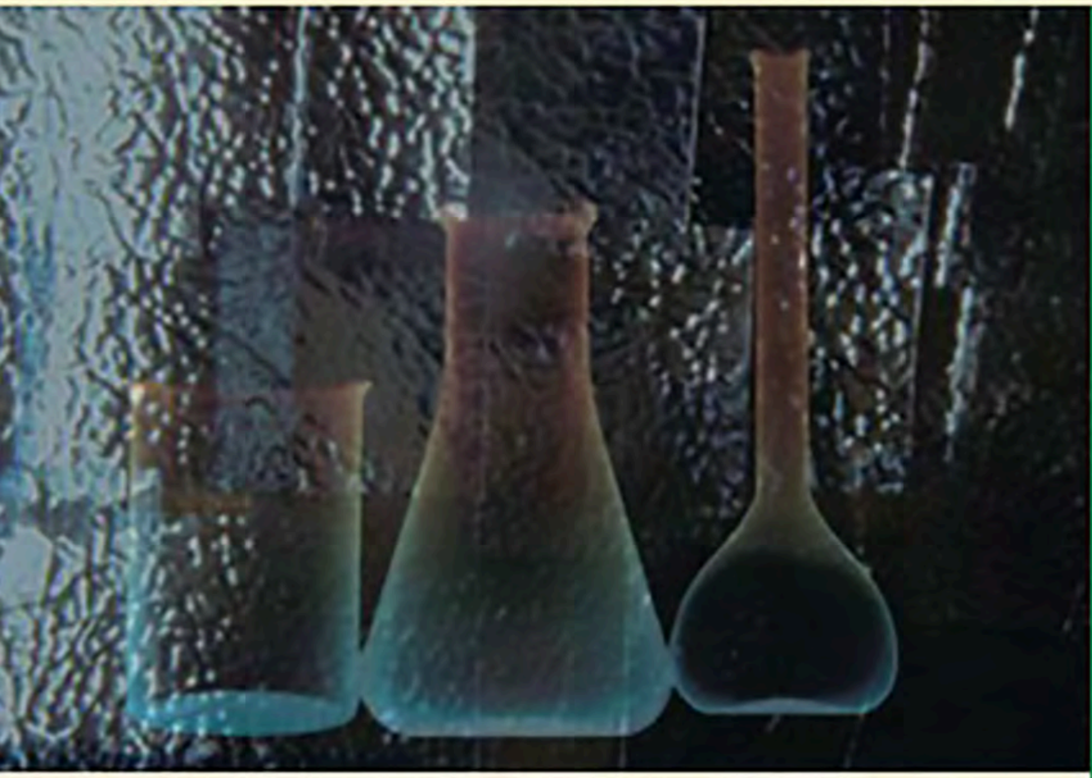
CHEMISTRY



ANSWERS

John Green
Sadru Damji

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3rd Edition

FOR USE WITH THE INTERNATIONAL BACCALAUREATE DIPLOMA PROGRAMME

CHAPTER 1 QUANTITATIVE CHEMISTRY

Page 4 Ex

1. D
2. C
3. B
4 (a) element; (b) mixture; (c) compound; (d) element; (e) compound
5. (a) mixture; (b) compound; (c) mixture; (d) element; (e) compound.

Page 5 Ex 1.1

1. D
2. C
3. C
4. D
5. C
6. D
7. a) 0.20 b) $1.2\cdot10^{23}$ c) $3.6\cdot10^{23}$
8. a) $3.61\text{x}10^{24}$ b) $5.4\text{x}10^{23}$

Page 7 Ex 1.2

1. D
2. A
3 a) 127.9 b) 106.4 c) 132.1 d) 126.1 e) 152.0 f) 233.3

Page 7 Ex 1.2.3

1. B
2. D
3. A
4. B
5. A
6. a) 51.1 g, b) 7.47 g, c) 10.7 g, d) 68.7 g, e) 1.90 g
7. a) 1.00, b) 3.00, c) 25.8, d) 5.44
8. a) 150 g mol^{-1}, b) 128 g mol^{-1}
9. $1.245\text{x}10^{23}$ molecules
10. a) $3.41\text{x}10^{-4}$, b) $5.68\text{x}10^{-3}$, c) $2.05\text{x}10^{22}$

Page 12 Ex1.2.4

1. D
2. C
3. B

4. D
5. B
6. C
7. A
8. B
9. D
10. B
11. 36.3%
12. a) Fe_2O_3 b) SiF_4 c) $C_2H_2O_4$
13. SnO_2
14. $CuSO_4.5H_2O$
15. 66700 g mol^{-1}
16. $K_2Cr_2O_7$
17. 354.5; 47.4% carbon, 2.56% hydrogen, 50.0% chlorine
18. a) 0.409 g carbon and 0.0453 g hydrogen b) 0.545 g oxygen c) $C_3H_4O_3$
19. $C_2H_5N_3O_2$; $C_4H_{10}N_6O_4$
20. 56.7%

Page 14 Ex 1.3

1. A
2. C
3. D
4. a) H_2SO_4, b) NaOH, c) HNO_3, d) NH_3, e) HCl,
   f) CH_3COOH, g) $CuSO_4$, h) CO, i) SO_2, j) $NaHCO_3$
5. a) NaCl b) CuS c) $ZnSO_4$ d) Al_2O_3 e) $Mg(NO_3)_2$
   f) $Ca_3(PO_4)_2$ g) HI h) $(NH_4)_2CO_3$ i) CH_4 j) PCl_5

CHAPTER 1 QUANTITATIVE CHEMISTRY

Page 17 Ex 1.3.1

1. C
2. B
3. A
4. a) $CaO + 2\ HNO_3 \rightarrow Ca(NO_3)_2 + H_2O$
   b) $2NH_3 + H_2SO_4 \rightarrow (NH_4)_2SO_4$
   c) $2HCl + ZnCO_3 \rightarrow ZnCl_2 + H_2O + CO_2$
   d) $SO_2 + 2\ Mg \rightarrow S + 2MgO$
   e) $Fe_3O_4 + 4\ H_2 \rightarrow 3Fe + 4H_2O$
   f) $2K + 2C_2H_5OH \rightarrow 2KC_2H_5O + H_2$
   g) $2Fe(OH)_3 \rightarrow Fe_2O_3 + 3H_2O$
   h) $CH_3CO_2H + 2\ O_2 \rightarrow 2CO_2 + 2\ H_2O$
   i) $2Pb(NO_3)_2 \rightarrow 2PbO + 4NO_2 + O_2$
   j) $2NaMnO_4 + 16HCl \rightarrow 2NaCl + 2MnCl_2 + 5Cl_2 + 8H_2O$

5. a) $CuCO_3 \rightarrow CuO + CO_2$
   b) $NiO + H_2SO_4 \rightarrow NiSO_4 + H_2O$
   c) $2\ Fe + 3\ Br_2 \rightarrow 2\ FeBr_3$
   d) $PbO_2 + 2\ CO \rightarrow Pb + 2\ CO_2$
   e) $2\ FeCl_2 + Cl_2 \rightarrow 2\ FeCl_3$
   f) $C_2H_5OH + 3\ O_2 \rightarrow 2\ CO_2 + 3\ H_2O$
   g) $Ag + 2\ HNO_3 \rightarrow AgNO_3 + NO_2 + H_2O$
   h) $MnO_2 + 4HCl \rightarrow MnCl_2 + Cl_2 + 2H_2O$
   i) $SO_2 + 2H_2S \rightarrow 3S + 2H_2O$
   j) $4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O$

Page 19 Ex 1.4

1. C
2. B
3. a) $2\ KClO_{3(s)} \rightarrow 2\ KCl_{(s)} + 3\ O_{2(g)}$
   b) 0.4 moles
   c) 2.45 g
4. 37.69 g
5. a) MnO_2 ; Mn_3O_4,
   b) $3\ MnO_2 \rightarrow Mn_3O_4 + O_2$,
   c) 0.353 g

CHAPTER 1 QUANTITATIVE CHEMISTRY

Page 21 Ex 1.4.1

1. a) Limiting reagent is Al, yield is 1.2 mol,
   b) Limiting reagent is I_2, yield is 2.57 g
   c) 1.03 g excess aluminium
2. a) Limiting reagent is SbF_3, CCl_4 is in excess
   b) 101.5 g
   c) 20.9 g
3. a) Limiting reagent is salicylic acid
   b) 1.30 kg
   c) 90.6%

Page 23 Ex 1.4.2

1. C
2. D
3. A
4. B
5. D
6. 30 cm^3 of oxygen remains unreacted
7. $1.20 \cdot 10^{23}$
8. 46.8 g mol^{-1}
9. 0.761 g dm^{-3}
10. 2.24×10^5 dm^3 (224 m^3)

CHAPTER 1 QUANTITATIVE CHEMISTRY

Page 25 Ex 1.4.3

1. A
2. A
3. C
4. B
5. D
6. C
7. a) 0.0139 moles, b) 83.2%
8. a) 1100 dm^3 b) 100 g (n.b. H_2)
9. Mass of gas in flask = 4.685 g;

   Volume of flask (assuming density of water = 1 kg dm^{-3}) = 0.8043 dm^3;

   The flask contains 0.03193 moles at this T & P, hence the molar mass = 146.7 g mol^{-1}.
10. The pressure in both flasks must be equal, therefore

$$P = \frac{nRT}{V} = \frac{x \times R \times 600}{V} = \frac{(2-x) \times R \times 300}{V} \Rightarrow 600x = 600 - 300x \Rightarrow x = \frac{6}{7}$$

Therefore there is 8/7 mol in the flask at 27 K and 6/7 mol in the flask at 127 K.

$$P = \frac{nRT}{V} = \frac{\frac{6}{7} \times 8.31 \times 400}{5} = 570\text{kPa}$$

Page 28 Ex 1.5

1. A
2. D
3. B
4. a) 0.75 mol dm^{-3}

   b) 0.0250 mol dm^{-3}

   c) 0.0811 mol dm^{-3}
5. a) 2.1 moles,

   b) 0.0020 moles,

   c) 2.55x10^{-3} moles
6. a) 0.4 dm^{-3} b) 2.94 dm^{-3} c) 0.720 dm^{-3} (=720 cm^{-3})
7. Weigh out precisely 2.922 g of solid sodium chloride (0.0500 moles) and make it up to 500 cm^3 of solution in a 500 cm^3 volumetric flask.
8. Measure out 240 cm^3 of 2.0 mol dm^{-3} hydrochloric acid (0.48 moles) and make this up to 1.2 dm^3 of solution.
9. 1.25 mol dm^{-3}
10. $[NO_{3-}]$ = 0.8 mol dm^{-3}, [Cl–] = 0 mol dm^{-3}, $[H^+]$ = 0.4 mol dm^{-3},

    $[Pb^{2+}]$ = 0.2 mol dm^{-3}

CHAPTER 1 QUANTITATIVE CHEMISTRY

Page 31 Ex 1.5.1

1. C
2. A
3. D
4. a) 0.0125 moles, b) 0.0125 moles, c) 0.625 mol dm^{-3}
5. a) $3.75x10^{-4}$ moles, b) $1.875x10^{-4}$ moles, c) 0.556 g dm^{-3}
6. a) Ag^+(aq) + Cl–$_{(aq)}$ → $AgCl_{(s)}$, b) $4.00x10^{-3}$ moles, c) $2.00\cdot10^{-3}$ moles,
   d) 90.66%

7 a) $5.01x10^{-4}$ moles, b) $2.51x10^{-3}$ moles, c) 0.711 g, d) 0.268 g, $x = 6$

8 a) 9.46 mol dm^{-3}, b) 105.7 cm^3

9 a) $6\ Fe^{2+}(aq) + Cr_2O_7^{2-}(aq) + 14\ H^+(aq) \rightarrow 6\ Fe^{3+}(aq) + 2\ Cr^{3+}(aq) + 7\ H_2O_{(l)}$,

b) $3.74x10^{-4}$ moles, c) $2.24\cdot10^{-3}$ moles, d) 96.4%

10. 122 g mol^{-1}, possibly benzoic acid (C_6H_5COOH)

Page 33 Ex 1.5.2

1. a) 0.0050, b) 0.010, c) 0.005, d) 0.9 g, e) 90%
2. 82.6%. It was assumed that the impurities in the marble reacted with neither acid nor alkali. It was assumed that none of the evolved carbon dioxide remained in solution to react with the alkali.
3. a) 12.0 g mol^{-1} b) 24.0 g mol^{-1} c) 36.0 g mol^{-1}.

   Answer b) is most likely as this molar mass corresponds to magnesium, which is a divalent metal, rather than to carbon or chlorine.

Page 35 Ex 1.5.3

1. C
2. C
3. A
4. a) $4.376x10^5$, b) $2.3x10^{-7}$, c) $4.15x10^8$, d) $3.72x10^{-2}$, e) $4.768x10^2$, f) $3.26x10^0$
5. a) 820000, b) 0.00629, c) 271 380 000 000, d) 0.0000002, e) 42, f) 0.589

Page 36 Ex 1.16

1. B
2. D
3. B
4. B

5 a) 0.028, b) 28, c) $3.76\cdot10^5$, d) 0.00175, e) $2x10^9$

CHAPTER 2 ATOMIC STRUCTURE

Page 50,51 Ex 2.1

1. D
2. B
3. C
4. A
5. C
6. a) electron; b) neutron; c) electron; d) proton; e) electron
7.

Element	Protons	Neutrons	Electrons
Helium	2	2	2
Nitrogen	7	7	7
Aluminium	13	14	13
Manganese	25	30	25
Iodine	53	74	53

8. a) Atoms that have the same atomic number (number of protons), but a different number of neutrons (mass number).

   b) Mass numbers 10 and 11 $^{10}_{5}B$ and $^{11}_{5}B$

   c) 10.8

9. The calcium phosphate, containing traces of the radioisotope, could be mixed into the soil, in the same proportions for all the plants being tested. The radioactivity of the leaves of the plants could then be monitored and the rate of increase in radioactivity, as a result of the radioisotope, compared.

10.

	No. Protons	No. Neutrons	No. Electrons	Atomic No.	Mass No.
Isotope 1	29	34	29	29	63
Isotope 2	29	36	29	29	65

therefore 72.5% ^{63}Cu and 27.5% ^{65}Cu

11.

Isotope	No. protons	No. neutrons	No. electrons
$^{3}_{1}H$	1	2	1
$^{15}_{7}N$	7	8	7
$^{57}_{26}Fe$	26	31	26
$^{90}_{38}Sr$	38	52	38
$^{235}_{92}U$	92	143	92

12.

Isotope	No. protons	No. neutrons	No. electrons
$^{3}_{1}H^{-}$	1	2	2
$^{24}_{12}Mg^{2+}$	12	12	10

CHAPTER 2 ATOMIC STRUCTURE

Page 54 Ex 2.2

1. a) They are bombarded with fast moving electrons.

b) The paths of the moving ions are deflected by a magnetic field.

c) They are collected on a metal plate and the current flowing to neutralise the charge on the plate is recorded. (A number of other possible correct answers)

2. A doubly charged germanium-70 would produce a peak at a mass of 35.

3. a) $^{188}_{76}\mathrm{Os}$ − 14%; $^{189}_{76}\mathrm{Os}$ − 17%;
$^{190}_{76}\mathrm{Os}$ − 27%; $^{192}_{76}\mathrm{Os}$ − 42% b) 190

4. Let % of ^{207}Pb and ^{208}Pb = y, $\therefore$% of ^{206}Pb = (100-2y)

206(100-2y) + 207y + 208y = 207.2 x 100

3y = 20720-20600; $\therefore$ y = 120/3 = 40

20% ^{206}Pb, 40% ^{207}Pb and 40% ^{208}Pb.

Page 59 Ex 2.3

1. C
2. A
3. D
4. C
5. C
6. B
7 D
8. a) 2,2
   b) 2,8,3
   c) 2,7
   d) 2,8,8
   e) 2,8,6
9. a) They are isotopes of the same element.

b) Chemical properties depend primarily on the number of electrons that an atom has and the nuclear charge affecting these. Both isotopes have the same number of electrons and the same nuclear charge.

10 a) Because the electrons in the hydrogen atom can only have certain allowed energies and light emission depends on transitions between these.

b) The different series correspond to transitions to a given level from a higher level. The transition from the next higher level is the largest component of this, hence this dictates the spectral region it occurs in.

c) As the allowed electron levels move to higher energy the difference in energy from the previous level becomes smaller, hence the difference in the frequencies of the light emitted by successive transitions becomes smaller.

Page 67 Ex 12.1

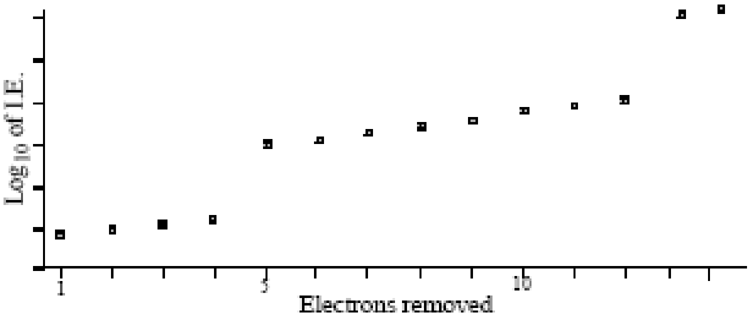
1. C
2. C
3. B
4. C
5. B
6. B
7. C
8. D
9. a) $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^5\ 4s^2$

   b)$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^4$

   c)$1s^2\ 2s^2\ 2p^6$

   d)$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^5$

   e)$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^1$
10. Na < Li < O < N < Ne
11. a)



b) Four electrons are lost relatively easily and they can be thought of as being in the highest energy level. The next eight are rather more difficult to remove and they may be thought of as being in the intermediate level. The remaining two electrons are very difficult to remove and can be thought of as forming the lowest energy level.

c) As successive electrons are removed, the electron–electron repulsion acting on the remaining electrons, which to some extent counteracts the attractive force of the nucleus, decreases. This means that as more electrons are removed from an energy level, (or as more electrons are removed, the remaining electrons are more attracted to the nucleus) so that the energy required to remove the remaining electrons increases.

12 a) In both cases the effective nuclear charge acting on the outermost electron is +1. The electron being lost in sodium however is further from the nucleus and so less strongly held by electrostatic forces than the electron in lithium.

b) In oxygen one of the 2p–orbitals is doubly filled. This means that there is increased repulsion between the two electrons sharing the orbital. This increased repulsion more than offsets the effect of the increase in nuclear charge on going from nitrogen to oxygen.

c) In beryllium the electron lost comes from a 2s energy level, whereas in boron the electron lost comes from a 2p orbital, which is at a higher energy than the 2s. This difference in energy of the 2s and 2p orbitals more than offsets the greater nuclear charge in boron.

