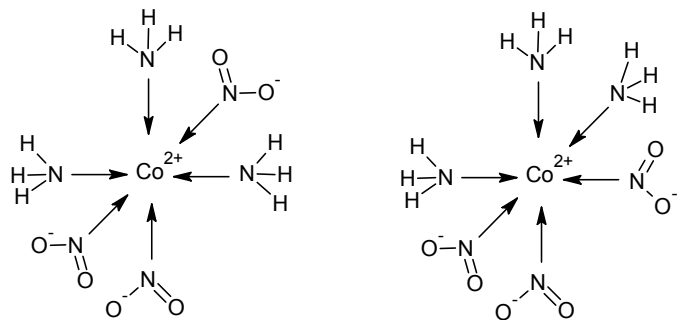
(a)



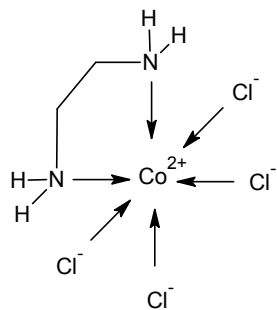
(b)



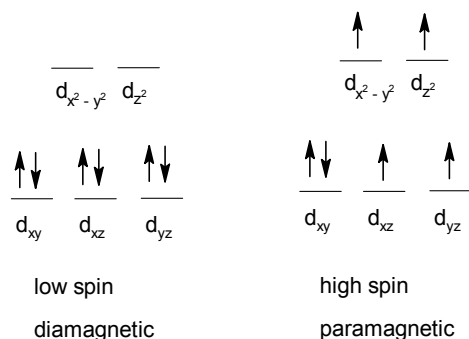
(c)



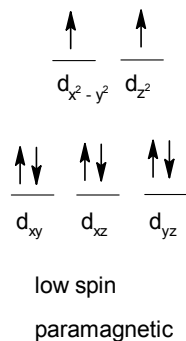
(d)



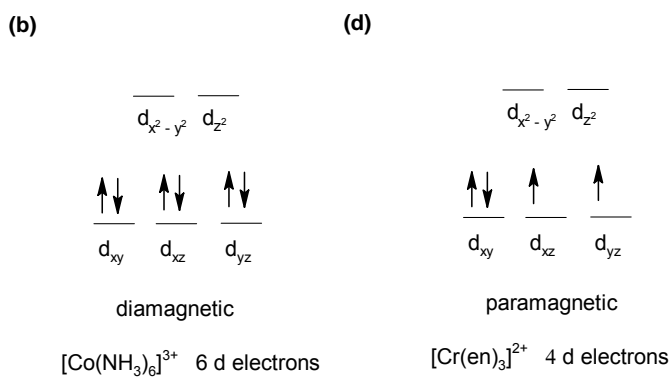
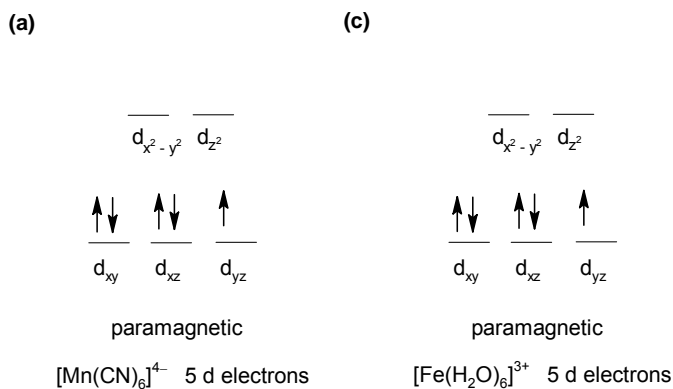
- 27.9 (a) *cis* and *trans* isomers
 (b) no isomers
 (c) no isomers
 (d) two enantiomers
 (e) no isomers
 (f) no isomers
- 27.10 (a) $[\text{Fe}(\text{en})_3]^{2+}$ has a stereocenter at Fe^{2+} giving rise to two enantiomers.
 (b) The cobalt ion in *trans*- $[\text{Co}(\text{en})_2\text{Br}_2]^+$ is 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 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 $[\text{Ru}(\text{H}_2\text{O})_6]^{2+}$, Ru^{2+} is in the +2 oxidation state.



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



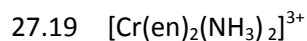
27.13



REVIEW QUESTIONS

- 27.15 (a) $[\text{Ar}] 3d^6$ Fe^{2+} and Co^{3+}
 (b) $[\text{Ar}] 3d^{10}$ Cu^+ and Zn^{2+}
 (c) $[\text{Ar}] 3d^5$ Mn^{2+} and Fe^{3+}
 (d) $[\text{Ar}] 3d^8$ Co^+ and Ni^{2+}

- 27.17 (a) $\text{Cr}_2\text{O}_3(\text{s}) + 2 \text{Al}(\text{s}) \longrightarrow \text{Al}_2\text{O}_3(\text{s}) + 2 \text{Cr}(\text{s})$
 (b) $\text{TiCl}_4(\text{l}) + 2 \text{Mg}(\text{s}) \longrightarrow \text{Ti}(\text{s}) + 2 \text{MgCl}_2(\text{s})$
 (c) $2 [\text{Ag}(\text{CN})_2]^- (\text{aq}) + \text{Zn}(\text{s}) \longrightarrow 2 \text{Ag}(\text{s}) + [\text{Zn}(\text{CN})_4]^{2-} (\text{aq})$
 (d) $3 \text{Mn}_3\text{O}_4(\text{s}) + 8 \text{Al}(\text{s}) \longrightarrow 9 \text{Mn}(\text{s}) + 4 \text{Al}_2\text{O}_3(\text{s})$



- 27.21 First, dissolve a known amount of CrCl_3 in a known volume of water. This process is repeated several times, except that sodium chloride is also added to the solution. The resulting solutions all have the same (known) total concentration of Cr^{3+} , and different (known) total concentrations of chloride. Excess $\text{AgNO}_3(\text{aq})$ is then added to each of these solutions. There will be a precipitate of silver chloride. After filtering, drying and weighing the precipitate, we

can determine how much chloride was available for precipitation in each solution. Since the total amount of chloride is known for each solution, we can determine the amount of chloride that was not available for precipitation in each case. This is the amount of chloride that was part of the complex. Since the total concentration of chromium is known in each case, we now know the ratio of chromium to complex-bound chloride for each solution. These values are then plotted against free chloride concentration – determined by the amount of precipitate. This plot should show whole number plateaus in ranges of chloride concentrations determined by the successive formation constants for the various species. We should be able to identify the ranges that correspond to $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$, $[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]^{2+}$ and $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]^+$. These correspond to 0, 1 and 2 bound chloride per chromium. According to the information given, we need to add diethylether to obtain $[\text{Cr}(\text{H}_2\text{O})_3\text{Cl}_3]$. Thus, an additional experiment wherein diethylether is added to a solution from the experiment described – before the precipitation reaction – in order to obtain the neutral complex species. The neutral compound will partition into the diethylether layer. It can be separated off, and the neutral complex can be obtained by evaporating the ether. Also, once the solutions with specific charged species are identified, we can evaporate the water and crystallize the distinct ionic solid compounds.

