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

<table>
<thead>
<tr>
<th>Pure</th>
<th>Mixture</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Compounds</strong></td>
<td><strong>Solutions</strong></td>
</tr>
<tr>
<td>(h) testosterone</td>
<td>(b) air</td>
</tr>
<tr>
<td>(f) sodium chloride</td>
<td>(c) vinegar</td>
</tr>
<tr>
<td>(g) athlete’s urine sample</td>
<td>(a) mud</td>
</tr>
<tr>
<td>(e) milk</td>
<td><strong>Elements</strong></td>
</tr>
<tr>
<td>(d) gold</td>
<td><strong>Homogeneous</strong></td>
</tr>
<tr>
<td><strong>Heterogeneous</strong></td>
<td></td>
</tr>
</tbody>
</table>
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 pm/0.001 pm = 10⁵. If the radius of the atom were 100 m, then the nucleus radius would be 100 m/10⁵ = 0.001 m = 1 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)$$^{69}_{31}\text{Ga}: 31\text{ protons}, 38\text{ neutrons}$$  
$$^{71}_{31}\text{Ga} (\%\text{ abundance, } 39.9\%): 31\text{ protons}, 40\text{ neutrons}$$

2.13 (a) 1.99875  
(b) 2.16522  
(c) 1.08329

2.14 Atomic weight of chlorine = \( \frac{75.77}{100} \times 34.96885 + \frac{24.23}{100} \times 36.96590 = 35.45 \)

2.18 10

2.19 (a) 59 g  
(b) \( 1.90 \times 10^{24} \) atoms

2.20 0.97 g
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 $^{57}_{27}$Co, $^{58}_{27}$Co, $^{60}_{27}$Co

2.37 $^{205}$Tl

2.39 50%.

2.41  
<table>
<thead>
<tr>
<th>Symbol</th>
<th>$^{65}$Cu</th>
<th>$^{86}$Kr</th>
<th>$^{195}$Pt</th>
<th>$^{81}$Br</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number of protons</td>
<td>29</td>
<td>36</td>
<td>78</td>
<td>35</td>
</tr>
<tr>
<td>Number of neutrons</td>
<td>36</td>
<td>50</td>
<td>117</td>
<td>46</td>
</tr>
<tr>
<td>Number of electrons in the neutral atom</td>
<td>29</td>
<td>36</td>
<td>78</td>
<td>35</td>
</tr>
<tr>
<td>Name of element</td>
<td>copper</td>
<td>krypton</td>
<td>platinum</td>
<td>bromine</td>
</tr>
</tbody>
</table>

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 25ºC  

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 x 10^-5 mol  
5.67 x 10^19 atoms  

2.61 (a) A_r^'(1H) = 1, A_r^'(11B) = 10.9241, A_r^'(24Mg) = 23.7994, and A_r^'(63Cu) = 62.4525  
(b) A_r^'(1H) = 1.0088, A_r^'(11B) = 11.0199, A_r^'(24Mg) = 24.0080, and A_r^'(63Cu) = 63  
(c) A_r^'(1H) = 1.0084, A_r^'(11B) = 11.0162, A_r^'(24Mg) = 24, and A_r^'(63Cu) = 62.9790  

2.63 \[ \delta^{13}C = \left( \frac{R_{sample} - R_{standard}}{R_{standard}} \right) \times 1000 \]  

\[ \delta^{13}C = \left[ \frac{218,248}{20,000,002} - 0.0112372 \right] / 0.112372 \times 1000 = -28.90 \] is consistent with a thermogenic sample  

<table>
<thead>
<tr>
<th>Biogenic Methane</th>
<th>Thermogenic Methane</th>
</tr>
</thead>
<tbody>
<tr>
<td>-100</td>
<td>0</td>
</tr>
</tbody>
</table>

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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 \text{radius of jar and the height of the jar in jelly bean length units. Squaring the first quantity, then dividing by } \pi \text{ 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\(_3\))\(_2\);
(b) equal amounts of Na\(^+\) and CH\(_2\)CO\(^2-\) in NaCO\(_2\)CH\(_3\)
(b) FeCl\(_2\) and FeCl\(_3\) are the compounds formed by Fe\(^{2+}\) and Fe\(^{3+}\), respectively
(c) Na\(_2\)S, Na\(_3\)PO\(_4\), 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 $^{1}$H are the most common isotopes of carbon, oxygen and hydrogen. The molar mass of the most abundant isotopologue, $^{12}$C$_2$$^{1}$H$_6$$^{16}$O, is 46.04189 g mol$^{-1}$. This is not in exact agreement with the experimental value.  

3.18  (a) 16.043 g mol$^{-1}$  
(b) 58.080 g mol$^{-1}$  
(c) 93.129 g mol$^{-1}$  

3.19  (a) 1.53 g  
(b) 4.60 g  
(c) 4.59 g  

3.23  A single chlorine atom  
C$_6$H$_3$Cl  
112.008002; 114.005052  

3.24  C$_6$H$_5$CHCH$_2$ or C$_8$H$_8$  

3.25  (a) C=O stretch - ketone, aldehyde or carboxylic acid  
(b) C-N-H bend of an amine  
(c) C≡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, $\text{NH}_4^+$, has one more proton than electron - hence the +1 charge.  
(b) phosphate, $\text{PO}_4^{3-}$, has three more electrons than protons - hence the −3 charge.  
(c) dihydrogen phosphate, $\text{H}_2\text{PO}_4^-$, has one more electron than protons - hence the −1 charge.

3.33  
$\text{Na}_2\text{CO}_3$ sodium carbonate  
$\text{BaCO}_3$ barium carbonate  
$\text{NaI}$ sodium iodide  
$\text{BaI}_2$ 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)

3.37  
(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 $\text{C}_2\text{H}_4$ comes really close to this value. If the data were from a low resolution spectrometer, we could not rule out $\text{H}_2\text{CN}$ (molecular mass = 28.01873), $\text{N}_2$ (molecular mass = 28.00614) and $\text{CO}$ (molecular mass = 27.99491).

3.43  
(a) carboxylic acid and aromatic ring  
absorption wavenumbers in cm$^{-1}$:  
(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) alcohol, nitrile, and aromatic ring  
3200-3550 broad peak due to alcohol (phenol) O-H stretch  
2210-2260 due to nitrile C≡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

3.45   (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 C≡N stretch (delete words- not given in Table 3.5)
(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
3.47   (a) 159.688 g mol\(^{-1}\)
       (b) 117.170 g mol\(^{-1}\)
       (c) 176.1241 g mol\(^{-1}\)
3.49   21 million kMol
3.51   (c)  CaS
3.53   (a) 305.4119 g mol\(^{-1}\)
       (b) 1.8\times10^{-4} 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 Cl₂ 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 CaCl₂
     (b) calcium, carbon and oxygen atoms are in a 1:1:3 ratio in CaCO₃
     (c) nitrogen and hydrogen atoms are in a 1:3 ratio in NH₃
     (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 Al³⁺ 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 C≡N stretch – not given in Table 3.5
1705-1725  due to ketone C=O stretch
1640-1670  due to C=C stretch

3.69  (a)  Look for the N-H stretch of CH$_3$CH$_2$NHCH$_3$ – a peak around 3250-3400 cm$^{-1}$ not seen for (CH$_3$)$_3$N.
(b)  Look for the ketone C=O stretch of CH$_3$COCH$_3$ – a peak around 1705-1725 cm$^{-1}$ – or the OH stretch – a broad peak around 2500-3300 cm$^{-1}$.
(c)  Look for the aldehyde C-H peaks (2 of them) of CH$_3$CH$_2$CHO, around 2700-2850 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 x 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.
4.13 (a) Covalent bonds hold the nitrogen atoms together in the N\textsubscript{2} molecules, inside the clathrate hydrate.
(b) Dispersion forces attract the N\textsubscript{2} and H\textsubscript{2}O molecules within the clathrate hydrate cage.
(c) Hydrogen bonding holds neighboring H\textsubscript{2}O together molecules to make the clathrate hydrate cage.
(d) Dispersion forces attract the N\textsubscript{2} and O\textsubscript{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\textsubscript{3}CH\textsubscript{3}(g); ozone, O\textsubscript{3}(g); and chloroform, CHCl\textsubscript{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.

4.25 In the troposphere, halocarbons have their greatest impact on radiative forcing. They are important greenhouse gases with a positive forcing.

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 CO$_2$ 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 CO$_2$ level. The CO$_2$ 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

(a) alkane
(b) alkene and alkane
(c) alkene, alkane and alcohol
(d) Benzaldehyde has aromatic and aldehyde functional groups
Presence of a strong oxidizing agent on Mars means the environment is hostile to many fragile molecules found on Earth. On the other hand, together with suitable reducing agents, a strong oxidizing agent such as hydrogen peroxide provides a potential rapid source of energy that evolving life forms might exploit. Here on Earth, animal forms of life exploit the readily available, strong oxidizing agent, O₂, to provide a quick source of energy.
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 SF\(_6\) has more bonds than CO\(_2\) 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\times10^6 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 O\(_2\)(g)
     3.0 mol of Al\(_2\)O\(_3\)(s)

5.5 (a) A small amount of solid sodium chloride in water has a higher chemical potential than a dilute solution of sodium chloride.
     (b) A dilute solution of sodium chloride is more stable than a small amount of solid sodium chloride in water.
5.6  (a) Neither. Chemical potential on both sides of these reactions are equal.
(b) A mixture of solid calcium carbonate in pure water has a higher chemical potential than a
mixture containing solid calcium carbonate and Ca\(^{2+}\)(aq) ions and CO\(_3\)^{2-}(aq) both at a
concentration of 6 × 10\(^{-5}\) mol L\(^{-1}\).
(c) A mixture containing solid calcium carbonate and Ca\(^{2+}\)(aq) ions and CO\(_3\)^{2-}(aq) both at a
concentration of 6 × 10\(^{-5}\) 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\(_2\)O are formed.

5.11  (a) CO is the limiting reactant
(b) 407 g of CH\(_3\)OH produced
(c) 14 g of H\(_2\) remain

5.12  (a) Fe\(_2\)O\(_3\) 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) H\(_2\)O(g) → H\(_2\)O(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 Cu²⁺(aq) ions is about 0.5 mol L⁻¹ and the concentration of Ag⁺(aq) ions is about 1 x 10⁻¹⁰ mol L⁻¹.
(b) A mixture containing some solid silver in an aqueous solution in which the concentration of Cu²⁺(aq) ions is about 0.5 mol L⁻¹ and the concentration of Ag⁺(aq) ions is about 1 x 10⁻¹⁰ 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 CO₂ = 36.6 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  TiO₁.₅ or Ti₂O₃

5.39  11.2%

5.41  66.7 kg

5.43  weight percent CuS in ore = 30 %
      weight percent Cu₂S in ore = 70 %

SUMMARY AND CONCEPTUAL QUESTIONS

5.45  (a) 8.8 g.
      (b) 1.5
      (c) FeBr₃
      (d) 2 Fe(s) + 3 Br₂(l) → 2 FeBr₃
      (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 Pt(NH₃)₂Cl₂ 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 H₂ to inflate the balloon. 0.107 − 0.050 mol = 0.057 mol of zinc remains.
(2) In this case, there is just enough zinc to consume all of the HCl. The same amount of H₂ 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 H₂ 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 x 10³ 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 dipoles vectors only partially cancel out, leaving a NET dipole moment.

6.13 (a) BFCl$_2$ is trigonal planar. It has a NET dipole because one of the three bonds is different – more polar – than the other two. If the three substituents on B were the same, as in BCl$_3$, then the bond dipoles would cancel.
(b) NH$_2$Cl 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 $CH_3-O\cdots\cdot\cdot\cdot O-H$

\[
\begin{array}{c}
| \\
CH_3CH_3
\end{array}
\]

shows the hydrogen bonding between neighbouring methanol molecules as they move past each other.
6.19  (a) bromine  
(b) butane

6.23  (a) ICl  
(b) Krypton  
(c) ethanol

6.24  (a) dispersion forces  
(b) hydrogen bonds and dispersion forces  
(c) dispersion forces

6.27  Mg\(^{2+}\)(aq) and Br\(^{-}\)(aq) are the main species present in solution when some magnesium bromide, MgBr\(_2\)(s), is dissolved in water.

6.28  (a) soluble  
\[
\text{LiNO}_3(s) \xrightarrow{H_2O} \text{Li}^+(aq) + \text{NO}_3^-(aq)
\]

(b) soluble  
\[
\text{CaCl}_2(s) \xrightarrow{H_2O} \text{Ca}^{2+}(aq) + 2 \text{Cl}^-(aq)
\]

(c) insoluble

(d) soluble  
\[
\text{NaCH}_3\text{COO}(s) \xrightarrow{H_2O} \text{Na}^+(aq) + \text{CH}_3\text{COO}^-(aq)
\]

6.29  (a) Ammonia, NH\(_3\)(g), is soluble in water because water molecules can make strong hydrogen bonds with ammonia molecules – O-H and H-N.  
(b) Hydrogen chloride, HCl(g), is soluble in water because water molecules can make strong hydrogen bonds with HCl molecules – O-H only.  
(c) Iodine, I\(_2\)(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, C\(_8\)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\(_6\)H\(_6\)(\(\ell\)), 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, \( \text{CH}_3\text{CH}_2\text{CH}_2\text{OH}(\ell) \), should be more soluble in hexane than butan-2,4-diol, \( \text{HOCH}_2\text{CH}_2\text{CH}_2\text{OH}(\ell) \). 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) \( \text{HBr(g)} + \text{H}_2\text{O(l)} \rightarrow \text{H}_3\text{O}^+(\text{aq}) + \text{Br}^-(\text{aq}) \)

(b) \( \text{HF(aq)} + \text{H}_2\text{O(l)} \xrightarrow{\text{only some ionised}} \text{H}_3\text{O}^+(\text{aq}) + \text{F}^-\text{(aq)} \)

(c) \( \text{HCOOH(aq)} + \text{H}_2\text{O(l)} \xrightarrow{\text{only some ionised}} \text{HCOO}^-\text{(aq)} + \text{H}_3\text{O}^+(\text{aq}) \)

(d) \( \text{C}_{12}\text{H}_{22}\text{O}_{11}(\text{s}) \xrightarrow{\text{H}_2\text{O}} \text{C}_{12}\text{H}_{22}\text{O}_{11}(\text{aq}) \)

6.36 (a) \( \text{Cu}^{2+}(\text{s}) + \text{CO}_3^{2-}\text{(aq)} \rightarrow \text{CuCO}_3\text{(s)} \)

\( \text{Na}^+\text{ and Cl}^-\text{ are spectator ions} \)

(b) No precipitate forms

(c) \( \text{Ni}^{2+}(\text{s}) + 2\text{OH}^-\text{(aq)} \rightarrow \text{Ni(OH)}_2\text{(s)} \)

\( \text{K}^+\text{ and Cl}^-\text{ are spectator ions} \)

6.37 \( \text{Fe}^{2+} \text{ is oxidized to Fe}^{3+} \text{. The oxidizing agent is MnO}_4^-\text{. MnO}_4^-\text{ is reduced to Mn}^{2+}\text{. Fe}^{2+} \text{ is the reducing agent.} \)

6.38 (a) \( \text{HCOOH is the acid reactant, while OH}^-\text{ is the base reactant.} \)

(b) \( \text{H}_2\text{CO}_3\text{ is the acid reactant, while NH}_3\text{ is the base reactant.} \)

(c) \( \text{H}_2\text{C}_2\text{H}_4\text{O}_6\text{ is the acid reactant, while HCO}_3^-\text{ is the base reactant.} \)

(d) \( \text{H}_3\text{O}^+\text{ is the acid reactant, while CH}_3\text{NH}_2\text{ is the base reactant.} \)

6.39 (a) \( \text{H}_3\text{O}^+(\text{aq}) + \text{OH}^-\text{(aq)} \rightarrow 2\text{H}_2\text{O(l)} \)

\( \text{Li}^+\text{ and Br}^-\text{ are spectator ions} \)

(b) \( \text{H}_2\text{CO}_3\text{(aq)} + \text{OH}^-\text{(aq)} \rightarrow \text{HCO}_3^-\text{(aq)} + \text{H}_2\text{O(l)} \)

and \( \text{HCO}_3^-\text{(aq)} + \text{OH}^-\text{(aq)} \rightarrow \text{CO}_3^{2-}\text{(aq)} + \text{H}_2\text{O(l)} \)

\( \text{K}^+\text{ is a spectator ion.} \)

(c) \( \text{H}_3\text{O}^+(\text{aq}) + \text{CH}_3\text{NH}_2\text{(aq)} \rightarrow \text{H}_2\text{O(l)} + \text{CH}_3\text{NH}_3^+(\text{aq}) \)

\( \text{NO}_3^-\text{ is a spectator ion} \)

(d) \( \text{H}_3\text{Citrate(aq)} + \text{OH}^-\text{(aq)} \rightarrow \text{H}_2\text{Citrate}^-\text{(aq)} + \text{H}_2\text{O(l)} \)

\( \text{H}_2\text{Citrate}^-\text{(aq)} + \text{OH}^-\text{(aq)} \rightarrow \text{HCitrate}^{2-}\text{(aq)} + \text{H}_2\text{O(l)} \)

\( \text{HCitrate}^{2-}\text{(aq)} + \text{OH}^-\text{(aq)} \rightarrow \text{Citrate}^{3-}\text{(aq)} + \text{H}_2\text{O(l)} \)

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

6.41

6.42  
(a) [Co(H$_2$O)$_6$]$^{2+}$(aq) + 4 Cl$^-$(aq) $\rightarrow$ [CoCl$_4$]$^{2-}$(aq) + 6 H$_2$O($\ell$)
Lewis base, Cl$^-$, competes successfully with the Lewis base, H$_2$O, to complex Co$^{2+}$.
(b) [Fe(H$_2$O)$_6$]$^{2+}$(aq) + 6 CN$^-$(aq) $\rightarrow$ [Fe(CN)$_6$]$^{4-}$(aq) + 6 H$_2$O($\ell$)
Lewis base, CN$^-$, competes successfully with the Lewis base, H$_2$O, to complex Fe$^{2+}$.
(c) [Ni(H$_2$O)$_6$]$^{2+}$(aq) + 2 CH$_3$NH$_2$(aq) $\rightarrow$ [Ni(CH$_3$NH$_2$)$_2$]$^{3+}$(aq) + 6 H$_2$O($\ell$)
Lewis base, CH$_3$NH$_2$, competes successfully with the Lewis base, H$_2$O, to complex Ni$^{2+}$.
(d) [Cu(H$_2$O)$_6$]$^{2+}$(aq) + 4 Cl$^-$(aq) + 2 NH$_3$(aq) $\rightarrow$ [Cu(NH$_3$)$_2$Cl$_4$]$^{2-}$(aq) + 6 H$_2$O($\ell$)
Lewis bases, Cl$^-$ and NH$_3$, compete successfully with the Lewis base, H$_2$O, 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 mol L$^{-1}$ NH$_4^+$ (aq) and 0.25 mol L$^{-1}$ SO$_4^{2-}$ (aq)
(b) 0.246 mol L$^{-1}$ Na$^+$ (aq) and 0.123 mol L$^{-1}$ CO$_3^{2-}$ (aq)
(c) 0.056 mol L$^{-1}$ H$_3$O$^+$ (aq) and NO$_3^-$ (aq)
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.

(a) Intramolecular forces.
(b) Intermolecular forces.
(c) Intramolecular forces.
(d) Intermolecular forces.

(a) C→O
(b) P→Cl
(c) B→O
(d) B→F

HF > HCl > HBr > HI

(a) BeCl₂ is non-polar.
(b) HBF₂ is polar. The negative end is at the two F atoms.
(c) CH₃Cl is polar. The negative end is at the Cl atom.
(d) SO₃ is non-polar.

(b) H₂S (g)

(b) HCOOH

(Kr) It is bigger with more electrons

(a) dispersion forces
(b) metallic bonds
(c) dipole-dipole and dispersion forces
(d) H-bonds and dispersion forces

(a) < (b) < (c) < (d). (a), (b) and (c) are gases at 25°C and 1 atm.

(a) higher.
(b) higher.
(c) unchanged.
(d) higher.
(e) smaller.
(f) higher.

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 Ca²⁺.
(b) The H end (the positive end) of water points to Br⁻.
(c) The H end (the positive end) of water points to Cr₂O₇²⁻.
(d) The O end (the negative end) of water points to NH₄⁺(aq).

6.85  H₂O(ℓ), Ag⁺(aq), NO₃⁻(aq), K⁺(aq) and Cl⁻(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,

\[ 2 \text{H}_2\text{O}(ℓ) \rightarrow \text{H}_3\text{O}⁺(aq) + \text{OH}⁻(aq) \]

6.91  Since barium sulfate, BaSO₄(s), precipitates from water, whereas iron (ii) sulfate does not, we conclude that BaSO₄(s) is insoluble in water (it has a very low solubility) whereas FeSO₄(s) is soluble.
6.93

\[
2\text{Cr}_2\text{O}_7^{2-}(aq) + 28\text{H}^+(aq) + 12\text{e}^- \rightarrow 4\text{Cr}^{3+}(aq) + 14\text{H}_2\text{O}(\ell)
\]

\[
3\text{C}_2\text{H}_5\text{OH}(aq) + 3\text{H}_2\text{O}(\ell) \rightarrow 3\text{CH}_3\text{COOH}(aq) + 12\text{H}^+(aq) + 12\text{e}^-
\]

Here, ethanol, \(\text{C}_2\text{H}_5\text{OH}\), is oxidized to acetic acid, \(\text{CH}_3\text{COOH}\). Dichromate, \(\text{Cr}_2\text{O}_7^{2-}\), is the oxidizing agent. \(\text{Cr}_2\text{O}_7^{2-}\) is reduced to \(\text{Cr}^{3+}\). 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, \(\text{Ba}^{2+}(aq)\) and \(\text{OH}^-(aq)\) are produced.

6.97 (a) \([\text{Fe}(\text{NH}_3)_6]^{2+}\)
(b) \([\text{Zn}(\text{CN})_4]^{2-}\)
(c) \([\text{MnF}_6]^{3+}\)
(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 \(\text{AgNO}_3(s)\), add it to the volumetric flask, add ~150 mL of de-ionized water, stopper the flask and shake to dissolve the \(\text{AgNO}_3\) and ensure a homogenenous solution. After the \(\text{AgNO}_3\) 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 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 \(\text{Na}_2\text{CO}_3 = 0.254 \text{ mol L}^{-1}\)
concentration of \(\text{Na}^+ = 0.508 \text{ mol L}^{-1}\)
concentration of \(\text{CO}_3^{2-} = 0.254 \text{ mol L}^{-1}\)

**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 CH₃COOH 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. Cu²⁺ 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

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**Chapter 7**

7.1 (a) 1 mol each of H⁺(aq) ions and OH⁻(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 Fe₂O₃(s) mixture is the system (initially – later it consists of Al₂O₃(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 Br₂(ℓ).
(b) metallic liquid, Hg(ℓ).
(c) ionic solid Na₂SO₄(s).
(d) molecular liquid CH₃CH₂OH(ℓ).
(e) 1 mol L⁻¹ concentration Cl⁻(aq).

7.17  (a) The standard enthalpy change of this reaction, Δ_rH°, 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, Δ_rH°, 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, Δ_rH°, 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, Br$_2$(ℓ), is the standard enthalpy change of the following reaction:
Br$_2$(ℓ) → Br$_2$(ℓ) at 25 °C

(b) The standard molar enthalpy of formation of solid iron (iii) chloride, FeCl$_3$(s), is the standard enthalpy change of the following reaction:
Fe(s) + Cl$_2$(g) → FeCl$_3$(s) at 25 °C

(c) The standard molar enthalpy of formation of solid sucrose, C$_{12}$H$_{22}$O$_{11}$(s), is the standard enthalpy change of the following reaction:
12 C(graphite) + 11 H$_2$(g) + $\frac{11}{2}$O$_2$(g) → C$_{12}$H$_{22}$O$_{11}$(s) at 25 °C

7.22  The standard molar enthalpy of formation of liquid methanol, CH$_3$OH(ℓ), is the standard enthalpy change of the following reaction:
C(graphite) + 2 H$_2$(g) + $\frac{1}{2}$O$_2$(g) → CH$_3$OH(ℓ) at 25 °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) H₂O(ℓ)
      (b) NaCl(s)
      (c) Hg(ℓ)
      (d) CH₄(g)
      (e) 2.00 mol L⁻¹ is the Na⁺(aq) concentration

7.47  90.3 kJ

7.49  (a) −601.24 kJ mol⁻¹
      (b) −1503.1 kJ

7.51  −905.47 kJ

7.53  −77.69 kJ

7.55  Δ₅H° = −352.9 kJ. Mass of Mg (s) = 7.24 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 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 °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  
(c) d subshell  
(d) $l$ is 0 and $m_l$ has the value 0  
(e) 3 orbitals  
(f) 7 values of $m_l$  

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) $n = 3$, $l = 3$, $m_l = \square -1$, $m_s = +\frac{1}{2}$ is not valid because $l$ must be less than or equal to $n - 1$.  

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8.27
(a) 90% isosurface of 1s orbital
50% isosurface of 1s orbital

(b) 90% isosurface of 2s orbital
90% isosurface of 1s orbital

8.28
s orbital 90% isosurface
p orbital 90% isosurface

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

8.32
[Ne] [↑↓] [↑] [↑] [↑] [↑]

3s
3p

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
\( Z^*(12\text{Mg}) = +2.85 \); \( Z^*(13\text{P}) = +4.8 \); \( Z^*(18\text{Ar}) = +6.75 \)

8.35
\( Z^*(16\text{O}) = +4.55 \); \( Z^*(16\text{O}^2) = +3.85 \)
Although $^{84}_{20}$Po has a lot more electrons than $^{11}_{1}$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.

\[ Z^*(Na) = +2.2; \quad Z^*(Si) = +4.15; \quad Z^*(Ar) = +6.75 \]

\[ Z^*(N^3-) = +2.85; \quad Z^*(S^3-) = -0.8 \]

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.

\[ Z^*(Na^+) = +6.85; \quad Z^*(Mg^{2+}) = +7.85; \quad Z^*(Al^{3+}) = +8.85 \]

The valence electrons of these three ions are increasingly tightly held. This is consistent with the trend in sizes – the ions decrease in size.

\[ Z^*(Mg^-) = +2.5; \quad Z^*(Cl^-) = +5.75 \]

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.

\[ Z^*(Ar^-) = +1.2 \]

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 $^\circ$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 $^\circ$C—and it does not conduct electricity.

8.47 C < B < Al < Na < K

8.49 K < Ca < Si < P

8.51 (a) $S^-$
(b) $Cl^-$

8.53 (a) C < B < Al
(b) Al < B < C
(c) carbon
8.55  (a) S < O < F  
(b) O  
(c) Cl  
(d) O^{2-}

8.59  2.179 x 10^{-18} 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  (a) 

(b) 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
(e) \( 1 + 3 + 5 + 7 = 16 \)

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 \([\text{Ar}]4s^2 3d^{10} 4p^6 = [\text{Kr}] \)

8.92  (a) Elements with atomic numbers 17, 18, and 19 – i.e. Cl, Ar and K – have the following effective nuclear charges: +6.1, +6.75 and +2.2, respectively.
Here, we see that argon is unreactive because it holds its electrons very tightly. It is therefore hard to remove an electron. Adding an electron produces an effective nuclear charge of +1.2 (1 less than that of K) – a much lower value. This is a very unfavorable process. Chlorine similarly holds its electrons very tightly, but it can add an electron to yield an anion with an effective nuclear charge of +5.75 (1 less than Ar). This is a very stable anion, making its formation via reaction of chlorine very favorable – chlorine is highly reactive. K is similarly very reactive. In this case, it is because the valence electron is easily lost – K forms the +1 cation.