13. a) Vanadium

b) $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^3\ 4s^2$

c) The electronic structure of the ion could not be that of an atom because the 3d level contains electrons, but there are no electrons in the 4s level. In neutral atoms electrons always at least partially fill the 4s before starting to fill the 3d.

14. a) The element is aluminium. (It must be in group 3 because 3 electrons are easily lost before a sudden increase in IE, but it cannot be boron because it contains at least 6 electrons.)

b) About 4.4 (just slightly greater than that for the last electron shown.)

c) They would be greater because even though the two elements have the same effective nuclear charge, the electrons being lost would be closer to the nucleus and hence more strongly attracted.

15. a) B and D

b) A – the first three electrons have much lower ionisation energies than the fourth.

c) A and D or E and D.

d) C – it has a high first ionisation energy and it must have more than four electrons in the outer shell as there is no sudden increase in ionisation energy.

CHAPTER 3 PERIODICITY

Page 72 Ex 3.1

1. A
2. C
3. a) 7

   b) 2

   c) One of Na, Mg, Al, Si, P, S, Ar

   d) One of F, Br, I, At

   e) Halogens

Page 75 Ex 3.2

1. C
2. D
3. D
4. C
5. Al, Mg, Ca, Ba, Cs
6. a) Decrease–the valence shell electrons are further away from the charge on the nucleus.

   b) Decrease – the nuclear charge increases and valence electrons are in the same main energy level thus pulling the valence electrons closer in.

   c) Increase – the increased electron–electron repulsion pushes the electrons further from the nucleus.

   d) Decrease – the valence electrons are further from the nucleus so are more easily lost.

   e) Decrease – the increasing nuclear charge attracts the valence electrons more strongly.

Page 80,81 Ex 3.3

1. C
2. A
3. B
4. A
5. A
6. a) $2\ Na + 2\ H_2O \rightarrow 2\ NaOH + H_2$

   b) The sodium would fizz around on the surface as a molten blob, slowly dissolving.

   c) Redox

   d) With lithium the reaction takes place gently and with potassium the reaction is so violent that the hydrogen ignites with a lilac flame.
7. a) Purple b) White c) Black d) Yellow-brown e) Yellow

8. a) $Ag^{+}_{(aq)}+Br^{-}_{(aq)} \rightarrow AgBr_{(s)}$

b) Add aqueous lead nitrate. If I^- is present a yellow precipitate forms. If Br^- is present the precipitate will be white $Pb^{2+}_{(aq)}+2I^{-}_{(aq)} \rightarrow PbI_{2\,(s)}$. Alternatively add chlorine water followed by an immiscible organic solvent (e.g. hexane) and if the organic solvent turns purple as a result of iodine dissolving in it, I– is present $Cl_{2\,(aq)} + 2\,I^{-}_{(aq)} \rightarrow I_{2\,(aq)} + 2Cl^{-}_{(aq)}$. If Br– was present the bromine formed will turn the organic layer brown $Br_{2\,(aq)} + 2\,I^{-}_{(aq)} \rightarrow I_{2\,(aq)} + 2\,Br^{-}_{(aq)}$.

9. a) Yes; the colourless (pale green solution) will turn yellow–brown;

$Cl_2 + 2\,Br^- \rightarrow Br_2 + 2\,Cl^-$

b) No reaction

c) Yes; the yellow–brown solution will turn to another yellow–brown solution and with excess bromine a black solid will form; $Br_2 + 2\,I^- \rightarrow I_2 + 2\,Br^-$

d) No reaction

10. a) Going from left to right the oxides change from basic to amphoteric to acidic in character.

Acidic, SO_2 (or SO_3 or oxides of P): $SO_2 + H_2O \rightleftharpoons HSO_3^{-} + H^{+}$

Basic, Na_2O (or MgO): $Na_2O + H_2O \rightarrow 2\,Na^{+} + 2\,OH^{-}$

b) The oxidising strength decreases going down the group. Going down the group the electron being gained is successively further away from the nucleus and hence are less strongly attracted.

c) The reducing strength increases going down the group. Going down the group the electrons are successively further away from the nucleus and hence are more easily lost.

Page 84 Ex 13.1

1. C

2. B

3. a) With sodium chloride there is no chemical reaction, the ions that exist in the solid just become free to move. In the case of phosphorus trichloride, there is a hydrolysis reaction to produce a solution containing ions:
$PCl_3 + 3H_2O \rightarrow H_3PO_3 + 3H^{+} + 3Cl^{-}$

b) i) Add aqueous silver nitrate to both solutions and a white precipitate would be formed in both cases.

ii) Test both solutions with blue litmus paper. The solution formed from the phosphorus trichloride is acidic and will turn it red, but that from the sodium chloride is neutral and so will not affect it.

4. **Basic** - Na_2O or MgO. These react with acids, but not with bases, e.g.
$Na_2O + 2\,HCl \rightarrow 2\,NaCl + H_2O$; $MgO + H_2SO_4 \rightarrow MgSO_4 + H_2O$

Amphoteric-Al_2O_3. This reacts with both acids and bases, e.g.
$Al_2O_3 + 6\,HCl \rightarrow 2\,AlCl_3 + 3\,H_2O$ & $Al_2O_3 + 2\,NaOH + 3\,H_2O \rightarrow 2\,NaAl(OH)_4$

Acidic - P_4O_{10}, P_4O_6, SO_2, or SO_3. These dissolve in water to form acidic solutions, e.g. $P_4O_{10} + 6\,H_2O \rightarrow 4\,H^{+} + 4\,H_2PO_4^{-}$; $SO_2 + H_2O \rightleftharpoons H^{+} + HSO_3^{-}$

5. The elements change from metallic (e.g. Na) to non–metallic (e.g. P) because as the charge on the nucleus increases going from left to right across the period, so do the ionisation energies and electronegativities of the elements. At the left hand side the elements bond by metallic bonding, with the valence electrons being delocalised. The chlorides are ionic because the elements readily lose electrons to form cations as a result of their low ionisation energies. The elements in the middle and right of the period are joined by covalent bonds, though in the centre this occurs as giant structures, whereas on the right hand side the structure is molecular. The chlorides of the elements in the middle and right of the period are all molecular covalent, because the ionisation energies are too high for cation formation.

Page 95 Ex

1. B
2. C
3. C
4. D
5. B
6. a) Elements in the s–block of the periodic table have a small number of electrons in their valence shell, that are relatively easily lost. The energy required to remove electrons from the filled inner shells is however so great that it is never energetically feasible. In the case of transition metals such as manganese the first few ionisation energies are somewhat higher, but even so manganese will always lose its two 4s electrons (the 3d electrons are buried under the 4s cloud). The ionisation energies for the 3d electrons are quite high, but there is no sudden rise in ionisation energy until all the 4s and 3d electrons have been lost, corresponding to the +7 state. Hence the precise oxidation state achieved depends on the oxidising agents present and the complex ions that can form.

   b) The hexaaquanickel(II) ion reacts with chloride ions from the acid to form the tetrachloronickel(II) complex ion:

   $[Ni(H_2O)_6]^{2+} + 4Cl^- \rightarrow NiCl_4^{2-} + 6H_2O$.

   The energies of the d–orbitals in the two ions are slightly different and hence they absorb light of a different wavelengths, giving slightly different colours.

   c) In order to form a bond to the metal ion, a species must have a lone pair of electrons that it can share with the ion to form a dative covalent bond (Lewis acid-base reaction). Ammonia has a lone pair of electrons on the nitrogen, but methane does not.

7. a) The blue and colourless solutions initially react to form a pale blue precipitate, but in the presence of excess ammonia this dissolves to form a dark blue solution.

   b) The colourless gas reacts to change the colour of the solution from orange to green due to Cr^{3+} ions.

   c) The pale green colour of the aqueous iron(II) sulfate darkens to a yellow–brown colour when it is heated with the colourless hydrogen peroxide. When aqueous sodium hydroxide is added a red–brown precipitate forms.

   d) When the black powder is added to the colourless hydrogen peroxide, there is an evolution of bubbles of a colourless gas. Finally the test tube contains a colourless liquid and the black powder remains unchanged.

8. Haber process and Contact process. (*Other answers possible*)

a) Iron metal, vanadium(V) oxide.

b) $N_2 + 3H_2 \rightleftharpoons 2NH_3$; $2SO_2 + O_2 \rightleftharpoons 2SO_3$

Both of these processes involve heterogeneous catalysts. These are in a different phase to the reactants (iron, for example provides an active surface on which the reaction occurs). A homogeneous catalyst is in the same phase as the reactants and is consumed in one step of the mechanism, but regenerated during a subsequent step.

9. a) $[Cu(H_2O)_6]^{2+}$ changing to $[CuCl_4]^{2-}$.

b) $[Cu(NH_3)_4]^{2+}$.

c) $[CoCl_4]^{2-}$ changing to $[Co(H_2O)_6]^{2+}$.

d) $Cr_2O_7^{2-}$ changing to CrO_4^{2-}.

e) MnO_4^- changing to MnO_4^{2-}.

10. a) Octahedral

b) +2 in $[Fe(CN)_6]^{4-}$ and +3 in $[Fe(CN)_6]^{3-}$

c) $^-$:CN. The presence of a lone pair allows complex formation.

11. a) The third ionisation energy of Ti is not much higher than the second ionisation energy, because it comes from a 3d orbital, which is of similar energy to the 4s orbital, hence Ti can quite easily lose a third electron. In the case of Ca the third electron would have to come from a 3p orbital, which is at a much higher energy, hence Ca does not readily lose a third electron.

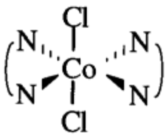
b) V^{3+} has electrons in the 3d sub–level. These electrons can move from one 3d orbital to another of higher energy and this process involves the absorption of light in the visible region of the spectrum, making the compound coloured. In the case of Sc^{3+} there are no electrons in the d–orbital, hence this cannot occur so the compounds are colourless.

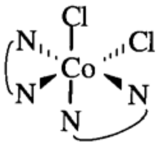
c) V^{3+} has electrons in the 3d sub–level which it can readily lose and hence act as a reducing agent, likewise it can accept another electron into this orbital and act as an oxidising agent. Sc^{3+} has a noble gas structure with filled electron shells. Losing an additional electron would require a great deal of energy and hence does not occur. Similarly because the nuclear charge is less than vanadium, gaining a single electron into an outer shell is not energetically feasible.

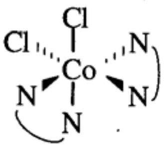
d) Cu^+ has a completely filled d–orbital hence electron transitions cannot occur between these and absorb light in the visible region. In Cu^{2+} there is a vacancy in the d–orbitals allowing such transitions and the absorption of light.

e) The complex has an octahedral geometry. Three identical ligands can either occupy sites all at 90° to each other, or a pair of identical ligands can be directly opposite each other.

12. a)







The left hand diagram and the right hand diagrams are geometrical isomers of each other; the left had being the 'trans–' form and the right hand ones both 'cis–' forms.

b) The pair of right hand diagrams are non–superimposable mirage image forms (i.e. enantiomers. It can be seen that the mirror image of the more symmetrical trans–form is superimposable on the original and so enantiomeric forms do not exist.

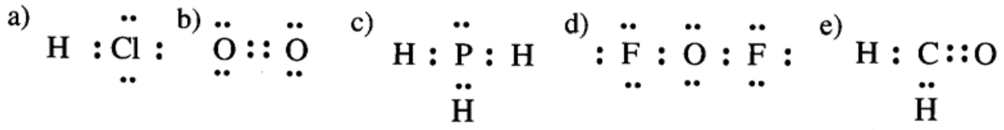
CHAPTER 4 BONDING

Page 101 Ex 4.1

1. D
2. D
3. B
4. a) potassium bromide b) lithium nitride c) barium sulfide
   d) aluminium iodide e) beryllium oxide
5. a) AB b) BA c) A_2B d) AB_3 e) B_3A_2

Page 106 Ex 4.2

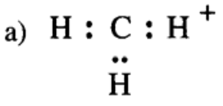
1. C
2. B
3. C
4. C
5. C
6. a) No compound (He is a noble gas) b) HCl c) NCl_3 d) SiF_4 e) P_2O_3
7. a) covalent b) covalent c) ionic d) covalent e) no compound
8.



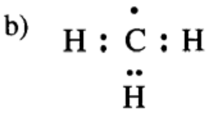
Page 111 Ex 14.1

1. A
2. A
3. a) tetrahedral b) trigonal pyramid c) non–linear, bent or ‘V’- shaped
   d) trigonal pyramid e) tetrahedral

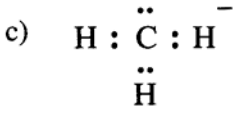
4.



trigonal planar
120°

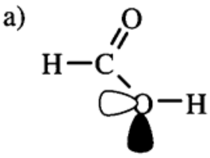


trigonal pyramid
~115°

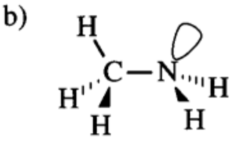


trigonal pyramid
~107°

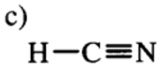
5.



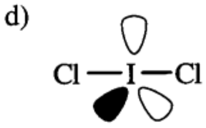
120° round C,
C–O–H ~104°



~109° round C,
~107° round N



180°



180°

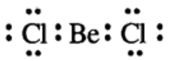
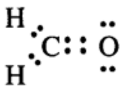
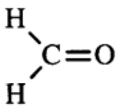
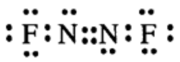
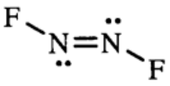
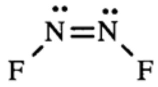
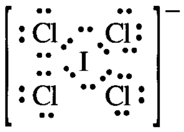
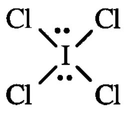
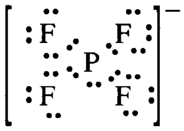
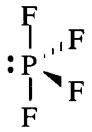
CHAPTER 4 BONDING

Page 113 Ex 14.1

1. C
2. C
3. a) non-polar b) polar c) slightly polar d) polar e) non-polar
4. a) N b) O c) F d) neither e) O
5. a) C-Cl will be the most polar, C=C the least polar

   b) A will be polar and B non- polar. In A the bond dipoles do not cancel whereas B has symmetrical electron distribution since the bond dipoles cancel.

   c) Put some of each liquid into a burette and allow it to run through the jet. Bring an electrically charged plastic rod close to, but not touching the stream of liquid. If the liquid is A, the stream will deflect and if it is B it will not deflect.
6.

Lewis structure	Diagram	Shape/ bond angle	Polarity
	Cl − Be − Cl	180° Linear	Non-polar
		120° Trigonal planar	Polar
	 	117° Planar	Non-polar polar
		90° Square planar	Non-polar
		~90° & 120° 'Saw-horse'	Polar

CHAPTER 4 BONDING

Page 117 Ex 14.2

1. C

2. a) Hybridisation is the combining of a number of atomic valence orbitals to form an equal number of identical orbitals of equal energy to be used in the formation of covalent bonds. In this case one s–orbital and two p–orbitals have combined to form three sp^2 hybrid orbitals.

   b) The shape of BF_3 is trigonal planar. This is also the shape of sp^2 hybrid orbitals.

   c) As the shape of the BF_4^- ion is tetrahedral, the hybridisation must be sp^3.

Page 118 Ex 14.2

1. D

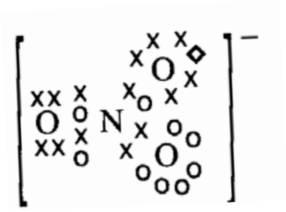
2. a) The single bond is a σ-bond. The double bond is a σ-bond and a π-bond. The triple bond is a σ-bond and two π-bonds.

   b) The shortest bond would be in C≡O, the bond in O=C=O would be intermediate in length and that in CH_3-OH would be the longest.

Page 121 Ex 14.3

1. B

2. a)



   b) This would predict that one of the nitrogen oxygen bonds would be shorter than the other two. Also with the charge all on one oxygen it is unlikely that it would have the precise trigonal planar symmetry found.

   c) The bonding is better described by considering the nitrogen and oxygen atoms to be joined by three σ-bonds and for there also to be a delocalised π-bond that connects all four atoms.

   d) The σ-bonds would be formed between sp^2 hybrid orbitals on the oxygen and nitrogen atoms. The delocalised π-bond would be the result of the interaction of the p-orbitals, on all of the atoms, that are at right angles to the sp^2 hybrid orbitals.

   e) The bond between the nitrogen and the oxygens would be equivalent to $1\frac{1}{3}$ bonds and each oxygen atom would carry a charge of $-\frac{1}{3}$

   f) It would be expected that the N–O bond length in the nitrate ion (bond order $1\frac{1}{3}$) would be longer than the N=O bond in nitric acid, but shorter than the N–O bond.

Page 125,126 Ex 4.3

1. D
2. A
3. B
4. D
5. B
6. a) These molecules have only van der Waals' forces between them. The strength of these forces increases with molar mass, so that the intermolecular forces are strongest in iodine, making it a solid, intermediate in bromine, hence it is a liquid, and least in chlorine, which is therefore a gas.

   b) Water molecules are held together by relatively strong hydrogen bonds. Sulfur is not sufficiently small and electronegative enough to give rise to hydrogen bonding in hydrogen sulfide, which therefore has a much lower boiling point as a result of the weaker intermolecular forces.

   c) Hydrogen bonding can occur between the -OH groups on the ethanol molecules, hence there are quite strong intermolecular forces between the molecules. Although methoxymethane contains an oxygen, there are no suitable hydrogen atoms for hydrogen bonding to take place, hence the intermolecular forces are only the much weaker dipole- dipole forces, resulting in a lower boiling point.

   d) The strength of the van der Waals' forces between these molecules will increase with the surface area of the molecule, hence they are weakest in the more spherical molecule, the weaker the forces and the lower the boiling point. The shape of pentan-3-ol is more spherical than pentan-1-ol, hence its lower boiling point.

   e) sulfur dioxide is a polar molecule and hence it will have dipole-dipole forces between its molecules. These are stronger than the van der Waals' forces between chlorine molecules, hence its higher boiling point, in spite of its lower molar mass.
7. The hydrides of fluorine, oxygen and nitrogen (HF, H_2O, H_3N) can all form hydrogen bonds between their molecules, whereas the hydrides of the elements lower down in the same group (e.g. HCl, H_2S and H_3P) only have van der Waals' forces and dipole-dipole interaction between their molecules. Hydrogen bonds are much stronger than van der Waals' forces and the dipole-dipole interaction, so the hydride of the first element in each group has the higher boiling point. Other differences would include the first element in each group having a higher melting point, a greater latent heat of fusion, a greater latent heat of vaporisation and high surface tension in the liquid state. Some more specific differences would include:

   - NH_3 is much more soluble in water than PH_3, this is partly because it can hydrogen bond to the solvent.