- 27.23 (a) 5.0×10^{11}
 (b) 250
 (c) 3.1×10^{-5} M

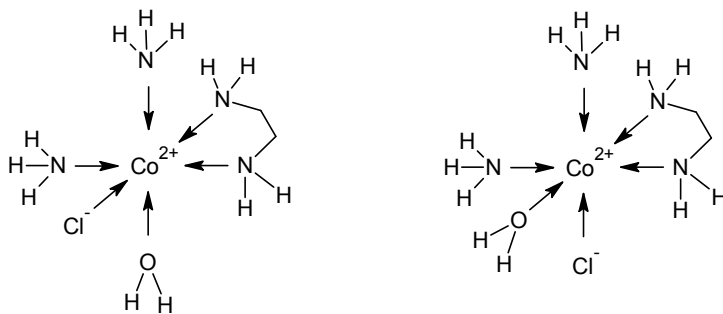
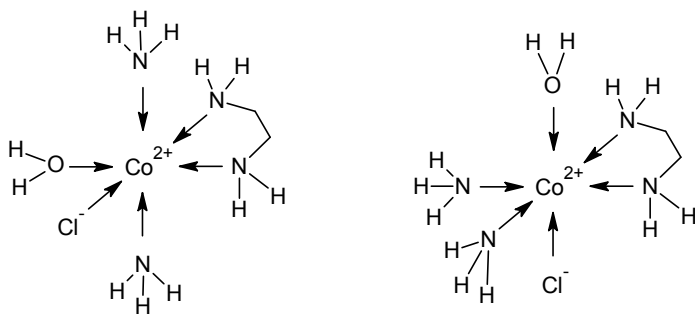
27.25

Complex	Co^{2+}	Ni^{2+}	Cu^{2+}	Zn^{2+}
K_f also known as β	7.7×10^4	5.6×10^8	6.8×10^{12}	2.9×10^9

Here we see the order $\text{Co}^{2+} < \text{Ni}^{2+} < \text{Cu}^{2+} > \text{Zn}^{2+}$ for the stability of the ammine complexes. This is consistent with the Irving-Williams series.

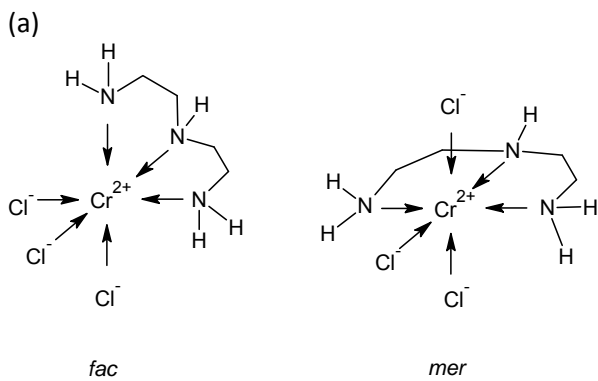
- 27.27 Two stereoisomers – *cis* and *trans*.

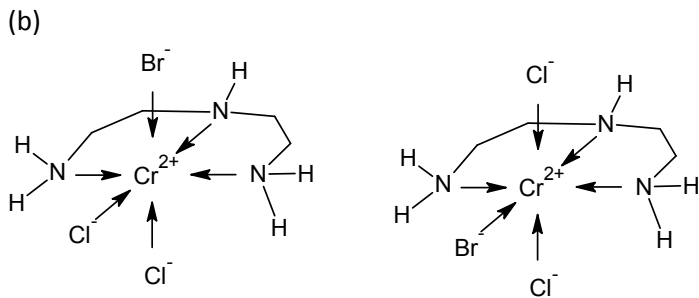
27.29



enantiomers

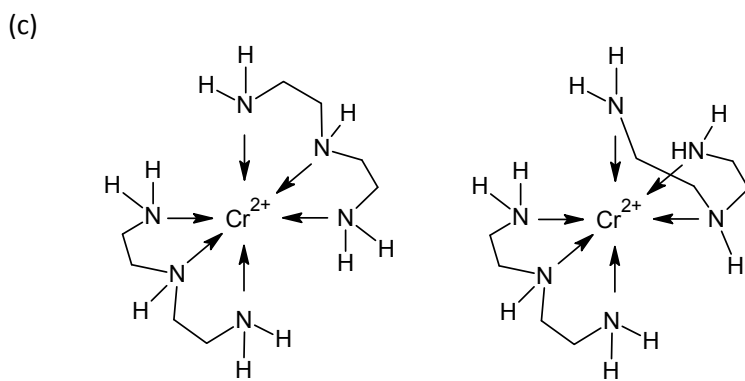
27.31





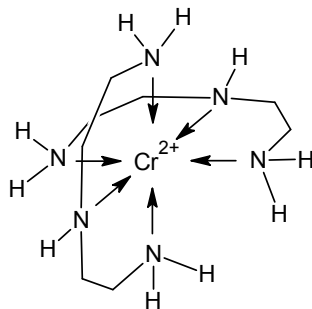
cis-mer

trans-mer



trans-fac

cis-fac

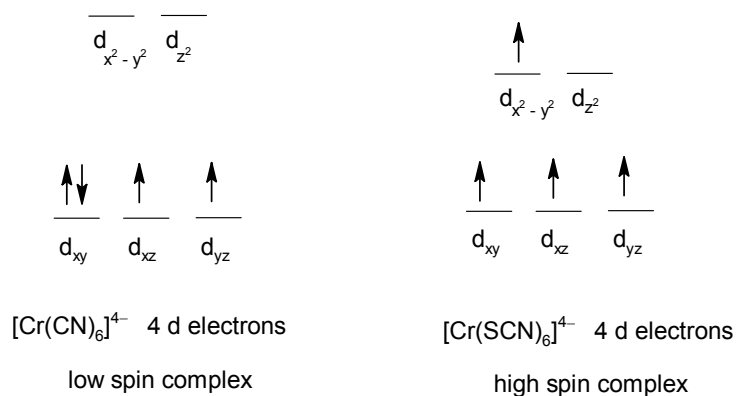


mer

27.33 A *trans* isomer would require the N atoms to be on opposite sides of the platinum. The $-\text{CH}_2\text{CH}_2-$ link between the N atoms is not long enough to allow this.

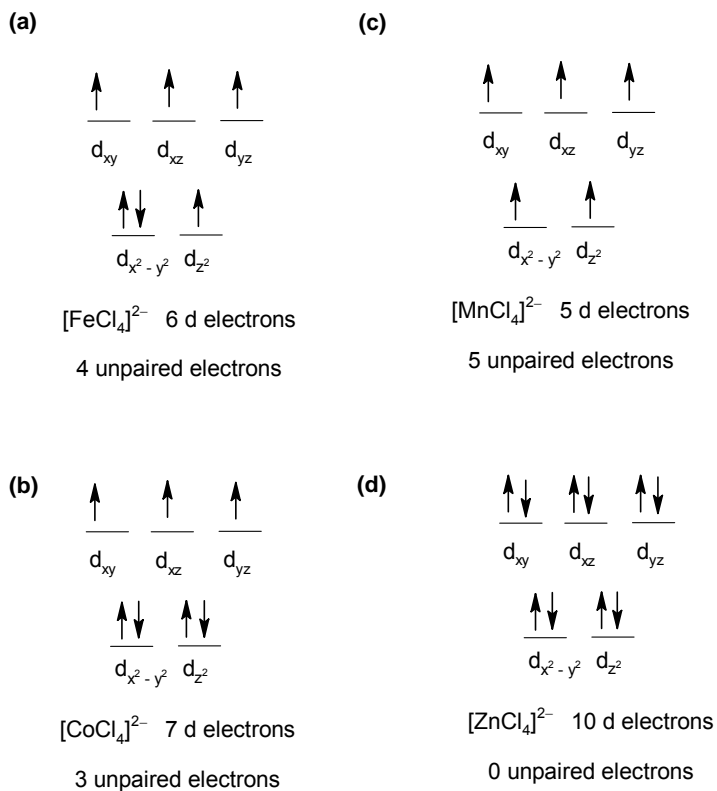
- 27.35 (a) False
 (b) False
 (c) True
 (d) False

