Answers to SelectedTextbook 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

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

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

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

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

2.5   (a) In CO, there is one carbon atom for every oxygen atom (or the ratio of C to O atoms is 1:1).
        (b) In CH_4, the C to H atom ratio is 1:4.
        (c) In C_2H_2, the C to H atom ratio is 1:1.
        (d) In $C_6H_{12}O_6$, 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 = 10^5. If the radius of the
        atom were 100 m, then the nucleus radius would be 100 m/10^5 = 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)$^{36}_{18}Ar$, $^{38}_{18}Ar$, $^{40}_{18}Ar$. % abundance of $^{40}_{18}Ar$ = 99.600 %
        (b)^{69}Ga: 31 protons, 38 neutrons
            ^{71}Ga (% abundance, 39.9 %): 31 protons, 40 neutrons

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

2.14   Atomic weight of chlorine $= \dfrac{75.77}{100} \times 34.96885 + \dfrac{24.23}{100} \times 36.96590 = 35.45$

2.18   10

2.19   (a) 59 g
        (b) 1.90 x 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

Symbol	^{65}Cu	^{86}Kr	^{195}Pt	^{81}Br
Number of protons	29	36	78	35
Number of neutrons	36	50	117	46
Number of electrons in the neutral atom	29	36	78	35
Name of element	copper	krypton	platinum	bromine

2.43 2

2.45 1

2.47 134.9 g

2.49 Two periods have 8 elements, two periods have 18 elements, and two periods have 32 elements.

2.51   (a) Bk
       (b) Br
       (c) B
       (d) Ba
       (e) Bi

2.53   (a) Si is a metalloid, while P is a non-metal
       (b) Si has some electrical conductivity, while P does not
       (c) Both Si and P are solids at 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 9.42×10^{-5} mol
       5.67×10^{19} atoms

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

2.63 $\delta^{13}C = -28.90$ is consistent with a thermogenic sample

2.65   We need the density of iron, (d), in order to determine the mass of 1 cm^3 of iron. Dividing this mass by the molar mass of iron, (b), determines the number of moles in 1 cm^3 of iron. Multiplying that number by Avogadro's constant, (c), provides the final answer – the number of atoms in 1 cm^3 of iron.

2.67   You could count how many jelly beans it takes to fill a smaller container – fewer jelly beans, easier to count – then multiply by the ratio of the volume of jar to that of the smaller container. If you only have the picture, you could count the number of jelly beans half way around the perimeter of the cylindrical jar, and from bottom to top of the jar. You have determined $\pi \times$ radius of jar and the height of the jar in jelly bean length units. Squaring the first quantity, then dividing by π and multiplying by the second quantity provides an estimate of the number of jelly beans in the jar.

Chapter 3

3.1 BN

3.2 Sodium chloride is held together in a lattice by strong ionic bonds – attraction between positively and negatively charged ions. Silicon carbide is a network solid. The atoms are similarly held together in a lattice, but in this case it is by covalent bonds. Covalent bonds are generally stronger than ionic bonds. Silicon carbide is expected to have the higher melting point. This is in fact the case – silicon carbide decomposes at 2730 ºC, while sodium chloride melts at 800ºC.

3.3 (a) S has 16 protons and 16 electrons. S^{2-} has 16 protons and 18 electrons.
(b) Al has 13 protons and 13 electrons. Al^{3+} has 13 protons and 10 electrons.
(c) H has 1 proton and 1 electron. H^+ has 1 proton and no electrons.

3.4 N^{3-}, O^{2-}, F^-, Na^+, Mg^{2+}, and Al^{3+} have 7, 8, 9, 11, 12 and 13 protons, respectively. All of these species have 10 electrons, the number of electrons in a neutral Ne atom (10 protons).

3.6 (a) equal amounts of Na^+ and F^- in NaF; twice as much NO_3^- as Cu^{2+} in $Cu(NO_3)_2$; equal amounts of Na^+ and $CH_3CO_2^-$ in $NaCO_2CH_3$
(b) $FeCl_2$ and $FeCl_3$ are the compounds formed by Fe^{2+} and Fe^{3+}, respectively
(c) Na_2S, Na_3PO_4, BaS and $Ba_3(PO_4)_2$

3.10 (a) 119.0 g mol^{-1}
(b) 53.5 g mol^{-1}
(c) 213 g mol^{-1}
(d) 120.3 g mol^{-1}

3.11 (a) 0.0250 mol
(b) 6.95 x 10^{-5} mol
(c) 5 x 10^3 mol

3.14 (a) electrons
(b) electrons and to a lesser extent Mg^{2+} ions (they are less mobile)
(c) Mg^{2+} and Cl^- ions
(d) Mg^{2+} and Cl^- ions

3.15 (b), (d) and (e) are molecular substances.

3.16 Silicon has a much higher melting point because it is a network solid. It does not consist of discrete molecules. Covalent bonding extends throughout a lattice giving the material exceptional strength. Sulfur consists of discrete S_8 molecules which are, in turn, held in a lattice by weaker intermolecular bonds.

3.17 ^{12}C, ^{16}O and ^1H are the most common isotopes of carbon, oxygen and hydrogen. The molar mass of the most abundant isotopologue, $^{12}C_2{}^1H_6{}^{16}O$, is 46.04189 g mol^{-1}. This is not in exact agreement with the experimental value.

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

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

3.23   A single chlorine atom
        C_6H_5Cl
        112.008002; 114.005052

3.24 $C_6H_5CHCH_2$ or C_8H_8

3.25   (a) C=O stretch - ketone, aldehyde or carboxylic acid
        (b) C-N-H bend of an amine
        (c) 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, NH_4^+, has one more proton than electron - hence the +1 charge.
        (b) phosphate, PO_4^{3-}, has three more electrons than protons - hence the −3 charge.
        (c) dihydrogen phosphate, $H_2PO_4^-$, has one more electron than protons - hence the −1 charge.

3.33 Na_2CO_3 sodium carbonate
        $BaCO_3$ barium carbonate
        NaI sodium iodide
        BaI_2 barium iodide

3.35   (a) chlorine trifluoride
        (b) nitrogen trichloride
        (c) strontium sulphate (ionic)
        (d) calcium nitrate (ionic)
        (e) xenon tetrafluoride
        (f) oxygen difluoride
        (g) potassium iodide (ionic)
        (h) aluminium sulphide (ionic with some covalent character)
        (i) phosphorus trichloride
        (j) potassium phosphate (ionic)

3.36   (a) NaOCl (ionic)

3.37   (iii) electrons are set free within a lattice of positive ions

3.39   A chemical reaction of oxygen requires breaking the oxygen-oxygen double bond, and generally
        forming other bonds. As such, the propensity of oxygen to react depends on the strength of the
        O=O bond, as well as the strength of bonds formed in the reaction. The boiling point of oxygen
        depends only on the strength of the weak intermolecular bonds between neighbouring oxygen
        molecules.

3.41   Only the calculated molecular mass, 28.03132, of C_2H_4 comes really close to this value. If the
        data were from a low resolution spectrometer, we could not rule out H_2CN (molecular mass =
        28.01873), N_2 (molecular mass = 28.00614) and CO (molecular mass = 27.99491).

3.43   Infrared spectroscopy and structure
        (a) absorption frequencies in cm^{-1}:
        2850-2980   due to alkyl C-H stretches
        3000-3100   due to aromatic C-H stretches
        2700-2850   due to aldehyde C-H stretch
        1720-1740   due to aldehyde C=O stretch
        1700-1725   due to carboxylic C=O stretch
        675-900, 1400-1500 and 1585-1600   due to aromatic C-C bends and stretches
        (b)
        3020-3100   due to alkene C-H stretches
        2850-2980   due to alkyl C-H stretches
        1730-1750   due to ester C=O stretch
        1640-1670   due to C=C stretch
        1000-1300   due to ester C-O stretch
         (c)
        3200-3550   due to alcohol O-H stretch
        2850-2980   due to alkyl C-H stretches
        1705-1725   due to ketone C=O stretch
        1000-1260   due to alcohol C-O stretch

3.45   (a) carboxylic acid and aromatic ring
        absorption wavenumbers in cm^{-1}:
        (b) ester and aromatic ring
        (c) alcohol, nitrile, and aromatic ring

3200-3550	broad peak due to alcohol (phenol) O-H stretch
2210-2260	due to nitrile 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

3.47   (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   CaS (c)

3.53   (a) 305.4119 g mol^{-1}
        (b) 1.8×10^{-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 Cl_2 molecules. In the solid state, the molecules are held together by weak intermolecular forces.

3.59   (a) silicon dioxide is a covalent network solid which melts at very high temperature
        carbon dioxide is a molecular substance which melts (sublimes at 1 atm pressure) at very low temperature
        (b) sodium sulfide is an ionic substance melting at high temperature
        hydrogen sulfide is a molecular substance which melts at very low temperature

3.61   (a) calcium and chloride ions are in a 1:2 ratio in $CaCl_2$
          (b) calcium, carbon and oxygen atoms are in a 1:1:3 ratio in $CaCO_3$
          (c) nitrogen and hydrogen atoms are in a 1:3 ratio in NH_3
          (d) silicon and carbon atoms are in a 1:1 ratio in SiC
          (e) hydrogen and chlorine atoms are in a 1:1 ratio in HCl

3.63 Al^{3+} is most attracted to water because it has the largest magnitude charge.

3.65

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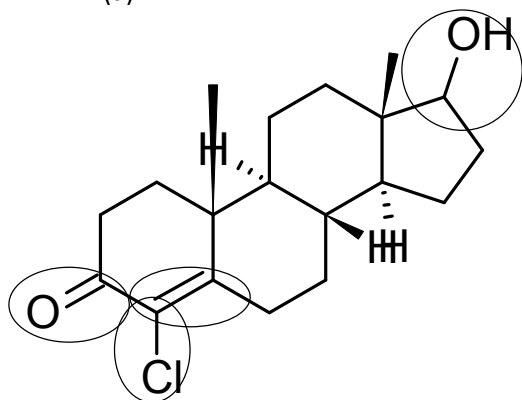
Clostebol has alkyl groups, an alkene, a ketone, a chloride and an alcohol group – the last four groups are circled.

(b) The testosterone molecular ion peak is at 288, whereas the clostebol molecular ion peak is at 322. There are peaks at both these positions, though the peak at 322 is smaller. It would appear that this mass spectrum does not rule out clostebol. However, chlorinated compounds generally show peaks associated with loss of a chlorine atom from the molecular ion. We therefore would expect to see a peak at 287. No such peak is seen. The peak at 322 must be due to some other compound. The data is consistent with the expert analysis.

3.67   absorption frequencies in cm^{-1}
         2850-2980   due to alkyl C-H stretches
         2210-2260   due to nitrile 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 $CH_3CH_2NHCH_3$ – a peak around 3250-3400 cm^{-1} not seen for $(CH_3)_3N$.
      (b) Look for the ketone C=O stretch of CH_3COCH_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_3CH_2CHO, 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 8.4×10^{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 petroluem extracted from fossil deposits. I am using a number of plastic products today – for example, the keyboard keys I am typing on, and the computer monitor I am viewing. Another fraction of the same petroleum was used to drive my car. Natural gas – from fossil deposits of mostly methane – is used to heat my house.

4.8
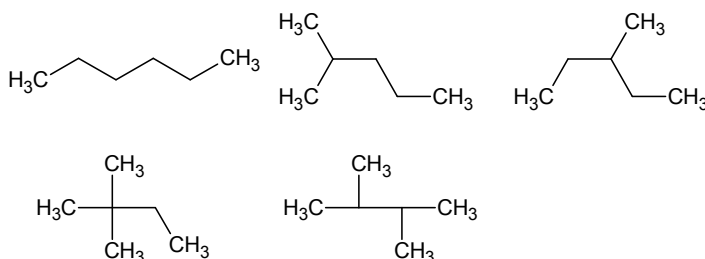
4.11   4

4.12
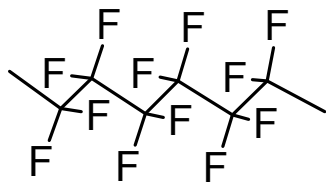
REVIEW QUESTIONS
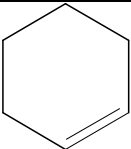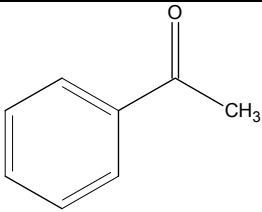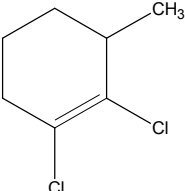
4.13   (a) Covalent bonds hold the nitrogen atoms together in the N_2 molecules, inside the clathrate hydrate.
(b) Dispersion forces attract the N_2 and H_2O molecules within the clathrate hydrate cage.
(c) Hydrogen bonding holds neighboring H_2O together molecules to make the clathrate hydrate cage.
(d) Dispersion forces attract the N_2 and O_2 molecules within the clathrate hydrate cage.

4.15   A greenhouse prevents convection of heat – a key component of the heat flow from the earth's surface out into the atmosphere. Greenhouse gases do not prevent convection. However, like the greenhouse walls and roof, they reflect some of the radiation emitted by the earth back down again. This occurs because much of the absorbed energy is re-emitted (a random process) back towards the earth, or spread to surrounding molecules by collisional de-excitation.

4.17 $CH_3CH_3(g)$; ozone, $O_3(g)$; and chloroform, $CHCl_3$

4.19   1750 is the beginning of the industrial revolution. Radiative forcing of our climate was subject only to natural fluctuations before that time.

4.21   Clouds cause cooling by reflecting incoming sunlight back out into space.

4.23   Increasing levels of tropospheric ozone has a positive radiative forcing effect.

4.24   Stratospheric ozone has a negative radiative forcing effect. It absorbs UV light preventing it from reaching the earth's surface. The stratosphere is heated, but the surface cools.

4.25   In the troposphere.

4.27   The radiative forcing and global warming potential of methane are both enhanced by methane's strong absorption of IR. However, the global warming potential also depends upon how long methane stays in the atmosphere before being eliminated by oxidation and subsequently returning to the surface in rain. The global warming potential of methane is an estimate of how much a given mass of methane will contribute to global warming relative to the same mass of carbon dioxide.

4.29   Consulting the ranking of levels of scientific uncertainty in Figure 2.20 of the 2007 IPCC summary report:

tropospheric carbon dioxide > tropospheric nitrous oxide > stratospheric ozone > jet contrails (we understand that its effect is very small) > solar irradiance

4.31   The advantages of using biofuels are as follows:
(1) They are renewable – we get a new crop each year.
(2) There is no net addition to atmospheric carbon dioxide. Atmospheric 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)		(b)	
(c)			

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

4.39

(a)
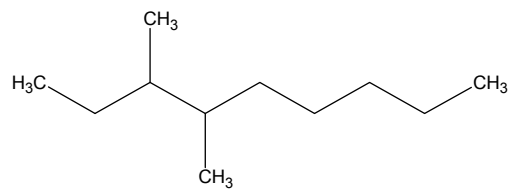
(b)
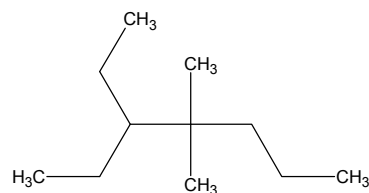
(c)
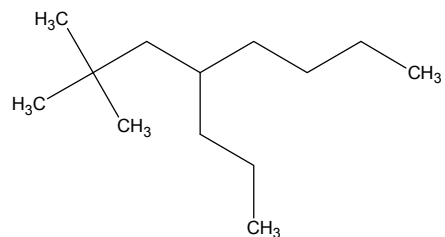
(d)
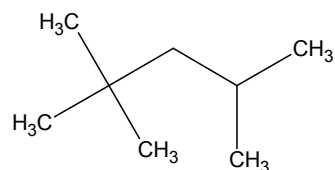
4.41
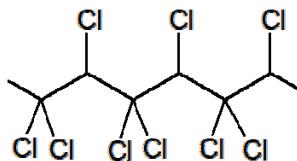
4.43   Presence of a strong oxidizing agent on mars means the environment is hostile to many fragile molecules found on earth. On the other hand, together with suitable reducing agents, a strong oxidizing agent such as hydrogen peroxide provides a potential rapid source of energy that evolving life forms might exploit. Here on earth, animal forms of life exploit the readily available, strong oxidizing agent, O_2, 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 2×10^6 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 $Al_2O_3(s)$

5.5   (a) A small amount of solid sodium chloride in water has a higher chemical potential than a dilute solution of sodium chloride.
        (b) A dilute solution of sodium chloride is more stable than a small amount of solid sodium chloride in water.

5.6 (a) Neither. Chemical potential on both sides of these reactions are equal.
(b) A mixture of solid calcium carbonate in pure water has a higher chemical potential than a mixture containing solid calcium carbonate and Ca^{2+}(aq) ions and CO_3^{2-}(aq) both at a concentration of 6×10^{-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_2O are formed.

5.11 (a) CO is the limiting reactant
(b) 407 g of CH_3OH produced
(c) 14 g of H_2 remain

5.12 (a) Fe_2O_3 is the limiting reactant
(b) 35.0 g of Fe

5.17 Theoretical yield of hydrogen = 15.7 g
Percent yield of hydrogen = 86.6 %

5.19 Mass percent of NiS = 13.8 %

5.20 (a) For the production of maleic anhydride by oxidation of benzene
(i) the C atom efficiency = 66.7%
the O atom efficiency = 33.3%
the H atom efficiency = 33.3%
(ii) the overall atom efficiency = 44.1%
(iii) the E-factor = 1.27

(b) For the production of maleic anhydride by oxidation of butene
(i) the C atom efficiency = 100.0%
the O atom efficiency = 50.0%
the H atom efficiency = 25.0%
(ii) the overall atom efficiency = 64.5%
(iii) the E-factor = 0.55

REVIEW QUESTIONS

5.21 (a) balanced for electrical charge and for all relevant atoms
(b) balanced for electrical charge and for all relevant atoms
(c) balanced for electrical charge and for all relevant atoms

5.23 (a) $H_2O(g) \longrightarrow H_2O(l)$ 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 Cu^{2+}(aq) ions is about 0.5 mol L^{-1} and the concentration of Ag^+(aq) ions is about 1×10^{-10} mol L^{-1}.

(b) A mixture containing some solid silver in an aqueous solution in which the concentration of Cu^{2+}(aq) ions is about 0.5 mol L^{-1} and the concentration of Ag^+(aq) ions is about 1×10^{-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 CO_2 = 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 $TiO_{1.5}$ or Ti_2O_3
5.39 11.2%

5.41 66.7 kg

5.43 weight percent CuS in ore = 30 %
weight percent Cu_2S in ore = 70 %

SUMMARY AND CONCEPTUAL QUESTIONS

5.45 (a) 8.8 g.
(b) 1.5
(c) $FeBr_3$
(d) 2 Fe(s) + 3 $Br_2(\ell)$ $\rightarrow$ 2 $FeBr_3$
(e) iron (III) bromide
(f) (i) **TRUE**
   (ii) **FALSE**
   (iii) **FALSE**
   (iv) **FALSE**

5.47   (a) 65.0% Pt by weight.
            9.3% N by weight.
            23.6% Cl by weight.
        (b) mass of ammonia required = 1.31 g.
            mass of $Pt(NH_3)_2Cl_2$ produced = 11.6 g.

5.49   (**1**) There is more than enough zinc. In this case, HCl is the limiting reactant – all of it reacts,
        producing enough H_2 to inflate the balloon. 0.107 – 0.050 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 H_2 is
        produced as in part (1) – i.e. enough to inflate the balloon. No zinc remains.
        (**3**) In this case, there is not enough zinc to consume all of the HCl. Zinc is the limiting reactant.
        Only 40% as much H_2 is produced as in part (1) – i.e. not enough to inflate the balloon. No zinc
        remains.