   - HF is a weak acid whereas HCl is a strong one. In part this is due to the fact that HF molecules are stabilised by being able to hydrogen bond to the water. Also, H–F is a relatively strong bond compared to H–Cl.

   - Ice (solid H_2O) is relatively hard and brittle. This is because it is held together by hydrogen bonding between the water molecules, which are stronger than other intermolecular forces, making it quite hard, and if the crystal is distorted these directional bonds break causing the crystal to cleave.

Page 126 Ex 4.4

1. a) The strength of metallic bonding and hence the boiling point, will increase with the number of electrons per atom that participate in the delocalised bonding. Also, the decreasing ionic size of the metal cations is another factor. Sodium has only one valence electron to contribute, hence its low boiling point, magnesium two, resulting in a greater boiling point, and aluminium three accounting for it having the highest boiling point.

   b) The bonding in metals is not between one atom and another, but between the cations and the mobile flux of electrons that surrounds them. This means that they can move relative to each other without the need to break bonds.

   c) The delocalised electrons are capable of moving freely throughout the solid, hence they are capable of conducting an electric current from one part of the solid to another.

Page 131,132 Ex 4.2

1. A
2. D
3. D
4. D
5. A
6. B
7. B
8. a) Silicon carbide b) Naphthalene c) Rubidium chloride d) Scandium
   e) Naphthalene f) Rubidium chloride g) Scandium h) Scandium
   i) Silicon carbide j) Rubidium chloride
9. a) Magnesium would be malleable, conduct electricity and have a higher melting point. Iodine would be brittle, would not conduct electricity and would have a lower melting point (any two of these differences).

   b) The mixture would have small grey and black particles visible. The compound would be a uniform white solid.

   c) MgI_2. It will be ionically bonded.

   d) When the compound is added to water it will dissolve, but neither component of the mixture would dissolve.

   e) When the mixture is shaken with the non-polar solvent, the iodine would dissolve in the solvent, but the magnesium would not. The magnesium could then be filtered off and the iodine recovered by evaporating the solvent.
10. Covalent bonds are not weak. Diamond one of the hardest known substances is held together only by covalent bonds. Many substances have molecular covalent bonding and in these, even though the covalent bonds are strong, there are relatively weak forces between the molecules. It is these that are overcome when a substance melts. It would be more accurate to state that ‘Sugar has a molecular covalent structure and the forces between the molecules are much weaker than the ionic bonds that exist in salt.’

11. Ethanoic acid dissolves in water because its -OH group can form hydrogen bonds to the water. Sodium ethanoate dissolves in water because it is an ionic solid and the strong hydration interaction between the ions and the polar water molecules enables the strong forces between the ions in the solid to be overcome. Ethyl ethanoate has two hydrocarbon regions which cannot bond to the water and these would disrupt the hydrogen bonding between water molecules if it were to dissolve, hence it is not soluble.

12. Going from left to right, sodium oxide has an ionic structure. There are quite strong electrostatic forces between the ions hence the melting point is quite high. In magnesium oxide, the bonding is also ionic, but the fact that there are equal numbers of the two ions and that these have double charges results in a very high melting point. Aluminium oxide and silicon dioxide have a giant covalent structures so that to melt them involves overcoming strong covalent bonds, resulting in a high melting point. The remaining oxides, those of phosphorus, sulfur and chlorine, have a molecular covalent structure, so that melting them only depends on overcoming relatively weaker intermolecular forces. The lower the molar mass of the compound, the lower the melting point and this accounts for the decrease in melting point of these from phosphorus, through sulfur to chlorine.

CHAPTER 5 ENERGETICS

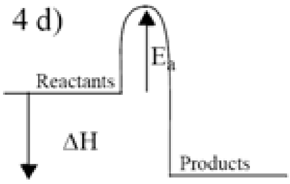
Page 137,138 Ex 5.1

1. B
2. C
3. A
4. a) $Mg(s) + H_2SO_4(aq) \rightarrow MgSO_4(aq) + H_2(g)$

   b) Exothermic

   c) The chemical potential energy of the reactants is higher than that of the ` products.

4 d)



5. a) Cl-Cl and O=O; absorbs energy

   b) Cl-O releases energy.

   c) It is the energy change when molar quantities of the reactants, as in the balanced equation, are completely converted to the products.

   d) Positive

   e) Endothermic

Page 140,141 Ex 5.2

1. B
2. C
3. B
4. C
5. D
6. A
7. D
8. Heat energy absorbed = $m.s.\Delta T$ = 100·4.18·4.5 = 1881J

   Amount of ammonium nitrate = m/M = 8.00/80.06 = 0.100 mol

   Enthalpy of solution = 1881/0.100 = 18810 J mol^{-1} = 18.8 kJ mol^{-1}
9. a) 3 cm^3 b) 2.3 g c) 0.050 moles

   d) $C_2H_5OH(l) + 3\ O_2(g) \rightarrow 2\ CO_2(g) + 3\ H_2O(l)$ e) 1350 x 0.050 = 67.4 kJ
10. a) Heat energy absorbed by the aluminium = $m.s.\Delta T$ = 0.1x875x80 = 7000J

    b) Heat energy absorbed by the water = $m.s.\Delta T$ = 500x4.18x80 = 167200J

    Total energy absorbed = 167200 +7000 = 174200J = 174.2 kJ

    c) Amount of butane = m/M = 14.5/58 = 0.25 moles

    d) Enthalpy of reaction = 174.2/0.25 = 697 kJ mol^{-1}

    e) Much of the heat generated by the combustion of the gas would be lost to the surroundings.

CHAPTER 5 ENERGETICS

Page 143 Ex 5.3

1. D
2. A
3. Let required enthalpy change = ΔH

   Applying Hess' law, $2.\Delta H + (-120) = (-800)$, $\Delta H = (120-800)/2 = -340$ kJ mol^{-1}
4. -126 kJ mol^{-1}
5. a) Weigh out a sample of the solid (i.e. CaO or $CaCO_3$). Take a known volume of dilute hydrochloric acid, so that the acid will be in excess. Measure the temperature of the acid and then add the solid. Stir the mixture, monitoring the temperature and record the maximum temperature reached.

   b) The calcium oxide, because the carbonate forms a gas and heat will be lost through the evolution of hot gas. OR The calcium carbonate, because the oxide is likely to have absorbed water vapour from the air converting it to the hydroxide.

   c) The specific heat capacity of dilute hydrochloric acid is required.

   d) Calculate the heat evolved in the two reactions ($m.s.\Delta T$) and knowing the number of moles of calcium compound taken in each case, calculate ΔH for the two reactions. The required enthalpy change is ΔH for the carbonate reaction minus ΔH for the reaction with the oxide.

Page 146.147 Ex 5.4

1. A
2. A
3. Equation: $2\ CO(g) + O_2(g) \rightarrow 2\ CO_2(g)$

   Bonds broken $2\cdot(C{\equiv}O) + O{=}O = (2\text{x}1073) + 496 = 2642$ kJ mol^{-1}

   Bonds made 4x743 = 2972 kJ mol^{-1}

   Overall enthalpy change = 2642 – 2972 = –330 kJ mol^{-1} for 2 moles of CO, so for 1 mole = –165 kJ mol^{-1}
4. Enthalpy change in breaking bonds = $(944) + (3\cdot242) = 1670$ kJ mol^{-1}

   Overall enthalpy change = 1670 – (6·N-Cl) = +688 kJ mol^{-1}

   Enthalpy of N-Cl bond = 1/6 (1670 - 688) = 164 kJ mol^{-1}
5. Equation: $C_3H_6\,(g) + H_2(g) \rightarrow C_3H_8(g)$.

   Bonds broken C-C + H-H = 348 + 436 = 784kJ mol^{-1}

   Bonds made $2\cdot(C\text{-}H) = 2\cdot412 = 824$ kJ mol^{-1}.

   Enthalpy change = 784 – 824 = –40 kJ mol^{-1}

   The actually value is much more exothermic than this value. The reason for this is that the bond angle in cyclopropane is 60°, much less than the normal tetrahedral angle of 109°. The resulting strain in the molecule increases the chemical potential energy of cyclopropane. This is released when it is converted to propane and the additional potential energy is converted to heat energy. Also, bond enthalpy values for C–C and C–H are only average values obtained from a series of compounds and are not exact values for the reaction.

6. The trend is one of decreasing bond strength with increasing atomic radius, going down the group. This is because the larger the radius, the further the bonding electrons are from the positively charged nucleus, hence the less strongly they are attracted and the weaker the bond.

   The difference between I-I and Br-Br is 58 kJ mol^{-1} and between Br-Br and Cl-Cl it is 50 kJ mol^{-1}, hence continuing this trend the difference between Cl-Cl and F-F would be expected to be 42 kJ mol^{-1}. This would give a F-F bond enthalpy of 285 kJ mol^{-1}.

   The F-F bond enthalpy is 158 kJ mol^{-1}, which is much less. The reason for this is repulsion between the inner electron shells and the fact that the strong attractive force of the nucleus draws electrons away from the region between the atoms.

Page 150 Ex 15.1

1. C
2. B
3. A
4. A
5. C
6. A
7. Enthalpy change to form 1 P atom = +354 kJ mol^{-1}

   Enthalpy change to form 5 H atoms = 5 x +218 kJ mol^{-1} = +1090 kJ mol^{-1}

   Enthalpy change to form 5 P-H bonds = 5 x +321 kJ mol^{-1} = -1605 kJ mol^{-1}

   Enthalpy of formation of PH_5 = +354+1090-1605 = -161 kJ mol^{-1}

8. a) Equation: $Zn(s) + Cl_2(g) \rightarrow ZnCl_2(s)$

   $\Delta H = \Delta H_f(ZnCl_2) - [\Delta H_f(Zn) + \Delta H_f(Cl_2)] = -416 - [0 + 0] = -416$ kJ mol^{-1}

   b) Equation: $2\ H_2S(g) + SO_2(g) \rightarrow 2\ H_2O(l_{)} + 3\ S(s)$

   $\Delta H = [2\Delta H_f(H_2O) + 3\Delta H_f(S)] - [2\Delta H_f(H_2S) + \Delta H_f(SO_2)] = -233$ kJ mol^{-1}

   c) Equation: $2\ Pb(NO_3)_2(s) \rightarrow 2\ PbO(s) + 4\ NO_2(g) + O_2(g)$

   $\Delta H = [2\Delta H_f(PbO) + 4\Delta H_f(NO_2) + \Delta H_f(O_2)] - [2\Delta H_f(Pb(NO_3)_2)] = +598$ kJ mol^{-1}

9. For the equation $CH_2Cl_2(l) + O_2(g) \rightarrow CO_2(g) + 2\ HCl(g)$, $\Delta H = -458$ kJ mol^{-1}.

   For the equation $CH_2Cl_2(l) + 2\ O_2(g) \rightarrow CO_2(g) + H_2O(l) + Cl_2(g)$
   $\Delta H = -560$ kJ mol^{-1}.

   The latter is much closer to the experimental value, so this is presumably the reaction occurring.

10. a) $4\ CH_3NHNH_2(l) + 5\ N_2O_4(g) \rightarrow 4\ CO_2(g) + 12\ H_2O(l) + 9\ N_2(g)$

    b) $[4\cdot(-395) + 12\cdot(-244)] - [4\cdot(+13) + 5\cdot(+9)] = -4605$ kJ mol^{-1}

    c) The products of the reaction are common, rather inert substances and so are unlikely to lead to pollution problems.

11. a) Burn both of the compounds in a calorimeter to measure their enthalpies of combustion and then combine these using a Hess' Law cycle to determine the enthalpy change for the hypothetical reaction.

    b) Bonds broken = C-C + O-H = 346 + 464 = 810 kJ mol^{-1}

    Bonds made = C-O + C-H = 358 + 413 = 771 kJ mol^{-1}.

    Enthalpy change = +39 kJ mol^{-1}

    c) $\Delta H = -280 - (-327) = +47$ kJ mol^{-1}

    d) The enthalpy of formation data will give the best agreement, because bond enthalpy data applies to general values for the bonds, the actual values of which vary slightly from molecule to molecule.

12. a) i $C_6H_{10}(g) + H_2(g) \rightarrow C_6H_{12}(g)$, ii $C_6H_6(g) + 3\ H_2(g) \rightarrow C_6H_{12}(g)$

    b) $\Delta H_i = \Delta H_{comb}(C_6H_{10}) + \Delta H_{comb}(H_2O) - \Delta H_{comb}(C_6H_{12})$

    $= -3752 - 286 + 3924 = -114$ kJ mol^{-1}

    $\Delta H_{ii} = \Delta H_{comb}(C_6H_6) + 3\ \Delta H_{comb}(H_2O) - \Delta H_{comb}(C_6H_{12})$

    $= -3273 - 3\text{x}286 + 3924 = -207$ kJ mol^{-1}

    c) It might be expected that as the hydrogenation of benzene requires 3 times the number of moles of hydrogen to give the same product, that the enthalpy change for the hydrogenation of benzene (ΔH_{ii}) might be 3 times the enthalpy change for the hydrogenation of cyclohexene (ΔH_i).

    d) This is not the case because benzene, as a result of the delocalised π-bond, is more stable than it would be if it had three separate double bonds, by 135 kJ mol^{-1} (= 3 x 114 - 207)according to this calculation.

Page 154,155 Ex15.2

1. C
2. C
3. B
4. A
5. B
6. -860 = +175 + 2x121 + 502 + 966 + 2xEA(Cl) - 2018

   EA(Cl) = ½ (-860 - 175 - 242 - 502 - 966 + 2018) = –363.5 kJ mol^{-1}

7. ΔH_f = +193 + ½ 158 + 590 - 348 - 891 = –377 kJ mol^{-1}

   If two moles of calcium were reacted with one mole of fluorine, then the formation of two moles of CaF would release 754 kJ mol^{-1}, but 1214 kJ mol^{-1} would be released if only one mole of CaF_2 was formed and the excess calcium remained unreacted so this is the reaction that occurs.

8. a) -100 = +285 + 112 + 732 - 342 + LE(AgBr)

   LE(AgBr) = -100 - 285 - 112 - 732 + 342 = +887 kJ mol^{-1}

   b) The experimentally determined lattice enthalpy above is considerably larger than that calculated on an electrostatic model (+758 kJ mol^{-1}). This signifies that there is significant covalent character to the bonding in silver bromide.

9. Theoretical ΔH_{sol} = +833 - 464 - 364 = +5 kJ mol^{-1}

Experimental ΔH_{sol} = +905 - 464 - 364 = +77 kJ mol^{-1}

In sodium chloride, which has an enthalpy of solution similar to the theoretical value for silver chloride, the positive enthalpy change on dissolving is sufficient to overcome the small endothermic enthalpy change, hence it is soluble. In silver chloride there is a high degree of covalent character to the bonding, which increases the lattice enthalpy. As a result the enthalpy of solution is much more endothermic and too high for the favourable entropy change to overcome. As a result silver chloride is insoluble.

Page 156 Ex 15.3

1. D

2. B

3. a) An increase in entropy. Increase in the number of moles of gas.

b) A decrease in entropy. Formation of a solid from aqueous solution.

c) A decrease in entropy. Decrease in the number of moles of gas.

d) A decrease in entropy. Decrease in the number of moles of gas.

e) Little change in entropy. Number of moles of gas constant.

4. a) ΔS = 109 + 5x70 - 300 = +159 J K^{-1} mol^{-1}

Positive as an increase in the number of moles and a liquid formed from a solid

b) ΔS = 142 - 118 - 83 = -59 J K^{-1} mol^{-1}

Negative as a decrease in the number of moles of gas

c) ΔS = 132 - 80 - 90 = -38 J K^{-1} mol^{-1}

Negative as a solid is formed from aqueous ions

Page 160 Ex 15.4

1. C

2. B

3. a) -334 J $mol^{-1}K^{-1}$ (= 3x201 - 269)

   b) -598 kJ mol^{-1} (= 83 - 3x227)

   c) 2007 J $mol^{-1}K^{-1}$ (= 598000/298)

   d) The total entropy change for the universe must be positive if a reaction is spontaneous. The total entropy change is the sum of the changes for the system and the surroundings.

   = 2007 - 334 = 1673 J $mol^{-1}K^{-1}$

   Therefore the reaction is spontaneous at 298K. As the temperature increases, the entropy change for the surroundings, which is positive becomes smaller. The optimum condition is therefore a low temperature.

4. For the *cis*- to the *trans*- isomer, $\Delta G = 64.1 - 67.1 = -3.0$ kJ mol^{-1}

   This is negative, therefore the product, the trans- isomer is the more stable. For ‘perfect equilibrium’ ΔG is zero:

   $\Delta G = \Delta H - T.\Delta S = -4400 - (-5).T = 0$. $T = 4400/5 = 880K$.

   The temperature at which the equilibrium is balanced would be 607°C.

5. a) The gradient represents the entropy change in the reaction. At the first gradient change the entropy reverses so that it becomes positive rather than negative. This means that the entropy of the products has increased, so probably the discontinuity is due to lead oxide becoming a gas. The second discontinuity is in the opposite direction, so corresponds to lead itself becoming a gas, making the entropy change less favourable.

   b) At temperatures below ~1000K carbon is a more powerful reductant than carbon monoxide, but above this temperature the reverse is true.

   c) (i)Hydrogen will not reduce Al_2O_3 at any temperature.

      (ii) It will reduce PbO at almost all temperatures shown on the graph.

      (iii) It will only reduce ZnO at temperatures below ~1500K.