(b) (i) \( Z^*(\text{Ne}^-) = +1.2 \)
(ii) \( Z^*(\text{Ar}^-) = +1.2 \)
(iii) \( Z^*(\text{Kr}^-) = +2.7 \)

The valence electron in these anions is weakly held. Though the effective nuclear charge of \( \text{Kr}^- \) is larger, its radius is so large that the electron is still quite weakly held. The neutral atoms all have much larger effective nuclear charges. They are quite unreactive with respect to formation of the anion. Nevertheless, krypton compounds have been synthesized – not so for neon and argon. This latter observation is consistent with \( \text{Kr}^- \) having the larger effective nuclear charge – making it more stable.
(c) Because $Z^*$ is so large for Ne, Ar and Kr atoms, the valence electrons are held very tightly. This reduces the polarizability of these atoms, and correspondingly reduces the dispersion forces between them. These elements occur mostly as monatomic gases. They have very low melting and boiling points.

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 \text{Mg}^+ to \text{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 Li$^{1+}$ 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 3200-3550 cm$^{-1}$) of butan-1-ol in the IR spectra.

9.3 The spectra on the right and left are those of propan-2-amine and propan-1-amine, respectively.
9.4  
(a) 1  
(b) 4  
(c) 3  
(d) 7  

9.5  
(a) 1 peak in both carbon-13 and proton spectra  
(b) 1 peak in both carbon-13 and proton spectra  
(c) 2 peaks in both carbon-13 and proton spectra  
(d) 1 peak in both carbon-13 and proton spectra  
(e) 1 peak in both carbon-13 and proton spectra  
(f) 1 peak in both carbon-13 and proton spectra  
(g) 2 peaks in both carbon-13 and proton spectra  
(h) 2 peaks in both carbon-13 and proton spectra  
(i) 2 peaks in carbon-13 spectrum and 1 peak in proton spectrum  

9.6  

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

9.7  

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

These are the Newman projections of the three eclipsed conformations. The conformation on the left has the highest energy. The other two have the same energy.
9.8 There is only one staggered and one eclipsed conformation of propane.

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

9.10 (a) C₅H₅N: one H atom is bonded to each C atom
(b) C₆H₁₂O: two H atoms are bonded to each C atom, except the C=O carbon
(c) C₈H₆NH: 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) \(-\text{Br} > -\text{CH}_2\text{CH}_3\text{OH} > -\text{CH}_2\text{CH}_3 > -\text{H}\)
(b) \(-\text{OH} > -\text{CO}_2\text{CH}_3 > -\text{CO}_2\text{H} > -\text{CH}_2\text{OH}\)
(c) \(-\text{Br} > -\text{Cl} > -\text{CH}_2\text{Br} > -\text{CH}_2\text{Cl}\)

9.22

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

9.23

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)

\[ \text{H} \]
\[ \text{CH}_3\text{−CH}_2\text{−C}≡\text{C}−\text{CH}_2\text{−CH}_2\text{−CH}_3 \]
\[ \text{H} \]

(b)

\[ \text{CH}_3\text{−CH}−\text{CH}_2−\text{CH}_2−\text{CH}_3 \]
\[ \text{CH}_3 \]

(c)

\[ \text{O} \]
\[ \text{CH}_3\text{−CH}−\text{C}−\text{H} \]
\[ \text{CH}_3 \]

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

9.39 Possible skeletal structures:
(a) \[
\begin{array}{c}
\text{C}_4\text{H}_8 \\
\text{H}_2\text{C}≡\text{CH}_3
\end{array}
\]
(b) \[
\begin{array}{c}
\text{C}_3\text{H}_6\text{O} \\
\text{H}_2\text{C}≡\text{O}−\text{CH}_3
\end{array}
\]
(c) \[
\begin{array}{c}
\text{C}_4\text{H}_9\text{Cl} \\
\text{H}_2\text{C}−\text{Cl}
\end{array}
\]

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

\( \text{cis} \) and \( \text{trans} \) 2-butene
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.

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

The methyl groups are in equatorial positions.

The methyl substituent has greater steric requirements than the electron lone pair – the former is in the more accommodating equatorial position.
9.57

(a)
\[
\begin{align*}
\text{H}_3\text{C} & \quad \text{H} & \quad \text{CH}_3 \\
\text{H}_3\text{C} & \quad \text{H} & \quad \text{CH}_3 \\
\end{align*}
\]
chiral centre

(b)
\[
\begin{align*}
\text{O} & \quad \text{H} \\
\end{align*}
\]
chiral centre

(c)
\[
\begin{align*}
\text{H}_3\text{C} & \quad \text{H} \\
\end{align*}
\]
achiral

the ring has a plane of
symmetry through C4
and the carbonyl bond

(d)
\[
\begin{align*}
\text{H} & \quad \text{Br} \\
\text{Br} & \quad \text{H} \\
\end{align*}
\]
two chiral centres

Depending on whether the stereocenters
are configured S,S or R,R, or S,R (R,S is
the same by symmetry), the molecule is
either chiral (former case - S,S and R,R
are enantiomers) or achiral (S,R = R,S is
called a meso compound)

(e)
\[
\begin{align*}
\text{H}_3\text{C} & \quad \text{H} \\
\end{align*}
\]
achiral

the ring has a plane of
symmetry through C4
and the carbonyl bond

9.59
37.0°

9.61

S configuration

R configuration

If a lone pair of electrons has
lower priority than H, then we
have the S configuration
here.

Of course, the configuration
will flip rapidly and no
chirality will result, except at
very low temperatures.

9.63

(a)

(b) 1\text{SO}_3\text{H} \quad 2\text{SH} \quad 3\text{OCH}_2\text{CH}_2\text{OH} \quad 4\text{NH}_2
9.65 The configurations at the chiral centers are:
(a) S  (b) S  (c) S

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

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

9.71

Ribose – three stereocenters indicated with circles. The 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
The two enantiomers of *trans*-1,2-dimethylcyclopentane – they are the non-superimposable mirror images of each other.

The stereocenters are denoted by solid white circles.

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.

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

(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 $\text{NH}_4^+$

\[
\begin{align*}
\text{CO} & \\
\text{CO} & \\
\text{SO}_4^{2-} & \\
\text{SO}_4^{2-} & \\
\end{align*}
\]

10.4 $\text{CH}_3\text{OH}$

10.5 $\text{NH}_2\text{OH}$

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10.6 (a) Acetylide ion, $\text{C}_2^-$, is isoelectronic with $\text{N}_2$.
(b) $\text{SO}_2$
(c) $\text{OH}^-$

10.9

The three resonance structures of nitrate, $\text{NO}_3^-$.

A structure for nitric acid, $\text{HNO}_3$

10.11

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

10.12

Equivalent resonance structures that together best describe the charge distribution within ozone.
10.13

Tetrahedral shape. The Cl—C—Cl bond angle is predicted to be 109.5°

10.16

BF₃ is trigonal planar. BF₄⁻ is tetrahedral.

10.17

(a) phosphate ion, PO₄³⁻, is tetrahedral

(b) phosphoric acid molecule, H₃PO₄, is tetrahedral at the P
(c) sulfate ion, \(\text{SO}_4^{2-}\), is tetrahedral

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

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

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

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 $sp^3$ orbitals, and methyl-carbon $sp^3$ orbitals. The remaining $sp^2$ orbital forms the $\sigma$ bond to oxygen.

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

The C=O double bond is formed from the unhybridized $p$ orbitals on each atom – both atoms are $sp^2$ hybridized with one unhybridized $p$ orbital. This $p-p$ bond is the C-O $\pi$ bond.
The N atoms have a linear arrangement of two electron regions. This means \( sp \) hybridization. An \( sp \) orbital from each N atom is used to make the N-N \( \sigma \) bond. The remaining \( sp \) orbitals accommodate the lone pairs – one on each atom.

The two remaining \( p \) orbitals on each atom overlap in pairs to form the two N-N \( \pi \) bonds. Specifically, the \( p_x \) orbitals overlap to form the \( \pi_x \) bond, while the \( p_y \) orbitals overlap to form the \( \pi_y \) bond.

\[ \begin{align*} 
: & \text{N} \equiv \text{N}: \\
\text{The N atoms have a linear arrangement of two electron regions. This means } & \text{sp hybridization. An sp orbital from each N atom is used to make the N-N } \sigma \text{ bond. The remaining sp orbitals accommodate the lone pairs – one on each atom.}
\end{align*} \]

\[ \begin{align*} 
: & \text{N} \equiv \text{N}: \\
\text{The two remaining } p \text{ orbitals on each atom overlap in pairs to form the two N-N } \pi \text{ bonds. Specifically, the } p_x \text{ orbitals overlap to form the } & \pi_x \text{ bond, while the } p_y \text{ orbitals overlap to form the } \pi_y \text{ bond.}
\end{align*} \]
The methyl C atom has the tetrahedral distribution of electron regions - \( sp^3 \) hybridization at the methyl carbon atoms. Three of the \( sp^3 \) orbitals overlap with s orbitals on H atoms to form the C-H bonds, while the fourth makes a bond with the carbonate C atom.

The carbonate C atom has a trigonal-planar arrangement of electron regions - \( sp^2 \) hybridization here. The C-C bond is formed from one of these \( sp^2 \) orbitals, and a methyl-carbon \( sp^3 \) orbital. The remaining two \( sp^2 \) orbitals form \( \sigma \) bonds to oxygen atoms.

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

What remains are a \( p \) orbital on each of the O atoms and the unhybridized \( p \) orbital on the carbonate carbon atom – three orbitals in all. Two electron pairs also remain. In a valence bond description, a \( \pi \) bond is formed using the \( p \) orbital on C and one of the O atom \( p \) orbitals. The other O-atom \( p \) orbital accommodates the remaining lone pair of electrons. This can be written in one of two equivalent ways – the resonance structures of carbonate. However, because of symmetry it is more accurate to think of the \( p \) orbital on C and both of the O atom \( p \) orbitals forming a delocalized \( \pi \) bond, though this goes beyond valence bond theory. We must think of the two O atom \( p \) orbitals being combined to form two delocalized (over the two O atoms) orbitals – analogous to orbital hybridization except that the orbitals are on different atoms (these are molecular orbitals). One of the delocalized orbitals forms a symmetric \( \pi \) bond with carbon, the other accommodates the remaining lone pair of electrons.

\[
\begin{align*}
10.25 \quad & H_2^+: (\sigma_{1s})^1 \\
& He_2^+: (\sigma_{1s})^2(\sigma_{1s}^*)^1 \\
& H_2^-: (\sigma_{1s})^2(\sigma_{1s}^*)^1
\end{align*}
\]

\( H_2^+ \) 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, \( \frac{1}{2} \).
10.27 Electron configuration of ground state $O_2^+$

\[ \text{[core electrons]} (\sigma_{2s})^2 (\sigma_{2s}^*)^2 (\pi_{2p})^2 (\pi_{2p})^2 (\sigma_{2p})^2 (\pi_{2p}^*)^1 \]

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

$O_2^+$ is expected to be paramagnetic. Its electron configuration shows an unpaired electron.

### REVIEW QUESTIONS

10.31 Elements in group 13 have 3 valences electrons. To obey the octet rule, such elements must form four bonds. Three of these bonds are formed by sharing each of the valence electrons with another atom. This gives the atom 6 valence electrons. To get 8, the atom must form a fourth “coordinate bond” wherein both electrons come from a different atom.

Elements in group 17 have 7 valence electrons. They can form an octet by forming a single bond.

10.33

(a) 

(b) 

(c) 

(d) 

10.35

(a) 

(b)
10.37

(a) $\text{SO}_2$

(b) $\text{NO}_2$

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

10.39

Average C-O bond order = $3/2$
10.41

(a)

\[ \cdot\text{O} \quad \text{N} \quad \cdot\text{O} \quad \]

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

(b)

\[ \cdot\text{O} \quad \text{N} \quad \cdot\text{O} \quad \quad \cdot\text{O} \quad \text{N} \quad \cdot\text{O} \quad \]

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

(c)

\[ \cdot\text{N} \quad \text{F} \quad \text{F} \quad \text{F} \quad \]

All atoms have zero formal charge.

(d)

\[ \cdot\text{O} \quad \text{N}^{+} \quad \cdot\text{O} \quad \text{O} \quad \text{H} \quad \]

Formal charges are as shown.

10.43

\[ \cdot\text{O} \quad \text{N} \quad \cdot\text{O} \quad \quad \cdot\text{O} \quad \text{N} \quad \cdot\text{O} \quad \]

If H\textsuperscript+ attaches to NO\textsubscript{2}\textsuperscript{−} (to form the acid HNO\textsubscript{2}), it attaches to an O atom – not N.
(a) \[ \cdot \cdot \cdot \text{O} \equiv \text{C} \equiv \cdot \cdot \cdot \]
There are two electron regions about the carbon atom. The electron geometry and the molecular geometry are linear.

(b) \[ \cdot \cdot \cdot \text{O} \equiv \text{N} \equiv \cdot \cdot \cdot \quad \cdot \cdot \cdot \text{O} \equiv \text{N} \equiv \cdot \cdot \cdot \]
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) \[ \cdot \cdot \cdot \text{O} \equiv \cdot \cdot \cdot \quad \cdot \cdot \cdot \text{O} \equiv \cdot \cdot \cdot \]
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) \[ \cdot \cdot \cdot \text{O} \equiv \cdot \cdot \cdot \quad \cdot \cdot \cdot \text{O} \equiv \cdot \cdot \cdot \]
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)
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 $\sigma$ 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 $\sigma$ bonds with C atoms.

(b+c) 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 120º.
The sulfur atom uses $sp^2$ orbitals to form two $\sigma$ bonds – one with each O atom.
The other $sp^3$ 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 $\pi$ 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 $\pi$ bonds - one with each of the O atoms.

(b) SO$_3$

The O-S-O bond angle is 120º.
The sulfur atom uses $sp^2$ orbitals to form three $\sigma$ 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 $\pi$ bonds - one with each of the O atoms. Otherwise, if we use just the $p$ orbital, then S can form only one S-O $\pi$ bond.

(c) SO$_3^{2-}$

The O-S-O bond angle is 109.5º.
The sulfur atom uses $sp^3$ orbitals to form three $\sigma$ 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 $\pi$ bonds - one with each of two O atoms.
(d) \( \text{SO}_4^{2-} \)

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 \( \text{CO}_2 \) the carbon atom uses two \( sp \) orbitals to form σ bonds with each O atom. Each of the two unhydridized \( p \) orbitals forms a π bond with an O atom. In \( \text{CO}_3^{2-} \), 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 unhydridized \( p \) 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) 

![O2- structure diagram]

The bond order in \( \text{O}_2^{2-} \) is 1.

(b) The molecular orbital theory electron configuration for \( \text{O}_2^{2-} \) is (using unhybridized orbitals)

\[
[\text{core electrons}] (\sigma^2_2s)^2 (\sigma^2_2p)^2 (\pi^2_2p)^2 (\sigma^*_2p)^2 (\pi^*_2p)^2 (\pi^*_2p)^2 
\]

Bond order = \( \frac{1}{2} \times (2 + 2 + 2 + 2 - 2 - 2 - 2) = 1 \)

(c) For \( \text{O}_2^{2-} \), 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

\((\sigma_{2s})^2(\sigma_{2s}^*)^2(\pi_{2p_z})^2(\pi_{2p_y})^2(\pi_{2p_x})^1\)

an unpaired electron \(\rightarrow\) paramagnetic

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

(b) \(\text{OF}^-\)

\((\sigma_{2s})^2(\sigma_{2s}^*)^2(\pi_{2p_z})^2(\pi_{2p_y})^2(\sigma_{2p_x})^2(\pi_{2p_y}^*)^2(\pi_{2p_z}^*)^2\)

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

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

(c) \(\text{O}_2^{2-}\)

\((\sigma_{2s})^2(\sigma_{2s}^*)^2(\pi_{2p_z})^2(\pi_{2p_y})^2(\sigma_{2p_x})^2(\pi_{2p_y}^*)^2(\pi_{2p_z}^*)^2\)

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

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

(d) \(\text{Ne}_2^+\)

\((\sigma_{2s})^2(\sigma_{2s}^*)^2(\pi_{2p_z})^2(\pi_{2p_y})^2(\sigma_{2p_x})^2(\pi_{2p_y}^*)^2(\pi_{2p_z}^*)^1\)

an unpaired electron \(\rightarrow\) paramagnetic

HOMO = \(\pi_{2p_y}^*\)

(e) \(\text{CN}\)

\((\sigma_{2s})^2(\sigma_{2s}^*)^2(\pi_{2p_z})^2(\pi_{2p_y})^2(\sigma_{2p_x})^1\)

an unpaired electron \(\rightarrow\) paramagnetic

HOMO = \(\pi_{2p_x}\)

**SUMMARY AND CONCEPTUAL QUESTIONS**

10.63

![NF₃ molecule](image)

NF₃ has four electron pairs about the central atom, and a trigonal pyramidal shape.

![OCl₂ molecule](image)

OCl₂ 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$_3$OH), 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 H$_3$N→BF$_3$ is tetrahedral. (b) In BF$_3$, the valence orbitals of boron are $sp^2$ hybridized. In H$_3$N→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 $32 \times 10^4$ L

11.5 650 balloons

11.6 136 kPa

11.10 121 gmol$^{-1}$

11.13 $P(C_2HBrClF_3) = 37.7$ kPa

$P(O_2) = 364$ 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 g mol\(^{-1}\)

11.23 (a) the dispersion forces in liquid O\(_2\) < (c) the dipole induced dipole interactions of O\(_2\) dissolved in H\(_2\)O < (b) the hydrogen bonding forces in liquid CH\(_3\)OH

11.25 (a) 167 mmHg
(b) the vapour and liquid are NOT at equilibrium – the vapour is supersaturated and vapour condenses to form more liquid.

11.26 0.50 g of water is not enough to achieve a partial pressure of 19.3 kPa. Instead, we achieve only 15 kPa.

With 2.0 g of water, the partial pressure of water would be 19.3 kPa.

11.27 (a) The density of liquid CO\(_2\) is less than that of solid CO\(_2\).
(b) gas phase
(c) No.

**REVIEW QUESTIONS**

11.29 \(T\) (80 km) < \(T\) (25 km) < \(T\) (110 km) < \(T\) (5 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 produce absorbs 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) \(c\) (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 atm = 30.0 kPa = 0.300 bar

11.37 0.117 L
11.39 9.7 atm

11.41 Molar volume (at 448.15 K and 1.00 bar) of H₂, CO₂ and SF₆ 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 x 10⁷ 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 cms⁻¹

11.63 4.58 cms⁻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 I₂ dissolves in methanol, CH₃OH, dispersion forces holding I₂ 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 °C  
(c) The equilibrium vapour pressure of ethanol is higher than that of water at 70 °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 \(T = -196 \, ^\circ\text{C}\) (i.e. \(T = 77 \, \text{K}\)), \(p = 76.5 \, \text{kPa}\)

11.83 1.624 kJ

11.87 CH\(_3\)Cl can be liquefied at or above room temperature, up to 416 K (143 °C) the critical temperature. Above the critical temperature, chloromethane cannot be liquefied – it can only be compressed into a supercritical fluid. Below the triple point temperature, 175.4 K (~97.8 °C), chloromethane cannot be liquefied – it solidifies upon compression. However, room temperature is between these limits on liquefaction.

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 O₂ and CO₂ at 25 °C has greater partial pressure of O₂ than CO₂. The partial pressures depend on the numbers of moles – 10.0 g of the lower molar mass O₂ has more moles than 10.0 g of CO₂.
(b) The lighter O₂ 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 g mL⁻¹ = 8200 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 m³ 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) 

\[
\begin{align*}
\text{ Nitrogen } & \quad \text{ Nitrogen } \\
\begin{array}{c}
\text{ Azide ion } \\
\text{ Nitrogen } \\
\text{ Azide ion}
\end{array}
\end{align*}
\]

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 °C.

11.101 (a) \( O_2 < B_2H_6 < H_2O \) - 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) \( x (O_2) = 0.17; x (N_2) = 0.83 \)

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 °C with 45% humidity than 0 °C with 95% humidity.

11.111  \(5.49 \times 10^{19}\) 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 CCl\(_2\)F\(_2\) until the dichlorodifluoromethane partial pressure inside the steel cylinder equals about 6.5 atm, the vapour pressure of CCl\(_2\)F\(_2\) at 25 °C. Here we assume that the cylinder is not so big that 25 kg of CCl\(_2\)F\(_2\) is not enough to fill the cylinder to this pressure – i.e. no bigger than about 780 L.

(c) The CCl\(_2\)F\(_2\) 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 CCl\(_2\)F\(_2\) 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
11.19

(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 x 10$^{-2}$ mol L$^{-1}$

12.5  The solubility of Li$_2$SO$_4$ in water decreases slightly as we increase the temperature from 10 °C. The amount of solid Li$_2$SO$_4$ 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 mol kg$^{-1}$
- 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 $-2.81 \, ^\circ\text{C}$
12.18 $1.40 \times 10^5$ g mol$^{-1}$
12.19 754 kPa
12.20 (a) volume = $4.19 \times 10^6$ nm$^3$
Surface area = $1.26 \times 10^5$ nm$^2$
(b) $2.4 \times 10^{14}$ spheres; surface area = $30$ m$^2$

**REVIEW QUESTIONS**

12.21 (a) $6.20 \times 10^{-6}$ mol L$^{-1}$ 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 molKg$^{-1}$
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 mol kg$^{-1}$ Na$_2$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 mol kg\(^{-1}\) ions
(c) 0.10 mol kg\(^{-1}\) MgCl\(_2\) solution \(\rightarrow\) 0.30 mol kg\(^{-1}\) ions
(b) 0.12 mol kg\(^{-1}\) K\(_2\)SO\(_4\) solution \(\rightarrow\) 0.36 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 Question answers necessary for this chapter.

**Chapter 13**

13.3  (a) \(Q = \frac{[PCl_3][Cl_2]}{[PCl_5]}\)

(b) \(Q = \frac{[CO]^2}{[CO_2]}\)

(c) \(Q = \frac{[Cu^{2+}][NH_3]^4}{[Cu(NH_3)_{4}^{2+}]}\)

(d) \(Q = \frac{[CH_3COO^-][H_3O^+]}{[CH_3COOH]}\)

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) \([NH_3] = 6.2 \times 10^{-4}\) mol L\(^{-1}\)

(b) \([NH_3] = 1.8 \times 10^{-2}\) mol L\(^{-1}\)

The cadmium solution has a higher ammonia concentration

13.7  (a) \([C_6H_{10}I_2] = 0.015\) mol L\(^{-1}\)

\([C_6H_{10}] = 0.035\) mol L\(^{-1}\)

(b) \(K = 0.082\)

13.10 \([H_2] = [I] = 1.54 \times 10^{-3}\) mol L\(^{-1}\)

\([HI] = 8.92 \times 10^{-7}\) mol L\(^{-1}\)

13.11 (b) \(K_2 = K_1^2\)
13.13 (a) \( K_2 = (K_2)^2 = (2.5 \times 10^{-29})^2 = 6.3 \times 10^{-58} \)
(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 \[ \text{butane} \] = 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.

\[ 2 \text{NOCl}(g) \rightleftharpoons 2 \text{NO}(g) + \text{Cl}_{2}(g) \quad \Delta H^\circ = 7.1 \text{ kJ mol}^{-1} \]

(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 SO₃ decreases if the temperature is increased?

\[ \text{SO}_2(g) + \frac{1}{2} \text{O}_2(g) \rightleftharpoons \frac{1}{2} \text{SO}_3(g) \quad \Delta H \thicksim -198 \text{ kJ mol}^{-1} \]

(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 H₂O and CO are both 0.014 mol L⁻¹

13.31 0.0002 g

13.33 \( [\text{NH}_3]_{\text{eqm}} = 0.66 \text{ mol L}^{-1} \)

\( [\text{N}_2]_{\text{eqm}} = 0.57 \text{ mol L}^{-1} \)

\( [\text{H}_2]_{\text{eqm}} = 1.71 \text{ mol L}^{-1} \)

\( \rho = 17.7 \text{ MPa} \)

13.35 \( 4.44 \times 10^{25} \)

13.37 (a) \( K = 0.041 \)

(b) \( K = 590 \)

13.39 (a) \( [\text{butane}] = 1.1 \text{ mol L}^{-1} \)

\( [\text{isobutane}] = 2.9 \text{ mol L}^{-1} \)

(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 BaCO₃(s)  
            (c)  (i) no net reaction  
            (d)  (iii) net reaction to form more BaO(s) and CO₂(g).  
            (e)  (iii) net reaction to form more BaO(s) and CO₂(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 SO₂Cl₂(g) dissociated in part (b) is less than that in part (b), 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)  \[ \text{HCOOH(aq)} + \text{H}_2\text{O(l)} \rightleftharpoons \text{HCOO}^-\text{(aq)} + \text{H}_3\text{O}^+(\text{aq}) \]  
      acid base conj. base conj. Acid

(b)  \[ \text{NH}_3\text{(aq)} + \text{H}_2\text{S(aq)} \rightleftharpoons \text{NH}_4^+(\text{aq}) + \text{HS}^-\text{(aq)} \]  
      base acid conj. acid conj. Base

(c)  \[ \text{HSO}_4^-\text{(aq)} + \text{OH}^-\text{(aq)} \rightleftharpoons \text{SO}_4^{2-}\text{(aq)} + \text{H}_2\text{O(l)} \]  
      acid base conj. base conj. acid

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

\[ \text{HC}_2\text{O}_4^-\text{(aq)} \] acting as a Brønsted-Lowry base:  
\[ \text{HC}_2\text{O}_4^-\text{(aq)} + \text{H}_3\text{O}^+(\text{aq}) \rightleftharpoons \text{H}_2\text{C}_2\text{O}_4\text{(aq)} + \text{H}_2\text{O(l)} \]

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 \( \text{K}_b = 7.1 \times 10^{-11} \)
    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\(_4\)NO\(_3\) has a pH < 7
    (c) An aqueous solution of AlCl\(_3\) has a pH < 7
    (d) An aqueous solution of Na\(_2\)HPO\(_4\) 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) \[
\begin{array}{c}
\text{H} \\
\text{C} \\
\text{H} \\
\text{H} \\
\end{array}
\]
Lewis Base

(b) \[
\begin{array}{c}
\text{H} \\
\text{C} \\
\text{N} \\
\text{C} \\
\end{array}
\]
Lewis Base

(c) \[
\begin{array}{c}
\text{Br} \\
\end{array}
\]
Lewis Base

(d) \[
\begin{array}{c}
\text{H} \\
\text{C} \\
\text{B} \\
\text{H} \\
\end{array}
\]
Lewis Acid

(e) \[
\begin{array}{c}
\text{H} \\
\text{C} \\
\text{Cl} \\
\text{H} \\
\end{array}
\]
Lewis base, through Cl atoms

(f) \[
\begin{array}{c}
\text{H} \\
\text{C} \\
\text{P} \\
\text{C} \\
\end{array}
\]
Lewis Base
14.19 \[ K_a = 6.87 \times 10^{-5} \]

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

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
\[ \text{pH} = 2.14; \% \text{ ionisation} = 2.4 \% \]

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

(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
\[ C < A < B \]
(b) according to amount of NaOH that can be consumed, we have
\[ B (0.001 \text{ mol L}^{-1}) < A (0.005 \text{ mol L}^{-1}) < C (0.006 \text{ mol L}^{-1}) \]

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

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

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

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

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

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

The dominant species at pH = 7.40 is H₂Lys⁺
14.42 (b) NH₃ and NH₄Cl 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 Na₂HPO₄(s) to NaH₂PO₄(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) ΔpH = 10.26 − 10.02 = 0.24
(b) (i) 11.02
   (ii) ΔpH = 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 × 10⁻⁷ mol L⁻¹