27.37

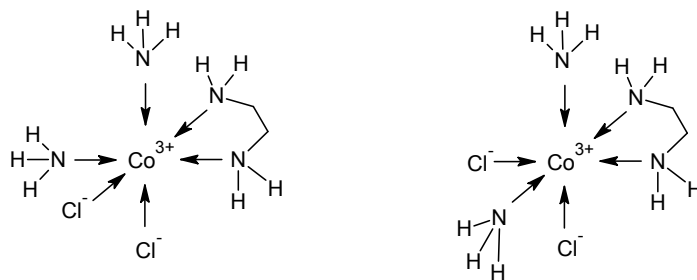
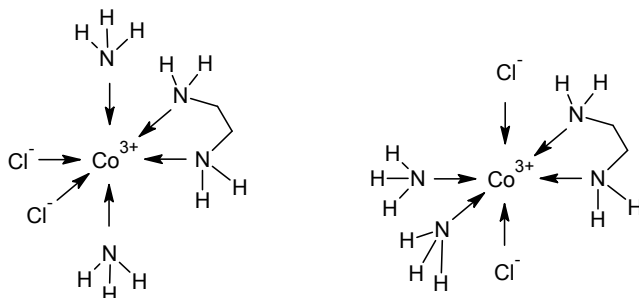


SCN^- is lower in the spectrochemical series than CN^- . It does not split the d orbital energies as much as cyanide.

27.39



- 27.41 (a) 6
 (b) Octahedral
 (c) +3
 (d) 0
 (e) diamagnetic
 (f)

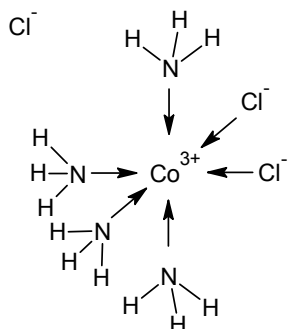


enantiomers

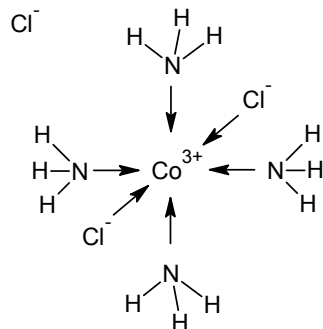
- 27.43 Hexaaquairon(II) is paramagnetic because it is a high spin complex with 4 unpaired electrons. When NH_3 is added to the solution the ammonia complex is formed. This complex is diamagnetic – it is the low spin complex with no unpaired electrons.
- 27.45 Low spin: no unpaired electrons.
 High spin: 4 unpaired electrons.

SUMMARY AND CONCEPTUAL QUESTIONS

27.47



cis-tetraamminedichlorocobalt(III) chloride



trans-tetraamminedichlorocobalt(III) chloride

- 27.49 (a) +2
(b) 6
(c) 1
(d) Paramagnetic

- 27.51 (a) $K = 5.792 \times 10^6$
(b) product-favoured
(c) Because the reaction is exothermic ($\Delta_r H^\circ = -160.8$ kJ), it is less product-favoured at higher temperatures. Consequently, it is possible to use this reaction to purify nickel metal. Specifically, one would react impure nickel with carbon monoxide at ordinary or even low temperature, where the product is highly favoured. The gaseous product is collected, then raised in temperature to reverse the reaction and deposit pure nickel.

Chapter 28

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

REVIEW QUESTIONS

- 28.1 Each Mg atom has 1 $2s$ and 3 $2p$ valence shell orbitals. Thus, there are $4N$ molecular orbitals formed from the valence orbitals of N Mg atoms. Each Mg atom contributes 2 valence electrons, while each molecular orbital can accommodate 2 electrons. Thus, $\frac{1}{4}$ of the available molecular orbitals are filled with electrons.
- 28.3 (a) Metal atoms that can form a solid solution in iron, as interstitial atoms, must be smaller than iron atoms. Iron atoms have a radius of 156 pm. Aluminum atoms have a radius of 118 pm. These are considerably smaller than Fe atoms, and might occupy interstitial sites in a solid solution with iron.

(b) Metal atoms that can form a solid solution in iron, as substitutional atoms, must be similar in size to iron atoms, and have similar electronegativity. Neighbouring elements in the same period as iron have similar size and similar electronic properties. Thus, Mn (radius = 161 pm) or Co (radius = 152 pm) might be expected to form such solid solutions.

- 28.5 The band gap of GaAs is 140 kJ mol^{-1} . The energy gap for an individual electron is this energy divided by Avagadro's number—i.e., $140 \text{ kJ mol}^{-1} / 6.022 \times 10^{23} = 2.32 \times 10^{-22} \text{ kJ} = 2.32 \times 10^{-19} \text{ J}$ (per photon)

The maximum wavelength of light that can excite a transition across the band corresponds to the minimum frequency that can do so. This corresponds to photon energy equal to the band gap.

$$E_g = h\nu = hc/\lambda$$

So,

$$\lambda = hc/E_g = 6.626 \times 10^{-34} \text{ J s} \times 2.998 \times 10^8 \text{ m s}^{-1} / 2.32 \times 10^{-19} \text{ J} = 8.54 \times 10^{-7} \text{ m} = 854 \text{ nm}$$

This corresponds to light in the near infrared region of the electromagnetic spectrum.

- 28.7 Pyrex, or borosilicate glass, is made by adding boron oxide to the melt. The glass that results upon rapid cooling (slow cooling produces opaque ceramic materials) has a lower thermal expansion coefficient (i.e., for a given increase in temperature its degree of expansion is less) than ordinary glass. Thermal expansion (or contraction upon cooling) causes strains in ordinary glass that can cause it to break. This is a problem for glass that is heated in an oven.

- 28.9 (a) Hydroplasticity is the property of materials that become plastic when water is added to them. Clays have this property. When wet, they are readily deformed into almost any desired shape. They retain this shape after deformation, allowing the wet clay to be heated in an oven—i.e., fired—to make the shape firm and rigid.

(b) A refractory material can withstand very high temperatures without deformation. They also have low thermal conductivities, making them useful for thermal insulation—especially under high temperature conditions. For example, the space shuttle uses refractory ceramic tiles in its heat shield to protect against the extreme temperature conditions of re-entry. The Columbia space shuttle disaster resulted from a missing heat shield tile.

SUMMARY AND CONCEPTUAL QUESTIONS

- 28.11 To operate a 700 W microwave oven, we would need N cells of the type described in 28.10, where
- $$700 \text{ W} = N \times 0.0925 \times 0.25 \text{ W} = N \times 0.0231 \text{ W},$$
- accounting for the 25% efficiency, i.e.,
- $$N = 700 / 0.0231 = 30300 \text{ cells required.}$$
- The total area of the solar panel = $30300 \text{ cm}^2 = 3.03 \text{ m}^2$.

28.13 In Table 28.1 of the text, the composition of pewter is given as 91% Sn, 7.5% Sb, 1.5% Cu. To get the density of pewter requires knowing the arrangement of the atoms and appropriate values for the atomic radii. Here, we will assume that the atoms are arranged pretty much the way they are in the bulk elements. We will calculate the density of pewter as a weighted average of the densities of the constituent elements. From www.webelements.com we get the bulk element densities:

Sn	7310 kg m ⁻³
Sb	6697 kg m ⁻³
Cu	8920 kg m ⁻³

From these densities, we get

$$0.91 \times 7310 + 0.075 \times 6697 + 0.015 \times 8920 \text{ kg m}^{-3} = 7288 \text{ kg m}^{-3}$$

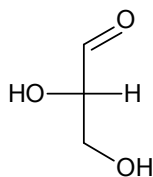
as the approximate density of pewter.