Page 162,163 Ex 6.1

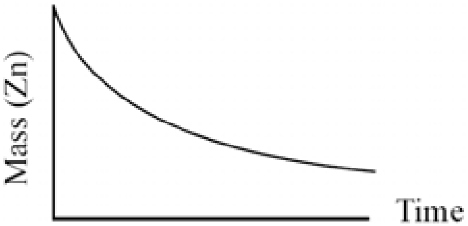
1. B
2. C
3. A
4. a) = 0.005/120 = $4.16\text{x}10^{-5}$ mol dm^{-3} s^{-1}

   b) i) H_2O_2 is consumed at a rate of $4.16\text{x}10^{-5}$ mol dm^{-3} s^{-1}

   ii) I^- ions are consumed at a rate of $8.32\text{x}10^{-5}$ mol dm^{-3} s^{-1}

   ii) is double i), because 2 moles of I^- are consumed for every mole of H_2O_2

5 (a)



b) The reaction rate is greatest at the start of the reaction. This can be seen by the fact that the gradient of the curve is greatest at the start of the reaction.

c) Possibilities include:

- Collecting the gas and recording its volume against time.
- Recording the change in total mass of the beaker and contents against time.
- Titrating samples from the reaction mixture with an aqueous alkali of known concentration.

Page 166 Ex 6.1

1. C
2. D
3. A
4. The determination of the reaction rate would be best determined using a spectrophotometer. Probably setting the wavelength to red (complimentary colour of green) or blue (complimentary colour of orange would yield acceptable results. (The best way would be to scan the complete spectrum of both dichromate(VI) and chromium(III) and then select the wavelength where they have the greatest difference in absorption.). Mix together aqueous dichromate(VI) and aqueous sulfur dioxide (suitable concentrations to give a reasonable rate of reaction would have to be determined by trial and error), then transfer the mixture rapidly to a cuvette in the spectrophotometer. Record the absorption of the solution at different times, or preferably continually using a link to a computer. Draw a graph of absorption against time. The relative rate can be determined from the gradient of the graph. If a concentration–absorption calibration has been carried out at the wavelength used, this can be converted to a concentration–time graph and the absolute rate calculated. The major precaution would be to measure the temperature and try to keep it constant.

5. Many possible answers, this is just a possible example.

   a) The reaction of marble (calcium carbonate) chips with hydrochloric acid.

   b) The variation of the total mass of the reaction system with time. As a gas with quite a high molar mass is evolved there is a significant change in total mass during the reaction. This technique is relatively easy to carry out and yet provides quite a high degree of precision.

   c) The concentration of hydrochloric acid. The acid was diluted before adding to the marble chips, but the total volume was kept constant.

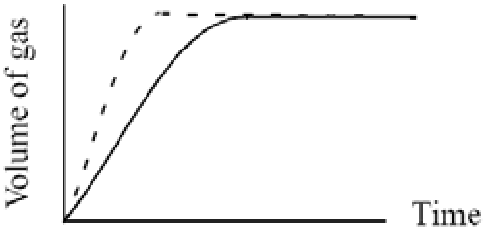
   d) The technique could be used to investigate the effect of temperature. This would be done by heating the acid to different temperatures before adding it to the marble chips. The precaution would be to monitor the temperature of the mixture during the course of the reaction and to use these values rather than the starting temperature of the acid as the cold marble chips will cause a drop in temperature.

Page 169,170 Ex 6.2

1. A
2. B
3. A
4. D
5. C
6. a) The rate of a chemical reaction depends on the collision rate between the reactants. Increasing the concentration of the reactants increases the collision rate and hence the reaction rate.

   b) In order for reaction to occur on collision, the energy of the collision must be greater than the activation energy for the reaction and the reactive parts of the molecule must come into contact during the collision.

   c) As the temperature is increased the kinetic energy of the particles increases and so the proportion of the collisions, with the required activation energy, and hence the rate, also increases. A small increase in the collision rate will also occur.
7. a) and b)



   c) The lead dioxide is acting as a catalyst.

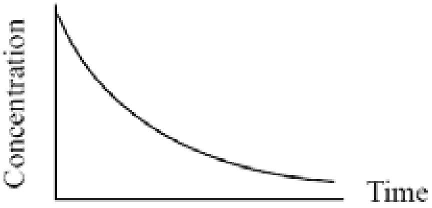
   d) By increasing the temperature.

CHAPTER 6 KINETICS

Page 173,174 Exercise 16.1

1. D
2. D
3. C
4. D
5. B
6. a) Comparing 1 and 2, doubling [CH_3COCH_3] doubles the rate of reaction. Comparing 2 and 4, halving [I_2] has no effect on the rate of reaction. Comparing 1 and 6, doubling [H^+] doubles the rate of reaction.

   The rate expression is: Rate = k.[CH_3-CO- CH_3].[H^+]

   b) The reaction is first order in CH_3-CO-CH_3. The reaction is zero order in I_2. The reaction is first order in H^+. The reaction is second order overall.

   c) Rate = k.[CH_3-CO-CH_3].[H^+] = $4x10^{-6}$ mol $dm^{-3}s^{-1}$, ∴ $k = 2x10^{-5}mol^{-1}dm^3s^{-1}$.
7. a) The reaction is first order in the ester. The fact that the first and second half–life are equal when the other reagent is in large excess demonstrates this.

   b) The half-life is 140 s, ∴ $k_1 = 4.95x10^{-3}\ s^{-1}$

   c) Because this is present in excess and so its concentration does not change significantly during the course of the reaction.

   d) The experiment could be repeated with a high concentration of ester and a low concentration of hydroxide ions.

   e) Rate = k_2.[ester].[OH^-], ∴ $k = 2.475x10^{-2}\ mol^{-1}\ dm^3\ s^{-1}$ If [OH^-] is virtually constant because it is present in excess, then Rate = (k_2.[OH^-]).[ester]. This gives first order kinetics with an apparent rate constant (k_2.[OH^-]) = 0.2.k_2 = $4.95x10^{-3}\ s^{-1}$.

Page 178 Ex 16.2

1. C
2. D
3. B
4. D
5. a) The reaction is second order in A and zero order in B, therefore Rate = k.$[A]^2$

   b) Substituting: $3.2x10^{-4} = k\cdot(0.2)^2$; $k = 3.2x10^{-4}/0.04 = 8x10^{-3}\ mol^{-1}\ dm^3\ s^{-1}$

   c) Rate = $k.[A]^2 = 8x10^{-3}\cdot(0.1)^2 = 8x10^{-5}mol\ dm^{-3}\ s^{-1}$

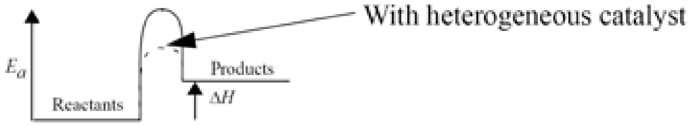
   d) (i) A+A → X (slow RDS) then X+B → C+D+A (fast)

   (ii) A+B → C+D (slow RDS) or other possibilities.

CHAPTER 6 KINETICS

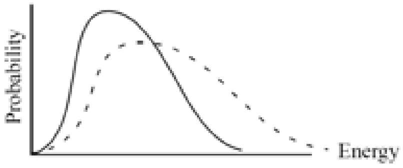
Page 180 Ex 16.3

1. A
2. A
3. D
4. (a) and (b)



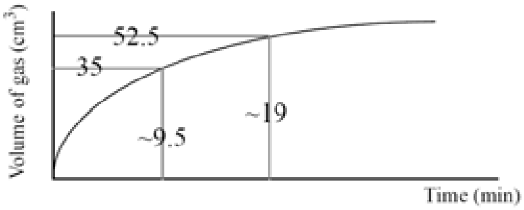
c) The reaction is endothermic, so the container will become cooler.

d) This would increase the rate of reaction. The reason for this is that the shape of the distribution of kinetic energies amongst the molecules will change so that a greater proportion of the molecules, and hence of the collisions, will have the required activation energy. There will also be a slight increase in the collision rate.



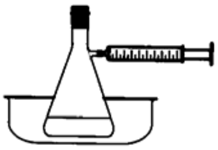
e) Increasing the pressure (and hence the concentration) of the gas.

f) The reaction could be monitored by shining a light, preferably a blue light, through the gas and recording the variation of the intensity of the light with time.



5. a) The reaction is first order because the first and second half lives are equal. In order to calculate the rate constant the concentration of the benzenediazonium chloride would need to be known.

b)



The precautions necessary would be to maintain the temperature, not only of the water bath, but of the whole apparatus (because of the effect of temperature on gas volume), constant.

c) In order to determine the activation energy the rate would have to be measured at different temperatures with all other conditions constant. The activation energy can be found from the gradient of a graph of ln(rate) against 1/*T* with all other conditions constant.

CHAPTER 7 EQUILIBRIUM

Page 183 Ex 7.1

1. C

2. a) $PCl_5\,(s) \rightleftharpoons PCl_3\,(s) + Cl_2\,(g)$

   b) i) It will start to dissociate.

   ii) The rate will decrease as its concentration decreases

   iii) Zero, because neither of the reactants are present to react.

   iv) The rate of the reverse reaction will increase as the concentrations of phosphorus(III) chloride and chlorine increase.

   v) Eventually they will become equal.

   vi) A state of equilibrium is achieved.

   vii) The flask will contain phosphorus(V) chloride, phosphorus(III) chloride and chlorine. The last two will have the same concentration, but this will be different to the concentration of phosphorus(V) chloride.

   c) No. A state of equilibrium will never be reached, because the products will escape and the reverse reaction will never reach a rate equal to the forward reaction.

Page 190-192 Ex 7.2

1. C
2. D
3. C
4. A
5. D
6. B
7. C
8. a) $N_2\,(g) + 3\,H_2\,(g) \rightleftharpoons 2\,NH_3\,(g)$ $K_c = [NH_3]^2/[N_2].[H_2]^3$

   b) $2SO_2\,(g) + O_2\,(g) \rightleftharpoons 2\,SO_3\,(g)$ $K_c = [SO_3]^2/[SO_2]^2.[O_2]$

   c) $NH_3\,(aq) + H_2O\,(l) \rightleftharpoons NH_4^+\,(aq) + OH^-\,(aq)$ $K_c = [NH_4^+].[OH^-]/[NH_3]$

   d) $H_2O\,(l) \rightleftharpoons H^+\,(aq) + OH^-\,(aq)$ $K_c = [H^+].[OH^-]$

   e) $2\,NO\,(g) + Cl_2\,(g) \rightleftharpoons 2\,NOCl\,(g)$ $K_c = [NOCl]^2/[NO]^2.[Cl_2]$

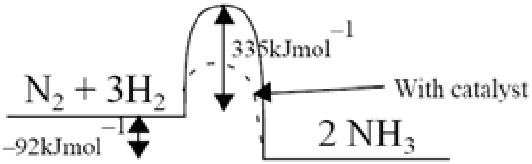
   f) $4NH_3\,(g) + 5\,O_2\,(g) \rightleftharpoons 6\,H_2O\,(g) + 4\,NO\,(g)$
   $K_c=[H_2O]^6.[NO]^4/[NH_3]^4.[O_2]^5$

   g) $CH_3NH_2\,(aq) + H_2O\,(l) \rightleftharpoons CH_3NH_3^+\,(aq) + OH^-\,(aq)$
   $K_c = [CH_3NH_3^+].[OH^-]/[CH_3NH_2]$

   h) $CH_3OH(l) + CH_3COOH(l) \rightleftharpoons CH_3COOCH_3(l) + H_2O(l)$
   $K_c=[CH_3COOCH_3].[H_2O]/[\ CH_3OH].[\ CH_3COOH]$

9. a) $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

b) and c)



d) Finely divided, because the reaction occurs on the surface of the catalyst, so increasing the surface area increases the rate of reaction.

e) It will increase the rate of both the forward and reverse reactions, by increasing the collision rates.

10. a) Initially the nitrogen monoxide and oxygen react to form nitrogen dioxide. The rate of this reaction will fall as the gases are consumed and their concentration falls. Initially there is no nitrogen dioxide, so the reverse reaction does not occur, but as nitrogen dioxide is formed by the forward reaction, the rate of the reverse reaction increases. Eventually the rates of forward and reverse reactions become equal.

b) $2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)$

c) Using air instead of oxygen decreases the concentration of oxygen and hence reduces the rate of the forward reaction, without affecting the reverse reaction. The equilibrium therefore shifts to the left, decreasing the concentration of NO_2, producing a lighter colour.

11.

Equilibrium	Effect of change	Balance by
a)	Shifts to the left	Increasing the temperature
b)	Shifts to the left	Increasing the pH (reducing [H^+])
c)	Shifts to the left	Decreasing the pressure
d)	Shifts to the right	Increasing the temperature
e)	Shifts to the right	Increasing [NH_3]

12. a) The equilibrium will shift to the left. According to Le Chatelier's principle, a decrease in temperature shifts the position of equilibrium in the direction of the exothermic change. In this case this is towards the left hand side or decreasing temperature shifts the equilibrium in the reverse direction to compensate for some of the heat taken away by reducing the temperature.

b) This will shift the position of equilibrium to the right, increasing the amount of hydrogen iodide. According to Le Chatelier's principle, adding more of a reagent shifts the position of equilibrium in the opposite direction.

c) Increasing the pressure will have no effect on the position of equilibrium. According to Le Chatelier's principle, increasing the presure shifts the equilibrium to the side with least moles of gas, but in this case there are two moles of gas on each side of the equilibrium.

13. a) The amount of yellow solid would increase and the amount of brown liquid would decrease. According to Le Chatelier's principle, increasing the pressure shifts the equilibrium to the side with least moles of gas. In this case this is the right hand side, so more of the yellow ICl_3 is formed.

b) According to Le Chatelier's principle, a decrease in temperature shifts the position of equilibrium in the direction of the exothermic change. If the amount of yellow solid increases, one can conclude that the forward reaction is exothermic.

14. a) $2\ SO_2\ (g)\ +\ O_2\ (g) \rightleftharpoons 2\ SO_3\ (g)$

b) i) Increase the rate of the forward reaction.

ii) Increases the rate of the reverse reaction.

iii) The proportions of the components will be unaffected.

c) Increasing the pressure shifts the position of equilibrium to the side with the least number of moles of gas. In this case this is the right hand side, so increasing the pressure would increase the amount of sulfur trioxide.

d) Because the forward reaction is exothermic, an increase in temperature would shift the equilibrium to the left, hence decreasing the proportion of sulfur trioxide.

Page 195,196 Ex 17.2

1. D

2. A

3. B

4. a) NH_4HS is a solid so that its concentration cannot vary, therefore it is omitted from the equilibrium constant expression, so that the units are just $[NH_3]\cdot[H_2S]$, i.e. $\text{mol}^2\ \text{dm}^{-6}$.

b) $K_c = [NH_3].[H_2S] = 0.00001$, $[NH_3] = [H_2S] = 3.16\cdot10^{-3}\ \text{mol dm}^{-3}$.

c) i) Increases the mass of solid.

ii) Decreases $[H_2S]$.

iii) Does not affect the value of K_c.

5. a) They show that the forward reaction of the equilibrium is exothermic as an increase in temperature causes a decrease in the amount of product.

b) $0.596\ \text{mol}^{-2}\text{dm}^6$.

6. a) $\frac{[COCl_2]}{[CO].[Cl_2]}$

b) $0.417\ \text{mol}^{-1}\ \text{dm}^3$

c) $[CO] = 1.60$; $[Cl_2] = 1.20$; $[COCl_2] = 0.400\ \text{mol dm}^{-3}$

d) $0.208\ \text{mol}^{-1}\ \text{dm}^3$

e) As the temperature is constant, the value of K_c must remain constant, so the system is now no longer at equilibrium. The equilibrium must shift to the right so as to increase the value of the equilibrium constant expression

f) Yes. Le Chatelier's principle states that an increase in total pressure (this will be required to reduce the volume) will shift the equilibrium in the direction of the least moles of gas. For this equilibrium this is a shift to the right, increasing the amount of product.

CHAPTER 7 EQUILIBRIUM

Page 200,202 Ex

1. C
2. A
3. B
4. a) The temperature at which the vapour pressure equals the external pressure.

   b) The lower the boiling point, the weaker the intermolecular forces.

   c) Between 69°C and 81°C. The vapour pressure of the mixture will be greater than that of hexane, but lower than that of cyclohexane. This means that the temperature required for it to equal the external pressure will be intermediate between the boiling points of the pure components.

   d) The vapour will be richer in the more volatile component, hexane. At the boiling point of the mixture, the vapour pressure of the hexane in the mixture would be greater than that of the cyclohexane.

   e) The proportion of the hexane in the distillate will continually increase and that of the cyclohexane decrease.

   f) Fractional distillation.

   g) The separation of the components of petroleum (crude oil) or the components of air.

Page 204 Ex

1. A
2. D

3. $$\Delta T = K \times \frac{n \times m_{st}}{M_{st}} \times \frac{1000}{m_{sv}}$$

$$M_{st} = K \times \frac{n \times m_{st}}{\Delta T} \times \frac{1000}{m_{sv}} = 20.1 \times \frac{1 \times 1.50}{4.7} \times \frac{1000}{50} = 128.3$$

4. $$K = \Delta T \times \frac{1}{n_{st}} \times \frac{m_{sv}}{1000} = 1.2 \times \frac{1}{0.0135} \times \frac{20}{1000} = 1.78 \text{ K mol}^{-1} \text{ kg.}$$

5. $$\Pi V = nRT$$

$$n = \frac{\Pi V}{RT} = \frac{330 \times 0.5}{8.31 \times 298} = 0.0666 \text{ moles}$$

From mass and molar mass, 5/150 = 0.0333 moles, therefore the solute must dissociate into two particles.

CHAPTER 7 EQUILIBRIUM

Page 206 Ex

1. D

2. D

3. Initially: $p(O_2) = 20$ kPa; $p(N_2) = 80$ kPa; $p(NO) = 0$

At equilibrium $p(O_2) = 19.4$ kPa; $p(N_2) = 79.4$ kPa; $p(NO) = 1.2$ kPa

4. a) Molar mass = 136, therefore $[Ca^{2+}] = [SO_4^{2-}] = 6.34/136 = 0.0466$ mol dm^{-3}

$K_{sp} = [Ca^{2+}].[SO_4^{2-}] = (0.0466)^2 = 2.17\times10^{-3}$ mol^{2}dm^{-6}

b) $[Ca^{2+}] = [SO_4^{2-}] = {}^{0.1}/_2$ (as V doubles when the solutions are mixed)

$[Ca^{2+}].[SO_4^{2-}] = (0.05)^2 = 2.5\times10^{-3}$

This is greater than 2.17×10^{-3}, so a precipitate will form

5. a) $K_{sp} = [Mg^{2+}].[OH^-]^2 = x.(2x)^2 = 4x^3 = 2x10^{-11}$; $x = 1.71\times10^{-4}$ mol dm–^{3}

In g dm^{-3} = $M_r \cdot n = 58 \cdot 1.71\cdot10^{-4} = 0.00992$ g dm^{-3}

b) $[OH^-] = 2 \cdot 1.71\times10^{-4} = 3.42\cdot10^{-4}$ mol dm^{-3}

c) $0.00992 \times 50/1000 = 4.96\times10^{-4}$ g

d) $$[Mg^{2+}] = \frac{2\times10^{-11}}{(10^{-2})^{-2}} = 2\times10^{-7}\ \text{mol dm}^{-3}$$

e) $2x10^{-7} \times 50/1000 \times 58 = 5.81\times10^{-7}$ g

The hydroxide ions displace the position of the equilibrium:

$Mg(OH)_2 \rightleftharpoons Mg^{2+} + 2\,OH^-$

to the left, hence decreasing the solubility (common ion effect).