**REVIEW QUESTIONS**

14.55 pH = 2.12
[OH⁻] = 1.3 × 10⁻¹² mol L⁻¹

14.57 [H₃O⁺] = 10⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻~-~-~⁻~-~-~-~⁻~-~-~⁻~-~-~⁻~-~-~⁻~-~-~⁻~-~-~⁻~-~-~⁻~-~-~⁻~-~-~⁻~-~-~⁻~-~-~⁻~-~-~⁻~-~-~⁻~-~-~⁻~-~-~⁻~-~-~⁻~-~-~⁻~-~-~⁻~-~-~⁻~-~-~⁻~-~-~⁻~-~-~⁻~-~-~⁻~-~-~⁻~-~-~⁻~-~-~⁻~-~-~⁻~-~-~⁻~-~-~⁻~-~-~⁻~-~-~⁻~-~-~⁻~-~-~⁻~-~-~⁻~-~-~⁻~-~-~⁻~-~-~⁻~-~-~⁻~-~-~⁻~-~-~⁻~-~-~⁻~-~-~⁻~-~-~⁻~-~-~⁻~-~-~⁻~-~-~⁻~-~-~⁻~-~-~⁻~-~-~⁻~-~-~⁻~-~-~⁻~-~-~⁻~-~-~⁻~-~-~⁻~-~-~⁻~-~-~⁻~-~-~⁻~-~-~⁻~-~-~⁻~-~-~⁻~-~-~⁻~-~-~⁻~-~-~⁻~-~-~⁻~-~-~⁻~-~-~⁻~-~-~⁻~-~-~⁻~-~-~⁻~-~-~⁻~-~-~⁻~-~-~⁻~-~-~⁻~-~-~⁻~-~-~⁻~-~-~⁻~-~-~⁻~-~-~⁻~-~-~⁻~-~-~⁻~-~-~⁻~-~-~⁻~-~-~⁻~-~-~⁻~-~-~⁻~-~-~⁻~-~-~⁻~-~-~⁻~-~-~⁻~-~-~⁻~-~-~⁻~-~-~⁻~-~-~⁻~-~-~⁻~-~-~⁻~-~-~⁻~-~-~⁻~-~-~⁻~-~-~⁻~-~-~⁻~-~-~⁻~-~-~⁻~-~-~⁻~-~-~⁻~-~-~⁻~-~-~⁻~-~-~⁻~-~-~⁻~-~-~⁻~-~-~⁻~-~-~⁻~-~-~⁻~-~-~⁻~-~-~⁻~-~-~⁻~-~-~⁻~-~-~⁻~-~-~⁻~-~-~⁻~-~-~⁻~-~-~⁻~-~-~⁻~-~-~⁻~-~-~⁻~-~-~⁻~-~-~⁻~-~-~⁻~-~-~⁻~-~-~⁻~-~-~⁻~-~-~⁻~-~-~⁻~-~-~⁻~-~-~⁻~-~-~⁻~-~-~⁻~-~-~⁻~-~-~⁻~-~-~⁻~-~-~⁻~-~-~⁻~-~-~⁻~-~-~⁻~-~-~⁻~-~-~⁻~-~-~⁻~-~-~⁻~-~-~⁻~-~-~⁻~-~-~⁻~-~-~⁻~-~-~⁻~-~-~⁻~-~-~⁻~-~-~⁻~-~-~⁻~-~-~⁻~-~-~⁻~-~-~⁻~-~-~⁻~-~-~⁻~-~-~⁻~-~-~⁻~-~-~⁻~-~-~⁻~-~-~⁻~-~-~⁻~-~-~⁻~-~-~⁻~-~-~⁻~-~-~⁻~-~-~⁻~-~-~⁻~-~-~⁻~-~-~⁻~-~-~⁻~-~-~⁻~-~-~⁻~-~-~⁻~-~-~⁻~-~-~⁻~-~-~⁻~-~-~⁻~-~-~⁻~-~-~⁻~-~-~⁻~-~-~{-}
14.59

\[
K_b \left( [(\text{CH}_3)_3\text{N}](\text{aq}) \right) = \frac{[(\text{CH}_3)_3\text{NH}^+][\text{OH}^-]}{[(\text{CH}_3)_3\text{N}]} = \left( \frac{[(\text{CH}_3)_3\text{N}][\text{H}_2\text{O}^+]}{[(\text{CH}_3)_3\text{NH}^+]} \frac{1}{[\text{H}_2\text{O}^+][\text{OH}^-]} \right)^{-1}
\]

\[
= \left( \frac{K_a \left( [(\text{CH}_3)_3\text{NH}^+ \right]}{K_w \left( [(\text{CH}_3)_3\text{NH}^+ \right]} \right)^{-1} = \frac{K_w}{K_a \left( [(\text{CH}_3)_3\text{NH}^+ \right]}
\]

\[
= \frac{10^{-14}}{10^{-9.80}} = \frac{10^{-14}}{10^{-9.80}} = 10^{-4.20} = 6.31 \times 10^{-5}
\]

14.61

HPO_4^{2-}(\text{aq}) \text{ ions acting as an acid:}

\[\text{HPO}_4^{2-}(\text{aq}) + \text{H}_2\text{O}(l) \rightleftharpoons \text{PO}_4^{3-}(\text{aq}) + \text{H}_3\text{O}^+(\text{aq})\]

HPO_4^{2-}(\text{aq}) \text{ ions acting as a base:}

\[\text{HPO}_4^{2-}(\text{aq}) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_2\text{PO}_4^-(\text{aq}) + \text{OH}^-(\text{aq})\]

14.63 (b) C_6H_5COOH (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) HCOOH(\text{aq}) (formic acid) is the strongest acid.

C_6H_5OH(\text{aq}) (phenol) is the weakest acid.

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

(c) C_6H_5OH(\text{aq}) (phenol) has the strongest conjugate base.

14.69 The 0.10 mol L^{-1} solution of (a) Na_2S(s) has the highest pH. The 0.10 mol L^{-1} solution of (f) AlCl_3(s) has the lowest pH.
14.71

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

(b) \(\text{Br}^-\) 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 affect on the pH

14.77

\[ [\text{NH}_4^+] = [\text{OH}^-] = 1.6 \times 10^{-3} \text{ mol L}^{-1} \]
\[ [\text{NH}_3] = 0.015 \text{ mol L}^{-1} \]
\[ [\text{H}_3\text{O}^+] = 6.25 \times 10^{-12} \text{ mol L}^{-1} \]
\(\text{pH} = 11.20\)
\(\% \text{ NH}_3\text{ ionized} = 1.1\%\)

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) \(\text{pH} = 6\), \(\text{H}_2\text{A}(aq)\) has the highest concentration
(ii) \(\text{pH} = 8\), \(\text{HA}^- (aq)\) has the highest concentration
(iii) \(\text{pH} = 10\), \(\text{HA}^- (aq)\) still has the highest concentration – but not by as wide a margin

(b) \(\text{pK}_{a1}\) and \(\text{pK}_{a2}\) can be seen in the plot.
\([\text{H}_2\text{A}(aq)] = [\text{HA}^- (aq)] \text{ when } \text{pH} = \text{pK}_{a1}\)
So, \(\text{pK}_{a1} \approx 6.4\)
\([\text{HA}^- (aq)] = [\text{A}^{2-} (aq)] \text{ when } \text{pH} = \text{pK}_{a2}\)
So, \(\text{pK}_{a1} \approx 10.3\)

(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
(a) ![Image](a.png)
(b) ![Image](b.png)
(c) ![Image](c.png)
(d) ![Image](d.png)

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 \(\text{Na}_2\text{CO}_3\) for every 1.000 mol of \(\text{NaHCO}_3\) 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) \([\text{H}_3\text{O}^+] = 2.1 \times 10^{-3} \text{ mol L}^{-1}\)
\([\text{C}_6\text{H}_5\text{NH}_3^{+}] = 0.178 \text{ mol L}^{-1}\)
\([\text{OH}^-] = 6.76 \times 10^{-12} \text{ mol L}^{-1}\)
(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.

![Graph of HCN and CN-](image)

**SUMMARY AND CONCEPTUAL QUESTIONS**

14.107 (a) 10 \(\text{H}_3\text{O}^+\) ions.
(b) 1 \(\text{H}_3\text{O}^+\) 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 \(\text{H}_3\text{O}^+\) 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.

\[ \text{HCO}_3^-(aq) + \text{OH}^-(aq) \rightarrow \text{CO}_3^{2-}(aq) + \text{H}_2\text{O}(\ell) \]

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.

\[ \text{CH}_3\text{COOH}(aq) + \text{H}_2\text{O}(\ell) \rightleftharpoons \text{CH}_3\text{COO}^-(aq) + \text{H}_3\text{O}^+(aq) \]

Increasing pH means decreasing \( \text{H}_3\text{O}^+ \), 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. 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)

\[ \text{AgI}(s) \rightleftharpoons \text{Ag}^+(aq) + \text{I}^-(aq) \]

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

(b)

\[ \text{BaF}_2(s) \rightleftharpoons \text{Ba}^{2+}(aq) + 2 \text{F}^-(aq) \]

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

(c)

\[ \text{Ag}_2\text{CO}_3(s) \rightleftharpoons 2 \text{Ag}^+(aq) + \text{CO}_3^{2-}(aq) \]

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

15.4 \( K_{sp} = 1.9 \times 10^{-7} \)
15.6  (a) \(1.3 \times 10^{-2}\) mol L\(^{-1}\)
(b) \(9.6 \times 10^{-3}\) g L\(^{-1}\)

15.8  (a) AgCl
(b) Ca(OH)\(_2\)
(c) Ca(OH)\(_2\)

15.10  The solubility of Ag\(_3\)PO\(_4\) is larger than that predicted using Ksp of the salt because the phosphate ion, PO\(_4^{3-}\), reacts with water to form HPO\(_4^{2-}\) (H\(_2\)PO\(_4\) and H\(_3\)PO\(_4\) upon further reaction with water). The concentration of PO\(_4^{3-}\) is consequently significantly reduced, and the reaction quotient for dissolution of Ag\(_3\)PO\(_4\) remains less than the solubility product for larger initial concentrations of Ag\(_3\)PO\(_4\) than predicted using Ksp.

15.13  (a) \(1.0 \times 10^{-2}\) mol L\(^{-1}\)
(b) \(1.1 \times 10^{-8}\) mol L\(^{-1}\)

15.15  (a) PbS(s)
(b) Ag\(_2\)CO\(_3\)(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 PbI\(_2\) can dissolve.

15.19  \(Q = 6.3 \times 10^{-8} < K_{sp} = 3.4 \times 10^{-7}\)
The mixture is not saturated. SrSO\(_4\)(s) will not precipitate.

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

15.22  \([OH^-] = 5.3 \times 10^{-6}\) 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 \(pK_a = -\log_{10}(3.5 \times 10^{-4}) = 3.5\), 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

15.25 (a) \( \text{PbSO}_4 (s) \rightleftharpoons \text{Pb}^{2+} (aq) + \text{SO}_4^{2-} (aq) \)
\[ Q = [\text{Pb}^{2+}] [\text{SO}_4^{2-}] = K_{sp} = 1.8 \times 10^{-8} \text{ at equilibrium.} \]

(b) \( \text{NiCO}_3 (s) \rightleftharpoons \text{Ni}^{2+} (aq) + \text{CO}_3^{2-} (aq) \)
\[ Q = [\text{Ni}^{2+}] [\text{CO}_3^{2-}] = K_{sp} = 1.4 \times 10^{-7} \text{ at equilibrium.} \]

(c) \( \text{Ag}_3\text{PO}_4 (s) \rightleftharpoons 3\text{Ag}^+ (aq) + \text{PO}_4^{3-} (aq) \)
\[ Q = [\text{Ag}^+]^3 [\text{PO}_4^{3-}] = K_{sp} = 1.3 \times 10^{-20} \text{ at equilibrium.} \]

15.27 \( \text{SrF}_2 (s) \rightleftharpoons \text{Sr}^{2+} (aq) + 2 \text{F}^- (aq) \)
\[ K_{sp} = 4.0 \times 10^{-9} \]

15.29 51 mg of \( \text{PbSO}_4 \) remains undissolved

15.31 (a) \( \text{PbCl}_2(s) \)
(b) \( \text{FeS}(s) \)
(c) \( \text{Fe(OH)}_2(s) \)

15.33 \( Q = 1.1 \times 10^{-6} > K_{sp} = 1.8 \times 10^{-8} \)
AgCl will precipitate out of solution

15.35 (a) \( Q = 2.4 \times 10^{-9} < K_{sp} = 6.6 \times 10^{-9} \)
NiCO\(_3\) will not precipitate

(b) \( Q = 2.4 \times 10^{-7} > K_{sp} = 6.6 \times 10^{-9} \)
NiCO\(_3\) will precipitate

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

15.39 \( \text{AuCl}(s) \rightleftharpoons \text{Au}^+(aq) + \text{Cl}^-(aq) \)
\[ \text{Au}^+(aq) + 2 \text{CN}^-(aq) \rightleftharpoons [\text{Au(CN)}_2]^-(aq) \]
\( \text{AuCl}(s) + 2 \text{CN}^-(aq) \rightleftharpoons [\text{Au(CN)}_2]^-(aq) + \text{Cl}^-(aq) \)
\[ K_{net} = 4.0 \times 10^{25} \]
SUMMARY AND CONCEPTUAL QUESTIONS

15.41  $5.51 \times 10^{-5}$

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

Chapter 16

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

16.4  CH$_3$CH$_2$OH is oxidized. CH$_3$CH$_2$OH is the reducing agent. Cr$_2$O$_7^{2-}$ is reduced. Cr$_2$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: $2$Ag$^+$(aq) + Ni(s) $\rightarrow$ 2Ag(s) + Ni$^{2+}$(aq)  
Electrons flow from the Ni(s) to the Ag(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
(a) \( \text{Zn(s)} | \text{Zn}^{2+}(aq) | \text{Ni}^{2+}(aq) | \text{Ni(s)} \)
(b) \( \text{C(s)} | \text{Fe}^{2+}(aq) | \text{Fe}^{3+}(aq) | \text{Ag}^+(aq) | \text{Ag(s)} \)
(c) \( \text{Mg(s)} | \text{Mg}^{2+}(aq) | \text{Br}_2(l) | \text{Br}^-(aq) | \text{Pt(s)} \)

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

16.9
See above – Exercise 16.8(b).

16.13
\[
\begin{align*}
\text{Zn(s)} & \rightarrow \text{Zn}^{2+}(aq) + 2 \text{e}^- \quad \text{at the anode} \\
2 \times (\text{Ag}^+(aq) + \text{e}^- & \rightarrow \text{Ag(s)}) \quad \text{at the cathode} \\
\text{Zn(s)} + 2 \text{Ag}^+(aq) & \rightarrow \text{Zn}^{2+}(aq) + 2 \text{Ag(s)} \\
\end{align*}
\]

\( E^\circ_{\text{cell}} = 1.56 \text{ V} \)

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) Fe^{2+}(aq) + Sn(s) → Fe(s) + Sn^{2+}(aq). This is NOT the direction of spontaneous reaction.  
(d) Zn^{2+}(aq) + Sn(s) → Zn(s) + Sn^{2+}(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 pH = 0, \( E_{\text{cell}} = +1.51 \text{ V} \)  
(b) At pH = 5.0, \( E_{\text{cell}} = +1.04 \text{ V} \)

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

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

16.27 \( \begin{align*} 2 \text{ H}_2\text{O}(l) + 2 \text{ e}^- & \rightarrow \text{ H}_2(g) + 2 \text{ OH}^-(aq) \quad \text{(Cathode reaction)} \\ 4 \text{ OH}^- (aq) & \rightarrow \text{ O}_2(g) + 2 \text{ H}_2\text{O}(l) + 4 \text{ e}^- \quad \text{(Anode reaction)} \end{align*} \)

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

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) \( \text{OS}(f) = -1 \) \( \text{OS}(P) = +5 \)
(b) \( \text{OS}(h) = +1 \) & \( \text{OS}(O) = -2 \) \( \text{OS}(As) = +5 \)
(c) \( \text{OS}(O) = -2 \) \( \text{OS}(U) = +4 \)
(d) \( \text{OS}(O) = -2 \) \( \text{OS}(N) = +5 \)
(e) \( \text{OS}(Cl) = -1 \) & \( \text{OS}(O) = -2 \) \( \text{OS}(P) = +5 \)
(f) \( \text{OS}(O) = -2 \) \( \text{OS}(Xe) = +6 \)

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

16.37  A voltaic cell is constructed using the reaction of chromium metal and aquated iron(ii) ions
\( 2 \text{Cr}(s) + 3 \text{Fe}^{2+}(aq) \rightarrow 2 \text{Cr}^{3+}(aq) + 3 \text{Fe}(s) \)
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 \( \text{Fe}^{2+}/\text{Fe} \) half-cell (the reduction half-cell) to the \( \text{Cr}/\text{Cr}^{3+} \) half-cell (the oxidation half-cell). The half-reaction at the anode is \( \text{Cr}(s) \rightarrow \text{Cr}^{3+}(aq) + 3 \text{e}^- \) and that at the cathode is \( \text{Fe}^{2+}(aq) + 2 \text{e}^- \rightarrow \text{Fe}(s) \).
16.39 (a) + (c)

(b)

\[ \text{Mg}(s) \rightarrow \text{Mg}^{2+}(aq) + 2e^- \] (oxidation half-reaction that occurs at the anode).  
\[ \text{Ag}^+(aq) + e^- \rightarrow \text{Ag}(s) \] (reduction half-reaction that occurs at the cathode)

\[ \text{Mg}(s) + 2\text{Ag}^+(aq) \rightarrow \text{Mg}^{2+}(aq) + 2\text{Ag}(s) \] (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) \[ E^\circ[\text{NO}_3^-(aq)\mid\text{NO}(g)] = 0.96 \text{ V} \]

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

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

16.47 (a) \( \text{Se}(s) \)
(b) \( \text{F}^-(aq) \)
(c) \( \text{F}_2(g), \text{Cl}_2(g) \)
(d) \( \text{F}_2(g), \text{Cl}_2(g), \text{Br}_2(\ell), \text{I}_2(s), \text{O}_2(g) \)
(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.  

\[ 6 \text{I}^-(aq) + 2 \text{NO}_3^-(aq) + 8 \text{H}^+(aq) \rightarrow 3 \text{I}_2(s) + 2 \text{NO}(g) + 4 \text{H}_2\text{O}(l) \] (Balanced equation)  

16.57  \( E_{\text{cell}} = +1.585 \text{ V} \)  

16.59  (a)  

(b)  

\[
\begin{align*}
\text{Cd}(s) & \rightarrow \text{Cd}^{2+}(aq) \\
\text{Ni}^{2+}(aq) & \rightarrow \text{Ni}(s)
\end{align*}
\]

(c) The Ni(s) electrode is the cathode – it is labeled +. The cadmium anode is labeled −.  
(d) \( E_{\text{cell}}^0 = +0.15 \text{ V} \)  
(e) from anode to cathode  
(f) The Na⁺(aq) ions in the salt bridge move from the anode compartment to the cathode compartment. The NO₃⁻(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 \( E_{\text{cell}} \) is still positive, the net reaction is in the same direction given in part (b).
16.61  (a) \( E_{\text{cell}}^o = +0.236 \text{ V}, \ K = 9.5 \times 10^7 \)
(b) \( E_{\text{cell}}^o = -0.531 \text{ V}, \ K = 1.1 \times 10^{-18} \)

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.
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.

16.78 C > A > D > B

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.

$$\Delta S = q / T = 10^6 \ J / 323.15 \ K = 3095 \ J/K,$$ 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 \[ \Delta S^\circ_{\text{sys}} = -134.23 \text{ JK}^{-1} \]
\[ \Delta H^\circ_{\text{sys}} = -657.01 \text{ kJ} \]
\[ \Delta S^\circ_{\text{univ}} = +2071 \text{ JK}^{-1} \]
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 \[ \Delta S^\circ = -198.76 \text{ JK}^{-1} \]
\[ \Delta H^\circ = -91.8 \text{ kJ} \]
\[ \Delta G^\circ = -32.6 \text{ kJ} \]

17.15  (a) \[ \frac{1}{2} \text{N}_2(g) + \frac{3}{2} \text{H}_2(g) \rightarrow \text{NH}_3(g) \]
(b) 2 Fe(s) + \( \frac{3}{2} \) O₂(g) \rightarrow Fe₂O₃(s)
(c) 3 C(s) + 3 H₂(g) + O₂(g) \rightarrow CH₃CH₂COOH(ℓ)
(d) Ni(s) is the element in its standard state. Its \( \Delta G^\circ = 0 \).

17.17 \[ \Delta G^\circ = -70.87 \text{ kJ} \]

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

17.19 \[ T = 838.7 \text{ K} \]

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

17.22 \[ \Delta G^\circ = -1.13 \text{ kJ} \]

17.25 \[ \Delta G^\circ = +120.023 \text{ kJ} \]
\[ K = 9.18 \times 10^{-22} \]

17.26 -41 kJ

17.27 +147 kJ. The reverse reaction is spontaneous.
17.28  (a) $E^\circ = 0.236$ V  
$\Delta_r G^\circ = -45.5$ kJ  
$K = 9.46 \times 10^7$
(b) $E^\circ = -0.531$ V  
$\Delta_r G^\circ = -102$ kJ  
$K = 7.58 \times 10^{17}$

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

17.32  (a) $\rho_{30^\circ C} = 1.37 \times 10^{-3}$ bar
(b) $\rho_{100^\circ C} = 6.20 \times 10^{-2}$ bar
(c) 62.5 kJ

REVIEW QUESTIONS

17.33  $\Delta S = q / T = 6.01 \times 10^3$ J mol$^{-1}$ / 273.15 K = 22.0 J K$^{-1}$ mol$^{-1}$

17.35  (a) NaCl(g) has more entropy than NaCl(aq), which has more entropy than NaCl(s).
The greatest disorder is in the gas state. NaCl(s) is a highly constrained arrangement of the ions.
Check:  $S^\circ[\text{NaCl(g)}] = 229.79 > S^\circ[\text{NaCl(aq)}] = 115.5 > S^\circ[\text{NaCl(s)}] = 72.11$ (all in J K$^{-1}$)

(b) H$_2$S(g) has more entropy than H$_2$O(g) because S is heavier than O. Heavier molecules have
more entropy (everything else equal). This is because energy distributed among heavier gas
molecules corresponds to a larger range of momenta—which means more ways of distributing the
energy. At the same temperature, molecules with less mass travel faster (on average).
Check:  $S^\circ[\text{H}_2\text{S(g)}] = 205.79 > S^\circ[\text{H}_2\text{O(g)}] = 188.84$

(c) C$_2$H$_4$(g) has more entropy than N$_2$(g) (with the same molar mass). More complex molecules have more entropy than less complex molecules with the same mass.
They have more internal motions which mean more ways of distributing energy.
Check:  $S^\circ[\text{C}_2\text{H}_4(g)] = 219.36 > S^\circ[\text{N}_2(g)] = 191.56$

(d) H$_2$SO$_4$(ℓ) has more entropy than H$_2$SO$_4$(aq).
On the surface, it would appear that since H$_2$SO$_4$(aq) explores a larger volume—the volume of its
aqueous environment—it should have a greater entropy than the same amount of H$_2$SO$_4$(ℓ).
(Note that standard entropies correspond to 1 M concentration in case of aqueous species.)
However, the aqueous sulfuric acid is strongly associated with water via the acid-base reaction.
The stronger forces in the ionized solution reduce its entropy, more than compensating for the
increase in entropy due to the greater freedom of the aqueous species.
Check:  $S^\circ[\text{H}_2\text{SO}_4(\ell)] = 156.9 > S^\circ[\text{H}_2\text{SO}_4(aq)] = 20.1$
17.37  $2\text{C(graphite)} + 3\text{H}_2(g) \rightarrow \text{C}_2\text{H}_6(g)$

$\Delta_S^o = 1 \times S^o(\text{C}_2\text{H}_6, g) - [2 \times S^o(\text{C, graphite}) + 3 \times S^o(\text{H}_2, g)]$

$= 229.60 \text{ JK}^{-1} \text{ mol}^{-1} - [2 \times 5.740 \text{ JK}^{-1} \text{ mol}^{-1} + 3 \times 130.684 \text{ JK}^{-1} \text{ mol}^{-1}]$

$= -173.93 \text{ JK}^{-1} \text{ mol}^{-1}$

17.41  

1. $\text{C(s)} + 2\text{H}_2(g) \rightarrow \text{CH}_4(g)$

$S^o_1 = S^o[\text{CH}_4(g)] - (S^o[\text{C(s)}] + 2 S^o[\text{H}_2(g)])$

$= 186.3 \text{ JK}^{-1} \text{ mol}^{-1} - (5.74 \text{ JK}^{-1} \text{ mol}^{-1} + 2 \times 130.7 \text{ JK}^{-1} \text{ mol}^{-1}) = -80.8 \text{ JK}^{-1} \text{ mol}^{-1}$

2. $\text{CH}_4(g) + \frac{1}{2}\text{O}_2(g) \rightarrow \text{CH}_3\text{OH}(l)$

$S^o_2 = S^o[\text{CH}_3\text{OH}(l)] - (S^o[\text{CH}_4(g)] + \frac{1}{2} S^o[\text{O}_2(g)])$

$= 126.8 \text{ JK}^{-1} \text{ mol}^{-1} - (186.3 \text{ JK}^{-1} \text{ mol}^{-1} + \frac{1}{2} \times 205.1 \text{ JK}^{-1} \text{ mol}^{-1}) = -162.1 \text{ JK}^{-1} \text{ mol}^{-1}$

3. $\text{C(s)} + 2\text{H}_2(g) + \frac{1}{2}\text{O}_2(g) \rightarrow \text{CH}_3\text{OH}(l)$

$S^o_3 = S^o[\text{CH}_3\text{OH}(l)] - (S^o[\text{C(s)}] + 2 S^o[\text{H}_2(g)] + \frac{1}{2} S^o[\text{O}_2(g)])$

$= 126.8 \text{ JK}^{-1} \text{ mol}^{-1} - (5.74 \text{ JK}^{-1} \text{ mol}^{-1} + 2 \times 130.7 \text{ JK}^{-1} \text{ mol}^{-1} + \frac{1}{2} \times 205.1 \text{ JK}^{-1} \text{ mol}^{-1})$

$= -242.9 \text{ JK}^{-1} \text{ mol}^{-1}$

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

$\Delta S^o_1 + \Delta S^o_2 = -80.8 \text{ JK}^{-1} \text{ mol}^{-1} - 162.1 \text{ JK}^{-1} \text{ mol}^{-1} = -242.9 \text{ JK}^{-1} \text{ mol}^{-1} = \Delta S^o_3$

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  $\text{H}_2(g) + \text{Cl}_2(g) \rightarrow 2\text{HCl(g)}$

$\Delta S^o_{sys} = 2 \times (S^o[\text{HCl(g)}] - (S^o[\text{H}_2(g)] + S^o[\text{Cl}_2(g)]))$

$= 2 \times 186.9 J K^{-1} mol^{-1} - (130.7 J K^{-1} mol^{-1} + 223.1 J K^{-1} mol^{-1}) = 20.0 J K^{-1} mol^{-1}$

$\Delta H^o_{sys} = 2 \times (-92.31) kJ mol^{-1} = (-184.62) kJ mol^{-1}$

$\Delta S^o_{sur} = \frac{-\Delta H^o_{sys}}{T} = \frac{-184.62 \times 10^3 J mol^{-1}}{298K} = +619.5 J K^{-1} mol^{-1}$

$\Delta S^o_{univ} = \Delta S^o_{sys} + \Delta S^o_{sur} = 20.0 J K^{-1} mol^{-1} + 619.5 J K^{-1} mol^{-1} = +639.5 J K^{-1} mol^{-1}$

This reaction is spontaneous in the forward direction, under the reaction mixture conditions specified.
17.45 $\text{H}_2\text{O}(l) \rightarrow \text{H}_2(g) + \frac{1}{2} \text{O}_2(g)$

\[ \Delta S^\circ_{\text{sys}} = (S^\circ[\text{H}_2(g)] + \frac{1}{2} S^\circ[\text{O}_2(g)]) - S^\circ[\text{H}_2\text{O}(l)] \]

\[ = (130.7 \text{ J K}^{-1} \text{ mol}^{-1} + \frac{1}{2} \times 205.1 \text{ J K}^{-1} \text{ mol}^{-1}) - 69.91 \text{ J K}^{-1} \text{ mol}^{-1} = 163.3 \text{ J K}^{-1} \text{ mol}^{-1} \]

\[ \Delta H^\circ_{\text{sys}} = (\Delta H^\circ[\text{H}_2(g)] + \frac{1}{2} \Delta H^\circ[\text{O}_2(g)]) - \Delta H^\circ[\text{H}_2\text{O}(l)] \]

\[ = -285.8 \text{ kJ mol}^{-1} - 0 - 0 = -285.8 \text{ kJ mol}^{-1} \]

\[ \Delta S^\circ_{\text{surr}} = -\frac{\Delta H^\circ_{\text{sys}}}{T} = -\frac{-285.8 \times 10^3 \text{ J mol}^{-1}}{298 \text{ K}} = -959.1 \text{ J K}^{-1} \text{ mol}^{-1} \]

\[ \Delta S^\circ_{\text{univ}} = \Delta S^\circ_{\text{sys}} + \Delta S^\circ_{\text{surr}} = 163.3 \text{ J K}^{-1} \text{ mol}^{-1} - 959.1 \text{ J K}^{-1} \text{ mol}^{-1} \]

\[ = -795.8 \text{ J K}^{-1} \text{ mol}^{-1} \]

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 $\text{COCl}_2(\text{g}) \rightarrow \text{CO}(\text{g}) + \text{Cl}_2(\text{g})$

Because one mole of gas is converted to two moles of gas, we know that the change in entropy is positive for this reaction. Since the reaction is NOT spontaneous at 25 °C, it must be endothermic—i.e., causing a positive change in the entropy of the surroundings. Increasing the temperature decreases the impact of the heat flow from the surroundings—i.e., the decrease in the entropy of the surroundings is not as great at higher $T$. At sufficiently high $T$, the system change in entropy will be the dominant term and the reaction will be spontaneous.