28.15 While hydrogen bonding is usually stronger than dispersion forces (locally), we cannot make a blanket statement that hydrogen bonding is always stronger. Dispersion forces increase with the size of the molecules involved and, more specifically, with the number of electrons. This is why iodine, a non-polar diatomic molecule, is a solid at normal temperature. Iodine atoms have many more electrons than O atoms and especially H atoms, and they are much further from the nucleus so are much more polarizable. The dispersion forces between iodine molecules are consequently substantial—even, based on the evidence of their phases at ambient temperature, more effective than the hydrogen bonding networks in water.

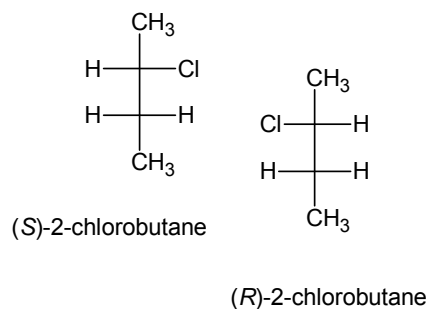
Chapter 29

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

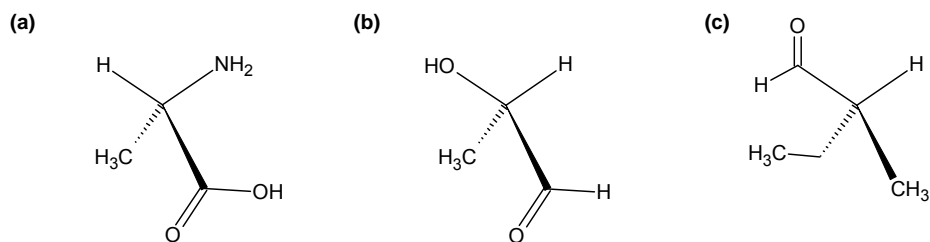
29.2



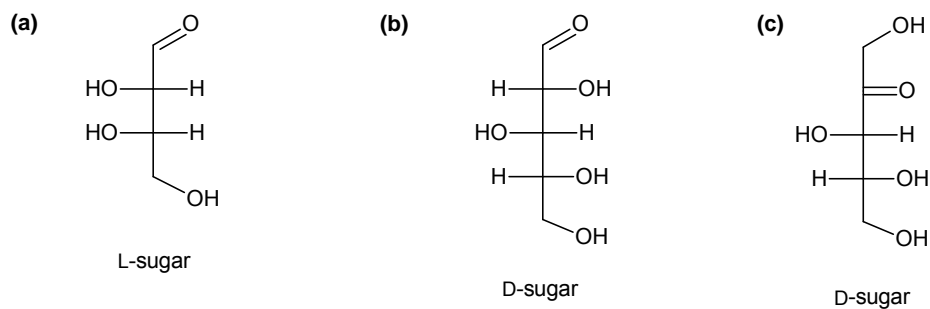
29.3



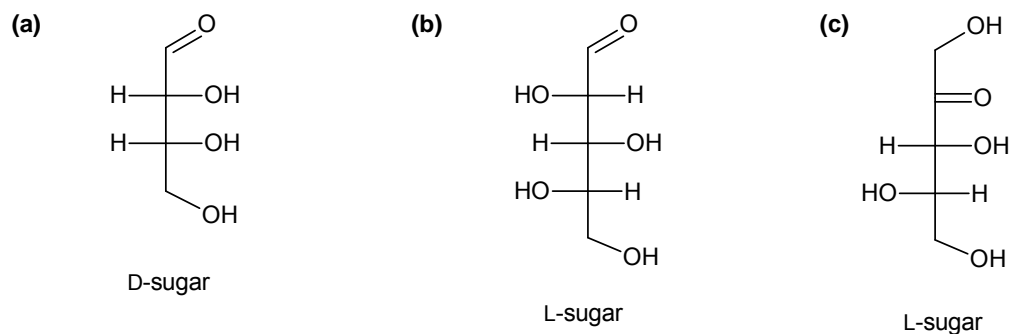
29.4



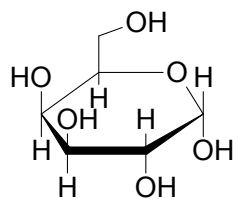
29.5



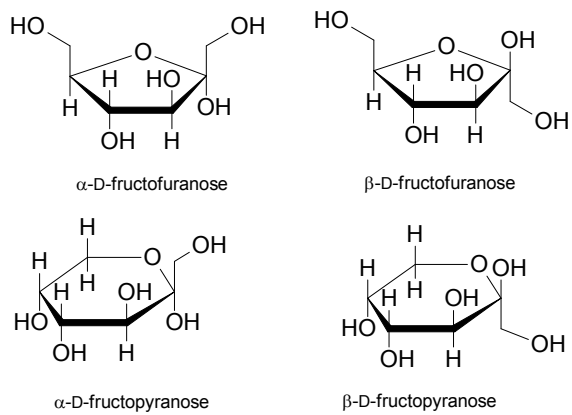
29.6



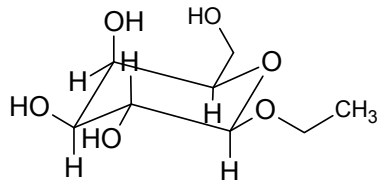
29.7



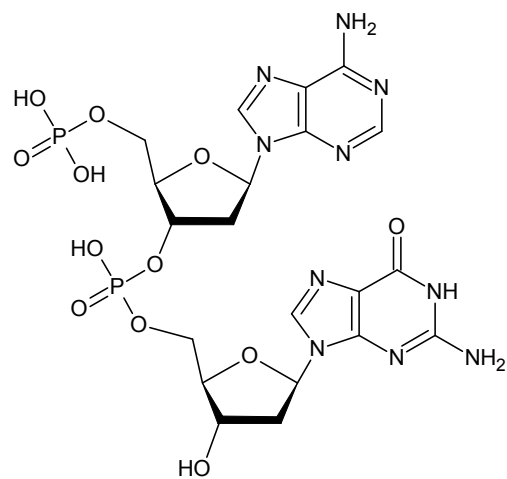
29.9



29.11



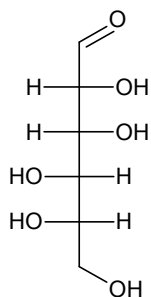
29.13



- 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.
- 29.17 RNA sequence 3'-CUAAUGGCAU-5' or UACGGUAAUC is complementary to DNA sequence GATTACCGTA.
- 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.
- 29.21 mRNA base sequence AUC-GGU gives rise to tRNA sequence, ACC-GAU.

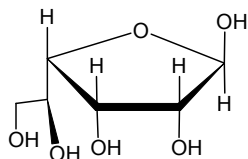
REVIEW QUESTIONS

- 29.23 (a)

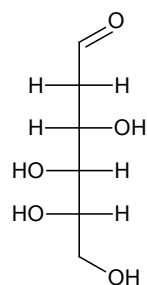


- (b) This is an L sugar – so-called because the hydroxyl on the bottom carbon stereocenter is on the left in this Fischer projection.