Chapter 6

6.1   (a) 108.99 mL
        (b) 109.06 mL
        (c) 100.01 mL
        (d) 100.00 mL
        (e) 100.03 mL
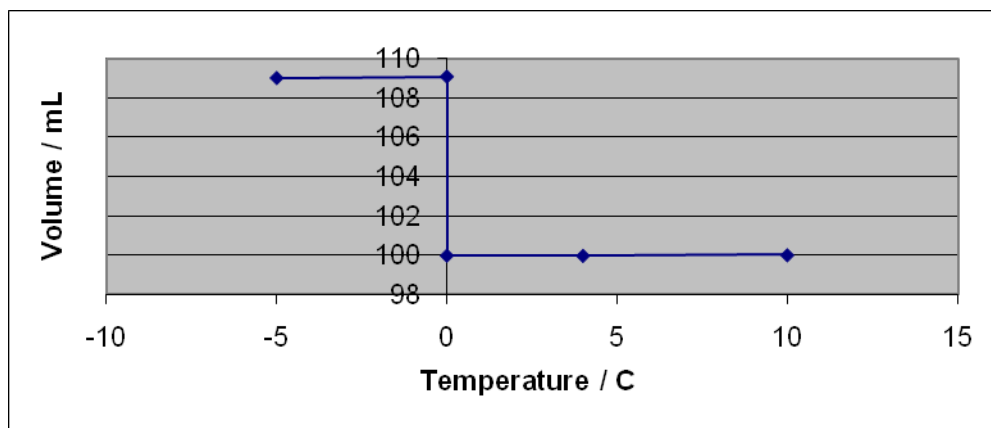
6.2   35 s

6.3   (a) 1.10×10^3 kJ
        (b) 727 kJ

6.4   diethyl ether > carbon disulfide > acetone > bromine > hexane > ethanol > water

6.5   The order of normal boiling points is the same as the order of enthalpy changes of vaporization.
        This is what we expect because both boiling point and enthalpy change of vaporization increase
        with increasing strength of intermolecular forces.

6.6   The surface tension is that which pulls the drop into a spherical shape – minimizing surface area. Since this force is smaller for diethyl ether we expect its drops to be even more distorted by gravity than those of water.

6.7   (a) The intermolecular force of attraction between water molecules and other water molecules or the molecules on the surface of the blade of grass is sufficient to allow water molecules to stick together on the blade of grass.
        (b) When a piece of paper burns, carbon-carbon and carbon-hydrogen bonds are broken while new bonds with oxygen are formed. Intramolecular forces are the losing (in the breaking reactant bonds) and winning forces (in the making of bonds) at work when paper burns.
        (c) Intermolecular forces holding water molecules together, and next to clothes fiber molecules, are overcome when wet clothes are hung out to dry.
        (d) Intermolecular forces cause water molecules to arrange themselves into a lattice of lowest potential energy. The freezer takes away the kinetic energy thereby liberated, leaving water in its crystalline, solid form – ice.

6.9   (a) H→F is more polar than H→I
        (b) B→C is less polar than B→F
        (c) C←Si is more polar than C→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_2Cl is trigonal pyramidal. It has a NET dipole because it is asymmetrical and has one bond different from the other two – N-Cl vs. N-H.
        (c) SCl_2 is bent like water. It has a NET dipole because the S-Cl bond dipoles only partially cancel out.

6.15   (a) Bent SO_2 has a net dipole. So, there are dipole-dipole forces between neighboring molecules.
        (b) Linear CO_2 has no net dipole. There are no dipole-dipole forces between these molecules – only dispersion forces.
        (c) HCl has just one polar bond, and so has a dipole moment. There are dipole-dipole forces between neighboring molecules.

6.17 CH3-O····· O-H
        |
        CH_3CH_3
shows the hydrogen bonding between neighbouring methanol molecules as they move past each other.

6.19 (a) bromine
(b) butane

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

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

6.27 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

$$LiNO_3(s) \xrightarrow{H_2O} Li^+(aq) + NO_3^-(aq)$$

(b) soluble

$$CaCl_2(s) \xrightarrow{H_2O} Ca^{2+}(aq) + 2\,Cl^-(aq)$$

(c) insoluble

(d) soluble

$$NaCH_3COO(s) \xrightarrow{H_2O} Na^+(aq) + CH_3COO^-(aq)$$

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, $C_8H_{18}(\ell)$ is non-polar and insoluble in water. Only dispersion-like forces can be made between water and octane. This interaction is weaker than the dispersion force between octane molecules.

6.30   (a) Benzene, $C_6H_6(\ell)$, is non-polar and soluble in non-polar octane. Dispersion forces are all that are at play in the pure substances and mixtures. The entropy of mixing is sufficient to drive dissolution.
(b) Water is polar and insoluble in non-polar octane. It turns out that reason for this is more subtle than appears. Dissolving octane in water decreases the entropy of neighboring water molecules. This effect overwhelms the entropy of mixing, and dissolution is not spontaneous.
(c) Iodine, $I_2(s)$, is non-polar and soluble in non-polar octane. Dispersion forces are all that are at play in the pure substances and mixtures. The entropy of mixing is sufficient to drive dissolution.

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

6.32   (a) $HBr(g) + H_2O(l) \longrightarrow H_3O^+(aq) + Br^-(aq)$

(b) $HF(aq) + H_2O(l) \xrightleftharpoons{\text{only some ionised}} H_3O^+(aq) + F^-(aq)$

(c) $HCOOH(aq) + H_2O(l) \xrightleftharpoons{\text{only some ionised}} HCOO^-(aq) + H_3O^+(aq)$

(d) $C_{12}H_{22}O_{11}(s) \xrightarrow{H_2O} C_{12}H_{22}O_{11}(aq)$

6.36   (a) $Cu^{2+}(s) + CO_3^{2-}(aq) \longrightarrow CuCO_3(s)$
Na^+ and Cl^- are spectator ions

(b) No precipitate forms

(c) $Ni^{2+}(s) + 2\ OH^-(aq) \longrightarrow Ni(OH)_2(s)$
K^+ and Cl^- are spectator ions

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

6.38   (a) HCOOH is the acid reactant, while OH^- is the base reactant.
(b) H_2CO_3 is the acid reactant, while NH_3 is the base reactant.
(c) $H_2C_4H_4O_6$ is the acid reactant, while HCO_3^- is the base reactant.
(d) H_3O^+ is the acid reactant, while CH_3NH_2 is the base reactant.

6.39   (a) $H_3O^+(aq) + OH^-(aq) \longrightarrow 2\ H_2O(l)$

              Li+ and Br− are spectator ions

    (b) $H_2CO_3(aq) + OH^-(aq) \longrightarrow HCO_3^-(aq) + H_2O(l)$

       and $HCO_3^-(aq) + OH^-(aq) \longrightarrow CO_3^{2-}(aq) + H_2O(l)$

           K^+ is a spectator ion.

    (c) $H_3O^+(aq) + CH_3NH_2(aq) \longrightarrow H_2O(l) + CH_3NH_3^+(aq)$

           NO_3^- is a spectator ion

    (d) $H_3Citrate(aq) + OH^-(aq) \longrightarrow H_2Citrate^-(aq) + H_2O(l)$

        $H_2Citrate^-(aq) + OH^-(aq) \longrightarrow HCitrate^{2-}(aq) + H_2O(l)$

        $HCitrate^{2-}(aq) + OH^-(aq) \longrightarrow Citrate^{3-}(aq) + H_2O(l)$

          Na^+ 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_3NH_2 is the Lewis base.
       (d) Cu^{2+} is the Lewis acid, while Cl^- and NH_3 are the Lewis bases.
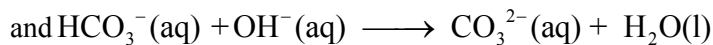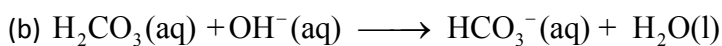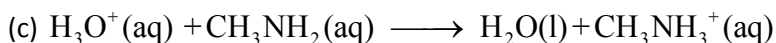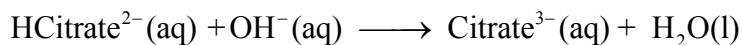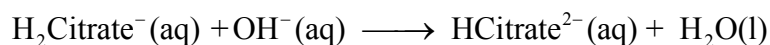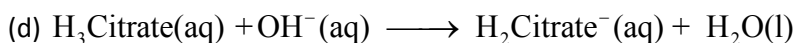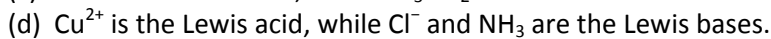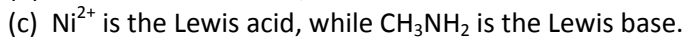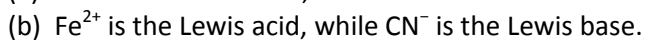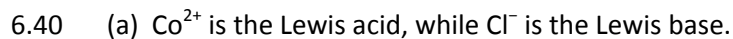
6.41
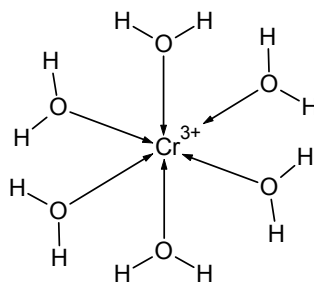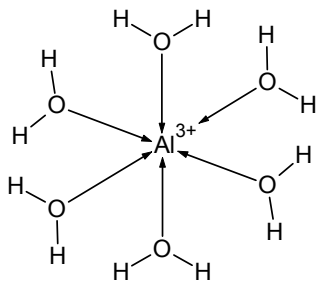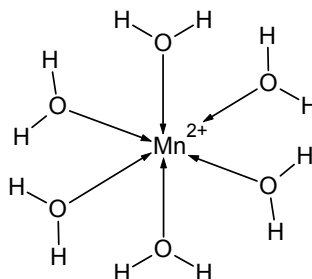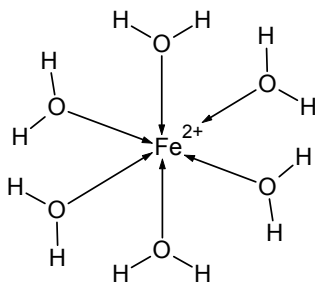
6.42   (a) $[Co(H_2O)_6]^{2+}(aq) + 4\,Cl^-(aq) \rightarrow [CoCl_4]^{2-}(aq) + 6\,H_2O(\ell)$
         Lewis base, Cl^-, competes successfully with the Lewis base, H_2O, to complex Co^{2+}.
         (b) $[Fe(H_2O)_6]^{2+}(aq) + 6\,CN^-(aq) \rightarrow [Fe(CN)_6]^{4-}(aq) + 6\,H_2O(\ell)$
         Lewis base, CN^-, competes successfully with the Lewis base, H_2O, to complex Fe^{2+}.
         (c) $[Ni(H_2O)_6]^{2+}(aq) + 2\,CH_3NH_2(aq) \rightarrow [Ni(CH_3NH_2)_2]^{2+}(aq) + 6\,H_2O(\ell)$
         Lewis base, CH_3NH_2, competes successfully with the Lewis base, H_2O, to complex Ni^{2+}.
         (d) $[Cu(H_2O)_6]^{2+}(aq) + 4\,Cl^-(aq) + 2\,NH_3(aq) \rightarrow [Cu(NH_3)_2Cl_4]^{2-}(aq) + 6\,H_2O(\ell)$
         Lewis bases, Cl^- and NH_3, compete successfully with the Lewis base, H_2O, to complex Cu^{2+}.

6.43   0.478 molL^{-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_3O^+(aq) and NO_3^-(aq)

REVIEW QUESTIONS

6.51   Water has a lower vapour pressure than hexane, 3.17 vs. 20.2 kPa at 25 °C. It takes a higher
         temperature to get 1 atm vapour from water, than it does from hexane – i.e. water has a higher
         boiling point.

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

6.55   (a) C→O
         (b) P→Cl
         (c) B→O
         (d) B→F

6.57   HF > HCl > HBr > HI

6.59   (a) $BeCl_2$ is non-polar.
         (b) HBF_2 is polar. The negative end is at the two F atoms.
         (c) CH_3Cl is polar. The negative end is at the Cl atom.
         (d) SO_3 is non-polar.

6.61 H_2S (g)

6.63   (b)   HCOOH

6.65   (Kr) It is bigger with more electrons

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

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

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

6.73   Propan-1-ol ($CH_3CH_2CH_2OH$) has a higher boiling point than methyl ethyl ether ($CH_3CH_2OCH_3$), a
        compound with the same empirical formula, because propan-1-ol molecules can form hydrogen
        bonds, whereas methyl ethyl ether cannot.

6.75   (a) O_2
        (b) SO_2
        (c) HF
        (d) GeH_4

6.77
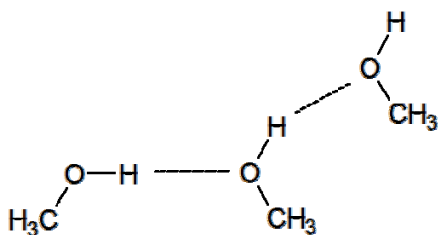
6.79   (a) Water has a higher viscosity than hexane, in spite of its smaller dispersion forces, because of
        its strong hydrogen bonds.
        (b) Glycerol (propan-1,2,3-triol, $HOCH_2CHOHCH_2OH$) is even more viscous than water because it
        has three O-H groups and can form more hydrogen bonds than water.

6.81   The melting point of fumaric acid (287 °C) is much higher than that of maleic acid (131 °C) even
        though these substances are just *cis* and *trans* isomers.
        Maleic acid makes a strong intramolecular hydrogen bond – this reduces opportunities for
        intermolecular hydrogen bonds, as an O and H are already hydrogen bonding. Strong
        intermolecular pairs of hydrogen bonds are formed between adjacent fumaric acid molecules.

6.83   (a) The O end (the negative end) of water points to Ca^{2+}.
        (b) The H end (the positive end) of water points to Br^-.
        (c) The H end (the positive end) of water points to $Cr_2O_7^{2-}$.
        (d) The O end (the negative end) of water points to $NH_4^+(aq)$.

6.85 $H_2O(\ell)$, $Ag^+(aq)$, $NO_3^-(aq)$, $K^+(aq)$ 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,
$$2\,H_2O(\ell) \rightarrow H_3O^+(aq) + OH^-(aq)$$

6.91   Since barium sulfate, $BaSO_4(s)$, precipitates from water, whereas iron (II) sulfate does not, we conclude that $BaSO_4(s)$ is insoluble in water (it has a very low solubility) whereas $FeSO_4(s)$ is soluble.

6.93
$$2\,Cr_2O_7^{2-}(aq) + 28\,H^+(aq) + 12\,e^- \longrightarrow 4\,Cr^{3+}(aq) + 14\,H_2O(\ell)$$
$$3\,C_2H_5OH(aq) + 3\,H_2O(\ell) \longrightarrow 3\,CH_3COOH(aq) + 12\,H^+(aq) + 12\,e^-$$
Here, ethanol, C_2H_5OH, is oxidized to acetic acid, CH_3COOH. Dichromate, $Cr_2O_7^{2-}$, is the oxidizing agent. $Cr_2O_7^{2-}$ is reduced to Cr^{3+}. Ethanol is the reducing agent.

6.95   When nitric acid dissolves in water, nitrate and hydronium ions are produced.
        When barium hydroxide dissolves in water, $Ba^{2+}(aq)$ and $OH^-(aq)$ are produced.

6.97   (a) $[Fe(NH_3)_6]^{2+}$
        (b) $[Zn(CN)_4]^{2-}$
        (c) $[MnF_6]^{4-}$
        (d) $[Fe(CN)_6]^{3-}$
        (e) $[CoCl_4]^{2-}$
        (f) $\{Ni(NH_3)_4(H_2O)_2\}^{2+}$

6.99   To prepare the desired solution, carefully weigh 0.849 g of $AgNO_3(s)$, add it to the volumetric flask, add ~150 mL of de-ionized water, stopper the flask and shake to dissolve the $AgNO_3$ and ensure a homogenenous solution. After the $AgNO_3$ has dissolved, top up the volume to the 250 mL mark with de-ionized water – add the additional de-ionized water in steps, swirling between each step to ensure a homogeneous solution.

6.101   1250 mL of 0.060 mol L^{-1} Na_2CO_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 Na_2CO_3 = 0.254 $molL^{-1}$
         concentration of Na^+ = 0.508 $molL^{-1}$
         concentration of CO_3^{2-} = 0.254 $molL^{-1}$

SUMMARY AND CONCEPTUAL QUESTIONS

6.111   (a) Kinetic energy of the water molecules within and on the surface of the bubble prevents its
         collapse. These "hot" molecules smash into their neighbours pushing open the bubble.
         (b) Bubbles form when the vapour pressure within the heated liquid slightly exceeds
         atmospheric pressure—enough to push open the bubble.

6.113   (a) Hydronium ions appear to diffuse very quickly through an aqueous solution—faster than
         they should be able to via diffusion—because the transfer of hydronium across a cluster of
         water molecules is achieved through successive H^+ ion transfers between adjacent water
         molecules.
         (b) Each proton transfer involves one O atom of a hydronium ion taking the pair of electrons
         from an H atom bonded to it, and another O atom (on a water molecule on the other side of the
         H) donating a lone pair of electrons to the released proton—i.e., accepting the proton.

6.115   (a) Here, the electrostatic attraction of the Ag^+ and Cl^- ions overcomes the dipole-ion forces
         between solvating water molecules and the ions to cause growth of the ionic lattice.
         (b) The lattice is an array of Ag^+ and Cl^- ions. It does not consist of distinct AgCl molecules.

6.117   (a) The electrons in the O–H bond of the CH_3COOH molecule go entirely to the O atom releasing
         a proton which attaches to a lone pair of electrons on a water molecule.
         (b) A covalent bond is broken and a new one made.

6.119   (a) Ammonia is the Lewis base, donating lone pairs of electrons to the copper atom, in the form
         of a coordinate bond. Cu^{2+} is the Lewis acid.
         (b) Ammonia molecules replace water molecules because the N in ammonia forms a stronger
         coordinate bond with copper than the O in water—ammonia is a better ligand.

6.121   (a) an acid-base reaction
         (b) precipitation reaction
         (c) acid-base, and complexation reaction
         (d) oxidation-reduction reaction

Chapter 7

7.1 (a) 1 mol each of 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 Fe_2O_3(s) mixture is the system (initially – later it consists of Al_2O_3(s) and iron). The flask and the laboratory bench are the surroundings.

7.6 (a) The volume of a balloon is a state function.
(b) The time it takes to drive from your home to your college or university is NOT a state function
(c) The temperature of the water in a coffee cup is a state function.
(d) The potential energy of a ball held in your hand is a state function.

7.7 333 kJ

7.10 32.1 kJ

7.11 0.16 kJ
7.12 heat evolved = 2.38 kJ

7.15 −56.3 kJ

7.16 (a) molecular liquid $Br_2(\ell)$.
(b) metallic liquid, $Hg(\ell)$.
(c) ionic solid Na_2SO_4(s).
(d molecular liquid $CH_3CH_2OH(\ell)$.
(e) 1 mol L^{-1} concentration Cl^-(aq).

7.17 (a) The standard enthalpy change of this reaction, $\Delta_r H°$, is the heat absorbed (hence a negative number when is evolved) at a constant temperature of 25 °C, when exactly 1.00 mol of CO(g) and 0.500 mol of O_2(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 CO_2(g) at 1 bar.
(b) The standard enthalpy change of this reaction, $\Delta_r H°$, 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 Mg^{2+}(aq) at 1.00 mol L^{-1} concentration and 1 mol H_2(g) at 1 bar partial pressure.
(c) The standard enthalpy change of this reaction, $\Delta_r H°$, 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 $H_2O(\ell)$.