17.49 (a) $2 \text{Al}(s) + 3 \text{Cl}_2(\text{g}) \rightarrow 2 \text{AlCl}_3(\text{s})$

\[ \Delta S^\circ = 2 \times S^\circ[\text{AlCl}_3(s)] - (2 \times S^\circ[\text{Al}(s)] + 3 \times S^\circ[\text{Cl}_2(\text{g})]) \]

\[ = 2 \times 110.67 \text{ J K}^{-1} \text{ mol}^{-1} - (2 \times 28.3 \text{ J K}^{-1} \text{ mol}^{-1} + 3 \times 223.066 \text{ J K}^{-1} \text{ mol}^{-1}) = -504.5 \text{ J K}^{-1} \text{ mol}^{-1} \]

\[ \Delta H^\circ = 2 \Delta H^\circ[\text{AlCl}_3(s)] - [0 + 0] = 2 \times (-704.2 \text{ kJ mol}^{-1}) = -1408.4 \text{ kJ mol}^{-1} \]

\[ \Delta G^\circ = \Delta H^\circ - T \Delta S^\circ = -1408.4 \text{ kJ mol}^{-1} - (298 \text{ K}) \times (-504.5 \text{ J K}^{-1} \text{ mol}^{-1}) / (1000 \text{ J / kJ}) \]

\[ = 1258.1 \text{ kJ mol}^{-1} \]

This reaction is spontaneous at 25 °C in a reaction mixture with all reagent species in their standard states. It is enthalpy driven—the negative enthalpy change more than compensates for the negative entropy change (positive $-T \Delta S^\circ$) at 25 °C.

(b) $6 \text{C}(\text{graphite}) + 3\text{H}_2(\text{g}) \rightarrow \text{C}_6\text{H}_6(\text{l})$

\[ \Delta S^\circ = 1 \times S^\circ[\text{C}_6\text{H}_6(\ell)] - (6 \times S^\circ[\text{C}(\text{graphite})] + 3 \times S^\circ[\text{H}_2(\text{g})]) \]

\[ = 172.8 \text{ J K}^{-1} \text{ mol}^{-1} - (6 \times 5.740 \text{ J K}^{-1} \text{ mol}^{-1} + 3 \times 130.684 \text{ J K}^{-1} \text{ mol}^{-1}) = -253.7 \text{ J K}^{-1} \text{ mol}^{-1} \]

\[ \Delta H^\circ = \Delta H^\circ[\text{C}_6\text{H}_6(\ell)] = 49.03 \text{ kJ mol}^{-1} \]

\[ \Delta G^\circ = \Delta H^\circ - T \Delta S^\circ = 49.03 \text{ kJ mol}^{-1} - (298 \text{ K}) \times (-253.7 \text{ J K}^{-1} \text{ mol}^{-1}) / (1000 \text{ J / kJ}) \]

\[ = 124.6 \text{ kJ mol}^{-1} \]

This reaction is NOT spontaneous at 25 °C in a reaction mixture with all reagent species in their standard states. Both enthalpy and entropy terms disfavour this process. It is NOT spontaneous at any temperature.
17.51 This problem is answered using thermochemical data from the NIST webbook (webbook.nist.gov).

\[ 2 \text{C(graphite)} + 2 \text{H}_2(g) + \text{O}_2(g) \rightarrow \text{CH}_3\text{COOH(l)} \]

\[ \Delta S^\circ = S^\circ[\text{CH}_3\text{COOH}(\ell)] - (2 \times S^\circ[\text{C(graphite)}] + 2 \times S^\circ[\text{H}_2(g)] + 1 \times S^\circ[\text{O}_2(g)]) \]

\[ = 158.0 \text{ J K}^{-1} \text{ mol}^{-1} - (2 \times 5.6 \text{ J K}^{-1} \text{ mol}^{-1} + 2 \times 130.680 \text{ J K}^{-1} \text{ mol}^{-1} + 205.152 \text{ J K}^{-1} \text{ mol}^{-1}) = -319.7 \text{ J K}^{-1} \text{ mol}^{-1} \]

\[ \Delta H^\circ = \Delta H^\circ[\text{CH}_3\text{COOH}(\ell)] = -483.52 \text{ kJ mol}^{-1} \]

\[ \Delta G^\circ = \Delta H^\circ - T \Delta S^\circ = -483.52 \text{ kJ mol}^{-1} - (298.15 \text{ K}) \times (-319.7 \text{ J K}^{-1} \text{ mol}^{-1}) / (1000 \text{ J} / \text{kJ}) \]

\[ = -388.2 \text{ kJ mol}^{-1} \]

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 \( \text{BaCO}_3(s) \rightarrow \text{BaO(s)} + \text{CO}_2(g) \)

\[ \Delta G^\circ = \Delta G^\circ[\text{BaO(s)}] + \Delta G^\circ[\text{CO}_2(g)] - \Delta G^\circ[\text{BaCO}_3(s)] = 219.7 \text{ kJ mol}^{-1} \]

\[ = -525.1 \text{ kJ mol}^{-1} + (-394.359 \text{ kJ mol}^{-1}) - 219.7 \text{ kJ mol}^{-1} \]

\[ = -1139.2 \text{ kJ mol}^{-1} \]

So,

\[ \Delta G^\circ[\text{BaCO}_3(s)] = -525.1 \text{ kJ mol}^{-1} + (-394.359 \text{ kJ mol}^{-1}) - 219.7 \text{ kJ mol}^{-1} = -1139.2 \text{ kJ mol}^{-1} \]

17.55 \( \text{Ni(CO)}_4(\ell) \rightarrow \text{Ni(s)} + 4 \text{CO(g)} \)

\[ \Delta G^\circ = \Delta G^\circ[\text{Ni(s)}] + 4 \Delta G^\circ[\text{CO(g)}] - \Delta G^\circ[\text{Ni(CO)}_4(\ell)] \]

\[ = 29.87 \text{ J K}^{-1} \text{ mol}^{-1} + 4 \times 197.674 \text{ J K}^{-1} \text{ mol}^{-1} - 320 \text{ J K}^{-1} \text{ mol}^{-1} = 501 \text{ J K}^{-1} \text{ mol}^{-1} \]

\[ \Delta H^\circ = \Delta H^\circ[\text{Ni(s)}] + 4 \Delta H^\circ[\text{CO(g)}] - \Delta H^\circ[\text{Ni(CO)}_4(\ell)] \]

\[ = 0 + 4 \times (-110.525 \text{ kJ mol}^{-1}) - (-632 \text{ kJ mol}^{-1}) = 190 \text{ kJ mol}^{-1} \]

Assuming \( \Delta H^\circ \) and \( \Delta S^\circ \) are temperature independent, we get the temperature where \( \text{Ni(CO)}_4(\ell) \) is in equilibrium with 1 bar CO(g) via

\[ T_{eq} = \Delta H^\circ / \Delta S^\circ = 190 \times 1000 \text{ J mol}^{-1} / (501 \text{ J K}^{-1} \text{ mol}^{-1}) = 379 \text{ K} = 106 \text{ ºC}. \]

17.57 \( \text{C}_2\text{H}_6(g) + \frac{7}{2}\text{O}_2(g) \rightarrow 2\text{CO}_2(g) + 3\text{H}_2\text{O(g)} \)

\[ \Delta G^\circ = 2 \Delta G^\circ[\text{CO}_2(g)] + 3 \Delta G^\circ[\text{H}_2\text{O(g)}] - (\Delta G^\circ[\text{C}_2\text{H}_6(g)] + \frac{7}{2} \Delta G^\circ[\text{O}_2(g)]) \]

\[ = 2 \times (-394.359 \text{ kJ mol}^{-1}) + 3 \times (-228.572 \text{ kJ mol}^{-1}) - (-32.82 \text{ kJ mol}^{-1} + \frac{7}{2} \times 0) = -1441.61 \text{ kJ mol}^{-1} \]

This is in accord with experience. Ethane is a component of natural gas—it is a fuel. Its combustion is highly favoured—it releases a lot of free energy.
17.59 \[ \frac{1}{2}N_2(g) + \frac{1}{2}O_2(g) \xrightarrow{\Delta} 2N\overset{\cdot}{O}(g) \quad \Delta G^\circ = +86.58 \text{ kJ mol}^{-1} \]

\[ \ln K = \frac{-\Delta G^\circ}{RT} = - \frac{86.58 \times 10^3 \text{ J mol}^{-1}}{8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 298 \text{ K}} \]

\[ = -34.95 \]

\[ K = e^{-34.95} = 6.63 \times 10^{-16} \]

*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 \[ N_2O_4(g) \rightleftharpoons 2 NO_2(g) \]

\[ \Delta G^\circ = -RT \ln K = -8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 298 \text{ K} \ln(0.14) \]

\[ = 4871 \text{ J mol}^{-1} = 4.871 \text{ kJ mol}^{-1} \]

\[ \Delta G^\circ = 2 \Delta G^\circ[NO_2(g)] - \Delta G^\circ[N_2O_4(g)] \]

\[ = 2 \times 51.31 \text{ kJ mol}^{-1} - (97.89 \text{ kJ mol}^{-1}) = 4.73 \text{ kJ mol}^{-1} \]

This is pretty close to the above value, based upon the equilibrium constant (with only two significant digits). Also, note that tabulated data are not always as accurate as the number of digits indicates.

17.63 C(graphite) + \(\frac{1}{2}\)O₂(g) + 2H₂(g) \(\xrightarrow{\Delta}\) CH₃OH(l)

\[ \Delta G^\circ = \Delta f G^\circ[CH_3OH(g)] = -166.27 \text{ kJ mol}^{-1} \]

This is the formation reaction for methanol.

\[ \ln K = \frac{-\Delta G^\circ}{RT} = - \frac{-166.27 \times 10^3 \text{ J mol}^{-1}}{8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 298 \text{ K}} \]

\[ = 67.11 \]

\[ K = e^{67.11} = 1.398 \times 10^{29} \]

This reaction is decidedly product-favoured at 25 °C (when all reagents are in their standard states). Another temperature is not needed to better favour the product.

17.65 (a) HCOOH(aq) (formic acid) is the strongest acid.

C₆H₅OH(aq) (phenol) is the weakest acid.

(b) HCOOH(aq) (formic acid) has the weakest conjugate base.

(c) C₆H₅OH(aq) (phenol) has the strongest conjugate base.
SUMMARY AND CONCEPTUAL QUESTIONS

17.67  \[2\text{HgO}(s) \rightarrow 2\text{Hg}(l) + \text{O}_2(g)\]

(a) \(\Delta S^\circ_{\text{sys}}\) is clearly positive—a gas is produced from a solid. \(\Delta H^\circ\) is surely positive—it is the reverse of a redox reaction between a metal and a non-metal. \(\Delta S^\circ_{\text{surr}}\) is correspondingly negative. \(\Delta G^\circ\) is positive at ordinary temperatures—otherwise, mercuric oxide would decompose in nature. At the temperatures Priestly studied, \(\Delta G^\circ\) is less than zero. The forward reaction proceeded, allowing Priestly to produce pure oxygen. Note that the mercury impurity is incredibly small because the vapour pressure of mercury is very small.

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

\[\Delta r S^\circ = 2 S^\circ[\text{Hg}(l)] + \frac{1}{2} S^\circ[\text{O}_2(g)] - 2 S^\circ[\text{HgO}(s)] = 2 \times 76.02 \text{ J K}^{-1} \text{ mol}^{-1} + 205.138 \text{ J K}^{-1} \text{ mol}^{-1} - 2 \times 70.29 \text{ J K}^{-1} \text{ mol}^{-1} = 216.60 \text{ J K}^{-1} \text{ mol}^{-1}
\]

\[\Delta r G^\circ = \Delta r H^\circ - T \Delta r S^\circ = 117 \text{ kJ mol}^{-1} - 298.15 \text{ K} \times 128.133 \text{ J K}^{-1} \text{ mol}^{-1}/(1000 \text{ J} / \text{kJ}) = 77.37 \text{ kJ mol}^{-1}
\]

We have \(\Delta r G^\circ\) at 25 °C, so we can calculate \(K\) at 25 °C (298 K) from

\[K = \frac{\exp{(-77.37 \times 10^3 \text{ J mol}^{-1})/(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(298 \text{ K})}}{117 \times 10^{-21}} = 3.1 \times 10^{-21}
\]

17.69  \[\text{CH}_3\text{OH}(l) \rightarrow \text{CH}_4(g) + \frac{1}{2}\text{O}_2(g)\]

(a) \(\Delta S^\circ = S^\circ[\text{CH}_4(g)] + \frac{1}{2} S^\circ[\text{O}_2(g)] - S^\circ[\text{CH}_3\text{OH}(l)] = 186.264 \text{ J K}^{-1} \text{ mol}^{-1} + \frac{1}{2} \times 205.138 \text{ J K}^{-1} \text{ mol}^{-1} - 160.7 \text{ J K}^{-1} \text{ mol}^{-1} = 128.133 \text{ J K}^{-1} \text{ mol}^{-1}
\]

A large positive entropy change is consistent with the production of 1.5 mol gas from 1 mol liquid.

(b) \(\Delta r G^\circ = \Delta r G^\circ[\text{CH}_4(g)] - \Delta r G^\circ[\text{CH}_3\text{OH}(l)] = -50.72 \text{ kJ mol}^{-1} - (-166.27 \text{ kJ mol}^{-1}) = 115.55 \text{ kJ mol}^{-1}
\]

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

(c) \(\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} / \text{kJ}) = 77.37 \text{ kJ mol}^{-1}
\]

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

\[\Delta r G^\circ = \Delta r H^\circ - T_{\text{sp}} \Delta r S^\circ = 0 \quad (\text{above } T_{\text{sp}}, \Delta r G^\circ < 0)
\]

\[T_{\text{sp}} = \Delta r H^\circ / \Delta r S^\circ = 77.37 \times 10^3 \text{ J mol}^{-1} / 115.55 \text{ J K}^{-1} \text{ mol}^{-1} = 669.5 \text{ K}
\]
17.71 (a) \[ S_8(s, \text{rhombic}) \rightarrow S_8(s, \text{monoclinic}) \]
\[ \Delta_r H^0 = 3.213 \text{ kJ mol}^{-1}, \Delta_r S^0 = 8.7 \text{ J K}^{-1} \text{ mol}^{-1} \]
\[ \Delta_r G^0 = \Delta_r H^0 - T \Delta_r S^0 = 3.213 \text{ kJ mol}^{-1} - 353.15 \text{ K} \times (8.7 \text{ J K}^{-1} \text{ mol}^{-1}) / (1000 \text{ J} / \text{kJ}) = 0.141 \text{ kJ mol}^{-1} \]

The rhombic form of \( S_8 \) solid is more stable than the monoclinic form at 80 °C.
\[ \Delta_r G^0 = \Delta_r H^0 - T \Delta_r S^0 = 3.213 \text{ kJ mol}^{-1} - 383.15 \text{ K} \times (8.7 \text{ J K}^{-1} \text{ mol}^{-1}) / (1000 \text{ J} / \text{kJ}) = -0.120 \text{ kJ mol}^{-1} \]

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

(b) \[ \Delta_r G^0 = \Delta_r H^0 - T_{\text{trans}} \Delta_r S^0 = 0 \]

at temperature, \( T_{\text{trans}} \), the temperature at which rhombic sulfur transforms to monoclinic sulfur.
\[ T_{\text{trans}} = \Delta_r H^0 / \Delta_r S^0 = 3.213 \times 10^3 \text{ J mol}^{-1} / (8.7 \text{ J K}^{-1} \text{ mol}^{-1}) = 369 \text{ K} = 96 \text{ °C} \]

17.73 \[ 4 \text{Ag(s) + O}_2(g) \rightarrow 2 \text{Ag}_2\text{O(s)} \]

(a) \[ \Delta_r H^0 = 2 \Delta_f H^0[\text{Ag}_2\text{O}(s)] = 2 \times (-31.05 \text{ kJ mol}^{-1}) = -62.10 \text{ kJ mol}^{-1} \]
\[ \Delta_r S^0 = 2 S^0[\text{Ag}_2\text{O}(s)] - (4 S^0[\text{Ag}(s)] + S^0[\text{O}_2(g)]) = 2 \times 121.3 \text{ J K}^{-1} \text{ mol}^{-1} - (4 \times 42.55 \text{ J K}^{-1} \text{ mol}^{-1} + 205.138 \text{ J K}^{-1} \text{ mol}^{-1}) = -132.738 \text{ J K}^{-1} \text{ mol}^{-1} \]
\[ \Delta_r G^0 = \Delta_r H^0 - T \Delta_r S^0 = -62.10 \text{ kJ mol}^{-1} - 298.15 \text{ K} \times (-132.738 \text{ J K}^{-1} \text{ mol}^{-1}) / (1000 \text{ J} / \text{kJ}) = -22.524 \text{ kJ mol}^{-1} \]

(b) \[ \ln K = - \frac{\Delta_r G^0}{RT} = - \frac{-22.524 \times 10^3 \text{ J mol}^{-1}}{8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 298.15 \text{ K}} = 9.087 \]
\[ K = e^{9.087} = 8.835 \times 10^3 = \frac{1}{p(O_2)} \]
So, \( p(O_2) = 1 / (8.835 \times 10^3) = 1.13 \times 10^{-4} \text{ bar} \)

(c) \[ \Delta_r G^0 = \Delta_r H^0 - T \Delta_r S^0 = 0 \]
at \( T = \Delta_r H^0 / \Delta_r S^0 = -62.10 \times 10^3 \text{ J mol}^{-1} / (-132.738 \text{ J K}^{-1} \text{ mol}^{-1}) = 468 \text{ K} \)

At this temperature, the vapour pressure of oxygen is 1.00 bar.
17.75 $\text{Hg}(\ell) \rightarrow \text{Hg}(g)$

$\Delta H^\circ = \Delta_H^o[\text{Hg}(g)] = 61.38 \text{ kJ mol}^{-1}$

$\Delta S^\circ = S^o[\text{Hg}(g)] - S^o[\text{Hg}(\ell)] = 174.97 \text{ J K}^{-1} \text{ mol}^{-1} - 76.02 \text{ J K}^{-1} \text{ mol}^{-1}$

$= 98.95 \text{ J K}^{-1} \text{ mol}^{-1}$

$\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ = 61.38 \text{ kJ mol}^{-1} - 298.15 \text{ K} \times (98.95 \text{ J K}^{-1} \text{ mol}^{-1}) / (1000 \text{ J} / \text{kJ}) = 31.88 \text{ kJ mol}^{-1}$

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

$K = 1.00$

$\Delta G^\circ = -RT \ln(K) = 0$

$= \Delta_H^\circ - T \Delta S^\circ$

So,

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

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

$K = 1.33 \times 10^{-3}$

$\Delta G^\circ = -RT \ln(K) = \Delta_H^\circ - T \Delta S^\circ$

Solve for $T$.

$T = \Delta H^\circ / (\Delta S^\circ - R \ln(K))$

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

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 ($\Delta G^\circ < 0$) are product-favoured. However, these reactions sometimes occur very slowly. $\Delta G^\circ$ 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 $\Delta S^\circ$ 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 $\Delta H^e = 0$

$\Delta G^e = \Delta H^e - T \Delta S^e < 0$

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 \[ \text{C}_6\text{H}_6(\text{s}) \rightarrow \text{C}_6\text{H}_6(\ell) \]
(a) \( \Delta H^\circ > 0 \)
   It takes energy (enthalpy) to break the intermolecular bonds holding the benzene molecules rigidly in their lattice positions.
(b) \( \Delta S^\circ > 0 \)
   A liquid has more disorder—more entropy—than the corresponding solid.
(c) \( \Delta G^\circ = 0 \) at 5.5 °C, the melting point, where the solid and liquid co-exist.
(d) \( \Delta G^\circ > 0 \) at 0.0 °C < the melting point, where the solid is the more stable phase.
(e) \( \Delta G^\circ < 0 \) at 25.0°C > the melting point, where the liquid is the more stable phase.

17.83 \[ \text{I}_2(\text{s}) \rightarrow \text{I}_2(\text{in CCl}_4 \text{ solution}) \]
\( \Delta G^\circ < 0 \)
This process is spontaneous—iodine dissolves readily in CCl₄.
\( \Delta S^\circ = (\Delta H^\circ - \Delta G^\circ) / T > 0 \) since \( \Delta H^\circ = 0 \)
This dissolution is an entropy-driven process.

17.85 (a) \[ \text{N}_2\text{H}_4(\ell) + \text{O}_2(\text{g}) \rightarrow \text{N}_2(\text{g}) + 2 \text{H}_2\text{O}(\ell) \]
This is an oxidation-reduction reaction—oxygen is the oxidizing agent and hydrazine is the reducing agent.
(b) \[ \Delta H^\circ = 2 \Delta H^\circ[\text{H}_2\text{O}(\ell)] - \Delta H^\circ[\text{N}_2\text{H}_4(\ell)] \]
\[ = 2 \times (-285.830 \text{ kJ mol}^{-1}) - (50.63 \text{ kJ mol}^{-1}) = -622.29 \text{ kJ mol}^{-1} \]
\[ \Delta S^\circ = 2 S^\circ[\text{H}_2\text{O}(\ell)] + S^\circ[\text{N}_2(\text{g})] - (S^\circ[\text{N}_2\text{H}_4(\ell)] + S^\circ[\text{O}_2(\text{g})]) \]
\[ = 2 \times (69.91 \text{ J K}^{-1} \text{ mol}^{-1}) + 191.61 \text{ J K}^{-1} \text{ mol}^{-1} - (121.21 \text{ J K}^{-1} \text{ mol}^{-1} + 205.138 \text{ J K}^{-1} \text{ mol}^{-1}) \]
\[ = 5.08 \text{ J K}^{-1} \text{ mol}^{-1} \]
\[ \Delta G^\circ = \Delta H^\circ - T \Delta S^\circ = -622.29 \text{ kJ mol}^{-1} - 298 \text{ K} \times 5.08 \text{ J K}^{-1} \text{ mol}^{-1} / (1000 \text{ J/kJ}) = -623.80 \text{ kJ mol}^{-1} \]

**Chapter 18**

18.2 For every 2 moles of NOCl consumed, there are 2 moles of NO and one mole of Cl₂ produced.
The relative rate of appearance of Cl₂ 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 mol L⁻¹ h⁻¹
In the last two hours: 0.002 mol L⁻¹ h⁻¹
The instantaneous rate of decay at \( t = 4.0 \text{ h} \): 0.0044 mol L⁻¹ h⁻¹

18.4 (a) Rate = \( k [\text{NO}_2][\text{O}_3] \)
(b) The rate triples.
(c) The rate is halved.

18.7 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 \(^{241}\text{Am} = 430 \text{ years} \)
\[ t_{1/2} \text{ of } ^{125}\text{I} = 63 \text{ years} \]
(b) \(^{125}\text{I} \)
(c) \( 1.57 \times 10^{15} \text{ atoms} \)

18.17 57.2 \text{ 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] \\

\begin{align*}
2 \text{NO} & \rightarrow \text{N}_2\text{O}_2 \\
\text{N}_2\text{O}_2 + \text{H}_2 & \rightarrow \text{N}_2\text{O} + \text{H}_2\text{O} \\
\text{N}_2\text{O} + \text{H}_2 & \rightarrow \text{N}_2 + \text{H}_2\text{O} \\
2 \text{NO} + 2 \text{H}_2 & \rightarrow \text{N}_2 + 2 \text{H}_2\text{O}
\end{align*}
\]

18.21 (a) \( 2\text{NH}_3(aq) + \text{OCl}^{-}(aq) \rightarrow \text{N}_2\text{H}_4(aq) + \text{H}_2\text{O}(\ell) + \text{Cl}^{-}(aq) \)
(b) step 2
(c) \[
\text{Rate} = k \ [\text{NH}_2\text{Cl}] [\text{NH}_3] \\
\]
(d) \( \text{NH}_2\text{Cl}, \text{N}_2\text{H}_5^{+} \text{ and OH}^{-} \)

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

(e) \((R)\text{-octan-2-ol} \)

\[ \text{H}_3\text{C} \quad \text{CH}_3 \]

\[ \text{H}_3\text{C} \quad \text{CH}_3 \]

\[ \text{H} \quad \text{OH} \]
18.23  (a) The rate of substitution will double  
(b) The rate of substitution will not change  
(c) 
\[
\text{CH}_3
\]
\[
C^+\]
\[
\text{CH}_3\quad \text{CH}_3
\]
(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 $\text{Cl}^-$, for this reaction.

18.31  (a) second order in $\text{NO}$ and first order in $\text{O}_2$  
(b) $\text{Rate} = k [\text{NO}]^2[\text{O}_2]$  
(c) 25 mol$^{-2}$ L$^2$ s$^{-1}$  
(d) $2.8 \times 10^{-5} \text{ mol L}^{-1} \text{ s}^{-1}$  
(e) $\text{O}_2 (g)$ reacts at rate $= 5.0 \times 10^{-5} \text{ mol L}^{-1} \text{ s}^{-1}$; i.e. one half the rate of NO. $\text{NO}_2(g)$ 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 $\text{NO}$ and first order in $\text{H}_2$  
(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 $[\text{CO}]$ 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

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 kJ mol

18.55

18.57  (a) Rate = \( k [\text{Cl}][\text{I}] \)
(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) Step 1 Slow \[ \text{H}_2\text{O}_2^{(aq)} + \text{I}^-^{(aq)} \rightarrow \text{H}_2\text{O}^{(l)} + \text{OI}^-^{(aq)} \] Step 2 Fast \[ \text{H}^+^{(aq)} + \text{OI}^-^{(aq)} \rightarrow \text{HOI}^{(aq)} \] Step 3 Fast \[ \text{HOI}^{(aq)} + \text{H}^+^{(aq)} + \text{I}^-^{(aq)} \rightarrow \text{I}_2^{(aq)} + \text{H}_2\text{O}^{(l)} \] \[ \text{H}_2\text{O}_2^{(aq)} + 2 \text{I}^-^{(aq)} + 2 \text{H}^+^{(aq)} \rightarrow 2 \text{H}_2\text{O}^{(l)} + \text{I}_2^{(aq)} \] (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) \( \text{NO}_2^{(g)} \) and \( \text{CO}^{(g)} \) are reactants. \( \text{NO}_3^{(g)} \) is an intermediate. \( \text{CO}_2^{(g)} \) and \( \text{NO}^{(g)} \) are products.