- (c)

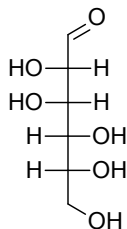


- 29.25

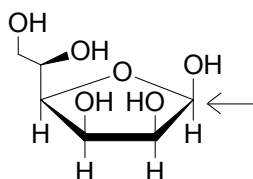


29.27 Ascorbic acid has the L configuration at the carbon next to the primary alcohol.

29.29 (a) A monosaccharide is a simple carbohydrate consisting of a single chain polyhydroxyl ketone or aldehyde. (e.g D-mannose)

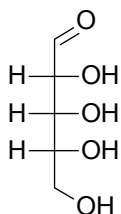


(b)

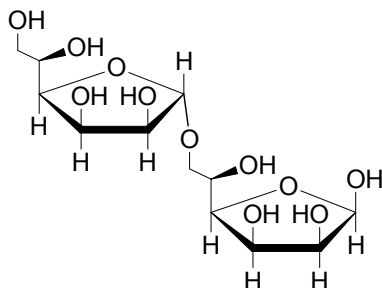


e.g. β -D-mannofuranose – the anomeric center is indicated by the arrow

(c) To make a Fischer projection, we construct the conformation of the carbon chain arranged vertically such that all C–C bonds point into the paper. To do this, we imagine that the carbon chain which otherwise curls into a spiral is flattened onto the plane of the paper – the other substituents on the chain point above the plane of the paper. These bonds are drawn as horizontal lines. The exact stereochemistry is preserved in the Fischer projection.

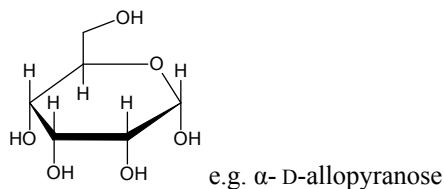


(d) A glycoside is the acetal formed from a monosaccharide and an alcohol. The alcohol is frequently another monosaccharide.



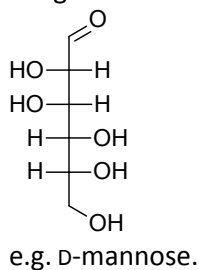
(e) Reducing sugars are sugars that can be reduced by Tollens reagent – a basic aqueous solution of AgNO_3 . Such sugars are aldoses in their open chain form. The ring form is also reducing because it can open up under basic conditions.

(f) Pyranose form is the six-membered ring form of an aldohexose – an aldehyde with 6 carbons.



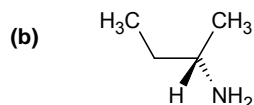
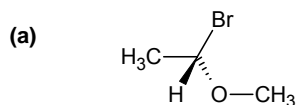
(g) A 1,4' link is a glycosidic linkage between C1 of one saccharide and C4 of another saccharide.

(h) A D-sugar has the D configuration at the carbon next to the primary alcohol.



- 29.31 D-allose and L-allose are enantiomers. In their pure forms, they have the same values of all physical properties except specific rotation. Thus, they have the same **(a)** melting point, **(b)** solubility in water, and **(d)** density.
(c) The specific rotations are equal in magnitude but opposite in sign.

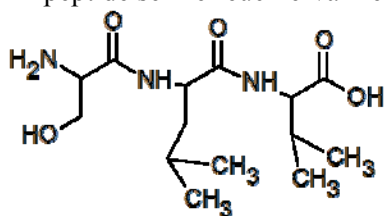
29.33



29.35 28% α -D-galactopyranose and 72% β -D-galactopyranose

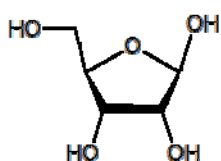
29.37 We see that alanine, leucine, and phenylalanine have non-polar R groups. Serine and aspartic acid have polar R groups. The R group of lysine is a non-polar chain with a polar end.

29.39 Tripeptide serine-leucine-valine:

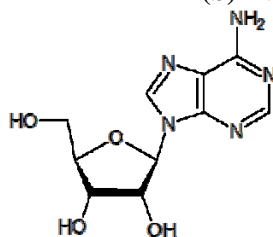


- 29.41 (a) The amino acid sequence in the protein is its primary structure.
(b) The way different peptide chains in the overall protein are arranged with respect to one another is the quaternary structure.
(c) The way the polypeptide chain is folded, including how amino acids which are far apart in the sequence end up in the overall molecule, is the tertiary structure.
(d) The way the amino acids near one another in the sequence arrange themselves is the secondary structure.

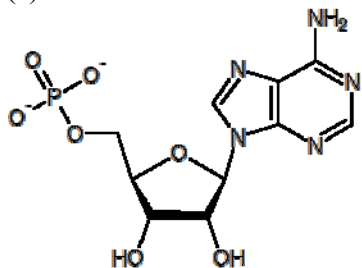
29.43 (a) Sugar ribose:



(b) Nucleoside adenosine:



(c) Nucleotide adenosine 5'-monophosphate:



29.45 ATGC and CGTA are not the same molecule. The nucleosides are differently arranged when connected at the 5' and 3' positions to phosphate.

29.47 (a) Transcription is the process wherein mRNA is produced complementary to a strand of DNA. The first step is the unwinding of the DNA double helix. An RNA strand complementary to a DNA strand is synthesized, next to the DNA strand. The RNA strand is then unwound from the DNA. It goes on to protein synthesis. The DNA returns to its double helix form.

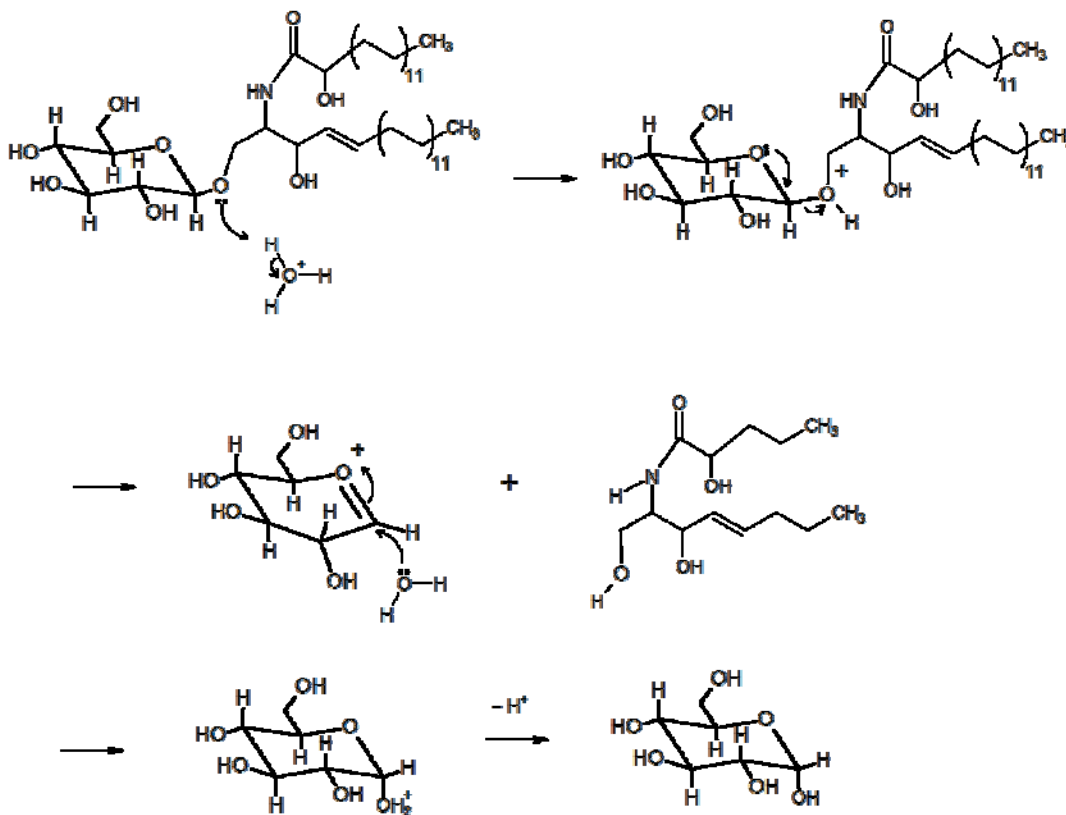
(b) Translation is the process wherein the codons of the mRNA are “read” and used to synthesize the specific coded protein. A process of sequentially “reading” the codons is coordinated with the process that makes a peptide linkage to the next amino acid in the specified sequence.