7.19 (a) 1.9 kJ

7.20 116.8 kJ

7.21 (a) The standard molar enthalpy of formation of bromine, $Br_2(\ell)$, is the standard enthalpy change of the following reaction:
$Br_2(\ell) \rightarrow Br_2(\ell)$ 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:
$Fe(s) + Cl_2(g) \rightarrow FeCl_3(s)$ 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:
$12\ C(graphite) + 11\ H_2(g) + \dfrac{11}{2} O_2(g) \rightarrow C_{12}H_{22}O_{11}(s)$ at 25 °C

7.22 The standard molar enthalpy of formation of liquid methanol, $CH_3OH(\ell)$, is the standard enthalpy change of the following reaction:
$C(graphite) + 2\ H_2(g) + \dfrac{1}{2} O_2(g) \rightarrow CH_3OH(\ell)$ 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) $H_2O(\ell)$
        (b) NaCl(s)
        (c) $Hg(\ell)$
        (d) $CH_4(g)$
        (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

$$\begin{array}{c}
\underline{2\ N_2(g) + 6\ H_2(g) + 5\ O_2(g)} \\
\uparrow\ -4\ \Delta_fH°[NH_3(g)] \qquad\qquad | \\
\underline{4\ NH_3(g) + O_2(g)} \quad | \qquad\qquad\qquad\qquad | \\
| \qquad\qquad | \quad 4\times\Delta_rH°[NO(g)] + 6\times\Delta_rH°[H_2O(g)] \\
4\times\Delta_rH°[NO(g)] + 6\times\Delta_rH°[H_2O(g)]\ | \qquad\qquad | \\
-\ 4\times\Delta_rH°[NH_3(g)] \qquad\quad | \qquad\qquad | \\
\downarrow \qquad\qquad \downarrow\ \underline{4\ NO(g) + 6\ H_2O(g)}
\end{array}$$
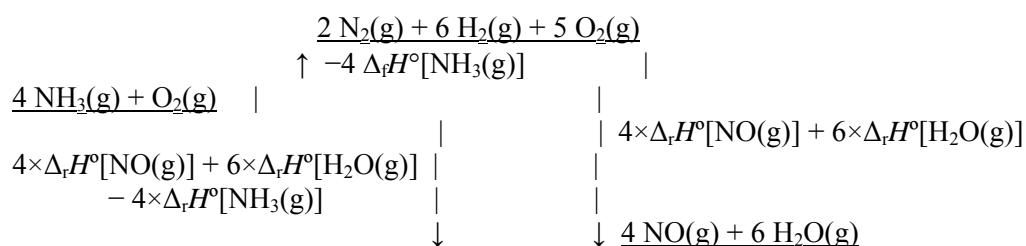
7.53 -77.69 kJ

7.55 $\Delta_rH°$ = -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, $\Delta_r H°$, 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, $\Delta_f H°$, 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　　$\Delta_r H°$ = −1433.5 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　　- 6.2×10^{10} 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, $Br_2(g)$
(b) Sodium, Na(s)
(c) Chlorine, $Cl_2(g)$
(d) The elements with atomic numbers 34, 35, 36, 37, and 38 are Se, Br, Kr and Rb. Rubidium, Rb, is the most powerful reducing agent.

8.5　C < Si < Al

8.7　(c)　　Li < Si < C < Ne

8.8　(a) The fourth ionization energy of Al is much larger than the third – more so than successive ionization energies usually increase. After removing three electrons from an aluminum atom – the result of the first three ionization steps – the atom (now an ion) is left with the electron configuration of Ne, a noble gas. Al^{3+} 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) Ba^{2+}
(c) K
(d) Se^{2-}
(e) Cl^-
(f) Pb^{2+}

8.14　(a) O^-
(b) Cl^-

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

8.16   (a) -1.46×10^5 Jmol^{-1} = -146 kJmol^{-1}
        (b) 182 KJmol^{-1}

8.18 2.043×10^{-18} J; 308.3 THz; 97.24 nm

8.19 2.2×10^{-25} nm

8.20
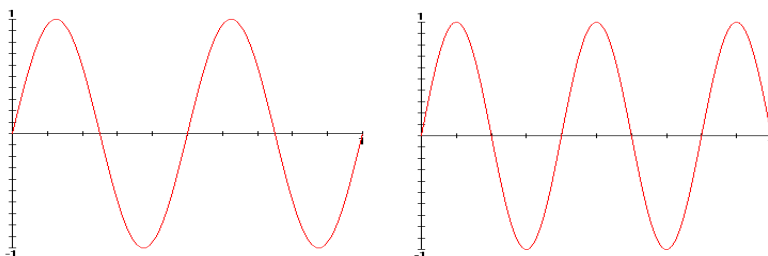
8.22   (a) valid
        (b) not valid
        (c) not valid

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

8.25   (a) $n = 4$, $l = 2$, $m_l = 0$, $m_s = 0$ is not valid because m_s is always ± ½ because s = ½
        for an electron. m_s is never equal to zero.
        (b) $n = 3$, $l = 1$, $m_l = -3$, $m_s = -$ ½ is not valid because $m_l = -3$ does not go with $l = 1$. $m_l = -1$, 0, or
        1 in this case.
        (c) $n = 3$, $l = 3$, $m_l =$ −1, $m_s = +$ ½ is not valid because l must be less than or equal to $n − 1$.

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

z

y

x

s obital 90% isosurface

p obital 90% isosurface
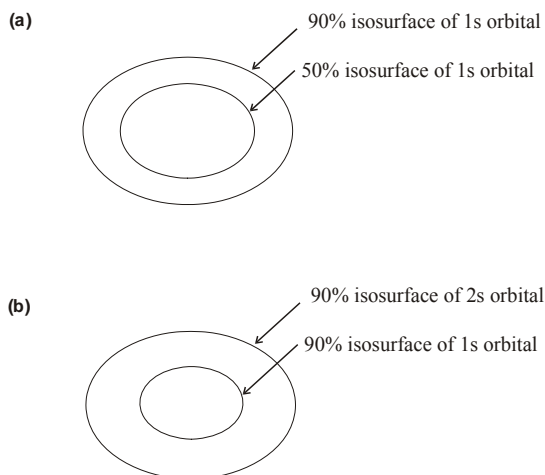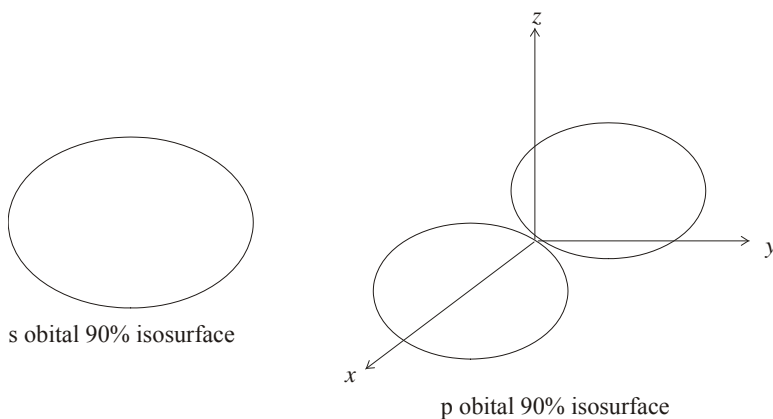
8.30   (a) 18
       (b) 10
       (c) 1
       (d) none
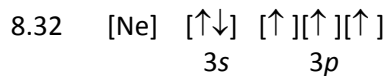
8.32   [Ne]   [↑↓] [↑][↑][↑]
               3s 3p
       The last five electrons correspond to the quantum numbers,
       $n = 3$,
       $l = 0$ and $m_l = 0$, and $m_s = -\frac{1}{2}$ or $+\frac{1}{2}$ 2 electron states
       $l = 1$ and $m_l = -1$, 0 or 1 and $m_s = +\frac{1}{2}$ 3 electron states

8.34 $Z^*(_{12}Mg) = +2.85$; $Z^*(_{15}P) = +4.8$; $Z^*(_{18}Ar) = +6.75$

8.35 $Z^*(_8O) = +4.55$; $Z^*(_8O^{2-}) = +3.85$

8.36 Although $_{84}$Po has a lot more electrons than $_{11}$Na, the electrons of Po are held so much more tightly that it is smaller. The effective nuclear charges, +5.45 and +2.2, show that even the valence electrons of Po are held more tightly than the valence electrons of Na. The valence electrons determine the size of the atom.

8.39 Z*(Na) = +2.2; Z*(Si) = +4.15; Z*(Ar) = +6.75

8.40 Z*(N^{3-}) = +2.85; 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.

8.41 Z*(Na^+) = +6.85; Z*(Mg^{2+}) = +7.85; 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.

8.42 Z*(Mg^-) = +2.5; 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.

8.43 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 °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 °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 2.179×10^{-18} J

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

8.63 (a) 10
      (b) $\boldsymbol{n = 5}$ to a level with $\boldsymbol{n = 1}$.
      (c) $\boldsymbol{n = 5}$ to the level with $\boldsymbol{n = 4}$.

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

8.67 0.145 nm

8.69

(a)
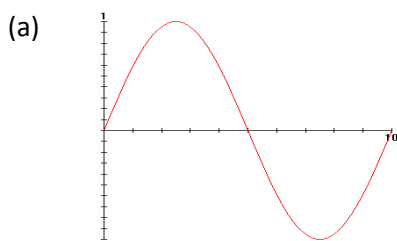
The wavelength of this wave is 10 cm.

(b)
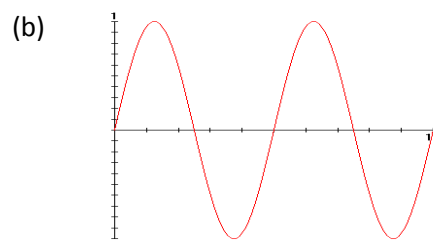
The wavelength of this wave is 5 cm.

(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 $2 \times 4 - 1 = 7$.
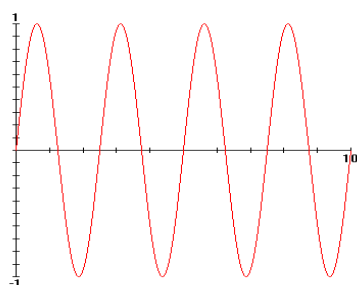
8.71 $n = 4$, $l = 1$ and $m_l = -1, 0, 1$

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 6*s*, 4*p*, 5*d*, and 4*f* are as follows:

$$6s \ \text{means} \ n = 6, \ l = 0$$
$$4p \ \text{means} \ n = 4, \ l = 1$$
$$5d \ \text{means} \ n = 5, \ l = 2$$
$$4f \ \text{means} \ n = 4, \ l = 3$$

(b) For a 4*p* orbital there are $n - 1 = 3$ radial nodes (spherical in shape) and $l = 1$ nodal planes. $3 + 1 = 4$ altogether

For a 6*d* 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 $[Ar]4s^2 3d^{10} 4p^3$
(b) $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6$ or $[Ar]4s^2 3d^{10} 4p^6 = [Kr]$

8.93   (i) $Z^*(Mg) = +2.85$
(ii)) $Z^*(Mg^+) = +3.2$
(iii) $Z^*(Mg^{2+}) = +7.85$
The increasing effective nuclear charge for these three species correlates with their sizes: Mg > Mg^+ > Mg^{2+}. Note, especially the jump from Mg^+ to Mg^{2+}.

8.95 $Z^*(N^{3-}) = +2.85$; $Z^*(O^{2-}) = +3.85$; $Z^*(F^-) = +4.85$
These effective nuclear charges correlate with the relative sizes of the ions: $F^- < O^{2-} < N^{3-}$

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 $^+$ 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

10.3 NH_4^+
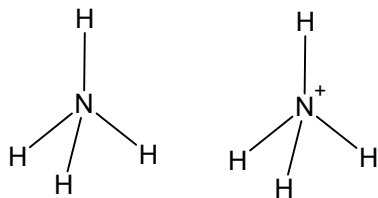
CO

SO_4^{2-}
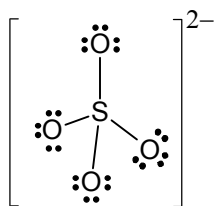
10.4
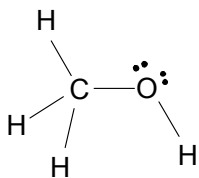
CH$_3$OH   NH$_2$OH
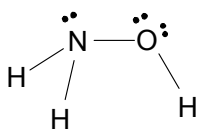
10.5
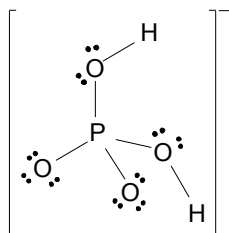
10.6   (a) Acetylide ion, C_2^{2-}, is isoelectronic with N_2.
        (b) SO_2
        (c) OH^-

10.9
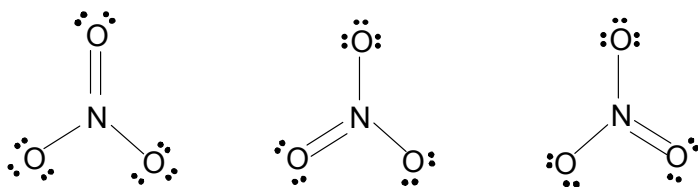
The three resonance structures of nitrate, NO_3^-.
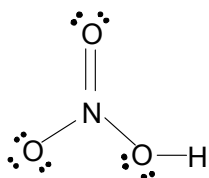
A structure for nitric acid, HNO_3

10.11
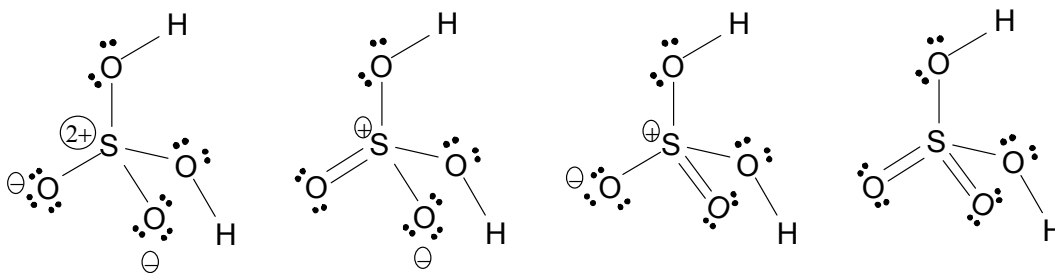
The structure on the right, with no formal charges, is the preferred Lewis structure.

10.12

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

10.13
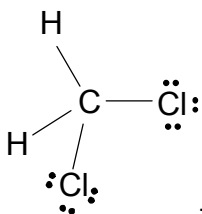
Tetrahedral shape. The Cl—C—Cl bond angle is predicted to be 109.5°

10.16

BF$_3$

BF$_4^-$
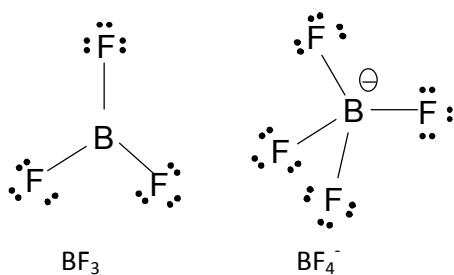
BF$_3$ is trigonal planar. BF$_4^-$ is tetrahedral.

10.17

(a) phosphate ion, PO$_4^{3-}$, is tetrahedral
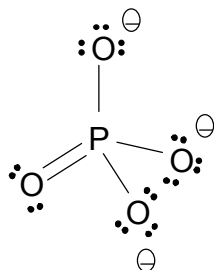
(b) phosphoric acid molecule, H$_3$PO$_4$, is tetrahedral at the P
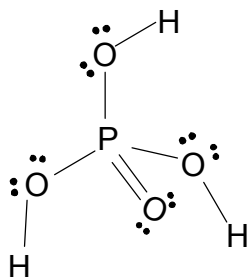
(c) sulfate ion, SO$_4^{2-}$, is tetrahedral
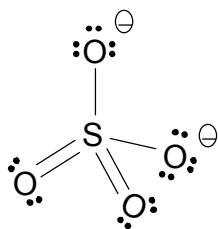
(d) sulfite ion, SO_3^{2-}, is trigonal pyramidal
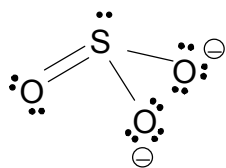
(e) ethanol is tetrahedral at the carbons and bent at the oxygen
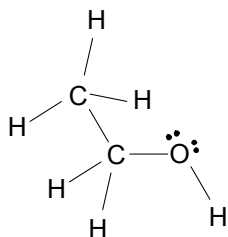
(f) Acetone, $CH_3C(O)CH_3$, is trigonal planar at the carbonyl carbon and tetrahedral at the methyl carbons.
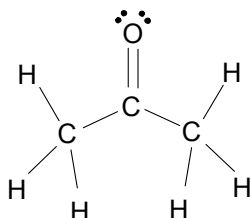
10.18
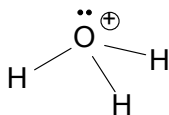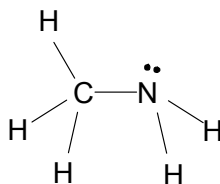
(a)   (b)

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

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

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

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

10.19
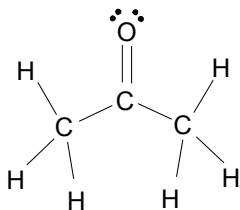
The methyl C atoms have the tetrahedral distribution of electron regions. This means sp^3 hybridization at the methyl carbon atoms. Three of the sp^3 orbitals overlap with s orbitals on H atoms to form the C-H bonds, while the fourth makes a bond with the carbonyl C atom.

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

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

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

10.20

:N≡N:
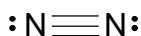
The N atoms have a linear arrangement of two electron regions. This means sp hybridization. An sp orbital from each N atom is used to make the N-N σ bond. The remaining sp orbitals accommodate the lone pairs – one on each atom.

The two remaining p orbitals on each atom overlap in pairs to form the two N-N π bonds. Specifically, the p_x orbitals overlap to form the π_x bond, while the p_y orbitals overlap to form the π_y bond.

10.21
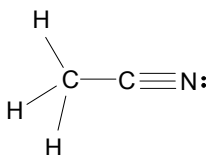
The H-C-H, H-C-C, and C-C-N bond angles are estimated to be 109.5º, 109.5º and 180º, respectively.

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

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

The two remaining p orbitals on the nitrile C and N atoms overlap in pairs to form the two C-N π bonds.
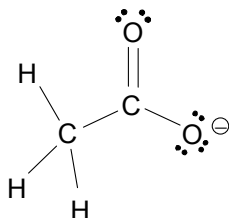
10.22

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

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

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

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

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

10.25 $H_2^+ : (\sigma_{1s})^1$

   $He_2^+ : (\sigma_{1s})^2 (\sigma_{1s}^*)^1$

   $H_2^- : (\sigma_{1s})^2 (\sigma_{1s}^*)^1$
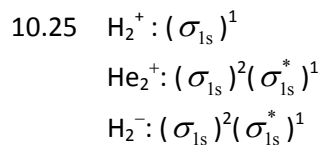
   H_2^+ has a bond order of ½. It should exist. But, it is weakly bound. He_2^+ and H_2^- have the same bond order.