(b) \[ \text{NO}_2^{(g)} \rightarrow \text{NO}^{(g)} + \text{NO}_3^{(g)} + \text{CO}^{(g)} \]

1 \( \text{NO}_2 \) appears as both reactant and product - it cancels from the net reaction
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)  \[
\begin{align*}
\text{H}_3\text{C} & \quad \text{CH}_2 \\
\text{CH}_3 & \quad \text{H}_2\text{C}
\end{align*}
\]

(b)  \[
\begin{align*}
\text{H}_3\text{C} & \quad \text{CH}_3 \\
\text{H}_2\text{C} & \quad \text{CH}_2 \\
\text{CH}_3 & \quad \text{H}_2\text{C}
\end{align*}
\]

(c)  \[
\begin{align*}
\text{H}_2\text{C} & \quad \text{CH}_2 \\
\text{CH}_3 & \quad \text{H}_2\text{C}
\end{align*}
\]

(d)  \[
\begin{align*}
\text{H}_3\text{C} & \quad \text{CH}_3 \\
\text{H}_2\text{C} & \quad \text{CH}_2 \\
\text{CH}_3 & \quad \text{H}_2\text{C}
\end{align*}
\]

19.4

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

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

(c)  \[
\begin{align*}
\text{Cl} & \quad \text{Cl} \\
\text{Cl} & \quad \text{H} \\
\text{H} & \quad \text{Cl}
\end{align*}
\]
cis  trans

(d)  \[
\begin{align*}
\text{H}_3\text{C} & \quad \text{C}_{\text{H}_3} \\
\text{H}_2\text{C} & \quad \text{H} \\
\text{H}_2\text{C} & \quad \text{Cl}_{\text{H}_3}
\end{align*}
\]
cis  trans
19.6
(a) –Br
(b) –Br
(c) –CH₂CH₃
(d) –OH
(e) –CH₂OH
(f) –CH=O

19.7
(a)

(b)

19.8
This is the Z isomer.

19.9
The two downfield lines, at about 139 and 113 ppm, are the two alkene carbon peaks.
19.10

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

19.13  (a)

(b)

(c)

(d)  
R → MgBr
→
19.14
(a) $\text{NH}_4^+$
Ammonium is an electrophile. It is attracted to concentrations of negative charge, and will donate a proton to proton acceptors – i.e. nucleophiles.

(b) $\text{CN}^-$
Cyanide is a nucleophile. It is attracted to concentrations of positive charge (i.e. regions of depleted electron density) such as acidic protons and carbonyl carbons.

(c) $\text{Br}^-$
Bromide is a nucleophile. It is attracted to concentrations of positive charge (i.e. regions of depleted electron density).

(d) $\text{CH}_3\text{NH}_2$
The amine N atom is a nucleophile. It is attracted to concentrations of positive charge (i.e. regions of depleted electron density).

(e) $\text{H} C\equiv\text{C} - \text{H}$
Acetylene is a nucleophile. It has a relatively loosely held cloud of $\pi$ electrons which electrophiles are attracted to – and vice versa.

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

19.16

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

19.20
1,2-dibromobutane
1,4-dibromobutane

19.21
(a) Addition of water to 3-methylhex-3-ene gives 3-methylhexan-3-ol,
(b) Addition of water to 1-methylcyclopentene gives 1-methylcyclopentanol
(c) Addition of water to 2,5-dimethylhept-2-ene gives 2,5-dimethylheptan-2-ol

19.22
(a) Butan-2-ol can be made by addition of water to but-1-ene or but-2-ene.
(b) 3-Methylpentan-3-ol can be made by addition of water to 3-methylpent-2-ene or 2-ethylbut-1-ene.
(c) 1,2-Dimethylcyclohexanol can be made by addition of water to 1,2-dimethylcyclohexene or 1,6-dimethylcyclohexene.
19.23 If the second bromine added to the other carbon – the one on the left, then the enantiomeric product would be formed. By symmetry, this pathway is just as likely as the one shown in Figure 19.30 of the text. The two enantiomeric products would be formed in equal amounts.

19.24

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

19.25 See Exercise 19.24 above

19.26 (a) Catalytic hydrogenation of (CH₃)₂C=CHCH₂CH₃ produces (CH₃)₂CHCH₂CH₂CH₃.
(b) Catalytic hydrogenation of 3,3-dimethylcyclopentene gives 3,3-dimethylcyclopentane.

19.27 (a)

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

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

19.30 The peak just above 3300 cm$^{-1}$ looks like an alkyne $\text{C}−\text{H}$ stretch, while the peak just above 2100 cm$^{-1}$ looks like an asymmetric alkyne $\text{C}=\text{C}$ stretch. There also appear to be alkyl $\text{C}−\text{H}$ 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 $^{13}\text{C}$ chemical shifts occur further downfield.

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

19.33

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

REVIEW QUESTIONS

19.37 \( \beta \)-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. \( \beta \)-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 \( \beta \)-carotene are between carbon 1 (the carbon connected to the chain) and carbon 2, whereas the ring double bonds in \( \alpha \)-carotene are between carbon 2 and carbon 3. Otherwise, the two molecules are identical.
The HOMO-LUMO gap for \( \alpha \)-carotene is larger than that for lycopene. Whereas \( \alpha \)-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) 

(b) 

19.45  
(a) 4-methylpent-1-ene  
(b) 3-heptene  
(c) 1,5-heptadiene  
(d) 2-methylhex-3-ene  

(a+b+c) All three of these molecules have cis-trans isomers.

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

19.57 \[ \text{CH}_3\text{CH}2\text{CH}2\text{CHCH}_3 + \text{HCl} \rightarrow \text{CH}_3\text{CH}2\text{CHClCH}_2\text{CH}_3 \text{ or } \text{CH}_3\text{CH}_2\text{CH}_2\text{CHClCH}_3 \]
19.59

The carbocation on the left is the more stable.

19.61

(a) 

(b) 

(c) 

(d) 

H3C-C+CH3

H3C-C+H

H2 & Pd

Br2

HBr

KMnO4, NaOH, H2O

H3C-CH3
19.63 Oxidative cleavage of \( \text{O} \) yields a single product, \( \text{O} \) because of symmetry. Oxidative cleavage of \( \text{O} \) gives two distinct products, \( \text{OH} \) + \( \text{HO} \).

19.65

19.67 (a) 6  
(b) 6  
(c) 3
19.69

\[
\text{H}_3\text{C} = \text{CH} \quad \text{1 equiv HBr} \quad \text{H}_3\text{C} \quad \text{CH}_2
\]

\[
\text{H}_3\text{C} = \text{CH} \quad \text{1 equiv Cl}_2 \quad \text{H}_3\text{C} \quad \text{Cl} \quad \text{Cl}
\]

\[
\text{H}_3\text{C} = \text{CH} \quad \text{H}_2 + \text{Lindlar catalyst} \quad \text{H}_3\text{C} \quad \text{H} \quad \text{H} \quad \text{H}
\]

19.71

\[
\text{H}_3\text{C} = \text{CH} \quad \text{NaNH}_2 \quad \text{H}_3\text{C} = \text{C}^- \quad \text{Na}^+
\]

\[
\text{CH}_3\text{Br} \quad \text{H}_2 + \text{Lindlar catalyst} \quad \text{H}_3\text{C} = \text{CH} \quad \text{H}_3\text{C} \quad \text{CH}_3
\]
19.73 (a)

\[ \text{1-hexene, 2-methylpent-2-ene, 2,3-dimethylbut-2-ene} \]

(b)

\[ \text{H}_3\text{C} - \text{CH} = \text{CH} - \text{CH}_3 \]

(c)

\[ \text{H}_3\text{C} - \text{CH} = \text{CH} - \text{CH}_3 \]

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.
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.
19.81

A

\[
\text{3 H}_2 \text{ Pd catalyst}
\]

B

KMnO_4 - suppose acidic conditions

\[
\text{NaNH}_2 - \text{followed by iodomethane}
\]

C

19.83 Treat acetylene with NaNH_2 to get acetylide, H\text{C}≡\text{C}^-. Add to 1-bromotridecane, CH_3(CH_2)_{12}Br to get CH_3(CH_2)_{12}C≡CH. Treat with NaNH_2 to get pentadecynylide. Add to 1-bromooctane, CH_3(CH_2)_{7}Br to get CH_3(CH_2)_{12}C≡C(CH_2)_{7}CH_3.
much slower

fast

slow

$E_{a1}$

$E_{a2}$

$\Delta H$

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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.

![1,3-dichlorobenzene structure]

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 $\pi$ system. It is aromatic, with $^1$H NMR shifts are at 6.4 and 7.4 ppm.

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

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

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

20.10

![Structures of 0-, m- and p-bromotoluenes]

20.11 D$_2$SO$_4$ sulfonates the benzene ring reversibly. On sulfonation, an H$^+$ is lost to the solvent (D$_2$SO$_4$). 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 (a) 

(b) 

(c) 

(d) 

(e)
20.15 Oxidizing \( m \)-chloroethylbenzene with \( \text{KMnO}_4 \) produces \( m \)-chlorobenzoic acid,

\[
\begin{align*}
\text{Oxidizing tetralin with } \text{KMnO}_4 \text{ produces } 1,2\text{-bezenedicarboxylic acid a.k.a. phthalic acid,}
\end{align*}
\]

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
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-tetramethylcyclooctatraene 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 anthacene – 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.
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 $1\frac{1}{2}$.

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

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.

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 NaNH₂. The sodium salt of the aromatic cation would be formed.

20.39

\[
\text{CH}_3\text{C}_6\text{H}_4\text{OH} \quad \text{CH}_3
\]

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

\[
\text{HO} - \text{C}_6\text{H}_4\text{OOH}
\]

1,2-benzenedicarboxylic acid a.k.a phthalic acid
20.41 (a) \( o \)-dinitrobenzene, \( m \)-dinitrobenzene and \( p \)-dinitrobenzene

\[
\begin{align*}
&\text{\( o \)-dinitrobenzene} \\
&\text{\( m \)-dinitrobenzene} \\
&\text{\( p \)-dinitrobenzene}
\end{align*}
\]

(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

\[
\begin{align*}
&\text{1-bromo-2,3-dimethylbenzene} \\
&\text{1-bromo-2,4-dimethylbenzene} \\
&\text{1-bromo-2,5-dimethylbenzene}
\end{align*}
\]
The products of bromination are \( o \)-bromomethoxybenzene and \( p \)-bromomethoxybenzene. The products of acylation are \( o \)-acetylmethoxybenzene and \( p \)-acetylmethoxybenzene.
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-acyltoluene.
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.

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

(a) $\text{CH}_3\text{CH}_2\text{Cl}$ with $\text{AlCl}_3$

\[
\begin{align*}
\text{-Benzene} + \text{CH}_3\text{CH}_2\text{Cl} + \text{AlCl}_3 & \rightarrow \text{H}_3\text{C} - \text{CH}_3 \\
+ & \quad \text{HCl}
\end{align*}
\]

(b) $\text{Benzene}$

\[
\begin{align*}
\text{-Benzene} + \text{CH}_3\text{CH}_2\text{Cl} + \text{AlCl}_3 & \rightarrow \text{H}_3\text{C} - \text{CH}_3 \\
+ & \quad \text{HCl}
\end{align*}
\]

(c) $\text{Benzoic acid}$

\[
\begin{align*}
\text{Benzoic acid} + \text{HNO}_3 + \text{H}_2\text{SO}_4 & \rightarrow \text{H}_3\text{C} - \text{CH}_3 \\
+ & \quad \text{H}_2\text{O}
\end{align*}
\]

(d) $\text{Diethylphenylamine}$

\[
\begin{align*}
\text{Diethylphenylamine} + \text{SO}_3 + \text{H}_2\text{SO}_4 & \rightarrow \text{H}_3\text{C} - \text{CH}_3 \\
+ & \quad \text{H}_2\text{O}
\end{align*}
\]

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

20.57 (a) $\text{o}$-Bromotoluene can be synthesized from benzene via a Friedel-Crafts methylation (i.e. treat with 1 equivalent $\text{CH}_3\text{Cl}$ and $\text{AlCl}_3$) to make toluene, followed by bromination (treat toluene with 1 equivalent $\text{Br}_2$ and $\text{FeBr}_3$) 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, $\text{o}$-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 $\text{CH}_3\text{Cl}$ and $\text{AlCl}_3$. Nitrate using $\text{HNO}_3$ and $\text{H}_2\text{SO}_4$ to get $\text{o}$- and $\text{p}$-nitrobenzene. Separate the para product. Oxidize it using $\text{KMnO}_4$ to obtain the desired $\text{p}$-nitrobenzoic acid.
20.61 (a) Methylate benzene using CH₃Cl and AlCl₃. Nitrate the toluene product using HNO₃ and H₂SO₄. Separate the ortho product. Oxidize using KMnO₄ to convert the methyl group to carboxylic acid.

(b) Methylate benzene using two equivalents of CH₃Cl and AlCl₃. 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

\[
\text{AlCl}_3 \quad \rightarrow \quad \text{HCl} \quad \rightarrow \quad \text{H}_2\text{O}
\]

20.69

\[
\text{Br} + \text{NO}_2^- \quad \rightarrow \quad \text{BrONO}_2^- \quad \rightarrow \quad \text{BrONO}_2^- \quad \rightarrow \quad \text{BrONO}_2^-
\]

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

\[
\text{Br} \quad \rightarrow \quad \text{Br} \quad \rightarrow \quad \text{Br}
\]

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

\[
\text{Br} \quad \rightarrow \quad \text{Br} \quad \rightarrow \quad \text{Br}
\]

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.
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

(a)

(b)

(c)

(d)
21.5
(a)  \[ \text{HO} \quad \begin{array}{c} \text{H}_3\text{C} \\ \text{H}_3\text{C} \end{array} \quad \text{HCl} \quad \begin{array}{c} \text{Cl} \\ \text{CH}_3 \end{array} \]

(b)  \[ \text{HO} \quad \begin{array}{c} \text{H}_3\text{C} \\ \text{H}_3\text{C} \end{array} \quad \text{PBr}_3 \quad \begin{array}{c} \text{Br} \\ \text{CH}_3 \end{array} \]

(c)  \[ \text{HO} \quad \begin{array}{c} \text{H}_3\text{C} \\ \text{H}_3\text{C} \end{array} \quad \text{PBr}_3 \quad \begin{array}{c} \text{Br} \\ \text{CH}_3 \end{array} \]

(d)  \[ \text{HO} \quad \begin{array}{c} \text{H}_3\text{C} \\ \text{H}_3\text{C} \end{array} \quad \text{SOCl}_2 \quad \begin{array}{c} \text{Cl} \\ \text{CH}_3 \end{array} \]

21.6
(a)  \[ \text{HO} \quad \begin{array}{c} \text{H}_3\text{C} \\ \text{H}_3\text{C} \end{array} \quad \text{PBr}_3 \quad \begin{array}{c} \text{Br} \\ \text{CH}_3 \end{array} \]

(b)  \[ \text{HO} \quad \begin{array}{c} \text{CH}_3 \\ \text{CH}_3 \end{array} \quad \text{HCl} \quad \begin{array}{c} \text{Cl} \\ \text{CH}_3 \end{array} \]

(c)  \[ \text{HO} \quad \begin{array}{c} \text{H}_3\text{C} \\ \text{H}_3\text{C} \end{array} \quad \text{SOCl}_2 \quad \begin{array}{c} \text{Cl} \\ \text{H}_3\text{C} \end{array} \]
21.8
(a) 
\[
\begin{array}{c}
\text{H}_3\text{C} & - & \text{Br} \\
\text{CH}_3 \\
\end{array}
\rightarrow
\begin{array}{c}
\text{H}_3\text{C} & - & \text{I} \\
\text{CH}_3 \\
\end{array}
\]
\text{LiI}

(b) 
\[
\begin{array}{c}
\text{Cl} & - & \text{H} \\
\text{CH}_3 & - & \text{CH}_3 \\
\text{CH}_3 \\
\end{array}
\rightarrow
\begin{array}{c}
\text{HS} & - & \text{H} \\
\text{H} & - & \text{CH}_3 \\
\text{CH}_3 \\
\end{array}
\]
\text{HS}^-

(c) 
\[
\begin{array}{c}
\text{C}_6\text{H}_5 & - & \text{Br} \\
\end{array}
\rightarrow
\begin{array}{c}
\text{C}_6\text{H}_5 & - & \text{C} = \text{N} \\
\end{array}
\]
\text{NaCN}

21.9
(a) 
\[
\begin{array}{c}
\text{H}_3\text{C} & - & \text{Br} \\
\end{array}
\rightarrow
\begin{array}{c}
\text{H}_3\text{C} & - & \text{OH} \\
\end{array}
\]
\text{NaOH}

(b) 
\[
\begin{array}{c}
\text{H}_3\text{C} & - & \text{Br} \\
\text{H}_3\text{C} \\
\end{array}
\rightarrow
\begin{array}{c}
\text{H}_3\text{C} & - & \text{N} = \text{N}^- \\
\text{N}^- \\
\end{array}
\]
\text{NaN}_3

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

21.11
\[
\begin{array}{c}
\text{H}_3\text{C} & - & \text{Br} & - & \text{H} \\
\text{CH}_3 & - & \text{CH}_3 \\
\end{array}
\rightarrow
\begin{array}{c}
\text{H}_3\text{C} & - & \text{H} \\
\text{CH}_3 & - & \text{O} \\
\text{CH}_3 \\
\end{array}
\]
\text{NaCH}_3\text{COO}

\text{(S)-2-bromohexane} \quad \text{(R)-2-hexyl acetate}
21.12

\[
\begin{align*}
\text{(R)-2-bromo-4-methylpentane} & \quad \text{HS}^- & \quad \text{4-methylpentane-(S)-2-thiol} \\
\end{align*}
\]

21.14  (a) CN\(^-\) (cyanide ion) reacts faster with \(\text{CH}_3\text{CH}_2\text{CH}_2\text{Br}\)  
(b) Reaction of \(\text{I}^-\) with \((\text{CH}_3)_2\text{CH}\text{CH}_2\text{Cl}\) 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 \textit{tert}-butyl alcohol concentration doubles the rate of reaction.

21.17

\[
\begin{align*}
\text{(S)-3-methyloctan-3-ol} & \quad \text{HBr} & \quad \text{(S)-3-bromo-3-methyloctane} \\
\quad & \quad & \text{+} \quad \text{(R)-3-bromo-3-methyloctane} \\
\end{align*}
\]

21.18

\[
\begin{align*}
\text{(S)-2-bromo-2-phenylbutane} & \quad \text{H}_2\text{O} & \quad \text{(S)-2-phenylbutan-2-ol} \\
\quad & \quad & \text{+} \quad \text{(R)-2-phenylbutan-2-ol} \\
\end{align*}
\]
21.19

(a) 

(b) 

(c) 

21.20

(a) 

(b) 

21.21 Rate of the elimination reaction triples.

21.22 (a) $S_n2$
(b) $E2$
(c) $S_n1$
21.23

\[
\begin{align*}
\text{Br} & \quad \text{Mg + ether} \\
H_3C & \quad \text{MgBr} \\
\text{CH}_3 & \quad \text{CH}_3 \\
\end{align*}
\]
Grignard reagent

\[
\begin{align*}
\text{MgBr} & \quad \text{D}_2\text{O} \\
H_3C & \quad \text{D} \\
\text{CH}_3 & \quad \text{CH}_3 \\
\end{align*}
\]

21.24

\[
\begin{align*}
\text{OH} & \quad \text{PBr}_3 \\
H_3C & \quad \text{CH}_3 \text{Br} \\
\text{CH}_3 & \quad \text{CH}_3 \text{Br} \\
\end{align*}
\]

\[
\begin{align*}
\text{Br} & \quad \text{Mg + ether} \\
H_3C & \quad \text{CH}_3 \text{MgBr} \\
\text{CH}_3 & \quad \text{CH}_3 \text{MgBr} \\
\end{align*}
\]

\[
\begin{align*}
\text{MgBr} & \quad \text{H}_2\text{O} \\
H_3C & \quad \text{CH}_3 \text{CH}_3 \\
\text{CH}_3 & \quad \text{CH}_3 \text{CH}_3 \\
\end{align*}
\]
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

\[
\begin{align*}
\text{F} & \quad \text{H} & \quad \text{Cl} \\
\text{F} & \quad \text{F} & \quad \text{Br}
\end{align*}
\]

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) $\text{Br}^-$

(b) $\text{Cl}^-$

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

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  
(a)  
\[
\begin{array}{c}
\text{H}_3\text{C} \text{-} \text{Cl} \\
\text{H}_3\text{C} \text{-} \text{CH}_3 \text{-} \text{Cl}
\end{array}
\]

(b)  
\[
\begin{array}{c}
\text{H}_3\text{C} \text{-} \text{Br} \\
\text{H}_3\text{C} \text{-} \text{CH}_3 \text{-} \text{Br}
\end{array}
\]

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  
\[
\begin{array}{c}
\text{H}_3\text{C} \text{-} \text{Cl} \\
\text{NaOH} \rightarrow \\
\text{H}_3\text{C} \text{-} \text{CH}_3 \text{-} \text{CH}_3
\end{array}
\]

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

21.47  
(a) E2  
(b) \( S_n1 \)
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

(a) \( \text{HCl} \rightarrow \)

(b) \( \text{HCl, dilute } \text{H}_2\text{SO}_4(\text{aq}) \rightarrow \)

(c) \( \text{HCl, Mg & ether} \rightarrow \)

(d) \( \text{H}_2 & \text{Pd catalyst} \rightarrow \)
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

\[
\begin{align*}
\text{1-bromobutane} &\quad > \quad \text{1-bromo-2-methylpropane} \\
\text{2-bromobutane} &\quad > \quad \text{2-bromo-2-methylpropane}
\end{align*}
\]

21.59

\[
\begin{align*}
\text{H}_3\text{C}-\text{OH} &\quad \overset{\text{NaNH}_2}{\Rightarrow} \quad \text{H}_3\text{C}-\text{O}^- \\
\text{H}_3\text{C}-\text{OH} &\quad \overset{\text{PBr}_3}{\Rightarrow} \quad \text{H}_3\text{C}-\text{Br}
\end{align*}
\]

\[
\begin{align*}
\text{H}_3\text{C}-\text{O}^- + \text{H}_3\text{C}-\text{Br} &\quad \Rightarrow \quad \text{H}_3\text{C}-\text{O}-\text{CH}_3
\end{align*}
\]

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 (±)-3-bromo-3-methylhexane, because it is an SN1 substitution. Once the carbocation is formed, the stereochemistry of the starting material is lost. The (R) and (S) products are equally likely.  

Chapter 22

22.2 (a) tertiary alcohol.  
(b) contains primary and secondary alcohol functional groups.  
(c) primary alcohol.  
(d) secondary alcohol.  
(e) phenol  
(f) phenol
22.3

(a) \[
\begin{array}{c}
\text{CH}_3 \\
\text{CH}_3 \\
\text{CH}_3 \\
\text{OH}
\end{array}
\]

(b) \[
\begin{array}{c}
\text{CH}_3 \\
\text{OH}
\end{array}
\]

(c) \[
\begin{array}{c}
\text{H}_3\text{C} \\
\text{OH}
\end{array}
\]

(d) \[
\begin{array}{c}
\text{H}_3\text{C} \\
\text{OH}
\end{array}
\]

(e) \[
\begin{array}{c}
\text{OH} \\
\text{Br}
\end{array}
\]

(f) \[
\begin{array}{c}
\text{OH} \\
\text{N} \\
\text{O} \\
\text{N} \\
\text{N}
\end{array}
\]

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

\[
\begin{align*}
\text{H}_3\text{C} & \quad \text{O} & \quad \text{OCH}_3 \\
\text{H}_3\text{C} & \quad \text{O} & \quad \text{OCH}_3 \\
\text{NaBH}_4 & \quad \longrightarrow & \quad \text{H}_3\text{C} & \quad \text{O} & \quad \text{OCH}_3 \\
\text{H}_3\text{C} & \quad \text{O} & \quad \text{OCH}_3 & \quad \text{LiAlH}_4 & \quad \longrightarrow & \quad \text{H}_3\text{C} & \quad \text{O} & \quad \text{OCH}_3
\end{align*}
\]

22.8

\[
\begin{align*}
\text{NaNH}_2 & \quad \longrightarrow & \quad \text{O} & \quad \text{Na}^+ \\
\text{H}_3\text{C} & \quad \text{O} & \quad \text{H} & \quad \text{H}_3\text{C} & \quad \text{O} & \quad \text{CH}_3
\end{align*}
\]

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

(a) \[
\begin{align*}
\text{CH}_3\text{OH} & \xrightarrow{\text{CrO}_3} \text{CHO} \\
& \\
\end{align*}
\]

(b) \[
\begin{align*}
\text{H}_3\text{C}-\text{C}-\text{CH}_2-\text{CH}_2-\text{OH} & \xrightarrow{\text{CrO}_3} \text{H}_3\text{C}-\text{C}-\text{CH}_2-\text{CH}_2-\text{CO}_2\text{H} \\
& \\
\end{align*}
\]

(c) \[
\begin{align*}
\text{H}_3\text{C}-\text{C}-\text{CH}_2-\text{CH}_2-\text{CH}_3 & \xrightarrow{\text{CrO}_3} \text{H}_3\text{C}-\text{C}-\text{CH}_2-\text{CH}_2-\text{CH}_3 \\
& \\
\end{align*}
\]

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

\[
\begin{align*}
\text{SO}_3 + \text{H}_2\text{SO}_4 & \xrightarrow{\text{NaOH, high T}} \text{HO} \\
& \text{Ph} \\
\text{Ph} & \xrightarrow{\text{CH}_3\text{Cl} + \text{AlCl}_3} \text{HO} + \text{HO} \\
& \text{Ph} \\
& \text{Ph} \\
\end{align*}
\]
22.15

\[
\begin{align*}
\text{ON} & \quad \text{O} \\
\text{Br} & \quad \text{OH} \\
\text{CH}_3 & \quad \text{O} \\
\text{O} & \quad \text{N} \\
\text{O} & \quad \text{O} \\
\end{align*}
\]

22.16

(a)

\[
\begin{align*}
\text{H}_3\text{C} & \quad \text{O} \quad \text{CH}_3 & \quad \text{HI} & \quad \text{H}_3\text{C} & \quad \text{I} + \text{H}_3\text{C} & \quad \text{OH}
\end{align*}
\]

(b)

\[
\begin{align*}
\text{C}_8\text{H}_{15} & \quad \text{O} \quad \text{CH}_3 & \quad \text{HI} & \quad \text{C}_8\text{H}_{15} & \quad \text{OH} + \text{H}_3\text{C} & \quad \text{I}
\end{align*}
\]

(c)

\[
\begin{align*}
\text{H}_3\text{C} & \quad \text{O} \quad \text{CH}_3 & \quad \text{HI} & \quad \text{H}_3\text{C} & \quad \text{CH}_3 \quad \text{OH} + \text{H}_3\text{C} & \quad \text{I}
\end{align*}
\]
22.17

\[
\begin{align*}
\text{H}_3\text{C} & \quad \text{O} \quad \text{H} \\
\text{H} & \quad \text{O}^- \quad \text{H} \\
\text{H}_3\text{C} & \quad \text{H} \\
\end{align*}
\]

22.18 (a) 2-butanethiol
(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

(a) \[ \text{CH}_3\text{O} - \text{CH}_3 \]