6 a) $ZnCO_{3\,(s)} \rightleftharpoons Zn^{2+}_{(aq)} + CO_3^{2-}{}_{(aq)}$

$Zn(OH)_{2\,(s)} \rightleftharpoons Zn^{2+}_{(aq)} + 2\,OH^-_{(aq)}$

b) $K_{sp}(ZnCO_3) = [Zn^{2+}].[CO_3^{2-}]$

$K_{sp}(Zn(OH)_2) = [Zn^{2+}].[OH^-]^2$

c) $ZnCO_3$: $x^2 = 1.4x10^{-11}$, therefore $x = 3.74x10^{-6}$ mol dm^{-3}

$Zn(OH)_2$: $4x^3 = 2.0x10^{-17}$, therefore $x = 1.71x10^{-6}$ mol dm^{-3}

Hence zinc carbonate is the more soluble

d) For $ZnCO_3$ to precipitate, $[Zn^{2+}] = 1.4\times10^{-11}/0.1 = 1.4\times10^{-10}$ mol dm^{-3}

For $Zn(OH)_2$ to precipitate, $[Zn^{2+}] = 2.0\times10^{-17}/(0.1)^2 = 2.0\times10^{-15}$ mol dm^{-3}

Therefore the hydroxide precipitates first.

CHAPTER 8 ACIDS AND BASES

Page 211 Ex 8.1

1. C
2. C
3. B
4. C
5. D

6 a) HCl; HPO_4^{2-}; $C_5H_5NH^+$; $H_3N–NH_3^{2+}$; $^-OOC–COOH$.

b) NO_3^-; I^-; SO_4^{2-}; NH_3; $HONH_2$

c) HSO_4^- and $N_2H_5^+$.

d) e.g. H_2O Conjugate base OH^- Conjugate acid H_3O^+

or HCO_3^- Conjugate base CO_3^{2-} Conjugate acid H_2CO_3

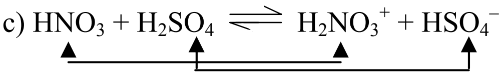
7 a) i) An acid is a species that can donate hydrogen ions to another species.

ii) A base is a substance that can accept a hydrogen ion from another species.

b) $HNO_3 + H_2SO_4 \rightleftharpoons H_2NO_3^+ + HSO_4^-$

Sulfuric acid donates a proton to nitric acid, and thus behaves as an acid.

c)



$HNO_3 + H_2SO_4 \rightleftharpoons H_2NO_3^+ + HSO_4^-$

d) Conjugate acid–base pair means that the two species are related by the gain/loss of only a single hydrogen ion (H^+).

8. a) Diprotic acids are acids in which each molecule of acid can donate two hydrogen ions.

b) An amphiprotic species is one that can both accept and donate hydrogen ions, i.e. they can act as both an acid and a base. For example the hydrogencarbonate ion can act as an acid to form the carbonate ion (CO_3^{2-}), or it can act as a base and form carbonic acid (H_2CO_3).

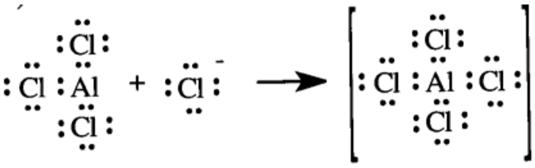
c) e.g. Water $H_2O(l) \rightleftharpoons OH^-(aq) + H^+(aq)$ and $H_2O(l) + H^+(aq) \rightleftharpoons H_3O^+(aq)$

or hydrogenphosphate $HPO_4^{2-}(aq) \rightleftharpoons H^+(aq) + PO_4^{3-}(aq)$

and $HPO_4^{2-}(aq) + H^+(aq) \rightleftharpoons H_2PO_4^-(aq)$

9. a) A Lewis acid is a species that can accept a non-bonding electron pair to form a dative covalent bond.

b)



c) A dative bond. Both of the electrons in the bond came from the chloride ion.

d) i) Trigonal planar

ii) Tetrahedral

10. a) Lewis base – the P in the PH_3 has a lone pair of electrons that it can donate.

    b) Lewis acid – the B in the BCl_3 has an incomplete valence shell, so can accept a pair of electrons.

    c) Lewis base – the S in the H_2S has a lone pair of electrons that it can donate.

    d) Lewis base – the S in the SF_4 has a lone pair of electrons that it can donate.

    e) Lewis acid – the Cu^{2+} has incomplete p and d orbitals, so it can accept a pair of electrons.

Page 212 Exercise 8.2

1. D
2. B
3. a) $Fe(s) + H_2SO_4(aq) \rightarrow FeSO_4 + H_2(g)$

   b) $PbCO_3(s) + 2\ HNO_3(aq) \rightarrow Pb(NO_3)_2(aq) + H_2O(l) + CO_2(g)$

   c) $ZnO(s) + 2\ HCl(aq) \rightarrow ZnCl_2(aq) + H_2O(l)$

   d) $Ca(OH)_2(s) + 2\ HNO_3(aq) \rightarrow Ca(NO_3)_2(aq) + 2\ H_2O(l)$

   e) $2\ NaHCO_3(s) + H_2SO_4(aq) \rightarrow Na_2SO_4(aq) + 2\ H_2O(l) + 2\ CO_2(g)$

   f) $H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$

Page 214 Ex 8.3

1. C
2. A
3. A
4. a) $NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$.

   The presence of hydroxide ions make the solution alkaline or NH_4^+ is a weak acid and OH^- is a strong base, thus the solution is basic.

   b) A base is a species that accepts a hydrogen ion, for example NH_3 accepts a hydrogen ion to form NH_4^+. Weak means that the base is not completely converted to hydroxide ions in aqueous solution, so aqueous ammonia molecules are in equilibrium with ammonium and hydroxide ions.

   c) A lower pH. The sodium hydroxide is totally converted to sodium and hydroxide ions, so $[OH^-] = 0.1$ mol dm^{-3} whereas in ammonia the ammonia is in equilibrium with the ammonium and hydroxide ions, so $[OH^-]$ is much less than 0.1 mol dm^{-3}. This means that the pH is lower in the ammonia solution.
5. a) $HCl(aq) + H_2O(l) \rightarrow H_3O^+(aq) + Cl^-(aq)$.

   The acid is fully dissociated.

   $CH_3COOH(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3COO^-(aq)$.

   The acid is only partially dissociated.

   b) The concentration of ions in the hydrochloric acid (strong acid) is much greater than that in the ethanoic acid (weak acid) so it has a much greater conductivity.

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c) If the acids were added to magnesium ribbon (or any other reactive metal or metal carbonate) the rate of reaction, and hence of evolution of gas, would be much greater for the strong acid. Or if titrated with a strong base, NaOH, the equivalence point with the strong acid will be 7, whereas with the weak acid, it will be greater than 7 (approximately 9).

Page 216 Ex 8.4

1. B
2. B
3. D
4. a) 10^{-3} mol dm^{-3}

   b) 10^{-11} mol dm^{-3}

   c) 1 mol dm^{-3}
5. a) 4

   b) 2

   c) 7
6. The hydrochloric acid is full dissociated and so $[H^+] = 5\cdot10^{-4}$ mol dm^{-3}, hence the pH is between 3 and 4. The ethanoic acid is only partially dissociated and so, even though its concentration is much greater than that of the hydrochloric acid, the concentration of hydrogen ions and hence the effect on universal indicator, is similar.
7. a) $n = \frac{m}{M} = \frac{0.63}{63} = 0.01, c = \frac{n}{v} = \frac{0.01}{0.1} = 0.1 \mathrm{mol dm}^{-3}$

   b) 1

   c) 10^{-13} mol dm^{-3}

   d) $HNO_2 \rightleftharpoons H^+ + NO_2^-$

   e) The pH would be greater than that of nitric acid, as nitrous acid is only partially dissociated, so the hydrogen ion concentration will be much lower than in nitric acid, giving a greater pH.
8. Hydrochloric acid is a strong monobasic acid ($HCl \rightarrow H^+ + Cl^-$), hence the $[H^+]$ = 0.01 mol dm^{-3} and the pH is 2. Sulfuric acid is a strong dibasic acid ($H_2SO_4 \rightarrow 2H^+ + SO_4^{2-}$), hence the $[H^+]$ = 0.02 mol dm^{-3} and the pH is less than 2. Ethanoic acid is a weak monobasic acid, and hence there is an equilibrium between the undissociated acid and the ions ($CH_3COOH + H_2O \rightleftharpoons H_3O^+ + CH_3COO^-$). This means that $[H^+]$ is much less than 0.01 mol dm^{-3} and hence the pH is much greater than 2.

CHAPTER 8 ACIDS AND BASES

Page 220,221 Ex 18.1

1. D
2. C
3. C
4. D
5. C
6. a) 1.14 b) 8.34 c) 1.48×10^{-6} mol dm^{-3} d) 0.00437 mol dm^{-3} e) 13.13
7. a) 0.00100 mol dm^{-3}

   b) 1.0×10^{-11} mol dm^{-3}

   c) Greater as each $Ba(OH)_2$ forms two OH^- ions.
8. a) 7.21

   b) $[H^+] = \sqrt{(0.02 \times 6.17 \times 10^{-8})} = 3.51 \times 10^{-5}$ mol dm^{-3}, therefore pH = 4.45

   c) 1.62×10^{-7} mol dm^{-3}
9. a) $K_a = \frac{[H^+].[A^-]}{[HA]} = \frac{(10^{-4.67})^2}{0.28} = 1.63 \times 10^{-9}\ \mathrm{mol\ dm^{-3}}$

   b) Weaker ($pK_a = 8.79$); the greater pK_a, the weaker the acid.

   c) $K_a = \frac{[H^+].[A^-]}{K_a} = \frac{(10^{-5})^2}{1.63 \times 10^{-9}} = 0.0613\ \mathrm{mol\ dm^{-3}}$
10. a) $HCN(aq) \rightleftharpoons H^+(aq) + CN^-(aq)$

    b) $[H^+] = \sqrt{(K_a.[HA])} = \sqrt{(10^{-9.3} \cdot 0.01)} = 2.24 \times 10^{-6}$ mol dm^{-3}, therefore pH = 5.65. This is much greater that of a strong acid of this concentration (pH = 2).

    c) Percentage = $\frac{100 \times [H^+]}{[HA]} = \frac{100 \times 2.24 \times 10^{-6}}{0.01} = 0.0224\%$

    If diluted, the percentage increases.

    d) pK_b of conjugate base = 14 - pK_a = 14 - 9.3 = 4.7

    $[OH^-] = \sqrt{(K_b.[A^-])} = \sqrt{(10^{-4.7} \cdot 0.1)} = 1.41 \cdot 10^{-3}$ mol dm^{-3},

    therefore $[H^+] = 7.08 \cdot 10^{-12}$ & pH = 11.15

Page 223,224 Ex 18.2

1. B
2. D
3. B
4. C
5. a)

$$K_b = \frac{[BH^+][OH^-]}{[B]} = \frac{0.1 \times 10^{-4.7}}{0.1} = 10^{-4.7} = 2.00 \times 10^{-5} \text{ mol dm}^{-3}$$

b) The solution must be more acidic, so the equilibrium given above must be displaced to the left. This requires the addition of more ammonium chloride.

c)

$$[BH^+] = \frac{K_b[B]}{[OH^-]} = \frac{2.00 \times 10^{-5} \times 0.1}{1 \times 10^{-5}}$$

= 0.2 mol dm^{-3}

d) Ethanoic acid and sodium ethanoate (or any similar strength weak acid and conjugate base).

6. a) A buffer solution is one that maintains an approximately constant pH when small amounts of acid or base are added to it.

b) $NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$. When a small amount of acid is added, the hydrogen ions from the acid will react with the hydroxide ions in the equilibrium above. This will cause the equilibrium to shift to the right, forming more hydroxide ions until their pH is restored to almost the original value. If a small amount of alkali is added, then the hydroxide ions will react with ammonium ions, displacing the above equilibrium to the left until the hydroxide ion concentration falls to almost its initial value.

Page 225 Ex 18.3

1. C
2. B
3. C
4. a) Slightly acidic – salt of a weak base and strong acid.

b) Neutral – salt of a strong base and a strong acid.

c) Slightly acidic – salt of a small, highly charged cation.

d) Slightly alkaline – salt of a strong base and a weak acid.

Page 227,228 Ex 18.4

1. A
2. B
3. C
4. a) Amount of HCl = $c.V = 0.2 \cdot 0.015 = 3\text{x}10^{-3}$ moles

HCl + $NH_3 \rightarrow NH_4Cl$, therefore amount of ammonia = $3\text{x}10^{-3}$ moles

$$c = \frac{n}{V} = \frac{3 \times 10^{-3}}{0.020} = 0.15$$

0.15 mol dm^{-3}

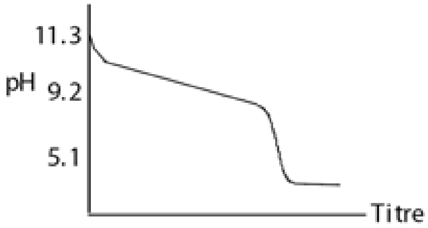
b) i) $[OH^-] = \sqrt{}(K_b.[B]) = \sqrt{}(10^{-4.7} \cdot 0.15) = 1.73\text{x}10^{-3}$;

pOH = 2.76, so pH = 14-2.76 = 11.24

ii) At the mid point [B] = $[BH^+]$, so pOH = pK_b = 4.7. pH = 14-4.7 = 9.3

iii) $[H^+] = \sqrt{}(K_a.[HA]) = \sqrt{}\ (10^{-9.3} \cdot 0.15) = 8.67 \cdot 10^{-6}$, therefore pH = 5.06

(c)



d) The section of the curve around pH 9 is the buffering region, this is because the addition of a small amount of acid or alkali has little effect on the pH.

e) Firstly the pH would remain at about pH 13 until almost the equivalence point. Secondly twice the volume of acid would be required to reach the equivalence point.

CHAPTER 8 ACIDS AND BASES

Page 229,230 Ex 18.5

1. B

2. a) Methyl orange

   b) Because the titration involves a weak base and a strong acid, the rapid change of pH at the end point will be from about 2 to 6. Methyl orange changes colour within this pH range.

   c) From red to yellow.

   d) The indicator is itself a weak acid, so enough alkali must be added to react with this as well as with the other acid present - this amount is assumed to be negligible.

   e) Bromophenol blue. Because its pK_a is 4.0, the mid point of its color change will be at about pH 4, which is within the expected pH change at the equivalence point.

3. a) Ethanoic acid is a weak acid, so only partially dissociated in aqueous solution.

   b) Phenolphthalein.

   c) The rapid change in pH at the equivalence point is only about 1 unit, too small for most indicators to completely change colour.

   d) For Curve b, when the volume of alkali added is twice that required for neutralisation, $[NH_3] = [NH_4^+]$ and hence the pH at this point is equal to the pK_a.

4. a) i). The sudden drop in pH would occur at ~12.5 cm^3 as H_2SO_4 is dibasic.

      ii) The sudden drop in pH at ~25 cm^3 would only go to ~pH = 6 and this would gradually fall as excess ethanoic acid is added.

   b) Phenolphthalein would be an appropriate indicator for all three as the rapid changes in pH at the equivalence point all pass through the range for phenolphthalein (10 to 8). Methyl orange, which changes between pH 4.5 and 3.0 would only change colour with the two strong acids, it would not change colour with ethanoic acid.

5. a) HS^-

   b) $H_2S_{(aq)} \rightleftharpoons HS^-_{(aq)} + H^+_{(aq)}$

   c) $c = \frac{m}{MV} = \frac{3.4}{34} = 0.10$ mol dm^{-3}

   d) $[H^+] = \sqrt{(K_a.[HA])} = \sqrt{(9.55\text{x}10^{-8}\cdot 0.1)} = 9.77\text{x}10^{-5}$ mol dm^{-3},

   therefore pH = 4.01

   e) A buffer solution is one that maintains an approximately constant pH when small amounts of acid or base are added to it.

   f) The hydroxide ions would react with the hydrogen ions. As a result the equilibrium in b) will shift to the right, producing more hydrogen ions, until the pH is restored to almost its original level.

   g) 0.196 mol dm^{-3}

   h) pH = 7.31

   i) $9.77\cdot 10^{-3}$ mol dm^{-3}. The concentration is so low that it would soon be consumed if an acid were added.

j) The solution has a pH of 4.01 (see d), so with bromothymol blue it will be yellow (the “acid” colour), and with methyl yellow it will also be yellow (the ‘alkali’ colour).

k) Indicators are weak acids/bases in which the colours of the acidic and basic forms (HIn and In^- in the equilibrium $HIn_{(aq)} \rightleftharpoons H^+_{(aq)} + In^-_{(aq)}$) have different colours. If an acid is added, the hydrogen ions drive the equilibrium to the left producing one colour. If an alkali is added, then this reacts with the hydrogen ions driving the equilibrium to the right, giving another colour. The pH at which this occurs will depend on the pK_a value of the acid.

l) Bromothymol blue would be the more suitable, because it would change colour when the pH reached about 7, near to the expected equivalence point. Methyl yellow is already in the alkaline form and so would never change colour if titrated with an alkali.

m) $S^{2-}(aq) + H_2O(l) \rightleftharpoons HS^-(aq) + OH^-(aq)$

n) The hydrogensulfide ion is amphiprotic, i.e. it can both gain and lose hydrogen ions.

o) 0.0891 mol dm^{-3}

p) $1.26 \cdot 10^{-13}$ mol dm^{-3}

q) Add either hydrogensulfide ions, or a dilute acid to convert sulfide ions to hydrogensulfide ions.