10.26 Li_2^- anion should exist. It is weakly bound with bond order, ½.

10.27   Electron configuration of ground state O_2^+

   $$[\text{core electrons}](\sigma_{2s})^2 (\sigma_{2s}^*)^2 (\pi_{2p_y})^2 (\pi_{2p_z})^2 (\sigma_{2p_x})^2 (\pi_{2p_y}^*)^1$$

   Bond order = 2 ½

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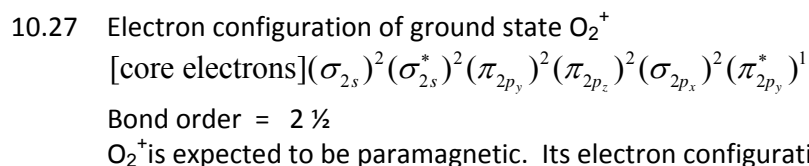
REVIEW QUESTIONS

10.31   4

10.33

(a)

(b)

(c)

(d)
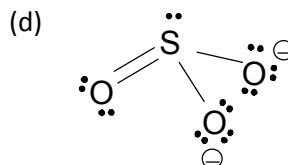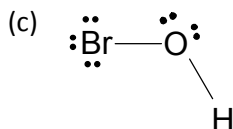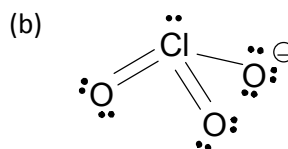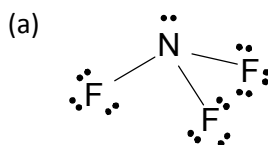
10.35
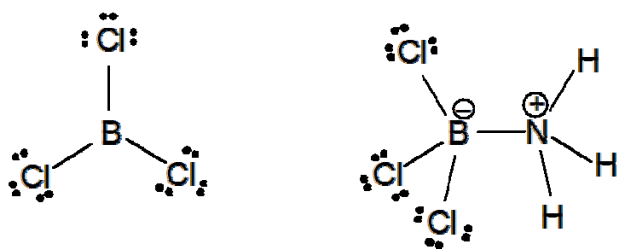
10.37

(a) SO_2
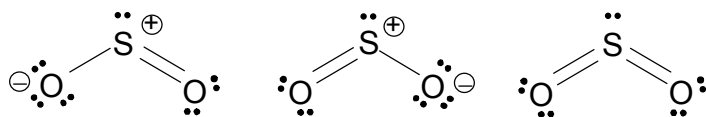
(b) NO_2
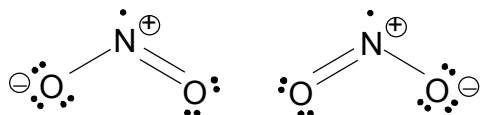
(c) SCN^-
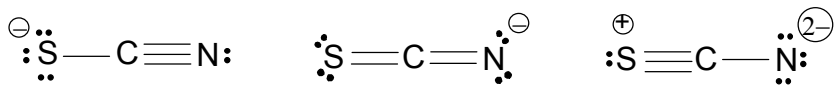
10.39

Average C-O bond order = 3/2

Chemistry, First Canadian Edition
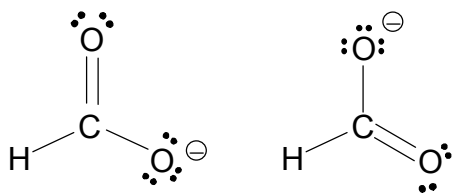
10.41
(a)
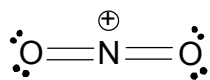
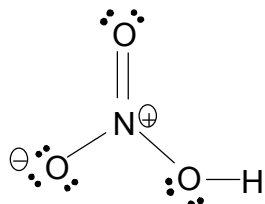Formal charges are zero on O's and +1 on N.

(b)
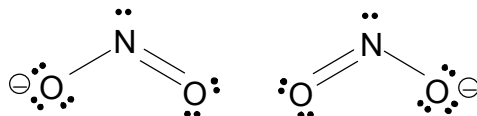
The N has a formal charge of zero. The formal charges on the two equivalent O's are zero and −1.
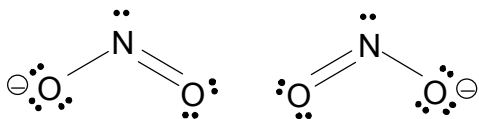
(c)
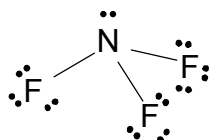
All atoms have zero formal charge.

(d)
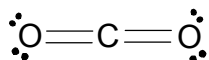

Formal charges are as shown.

10.43

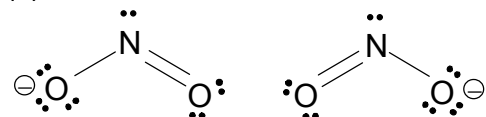If H^+ attaches to NO_2^- (to form the acid HNO_2), it attaches to an O atom – not N.

10.45

(a)

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

(b)

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

(c)

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

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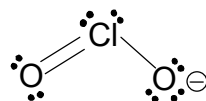
There are four electron regions about the oxygen atom. The electron geometry is tetrahedral, while the molecular geometry is bent – there are two lone pairs on the central atom. This molecule is likely more bent than O_3 or NO_2^-, because there are two lone pairs on the central atom in this case.

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

10.49
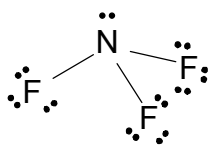
The molecular geometry is trigonal pyramidal – there is a lone pair – while the electron geometry about the N atom is tetrahedral.

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

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

10.53

(a) SO_2
The O-S-O bond angle is about 120º.
The sulfur atom uses sp^2 orbitals to form two σ bonds – one with each O atom. The other sp^2 orbital accommodates a lone pair. We can describe the Lewis structure with only one double S-O bond with the remaining unhybridized p orbital. It forms a π bond with just one of the O atoms.
However, the structure with two S-O double bonds minimizes formal charges and, as such, is preferred. To describe the bonding in this case requires the use of a 1 d orbital on S – since in this structure, S accommodates 10 electrons in its valence shell. Two pd orbitals on S form two π bonds - one with each of the O atoms.

(b) SO_3
The O-S-O bond angle is 120º.
The sulfur atom uses sp^2 orbitals to form three σ bonds – one with each O atom. In accord with the formal charge minimized structure, we use three pd^2 orbitals on S to form three π bonds - one with each of the O atoms. Otherwise, if we use just the p orbital, then S can form only one S-O π bond.

(c) SO_3^{2-}
The O-S-O bond angle is 109.5º.
The sulfur atom uses sp^3 orbitals to form three σ bonds – one with each O atom. The other sp^3 orbital accommodates a lone pair on S.
In accord with the formal charge minimized structure, we use two pd orbitals on S to form two π bonds - one with each of two O atoms.

(d) SO_4^{2-}
The O-S-O bond angle is 109.5º.

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

10.55   In linear CO_2 the carbon atom uses two sp orbitals to form σ bonds with each O atom. Each of the two unhydridized p orbitals forms a π bond with an O atom. In $CO_3{}^{2-}$, there are two single C-O bonds and one double C-O bond, giving rise to three equivalent resonance structures. The carbon atom uses three sp^2 orbitals to form σ bonds with each of the three O atoms. The 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 120º, 109.5º (actually 104º), 109.5º and 120º, respectively.
(b) According to the valence bond model, carbon atoms 1, 2, and 3 are sp^2, sp^2 and sp^3 hybridized, respectively.

10.59
(a)
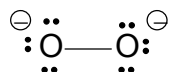
The bond order in $O_2{}^{2-}$ is 1.

(b) The molecular orbital theory electron configuration for $O_2{}^{2-}$ is (using unhybridized orbitals)
$$[\text{core electrons}](\sigma_{2s})^2(\sigma_{2s}^*)^2(\pi_{2p_y})^2(\pi_{2p_z})^2(\sigma_{2p_x})^2(\pi_{2p_y}^*)^2(\pi_{2p_z}^*)^2$$
bond order $= \frac{1}{2} \times (2 + 2 + 2 + 2 - 2 - 2 - 2) = 1$
(c) For $O_2{}^{2-}$, the valence bond description and the molecular orbital description predict the same bond order and the same magnetic behaviour (i.e. diamagnetic – NOT paramagnetic – there are no unpaired electrons in either description).

10.61   Molecular orbital; theory electron configurations (core electrons omitted):
(a) NO
$$(\sigma_{2s})^2(\sigma_{2s}^*)^2(\pi_{2p_y})^2(\pi_{2p_z})^2(\sigma_{2p_x})^2(\pi_{2p_y}^*)^1$$
an unpaired electron → paramagnetic
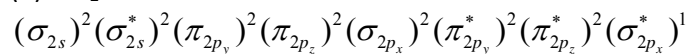HOMO $= \pi_{2p_y}^*$ or $\pi_{2p_z}^*$ ← same energy (by symmetry)

(b) OF^-
$$(\sigma_{2s})^2(\sigma_{2s}^*)^2(\pi_{2p_y})^2(\pi_{2p_z})^2(\sigma_{2p_x})^2(\pi_{2p_y}^*)^2(\pi_{2p_z}^*)^2$$
no unpaired electrons → NOT paramagnetic – i.e. diamagnetic
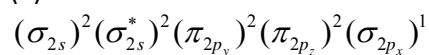HOMO $= \pi_{2p_y}^*$ or $\pi_{2p_z}^*$ ← same energy (by symmetry)

(c) $O_2{}^{2-}$
$$(\sigma_{2s})^2(\sigma_{2s}^*)^2(\pi_{2p_y})^2(\pi_{2p_z})^2(\sigma_{2p_x})^2(\pi_{2p_y}^*)^2(\pi_{2p_z}^*)^2$$
no unpaired electrons → NOT paramagnetic – i.e. diamagnetic

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

(d) Ne_2^+

$$(\sigma_{2s})^2(\sigma^*_{2s})^2(\pi_{2p_y})^2(\pi_{2p_z})^2(\sigma_{2p_x})^2(\pi^*_{2p_y})^2(\pi^*_{2p_z})^2(\sigma^*_{2p_x})^1$$

an unpaired electron → paramagnetic

HOMO = $\sigma^*_{2p_x}$

(e) CN

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

an unpaired electron → paramagnetic

HOMO = σ_{2p_x}

SUMMARY AND CONCEPTUAL QUESTIONS

10.63
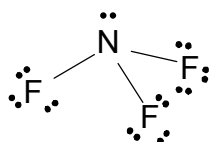
NF_3 has four electron pairs about the central atom, and a trigonal pyramidal shape.
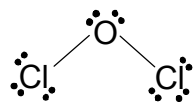
OCl_2 has four electron pairs about the central atom, and a bent shape.

10.65   The average C-O bond order in formate (HCO_2^-) is 1.5 – there are two equivalent C-O bonds
represented as a single and a double bond in the two resonance structures.
In methanol (CH_3OH), the C-O bond is just a single bond – there is just one structure.
In carbonate (CO_3^{2-}), there are three equivalent C-O bonds. One is a double bond, while the
other two are single bonds. The average bond order is 4/3 = 1.3333.
Formate has the strongest C-O bond, which is expected to be the shortest.
Methanol has the weakest C-O bond, which is expected to be the longest.

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

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

10.69   (a) Angles 1, 2, and 3 equal about 120 º, 180º and 120º, 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 120º, 109.5º (actually 104º) and 120º, 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 $H_3N{\rightarrow}BF_3$ is tetrahedral.
(b) In BF_3, the valence orbitals of boron are sp^2 hybridized.
In $H_3N{\rightarrow}BF_3$, 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 32×10^4 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, $\dfrac{\text{Rate of effusion of } SF_6}{\text{Rate of effusion of He}}$ = 0.166

and $\dfrac{\text{Rate of effusion of } N_2}{\text{Rate of effusion of He}}$ = 0.378

11.19 160 $gmol^{-1}$

11.23 (a) the dispersion forces in liquid O_2 < (c) the dipole induced dipole interactions of O_2 dissolved in H_2O < (b) the hydrogen bonding forces in liquid CH_3OH

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

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

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

11.27 (a) The density of liquid CO_2 is less than that of solid CO_2.
       (b) gas phase
       (c) No.

11.29 T (80 km) < T (25 km) < T (110 km) < T (5 km)

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 H_2, CO_2 and SF_6 are 37.277, 37.218 and 37.157 Lmol^{-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 1.22×10^7 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_{Total} = 580 kPa
       $P(H_2)$ = 412 kPa
       $P(Ar)$ = 168 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 kPa. Using van der Waals equation, p = 2991 kPa.

11.71 When solid I_2 dissolves in methanol, CH_3OH, dispersion forces holding I_2 molecules in their lattice positions must be overcome. Hydrogen bonding forces between methanol molecules are disrupted when methanol solvates iodine. The solvation forces between methanol and iodine are dipole induced dipole interactions.

11.75 (a) 18.7 kPa
       (b) At about 75 °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
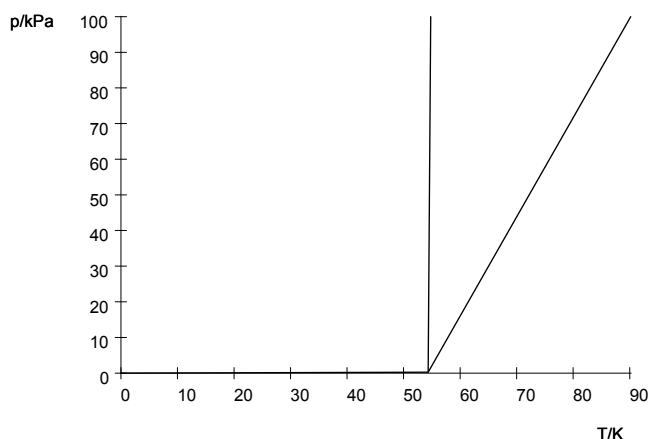
This phase diagram is constructed by (1) connecting (T = 0 K, p = 0 kPa) to the triple point, (T = 54.34 K, p = 0.267 kPa), to get the solid-gas coexistence curve, (2) connecting the triple point to the normal melting point, (T = 54.8 K, p = 100 kPa), to get the solid-liquid coexistence curve, and (3) connecting the triple point to the normal boiling point, (T = 90.18 K, p = 100 kPa), to get the liquid-gas coexistence curve.
At T = −196 °C (i.e. T = 77 K), p = 76.5 kPa

11.83   1.624 kJ

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

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

SUMMARY AND CONCEPTUAL QUESTIONS

11.91   306 K

11.93   (a) A 1.0-L flask containing 10.0 g each of O_2 and CO_2 at 25 °C has greater partial pressure of O_2 than CO_2. The partial pressures depend on the numbers of moles – 10.0 g of the lower molar mass O_2 has more moles than 10.0 g of CO_2.
(b) The lighter O_2 molecules have greater average speed – average speed is proportional to $M^{-1/2}$.

11.95   (a) This is NOT a gas. An ideal gas would expand 100 fold if its pressure were changed from 100 bar to 1 bar (atmospheric pressure). Only a liquid or solid is so incompressible as to expand only 10% when relieved of such a large pressure.
(b) This is NOT a gas. A density of 8.2 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 m^3 as the same volume of air, at the same temperature and pressure, is definitely a gas (assuming the temperature and pressure are not unusual).

11.97   (a) 46.0 g

(b)
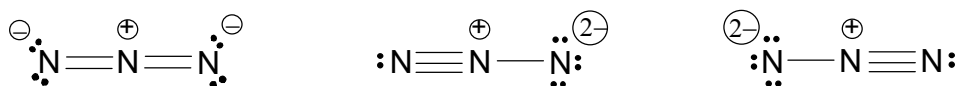
The structure on the left is the most reasonable.

(c) The azide ion is linear.

11.99   0.61 kPa corresponds to essentially zero pressure in the given phase diagram. To solidify carbon dioxide requires a temperature no greater than −90 °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 × 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 ºC

(b)   At 25 °C, there is net evaporation of liquid CCl_2F_2 until the dichlorodifluoromethane partial pressure inside the steel cylinder equals about 6.5 atm, the vapour pressure of CCl_2F_2 at 25 °C. Here we assume that the cylinder is not so big that 25 kg of CCl_2F_2 is not enough to fill the cylinder to this pressure – i.e. no bigger than about 780 L.

(c) The CCl_2F_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_2F_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

11.119
    (a)
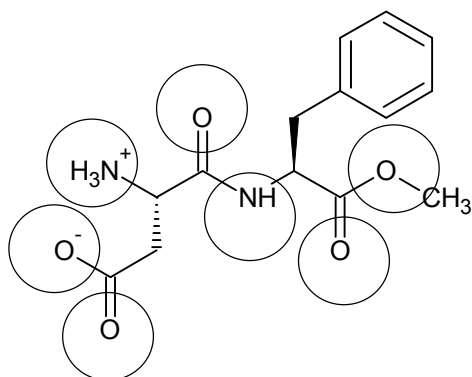
(b) Aspartame is capable of hydrogen bonding. Sites of hydrogen bonding are circled on the structure.

Chapter 12

12.2 (a) The lattice enthalpy of LiCl(s) is larger than that of KCl(s) because the Li^+ ion is smaller than K^+ and so gets closer to Cl^-. The electrostatic potential energy is lower – it takes more energy to break the ionic bonds.

(b) The enthalpy of aquation of Li^+ and Cl^- is larger in magnitude than that of K^+ and Cl^- (they are both negative) because the Li^+ ion is smaller than K^+. The interaction of water molecules with Li^+ is stronger than with K^+ because they get closer to the smaller lithium ions.

12.4 1.12×10^{-2} molL^{-1}

12.5 The solubility of Li_2SO_4 in water decreases slightly as we increase the temperature from 10 °C. The amount of solid Li_2SO_4 in the second beaker will increase a little.

The solubility of LiCl in water increases slightly as we increase the temperature from 10 °C. The amount of solid LiCl in the first beaker will decrease.

12.7 mole fraction = 0.00210
molality = 0.117 molkg^{-1}
mass percent = 3.85 %

12.8 19.85 kPa

12.10 4.66 kPa

12.12 The freezing point of the solution is −5.25 °C. The added ethylene glycol is not enough to prevent freezing at −25 °C.

12.14 472 g mol^{-1}

12.16 −2.81 ºC

12.18 1.40×10^5 g mol^{-1}

12.19 754 kPa

12.20 (a) volume = 4.19×10^6 nm^3
Surface area = 1.26×10^5 nm^2
(b) 2.4×10^{14} spheres; surface area = 30 m^2

REVIEW QUESTIONS

12.21 (a) 6.20×10^{-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_2SO_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_2SO_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 answers necessary for this chapter.

Chapter 13

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

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

(c) $Q = \dfrac{[Cu^{2+}][NH_3]^4}{[Cu(NH_3)_4^{2+}]}$

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

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 x 10^{-2} mol L^{-1}
The cadmium solution has a higher ammonia concentration

13.7   (a) [C$_6$H$_{10}$I$_2$] = 0.015 mol L^{-1}
     [C$_6$H$_{10}$] = 0.035 mol L^{-1}
(b) K = 0.082

13.10   [H$_2$] = [I$_2$] = 1.54 × 10^{-3} mol L^{-1}
[HI] = 8.92 × 10^{-3} 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   [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.

$$2\,NOCl(g) \;\rightleftharpoons\; 2\,NO(g)\,+\,Cl_2(g) \qquad \Delta_{rxn}H^\circ = +77.1\,kJ\,mol^{-1}$$
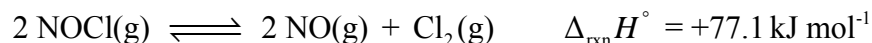
(i) Initially, the mixture is at equilibrium. So, $Q = K$. When temperature increases, the equilibrium constant generally changes. For an endothermic reaction such as this, the equilibrium constant increases. Now, $Q < K'$ where K' is the new equilibrium constant. Q has not changed – at least at first. 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 SO_3 decreases if the temperature is increased?

$$2\,SO_2(g)\,+\,O_2(g) \;\rightleftharpoons\; 2\,SO_3(g) \qquad \Delta_{rxn}H^\circ = -198\,kJ\,mol^{-1}$$
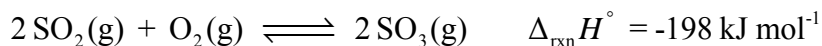
(i) Initially, the mixture is at equilibrium. So, $Q = K$. For an exothermic reaction such as this, the equilibrium constant decreases. Now, $Q > K'$ where K' is the new equilibrium constant. To return to equilibrium, Q must decrease – i.e. the reaction proceeds in the reverse direction to return to 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 x 10^{-4}) < K (4.0 x 10^{-4}), the reaction proceeds in the forward direction

13.21 $K = 1.2$

13.25 $K = 9.3 \times 10^{-5}$

13.29   (a) $K = 1.6$
       (b) The new equilibrium concentrations of H_2O and CO are both 0.014 mol L^{-1}

13.31   0.0002 g

13.33 $[NH_3]_{eqm} = 0.66$ mol L^{-1}
       $[N_2]_{eqm} = 0.57$ mol L^{-1}
       $[H_2]_{eqm} = 1.71$ mol L^{-1}
       $p = 17.7$ MPa

13.35 4.44×10^{25}

13.37   (a) $K = 0.041$
       (b) $K = 590$

13.39   (a) [butane] = 1.1 mol L^{-1}
         [isobutane] = 2.9 mol L^{-1}
       (b) same as in part (a)

13.41   (a) All three gases increase in concentration.
       (b) All three gases increase in concentration.
       (c) A net decrease in all gas concentrations.
       (d) Product gases decrease in concentration, while reactant gases increase in concentration.