(b) \[ \text{OH} \quad \text{H} \quad \text{O} \quad \text{CH}_3 \]

(c) \[ \text{H}_3\text{C} - \text{OH} - \text{CH}_3 \]

(d) \[ \text{H} \quad \text{H} \quad \text{HO} \quad \text{CH}_3 \]

(e) \[ \text{OH} \quad \text{CH}_3 \quad \text{O} \quad \text{CH}_3 \]
22.29

1-pentanol

CH₃
OH

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

CH₃
OH

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

CH₃
CH₃

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

CH₃
OH

2-pentanol

CH₃

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

CH₃

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

CH₃

3-pentanol
22.31

1-butyl methyl ether

2-butyl methyl ether

2-methylpropyl 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)
22.41

\[
\text{H}_3\text{C} \quad \text{CH}_3 \\
\text{O} \quad \text{CH}_3 \\
\text{CH}_3 \quad \text{LiAlH}_4
\]

\[
\rightarrow \quad \text{H}_3\text{C} \quad \text{OH} \\
\text{CH}_3 \\
\text{CH}_3
\]

\[
\text{NaNH}_2 \quad \text{CH}_3\text{CH}_2\text{I} \quad \rightarrow \quad \text{H}_3\text{C} \quad \text{O} \\
\text{CH}_3 \quad \text{CH}_3
\]

22.43

(a)

\[
\text{OH} \quad \text{OCl}^- \text{ in acetic acid} \quad \rightarrow \quad \text{O} \\
\]

(b)

\[
\text{H}_3\text{C} \quad \text{OH} \quad \text{CH}_3 \quad \text{OCl}^- \text{ in acetic acid} \quad \rightarrow \quad \text{H}_3\text{C} \quad \text{O} \\
\text{CH}_3 \quad \text{CH}_3
\]

(c)

\[
\text{OH} \quad \text{OCl}^- \text{ in acetic acid} \quad \rightarrow \quad \text{O} \\
\text{H}_3\text{C} \quad \text{CH}_3
\]
\[
\begin{align*}
\text{H}_3\text{C} - \text{O} - \text{CH}_3 & \xrightarrow{\text{HI}} \text{H}_3\text{C} - \text{O} - \text{CH}_3 & \rightarrow & \text{H}_3\text{C} - \text{O} - \text{CH}_3 & + & \text{H}_3\text{C} - \text{I} \\
\text{H}_3\text{C} - \text{O} - \text{CH}_3 & \xrightarrow{\text{HI}} \text{H}_3\text{C} - \text{O} - \text{CH}_3 & \rightarrow & \text{H}_3\text{C} - \text{O} - \text{CH}_3 & + & \text{H}_3\text{C} - \text{I} \\
\text{H}_3\text{C} - \text{O} - \text{CH}_3 & \xrightarrow{\text{HI}} \text{H}_3\text{C} - \text{O} - \text{CH}_3 & \rightarrow & \text{H}_3\text{C} - \text{O} - \text{CH}_3 & + & \text{H}_3\text{C} - \text{I} \\
\text{H}_3\text{C} - \text{O} - \text{CH}_3 & \xrightarrow{\text{HI}} \text{H}_3\text{C} - \text{O} - \text{CH}_3 & \rightarrow & \text{H}_3\text{C} - \text{O} - \text{CH}_3 & + & \text{H}_3\text{C} - \text{I} \\
\end{align*}
\]
(a) 
\[
\begin{align*}
\text{O} & \text{H} \\
\text{C} & \text{H} \\
\text{H} & \text{H} \\
\text{C} & \text{H} \\
\text{H} & \text{H} \\
\text{O} & \text{H} \\
\text{C} & \text{H} \\
\text{H} & \text{H} \\
\text{C} & \text{H} \\
\text{H} & \text{H}
\end{align*}
\]
\[\text{PCC} \quad \rightarrow \quad \text{C} \quad \text{H} \quad \text{O} \]

(b) 
\[
\begin{align*}
\text{O} & \text{H} \\
\text{C} & \text{H} \\
\text{H} & \text{H} \\
\text{C} & \text{H} \\
\text{H} & \text{H} \\
\text{O} & \text{H} \\
\text{C} & \text{H} \\
\text{H} & \text{H} \\
\text{C} & \text{H} \\
\text{H} & \text{H}
\end{align*}
\]
\[\text{HBr} \quad \rightarrow \quad \text{C} \quad \text{H} \quad \text{O} \quad + \quad \text{Br} \quad \text{C} \quad \text{H} \quad \text{H} \]

(c) 
\[
\begin{align*}
\text{H}_2\text{C} & \text{C} \quad \text{H} \quad \text{C} \\
\text{O} & \text{O} \\
\text{C} & \text{H} \\
\text{H} & \text{H} \\
\text{C} & \text{H} \\
\text{H} & \text{H} \\
\text{C} & \text{H} \\
\text{H} & \text{H} \\
\text{C} & \text{H} \\
\text{H} & \text{H}
\end{align*}
\]
\[1. \text{LiAlH}_4 \quad \rightarrow \quad \text{H}_2\text{C} \quad \text{C} \quad \text{H} \quad \text{C} \quad + \quad \text{H}_3\text{C} \quad \text{O} \quad \text{H} \]

(c) 
\[
\begin{align*}
\text{H} & \text{H} \\
\text{H} & \text{H} \\
\text{H} & \text{H} \\
\text{H} & \text{H} \\
\text{C} & \text{H} \\
\text{H} & \text{H} \\
\text{C} & \text{H} \\
\text{H} & \text{H} \\
\text{C} & \text{H} \\
\text{H} & \text{H}
\end{align*}
\]
\[\text{HBr} \quad \rightarrow \quad \text{H}_2\text{C} \quad \text{C} \quad \text{H} \quad \text{C} \quad + \quad \text{Br} \quad \text{C} \quad \text{H} \quad \text{H} \]

Chemistry, First Canadian Edition
(a)\[ \text{PCC} \rightarrow \text{H}_3\text{C}-\text{CH(OH)}\text{CH}_3 \rightarrow \text{H}_3\text{C}-\text{CHO} \]

(b)\[ \text{CrO}_3 \rightarrow \text{H}_3\text{C}-\text{CH(OH)}\text{CH}_3 \rightarrow \text{H}_3\text{C}-\text{CHO} \]

(c)\[ \text{NaNH}_2 \rightarrow \text{H}_3\text{C}-\text{CH(OH)}\text{CH}_3 \rightarrow \text{H}_3\text{C}-\text{CH(OH)}^-\text{Na}^+ \]

(d)\[ \text{PCl}_3 \rightarrow \text{H}_3\text{C}-\text{CH(OH)}\text{CH}_3 \rightarrow \text{ClH}_3\text{C}-\text{CH} \]
(a) \[ \text{KMnO}_4 \ & \ H_2\text{SO}_4 \quad \text{strongly oxidizing conditions} \]

oxidation takes place at the benzyl position - in addition to the alcohol intermediates are stabilized by the neighboring phenyl ring

(b) \[ \text{H}_2\text{SO}_4 \]

(c) \[ \text{PBr}_3 \]

(d) \[ \text{CrO}_3 \]

(e) \[ \text{PCC} \]
22.53

(a) \( \text{H}_3\text{C} - \text{OH} \xrightarrow{\text{PBr}_3} \text{H}_3\text{C} - \text{Br} \)

(b) \( \text{H}_3\text{C} - \text{OH} \xrightarrow{\text{CrO}_3} \text{H}_3\text{C} - \text{O} - \text{OH} \)

(c) \( \text{H}_3\text{C} - \text{OH} \xrightarrow{\text{NaNH}_2} \text{H}_3\text{C} - \text{O}^-\text{Na}^+ \)

(d) \( \text{H}_3\text{C} - \text{OH} \xrightarrow{\text{PCC}} \text{H}_3\text{C} - \text{O} \)
22.55

(a) \[
\text{OH} \quad \overset{\text{CrO}_3}{\longrightarrow} \quad \text{O}
\]

(b) \[
\text{H}^+ \quad \overset{\text{PCC}}{\longrightarrow} \quad \text{H}^+ \quad \text{O}
\]

(c) \[
\text{CH}_3 \quad \overset{\text{CrO}_3}{\longrightarrow} \quad \text{CH}_3 \quad \text{O}
\]

22.57

(a) \[
\text{OH} \quad \overset{\text{Na}_2\text{CrO}_3}{\longrightarrow} \quad \text{O}
\]

(b) \[
\text{H}_3\text{C} \quad \overset{\text{SH}^-}{\longrightarrow} \quad \text{H}_3\text{C} \quad \text{SH}
\]

(c) \[
\text{SH} \quad \overset{\text{Br}_2}{\longrightarrow} \quad \text{S-S}
\]
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 NaHCO₃.

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 −OCH₂CH₂O− 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 S₄2 substitution by (in this case) phenoxide. The trouble is that phenyl halides are not amenable to S₄2 substitution. Nucleophilic attack will not occur at an aromatic carbon atom.

22.69

The cis isomer will oxidize faster with CrO₃ − the hydroxyl group is axial in this isomer.
22.71

\[ \text{Cl} \overset{\text{O-H}}{\text{Cl}} \rightarrow \text{Cl} \overset{\text{O}}{\text{Cl}} \]

22.73 Dehydration reaction

\[ \text{H}_3\text{C} \overset{\text{O}}{\text{R}} \rightarrow \text{H}_3\text{C} \overset{\text{O}}{\text{R}} \]

neutralize
Chapter 23

23.2  (a) 2-methylpentan-3-one  
      (b) 3-phenylpropanal  
      (c) 2,6-octandione  
      (d) trans-2-methylcyclohexanecarbaldehyde  
      (e) 1,5-pentanediol  
      (f) cis-2,5-dimethylcyclohexanone
23.5

(a) \[ \text{H}_3\text{C}-\text{CH}-(\text{CH}_3)_{\text{O}}-\text{H} \xrightarrow{\text{PCC}} \text{H}_3\text{C}-\text{CH}-(\text{CH}_3)_{\text{O}}-\text{CH}_3 \]

(b) \[ \text{H}_3\text{C}-\text{CH}-(\text{CH}_3)_{\text{O}}-\text{CH} \xrightarrow{\text{H}_2\text{SO}_4 \text{ & HgSO}_4} \text{H}_3\text{C}-\text{CH}-(\text{CH}_3)_{\text{O}}-\text{CH}_3 \]

(c) \[ \text{H}_3\text{C}-\text{CH}-(\text{CH}_3)_{\text{O}}-\text{CH}_2 \xrightarrow{\text{KMnO}_4 \text{ & H}_3\text{O}^+} \text{H}_3\text{C}-\text{CH}-(\text{CH}_3)_{\text{O}}-\text{CH}_3 + \text{CO}_2 \]

23.6

23.7

23.8
23.9

\[
\begin{align*}
R_1 R_2 O & \quad \leftrightarrow \quad R_1 R_2 O^+ H^- \\
R_1 R_2 O^+ H^- & \quad \leftrightarrow \quad R_1 R_2 O H^+ \\
R_1 R_2 O H^+ & \quad \leftrightarrow \quad R_1 R_2 O^- H^+ \\
R_1 R_2 O^- H^+ & \quad \leftrightarrow \quad R_1 R_2 O^- H^+ 
\end{align*}
\]

23.10

ethanol) 
(1 equivalent of ethanol) 
(2 equivalents of

23.11

\[
\begin{align*}
& \text{苯} \\
& \text{四氢化硅}
\end{align*}
\]
protection step

\[
\begin{align*}
\text{H-CO-O-CH}_3 &\quad \rightarrow \quad \text{H-CO-O-CH}_3 \\
\text{HO-OH} &\quad \rightarrow \quad \text{HO-OH}
\end{align*}
\]

acid catalyzed

deprotection step

\[
\begin{align*}
\text{H-OH} &\quad \rightarrow \quad \text{H-CO-}
\end{align*}
\]

acid catalyzed

23.13

(a) \[\text{N}^\text{CH}_3\] \\
(b) \[\text{OH-O-CH}_3\]

(c) \[\text{OH}\]

23.14

\[
\begin{align*}
\text{H}_3\text{C-C} &\quad + \quad \text{H}_2\text{N-CH}_3 \\
\text{CH}_3 &\quad \rightarrow \quad \text{N}^\text{CH}_3
\end{align*}
\]
23.15
(a) ![Image of structure]
(b) ![Image of structure]
(c) ![Image of structure]

23.16
\[
\begin{align*}
\text{O} & \quad \text{H}_3\text{C} \\
\text{HO} & \quad \text{CH}_3 \\
\end{align*}
\begin{align*}
\text{CH}_3 & \quad \text{H}_3\text{C} \\
\text{CH}_3 & \quad \text{HO} \\
\end{align*}
\begin{align*}
\text{O} & \quad \text{CH}_3 \\
\text{O} & \quad \text{CH}_3 \\
\end{align*}
\begin{align*}
\xrightarrow{\text{O}} & \quad \text{O} \\
\text{H}_3\text{C} & \quad \text{CH}_3 \\
\end{align*}

23.17
(a) ![Image of structure]
(b) ![Image of structure]
(c) ![Image of structure]

\text{Ag}^+(\text{aq}) \ & \ \text{NH}_3(\text{aq}) \quad \text{no reaction}

\text{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

(a) [Diagram of a ketone]

(b) [Diagram of a diacetic acid]

(c) [Diagram of a phenyl ketone]

(d) [Diagram of a bromo ketone]

23.25

pentanal
3-methylbutanal
2-methylbutanal
2,2-dimethylpropanal
2-pentanone
3-methylbutanone
3-pentanone

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

(a) 
\[
\text{CH}_3\text{C}(-\text{CH}_2\text{CH}_3)\text{CH}_3 \xrightarrow{\text{dilute H}_2\text{SO}_4} \text{CH}_3\text{C}(-\text{CH}_2\text{CH}_3)\text{OH}
\]

(b) 
\[
\text{CH}_3\text{C}(-\text{CH}_2\text{CH}_3)\text{OH} \xrightarrow{\text{CrO}_3} \text{CH}_3\text{C}(-\text{CH}_2\text{CH}_3)\text{CO}_2\text{H}
\]

CH₃COCl & AlCl₃

\[
\text{H}_3\text{C}-\text{O}-\text{C}(-\text{CH}_2\text{CH}_3)\text{C}_{6}\text{H}_5 \xrightarrow{1. \text{NaBH}_4} \text{H}_3\text{C}-\text{OH} \xrightarrow{2. \text{H}_3\text{O}^+} \text{H}_3\text{C}-\text{O}(-\text{CH}_2\text{CH}_3)\text{C}_{6}\text{H}_5
\]

23.31

\[
\text{H}_3\text{C}-\text{CH}_2\text{CH}_3
\]

B

23.33

(a) 
\[
\text{Ph}-\text{CO} \xrightarrow{\text{NaBH}_4, \text{then H}_3\text{O}^+} \text{Ph}-\text{CH}_2\text{OH}
\]

(b) 
\[
\text{Ph}-\text{CHO} \xrightarrow{\text{Tollens: AgNO}_3(aq) \ & \ NH}_3(aq)} \text{Ph}-\text{CH(OH)}
\]
(c) \[ \text{CH}_3\text{C} = \text{O} \quad \xrightarrow{\text{NH}_2\text{OH}} \quad \text{CH}_3\text{C} = \text{NOH} \]

(d) \[ \text{CH}_3\text{C} = \text{O} \quad \xrightarrow{\text{H}_3\text{C} - \text{Mg} \quad \text{Br}} \quad \xrightarrow{\text{H}_2\text{O}^+} \quad \text{CH}_3\text{C} = \text{OH} \]

(e) \[ \text{CH}_3\text{C} = \text{O} \quad \xrightarrow{\text{CH}_3\text{OH}, \quad \text{H}^+ \text{catalyst}} \quad \text{CH}_3\text{C} = \text{O} \quad \text{CH}_3 \]

23.35

(a) \[ \text{CH}_3\text{C} = \text{O} \quad \xrightarrow{\text{NaBH}_4, \quad \text{then H}_2\text{O}^+} \quad \text{H}_2\text{O} = \text{H}^+ \]

(b) \[ \text{CH}_3\text{C} = \text{O} \quad \xrightarrow{\text{H}_3\text{C} - \text{Mg} \quad \text{Br}} \quad \text{H}_3\text{C} - \text{CH}_3 \]

(c) \[ \text{CH}_3\text{C} = \text{O} \quad \xrightarrow{\text{NH}_2\text{CH}_3} \quad \text{CH}_3\text{C} = \text{NCH}_3 \]

(d) \[ \text{CH}_3\text{C} = \text{O} \quad \xrightarrow{\text{CH}_3\text{SH}} \quad \text{CH}_3\text{C} = \text{SCH}_3 \]

It adds to the electron deficient carbonyl carbon.

Water is eliminated in a subsequent step.

Nucleophile is CH$_3$SH attacking with an S lone pair.
23.37 The reaction of phenylmagnesium bromide with butan-2-one produces a racemic mixture of 2-phenylbutan-2-ol.

23.39

(a)

\[
\begin{align*}
\text{phenylmagnesium bromide} & + \text{butan-2-one} \\
\rightarrow & \text{a hemiacetal}
\end{align*}
\]

(b)

\[
\begin{align*}
\text{butan-2-one} & + \text{pentanal} \\
\rightarrow & \text{a hemiacetal}
\end{align*}
\]
23.41

add another ketone with the same steps

23.43

(a)  
\[
\begin{array}{c}
\text{CH}_3 \text{C} \text{C} \text{H}_3 \\
\text{O} \\
\text{CH}_3 \text{MgBr}
\end{array}
\quad \rightarrow
\quad \begin{array}{c}
\text{CH}_3 \text{C} \text{C} \text{H}_3 \\
\text{HO} \text{CH}_3
\end{array}
\]

(b)  
\[
\begin{array}{c}
\text{C}_8 \text{H}_8 \\
\text{O} \\
\text{CH}_3 \text{MgBr}
\end{array}
\quad \rightarrow
\quad \begin{array}{c}
\text{C}_8 \text{H}_8 \\
\text{HO} \text{CH}_3
\end{array}
\]

(c)  
\[
\begin{array}{c}
\text{CH}_3 \text{C} \text{C} \text{C} \text{H}_3 \\
\text{O} \\
\text{CH}_3 \text{MgBr}
\end{array}
\quad \rightarrow
\quad \begin{array}{c}
\text{CH}_3 \text{C} \text{C} \text{C} \text{H}_3 \\
\text{HO} \text{CH}_3 \text{CH}_3
\end{array}
\]
(a) 

\[
\text{CH}_3\text{CH} = \text{CH} - \text{CO} \quad \xrightarrow{\text{CH}_2\text{MgBr}} \quad \text{CH}_3\text{CH} = \text{CH} - \text{CH}_2\text{OH}
\]

(b) 

\[
\text{CH}_3\text{C} = \text{CHCH}_3 \quad \xrightarrow{\text{C}_6\text{H}_{5}\text{MgBr}} \quad \text{CH}_3\text{C} = \text{CHCH}_3 \quad \text{CH}_3\text{CH}_2\text{OH}
\]

(c) 

\[
\text{CH}_3\text{C} = \text{C} \quad \xrightarrow{\text{CH}_3\text{CH}_2\text{MgBr}} \quad \text{CH}_3\text{C} = \text{C} \quad \text{CH}_3\text{OH}
\]

(d) 

\[
\text{C}_6\text{H}_{5}\text{CH} = \text{CH} \quad \xrightarrow{\text{C}_6\text{H}_{5}\text{MgBr}} \quad \text{C}_6\text{H}_{5}\text{CH} = \text{CH} \quad \text{CH}_3\text{OH}
\]
(a) 
\[
\begin{align*}
\text{H} & \hspace{1em} \text{H} \\
\text{O} & \hspace{1em} \text{H} \hspace{1em} \text{CH}_3 \\
\text{H}_2\text{C} & \hspace{1em} \text{MgBr} & \hspace{0.5em} \text{CH}_3 \\
\text{H} & \hspace{1em} \text{H} \hspace{1em} \text{CH}_3
\end{align*}
\]

(b) 
\[
\begin{align*}
\text{H} & \hspace{1em} \text{H} \\
\text{O} & \hspace{1em} \text{H} \\
\text{H}_2\text{C} & \hspace{0.5em} \text{MgBr} \\
\text{H}_2\text{C} & \hspace{0.5em} \text{MgBr} & \hspace{0.5em} \text{OH} \\
\text{H} & \hspace{1em} \text{H} \\
\text{H}_2\text{C} & \hspace{1em} \text{MgBr} \\
\text{H}_2\text{C} & \hspace{1em} \text{MgBr} & \hspace{0.5em} \text{OH}
\end{align*}
\]

(c) 
\[
\begin{align*}
\text{H} & \hspace{1em} \text{H} \\
\text{O} & \hspace{1em} \text{H} \\
\text{H}_2\text{C} & \hspace{1.5em} \text{MgBr} \\
\text{H}_2\text{C} & \hspace{1.5em} \text{MgBr} & \hspace{1em} \text{OH} \\
\text{H}_2\text{C} & \hspace{1em} \text{MgBr} \\
\text{H}_2\text{C} & \hspace{1em} \text{MgBr} & \hspace{1em} \text{OH}
\end{align*}
\]

this choice leads to an additional aldehyde product which could then react with the Grignard reagent to form yet additional products.
23.49

(a) 
\[ \text{add } H_2O \rightarrow \text{add } H_2O \rightarrow \]

(b) 
\[ \text{add } NH_3 \rightarrow \]

(c) 
\[ \text{add } CH_3OH \rightarrow \]

(d) 
\[ \text{add } CH_3CH_2SH \rightarrow \]
SUMMARY AND CONCEPTUAL QUESTIONS

23.51

(a) $\text{NaBH}_4$ then $H^+$ separation is necessary chromatography is the likely choice distillation would be difficult on account of the similarity of the two products

(b) $\text{H}_2$ & Pd there may be a conjugate addition product in addition to this one the conjugate addition product can add another equivalent of phenylmagnesium bromide

(c) $\text{H}_2$ & Pd

(d) $\text{MgBr}$
(a) \[ \text{CH}_3\text{CH}_2\text{OH} \quad \xrightarrow{\text{NH}_2\text{OH}} \quad \text{CH}_3\text{CH}_2\text{NH}_2\text{OH} \]

(b) \[ \text{CH}_3\text{CH}_2\text{OH} \quad \xrightarrow{\text{H}^+} \quad \text{CH}_3\text{CH}_2\text{OH} \quad \xrightarrow{\text{H}^+} \quad \text{CH}_3\text{CH}_2\text{CH}_2\text{O} \]

(c) \[ \text{CH}_3\text{CH}_2\text{OH} \quad \xrightarrow{\text{H}^+} \quad \text{CH}_3\text{CH}_2\text{OH} \quad \xrightarrow{\text{H}^+} \quad \text{CH}_3\text{CH}_2\text{CH}_2\text{O} \]
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

(a) 

\[
\begin{align*}
\text{H}_3\text{C} & \text{CH}_3 \\
\text{CH}_3 & \text{CH}_3
\end{align*}
\]
\[
\text{O} \rightarrow \\
\text{H}_3\text{C} & \text{CH}_3
\]

(b) 

\[
\text{NaOCl} \\
\rightarrow \\
\text{H}_3\text{C} & \text{CH}_3
\]

(c) 

\[
\text{Br}_2 \text{ & FeBr}_3 \\
\rightarrow \\
\text{H}_3\text{C} & \text{CH}_3
\]

(d) 

\[
\text{CH}_3\text{OH} \text{ & H}^+ \\
\rightarrow \\
\text{H}_3\text{C} & \text{CH}_3
\]

\[
\text{O} \text{OCH}_3 \text{Br}
\]
(a) 1,4 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.
24.2

(a) \[
\text{CH}_3 \text{OH}
\]

(b) \[
\text{CH}_3 \text{OH}
\]

(c) \[
\text{O}
\]

(d) \[
\text{O}
\]

24.3

(a) \[
\text{CH}_3 \text{Cl}
\]

(b) \[
\text{O}
\]

(c) \[
\text{NH}
\]

(d) \[
\text{CH}_3 \text{NCH}_3 \text{CH}_3
\]

(e) \[
\text{O}
\]

(f) \[
\text{O}
\]

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) \[ CH_3O\overset{\text{C}}{\text{O}}CH_3 \]

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

(b) \[ CH_3\overset{\text{N}}{\text{O}}CH_3 \]

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

(c) \[ CH_3\overset{\text{C}}{\text{O}}Cl \]

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 \(^1\)H NMR spectra, the molecules are distinguished by possible splitting of the hydroxyl H peak in the case of 4-hydroxycyclohexanone, and (more importantly) by the extra downfield peak due to the methine H−C−O.
24.8

(a) 

\[
\text{CH}_3\text{CO}_2\text{H} \quad \text{NaOCH}_3 \quad \text{CH}_3\text{CO}_2\text{OCH}_3
\]

(b) 

\[
\text{H}_3\text{C}\text{CCH}_2\text{CO}_2\text{H} \quad \text{KOH} \quad \text{H}_3\text{C}\text{CCH}_2\text{CO}_2\text{K}^+
\]

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

24.10 (a) CH\textsubscript{3}CH\textsubscript{2}CO\textsubscript{2}H < BrCH\textsubscript{2}CH\textsubscript{3}CO\textsubscript{2}H < BrCH\textsubscript{3}CO\textsubscript{2}H
(b) ethanol < benzoic acid < p-cyanobenzoic acid

24.11 (a) CH\textsubscript{3}COCl > CH\textsubscript{3}CO\textsubscript{2}CH\textsubscript{3} (b) CH\textsubscript{3}CH\textsubscript{2}CO\textsubscript{2}CH\textsubscript{3} > (CH\textsubscript{3})\textsubscript{2}CHCONH\textsubscript{2} (c) CH\textsubscript{3}CO\textsubscript{2}COCH\textsubscript{3} > CH\textsubscript{3}CO\textsubscript{2}CH\textsubscript{3} (d) CH\textsubscript{3}CO\textsubscript{2}CH\textsubscript{3} > CH\textsubscript{3}CHO

24.12 The fluorine substituents in CF\textsubscript{3}CO\textsubscript{2}CH\textsubscript{3} are electron withdrawing, making the carbonyl carbon more electron deficient (attracting nucleophiles) and stabilizing the four coordinate intermediate which has additional electron density due to the bonded nucleophile.