SUMMARY AND CONCEPTUAL QUESTIONS

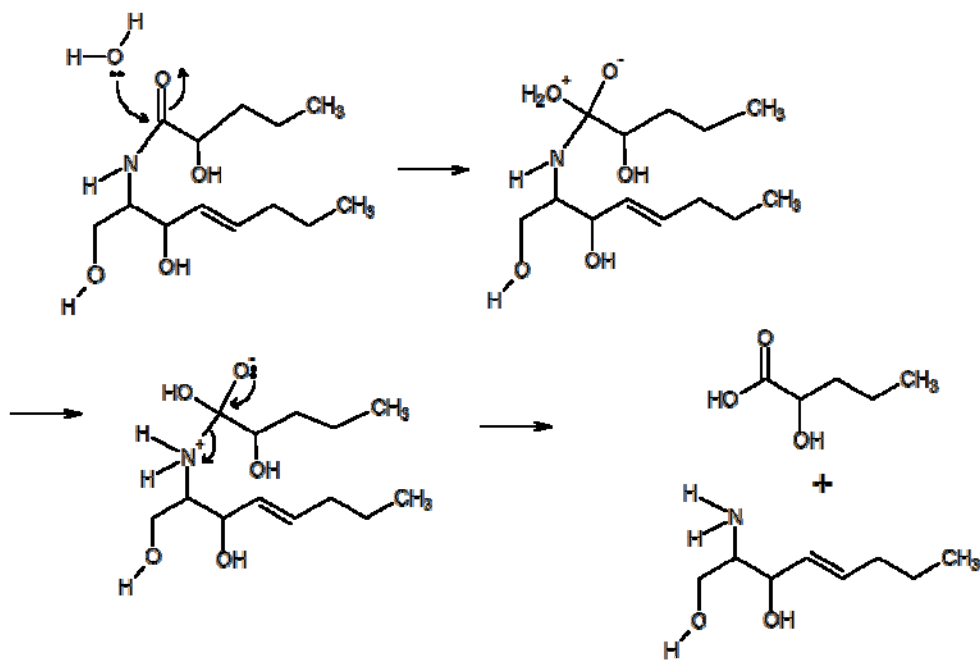
29.49 Raffinose is not a reducing sugar. The glycosidic linkages cannot be hydrolyzed under basic conditions.

29.51 (a) Glucocerebroside has hydroxyl, acetal, amide, alkene and alkyl functional groups.

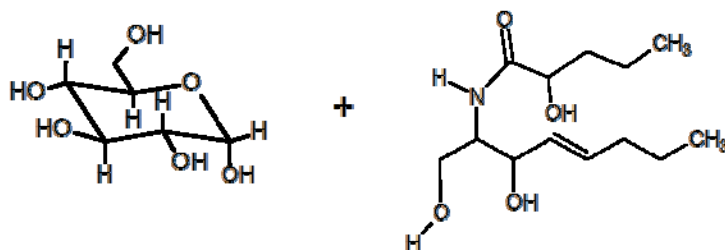
(b) Hydrolysis of glycosidic linkage:



Hydrolysis of amide



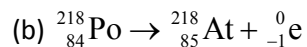
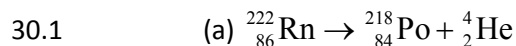
(c)



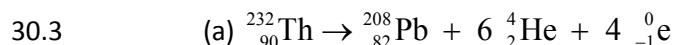
- 29.53 (a) The complementary strand of DNA is (5')—GAATCGCGT—(3')
- (b) The complementary strand of mRNA is (5')—GAAUCGCGU—(3')
- (c) The three anticodons are (5')—UUC—(3'), (5')—CGA—(3'), and (5')—ACG—(3'). They are complementary to the three codons of the mRNA, (5')—GAA—(3'), (5')—UCG—(3'), and (5')—CGU—(3').
- (d) (5')—GAA—(3') codes for Glu, glutamic acid, (5')—UCG—(3') codes for Ser, serine, and (5')—CGU—(3') codes for Arg, arginine.

Chapter 30

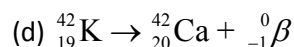
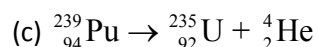
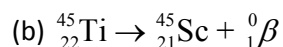
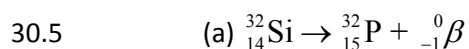
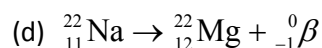
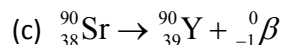
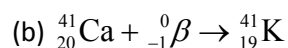
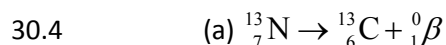
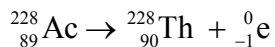
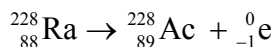
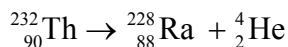
In these solutions, the symbols ${}_{-1}^0\text{e}$ and ${}_{-1}^0\beta$ can be used interchangeably, as can ${}_{2}^4\text{He}$ and ${}_{2}^4\alpha$.



30.2 $E_{\text{photon}} = 9.9 \times 10^{-14} \text{ J}$
 $E = 60 \text{ GJ mol}^{-1}$



(b)



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 ± 52 years

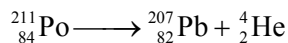
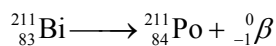
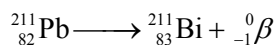
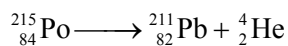
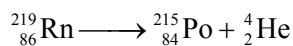
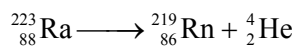
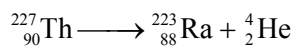
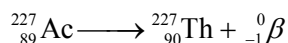
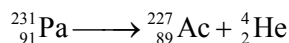
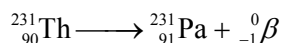
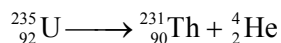
- 30.11 The isolated sample consists of the fraction, $20 / 50 = 0.40$, of the original threonine. Since the isolated sample weighs 60.0 mg, there must have been $60.0\text{mg} / 0.40 = 150.0\text{ mg}$ of threonine in the original sample.