13.43   (a) (i) no net reaction
       (b) (ii) net reaction to form more $BaCO_3(s)$
       (c) (i) no net reaction
       (d) (iii) net reaction to form more BaO(s) and $CO_2(g)$.
       (e) (iii) net reaction to form more BaO(s) and $CO_2(g)$.

13.45 $[PCl_5]_{eqm} = 0.0198$ mol L^{-1}
       $[PCl_3]_{eqm} = 0.0232$ mol L^{-1}
       $[Cl_2]_{eqm} = 0.0404$ 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 $SO_2Cl_2(g)$ 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) $$HCOOH(aq) + H_2O(l) \rightleftharpoons HCOO^-(aq) + H_3O^+(aq)$$
               acid   base   conj. base   conj. Acid

        (b) $$NH_3(aq) + H_2S(aq) \rightleftharpoons NH_4^+(aq) + HS^-(aq)$$
               base   acid   conj. acid   conj. Base

        (c) $$HSO_4^-(aq) + OH^-(aq) \rightleftharpoons SO_4^{2-}(aq) + H_2O(l)$$
               acid   base   conj. base   conj. acid

14.3 $HC_2O_4^-(aq)$ acting as a Brønsted-Lowry acid:
        $$HC_2O_4^-(aq) + OH^-(aq) \rightleftharpoons C_2O_4^{2-}(aq) + H_2O(l)$$

        $HC_2O_4^-(aq)$ acting as a Brønsted-Lowry base:
        $$HC_2O_4^-(aq) + H_3O^+(aq) \rightleftharpoons H_2C_2O_4(aq) + H_2O(l)$$

14.5 $[H_3O^+]$ = 4.0×10^{-3} mol L^{-1}
        $[OH^-]$ = 2.5×10^{-12} mol L^{-1}

14.7   (a) pOH = 2.9; pH=11.1
        (b) $[H_3O^+]$ = 4.79×10^{-5} mol L^{-1}; $[OH^-]$ = 2.09×10^{-10} mol L^{-1}
        (c)) pOH = 3.54; $[OH^-]$ = 2.88×10^{-4} mol L^{-1}

14.9   (a) pK_a = 4.2
        (b) aquated chloroacetic acid is a stronger acid than aquated benzoic acid

14.10   It fits between benzoic and acetic acids in Table 14.5.

14.12 K_b = 7.1×10^{-11}
        It fits between dihydrogenphosphate and fluoride in Table 14.5.

14.13   (a) An aqueous solution of KBr has a pH of 7.
         (b) An aqueous solution of NH_4NO_3 has a pH < 7
         (c) An aqueous solution of $AlCl_3$ has a pH < 7
         (d) An aqueous solution of Na_2HPO_4 has pH > 7

14.15   (a) The H attached to N has the greatest concentration of positive charge. As such, this is the
         most acidic hydrogen atom.
         (b) The unprotonated ring nitrogen has the greatest concentration of negative charge. It is the
         most basic nitrogen atom in imidazole.

14.16   CO a Lewis base.

14.17
         (a)   (b)

                   Lewis Base   Lewis Base

         (c)   (d)

                   Lewis Base
                                                                  Lewis Acid

         (e)   (f)
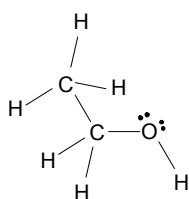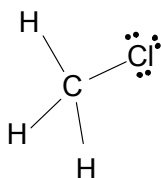
         Lewis base, through Cl atoms
                                                                  Lewis Base
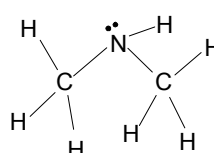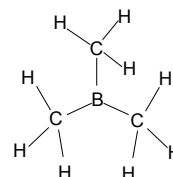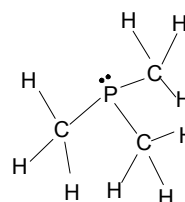
14.19 K_a = 6.87 x 10^{-5}

14.22 $[CH_3COO^-]$ = $[H_3O^+]$ = 0.0013 mol L^{-1}
         $[CH_3COOH]$ = 0.0987 mol L^{-1}
         pH= 2.89
         % acetic acid ionized = 1.3 %

14.24   The results shown in Table 14.7 are correct.

14.25   The results shown in Table 14.8 are correct.

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

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

       (b) 0.18%

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

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

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

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

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

       (b) At pH = 9.0
           (i) 1.33 x10^{-7}
           (ii) 1.6 x 10^{-2}
           (iii) 2.78 x 10^3
       At pH = 9.0, the dominant species is HPO$_4^{2-}$

14.36 (a) phenylalanine

$$\frac{[H_2Phe^+]}{[HPhe]} = \frac{[H_3O^+]}{K_{a1}} = \frac{10^{-7.40}}{10^{-1.83}} = 10^{-5.57} = 2.7 \times 10^{-6}$$

$$\frac{[HPhe]}{[Phe^-]} = \frac{[H_3O^+]}{K_{a2}} = \frac{10^{-7.40}}{10^{-9.13}} = 10^{1.73} = 54$$

The dominant species at pH = 7.40 is HPhe.
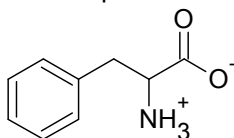
(b) glutamic acid

$$\frac{[H_3Glu^+]}{[H_2Glu]} = \frac{[H_3O^+]}{K_{a1}} = \frac{10^{-7.40}}{10^{-2.19}} = 10^{-5.21} = 6.2 \times 10^{-6}$$

$$\frac{[H_2Glu]}{[HGlu^-]} = \frac{[H_3O^+]}{K_{a2}} = \frac{10^{-7.40}}{10^{-4.25}} = 10^{-3.15} = 7.1 \times 10^{-4}$$

$$\frac{[HGlu^-]}{[Glu^{2-}]} = \frac{[H_3O^+]}{K_{a3}} = \frac{10^{-7.40}}{10^{-9.67}} = 10^{2.27} = 190$$

The dominant species at pH = 7.40 is HGlu⁻
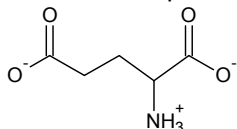
(c) lysine

$$\frac{[H_3Lys^{2+}]}{[H_2Lys^+]} = \frac{[H_3O^+]}{K_{a1}} = \frac{10^{-7.40}}{10^{-2.18}} = 10^{-5.22} = 6.0 \times 10^{-6}$$

$$\frac{[H_2Lys^+]}{[HLys]} = \frac{[H_3O^+]}{K_{a2}} = \frac{10^{-7.40}}{10^{-8.95}} = 10^{1.55} = 35$$

$$\frac{[HLys]}{[Lys^-]} = \frac{[H_3O^+]}{K_{a3}} = \frac{10^{-7.40}}{10^{-10.53}} = 10^{3.13} = 1350$$

The dominant species at pH = 7.40 is H_2Lys^+
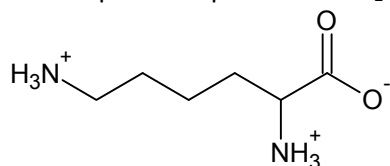
14.40 pH = 4.13

14.42 (b) NH_3 and NH_4Cl would make a buffer solution near pH = 9

14.43 If we prepare a (not too dilute) solution with a 2.0 to 1 ratio (on a moles basis) of $Na_2HPO_4(s)$ to $NaH_2PO_4(s)$, 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}

14.56 K_b = 6.31 x 10^{-5}

14.57 $[H_3O^+]$ = 10^{-pH} = $10^{-3.75}$ = 1.78×10^{-4} mol L^{-1}
       The solution is acidic (pH < 7).

14.59

$$K_b\left((CH_3)_3\,N(aq)\right) \;=\; \frac{[(CH_3)_3\,NH^+][OH^-]}{[(CH_3)_3\,N]} \;=\; \left(\frac{[(CH_3)_3\,N][H_3O^+]}{[(CH_3)_3\,NH^+]}\,\frac{1}{[H_3O^+][OH^-]}\right)^{-1}$$

$$=\; \left(K_a\left((CH_3)_3\,NH^+\right)\frac{1}{K_w}\right)^{-1} \;=\; \frac{K_w}{K_a\left((CH_3)_3\,NH^+\right)}$$

$$=\; \frac{10^{-14}}{10^{-pK_a}} \;=\; \frac{10^{-14}}{10^{-9.80}} \;=\; 10^{-4.20} \;=\; 6.31\times10^{-5}$$

14.61

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

$$HPO_4{}^{2-}\left(aq\right) + H_2O(l) \rightleftharpoons PO_4{}^{3-}\left(aq\right) + H_3O^+(aq)$$

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

$$HPO_4{}^{2-}\left(aq\right) + H_2O(l) \rightleftharpoons H_2PO_4{}^-\left(aq\right) + OH^-\left(aq\right)$$
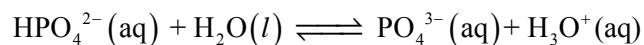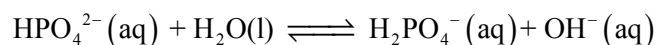
14.63　(b) ClC$_6$H$_4$COOH (p$K_a = 2.88$) is the stronger acid, stronger than benzoic acid (p$K_a = 4.20$). The acid with the lowest pK_a value is the strongest.

14.65　(a) HCOOH(aq) (formic acid) is the strongest acid.
　　　　C$_6$H$_5$OH(aq) (phenol) is the weakest acid.
　　　　(b) HCOOH(aq) (formic acid) has the weakest conjugate base.
　　　　(c) C$_6$H$_5$OH(aq) (phenol) has the strongest conjugate base.

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

14.71
  (a)
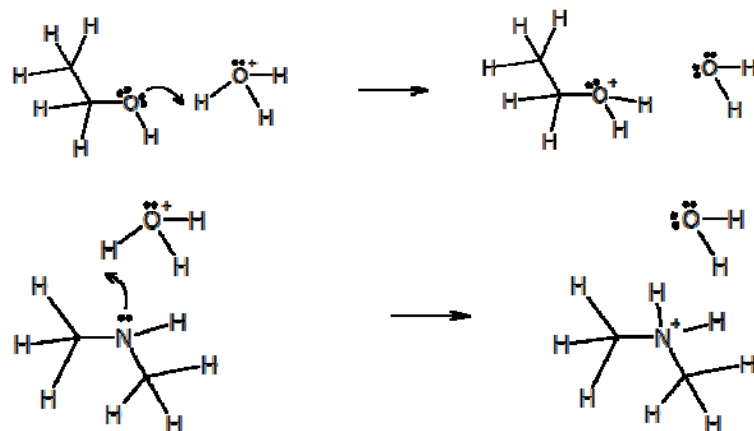
trimethyl phosphine, $(CH_3)_3P$, plus H_3O^+ is similar to dimethyl amine, $(CH_3)_2NH$, plus H_3O^+

(b)
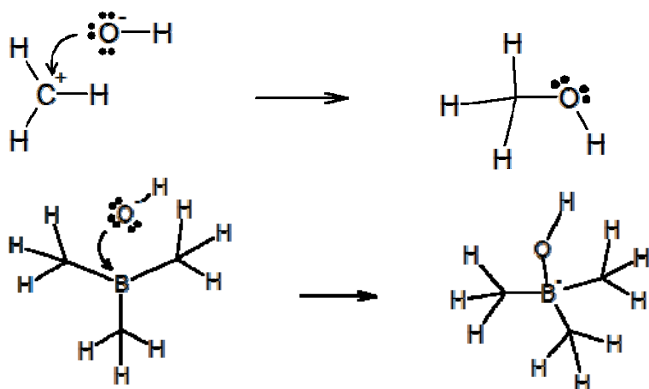
               Br^- does not behave as a Lewis acid

14.73 $[H_3O^+] = 1.58 \times 10^{-4}$ 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 $[NH_4^+] = [OH^-] = 1.6 \times 10^{-3}$ mol L^{-1}
       $[NH_3] = 0.015$ mol L^{-1}
       $[H_3O^+] = 6.25 \times 10^{-12}$ mol L^{-1}
       pH = 11.20
       % NH_3 ionized = 1.1 %

11.79 (i) 0.054 %
       (ii) 0.17 %
       (iii) 5.4 %

14.81   (a) [OH−] = 9.2×10^{-5} mol L^{-1}
        [$N_2H_5^+$] = 9.2×10^{-5} mol L^{-1}
        [$N_2H_6^{2+}$] = 9.0×10^{-16} mol L^{-1}

        (b) pH = 9.96

14.83   At pH = 3.00, [CH_3NH_2]/[$CH_3NH_3^+$] = 0.42
        At pH =7.00, [CH_3NH_2]/[$CH_3NH_3^+$] = 4200
        At pH = 11.00, [CH_3NH_2]/[$CH_3NH_3^+$] = 4.2×10^7
        When pH = pKa = 3.38, [CH_3NH_2] =[$CH_3NH_3^+$]

14.85   (a) At
        (i) pH = 6, $H_2A(aq)$ has the highest concentration
        (ii) pH = 8, $HA^-(aq)$ has the highest concentration
        (iii) pH = 10, $HA^-(aq)$ still has the highest concentration – but not by as wide a margin

        (b) pK_{a1} and pK_{a2} can be seen in the plot.
        [$H_2A(aq)$] = [$HA^-(aq)$] when pH = pK_{a1}
        So, pK_{a1} = about 6.4
        [$HA^-(aq)$] = [$A^{2-}(aq)$] when pH = pK_{a2}
        So, pK_{a1} = about 10.3

        (c) Since pK_{a1} = 6.38 and pK_{a2} = 10.32 for carbonic acid, the acid is very likely carbonic acid.

14.87

(a)

H_3Glu^+

(b)

H_2Glu

(c)

$HGlu^-$

(d)

Glu^{2-}
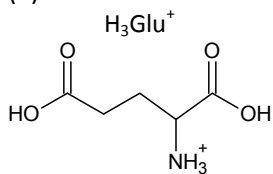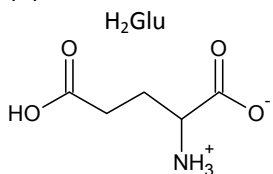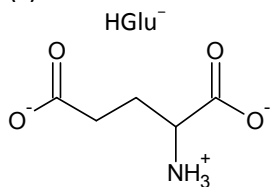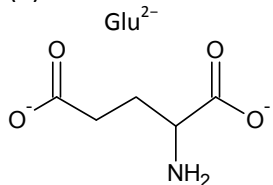
14.89   3.89

14.91   (a) 3.59
        (b) 2.24

14.93   The buffer solution is prepared by adding 0.479 mol of Na_2CO_3 for every 1.000 mol of $NaHCO_3$ added to water to give a not-too-dilute concentration (so we have a buffer with some capacity).
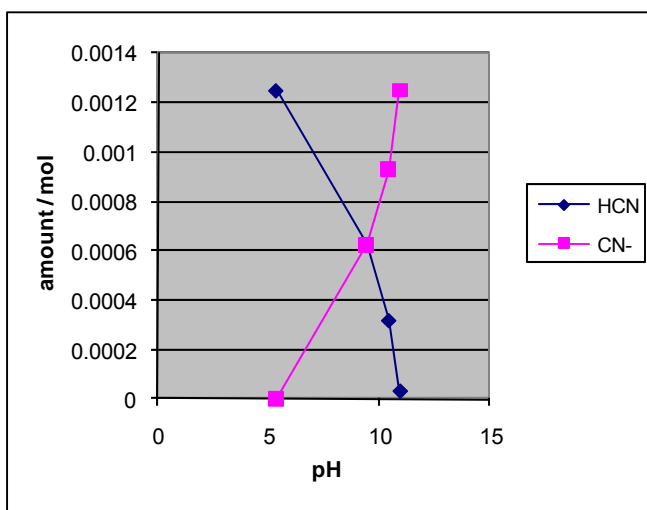
14.95   (a) 4.95
        (b) 5.05

14.99   0.167 mol L^{-1}

14.101 (a) 7.46
        (b) 7.28

14.103 (a) 0.180 mol L^{-1}
        (b) $[H_3O^+] = 2.1 \times 10^{-3}$ mol L^{-1}
            $[C_6H_5NH_3^+] = 0.178$ mol L^{-1}
            $[OH^-] = 6.76 \times 10^{-12}$ 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 ≈ 10.93.
        Indicators which change colour in the neighborhood of pH = 11 include
        alizarine yellow R.

SUMMARY AND CONCEPTUAL QUESTIONS

14.107 (a) 10 H_3O^+ ions.
        (b) 1 H_3O^+ ion
        (c) If the pH were 4, then there would likely not be any hydronium ions in the cube. To visualize
        pH = 4, you would have to imagine the cube as a snapshot taken from a larger quantity of water.
        If many such snapshots were considered, then about 1 in 10 of them would have a single
        hydronium ion.
        (d) If the H_3O^+ ion to water molecule ratio is 100:55000 = 1:550 when pH = 1.0, then this ratio is
        1:55000000 when pH = 6.0 (i.e. a hydronium concentration 10^5 times smaller).

14.109 A buffer solution contains a not-too-dilute solution of both a weak acid and a weak base. When
        a strong base is added, the weak acid reacts with it and consumes most of it. In the case of a
        carbonate/hydrogencarbonate buffer, the hydrogencarbonate reacts with the added base.
        $HCO_3^-(aq) + OH^-(aq) \rightarrow CO_3^{2-}(aq) + H_2O(\ell)$

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.

$CH_3COOH(aq) + H_2O(\ell) \rightleftharpoons CH_3COO^-(aq) + H_3O^+(aq)$
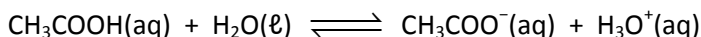
Increasing pH means decreasing H_3O^+ which, according to Le Chatelier's principle, causes a shift in the equilibrium to the right – i.e. depleted acetic acid and increased acetate.

(b) From the buffer equation,

$$[H_3O^+] = \frac{[CH_3COOH]}{[CH_3COO^-]} \times 1.8 \times 10^{-5} = 10^{-4}$$

at pH = 4. Here, we see that $[CH_3COOH] / [CH_3COO^-]$ must be greater than 1 – i.e. acetic acid predominates.

At pH = 6, the right side of the above equation is 10^{-6} and $[CH_3COOH] / [CH_3COO^-]$ must be less than 1 – i.e. acetate predominates.

(c) From the buffer equation, we see that $[H_3O^+]$ = K_a = 1.8×10^{-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)

$AgI(s) \rightleftharpoons Ag^+(aq) + I^-(aq)$

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

(b)

$BaF_2(s) \rightleftharpoons Ba^{2+}(aq) + 2\,F^-(aq)$
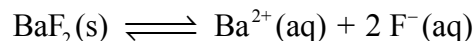
$Q = [Ba^{2+}][F^-]^2 = K_{sp} = 1.7 \times 10^{-6}$ at equilibrium

(c)

$Ag_2CO_3(s) \rightleftharpoons 2\,Ag^+(aq) + CO_3^{2-}(aq)$
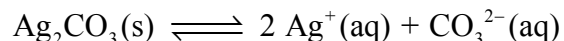
$Q = [Ag^+]^2[CO_3^{2-}] = K_{sp} = 8.1 \times 10^{-12}$ at equilibrium

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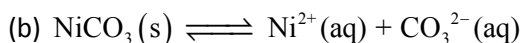
15.6   (a) 1.3×10^{-2} molL^{-1}
        (b) 9.6×10^{-1} g L^{-1}

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

15.10 The solubility of Ag_3PO_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} ($H_2PO_4^-$ and H_3PO_4 upon further reaction with water). The concentration of PO_4^{-3} is consequently significantly reduced, and the reaction quotient for dissolution of Ag_3PO_4 remains less than the solubility product for larger initial concentrations of Ag_3PO_4 than predicted using K_{sp}.