24.13

(a) 

\[
\text{H}_3\text{C}\text{CCH}_2\text{CO}_2\text{H} \quad \text{CH}_3\text{OH} \quad \text{H}_3\text{C}\text{CCH}_2\text{CO}_2\text{OCH}_3
\]

(b) 

\[
\text{H}_3\text{C}\text{CCH}_2\text{Cl} \quad \text{CH}_3\text{CH}_2\text{OH} \quad \text{H}_3\text{C}\text{CCH}_2\text{CO}_2\text{CH}_3
\]

(c) 

\[
\text{H}_3\text{C}\text{CCH}_2\text{Cl} \quad \text{HOCH}_2\text{CH}_2\text{OH} \quad \text{H}_3\text{C}\text{CCH}_2\text{CO}_2\text{CH}_2\text{OH}
\]
24.14

\[
\begin{align*}
\text{H}_3\text{C} & \quad \text{N} \\
\text{H} & \quad \text{H} \\
\text{N} & \quad \text{H} \\
\text{H} & \quad \text{H} \\
\text{O} - & \quad \text{N} \\
\end{align*}
\]

\[
\begin{align*}
\text{H}_3\text{C} & \quad \text{N} \\
\text{H} & \quad \text{H} \\
\text{N} & \quad \text{H} \\
\text{H} & \quad \text{H} \\
\text{Cl} & \quad \text{O}
\end{align*}
\]

24.15

(a)

\[
\begin{align*}
\text{H}_3\text{C} & \quad \text{O} \\
\end{align*}
\]

\[
\begin{align*}
\text{NH}_3 & \quad \rightarrow \\
\text{H}_3\text{C} & \quad \text{O} \\
\text{NH}_2 & \quad \text{H}
\end{align*}
\]

(b)

\[
\begin{align*}
\text{H}_3\text{C} & \quad \text{O} \\
\text{Cl} & \quad \text{CH}_3\text{NH}_2
\end{align*}
\]

\[
\begin{align*}
\text{H}_3\text{C} & \quad \text{O} \\
\text{NH}_3 & \quad \rightarrow \\
\text{H}_3\text{C} & \quad \text{O} \\
\text{NH}_3 & \quad \text{CH}_3
\end{align*}
\]

(c)

\[
\begin{align*}
\text{H}_3\text{C} & \quad \text{O} \\
\text{NH}_3 & \quad \rightarrow \\
\text{H}_3\text{C} & \quad \text{O} \\
\text{NH}_3 & \quad \text{CH}_3
\end{align*}
\]

(d)

\[
\begin{align*}
\text{H}_3\text{C} & \quad \text{Cl} \\
\end{align*}
\]

\[
\begin{align*}
\text{H}_3\text{C} & \quad \text{N} \\
\text{H} & \quad \text{CH}_3 \\
\text{H} & \quad \text{CH}_3 \\
\text{H} & \quad \text{H} \\
\end{align*}
\]
24.16

24.17

24.18

(a) 

(b)
24.19

(a)  
\[ \text{H}_3\text{C}-\text{CH}_2-\text{O}-\text{CH}_3 \xrightarrow{\text{LiAlH}_4} \text{H}_3\text{C}-\text{CH}_2-\text{OH} + \text{H}_3\text{C}-\text{OH} \]

(b)  
\[ \text{PhO}-\text{O}-\text{Ph} \xrightarrow{\text{LiAlH}_4} \text{PhCH}_2-\text{OH} + \text{PhOH} \]

24.20

(a)  
\[ \text{PhO}-\text{O}-\text{CH}_3 \xrightarrow{2 \text{CH}_3\text{MgBr}} \text{PhCH}_3-\text{CH}_3 \]

(b)  
\[ \text{H}_3\text{C}-\text{O}-\text{CH}_3 \xrightarrow{2 \text{PhMgBr}} \text{PhCH}_3\text{C}-\text{OH} \]

(c)  
\[ \text{H}_3\text{C}-\text{CH}_2-\text{O}-\text{CH}_3 \xrightarrow{\text{H}_3\text{C}-\text{MgBr}} \text{H}_3\text{C}-\text{CHCH}_2-\text{CH}_3 \]
24.21

(a) \( \text{H}_2\text{O}^{+}(\text{aq}) \) & heat

(b) \( \text{LiAlH}_4 \)

(c) \( \text{LiAlH}_4 \)

24.22

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

(b) \( \text{(CH}_3\text{)}_3\text{CCOCH}_3 \) 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, CH\(_3\)CO\(_2\)H.

(d) The methylene H’s between the two carbonyl C’s are acidic in 1,3-Cyclohexanedione.
24.24

(a) 

\[
\begin{align*}
\text{CH}_3 & \quad \text{O} & \quad \text{H} & \quad \text{H} & \quad - & \quad \text{H}^+ \\
\text{H}_3\text{C} & \quad - & \quad \text{C} & \quad \text{O} & \quad \text{H} & \quad \text{H}
\end{align*}
\]

(b) 

\[
\begin{align*}
\text{CH}_3 & \quad \text{O} & \quad \text{CH}_3 & \quad \text{O} & \quad \text{H} & \quad \text{H} & \quad - & \quad \text{H}^+ \\
\text{H}_3\text{C} & \quad & \text{CH}_2 & \quad & \text{CH}_3 & \quad & \text{CH}_3 & \quad & \text{CH}_3
\end{align*}
\]

(c) 

\[
\begin{align*}
\text{CH}_3 & \quad \text{O} & \quad \text{CH}_3 & \quad \text{O} & \quad \text{H} & \quad \text{H} & \quad - & \quad \text{H}^+ \\
\text{CH}_3 & \quad & \text{CH}_3 & \quad & \text{C} & \quad & \text{O} & \quad \text{CH}_3 & \quad & \text{CH}_3
\end{align*}
\]

24.25

\[
\begin{align*}
\text{CH}_3 & \quad \text{O} & \quad \text{CH}_3 & \quad \text{O} & \quad \text{H} & \quad \text{H} & \quad - & \quad \text{H}^+ \\
\text{H}_3\text{C} & \quad & \text{CH} & \quad & \text{O} & \quad \text{CH}_3 & \quad & \text{O} & \quad \text{H} & \quad \text{H}
\end{align*}
\]
24.26

(a) 

\[
\begin{align*}
\text{H}_3\text{C} & \quad \text{NaCH}_2\text{CH}_2\text{O} \\
\text{O} & \quad \rightarrow \\
\text{O} & \quad \text{H} \\
\text{CH}_3 & \quad \text{CH}_3 \\
\end{align*}
\]

(b) 

\[
\begin{align*}
\text{H}_3\text{C} & \quad \text{Br} \\
\text{H} & \quad \rightarrow \\
\text{CH}_3 & \quad \text{H} \\
\text{HCl(aq)} & \quad \text{heat} \\
\text{CH}_3 \text{CO} & \quad \rightarrow \\
\text{OH} & \quad \text{H} \\
\end{align*}
\]

(c) 

\[
\begin{align*}
\text{H}_3\text{C} & \quad \text{CH}_3 \\
\text{Br} & \quad \rightarrow \\
\text{CH}_3 & \quad \text{Br} \\
\text{HCl(aq)} & \quad \text{heat} \\
\text{CH}_3 & \quad \text{O} \\
\text{CH}_3 & \quad \text{CH}_3 \\
\end{align*}
\]
24.27

hexanoic acid

4-methylpentanoic acid

3-methylpentanoic acid

2-methylpentanoic acid

3,3-dimethylbutanoic acid

2,3-dimethylbutanoic acid

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

(b) cyclohex-1-enecarboxamide

(c) cyclopentanecarbonitrile

(d) methyl but-2-enoate ethyl propenoate ethenyl propanoate

24.33

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

24.41

24.43
24.45

(a)

\[
\begin{align*}
\text{Cl} & \quad \text{R}_1 \quad \text{O} \\
\text{R}_2 - \text{Mg} & \quad \text{Br}
\end{align*}
\]

\[
\xrightarrow{\text{OH}}
\]

\[
\text{R}_2 \quad \text{Mg} \quad \text{Br}
\]

(b)

\[
\begin{align*}
\text{CH}_3 & \quad \text{Cl} \\
\text{H}_3\text{C} & \quad \text{CH}_3
\end{align*}
\]

\[
\xrightarrow{\text{CH}_3\text{MgBr then H}_2\text{O}^+}
\]

\[
\text{CH}_3 \quad \text{CH}_3 \quad \text{OH}
\]

(b)

\[
\begin{align*}
\text{CH}_3 \quad \text{CH}_3 & \quad \text{Cl} \\
\text{CH}_3 \quad \text{CH}_3
\end{align*}
\]

\[
\xrightarrow{\text{CH}_3\text{MgBr then H}_2\text{O}^+}
\]

\[
\text{CH}_3 \quad \text{CH}_3
\]
(a) Excess CH$_3$MgBr in ether then H$_3$O$^+$

(b) NaOH(aq)

(c) CH$_3$NH$_2$

(d) LiAlH$_4$ then H$_3$O$^+$

(e) 

(f)
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.

The first two enols shown are the most stable because the 2 carbon H’s are more acidic – they are α to two carbonyls.
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.
HCl(aq) & heat

CH₃CHOH

CH₃CH₂OH
SUMMARY AND CONCEPTUAL QUESTIONS

24.61

(a)

\[
\begin{align*}
\text{Br} & \quad \text{O} \\
\text{C} & \quad \text{H}_2\text{C} \\
\text{O} & \quad \text{H}_2\text{C} \\
\end{align*}
\]

\[
\text{SOCl}_2 ightarrow 
\begin{align*}
\text{Br} & \quad \text{O} \\
\text{C} & \quad \text{H}_2\text{C} \\
\text{O} & \quad \text{H}_2\text{C} \\
\end{align*}
\]

(b)

\[
\begin{align*}
\text{CH}_2\text{C} & \quad \text{NH}_2 \\
\text{O} & \quad \text{O} \\
\text{SOCl}_2 & \quad \text{SOCl}_2 \\
\end{align*}
\]

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

(a) \[ \text{Br} \quad \text{Mg in ether} \quad \text{Mg}^{\text{Br}} \quad \text{CH}_3 \quad \text{O} \quad \text{CH}_3 \quad \text{O} \quad \text{CH}_3 \quad \text{Mg} \quad \text{Br} \quad \text{Mg}^{\text{Br}} \quad \text{CH}_3 \quad \text{O} \quad \text{CH}_3 \quad \text{O} \quad \text{CH}_3 \]

(b) \[ \text{O} \quad \text{CH}_3 \quad \text{H}_3\text{C} - \text{Mg} \quad \text{Br} \quad \text{O} \quad \text{CH}_3 \]

(c) \[ \text{H}_3\text{C} - \text{Cl} \quad \text{AlCl}_3 \quad \text{O} \quad \text{CH}_3 \quad \text{O} \quad \text{CH}_3 \]

Chemistry, First Canadian Edition
(a)  

\[
\text{\begin{align*} 
\text{O} & \quad \text{\begin{align} 
\text{LiAlH}_4 \quad \rightarrow \quad \text{O} \\
\text{H}_2\text{C} & \quad \text{\begin{align} 
\text{H}_2\text{C} & \quad \text{H}_2\text{O} \\
\text{H}_3\text{C} & \quad \text{H}_3\text{C} \\
\end{align}} \\
\end{align*}} 
\end{align}} 
\]

(b)  

\[
\text{\begin{align*} 
\text{O} & \quad \text{\begin{align} 
\text{CH}_2\text{OH} & \quad \text{\begin{align} 
\text{CH}_2\text{OH} & \quad \text{\begin{align}} 
\text{H}_3\text{C} & \quad \text{H}_3\text{C} \\
\text{H}_3\text{C} & \quad \text{H}_3\text{C} \\
\end{align}} \\
\end{align}} \\
\end{align*}} 
\]

(c)  

\[
\text{\begin{align*} 
\text{O} & \quad \text{\begin{align} 
\text{SOCl}_2 \quad \rightarrow \quad \text{Cl} \\
\text{H}_3\text{C} & \quad \text{H}_3\text{C} \\
\end{align}} \\
\end{align*}} 
\]

(d)  

\[
\text{\begin{align*} 
\text{O} & \quad \text{\begin{align} 
\text{NaOH} \quad \rightarrow \quad \text{Cl} \\
\text{H}_3\text{C} & \quad \text{H}_3\text{C} \\
\end{align}} \\
\end{align*}} 
\]
(a) $\text{CH}_3\text{CH}_3\text{I} \xrightarrow{\text{NaCN}} \text{CH}_3\text{CH}_3\text{N} \xrightarrow{\text{LiAlH}_4} \text{CH}_3\text{CH}_3\text{NH}_2$

(b) $\text{PhBr} \xrightarrow{\text{Mg in ether}} \text{PhMgBr}$

24.71

$\text{H}_3\text{C}\text{CH}_3\text{O}^-\text{Cl} \xrightarrow{\text{Na}^+} \text{H}_3\text{C}\text{CH}_3\text{O}^-\text{Cl} \xrightarrow{\text{Na}^+} \text{H}_3\text{C}\text{CH}_3\text{O}^-\text{N}^+\text{N} \xrightarrow{\text{Na}^+, \text{Cl}^-} \text{H}_3\text{C}\text{CH}_3\text{O}^-\text{N}^+\text{N}$
24.73

\[
\begin{align*}
\text{Br} & \quad \text{Mg in ether} \\
\text{CH}_3 & \\
\rightarrow & \\
\text{Br} & \quad \text{Mg} \\
\text{CH}_3 & \\
\end{align*}
\]

1 equiv

\[
\begin{align*}
\text{Cl} & \quad \text{O} \\
\text{N} \quad \text{CH}_3 \\
\quad \text{CH}_3 & \\
\rightarrow & \\
\text{H}_3\text{C} & \quad \text{O} \\
\text{N} \quad \text{CH}_3 \\
\quad \text{CH}_3 & \\
\end{align*}
\]
First step

\[
\begin{align*}
&\text{H}_2\text{O}\text{O}^+ \quad \text{H}_2\text{O}^-
\end{align*}
\]

Polymerization step

The amine group attacks the carboxylic acid on another molecule, extending the chain by another monomer. This process repeats many times.
24.77

\[ \text{CH}_3\text{CHOH} \quad \text{CH}_3\text{C(OH)CH}_3 \quad \text{CH}_3\text{C}_2\text{H}_5 \quad \text{CH}_3\text{C}_2\text{H}_5 \text{OH} \]

24.79

\[ \text{H}_3\text{C}_2\text{OCH}_2\text{CH}_3 \quad \text{H}_3\text{O}^+ \quad \text{H}_3\text{C}_2\text{OH} \]

24.81

(a)

(b)

\[ \text{H}_3\text{C}_2\text{OCH}_2\text{CH}_3 + \text{H}_3\text{C}_2\text{NHCH}_3 \quad \rightarrow \quad \text{H}_3\text{C}_2\text{OCH}_2\text{CH}_3 \quad \text{H}_3\text{C}_2\text{NHCH}_3 \]

(b)

\[ \text{H}_3\text{C}_2\text{OCH}_2\text{CH}_3 + \text{H}_3\text{C}_2\text{NHCH}_3 \quad \rightarrow \quad \text{H}_3\text{C}_2\text{OCH}_2\text{CH}_3 \quad \text{H}_3\text{C}_2\text{NHCH}_3 \]
(d) A twofold excess of diethylamine is required because both LSD and diethyl acetamide are produced.
[Diagram with chemical structures and reactions]
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) CH₃CH₂NH₂  
(b) NaOH  
(c) CH₃NHCH₃  
(d) (CH₃)₃N

25.6  

\[ \text{CH₃} \text{NH} \text{H} + \text{HBr} \rightarrow \text{CH₃} \text{NH}^+ \text{Br}^- \]
25.7

(a) 
\[ 3 \text{CH}_3\text{Cl} + \text{NH}_3 \rightarrow \text{H}_3\text{C} - \text{N} - \text{CH}_3 \]

(b) 
\[ 4 \text{CH}_3\text{Br} + \text{NH}_3 \rightarrow \text{H}_3\text{C} + \text{N}^+ - \text{CH}_3 \text{Br}^- \]

25.8

\[ \text{BrCH}_2\text{CH}_2\text{Br} + \text{H}_2\text{N} - \text{CH}_3 \rightarrow \text{NCH}_3\text{CH}_3 \]

25.9

(a) 
\[ \text{CH}_3\text{NH}_3 \rightarrow \text{CH}_3\text{NH}_3\text{Br} \]

(b) 
\[ \text{CH}_3\text{NH}_3 \rightarrow \text{CH}_3\text{Cl} \text{ & AlCl}_3 \rightarrow \text{CH}_3\text{NH}_3 \]

(c) 
\[ \text{CH}_3\text{NH}_3 \rightarrow \text{CH}_3\text{COCl} \text{ & AlCl}_3 \rightarrow \text{CH}_3\text{NH}_3 \]

25.10

\[ \text{CH}_3\text{NO}^+ \rightarrow \text{CH}_3\text{NO} \rightarrow \text{CH}_3\text{NO} \]
25.11

![Chemical Structure]

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)  

![Chemical Structures]
25.23
\[
\begin{align*}
&\text{N} \quad \text{CH}_3 \\
&\text{H}_2\text{N} - \text{CO} \\
&\text{H}_2\text{N} - \text{CH}_3
\end{align*}
\]

\[3 \succ 1 \succ 2\]

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

\[
\begin{align*}
\text{OH} & \quad \text{H}_2\text{SO}_4 \quad \text{then neutralize} \\
\text{N} & \quad \text{CH}_3
\end{align*}
\]

Tropidine

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

25.29 Atropine

\[
\begin{align*}
\text{OH} & \quad \text{H}_2\text{SO}_4 \quad \text{then neutralize} \\
\text{N} & \quad \text{CH}_3
\end{align*}
\]

\[+\]

\[
\begin{align*}
\text{OH} & \quad \text{H}_2\text{SO}_4 \quad \text{then neutralize} \\
\text{N} & \quad \text{CH}_3
\end{align*}
\]

Atropine
Nitration at the 2 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.
25.33

(a) 

[Chemical structure diagram]

(b) 

[Chemical structure diagram]

(c) 

[Chemical structure diagram]

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)

\[
\text{H}_3\text{C} - \text{NH}_2 \quad \xrightarrow{\text{Br}_2 (1 \text{ equivalent})} \quad \text{H}_3\text{C} - \text{Br} - \text{NH}_2 + \text{H}_2\text{C} - \text{NH}_2 - \text{Br}
\]

(b)

\[
\text{H}_3\text{C} - \text{NH}_2 \quad \xrightarrow{\text{CH}_3\text{I (excess)}} \quad \text{H}_3\text{C} - \text{N}^+\text{CH}_3 - \text{I}^-
\]

(c)

\[
\text{H}_3\text{C} - \text{NH}_2 \quad \xrightarrow{\text{CH}_3\text{COCl & pyridine}} \quad \text{H}_3\text{C} - \text{NH}_2 - \text{CH}_3
\]

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 $24 = 16$ 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$_2$O$_3$ which is amphoteric.

26.3 \[ 2 \text{H}_2(g) + \text{O}_2(g) \rightarrow 2 \text{H}_2\text{O}(\ell) \]
\[ \text{H}_2(g) + \text{Cl}_2(g) \rightarrow 2 \text{HCl}(g) \]
\[ 3 \text{H}_2(g) + \text{N}_2(g) \rightarrow 2 \text{NH}_3(g) \]

26.4 \[ 2 \text{K}(s) + \text{H}_2(g) \rightarrow 2 \text{KH}(s) \]
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 \[ 2 \text{Na}(s) + \text{Cl}_2(g) \rightarrow 2 \text{NaCl}(s) \text{ (exothermic reaction)} \]
NaCl is a colourless ionic with high melting point. It is soluble in water.

26.6 (a) \[ 2 \text{Cl}^-(aq) \rightarrow \text{Cl}_2(aq) + 2 \text{e}^- \text{ (reaction at anode, Cl}^\text{−} \text{is oxidized)} \]
\[ 2 \text{H}_2\text{O}(\ell) + 2 \text{e}^- \rightarrow 2 \text{OH}^-(aq) + \text{H}_2(g) \text{ (reaction at cathode, H}_2\text{O is reduced)} \]
(b) \[ 2 \text{I}^-(aq) \rightarrow \text{I}_2(aq) + 2 \text{e}^- \text{ (reaction at anode, I}^\text{−} \text{is oxidized)} \]
Same reduction reaction as in part (a)

26.7 \[ 2 \text{Ba}(s) + \text{O}_2(g) \rightarrow 2 \text{BaO}(s) \text{ (exothermic reaction)} \]
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) \[ \text{Ga(OH)}_3(s) + 3 \text{HCl}(aq) \rightarrow \text{GaCl}_3(aq) + 3 \text{H}_2\text{O}(\ell) \]
\[ \text{Ga(OH)}_3(s) + 3 \text{NaOH}(aq) \rightarrow \text{Na}_3\text{GaO}_3(aq) + 3 \text{H}_2\text{O}(\ell) \]
(b) Ga$^{3+}$(aq) is a stronger acid than Al$^{3+}$. 
(c) 2.77 L

26.10 \[ \text{Al}(s) + 3 \text{HCl}(aq) \rightarrow \text{AlCl}_3(aq) + \frac{3}{2} \text{H}_2(g) \]
\[ \text{Al}(s) + \frac{3}{2} \text{Cl}_2(g) \rightarrow \text{AlCl}_3(s) \]
\[ \text{Al}(s) + \frac{3}{2} \text{O}_2(g) \rightarrow \frac{1}{2} \text{Al}_2\text{O}_3(s) \]
26.11 In SiO₂, silicon forms a network of single bonds with oxygen – i.e. we get a covalently bonded network solid. The melting point of SiO₂ is therefore very high. The bonding in CO₂ is also covalent, but CO₂ is molecular. The intermolecular forces of attraction (dispersion forces) between CO₂ molecules are weak and are easily broken. Carbon dioxide is gas at ordinary temperatures.

26.12 PbCl₄

26.13 (a) 
\[ \begin{array}{c}
\vdots N \vdots \vdots \\
\vdots O \vdots \\
\end{array} \quad \longleftrightarrow \quad \begin{array}{c}
\vdots N \vdots \\
\vdots N \vdots \\
\vdots O \vdots \\
\end{array}\]

(b) exothermic

26.14

26.15

26.16 (a) F₂ can oxidize Cl⁻ (X = F, Y = Cl) for example, whereas (b) Cl₂ cannot oxidize F⁻ (X = Cl, Y = F).

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

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) \(Z^*(Ar^-) = +1.2;\) \(Z^*(K^-) = +1.85;\) \(Z^*(Cl^-) = +5.75\)

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 \( \text{BeCl}_2 \), \( \text{BCl}_3 \), \( \text{AlCl}_3 \), \( \text{TiCl}_4 \) and \( \text{FeCl}_3 \) are typically covalent, because of the small size of and high charge of the cations which make them highly polarizing. In contrast, \( \text{K}^+ \) and \( \text{Ag}^+ \), 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) \( \text{Al}_2^3+ \) is highly polarizing, giving covalent character to bonds with halides. However, since the small fluoride ion is rather non-polarizable, \( \text{AlF}_3 \) is essentially an ionic compound – the bonding has very little covalent character. It contrast, chloride and especially bromide are much more polarizable. Bonds in \( \text{AlCl}_3 \), and \( \text{AlBr}_3 \) have significantly more covalent character. These compounds more readily melt to form liquids of mobile \( \text{AlCl}_3 \), and \( \text{AlBr}_3 \) molecules.

(c) Singly charged cations, \( \text{K}^+ \), \( \text{Ag}^+ \) and \( \text{NH}_4^+ \), are not very polarizing. They do not attract water molecules strongly enough to hold them as coordinating ligands in the ionic crystal lattices of \( \text{KCl} \), \( \text{AgNO}_3 \) and \( \text{NH}_4\text{NO}_3 \). In contrast, the polarizing doubly and triply charged cations, \( \text{Mg}^{2+} \), \( \text{Fe}^{3+} \) and \( \text{Cr}^{3+} \), retain coordinated water ligands when their salts are precipitated from aqueous solution – i.e. they crystallize as hydrated compounds.

(d) The smaller \( \text{Li}^+ \) ion is more polarizing than the larger \( \text{Rb}^+ \) ion. Consequently, \( \text{Li}^+ \) holds water ligands about it rather tightly, and its mobility in water is that of \( [\text{Li(H}_2\text{O})_4]^+ \) 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 \( \text{Be}^{2+} \) (2455 kJ mol\(^{-1}\)) is greater than that of \( \text{Ba}^{2+} \) (1275 kJ mol\(^{-1}\)) because the former is much smaller.

(b) The molar enthalpy change of hydration of \( \text{Fe}^{3+} \) (4340 kJ mol\(^{-1}\)) is greater than that of \( \text{Fe}^{2+} \) (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 \( \text{Pb}^{4+} \) 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 \[ \Delta H^\circ = 131.30 \text{ kJ} \]
\[ \Delta S^\circ = 134.0 \text{ J/K} \]
\[ \Delta G^\circ = 91.3 \text{ kJ} \]

26.31 Na(s) + \( \frac{1}{2} \) F\(_2\)(g) \( \rightarrow \) NaF(s)
Na(s) + \( \frac{1}{2} \) Cl\(_2\)(g) \( \rightarrow \) NaCl(s)
Na(s) + \( \frac{1}{2} \) Br\(_2\)(ℓ) \( \rightarrow \) NaBr(s)
Na(s) + \( \frac{1}{2} \) I\(_2\)(s) \( \rightarrow \) NaI(s)

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

26.33 Mg(s) + \( \frac{1}{2} \) O\(_2\)(g) \( \rightarrow \) MgO(s)
3 Mg(s) + N\(_2\)(g) \( \rightarrow \) Mg\(_3\)N\(_2\)(s)

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 \[ \text{AlCl}_4^- \text{ is tetrahedral} \]

26.47 (a) BCl\(_3\)(g) + 3 H\(_2\)O(ℓ) \( \rightarrow \) B(OH)\(_3\)(s) + 3 HCl(aq)
(b) \( -110.5 \text{ kJ} \)
26.49 \[ \text{SiO}_2(s) + 2 \text{C(s)} \rightarrow \text{Si(ℓ)} + 2 \text{CO(g)} \]
\[ \text{Si(s)} + 2 \text{Cl}_2(g) \rightarrow \text{SiCl}_4(ℓ) \] (The SiCl_4(ℓ) is purified by distillation)
\[ \text{SiCl}_4(g) + 2 \text{Mg(s)} \rightarrow 2 \text{MgCl}_2 + \text{Si(s)} \]

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.

26.51 (a) \[ \text{Si} + 2 \text{CH}_3\text{Cl} \rightarrow (\text{CH}_3)_2\text{SiCl}_2 \]
(b) 83.5 kPa
(c) 12.2 g

26.53 \[ \text{Ca(OH)}_2(s) + \text{H}_3\text{PO}_4(aq) \rightarrow \text{CaHPO}_4(s) + 2 \text{H}_2\text{O(ℓ)} \]

26.55 \[ \Delta_r H^\circ = -58.02 \text{ kJ} \]
\[ \Delta_r G^\circ = -5.40 \text{ kJ} \]

The reaction is exothermic and slightly product-favoured under standard conditions.

26.57 \[ 5 \text{N}_2\text{H}_5^+(aq) + 4 \text{IO}_3^-(aq) \rightarrow 5 \text{N}_2(g) + \text{H}^+(aq) + 2 \text{I}_2(s) + 12 \text{H}_2\text{O(ℓ)} \]
\[ E^\circ = 1.43 \text{ V} \]

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.