REVIEW QUESTIONS

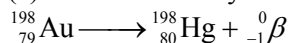
- 30.13 (a) ${}_{26}^{54}\text{Fe} + {}_2^4\text{He} \longrightarrow 2{}_0^1\text{n} + {}_{28}^{56}\text{Ni}$
 (b) ${}_{13}^{27}\text{Al} + {}_2^4\text{He} \longrightarrow {}_{15}^{30}\text{P} + {}_0^1\text{n}$
 (c) ${}_{16}^{32}\text{S} + {}_0^1\text{n} \longrightarrow {}_1^1\text{H} + {}_{15}^{32}\text{P}$
 (d) ${}_{42}^{96}\text{Mo} + {}_1^2\text{H} \longrightarrow {}_0^1\text{n} + {}_{43}^{97}\text{Tc}$
 (e) ${}_{42}^{98}\text{Mo} + {}_0^1\text{n} \longrightarrow {}_{43}^{99}\text{Tc} + {}_{-1}^0\beta$
 (f) ${}_{9}^{18}\text{F} \longrightarrow {}_8^{18}\text{O} + {}_{-1}^0\beta$

- 30.15 (a) ${}_{47}^{111}\text{Ag} \longrightarrow {}_{48}^{111}\text{Cd} + {}_{-1}^0\beta$
 (b) ${}_{36}^{87}\text{Kr} \longrightarrow {}_{-1}^0\beta + {}_{37}^{87}\text{Rb}$
 (c) ${}_{91}^{231}\text{Pa} \longrightarrow {}_{89}^{227}\text{Ac} + {}_2^4\text{He}$
 (d) ${}_{90}^{230}\text{Th} \longrightarrow {}_2^4\text{He} + {}_{88}^{226}\text{Ra}$
 (e) ${}_{35}^{82}\text{Br} \longrightarrow {}_{36}^{82}\text{Kr} + {}_{-1}^0\beta$
 (f) ${}_{11}^{24}\text{Na} \longrightarrow {}_{12}^{24}\text{Mg} + {}_{-1}^0\beta$

30.17

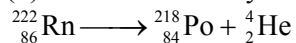


- 30.19 (a) Gold-198 decays to mercury-198.



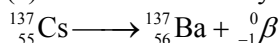
The atomic number increases by 1, while the mass number does not change. This is beta decay.

- (b) Radon-222 decays to polonium-218.



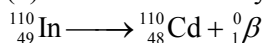
The atomic number decreases by 2, while the mass number decreases by 4. This is alpha decay.

- (c) Cesium-137 decays to barium-137.



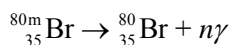
This is beta decay.

- (d) Indium-110 decays to cadmium-110.



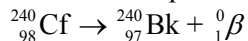
This is positron emission.

- 30.21 (a) Bromine-80m is a metastable state of bromine. It most likely decays by gamma emission to form bromine-80.



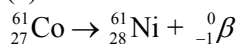
n is the number of gamma photons emitted.

- (b) Californium-240 is beyond—in mass and atomic number—the band of stability. However, its neutron to proton ratio is very low. It most likely decays by positron emission.

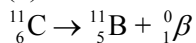


Alternatively: ${}_{98}^{240}\text{Cf} \rightarrow {}_{96}^{236}\text{Cm} + {}_2^4\text{He}$

- (c) Cobalt-61 has a high neutron to proton ratio. It most likely decays by beta emission.



- (d) Carbon-11 has a low neutron to proton ratio. It most likely decays by positron emission.



- 30.23 (a) Of the nuclei ${}^3\text{H}$, ${}^{16}\text{O}$, ${}^{20}\text{F}$ and ${}^{13}\text{N}$

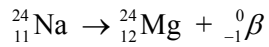
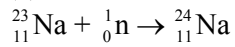
${}^3\text{H}$ and ${}^{20}\text{F}$ have high neutron to proton ratios and are likely to decay by beta emission.

- (b) Of the nuclei ${}^{238}\text{U}$, ${}^{19}\text{F}$, ${}^{22}\text{Na}$ and ${}^{24}\text{Na}$

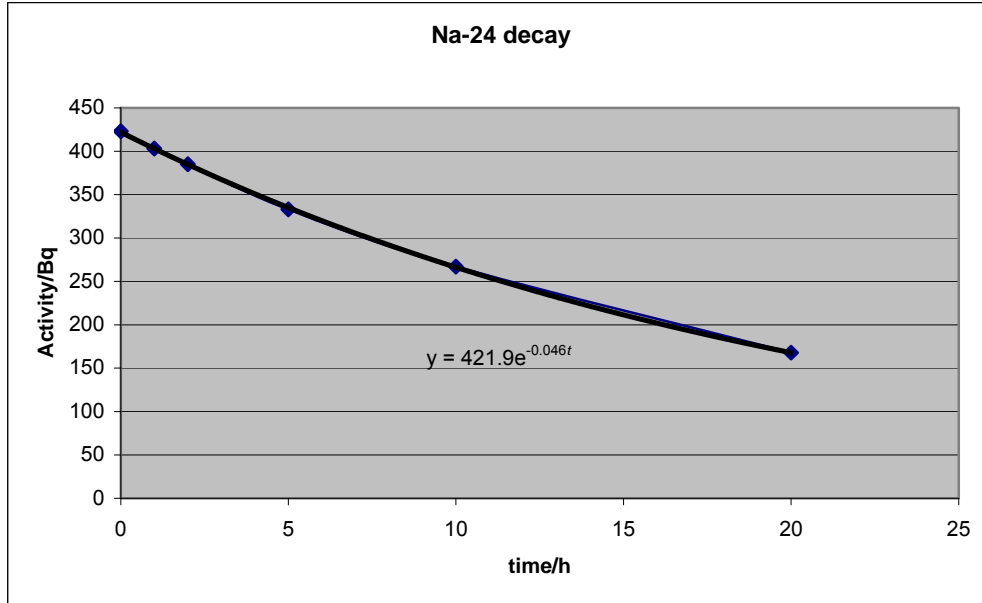
${}^{22}\text{Na}$ has a low neutron to proton ratio and is likely to decay by positron emission.

- 30.25 For ^{10}B ,
 $\Delta m = 5 \times 1.00783 + 5 \times 1.00867 - 10.01294 \text{ g mol}^{-1} = 0.069510 \text{ g mol}^{-1} = 6.9510 \times 10^{-5} \text{ kg mol}^{-1}$
 $E_b = \Delta m c^2$
 $= 6.9510 \times 10^{-5} \text{ kg mol}^{-1} \times (2.998 \times 10^8 \text{ m s}^{-1})^2$
 $= 6.248 \times 10^{12} \text{ J mol}^{-1} = 6.248 \times 10^9 \text{ kJ mol}^{-1}$
 Per nucleon,
 $E_b / n = 6.248 \times 10^9 \text{ kJ mol}^{-1} / 10 = 6.248 \times 10^8 \text{ kJ mol}^{-1} \text{ nucleons}$
 For ^{11}B ,
 $\Delta m = 5 \times 1.00783 + 6 \times 1.00867 - 11.00931 \text{ g mol}^{-1} = 0.081805 \text{ g mol}^{-1} = 8.1805 \times 10^{-5} \text{ kg mol}^{-1}$
 $E_b = \Delta m c^2$
 $= 8.1805 \times 10^{-5} \text{ kg mol}^{-1} \times (2.998 \times 10^8 \text{ m s}^{-1})^2$
 $= 7.353 \times 10^{12} \text{ J mol}^{-1} = 7.353 \times 10^9 \text{ kJ mol}^{-1}$
 Per nucleon,
 $E_b / n = 7.353 \times 10^9 \text{ kJ mol}^{-1} / 11 = 6.684 \times 10^8 \text{ kJ mol}^{-1} \text{ nucleons}$
 We see that ^{11}B is the more stable nucleus—it has a higher binding energy per nucleon.
- 30.31 64 h corresponds to $64 \text{ h} / 12.7 \text{ h} = 5.04$ half-lives. At this time, the mass of ^{64}Cu is
 $25.0 \mu\text{g} \times (1/2)^{5.04} = 0.760 \mu\text{g}$
- 30.33 (a) $^{131}_{53}\text{I} \rightarrow ^{131}_{54}\text{Xe} + ^0_{-1}\beta$
 (b) 40.2 days corresponds to $40.2 \text{ days} / 8.04 \text{ days} = 5.00$ half-lives. At this time, the mass of ^{198}Au is
 $2.4 \mu\text{g} \times (1/2)^5 = 0.075 \mu\text{g}$
- 30.35 13 days corresponds to $13 \text{ days} / (78.25 / 24) \text{ days} = 4.0$ half-lives. At this time, the mass of ^{67}Ga is
 $0.015 \text{ mg} \times (1/2)^{4.0} = 9.4 \times 10^{-4} \text{ mg}$
- 30.37 (a) $^{222}_{86}\text{Rn} \rightarrow ^{218}_{84}\text{Po} + ^4_2\text{He}$
 (b) 20.0% of ^{222}Rn remains after n half-lives.
 $0.200 = (1/2)^n$
 $n = \ln(0.200) / \ln(1/2) = 2.32$
 2.32 half-lives corresponds to $2.32 \times 3.82 \text{ days} = 8.87 \text{ days}$
- 30.39 0.72 of the ^{14}C remains after n half-lives.
 $0.72 = (1/2)^n$
 $n = \ln(0.72) / \ln(1/2) = 0.47$
 0.47 half-lives corresponds to $0.17 \times 5.73 \times 10^3 \text{ years} = 2700 \text{ years}$
 This is the age of the bone fragment.
- 30.41 (a) A cobalt-60 source will drop to 1/8 of its original activity after n half-lives.
 $0.125 = (1/2)^n$
 $n = \ln(0.125) / \ln(1/2) = 3$
 3 half-lives corresponds to $3 \times 5.27 \text{ years} = 15.81 \text{ years}$
 (b) 1 year corresponds to $1 / 5.27 = 0.190$ half-lives. At this time, the fraction of ^{60}Co remaining is
 $(1/2)^{0.190} = 0.877$