CHAPTER 9 OXIDATION AND REDUCTION

Page 235,236 Ex 9.1

1. B
2. D
3. B
4. C
5. C
6. a) +2 b) 0 c) +4 d) +4 e) +1 f) –2 g) +4 h) +1 i) +5 j) +6
7. a) Any compound of Fe^{2+} e.g. $FeSO_4$, $FeCl_2$ etc.

   b) NH_3, NH_4^+ c) MnO_4^- d) CH_2Cl_2, CH_2O e) PCl_5, $POCl_3$, P_4O_{10} (P_2O_5)
8. a) +2 to +1, reduced b) +4 to +4, neither c) –3 to +1, oxidised

   d) –2 to +2, oxidised e) +2 to +2½, oxidised
9. a) The nitrogen in the hydrazine has an oxidation state of -2 and in dinitrogen tetroxide it is +4. In the element the oxidation state is zero, so in the case of hydrazine the nitrogen is oxidised and in the case of dinitrogen tetroxide it is reduced.

   b) $2N_2H_4 + N_2O_4 \rightarrow 3N_2 + 4H_2O$

   c) The products are both common, stable, inert, non– toxic species and hence cannot be considered pollutants.
10. a) $(NH_4)_2Cr_2O_7$

    b) This gives the oxidation number of the chromium in the dichromate ion.

    c) There are two chromium atoms, each of which change their oxidation state from +6 to +3, so the total change in oxidation state is -6.

    d) -3

    e) There are two nitrogens and a total increase in oxidation number of +6, therefore each increases by +3.

    f) 0

    g) N_2

    h) Orange to green.

    i) The reaction is exothermic.

CHAPTER 9 OXIDATION AND REDUCTION

Page 237, 238 Ex 9.2

1. D
2. A
3. B
4. a) $Zn \rightarrow Zn^{2+} + 2e^-$
   b) $Br_2 + 2\ e^- \rightarrow 2\ Br^-$
   c) $H_2S \rightarrow S + 2\ H^+ + 2\ e^-$
   d) $HNO_3 + H^+ + e^- \rightarrow NO_2 + H_2O$
   e) $VO_3^- + 6\ H^+ + 2\ e^- \rightarrow V^{3+} + 3\ H_2O$
5. a) $PbO_2 + 4\ H^+ + Sn^{2+} \rightarrow Sn^{4+} + Pb^{2+} + 2\ H_2O$
   b) $2\ Co^{3+} + Sn^{2+} \rightarrow Sn^{4+} + 2\ Co^{2+}$
   c) $PbO_2 + 2\ H^+ + NO_2^- \rightarrow NO_3^- + Pb^{2+} + H_2O$
   d) $ClO_3^- + 6\ H^+ + 3\ Sn^{2+} \rightarrow 3\ Sn^{4+} + Cl^- + 3\ H_2O$
   e) $ClO_3^- + 3\ NO_2^- \rightarrow 3\ NO_3^- + Cl^-$
6. a) $Mg + Pb^{2+} \rightarrow Mg^{2+} + Pb$
   b) $SO_2 + I_2 + 2\ H_2O \rightarrow SO_4^{2-} + 2\ I^- + 4\ H^+$
   c) $H_2O_2 + 2\ H^+ + 2\ Fe^{2+} \rightarrow 2\ Fe^{3+} + 2\ H_2O$
   d) $3\ Zn + Cr_2O_7^{2-} + 14\ H^+ \rightarrow 3\ Zn^{2+} + 2\ Cr^{3+} + 7\ H_2O$
   e) $6\ MnO_4^- + 5\ CH_3OH + 18\ H^+ \rightarrow 6\ Mn^{2+} + 5\ CO_2 + 19\ H_2O$
7. a) +5 in ClO_3^-; -1 in Cl^-; +7 in ClO_4^-
   b) $ClO_3^- + H_2O \rightarrow ClO_4^- + 2\ H^+ + 2\ e^-$
   c) $ClO_3^- + 6\ H^+ + 6\ e^- \rightarrow Cl^- + 3\ H_2O$
   d) $4\ KClO_3 \rightarrow 3\ KClO_4 + KCl$
   e) When combining the half equations the water and hydrogen ion terms cancel out, so no other reagent is needed.
8. a) $C_2H_5OH + H_2O \rightarrow CH_3COOH + 4\ H^+ + 4\ e^-$
   b) -2 to 0
   c) $O_2 + 4\ H^+ + 4\ e^- \rightarrow 2\ H_2O$
   d) $C_2H_5OH + O_2 \rightarrow CH_3COOH + H_2O$
   e) The activation energy for reactions involving molecular oxygen is quite high owing to the strength of the O=O bond. The bacteria produce enzymes that catalyse the change by reducing this activation energy.

CHAPTER 9 OXIDATION AND REDUCTION

Page 240,241 Ex

1. A
2. B
3. C
4. a) +2 to +1

   b) A blue solution and a colourless solution react to give a brown solution and a white precipitate.

   c) $I_2 + 2\ S_2O_3^{2-} \rightarrow 2\ I^- + S_4O_6^{2-}$

   d) +2 to +2½

   e) Starch solution. The solution will change from blue to colourless.

   f) Moles of $S_2O_3^{2-} = c \text{ x } V = 0.2 \text{ x } 0.015 = 3\cdot10^{-3}$

   Moles of $Cu^{2+} = 2 \text{ x moles of } I_2 = \text{moles of } S_2O_3^{2-} = 3\text{x}10^{-3}$

   $[Cu^{2+}] = n/V = 3\text{x}10^{-3}/0.02 = 0.15 \text{ mol dm}^{-3}$
5. a) From colourless to purple (from excess MnO_4^-).

   b) Moles $Fe^{2+} = m/M_r = 2.00/55.85 = 0.0358$

   $MnO_4^- + 8\ H^+ + 5\ Fe^{2+} \rightarrow Mn^{2+} + 4\ H_2O + 5\ Fe^{3+}$

   Moles $MnO_4^- = {}^1/_5$ moles Fe $= 0.0358/5 = 7.16\cdot10^{-3}$

   Volume required $= n/V = 7.16\text{x}10^{-3}/0.2 = 0.0358 \text{ dm}^3 = 35.8 \text{ cm}^3$

Page 242 Exercise 9.3

1. B
2. B
3. B
4. a) A pale green gas and a colourless solution reacting to form a red–brown solution.

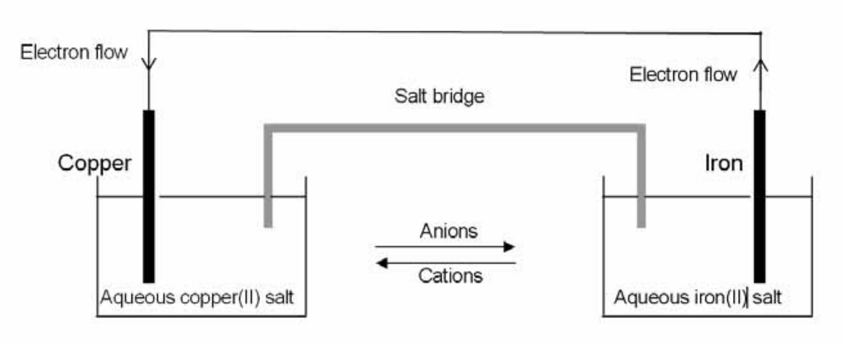
   b) There would be no reaction; the bromine would remain a red–brown colour.

   c) Chlorine is a more powerful oxidising agent than bromine. Hence in the first case the chlorine is able to oxidise the bromide ions to bromine, but in the second case the bromine is not a powerful enough oxidising agent to oxidise chloride ions to chlorine.
5. You could put strips of the metal M into aqueous solutions of salts of metals such as copper sulfate, zinc chloride and magnesium nitrate. If a layer of the metal in solution forms on the surface of metal M, then metal M is more reactive than the metal in solution.

   Alternatively strips of the other metals, such as copper, zinc etc. could be placed in an aqueous solution of MSO_4. If a layer of the metal M forms on the surface of the metal strip, then the metal that the strip is made from is more reactive than metal M.

Page 244 Ex 9.4

1. A
2. D
3. B
4. a) and b)



c) At the copper electrode: $Cu^{2+} + 2e^- \rightarrow Cu$

At the iron electrode: $Fe \rightarrow Fe^{2+} + 2e^-$

d) The copper electrode is the cathode (reduction is occurring) and the iron electrode is the anode (oxidation is occurring).

e) The salt bridge allows for the flow of ions between the two solutions, so as to maintain their electrical neutrality.

5. The two metals furthest apart in the reactivity series will be the pair that will produce the greatest potential difference. Inspection of the series will show that magnesium and copper are the two farthest apart. The more reactive metal will be oxidised, hence that electrode (Mg) will be the anode, ions of the less reactive metal will be reduced, hence that electrode (Cu) will be the cathode.

CHAPTER 9 OXIDATION AND REDUCTION

Page 248,249 Ex

1. D
2. C
3. A
4. a) A temperature of 298K, all concentrations 1 mol dm^{-3}, (pressure of 101.3 kPa less vital here).

   b) A standard hydrogen electrode.

   c) A high resistance voltmeter.

   d) A piece of filter paper dipped in aqueous potassium nitrate (many other possibilities).

   e) i) From the manganese to the silver.

      ii) A new layer of silver metal will form on the surface.

      iii) The manganese electrode will slowly dissolve.

      iv) The cations will move towards the silver electrode and the anions will move towards the manganese electrode.

   f) $Ag(s)|Ag^{+}(aq)||Mn^{2+}(aq)|Mn(s)$

   g) –1.98 V

   h) $\Delta G = -z.F.E^{\ominus} = -2 \cdot 96500 \cdot (-1.98) = +382$ kJ mol^{-1}. Therefore as ΔG is large and positive, the reaction is not spontaneous.

   i) Decrease. The silver equilibrium ($Ag^{+} + e^{-} \rightleftharpoons Ag$) will shift to the left, making its potential more negative, hence the difference in electrode potentials will be smaller.

Page 250 Ex 9.5

1. B
2. C
3. B
4. a) ionic

   b) i) No; ii) Yes; iii) Yes

   c) i) Electrolysis; ii) Electrolyte; iii) Electrodes

   d) Anode + positive; cathode – negative

   e) The anode.
5. a) The ions in the solid are firmly held in fixed places and so are not able to move and carry the current.

   b) It could be melted, or it could be dissolved in water.

   c) $2\ Cl^{-} \rightarrow Cl_2 + 2\ e^{-}$

   d) Bubbles of yellow–green gas.

   e) $Cu^{2+} + 2\ e^{-} \rightarrow Cu$

   f) A layer of a red–brown solid

   g) Reduction, because the copper ions are gaining electrons.

CHAPTER 9 OXIDATION AND REDUCTION

Page 253 Ex 19.2

1. D

2. A

3. D

4. a) The chloride ion.

   b) Oxidation.

   c) The ion from the calcium chloride.

   d) $2\ Cl^- \rightarrow Cl_2 + 2\ e^-$

   e) Bubbles of yellow–green gas would be evolved.

   f) If the chloride ion concentration was quite low, then the water might be oxidised to oxygen, rather than the chloride ions to chlorine.

   g) The calcium ion.

   h) The water will be changed most easily.

   i) $2\ H_2O + 2\ e^- \rightarrow H_2 + 2\ OH^-$

   j) Bubbles of colourless gas would be evolved.

   k) The solution would eventually become calcium hydroxide.

   l) ΔG is probably positive as energy is required for the change to occur.

5. a) The Faraday constant represents the electrical charge carried by one mole of electrons.

   b) $Q = I \text{ x } t = 0.2 \cdot (5\text{x}60\text{x}60) = 3600$ C

   c) Amount of electrons passed = 0.0373 mol.

   Reaction is $Cu^{2+} + 2e^- \rightarrow Cu$

   Amount of Cu = ½ amount of electrons = 0.01865 mol.

   Mass of Cu = $n.M$ = 0.01865x63.55 = 1.185 g

CHAPTER 10 0RGANIC CHEMISTRY

Page 263,264 Exercise 20.1

1. B
2. A
3. A
4. D
5. D
6. D
7. A
8. A
9. B
10. D
11. a) Homologous series

    b) $C_nH_{2n+1}NO_2$

    c) The boiling points would increase with increasing numbers of carbon atoms, owing to an increase in the strength of the van der Waals' forces between the molecules.

    d) i) More soluble in water because the oxygens on the nitro groups can hydrogen bond to the water molecules.

    ii) Less volatile because the nitro group would make the molecules polar and so dipole-dipole bonds will exist between them, increasing the boiling point.

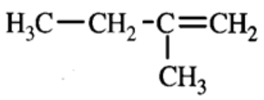
    e) Compounds in the same homologous series tend to have similar chemical reactions, so the product would be $C_5H_{11}NH_2$.

12. a) $CH_3–CH_2–CH_2–CH_2–CH_3$

    b) $CH_3–CH_2–CH(C_2H_5)–CH_2–CH_2–CH_3$

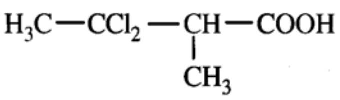
    c) $CH_3–CH_2–Br$

    d)



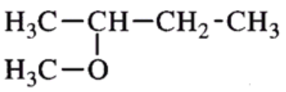
$H_3C-CH_2-\underset{\displaystyle CH_3}{\underset{|}{C}}=CH_2$

e)



$H_3C-CCl_2-\underset{\displaystyle CH_3}{\underset{|}{CH}}-COOH$

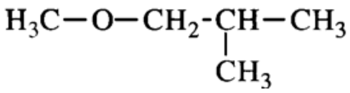
13. a)



$H_3C-\overset{}{\underset{\displaystyle H_3C-O}{\underset{|}{CH}}}-CH_2-CH_3$

or $CH_3CH_2\text{-}O\text{-}CH_2\text{-}CH_2\text{-}CH_3$

b)



$H_3C-O-CH_2-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_3$

c) $CH_3–CH_2–CH_2–CH_2–CH_2–O–H$

14.

$CH_3–CH_2–CH_2–CH_2–CH_2–CH_3$	Hexane
$CH_3–CH_2–CH_2–CH(CH_3)–CH_3$	2–methylpentane
$CH_3–CH_2–CH(CH_3)–CH_2–CH_3$	3–methylpentane
$CH_3\text{\_}CH(CH_3)–CH(CH_3)–CH_3$	2,3–dimethylbutane
$CH_3\text{\_}C(CH_3)_2–CH_2–CH_3$	2,2–dimethylbutane

15. a) Methylpropene
    b) 3–chloropentane
    c) 3–iodobutan–1–ol
    d) 4–hydroxy–4–methylpentanoic acid

Page 269,270 Exercise 10.3

1. A
2. C
3. A
4. D
5. B
6. D
7. a) CH_3-CH_2-CH=CH-CH_3

   b) $C_5H_{10\,(l)} + 7\frac{1}{2}\ O_{2\,(g)} \rightarrow 5\ CO_{2\,(g)} + 5\ H_2O_{(l)}$

   c) Heat energy.

   d) Carbon monoxide, or carbon.

   e) Carbon monoxide is a toxic gas, carbon particles contribute to smog formation.

   f) CH_3-CH(CH_3)-CH=CH_2; 3-methylbut-1-ene.

8. a)Bromoethane,; CH_3-CH_2-Br

   b) Addition reactions

   c) Hydrogen gas and a nickel catalyst

   d) The starting material would turn bromine water from orange to colourless, whereas the product would not do this.

   e) A high pressure (~70 atm), a temperature of about 300°C and a phosphoric acid catalyst.

   f) But-2-ene

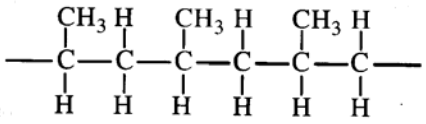
   g) CH_3-CH_2-CH(OH)-CH_3

9. a) A *monomer* is a small molecule that can form two or more covalent bonds to other similar molecules in order to form a large molecule.

   A *polymer* is a large molecule formed by the joining together of a large number of small molecules.

   b) [-CH_2CHCl-]$_n$. formed from CH_2=CHCl.

   c)



Page 273 Ex 10.4

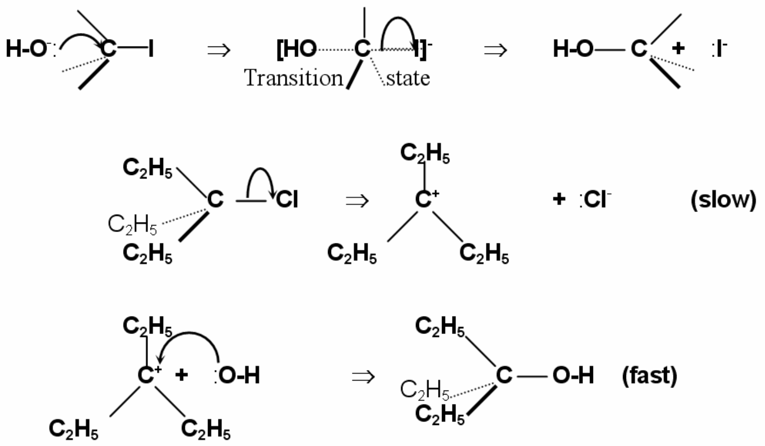
1. D
2. A
3. a) Acidified potassium dichromate(VI)

   b) From orange to green.

   c) Bubbles of carbon dioxide gas would be evolved.

Page 274 Ex 10.5

1. D
2. B
3. B
4. $C_2H_5\text{–}I + OH^- \rightarrow C_2H_5\text{–}OH + Br^-$
5.



Heterolytic fission means the breaking of a covalent bond so that both of the bonding electrons go to the same atom, as for the breaking of the C-Cl bond in the first step of the mechanism.

A **carbocation** intermediate is an intermediate, that is a species formed in one step of a reaction and consumed in a subsequent step, that involves a carbon carrying a positive charge. The $(C_2H_5)_3C^+$ species is an example of a carbocation intermediate.