(b) \[ \Delta_r S^\circ = 141 \text{ J K}^{-1} \]
\[ K = 141 \]
(c) \[ \Delta_r H^*[\text{N}_2\text{O}_3(g)] = 83.71 \text{ kJ} \]

26.61 \[ \Delta_r H^* = -884 \text{ kJ} \]
\[ \Delta_r G^* = -841 \text{ kJ} \]

This reaction is product-favoured – \( \Delta_r G^* < 0 \) – and it is exothermic which means that it is less product-favoured at higher temperature.
26.63
\[ \begin{align*}
\text{ON(S) } &= +1 \\
\text{ON(S) } &= +2 \\
\text{ON(S) } &= +4
\end{align*} \]

26.65 Any species with reduction potential greater than that of chlorine (i.e. > 1.36 V) can be used. For example,
- \[ \text{F}_2(g) + 2 \text{Cl}^-(aq) \rightarrow 2 \text{F}^-(aq) + \text{Cl}_2(g) \]
- \[ \text{H}_2\text{O}_2(aq) + 2 \text{H}^+(aq) + 2 \text{Cl}^-(aq) \rightarrow 2 \text{H}_2\text{O}(\ell) + \text{Cl}_2(g) \]
- \[ \text{PbO}_2(s) + \text{SO}_4^{2-}(aq) + 4 \text{H}^+(aq) + 2 \text{Cl}^-(aq) \rightarrow \text{PbSO}_4(s) + 2 \text{H}_2\text{O}(\ell) + \text{Cl}_2(g) \]
- \[ 2 \text{MnO}_4^-(aq) + 16 \text{H}^+(aq) + 10 \text{Cl}^-(aq) \rightarrow 2 \text{Mn}^{2+}(aq) + 8 \text{H}_2\text{O}(\ell) + 5 \text{Cl}_2(g) \]

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

26.69
\[ \text{Br} \quad \text{F} \]

26.71 1.6 kg

**SUMMARY AND CONCEPTUAL QUESTIONS**

26.73 \( \text{P}_4\text{O}_{10}(s) \) and \( \text{SO}_3(g) \) are acidic oxides—potassium and sulfur are non-metals.
- \[ \text{P}_4(s) + 5 \text{O}_2(g) \rightarrow \text{P}_4\text{O}_{10}(s) \]
- \[ \text{S}_8(s) + 12 \text{O}_2(g) \rightarrow 8 \text{SO}_3(g) \]

The acidic oxides react with water to form acidic solutions:
- \[ \text{P}_4\text{O}_{10}(s) + 6 \text{H}_2\text{O}(\ell) \rightarrow 4 \text{H}_3\text{PO}_4(aq) \]
- \[ \text{SO}_3(g) + \text{H}_2\text{O}(\ell) \rightarrow \text{HSO}_4(aq) \]
26.75 \( \text{S}^2-, \text{Cl}^-, \text{K}^+ \) and \( \text{Ca}^{2+} \) 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) \( 2 \text{Na}(s) + \text{Br}_2(\ell) \rightarrow 2 \text{NaBr}(s) \)
(b) \( 2 \text{Mg}(s) + \text{O}_2(g) \rightarrow 2 \text{MgO}(s) \)
(c) \( 2 \text{Al}(s) + 3 \text{F}_2(g) \rightarrow 2 \text{AlF}_3(s) \)
(d) \( \text{C}(s) + \text{O}_2(g) \rightarrow \text{CO}_2(g) \)

26.81 (a) Electrolysis of aqueous sodium chloride:
\[ 2 \text{Na}^+(aq) + 2 \text{Cl}^-(aq) + 2 \text{H}_2\text{O}(\ell) \rightarrow 2 \text{Na}^+(aq) + 2 \text{OH}^-(aq) + \text{Cl}_2(g) + \text{H}_2(g) \]
(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) Li(s) and Be(s) are metals
B(s) is a metalloid
C(s), N\(_2\)(g), O\(_2\)(g), F\(_2\)(g) and Ne(g) are non-metallic substances.
(b) + (c) Li(s), Be(s) and B(s) are silver-white shiny, with metallic appearance. C is a black solid (graphite) or a lustrous transparent very hard crystalline material (diamond). N\(_2\)(g), O\(_2\)(g), F\(_2\)(g) and Ne(g) are all gases, colourless except for a yellow tinge in the case of fluorine.

26.85 (a) \( 2 \text{KClO}_3(s) \text{ heat} \rightarrow 2 \text{KCl} + 3 \text{O}_2(g) \)
(b) \( 2 \text{H}_2\text{S}(g) + 3 \text{O}_2(g) \rightarrow 2 \text{H}_2\text{O}(\ell) + 2 \text{SO}_2(g) \)
(c) \( 2 \text{Na}(s) + \text{O}_2(g) \rightarrow \text{Na}_2\text{O}_2(s) \)
(d) \( \text{P}_4(s) + 3 \text{OH}^-(aq) + 3 \text{H}_2\text{O}(\ell) \rightarrow \text{PH}_3(g) + 3 \text{H}_2\text{PO}_4^-(aq) \)
(e) \( 2 \text{NH}_4\text{NO}_3(s) \text{ heat} \rightarrow \text{N}_2\text{O}(g) + 2 \text{H}_2\text{O}(g) \)
(f) \( 2 \text{In}(s) + 3 \text{Br}_2(\ell) \rightarrow 2 \text{InBr}_3(s) \)
(g) \( \text{SnCl}_4(\ell) + 4 \text{H}_2\text{O}(\ell) \rightarrow \text{Sn(OH)}_4(aq) + 4 \text{H}^+(aq) \)

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.
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 Ca(OH)\textsubscript{2}(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, CaCO\textsubscript{3}(s). CO\textsubscript{2}(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\textsubscript{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 g as the mass of the oxide. If we take the decomposition reaction to be (M is replaced by M\textsubscript{2} in case of a univalent metal, etc.)

\[
\text{MCO}_3(s) \ + \ \text{heat} \rightarrow \ \text{MO(s)} \ + \ \text{CO}_2(g),
\]

then the molar mass of MO(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. A = BaCO\textsubscript{3}(s) B = BaO(s) C = CaCO\textsubscript{3}(s) D = BaCl\textsubscript{2}(s) E = BaSO\textsubscript{4}(s)

### Chapter 27

27.1 (a) methyl amine, CH\textsubscript{3}NH\textsubscript{2} , (b) methyl nitrile, CH\textsubscript{3}CN , (c) azide, N\textsubscript{3}\textsuperscript{-} and (e) bromide, Br\textsuperscript{-} are monodentate ligands.

(d) en - ethylenediamine, H\textsubscript{2}NCH\textsubscript{2}CH\textsubscript{2}NH\textsubscript{2} and (f) phen - phenanthroline, C\textsubscript{12}H\textsubscript{8}N\textsubscript{2} are bidentate (special case of polydentate) ligands

27.2 NH\textsubscript{4}\textsuperscript{+} has no lone pairs and does not serve as a ligand.

27.3 (a) [Co(NH\textsubscript{3})\textsubscript{3}Cl\textsubscript{3}]

(b) (i) oxidation number: +3. coordination number: 6

(ii) oxidation number: +2. coordination number: 6

27.4 (a) 2.0 × 10\textsuperscript{-6} M

(b) 4.0 × 10\textsuperscript{-6} M

(c) 5.0 × 10\textsuperscript{4}
27.5  (i) \( \Delta G^\circ = -67.2 \text{ kJ mol}^{-1} \)

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  

\[
[\text{Co(NH}_3\text{)}_5 \text{Br}] \text{SO}_4(\text{aq}) + \text{BaCl}_2(\text{aq}) \rightarrow [\text{Co(NH}_3\text{)}_5 \text{Br}] \text{Cl}_2(\text{aq}) + \text{BaSO}_4(\text{s})
\]
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) \([\text{Fe(en)}_3]^{2+}\) has a stereocenter at \(\text{Fe}^{2+}\) giving rise to two enantiomers.  
(b) The cobalt ion in *trans*-[\(\text{Co(en)}_2\text{Br}_2\)]\(^+\) is a stereocenter, giving rise to two isomers – the *cis* and *trans* species.  
(c) The cobalt ion in *fac*-[\(\text{Co(en)}(\text{H}_2\text{O})\text{Cl}_3\)] is a stereocenter, giving rise to two isomers – the *fac* and *mer* species  
(d) The platinum ion in [\(\text{Pt(NH}_3)(\text{H}_2\text{O})(\text{Cl})(\text{NO}_2)\)] is a stereocenter. For example, the \(\text{NH}_3\) ligand can be *trans* to any of the other three ligands.  

27.11  \([\text{Ti(OH}_2)_6]^{3+}\) < \([\text{Ti(NH}_3)_6]^{3+}\) < \([\text{Ti(CN)}_6]^{3-}\)  

27.12  (a) In [\(\text{Ru(H}_2\text{O})_6\)]\(^{2+}\), \(\text{Ru}^{2+}\) is in the +2 oxidation state.  

\[
\begin{array}{c}
\downarrow \\
\downarrow \\
\downarrow \\
\uparrow \\
\uparrow \\
\uparrow \\
\end{array}
\quad
\begin{array}{c}
\uparrow \\
\uparrow \\
\uparrow \\
\downarrow \\
\downarrow \\
\downarrow \\
\end{array}
\]

\(d_{x^2-y^2} \quad d_{z^2} \quad d_{x'y'} \quad d_{xz} \quad d_{yz} \quad d_{xy}\)

*low spin* \quad *diamagnetic*  
*high spin* \quad *paramagnetic*  

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

\[
\begin{array}{c}
\uparrow \\
\uparrow \\
\uparrow \\
\downarrow \\
\downarrow \\
\downarrow \\
\end{array}
\quad
\begin{array}{c}
\uparrow \\
\uparrow \\
\uparrow \\
\downarrow \\
\downarrow \\
\downarrow \\
\end{array}
\]

\(d_{x^2-y^2} \quad d_{z^2} \quad d_{x'y'} \quad d_{xz} \quad d_{yz} \quad d_{xy}\)

*low spin*  
*paramagnetic*
27.13

(a) \[ \text{paramagnetic} \]
\[ [\text{Mn(CN)}_6]^{4-} \quad 5 \text{ d electrons} \]

(b) \[ \text{diamagnetic} \]
\[ [\text{Co(NH}_3)_6]^{3+} \quad 6 \text{ d electrons} \]

27.15

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

27.17

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

27.19 \[ [\text{Cr(en)}_2(\text{NH}_3)_2]^{3+} \]
First, dissolve a known amount of CrCl₃ 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 Cr³⁺, and different (known) total concentrations of chloride. Excess AgNO₃(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 [Cr(H₂O)₆]³⁺, [Cr(H₂O)₅Cl]²⁺ and [Cr(H₂O)₄Cl₂]⁺. These correspond to 0, 1 and 2 bound chloride per chromium. According to the information given, we need to add diethylether to obtain [Cr(H₂O)₃Cl₃]. 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) \(5.0 \times 10^{11}\)  
(b) 250  
(c) \(3.1 \times 10^{-5}\) M

27.25

<table>
<thead>
<tr>
<th>Complex</th>
<th>Co²⁺</th>
<th>Ni²⁺</th>
<th>Cu²⁺</th>
<th>Zn²⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>(K_f) also known as (\beta)</td>
<td>(7.7 \times 10^7)</td>
<td>(5.6 \times 10^8)</td>
<td>(6.8 \times 10^{12})</td>
<td>(2.9 \times 10^9)</td>
</tr>
</tbody>
</table>

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

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

27.37

\[
\begin{array}{cc}
\uparrow & \uparrow \\
\downarrow & \downarrow \\
\hline
\mathbf{d}_{xy} & \mathbf{d}_{xz} \\
\mathbf{d}_{yz} & \mathbf{d}_{x^2-y^2} \\
\mathbf{d}_{y^2} & \mathbf{d}_{z^2}
\end{array}
\]

\[
\begin{array}{cc}
\uparrow & \uparrow \\
\uparrow & \uparrow \\
\hline
\mathbf{d}_{xy} & \mathbf{d}_{xz} \\
\mathbf{d}_{yz} & \mathbf{d}_{x^2-y^2} \\
\mathbf{d}_{y^2} & \mathbf{d}_{z^2}
\end{array}
\]

\[\text{[Cr(CN)₆]}^{3−}\text{ 4 d electrons  low spin complex}\]

\[\text{[Cr(SCN)₆]}^{3−}\text{ 4 d electrons  high spin complex}\]

SCN\text{−} is lower in the spectrochemical series than CN\text{−}. It does not split the d orbital energies as much as cyanide.

27.39

(a)  
\[
\begin{array}{cc}
\uparrow & \uparrow \\
\downarrow & \downarrow \\
\hline
\mathbf{d}_{xy} & \mathbf{d}_{xz} \\
\mathbf{d}_{yz} & \mathbf{d}_{x^2-y^2} \\
\mathbf{d}_{y^2} & \mathbf{d}_{z^2}
\end{array}
\]

\[\text{[FeCl₄]}^{2−}\text{ 6 d electrons  4 unpaired electrons}\]

(b)  
\[
\begin{array}{cc}
\uparrow & \uparrow \\
\downarrow & \downarrow \\
\hline
\mathbf{d}_{xy} & \mathbf{d}_{xz} \\
\mathbf{d}_{yz} & \mathbf{d}_{x^2-y^2} \\
\mathbf{d}_{y^2} & \mathbf{d}_{z^2}
\end{array}
\]

\[\text{[CoCl₄]}^{2−}\text{ 7 d electrons  3 unpaired electrons}\]

(c)  
\[
\begin{array}{cc}
\uparrow & \uparrow \\
\downarrow & \downarrow \\
\hline
\mathbf{d}_{xy} & \mathbf{d}_{xz} \\
\mathbf{d}_{yz} & \mathbf{d}_{x^2-y^2} \\
\mathbf{d}_{y^2} & \mathbf{d}_{z^2}
\end{array}
\]

\[\text{[MnCl₄]}^{2−}\text{ 5 d electrons  5 unpaired electrons}\]

(d)  
\[
\begin{array}{cc}
\uparrow & \uparrow \\
\downarrow & \downarrow \\
\hline
\mathbf{d}_{xy} & \mathbf{d}_{xz} \\
\mathbf{d}_{yz} & \mathbf{d}_{x^2-y^2} \\
\mathbf{d}_{y^2} & \mathbf{d}_{z^2}
\end{array}
\]

\[\text{[ZnCl₄]}^{2−}\text{ 10 d electrons  0 unpaired electrons}\]
27.41  
(a) 6  
(b) Octahedral  
(c) +3  
(d) 0  
(e) diamagnetic  
(f)  

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 (\( \Delta H^\circ = -160.8 \text{ kJ} \)), 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.

(c) \( r = 227 \text{ pm}, \chi = 0.8 \). K could not be a substitutional impurity.  
(d) \( r = 154 \text{ pm}, \chi = 1.8 \). Pb could be a substitutional impurity (but not as good as Sn).
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.

$$E_g = h \nu = h c / \lambda,$$

So,

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

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 cm$^2$ $= 3.03$ m$^2$.  

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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:

\[
\begin{align*}
\text{Sn} & : 7310 \text{ kg m}^{-3} \\
\text{Sb} & : 6697 \text{ kg m}^{-3} \\
\text{Cu} & : 8920 \text{ kg m}^{-3}
\end{align*}
\]

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

29.2

![Threose structure](image)

29.3

![2-chlorobutane structures](image)

(S)-2-chlorobutane

(R)-2-chlorobutane
α-D-ribofuranose

β-D-ribofuranose

α-D-fructofuranose

β-D-fructofuranose

α-D-fructopyranose

β-D-fructopyranose

β-D-mannopyranose

β-D-galactopyranose

β-D-mannopyranose and β-D-galactopyranose should be about equally stable
29.11

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

29.13

29.14

29.15 DNA sequence 3’-CCGATTAGGCA-5’ is complementary to GGCTAATCCGT (by default this is 5’ to 3’). Arranged 5’ to 3’, this sequence is ACGGATTAGCC.
29.16

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

29.18 RNA sequence UUCGCAAGAGU was transcribed from DNA sequence ACTCTGCGAA.

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

29.20 CUU-AUG-GCU-UGG-CCC-UAA codes for the polypeptide, Leu-Met-Ala-Trp-Pro-stop
i.e. leucine, methionine, alanine, tryptophan and proline are linked together, in this order, then the chain is terminated at proline.

29.21 mRNA base sequence AUC-GGU gives rise to tRNA sequence, ACC-GAU.

29.22 mRNA base sequence AUC-GGU arose from transcription of DNA sequence, ACC-GAT.
29.23  (a) 

(b) This is an \( \alpha \) 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 \( \alpha \) configuration at the carbon next to the primary alcohol.
(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 AgNO₃. 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.

\[
\begin{align*}
\text{H} & \quad \text{O} \\
\text{O} & \quad \text{H} \\
\text{H} & \quad \text{H} \\
\text{O} & \quad \text{H} \\
\text{H} & \quad \text{H} \\
\text{O} & \quad \text{H}
\end{align*}
\]

\[\text{e.g. } \alpha-\text{D}-\text{allopyranose}\]

(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.

\[
\begin{align*}
\text{O} & \quad \text{H} \\
\text{H} & \quad \text{O} \\
\text{H} & \quad \text{H} \\
\text{H} & \quad \text{O} \\
\text{OH} & \quad \text{H}
\end{align*}
\]

\[\text{e.g. } \text{D}-\text{mannose}.\]

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% \(\alpha\)-D-galactopyranose and 72% \(\beta\)-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
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 \(^0\)e and \(^0\)β can be used interchangeably, as can \(^4\)He and \(^4\)α.

30.1  
(a) \(^{222}\)Rn \(\rightarrow\) \(^{218}\)Po + \(^4\)He
(b) \(^{218}\)Po \(\rightarrow\) \(^{218}\)At + \(^0\)e

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

30.3  
(a) \(^{232}\)Th \(\rightarrow\) \(^{208}\)Pb + 6 \(^2\)He + 4 \(^0\)e
(b) \(^{232}\)Th \(\rightarrow\) \(^{228}\)Ra + \(^4\)He

\(^{228}\)Ra \(\rightarrow\) \(^{228}\)Ac + \(^0\)e

\(^{228}\)Ac \(\rightarrow\) \(^{228}\)Th + \(^0\)e

30.4  
(a) \(^{15}\)N \(\rightarrow\) \(^{15}\)C + \(^0\)β
(b) \(^{41}\)Ca + \(^0\)β \(\rightarrow\) \(^{41}\)K
(c) \(^{90}\)Sr \(\rightarrow\) \(^{90}\)Y + \(^0\)β
(d) \(^{23}\)Na \(\rightarrow\) \(^{23}\)Mg + \(^0\)β
30.5
(a) $^{32}_{14}\text{Si} \rightarrow ^{32}_{15}\text{P} + ^0_0\beta$
(b) $^{45}_{22}\text{Ti} \rightarrow ^{45}_{21}\text{Sc} + ^0_0\beta$
(c) $^{239}_{94}\text{Pu} \rightarrow ^{235}_{92}\text{U} + ^4_2\text{He}$
(d) $^{42}_{19}\text{K} \rightarrow ^{42}_{20}\text{Ca} + ^0_{-1}\beta$

30.6
$3.087 \times 10^9 \text{kJ mol}^{-1}$
$5.145 \times 10^8 \text{ kJ mol}^{-1} \text{ nucleons}$

30.7
(a) 0.094 mg
(b) 36.9 years
(c) 81.7 years

30.8
26.9 days

30.9
6200 years

30.10 The sample is $t = 3010$ years old.
The ring data give the age of the tree to be $2853 \pm 52$ years

30.11 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) $^{54}_{26}\text{Fe} + ^4_2\text{He} \rightarrow ^{56}_{28}\text{Ni} + ^1_0\text{n}$
(b) $^{27}_{13}\text{Al} + ^4_2\text{He} \rightarrow ^{28}_{15}\text{P} + ^0_0\text{n}$
(c) $^{32}_{16}\text{S} + ^1_0\text{n} \rightarrow ^1_1\text{H} + ^{32}_{14}\text{P}$
(d) $^{98}_{42}\text{Mo} + ^1_0\text{n} \rightarrow ^1_0\text{n} + ^{97}_{43}\text{Tc}$
(e) $^{98}_{42}\text{Mo} + ^1_0\text{n} \rightarrow ^{99}_{43}\text{Tc} + ^0_{-1}\beta$
(f) $^{18}_{9}\text{F} \rightarrow ^{18}_{8}\text{O} + ^0_0\beta$

30.15
(a) $^{111}_{47}\text{Ag} \rightarrow ^{111}_{48}\text{Cd} + ^0_{-1}\beta$
(b) $^{82}_{36}\text{Kr} \rightarrow ^0_{-1}\beta + ^{83}_{37}\text{Rb}$
(c) $^{231}_{91}\text{Pa} \rightarrow ^{227}_{89}\text{Ac} + ^4_2\text{He}$
(d) $^{230}_{90}\text{Th} \rightarrow ^{4}_2\text{He} + ^{226}_{88}\text{Ra}$
(e) $^{82}_{35}\text{Br} \rightarrow ^{82}_{36}\text{Kr} + ^0_{-1}\beta$
(f) $^{24}_{11}\text{Na} \rightarrow ^{24}_{12}\text{Mg} + ^0_{-1}\beta$
30.17

\[ ^{235}\text{U} \rightarrow ^{231}\text{Th} + \frac{3}{2}\text{He} \]
\[ ^{231}\text{Th} \rightarrow ^{231}\text{Pa} + _{-1}\beta \]
\[ ^{231}\text{Pa} \rightarrow ^{227}\text{Ac} + \frac{3}{2}\text{He} \]
\[ ^{227}\text{Ac} \rightarrow ^{227}\text{Th} + _{-1}\beta \]
\[ ^{227}\text{Th} \rightarrow ^{223}\text{Ra} + \frac{3}{2}\text{He} \]
\[ ^{223}\text{Ra} \rightarrow ^{219}\text{Rn} + \frac{3}{2}\text{He} \]
\[ ^{219}\text{Rn} \rightarrow ^{215}\text{Po} + \frac{3}{2}\text{He} \]
\[ ^{215}\text{Po} \rightarrow ^{211}\text{Pb} + \frac{3}{2}\text{He} \]
\[ ^{211}\text{Pb} \rightarrow ^{211}\text{Bi} + _{-1}\beta \]
\[ ^{211}\text{Bi} \rightarrow ^{211}\text{Po} + _{-1}\beta \]
\[ ^{211}\text{Po} \rightarrow ^{207}\text{Pb} + \frac{3}{2}\text{He} \]

30.19

(a) Gold-198 decays to mercury-198.
\[ ^{198}\text{Au} \rightarrow ^{198}\text{Hg} + _{-1}\beta \]
The atomic number increases by 1, while the mass number does not change. This is beta decay.

(b) Radon-222 decays to polonium-218.
\[ ^{222}\text{Rn} \rightarrow ^{218}\text{Po} + \frac{3}{2}\text{He} \]
The atomic number decreases by 2, while the mass number decreases by 4. This is alpha decay.

(c) Cesium-137 decays to barium-137.
\[ ^{137}\text{Cs} \rightarrow ^{137}\text{Ba} + _{-1}\beta \]
This is beta decay.

(d) Indium-110 decays to cadmium-110.
\[ ^{110}\text{In} \rightarrow ^{110}\text{Cd} + _{0}\beta \]
This is positron emission.
(a) Bromine-80m is a metastable state of bromine. It most likely decays by gamma emission to form bromine-80.
\[ {}^{80}\text{Br} \rightarrow {}^{80}\text{Br} + n\gamma \]
\( n \) 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.
\[ {}^{240}\text{Cf} \rightarrow {}^{236}\text{Bk} + ^0\beta \]
Alternatively:
\[ {}^{240}\text{Cf} \rightarrow {}^{236}\text{Cm} + ^2\text{He} \]

(c) Cobalt-61 has a high neutron to proton ratio. It most likely decays by beta emission.
\[ {}^{61}\text{Co} \rightarrow {}^{58}\text{Ni} + ^0\beta \]

(d) Carbon-11 has a low neutron to proton ratio. It most likely decays by positron emission.
\[ ^{11}\text{C} \rightarrow ^{11}\text{B} + ^0\beta \]

(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.

For \( {}^{10}\text{B} \),
\[ \Delta m = 5 \times 1.00783 + 5 \times 1.00867 - 10.01294 \text{ g mol}^{-1} = 0.069510 \text{ g mol}^{-1} = 6.9510 \times 10^{-5} \text{ kg mol}^{-1} \]
\[ E_b = \Delta m c^2 \]
\[ = 6.9510 \times 10^{-5} \text{ kg mol}^{-1} \times (2.998 \times 10^8 \text{ m s}^{-1})^2 \]
\[ = 6.248 \times 10^{12} \text{ J mol}^{-1} = 6.248 \times 10^9 \text{ kJ mol}^{-1} \]

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 \( {}^{11}\text{B} \),
\[ \Delta m = 5 \times 1.00783 + 6 \times 1.00867 - 11.00931 \text{ g mol}^{-1} = 0.081805 \text{ g mol}^{-1} = 8.1805 \times 10^{-5} \text{ kg mol}^{-1} \]
\[ E_b = \Delta m c^2 \]
\[ = 8.1805 \times 10^{-5} \text{ kg mol}^{-1} \times (2.998 \times 10^8 \text{ m s}^{-1})^2 \]
\[ = 7.353 \times 10^{12} \text{ J mol}^{-1} = 7.353 \times 10^9 \text{ kJ mol}^{-1} \]

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 \( {}^{11}\text{B} \) is the more stable nucleus—it has a higher binding energy per nucleon.

For \( {}^{40}\text{Ca} \),
\[ \Delta m = 20 \times 1.00783 + 20 \times 1.00867 - 39.96259 \text{ g mol}^{-1} = 0.36721 \text{ g mol}^{-1} = 3.6721 \times 10^{-4} \text{ kg mol}^{-1} \]
\[ E_b = \Delta m c^2 \]
\[ = 3.6721 \times 10^{-4} \text{ kg mol}^{-1} \times (2.998 \times 10^8 \text{ m s}^{-1})^2 \]
\[ = 3.300 \times 10^{13} \text{ J mol}^{-1} = 3.300 \times 10^{10} \text{ kJ mol}^{-1} \]

Per nucleon,
\[ E_b / n = 3.300 \times 10^{10} \text{ kJ mol}^{-1} / 40 = 8.252 \times 10^8 \text{ kJ mol}^{-1} \text{ nucleons} \]
This result is consistent with Figure 30.6.
For $^{16}\text{O},$
\[\Delta m = 8 \times 1.00783 + 8 \times 1.00867 - 15.99492 \text{ g mol}^{-1} = 0.13700 \text{ g mol}^{-1} = 1.3700 \times 10^{-4} \text{ kg mol}^{-1}\]

\[E_b = \Delta m c^2 = 1.3700 \times 10^{-4} \text{ kg mol}^{-1} \times (2.998 \times 10^8 \text{ m s}^{-1})^2 = 1.231 \times 10^{13} \text{ J mol}^{-1} = 1.231 \times 10^{10} \text{ kJ mol}^{-1}\]

Per nucleon,
\[E_b / n = 1.231 \times 10^{10} \text{ kJ mol}^{-1} / 16 = 7.696 \times 10^8 \text{ kJ mol}^{-1} \text{ nucleons}\]

64 h corresponds to 64 h / 12.7 h = 5.04 half-lives. At this time, the mass of $^{64}\text{Cu}$ is 25.0 $\mu$g $\times (1/2)^{5.04} = 0.760$ $\mu$g

(a) $^{131}\text{I} \rightarrow ^{131}\text{Xe} + ^{0}_\beta\beta$
(b) 40.2 days corresponds to 40.2 days / 8.04 days = 5.00 half-lives. At this time, the mass of $^{198}\text{Au}$ is $2.4 \mu$g $\times (1/2)^2 = 0.075 \mu$g

13 days corresponds to 13 days / (78.25 / 24) days = 4.0 half-lives. At this time, the mass of $^{67}\text{Ga}$ is $0.015 \text{ mg} \times (1/2)^{4.0} = 9.4 \times 10^{-4} \text{ mg}\]

(a) $^{222}\text{Rn} \rightarrow ^{218}\text{Po} + ^{4}_2\text{He}$
(b) 20.0% of $^{222}\text{Rn}$ 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 days = 8.87 days

0.72 of the $^{14}\text{C}$ 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 $0.17 \times 5.73 \times 10^3$ years = 2700 years
This is the age of the bone fragment.

(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 $3 \times 5.27$ years = 15.81 years
(b) 1 year corresponds to $1 / 5.27 = 0.190$ half-lives. At this time, the fraction of $^{60}\text{Co}$ remaining is $(1/2)^{0.190} = 0.877$
The data is clearly well fit by a simple exponential decay, $421.9 e^{-0.046t}$. The parameters of this fit are well approximated using just the first and last data. $k = 0.046$ corresponds to $t_{1/2} = \frac{\ln 2}{k} = \frac{\ln 2}{0.046} \text{ h} = 15 \text{ h}$
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 $^{87}\text{Rb}$ 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 $^{235}\text{U}$ 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, $^{15}\text{O}$, carry out the reaction, and then sample the water and look for $^{15}\text{O}$ that could only have come from methanol. The same experiment could be carried out with labelled acetic acid to see if acid $^{15}\text{O}$ ends up in the water product.
30.69 The number of atoms in 1.0 mg of $^{238}\text{U}$ 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 Bq = 1 s$^{-1}$)

$$k = \frac{\Delta N / \Delta t}{N} = 12 \text{ s}^{-1} / 2.530 \times 10^{18} = 4.74 \times 10^{-18} \text{ s}^{-1}$$

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

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