15.13 (a) 1.0×10^{-5} mol L^{-1}
       (b) 1.1×10^{-8} mol L^{-1}

15.15 (a) PbS(s)
       (b) Ag_2CO_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}
       $[Pb^{2+}] = 4.4 \times 10^{-3}$ 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.
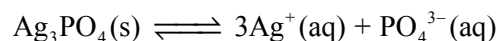
REVIEW QUESTIONS

15.25   (a) $PbSO_4(s) \rightleftharpoons Pb^{2+}(aq) + SO_4^{2-}(aq)$
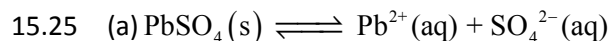
$Q = [Pb^{2+}][SO_4^{2-}] = K_{sp} = 1.8 \times 10^{-8}$ at equilibrium.

(b) $NiCO_3(s) \rightleftharpoons Ni^{2+}(aq) + CO_3^{2-}(aq)$

$Q = [Ni^{2+}][CO_3^{2-}] = K_{sp} = 1.4 \times 10^{-7}$ at equilibrium.

(c)
$Ag_3PO_4(s) \rightleftharpoons 3Ag^+(aq) + PO_4^{3-}(aq)$

$Q = [Ag^+]^3[PO_4^{3-}] = K_{sp} = 1.3 \times 10^{-20}$ at equilibrium.
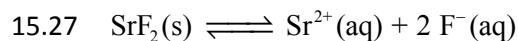
15.27 $SrF_2(s) \rightleftharpoons Sr^{2+}(aq) + 2\,F^-(aq)$
$K_{sp} = 4.0 \times 10^{-9}$

15.29   51 mg of $PbSO_4$ remains undissolved

15.31   (a) $PbCl_2(s)$
(b) $FeS(s)$
(c) $Fe(OH)_2(s)$
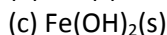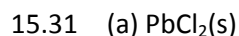
15.33 $Q = 1.1 \times 10^{-6} > K_{sp} = 1.8 \times 10^{-8}$
AgCl will precipitate out of solution

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

15.39

$AuCl(s) \rightleftharpoons Au^+(aq) + Cl^-(aq)$

$\underline{Au^+(aq) + 2\,CN^-(aq) \rightleftharpoons [Au(CN)_2]^-(aq)}$

$AuCl(s) + 2\,CN^-(aq) \rightleftharpoons [Au(CN)_2]^-(aq) + Cl^-(aq)$
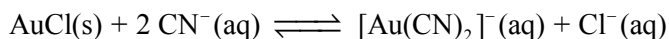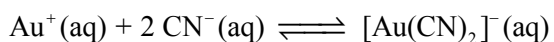
$K_{net} = 4.0 \times 10^{25}$

SUMMARY AND CONCEPTUAL QUESTIONS

15.41 5.51×10^{-5}

15.43 1.4×10^{-4} mol L^{-1}

Chapter 16

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

16.4 CH_3CH_2OH is oxidized. CH_3CH_2OH is the reducing agent. $Cr_2O_7^{2-}$ is reduced. $Cr_2O_7^{2-}$ 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 : $2Ag^+(aq) + Ni(s) \rightarrow 2Ag(s) + Ni^{2+}(aq)$
        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
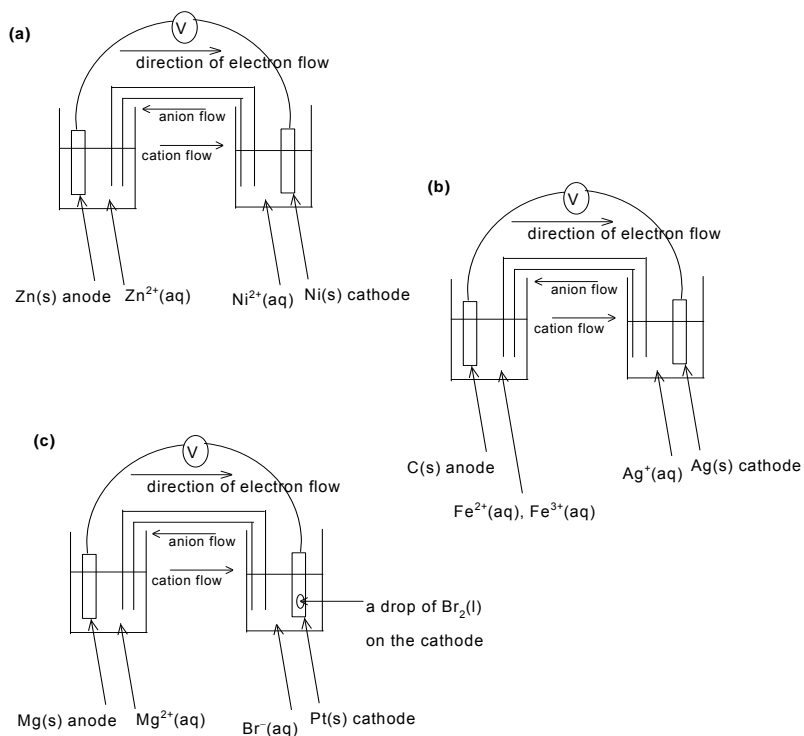
16.8   (a) $E^\circ[\ Ni^{2+}(aq)|Ni(s)\ ]\ =\ -0.25$ V
        (b) $E^\circ[Cl_2(g)|Cl^-(aq)|Pt(s)\ ]\ =\ 1.36$ V

16.9   See above – Exercise 16.8(b).

16.13

$$Zn(s)\ \rightarrow Zn^{2+}(aq)+2\ e^- \qquad\qquad \text{at the anode}$$

$$\underline{2\times(Ag^+(aq)+e^- \rightarrow Ag(s))} \qquad\qquad \text{at the cathode}$$

$$Zn(s)+2\ Ag^+(aq) \rightarrow Zn^{2+}(aq)+2\ Ag(s)$$
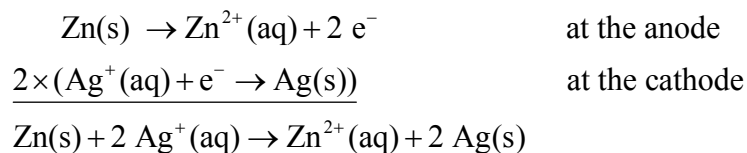
$E^\circ_{cell}\ = 1.56$ V

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

16.17   (a) Aluminum
        (b) Aluminum and zinc
        (c) $Fe^{2+}(aq) + Sn(s) \rightarrow Fe(s) + Sn^{2+}(aq)$. This is NOT the direction of spontaneous reaction.
        (d) $Zn^{2+}(aq) + Sn(s) \rightarrow Zn(s) + Sn^{2+}(aq)$. This is NOT the direction of spontaneous reaction.

16.20 $E^\circ_{cell}\ = + 1.24$ V
16.22   0.041 mol L^{-1}

16.23   (a) At pH = 0, $E_{cell}\ = + 1.51$ V
        (b) At pH = 5.0, $E_{cell}\ = + 1.04$ V

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

16.25 $K = 1.2$ x 10^{-19}

16.27 $2\ H_2O(l) + 2\ e^- \longrightarrow H_2(g) + 2\ OH^-(aq)$ (Cathode reaction)
        $4\ OH^-(aq) \longrightarrow O_2(g) +2\ H_2O(l) + 4\ e^-$ (Anode reaction)
        $E^\circ_{cell}\ = -1.23$ V

16.28   The brass fittings provide cathodes where oxygen is reduced to water. The steel provides the anode where iron is oxidized to Fe^{2+}. Of course, the steel can provide its own cathode and can corrode without brass fittings. However, because copper (the principal component of brass) is a more noble metal than iron, when it is in contact with iron there is a slight polarization at the junction, with iron becoming slightly positively charged. This makes the oxidation process at the surface of iron more favorable. At the same time, the slight negative charge on the brass makes the reduction of oxygen more favorable.
The rate of corrosion varies from city to city because it depends upon the ionic strength – the total concentration of ions – of the city water. Ions in the water carry current from the anode to cathode – to complete the circuit. The conductivity of the water increases with ion concentration.

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

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


REVIEW QUESTIONS

16.31   (a) OS(f) = −1 OS(P) = +5
(b) OS(h) = +1 & OS(O) = −2 OS(As) = +5
(c) OS(O) = −2 OS(U) = +4
(d) OS(O) = −2 OS(N) = +5
(e) OS(Cl) = −1 & OS(O) = −2 OS(P) = +5
(f) OS(O) = −2 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) $Sn(s) + 2 H^+(aq) \longrightarrow Sn^{2+}(aq) + H_2(g)$

(b) $Cr_2O_7^{2-}(aq) + 6 Fe^{2+}(aq) + 14 H^+(aq) \longrightarrow 2 Cr^{3+}(aq) + 6 Fe^{3+}(aq) + 7 H_2O(l)$

(c) $MnO_2(s) + 2 Cl^-(aq) + 4 H^+(aq) \longrightarrow Mn^{2+}(aq) + Cl_2(g) + 2 H_2O(l)$

(d) $HCHO(aq) + 2 Ag^+(aq) + H_2O(l) \longrightarrow HCOOH(aq) + 2 Ag(s) + 2 H^+(aq)$

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

16.39

(a) + (c)
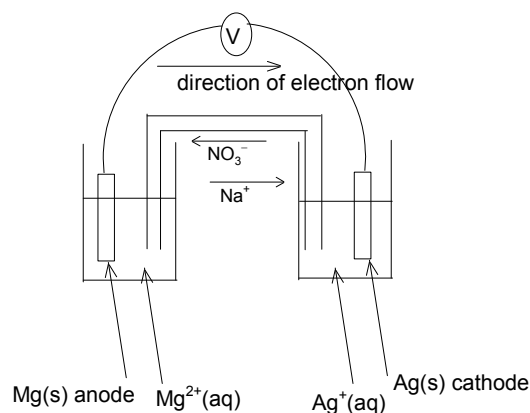
(b)　　$Mg(s) \longrightarrow Mg^{2+}(aq) + 2 e^-$ (oxidation half-reaction that occurs at the anode).

$Ag^+(aq) + e^- \longrightarrow Ag(s)$ (reduction half-reaction that occurs at the cathode)

$Mg(s) + 2Ag^+(aq) \rightarrow Mg^{2+}(aq) + 2Ag(s)$ (net reaction in the cell)

16.41　(a) + 0.78 V

(b) = −0.32 V

16.43　(a) when

$$Q = \frac{p(NO)}{[NO_3^-][H^+]^4} = 1.00$$

(b) $E°[\,NO_3^-(aq)\,|\,NO(g)\,] = 0.96$ V
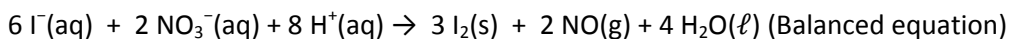
16.45　(a) To make a cell with potential close to 1.1 V, using the $Zn^{2+}(aq)\,|\,Zn(s)$ half-cell, we could use the $Cu^{2+}(aq)\,|\,Cu(s)$ half-cell as the cathode and the $Zn^{2+}(aq)\,|\,Zn(s)$ half-cell as the anode.
$E°_{cell} = E°[Cu^{2+}(aq)|\,Cu(s)] - E°[Zn^{2+}(aq)|Zn(s)] = 0.337$ V $- (-0.763$ V$) = 1.10$ V

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

16.47 (a) Se(s)
       (b) F⁻(aq)
       (c) $F_2(g)$, $Cl_2(g)$
       (d) $F_2(g)$, $Cl_2(g)$, $Br_2(\ell)$, $I_2(s)$, $O_2(g)$
       (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
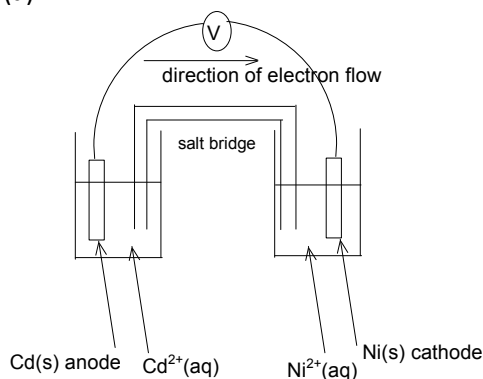   (d) is the direction of spontaneous reaction

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 $Cu(NO_3)_2$ causes a brown colour and a
       precipitate to form because the nitrate ion oxidizes iodide under these conditions. The I_2 that is
       formed first reacts with iodide to form the brown I_3^-(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
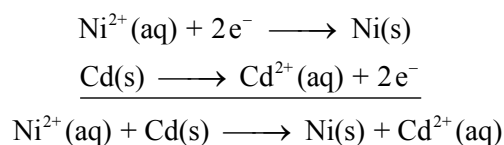   conditions – there is no reaction.
       $6\,I^-(aq)\ +\ 2\,NO_3^-(aq) + 8\,H^+(aq) \rightarrow\ 3\,I_2(s)\ +\ 2\,NO(g) + 4\,H_2O(\ell)$ (Balanced equation)

16.57 E_{cell} = + 1.585 V

16.59 (a)

       (b)

$$Ni^{2+}(aq) + 2\,e^- \longrightarrow Ni(s)$$
$$\underline{Cd(s) \longrightarrow Cd^{2+}(aq) + 2\,e^-}$$
$$Ni^{2+}(aq) + Cd(s) \longrightarrow Ni(s) + Cd^{2+}(aq)$$

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

(d) $E°_{cell} = +0.15$ 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 $NO_3^-(aq)$ ions move from the cathode compartment to the anode compartment.
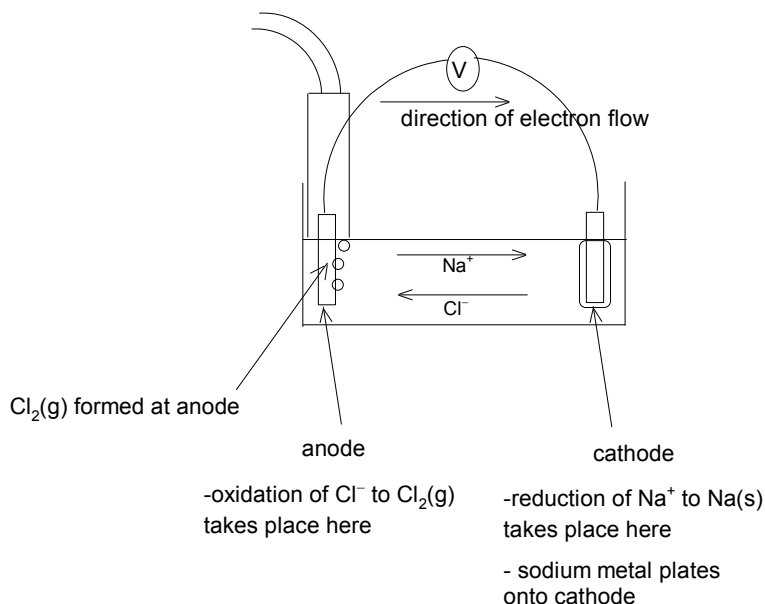(g) $K = 1.2 \times 10^5$
(h) $E_{cell} = +0.21$ V
    Since E_{cell} is still positive, the net reaction is in the same direction given in part (b).

16.61   (a) $E°_{cell} = +0.236$ V, $K = 9.5 \times 10^7$
        (b) $E°_{cell} = -0.531$ V, $K = 1.1 \times 10^{-18}$

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

16.67

direction of electron flow

V

Na⁺

Cl⁻

$Cl_2(g)$ formed at anode

anode
-oxidation of Cl^- to $Cl_2(g)$ takes place here

cathode
-reduction of Na^+ to $Na(s)$ takes place here
- sodium metal plates onto cathode

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

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

16.73

electron flow   electron flow

− | +

Fe(s) cathode

inert electrode

pipeline serves as cathode in this electrolytic cell

serves as anode

$O_2(g) + 4\,H^+(aq) + 2\,e^- \longrightarrow 2\,H_2O(l)$

$2\,H_2O(l) \longrightarrow O_2(g) + 4\,H^+(aq) + 2\,e^-$

Cl^- flow

Na^+ and Mg^{2+} flow
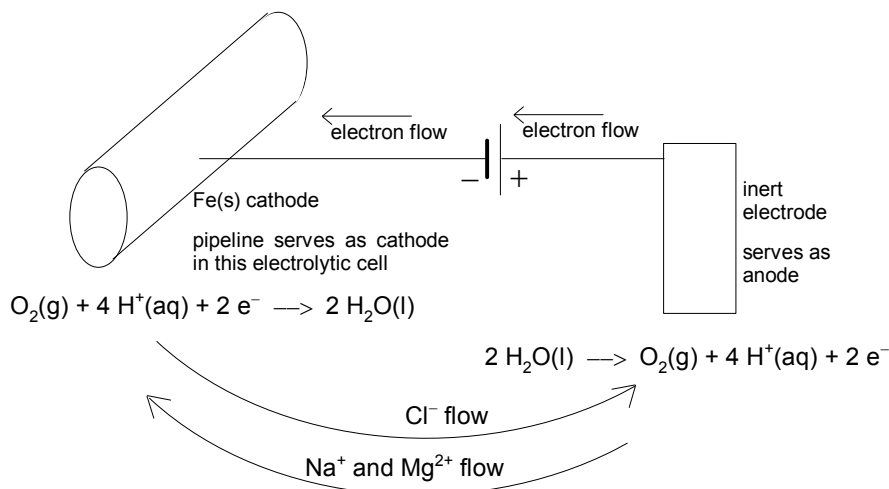
By keeping the pipeline at a higher potential than the inert electrode, the pipeline behaves like a metal even more noble - it does not corrode.

SUMMARY AND CONCEPTUAL QUESTIONS

16.75   (a) In this case, the iron screws in contact with the more noble copper alloy corrode rapidly. They crumble, leaving holes in the copper alloy sheets where water leaks in.
(b) In this case, the iron wrench is the more noble metal. It accelerates the corrosion of the aluminum in contact with it by polarizing the aluminum, making it slightly positive. The aluminum corrodes rapidly leaving a wrench-shaped hole in the hull.

16.77   If the emf is applied in the wrong direction, the corrosion of the pipeline will be accelerated. The potential of the pipeline is lowered – it is charged positively – and the oxidation (of Fe(s)) half reaction is made more favourable.

Chapter 17

17.1   The change in entropy for a reversible process (i.e. add the heat very slowly) is just heat flow into the system divided by temperature. Therefore, the entropy of the water and hexane change by the same amount – it depends only on the temperature of the system and the amount of heat added.
$\Delta S = q\,/\,T = 10^6\,J\,/\,323.15\,K = 3095\,J/K$, for both the water and hexane.

17.3   121 J/K

17.5   (a) 1 mol of O_3(g)
        (b) 1 mol of $SnCl_4$(g)
        (c) 3 mol of O_2(g)

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

17.10 ΔS^o_{sys} = -134.23 JK^{-1}
        ΔH^o_{sys} = -657.01 kJ
        ΔS^o_{univ} = +2071 JK^{-1}
        Since the change in entropy for the universe upon forward reaction is positive, the reaction is spontaneous.

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

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

17.15   (a) $\frac{1}{2}$ N_2(g) + $\frac{3}{2}$ H_2(g) → NH_3(g)

        (b) 2 Fe(s) + $\frac{3}{2}$ O_2(g) → Fe_2O_3(s)

        (c) 3 C(s) + 3 H_2(g) + O_2(g) → CH_3CH_2COOH(ℓ)
        (d) Ni(s) is the element in its standard state. Its $\Delta_f G^\circ$ = 0.

17.17 $\Delta_r G^o$ = -70.87 kJ

17.18 $\Delta_r G^o$ = -142.12kJ
        The reaction is spontaneous in the forward direction

17.19 T= 838.7 K

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

17.22 $\Delta_r G^o$ = - 1.13 kJ

17.25 $\Delta_r G^o$ = +120.023 kJ
        K = 9.18 x 10^{-22}

17.26   -41 kJ

17.27   + 147 kJ. The reverse reaction is spontaneous.