Page 276,277 Exercise 10.5

1. A
2. B
3. D
4. D
5. A

6. Firstly warm with aqueous sodium hydroxide to hydrolyse the chloroalkane to a secondary alcohol:

   $$CH_3\text{–}CHCl\text{–}CH_3 + OH^- \rightarrow CH_3\text{–}CH(OH)\text{–}CH_3 + Cl^-$$

   The heat the secondary alcohol with acidified potassium dichromate(VI) solution to oxidise it to the ketone:

   $$CH_3\text{–}CH(OH)\text{–}CH_3 + [O] \rightarrow CH_3\text{–}CO\text{–}CH_3 + H_2O$$

7. Firstly reflux the ethanol with excess concentrated acidified potassium dichromate(VI) solution to oxidise it to ethanoic acid:

   $$CH_3\text{–}CH_2\text{–}OH + 2\,[O] \rightarrow CH_3\text{–}CO\text{–}OH + H_2O$$

   Then heat the ethanoic acid produced with some more ethanol, in the presence of a trace of concentrated sulphuric acid to produce an ester.

   $$CH_3\text{–}CO\text{–}OH + CH_3\text{–}CH_2\text{–}OH \rightarrow CH_3\text{–}CO\text{–}O\text{–}CH_2\text{–}CH_3 + H_2O$$

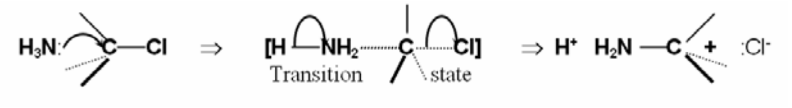
   The ester in this case is ethyl ethanoate.

Page 279 Ex 20.2

1. B
2. B
3. C
4. a) $C_4H_9\text{–}Cl + NH_3 \rightarrow C_4H_9\text{–}NH_2 + H^+ + Cl^-$

   b) S_N2

   c)



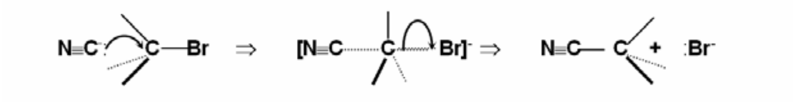
   A nucleophile is a species, like ammonia, which has a lone pair of electrons that it can use to form a bond to a carbon carrying a partial positive charge.

   A transition state is a transient state, labelled in the above diagram, that exists when the new bonds in the products are starting to form and the old bonds in the reactants have not fully broken.

   d) 1-bromobutane would react more rapidly because the carbon-bromine bond is weaker than the carbon-chlorine bond, lowering the activation energy.

5. a) $CH_3\text{—}C\equiv N$; the left hand carbon is sp^3 hybridized, the right hand one sp.

   b) $C_2H_5\text{–}Br + CN^- \rightarrow C_2H_5\text{–}CN + Br^-$



   c) $C_2H_5\text{–}C\equiv N + 2\,H_2 \rightarrow C_2H_5\text{–}CH_2\text{–}NH_2$

   The reaction is catalysed by finely divided nickel.

   The product is prop-1-ylamine.

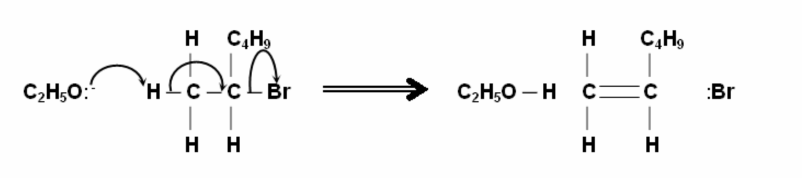
Page 281 Ex 20.3

1. A
2. D
3. B
4. If the reaction is carried out with dilute aqueous sodium hydroxide at ~60°C, then the hydroxide ion acts as a nucleophile, attacking the carbon of the 1-bromopropane bonded to the bromine, causing it to undergo hydrolysis to form propan-1-ol.
   If the reaction is carried out with concentrated alcoholic sodium hydroxide at ~100°C, then the hydroxide ion is converted to the ethoxide ion, which acts as a base, removing a hydrogen ion from a carbon of the 1-bromopropane neighbouring the one that is attached to the bromine, causing it to undergo an elimination reaction to form propene.
5. a) Elimination

   b) The hydroxide ion firstly reacts with the ethanol to form the ethoxide ion:

   $C_2H_5OH + OH^- \rightleftharpoons C_2H_5O^- + H_2O$

   This then acts as a base, removing a hydrogen ion from a carbon of the 2-bromohexane neighbouring the one that is attached to the bromine, causing it to undergo an elimination reaction to form hexane:

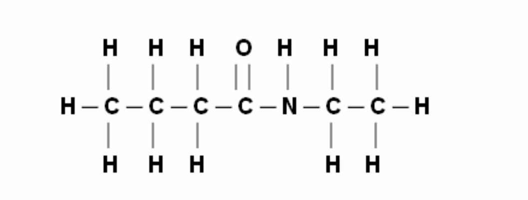


   c) The base can either remove a hydrogen from the first carbon of the chain, as shown above, to give hex-1-ene, alternatively it can remove a hydrogen from the third carbon of the chain to give hex-2-ene.

   d) If it were warmed with dilute aqueous alkali then the hex-2-ene would undergo hydrolysis to form hexan-2-ol.

Page 283 Ex 20.4

1. A
2. B
3. D
4. $C_3H_7\text{–CO–OH} + C_2H_5\text{–}NH_2 \rightarrow C_3H_7\text{–CO–NH–}C_2H_5 + H_2O$



5. a) Methanol and butanoic acid

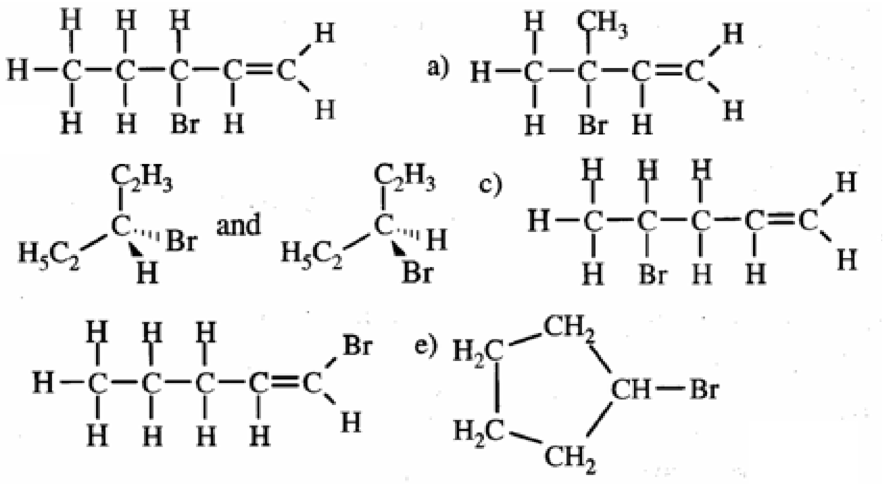
b) $C_3H_7–CO–OH + CH_3–OH \rightleftharpoons C_3H_7–CO–O–CH_3 + H_2O$

c) Apart from the reactants, a trace of concentrated sulphuric acid is needed.

d) Like all esters, methyl butanoate will have a sweet odour.

Page 288 Ex 20.6

1. C
2. C
3. C
4.



5. a) *Optically active* means that the substance will rotate the plane of polarisation of polarised light. A *racemic mixture* is one that contains equal amounts of two enantiomers.

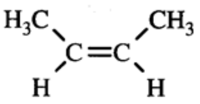
b) The natural lactic acid would comprise just one enantiomer, whereas the synthetic product would be a racemic mixture.

c) If polarised light were passed through a solution of the sample in a polarimeter, the synthetic product would have no effect, but the natural product would rotate the plane of polarisation of the light.

6. a) Because it contains an asymmetric/chiral carbon atom (labelled *),

$C_2H_5–{}^*CHBr–CH_3$, the molecule can exist in two enantiomeric forms.

b) If the starting alkene was orientated:



Then the attack from the H–Br could occur from either above or below the molecule and these produce the two different enantiomers. These are equally probable and hence there are equal amounts of the two enantiomers and the mixture would therefore be optically inactive.

CHAPTER 11 MEASUREMENT AND DATA PROCESSING

Page 298 Ex 11.1

1. C
2. B
3. B
4. D
5. C
6. A

Page 298 Ex 11.2

1. C
2. A
3. B
4. a) 22.85 ± 0.15

   b) 939.0 ± 0.2

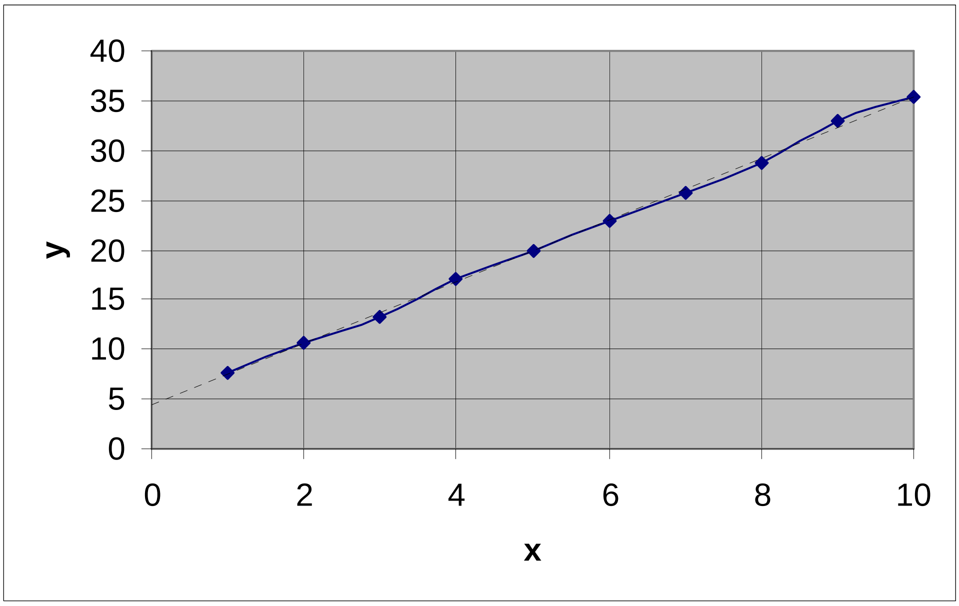
   c) 55.1 ± 0.8

   d) 30.2 ± 1.3 (or maybe 30± 1?)

   e) 13700 ± 200

Page 298 Ex 11.3

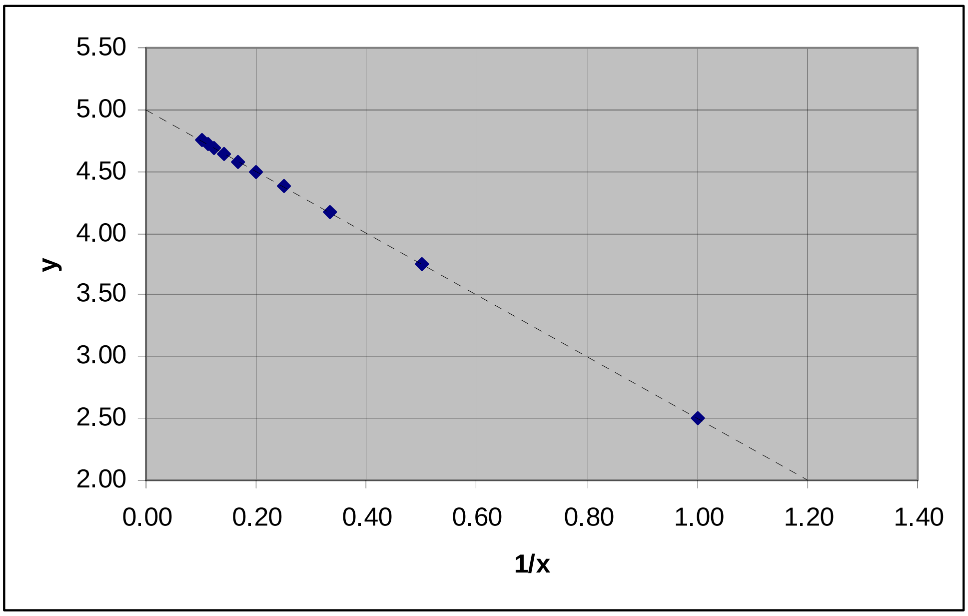
1. From the graph, the intercept is 4 and the gradient is 3.1



2 Rearrange to give $y = T - {}^{5}/_{S}\,({}^{1}/_{x})$.

This is an inverse relationship and so requires a graph of ${}^{1}/_{x}$ against y.

When ${}^{1}/_{x} = 0$, $y = T$; gradient $= -{}^{5}/_{S}$:



From the intercept (when ${}^{1}/_{x} = 0$) T = 5 and from the gradient (=-2.5) S = 2

(Note how important the ${}^{1}/_{x} = 1.0$ point is!)

CHAPTER 12 (OPTION A) MODERN ANALYTICAL CHEMISTRY

Page 301 Ex A2

1. A
2. D
3. a) UV-visible spectroscopy (though atomic absorption would be better still)

   b) Gas-liquid chromatography

   c) NMR spectroscopy

   d) Column chromatography

   e) Mass spectrometry

   (consult text for reasons)
4. Of the techniques mentioned in this chapter, the most obvious examples would be NMR spectroscopy, though the development of the MRI body scanner, chromatographic techniques (liquid and gas) to detect levels of drugs and other substances in the blood and other body fluids and atomic absorption to measure the levels of metals in these fluids.

Page 304 Ex A3

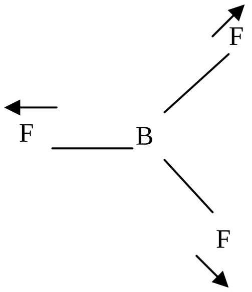
1. D
2. ~1200 cm^{-1} due to C-O bonds and ~3000 cm^{-1} due to C-H bonds.

   Groups that would seem to be absent are C=O (no peak near 1700 cm^{-1}) and O-H (no peak near 3200 cm^{-1}).

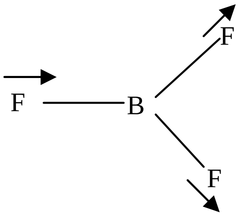
   Given access to a library of IR spectra this spectrum could be matched to that of a known compound and hence it could be identified.
3. a) Changes in the vibrational energy levels (bending and stretching) of the covalent bonds.

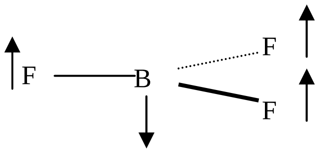
   b) In order to be infrared active the vibration must lead to a change in the dipole of the molecule.

   c) The symmetric stretching mode (all bonds moving in phase) would not be infrared active as the polarity of the molecule remains zero throughout:



Both the asymmetric stretching (one bond lengthens whilst the other two shorten) and bending mode (the B goes up, whilst the Fs go down) would be infrared active as the molecule becomes polar as a result of these deformations:





4. The wavenumber is equal to 1/wavelength in cm = 100/wavelength in m (λ). The wavelength is equal to the speed of light (c) divided by the frequency (f), ($\lambda = c/f$) hence wavenumber = 100f/c.

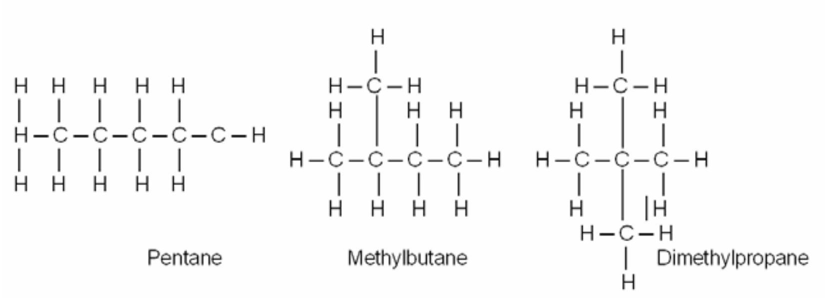
   Hence if the wavenumber is 3652 cm^{-1}, the wavelength will be 0.000274 cm or 2.74×10^{-6} m (= 100/3652) and the frequency will be 1.095×10^{14} Hz (= $3\times10^{8}/2.74\times10^{-6}$).

Page 306,307 Ex

1. a) In 100 g there is 83.3 g (= 83.3/12 = 6.94 mol) of carbon and 16.7 g (=(100-83.3)/1 = 16.7 mol) of hydrogen. The molar C:H ratio is therefore 1:2.4 (= 16.7/6.94) or 5:12, hence its empirical formula is C_5H_{12}.

   b) If the molecular formula was C_5H_{12} then it would be anticipated that the mass of the molecular ion (the fragment with the greatest mass) would be at 72. Anything greater than this would indicate a molecular formula which is a multiple of C_5H_{12}. (Though that would be difficult, from a bonding point of view, in this case!) If the precise value of the molecular ion could be determined, then the presence of oxygen and nitrogen could be eliminated as to a high precision the mass would be different to that of molecules containing O or N (O = 15.994, CH_4 = 16.0427; N = 14.0067, CH_2 = 14.0269).

   c) The possible isomers are:



   Pentane would have regularly spaced peaks resulting from the loss of successive CH_3 and CH_2 groups.

   Methylpentane would fragment more readily where the chain branches, giving rise to large peaks at 57 (=72-15) and 43 (=72-29).

   Dimethylpropane would tend to readily lose just a CH_3 group and so would have a very large peak at 57.

2. a) The molecular ion peak (E) is at 74. As the mass of -COOH is 45, the mass of the hydrocarbon chain must be 29 (74-45), hence it must be C_2H_5-COOH; propanoic acid.

   b) A is $C_2H_5^+$; B is also $C_2H_5^+$, but containing one ^{13}C atom; C is $COOH^+$; D is $C_3H_5O_2^+$;E is the molecular ion $C_3H_6O_2^+$; F is the molecular ion $C_3H_6O_2^+$, but containing one ^{13}C atom.

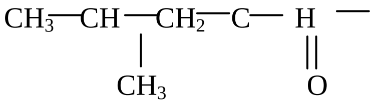
3. a) There are two Cl atoms in $C_2H_2Cl_2$, so there are three isotopic combinations: $^{35}Cl+^{35}Cl$; $^{37}Cl+^{35}Cl$; $^{37}Cl+^{37}Cl$ giving rise to molecular ion peaks at 97; 99 and 101 respectively.
   The relative intensities of these would be 9 (¾×¾) : 6 (¼×¾×2) : 1 (¼×¼).

b) If it were the 1.1 isomer then a CCl_2^+ fragment at around 84 would be possible, but this could not be produced from the 1.2 isomer.

c) If the mass spectrum of the two isomers were compared, then there would be subtle differences between them and the identity of the isomer could be determined by comparing the spectrum it gave with these sample spectra. A simpler way would be to see whether it was a polar molecule by seeing if a charged rod caused a stream of the liquid to deflect.