30.43 (a)

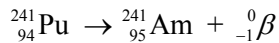
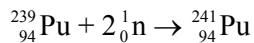


(b)



The data is clearly well fit by a simple exponential decay, $421.9 e^{-0.046 t}$. The parameters of this fit are well approximated using just the first and last data. $k = 0.046$ corresponds to $t_{1/2} = \ln 2 / k = \ln 2 / 0.046 \text{ h} = 15 \text{ h}$

30.45



30.47 ${}_{92}^{238}\text{U} + {}_6^{12}\text{C} \rightarrow {}_{98}^{246}\text{Cf} + 4{}_0^1\text{n}$

It must be carbon-12.

30.49 (a) ${}_{48}^{114}\text{Cd} + {}_1^2\text{H} \rightarrow {}_{48}^{115}\text{Cd} + {}_1^1\text{H}$

(b) ${}_3^6\text{Li} + {}_1^2\text{H} \rightarrow {}_4^7\text{Be} + {}_0^1\text{n}$

(c) ${}_{20}^{40}\text{Ca} + {}_1^2\text{H} \rightarrow {}_{19}^{38}\text{K} + {}_2^4\text{He}$

(d) ${}_{29}^{63}\text{Cu} + {}_1^2\text{H} \rightarrow {}_{30}^{65}\text{Zn} + \gamma$

30.51 ${}_{5}^{10}\text{B} + {}_0^1\text{n} \rightarrow {}_3^7\text{Li} + {}_2^4\text{He}$

30.53 ${}_3^6\text{Li} + {}_0^1\text{n} \rightarrow {}_1^3\text{H} + {}_2^4\text{He}$

SUMMARY AND CONCEPTUAL QUESTIONS

- 30.55 Carbon-14 levels in the atmosphere are in steady state—determined by the flux of cosmic rays that produce it in the upper atmosphere. Plants take up carbon-14 (via carbon dioxide) in proportion to its concentration in the atmosphere. When they die, no more carbon-14 is absorbed. The relative amount of carbon-14 (to carbon-12) decays exponentially with the known half-life of carbon-14. Measuring this isotope ratio allows the age of the sample to be determined—via the logarithm of the isotope ratio divided by its initial value (the atmospheric level). The method, as described here, assumes the atmospheric level has remained constant. This level is known to have varied by up to 10% in the past. The method can be corrected for this variation, however. Nevertheless, the method is limited to objects between 100 and 40,000 years old. There has not been enough carbon-14 decay in objects less than 100 years old, while the level of carbon-14 is too small to give an accurate age measurement beyond 40,000 years.
- 30.57 Radiation can cause transmutation of elements within cells, or can simply ionize or otherwise disrupt cellular molecules. The resulting chemical reactions can significantly affect cellular function and even damage DNA molecules. This can lead to cell death, if the cell is unable to repair the damage at the rate it occurs. Thus, exposure of humans to radiation can cause radiation sickness and even death, at sufficiently exposure levels. The killing of tissue by radiation can be used to treat diseases such as cancer, however. By focusing radiation on a tumour, we can kill the cancer tissue and possibly cure the patient.
- 30.59 The amount of ^{87}Rb is decreased by the factor,
$$0.951 = (1/2)^n$$
$$n = \ln(0.951) / \ln(1/2) = 0.072 \text{ half-lives}$$
This corresponds to $0.072 \times 4.8 \times 10^{10} \text{ years} = 3.5 \times 10^9 \text{ years}$.
- 30.61 The amount of ^{235}U decreases by the factor
$$0.72 / 3.0 = 0.24 = (1/2)^n$$
$$n = \ln(0.75) / \ln(1/2) = 2.06 \text{ half-lives}$$
This corresponds to $2.06 \times 7.04 \times 10^8 \text{ years} = 1.45 \times 10^9 \text{ years}$.
- 30.63 Amount of $^{235}\text{U} = 1000 \text{ g} / 235.0439 \text{ g mol}^{-1} = 4.255 \text{ mol}$
Amount of energy released by fission of uranium 235 = $4.255 \text{ mol} \times 2.1 \times 10^{10} \text{ kJ mol}^{-1} = 8.9 \times 10^{10} \text{ kJ}$
To obtain the same amount of energy from coal requires
 $8.9 \times 10^{10} \text{ kJ} / 2.9 \times 10^7 \text{ kJ t}^{-1} = 3100 \text{ t of coal}$
- 30.65 The time between the sample injection and the taking of the blood sample is negligible compared to the half-life of tritium. This is a sample dilution problem. A 1.0 mL sample was injected, and a 1.0 mL blood sample was taken. The activities measured are proportional to the sample concentrations. The ratio of the activities equals the ratio of the blood volume to 1.0 mL. The blood volume is just
 $2.0 \times 10^6 \text{ Bq} / 1.5 \times 10^4 \text{ Bq} \times 1.0 \text{ mL} = 130 \text{ mL}$
- 30.67 We could label the methanol with the radioactive isotope, ^{15}O , carry out the reaction, and then sample the water and look for ^{15}O that could only have come from methanol. The same experiment could be carried out with labelled acetic acid to see if acid ^{15}O ends up in the water product.

30.69 The number of atoms in 1.0 mg of ^{238}U is

$$6.022 \times 10^{23} \text{ mol} \times 1.0 \times 10^{-3} \text{ g} / 238.050782 \text{ g mol}^{-1} = 2.530 \times 10^{18}$$

From $\Delta N / \Delta t = -kN$

we get (note that $1 \text{ Bq} = 1 \text{ s}^{-1}$)

$$k = (\Delta N / \Delta t) / N$$

$$= 12 \text{ s}^{-1} / 2.530 \times 10^{18} = 4.74 \times 10^{-18} \text{ s}^{-1}$$

$$= 4.74 \times 10^{-18} \text{ s}^{-1} \times (60 \times 60 \times 24 \times 365) \text{ s y}^{-1} = 1.50 \times 10^{-10} \text{ y}^{-1}$$

$$t_{1/2} = \ln(2) / k = 4.6 \times 10^9 \text{ y}$$

This is close to the literature value, and consistent with the uncertainty expected with a measurement of only 12 events.