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

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

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

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

REVIEW QUESTIONS

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

17.35 (a) $NaCl(g)$
       (b) $H_2S(g)$
       (c) $C_2H_4(g)$
       (d) $H_2SO_4(\ell)$

17.37
$$\Delta_r S^\circ = 1 \times S^\circ(C_2H_6, g) - [2 \times S^\circ(C, graphite) + 3 \times S^\circ(H_2, g)]$$
$$= 229.60 \text{ J K}^{-1} \text{mol}^{-1} - [2 \times 5.740 \text{ J K}^{-1} \text{mol}^{-1} + 3 \times 130.684 \text{ J K}^{-1} \text{mol}^{-1}]$$
$$= -173.93 \text{ J K}^{-1} \text{mol}^{-1}$$

17.41 1. $C(s) = C(graphite)$
       $\Delta_r S^o_1 = S^o[CH_4(g)] - (S^o[C(s)] + 2 S^o[H_2(g)])$
       $= 186.3 \text{ J K}^{-1} \text{mol}^{-1} - (5.74 \text{ J K}^{-1} \text{mol}^{-1} + 2 \times 130.7 \text{ J K}^{-1} \text{mol}^{-1}) = -80.8 \text{ J K}^{-1} \text{mol}^{-1}$

       2. $\Delta_r S^o_2 = S^o[CH_3OH(\ell)] - (S^o[CH_4(g)] + \frac{1}{2} S^o[O_2(g)])$
       $= 126.8 \text{ J K}^{-1} \text{mol}^{-1} - (186.3 \text{ J K}^{-1} \text{mol}^{-1} + \frac{1}{2} \times 205.1 \text{ J K}^{-1} \text{mol}^{-1}) = -162.1 \text{ J K}^{-1} \text{mol}^{-1}$

       3. $\Delta_r S^o_3 = S^o[CH_3OH(\ell)] - (S^o[C(s)] + 2 S^o[H_2(g)] + \frac{1}{2} S^o[O_2(g)])$
       $= 126.8 \text{ J K}^{-1} \text{mol}^{-1} - (5.74 \text{ J K}^{-1} \text{mol}^{-1} + 2 \times 130.7 \text{ J K}^{-1} \text{mol}^{-1} + \frac{1}{2} \times 205.1 \text{ J K}^{-1} \text{mol}^{-1})$
       $= -242.9 \text{ J K}^{-1} \text{mol}^{-1}$

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

$\Delta_r S^o_1 + \Delta_r S^o_2 = -80.8 \text{ J K}^{-1} \text{mol}^{-1} - 162.1 \text{ J K}^{-1} \text{mol}^{-1} = -242.9 \text{ J K}^{-1} \text{mol}^{-1} = \Delta_r S^o_3$

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

$$\Delta S^{\circ}_{univ} = \Delta S^{\circ}_{sys} + \Delta S^{\circ}_{surr} = 20.0 \, \mathrm{J\,K^{-1}\,mol^{-1}} + 619.5 \, \mathrm{J\,K^{-1}\,mol^{-1}}$$
$$= +639.5 \, \mathrm{J\,K^{-1}\,mol^{-1}}$$

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

17.45 $H_2O(l) \longrightarrow H_2(g) + \frac{1}{2} O_2(g)$
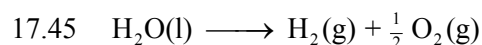
$\Delta S^{\circ}_{sys} = (\, S^{\circ}[H_2(g)] + \frac{1}{2}\, S^{\circ}[O_2(g)]\,) - S^{\circ}[H_2O(\ell)]$
$\qquad = (\, 130.7 \, \mathrm{J\,K^{-1}\,mol^{-1}} + \frac{1}{2} \times 205.1 \, \mathrm{J\,K^{-1}\,mol^{-1}}) - 69.91 \, \mathrm{J\,K^{-1}\,mol^{-1}} = 163.3 \, \mathrm{J\,K^{-1}\,mol^{-1}}$
$\Delta H^{\circ}_{sys} = (\Delta_f H^{\circ}[H_2(g)] + \frac{1}{2}\, \Delta_f H^{\circ}[O_2(g)]\,) - \Delta_f H^{\circ}[H_2O(\ell)]$
$\qquad = -285.8 \, \mathrm{kJ\,mol^{-1}} - 0 - 0 = -285.8 \, \mathrm{kJ\,mol^{-1}}$

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

$$\Delta S^{\circ}_{univ} = \Delta S^{\circ}_{sys} + \Delta S^{\circ}_{surr} = 163.3 \, \mathrm{J\,K^{-1}\,mol^{-1}} - 959.1 \, \mathrm{J\,K^{-1}\,mol^{-1}}$$
$$= -795.8 \, \mathrm{J\,K^{-1}\,mol^{-1}}$$

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, $p(H_2) = p(O_2) = 1$ bar.

17.47   At sufficiently high T, the system change in entropy will be the dominant term and the reaction will be spontaneous.

17.49   (a) = $-1258.1 \, \mathrm{kJ\,mol^{-1}}$
This reaction is spontaneous. It is enthalpy driven.
(b) = $124.6 \, \mathrm{kJ\,mol^{-1}}$
This reaction is NOT spontaneous. Both enthalpy and entropy terms disfavour this process.

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

17.53   = $-1139.2 \, \mathrm{kJ\,mol^{-1}}$

17.55   = 106 °C.

17.57   = $-1441.61 \, \mathrm{kJ\,mol^{-1}}$ This is in accord with experience.

17.59 K is very small, in accord with a positive standard free energy change—the forward reaction is NOT favoured in a reaction mixture at 25 °C and all reactants and products in their standard states (i.e., the conditions that apply for specification of the underlined standard free energy change of reaction).

17.61   = $4.73 \, \mathrm{kJ\,mol^{-1}}$

17.63   = $-166.27 \, \mathrm{kJ\,mol^{-1}}$

17.65 = 92.4 ºC

SUMMARY AND CONCEPTUAL QUESTIONS

17.67 (a) $\Delta_r S^\circ = 2\ S^\circ[Hg(\ell)] + S^\circ[O_2(g)] - 2\ S^\circ[HgO(s)]$

$= 2 \times 76.02\ J\ K^{-1}\ mol^{-1} + 205.138\ J\ K^{-1}\ mol^{-1} - 2 \times 70.29\ J\ K^{-1}\ mol^{-1} =$
$216.60\ J\ K^{-1}\ mol^{-1}$ √

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

A positive $\Delta_r H^\circ$ corresponds to a negative ΔH°_{surr} and a negative ΔS°_{surr}. √

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

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

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

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

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

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

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

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

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

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

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

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

$T_{spon} = \Delta_r H^\circ /\ \Delta_r S^\circ = 77.37 \times 10^3\ J\ mol^{-1} /\ 115.55\ J\ K^{-1}\ mol^{-1} = 669.5\ K$

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

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

$\Delta_r G^\circ = \Delta_r H^\circ - T\ \Delta_r S^\circ = 3.213\ kJ\ mol^{-1} - 383.15\ K \times (8.7\ J\ K^{-1}\ mol^{-1})\ /\ (1000\ J\ /kJ) =$
$-0.120\ kJ\ mol^{-1}$

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

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

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

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

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

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

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

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

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

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

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

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17.75 $Hg(\ell) \rightarrow Hg(g)$

$\Delta_rH° = \Delta_fH°[Hg(g)] = 61.38 \text{ kJ mol}^{-1}$

$\Delta_rS° = S°[Hg(g)] - S°[Hg(\ell)] = 174.97 \text{ J K}^{-1}\text{ mol}^{-1} - 76.02 \text{ J K}^{-1}\text{ mol}^{-1}$
$= 98.95 \text{ J K}^{-1}\text{ mol}^{-1}$

$\Delta_rG° = \Delta_rH° - T\Delta_rS° = 61.38 \text{ kJ mol}^{-1} - 298.15 \text{ K} \times (98.95 \text{ J K}^{-1}\text{ mol}^{-1}) / (1000 \text{ J /kJ}) = 31.88 \text{ kJ mol}^{-1}$

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

$\quad K = 1.00$

$\Delta_rG° = -RT \ln(K) = 0$

$\quad = \Delta_rH° - T\Delta_rS°$

So,

$T = \Delta_rH° / \Delta_rS° = 61.38 \times 10^3 \text{ J mol}^{-1}/ 98.95 \text{ J K}^{-1}\text{ mol}^{-1} = 620 \text{ K}$

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

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

$\Delta_rG° = -RT \ln(K) = \Delta_rH° - T\Delta_rS°$

Solve for T.

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

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 ($\Delta_rG° < 0$) are product-favoured. However, these reactions sometimes occur very slowly. $\Delta_rG°$ 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 $\Delta_rS°$ 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 $\Delta_rH° = 0$

$\quad\quad \Delta_rG° = \Delta_rH° - T\Delta_rS° < 0$

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 $C_6H_6(s) \rightarrow C_6H_6(\ell)$
(a) $\Delta_rH° > 0$
It takes energy (enthalpy) to break the intermolecular bonds holding the benzene molecules rigidly in their lattice positions.
(b) $\Delta_rS° > 0$
A liquid has more disorder—more entropy—than the corresponding solid.
(c) $\Delta_rG° = 0$ at 5.5 °C, the melting point, where the solid and liquid co-exist.
(d) $\Delta_rG° > 0$ at 0.0 °C < the melting point, where the solid is the more stable phase.
(e) $\Delta_rG° < 0$ at 25.0°C > the melting point, where the liquid is the more stable phase.

17.83 $\Delta_rG° < 0$
This process is spontaneous—iodine dissolves readily in CCl_4.
$\Delta_rS° = (\Delta_rH° - \Delta_rG°)/T > 0$ since $\Delta_rH° = 0$
This dissolution is an entropy-driven process.

17.85 (a) $N_2H_4(\ell) + O_2(g) \rightarrow N_2(g) + 2\ H_2O(\ell)$
This is an oxidation-reduction reaction—oxygen is the oxidizing agent and hydrazine is the reducing agent.

(b) $\Delta_rH° = -622.29$ kJ mol^{-1}
$\Delta_rS° = 5.08$ J K^{-1} mol^{-1}
$\Delta_rG° = -623.80$ kJ mol^{-1}

Chapter 18

18.2 For every 2 moles of NOCl consumed, there are 2 moles of NO and one mole of Cl_2 produced. The relative rate of appearance of Cl_2 is ½ the rate of appearance of NO which equals the rate of disappearance of NOCl.

18.3 In the first two hours: 0.0085 mol L^{-1} h^{-1}
In the last two hours: 0.002 mol L^{-1} h^{-1}
The instantaneous rate of decay at t = 4.0 h: 0.0044 mol L^{-1} h^{-1}

18.4 (a) Rate = $k\ [NO_2][O_3]$
(b) The rate triples.
(c) The rate is halved.

18.7 Rate = $k\ [NO]^2[O_2]$
$k = 7100$ mol^{-2} L^2 s^{-1}

18.9 0.0035 mol L^{-1}

18.11 0.00217 mol L^{-1}

18.13 The plot of ln($[N_2O_5]$) versus time gives a straight line. The reaction is first order.

18.15 (a) $t_{1/2}$ of ^{241}Am = 430 years
$t_{1/2}$ of ^{125}I = 63 years
(b) ^{125}I
(c) 1.57×10^{15} atoms
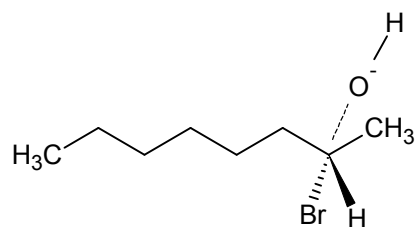
18.17 57.2 kJmol^{-1}

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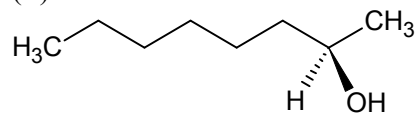The rate equation for the third step: Rate = k [N$_2$O] [H$_2$]

$$2\,NO \longrightarrow N_2O_2$$
$$N_2O_2 + H_2 \longrightarrow N_2O + H_2O$$
$$\underline{N_2O + H_2 \longrightarrow N_2 + H_2O}$$
$$2\,NO + 2\,H_2 \longrightarrow N_2 + 2\,H_2O$$
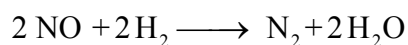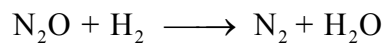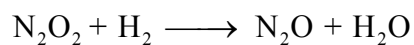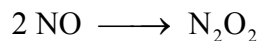
18.21 (a) 2NH$_3$(aq) + OCl$^-$(aq) → N$_2$H$_4$(aq) + H$_2$O(ℓ) + Cl$^-$(aq)
(b) step 2
(c) Rate = k [NH$_2$Cl] [NH$_3$]
(d) NH$_2$Cl, N$_2$H$_5^+$ and OH$^-$

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

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

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

$$CH_3 - \overset{+}{C}(CH_3)(CH_3)$$

(structure of tert-butyl carbocation: central $\overset{+}{C}$ bonded to three CH_3 groups)
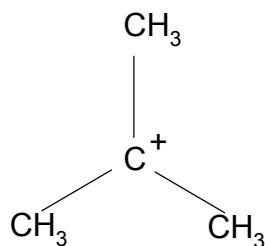
        (d) Whether or not inversion takes place is irrelevant here because the product is the same in both cases – due to symmetry.
        (e) The proportion of this reaction that proceeds by the S_N2 mechanism is negligible because the rate of the S_N1 mechanism is enhanced by the relatively stable carbocation 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 3.0×10^{-4} mol L^{-1} 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 1.8×10^{-3} mol L^{-1} h^{-1}. The rate of reaction is the rate of change of Cl$^-$, for this reaction.

18.31   (a) second order in NO and first order in O_2
        (b) $Rate = k\ [NO]^2[O_2]$
        (c) 25 mol^{-2} L^2 s^{-1}
        (d) 2.8×10^{-5} mol L^{-1} s^{-1}
        (e) O_2 (g) reacts at rate = 5.0×10^{-5} mol L^{-1} s^{-1}; i.e. one half the rate of NO. NO_2(g) forms at the same rate as NO, 1.0×10^{-4} mol L^{-1} s^{-1}.

18.33   (a) The reaction is second order in NO and first order in H_2
        (b) $Rate = k\ [NO]^2[H_2]$
        (c) 6.32 mol^{-2} L^2 s^{-1}
        (d) 0.159 mol L^{-1} s^{-1}

18.35   (a) $Rate = k\ [CO]^2[O_2]$
        (b) second order in [CO] and first order in [O_2]
        (c) 4.6 mol^{-2} L^2 min^{-1}

18.37 (a) 0.58
       (b) 1280 s

18.39 495 min^{-1}

18.43 105 min

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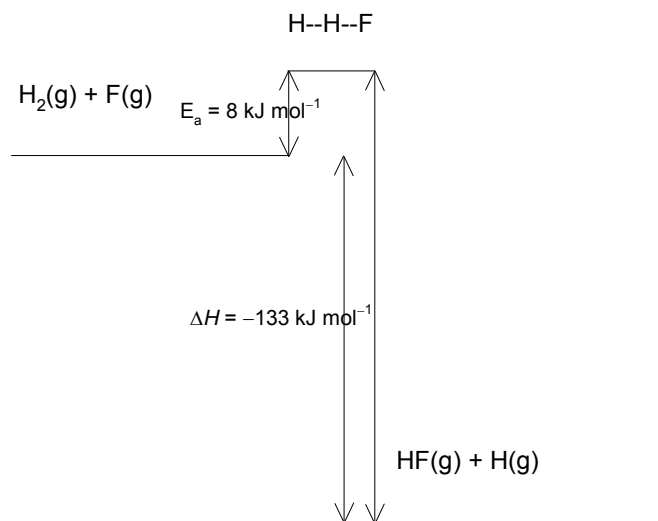   reaction.
       $k = 0.021$ s^{-1}

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

18.49 (a) 23 min
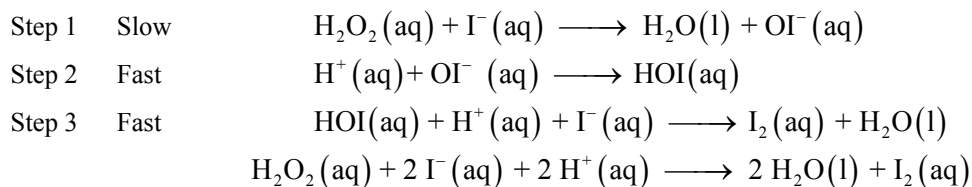   (b) 77 min

18.51 36 s

18.53 84.9 kJmol^{-1}

18.55

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

18.59 (a) Step 2
       (b) Rate = k_2 [O$_3$] [O]

18.61 (a)

Step 1	Slow	$H_2O_2(aq) + I^-(aq) \longrightarrow H_2O(l) + OI^-(aq)$
Step 2	Fast	$H^+(aq) + OI^-(aq) \longrightarrow HOI(aq)$
Step 3	Fast	$HOI(aq) + H^+(aq) + I^-(aq) \longrightarrow I_2(aq) + H_2O(l)$

$$H_2O_2(aq) + 2\,I^-(aq) + 2\,H^+(aq) \longrightarrow 2\,H_2O(l) + I_2(aq)$$

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

(c) Rate $= k_2\,[H_2O_2]\,[I^-]$

18.63 (a) $NO_2(g)$ and $CO(g)$ are reactants.
NO$_3$(g) is an intermediate.
CO_2(g) and NO(g) are products.

(b)

slow

fast

E_{a1}

E_{a2}

NO + NO$_3$ + CO

2 NO$_2$ + CO

ΔH

1 NO$_2$ appears as both reactant and
product - it cancels from the net reaction

NO$_2$ + NO + CO$_2$
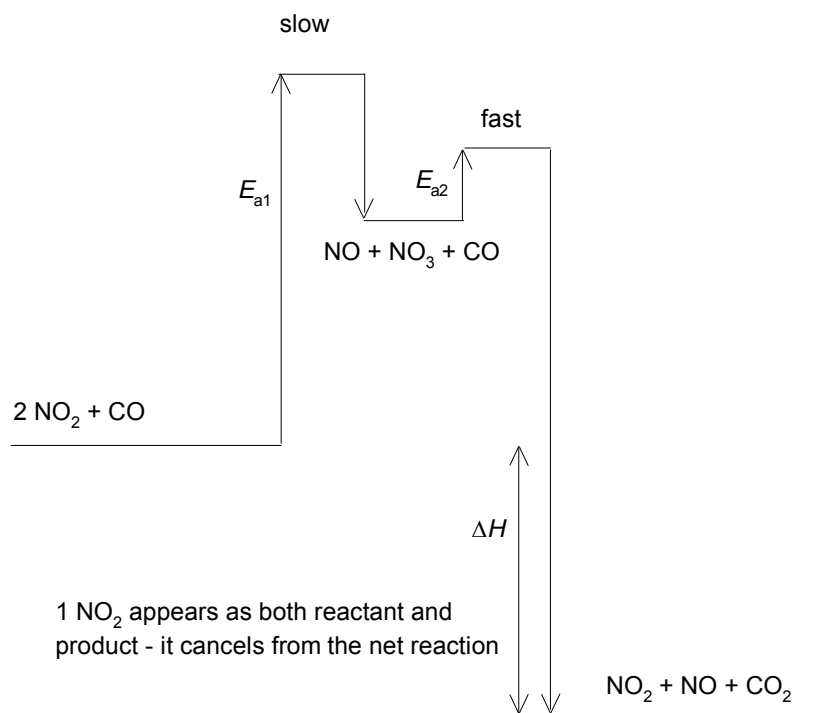
SUMMARY AND CONCEPTUAL QUESTIONS

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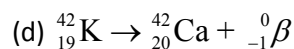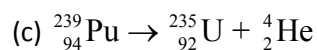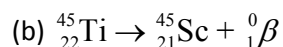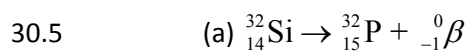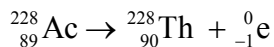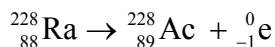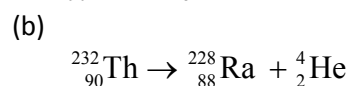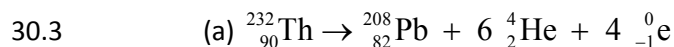   (d) False
          It is possible that the reaction proceeds via a single ternary process. Ternary processes are infrequent, but they can play important roles.

Chapter 30

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

30.1   (a) $_{86}^{222}Rn \rightarrow\ _{84}^{218}Po + _{2}^{4}He$

(b) $_{84}^{218}Po \rightarrow\ _{85}^{218}At + _{-1}^{0}e$
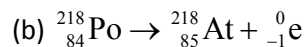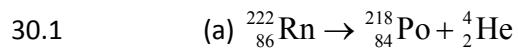
30.2 $E_{photon} = 9.9 \times 10^{-14}$ J
$E = 60$ GJ mol^{-1}

30.3   (a) $_{90}^{232}Th \rightarrow\ _{82}^{208}Pb\ +\ 6\ _{2}^{4}He\ +\ 4\ _{-1}^{0}e$

(b)

$$_{90}^{232}Th \rightarrow\ _{88}^{228}Ra\ +\ _{2}^{4}He$$

$$_{88}^{228}Ra \rightarrow\ _{89}^{228}Ac\ +\ _{-1}^{0}e$$

$$_{89}^{228}Ac \rightarrow\ _{90}^{228}Th\ +\ _{-1}^{0}e$$

30.4   (a) $_{7}^{13}N \rightarrow\ _{6}^{13}C + _{1}^{0}\beta$

(b) $_{20}^{41}Ca + _{-1}^{0}\beta \rightarrow\ _{19}^{41}K$

(c) $_{38}^{90}Sr \rightarrow\ _{39}^{90}Y + _{-1}^{0}\beta$

(d) $_{11}^{22}Na \rightarrow\ _{12}^{22}Mg + _{-1}^{0}\beta$

30.5   (a) $_{14}^{32}Si \rightarrow\ _{15}^{32}P + _{-1}^{0}\beta$

(b) $_{22}^{45}Ti \rightarrow\ _{21}^{45}Sc + _{1}^{0}\beta$

(c) $_{94}^{239}Pu \rightarrow\ _{92}^{235}U + _{2}^{4}He$

(d) $_{19}^{42}K \rightarrow\ _{20}^{42}Ca + _{-1}^{0}\beta$
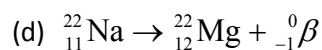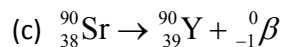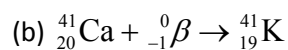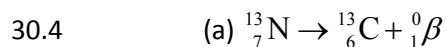
30.6   3.087 x 10^9 KJmol^{-1}
5.145 × 10^8 kJ mol^{-1} nucleons

30.7   (a) 0.094 mg
(b) 36.9 years
(c) 81.7 years

30.8   26.9 days

30.9   6200 years

30.10   The sample is t = 3010 years old.
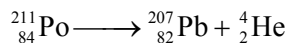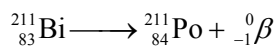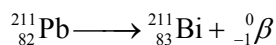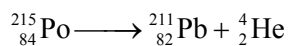The ring data give the age of the tree to be 2853 ± 52 years

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

REVIEW QUESTIONS

30.13 (a) $^{54}_{26}\text{Fe} + ^{4}_{2}\text{He} \longrightarrow 2^{1}_{0}\text{n} + ^{56}_{28}\text{Ni}$

(b) $^{27}_{13}\text{Al} + ^{4}_{2}\text{He} \longrightarrow ^{30}_{15}\text{P} + ^{1}_{0}\text{n}$
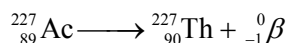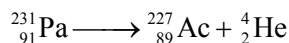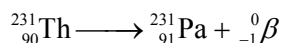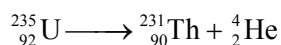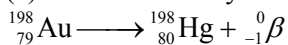
(c) $^{32}_{16}\text{S} + ^{1}_{0}\text{n} \longrightarrow ^{1}_{1}\text{H} + ^{32}_{15}\text{P}$

(d) $^{96}_{42}\text{Mo} + ^{2}_{1}\text{H} \longrightarrow ^{1}_{0}\text{n} + ^{97}_{43}\text{Tc}$

(e) $^{98}_{42}\text{Mo} + ^{1}_{0}\text{n} \longrightarrow ^{99}_{43}\text{Tc} + ^{0}_{-1}\beta$

(f) $^{18}_{9}\text{F} \longrightarrow ^{18}_{8}\text{O} + ^{0}_{1}\beta$

30.15 (a) $^{111}_{47}\text{Ag} \longrightarrow ^{111}_{48}\text{Cd} + ^{0}_{-1}\beta$

(b) $^{87}_{36}\text{Kr} \longrightarrow ^{0}_{-1}\beta + ^{87}_{37}\text{Rb}$

(c) $^{231}_{91}\text{Pa} \longrightarrow ^{227}_{89}\text{Ac} + ^{4}_{2}\text{He}$

(d) $^{230}_{90}\text{Th} \longrightarrow ^{4}_{2}\text{He} + ^{226}_{88}\text{Ra}$

(e) $^{82}_{35}\text{Br} \longrightarrow ^{82}_{36}\text{Kr} + ^{0}_{-1}\beta$

(f) $^{24}_{11}\text{Na} \longrightarrow ^{24}_{12}\text{Mg} + ^{0}_{-1}\beta$

30.17

$^{235}_{92}\text{U} \longrightarrow ^{231}_{90}\text{Th} + ^{4}_{2}\text{He}$

$^{231}_{90}\text{Th} \longrightarrow ^{231}_{91}\text{Pa} + ^{0}_{-1}\beta$

$^{231}_{91}\text{Pa} \longrightarrow ^{227}_{89}\text{Ac} + ^{4}_{2}\text{He}$

$^{227}_{89}\text{Ac} \longrightarrow ^{227}_{90}\text{Th} + ^{0}_{-1}\beta$

$^{227}_{90}\text{Th} \longrightarrow ^{223}_{88}\text{Ra} + ^{4}_{2}\text{He}$

$^{223}_{88}\text{Ra} \longrightarrow ^{219}_{86}\text{Rn} + ^{4}_{2}\text{He}$

$^{219}_{86}\text{Rn} \longrightarrow ^{215}_{84}\text{Po} + ^{4}_{2}\text{He}$

$^{215}_{84}\text{Po} \longrightarrow ^{211}_{82}\text{Pb} + ^{4}_{2}\text{He}$

$^{211}_{82}\text{Pb} \longrightarrow ^{211}_{83}\text{Bi} + ^{0}_{-1}\beta$

$^{211}_{83}\text{Bi} \longrightarrow ^{211}_{84}\text{Po} + ^{0}_{-1}\beta$

$^{211}_{84}\text{Po} \longrightarrow ^{207}_{82}\text{Pb} + ^{4}_{2}\text{He}$

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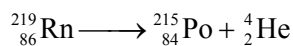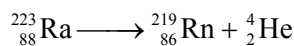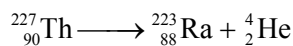
30.19 (a) Gold-198 decays to mercury-198.

$$^{198}_{79}\text{Au} \longrightarrow {}^{198}_{80}\text{Hg} + {}^{0}_{-1}\beta$$
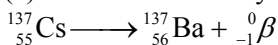
The atomic number increases by 1, while the mass number does not change. This is beta decay.
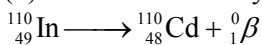
(b) Radon-222 decays to polonium-218.

$$^{222}_{86}\text{Rn} \longrightarrow {}^{218}_{84}\text{Po} + {}^{4}_{2}\text{He}$$
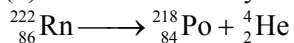
The atomic number decreases by 2, while the mass number decreases by 4. This is alpha decay.

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

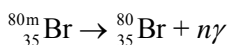$$^{137}_{55}\text{Cs} \longrightarrow {}^{137}_{56}\text{Ba} + {}^{0}_{-1}\beta$$

This is beta decay.

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

$$^{110}_{49}\text{In} \longrightarrow {}^{110}_{48}\text{Cd} + {}^{0}_{1}\beta$$

This is positron emission.

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

$$^{80m}_{35}\text{Br} \rightarrow {}^{80}_{35}\text{Br} + n\gamma$$

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.
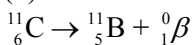
$$^{240}_{98}\text{Cf} \rightarrow {}^{240}_{97}\text{Bk} + {}^{0}_{1}\beta$$
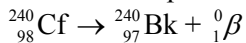
Alternatively: $^{240}_{98}\text{Cf} \rightarrow {}^{236}_{96}\text{Cm} + {}^{4}_{2}\text{He}$

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

$$^{61}_{27}\text{Co} \rightarrow {}^{61}_{28}\text{Ni} + {}^{0}_{-1}\beta$$
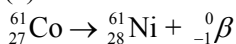
(d) Carbon-11 has a low neutron to proton ratio. It most likely decays by positron emission.

$$^{11}_{6}\text{C} \rightarrow {}^{11}_{5}\text{B} + {}^{0}_{1}\beta$$

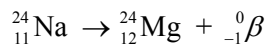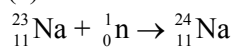30.23 (a) Of the nuclei ^{3}H ^{16}O ^{20}F and ^{13}N

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

(b) Of the nuclei ^{238}U ^{19}F ^{22}Na and ^{24}Na

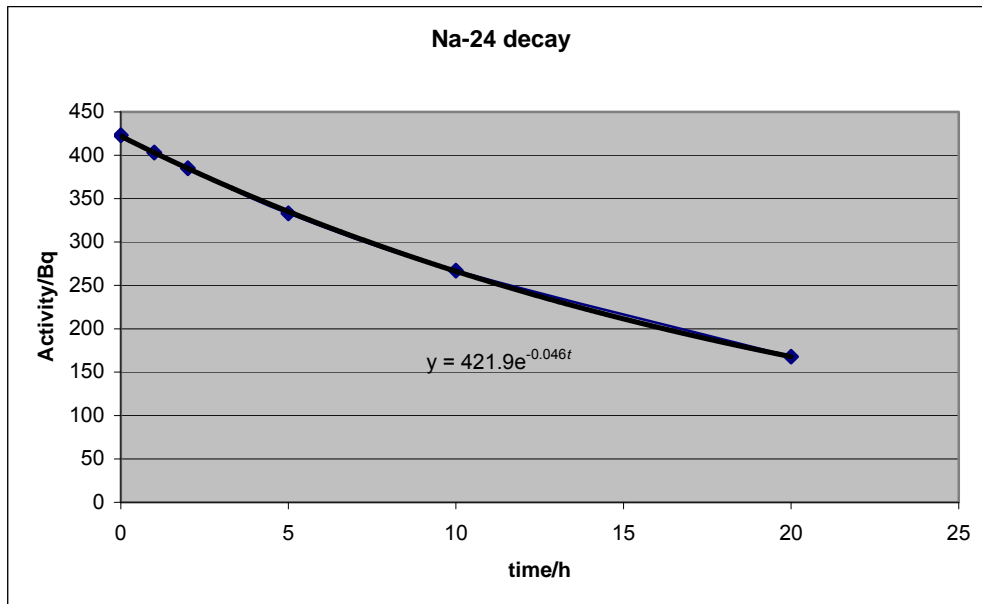^{22}Na has a low neutron to proton ratio and is likely to decay by positron emission.

30.25   For ^{10}B,
$\Delta m = 5 \times 1.00783 + 5 \times 1.00867 - 10.01294$ g mol^{-1} = 0.069510 g mol^{-1} =
6.9510×10^{-5} kg mol^{-1}
$E_b = \Delta m\, c^2$
$\qquad = 6.9510 \times 10^{-5}$ kg mol$^{-1} \times (2.998 \times 10^8$ m s$^{-1})^2$
$\qquad = 6.248 \times 10^{12}$ J mol^{-1} = 6.248×10^9 kJ mol^{-1}
Per nucleon,
$E_b / n = 6.248 \times 10^9$ kJ mol^{-1} / 10 = 6.248×10^8 kJ mol^{-1} nucleons
For ^{11}B,
$\Delta m = 5 \times 1.00783 + 6 \times 1.00867 - 11.00931$ g mol^{-1} = 0.081805 g mol^{-1} =
8. 1805×10^{-5} kg mol^{-1}
$E_b = \Delta m\, c^2$
$\qquad = 8. 1805 \times 10^{-5}$ kg mol$^{-1} \times (2.998 \times 10^8$ m s$^{-1})^2$
$\qquad = 7.353 \times 10^{12}$ J mol^{-1} = 7.353×10^9 kJ mol^{-1}
Per nucleon,
$E_b / n = 7.353 \times 10^9$ kJ mol^{-1} / 11 = 6.684×10^8 kJ mol^{-1} nucleons
We see that ^{11}B is the more stable nucleus—it has a higher binding energy per nucleon.

30.31   64 h corresponds to 64 h / 12.7 h = 5.04 half-lives. At this time, the mass of ^{64}Cu is
25.0 µg $\times (1/2)^{5.04}$ = 0.760 µg

30.33   (a) $^{131}_{53}\text{I} \rightarrow\ ^{131}_{54}\text{Xe} +\ ^{0}_{-1}\beta$
(b) 40.2 days corresponds to 40.2 days / 8.04 days = 5.00 half-lives. At this time, the mass of
^{198}Au is
$\qquad$ 2.4 µg $\times (1/2)^5$ = 0.075 µg

30.35   13 days corresponds to 13 days / (78.25 / 24) days = 4.0 half-lives. At this time, the mass of
^{67}Ga is
0.015 mg $\times (1/2)^{4.0}$ = 9.4 $\times 10^{-4}$ mg

30.37   (a) $^{222}_{86}\text{Rn} \rightarrow\ ^{218}_{84}\text{Po} +\ ^{4}_{2}\text{He}$
(b) 20.0% of ^{222}Rn remains after n half-lives.
$\qquad$ 0.200 = $(1/2)^n$
$\qquad n = \ln(0.200) / \ln(1/2) = 2.32$
$\qquad$ 2.32 half-lives corresponds to 2.32 $\times$ 3.82 days = 8.87 days

30.39   0.72 of the ^{14}C remains after n half-lives.
0.72 = $(1/2)^n$
$n = \ln(0.72) / \ln(1/2) = 0.47$
0.47 half-lives corresponds to 0.17 $\times$ 5.73 $\times 10^3$ years = 2700 years
This is the age of the bone fragment.

30.41   (a) A cobalt-60 source will drop to 1/8 of its original activity after n half-lives.
$\qquad$ 0.125 = $(1/2)^n$
$\qquad n = \ln(0.125) / \ln(1/2) = 3$
$\qquad$ 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}Co
remaining is
$\qquad (1/2)^{0.190} = 0.877$

30.43 (a)

$$^{23}_{11}\text{Na} + ^{1}_{0}\text{n} \rightarrow ^{24}_{11}\text{Na}$$

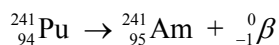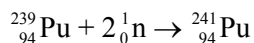$$^{24}_{11}\text{Na} \rightarrow ^{24}_{12}\text{Mg} + ^{0}_{-1}\beta$$

(b)

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

30.45

$$^{239}_{94}\text{Pu} + 2^{1}_{0}\text{n} \rightarrow ^{241}_{94}\text{Pu}$$

$$^{241}_{94}\text{Pu} \rightarrow ^{241}_{95}\text{Am} + ^{0}_{-1}\beta$$

30.47 $^{238}_{92}\text{U} + ^{12}_{6}\text{C} \rightarrow ^{246}_{98}\text{Cf} + 4^{1}_{0}\text{n}$

It must be carbon-12.

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

(b) $^{6}_{3}\text{Li} + ^{2}_{1}\text{H} \longrightarrow ^{7}_{4}\text{Be} + ^{1}_{0}\text{n}$

(c) $^{40}_{20}\text{Ca} + ^{2}_{1}\text{H} \longrightarrow ^{38}_{19}\text{K} + ^{4}_{2}\text{He}$

(d) $^{63}_{29}\text{Cu} + ^{2}_{1}\text{H} \longrightarrow ^{65}_{30}\text{Zn} + \gamma$

30.51 $^{10}_{5}\text{B} + ^{1}_{0}\text{n} \longrightarrow ^{7}_{3}\text{Li} + ^{4}_{2}\text{He}$

30.53 $^{6}_{3}\text{Li} + ^{1}_{0}\text{n} \rightarrow ^{3}_{1}\text{H} + ^{4}_{2}\text{He}$

SUMMARY AND CONCEPTUAL QUESTIONS

30.55 Carbon-14 levels in the atmosphere are in steady state—determined by the flux of cosmic rays that produce it in the upper atmosphere. Plants take up carbon-14 (via carbon dioxide) in proportion to its concentration in the atmosphere. When they die, no more carbon-14 is absorbed. The relative amount of carbon-14 (to carbon-12) decays exponentially with the known half-life of carbon-14. Measuring this isotope ratio allows the age of the sample to be determined—via the logarithm of the isotope ratio divided by its initial value (the atmospheric level). The method, as described here, assumes the atmospheric level has remained constant. This level is known to have varied by up to 10% in the past. The method can be corrected for this variation, however. Nevertheless, the method is limited to objects between 100 and 40,000 years old. There has not been enough carbon-14 decay in objects less than 100 years old, while the level of carbon-14 is too small to give an accurate age measurement beyond 40,000 years.

30.57 Radiation can cause transmutation of elements within cells, or can simply ionize or otherwise disrupt cellular molecules. The resulting chemical reactions can significantly affect cellular function and even damage DNA molecules. This can lead to cell death, if the cell is unable to repair the damage at the rate it occurs. Thus, exposure of humans to radiation can cause radiation sickness and even death, at sufficiently exposure levels. The killing of tissue by radiation can be used to treat diseases such as cancer, however. By focusing radiation on a tumour, we can kill the cancer tissue and possibly cure the patient.

30.59 The amount of ^{87}Rb is decreased by the factor,
$$0.951 = (1/2)^n$$
$$n = \ln(0.951) / \ln(1/2) = 0.072 \text{ half-lives}$$
This corresponds to $0.072 \times 4.8 \times 10^{10}$ years $= 3.5 \times 10^9$ years.

30.61 The amount of ^{235}U decreases by the factor
$$0.72 / 3.0 = 0.24 = (1/2)^n$$
$$n = \ln(0.75) / \ln(1/2) = 2.06 \text{ half-lives}$$
This corresponds to $2.06 \times 7.04 \times 10^8$ years $= 1.45 \times 10^9$ years.

30.63 Amount of ^{235}U $= 1000$ g $/ 235.0439$ g mol$^{-1} = 4.255$ mol
Amount of energy released by fission of uranium 235 $= 4.255$ mol $\times 2.1 \times 10^{10}$ kJ mol$^{-1} =$ 8.9×10^{10} kJ
To obtain the same amount of energy from coal requires
8.9×10^{10} kJ $/ 2.9 \times 10^7$ kJ t$^{-1} = 3100$ 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
2.0×10^6 Bq $/ 1.5 \times 10^4$ Bq $\times 1.0$ mL $= 130$ mL

30.67 We could label the methanol with the radioactive isotope, ^{15}O, carry out the reaction, and then sample the water and look for ^{15}O that could only have come from methanol. The same experiment could be carried out with labelled acetic acid to see if acid ^{15}O ends up in the water product.

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

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

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

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

$$k = (\Delta N / \Delta t) / N$$
$$= 12 \text{ s}^{-1} / 2.530 \times 10^{18} = 4.74 \times 10^{-18} \text{ s}^{-1}$$
$$= 4.74 \times 10^{-18} \text{ s}^{-1} \times (60 \times 60 \times 24 \times 365) \text{ s y}^{-1} = 1.50 \times 10^{-10} \text{ y}^{-1}$$
$$t_{1/2} = \ln(2) / k = 4.6 \times 10^{9} \text{ y}$$

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