Page 310 Ex

1. 3 methylbutanal is:



$CH_3-\underset{|\atop CH_3}{CH}-CH_2-\underset{\|\atop O}{C}-H$

It can be seen that there are hydrogens in 4 different environments so there will be four peaks at ~1 (both CH_3 groups), ~1.7 (CH), ~ 2.2 (CH_2) and ~9.7 (CO-H), with areas under the peak in the ratio of 6 : 1 : 2 :1.
The isomer dimethylpropanal, $(CH_3)_3C\text{-}CO\text{-}H$, would have just 2 widely separated peaks with a 9:1 ratio.

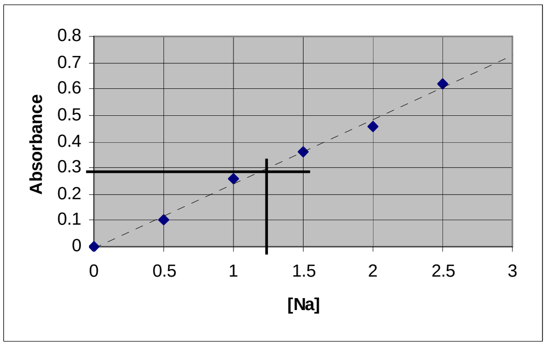
2. The molecule has hydrogens in 4 different environments. The absorption at 4.1 probably corresponds to $–CH_2–O$, and that at 2.1 to $CH_3\text{-}CO–$, hence the compound is probably an ester. There are 2 other environments at lower shifts, hence the molecule is probably
$CH_3–CO–O–CH_2–CH_2–CH_3$, prop-1-yl ethanoate. Going from left to right through the formula as written, the $CH_3–CO–$ at 2.1 is a singlet because there are no hydrogens on neighbouring carbons; the at 4.1 is a triplet because it is split by the two hydrogens on the neighbouring carbon atom; the hydrogens on the next $–CH_2–$ with a signal around 1.8 are split by both the $–CH_2–O$ on one side and the CH_3- on the other giving a complex pattern; finally the $CH_3–$ at 0.9 is split into a triplet by the neighbouring $–CH_2–$.

3. A nucleus will only generate a NMR signal if the nucleus of an atom has a residual spin, which will cause it to align itself either with or against an external magnetic field. Each proton and neutron has a spin, but as far as possible these “pair up” so that there is no resultant spin. This is the case in isotopes with an even number of nucleons, such as ^{16}O. If however there is an odd number of nucleons, then there must be a residual spin, as for example in ^{19}F, and the nucleus can give rise to an NMR signal. The precise frequency at which this occurs depends on the electron density near the nucleus as, when placed in a magnetic field the electrons generate their own magnetic field so as to oppose the external one. This means that because there are fewer electrons around a F-atom F-F than in H-F, the F-nucleus in F-F will experience a stronger field and hence absorb radiation of frequency than the F-nucleus in H-F.

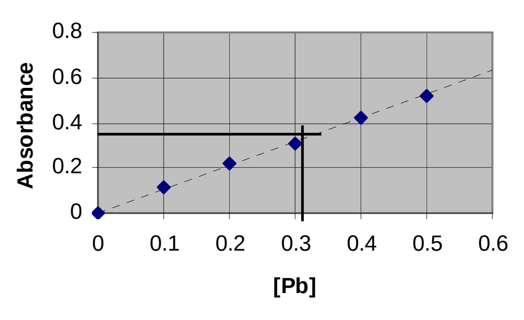
Page 312 Ex A6

1. B

2. The concentration of Na^+ is 1.25 mg dm^{-3} (see graph).



3. The concentration of Pb^{2+} is 0.31 ppm (see graph).



Page 317 Ex A10

1. Firstly a vertical column fitted with a tap would be filled with a suitable stationary phase (for example fine silica) in a suitable solvent (for example ethanol) and liquid allowed to drip from the tap until the surface of the liquid was just level with the top of the solid. The mixture of dyes would then be added to top of the column and again the tap opened, so the liquid dripped out at a slow rate (say about 10 drops per minute) until the liquid was again level with the solid. Fresh solvent should then be added so that the level of the liquid never falls below the surface of the solid. As time passes the coloured band of the dyes should pass downwards and gradually separate into the different components. Fresh receivers can be placed to collect the different components as they drip from the bottom of the column. The solid dyes can then be obtained by evaporating the solvent.

2. (a) A piece of chromatography paper is taken and a pencil line drawn about 1 cm from the bottom end. A small dot of the liquid dye mixture is then placed on this line and allowed to dry. A suitable eluent (for example butanol) is placed in a beaker to a depth of about ½ cm, the piece of paper stood in this so the pencil line is just above the surface of the liquid, and the beaker tightly covered. The eluent will rise through the paper by capilliary action and as it does so the dyes will also move upwards. Those that bond most strongly to the solvent will be carried up quickly, whilst those that bond most strongly to the droplets of water held stationary in the pores of the paper will move much slower. Hence the mixture of dyes will separate.

b) The R_f value is the distance moved by the component divided by the distance moved by the solvent front, hence it can be determined for each component by measuring these values. A R_f of 0.0 means the component has not moved whilst one of 1.0 means that it has moved at the same rate as the eluent.

c) If an illegal substance was suspected then a spot of this should be placed on the pencil line about 1 cm away from the dye mixture. When the eluent has almost reached the top of the paper the mixture should be examined to see if there is a component of the mixture that is producing a spot of a similar colour that has travelled about the same distance as the spot of the illegal substance.

3. a) In the case of paper chromatography the mobile phase is the solvent used to elute the chromatogram. The stationary phase is droplets of water firmly held in the pores of the paper. In the case of the chromatogram illustrated, the red dye bonds more strongly to the mobile, non-aqueous, phase whilst the yellow dye bonds more strongly to the aqueous phase held in the pores of the paper.

b) The R_f value of the red dye is

c) Generally GLC and HPLC can both deal with a greater variety of mixtures, provide better separation of the components and are far more sensitive than paper chromatography.

d) GLC can generally provide greater sensitivity than HPLC for readily volatile components, for example trying to find traces of benzene in gasoline. HPLC is better when substances are likely to decompose around the temperature needed to vapourise them, for example looking at the amounts of different sugars in a sample of hydrolysed honey.

4. a) The butan-1-ol is more strongly attracted to the packing of the column, which comprises the stationary phase, and hence it moves through the column more slowly than the 2.2-dimethylpropanol which being more weakly attracted passes more rapidly.

b) The relative amounts of the alcohols could be found from the relative areas under the peaks that they produce.

c) Frequently a flammable gas, such as hydrogen, is used as the carrier and burnt at the end of the column, with two electrodes in the flame testing its electrical conductivity. As other compounds elute they burn and produce ions that increase the conductivity of the flame and this can be measured. A slightly less sensitive alternative is to use an inert carrier gas and measure the thermal conductivity of the gas as it emerges. The presence of other compounds in the carrier gas will affect the thermal conductivity.

d) If the temperature of the column was increased, then the time taken for components to elute would decrease.

Page 321 Ex A8

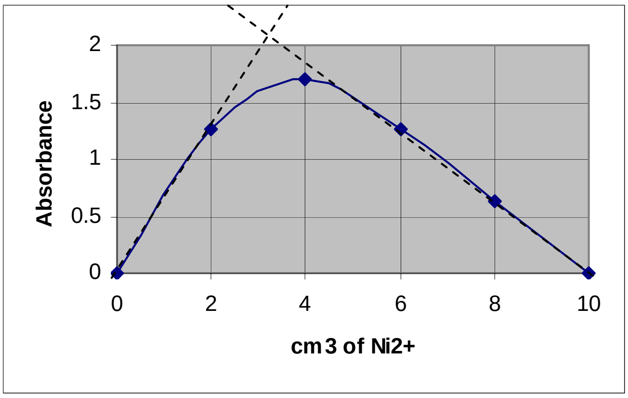
1. B
2. C

3. a) In an isolated atom of a transition metal the d-orbitals are all of an equal energy, but when surrounded by ligands in solution, the electrical fields from these affect the different d-orbitals to different extents as a result of their different shapes. As a result the d-orbitals usually split into two groups of different energies. The energy difference between these levels corresponds to a quantum of light in the visible region, hence the solutions absorb light of particular frequencies, to excite electrons from the lower to the upper d-orbitals, and the solution appears the complementary colour. The precise difference in energy between the d-orbitals depends upon the nature of the ligands surrounding the metal ion, so that changing the nature of the ligand will affect the colour of the solution.

b) Nickel sulphate will appear green because the solution absorbs red light so that he light passing unaffected (green as well as yellow+blue) appears green.

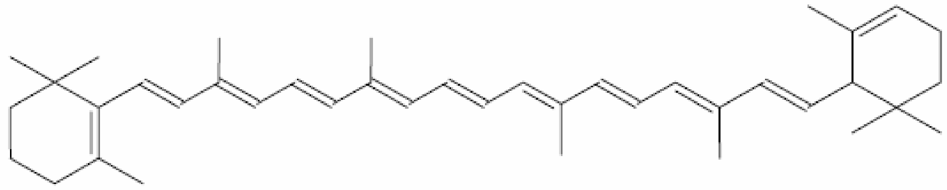
c) If the concentration of the salt is doubled then the intensity of the passing light will decrease by a factor of 10 ($I = I_o \times 10^{-\varepsilon.c.l}$). To restore the light to its former intensity the path length would have to be decreased by a factor of 10.

d)



By extrapolation from the two sides it can be seen that the maximum absorption would be when the volume of Ni^{2+} was ~3.3 cm^3. and the volume of the ligand 6.7 cm^3. As they are of equal concentrations, this would imply that the Ni^{2+}:ligand ratio in the complex ion was 1:2.

4. One coloured substance would be α-carotene, the structure of which is shown below:



It can be seen that there is along hydrocarbon chain containing conjugated double bonds (alternate single and double bonds), which extends into the rings at both ends. This leads to a large delocalised π-bond, for which the difference in energy between the highest filled and lowest unfilled energy level will correspond to a quanta of light in the blue and green regions of the visible spectrum. The molecule absorbs light of these colours but yellow, orange and red light pass unchanged, hence its colour.

CHAPTER 13 (OPTION B) HUMAN BIOCHEMISTRY

Page 359 B1 Energy

1. Heat evolved per g, $\Delta H = m_{\text{water equivalent}} \times c_{\text{water}} \times \Delta T$

$= 532\text{ g} \times 4.184\text{ J g}^{-1}\ °\text{C}^{-1} \times 6.60°\text{C}$

$= 14700\text{ J} = 14.7\text{ kJ}$ (answer to 3 significant figures)

Page 359 B2 Proteins

2: Glycine is the simplest amino acid in which the carbon atom is not chiral , that is the molecule is symmetrical. Alanine, on the other hand, has a carbon with four different groups on it, that is it contains a chiral carbon and the molecule is asymmetric (not that it is the molecule that is asymmetric, and not the carbon atom).

3. $HOOCCH(CH_3)NH_2 + HOOCCH(CH_3)NH_2 \rightarrow HOOCCH(CH_3)NHOCCH(CH_3)NH_2 + H_2O$; the peptide linkage in which the N atom is boned to the carbonyl group, -C=O.

4. (i) Ala-Ala-Ala; Ala-Ala-Gly; Ala-Gly-Ala; Gly-Ala-Ala;

Ala-Gly-Gly; Gly-Ala-Gly; Gly-Gly-Ala; Gly-Gly-Gly (total = $2^3 = 8$)

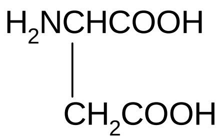
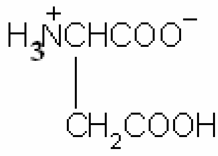
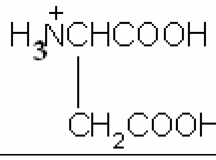
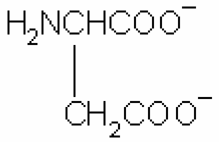
(ii) With three different amino acids: $3^3 = 27$

(iii) 6 (3 x 2 x 1): If the amino acids are 1, 2 and 3 then the combinations are:

1-2-3; 1-3-2; 2-3-1; 2-1-3; 3-1-2 and 3-2-1

5. Chromatography and electrophoresis, see Chapter 12 for more details about chromatography and electrophoresis

6.

 $H_2NCH(CH_2COOH)COOH$	 $H_3\overset{+}{N}CH(CH_2COOH)COO^-$	 $H_3\overset{+}{N}CH(CH_2COOH)COOH$	 $H_2NCH(CH_2COO^-)COO^-$
Aspartic acid	At pH = 2.8	At pH = 1.0	At pH = 11.0
	Zwitter ion where the positive and negative charges are identical (or balanced)	In an acidic solution, the lone electron pair of the nitrogen accepts a proton	In an alkaline solution, the -COOH groups donate protons and are converted to the carboxylate ions

7. The **primary** structure gives the sequence or order of amino acids which make up the protein, for example tyr-lys-cys-tyr-leu (each amino acid is represented by the three-letter code).

The **secondary** structure shows how the polypeptide chain folds or aligns itself in a repeating pattern due to hydrogen bonding.

In the **tertiary** structure, the chains fold or are uniquely twisted to give it 3-D shape.

Quaternary structures exist only in proteins that are composed of more than one polypeptide chain which are held together by hydrophobic interactions, hydrogen bonding and ionic bonding.

8. Major functions include structural proteins (for example, collagen the fibrous connective tissue in tendons and cartilage), enzymes (for example DNA polymerase that replicates DNA), hormones (for example, insulin that regulates glucose metabolism), immunoproteins (protective proteins such as antibodies that form complexes with foreign proteins), transport proteins (for example, hemoglobin that transports oxygen in blood) and energy source (for example casein, a milk protein).

Page 359 B3 Carbohydrates

9. CH_2O

   Carbonyl C=O group

   Hydroxyl –O-H groups (at least two)

10. C_1 and C_6 are not chiral, others are. Each of C_2 to C_5 contains a H atom, -OH and two different groups (making these four C atoms chiral). It exhibits stereoisomerism.

11. The only difference is that in α-glucose, the –OH on C_1 is below the ring where as in β-g;ucose the –OH is above the ring.

12. Condensation reaction takes place with the elimination of water. It forms the C–O–C bond between the rings (called the glycoside or ether linkage). The bond forms between the C_1 of one glucose molecule and C_4 of another molecule, thus called the 1→ 4 linkage.

$$C_6H_{12}O_6 + C_6H_{12}O_6 \rightarrow C_{12}H_{22}O_{11} + H_2O$$

   Hydrolysis of the glucoside linkage takes place (reverse of condensation reaction), and two glucose monosaccharides are formed.

13. Both contain the 1→ 4 glycoside (ether) linkage between the monosaccharides. Amylopectin also contains the 1→ 6 ether linkage which leads to branching in the structure of the starch.

14. Maltose: α-glucose (and α-glucose)

    Sucrose: α-glucose and β-fructose

    Starch: α-glucose (and α-glucose)

15. They contain several –OH (hydroxyl) groups that can form hydrogen bonds with water.

16. Amylopectin (a branched polymer containing 1→4 and 1→6 glycoside linkages) is part of the plant starch. Glycogen is found in animal tissue which has shorter chains but is more branched.

CHAPTER 13 (OPTION B) HUMAN BIOCHEMISTRY

Page 359,360 B4 Lipids

17. The iodine number indicates the number of double bonds present in a fat or oil. The higher the iodine number, the greater the degree of unsaturation (iodine number is the number of moles of I_2 reacting with one mole of fat/oil).

18. M(acid) = [18(12.0) + 30(1.0) + 2(16.0)] = 278.0 g mol^{-1}

$$n(\text{acid}) = \frac{2.78\,g}{278.0\,g\,mol^{-1}} = 0.0100\,mol$$

$$n(I_2) = \frac{7.62\,g}{253.8\,g\,mol^{-1}} = 0.0300\,\text{mol}\ I_2$$

Thus one mole acid will react with four moles of iodine and therefore contains 3 C=C double bonds.

19. A triglyceride is formed from one molecule of glycerol (propan-1,2,3-triol, $CH_2(OH)CH(OH)CH_2OH$) and three of fatty aliphatic acids (R–COOH, which can be the same or different fatty acids) which are carboxylic acids with long, straight-chain, hydrocarbons. Fats contain no unsaturation in the hydrocarbon chain, whereas oils contain at least one C=C and are thus unsaturated. The arrangement around the double bonds is cis meaning the alkyl groups across the C=C bond are on the same side. Triglycerides are un-ionised lipids (unlike phospholids that are ionised):

Phospholipids are complex lipids containing phosphorus and similar to triglycerides in their structure except that one fatty acid is replaced by a phosphate that contains a polar group; lecithin contains choline ($(CH_3)_3N^+CH_2CH_2OH$). The R groups of the fatty acids are non-polar tails whereas the phosphate group is the polar head of the molecule. Such molecules are called amphipathic.

The steroid skeleton is a characteristic molecular tetracyclic fused carbon ring structure consisting of three cyclohexane rings and a cyclopentane ring, Hence the structure is not related to that of fats/oils or phospholipids.

20. Both are triglycerides made from one propan-1,2,3-triol and three fatty acids. In fats, the hydrocarbon chain is saturated and contains no C=C double bonds. Oils contain one or more C=C double bonds (in one or more of the hydrocarbon chains). The hydrocarbon chains are able to pack more closely (or tightly) in the fats, experience greater van der Waals' forces and have higher melting points (exist as solids). The presence of double bonds means the hydrocarbon chains can not pack as closely, experience weaker interparticle forces and have lower boiling points (are liquids).

21. (a) The R group attached to the-COOH is saturated: C_nH_{2n-1}. Thus the long chain hydrocarbons can pack closer together, experience greater van der Waals' forces and it is a solid at room temperature.

(b) There are two less H atoms in oleic acid suggesting it has one C=C double bond present in the hydrocarbon chain. These chains can no longer pack as closely as in the case of the saturated hydrocarbons, experience less interparticle forces and the acid is a liquid at room temperature.

(c) Linoleic acid, with four less Hydrogen atoms compared to stearic acid must contain two C=C double bonds. As the number of C=C double bonds increases, it becomes increasingly more difficult for the hydrocarbon chains to pack closer together, thus further lowing the melting point.

22. Triglycerides contain carbon, hydrogen and oxygen (in a reduced form) with a low proportion of oxygen (for example, compare an unsaturated fatty acid with the formula $C_{17}H_{31}COOH$ compared to a trisaccharide $C_{18}H_{32}O_{16}$ with the same number of carbon atoms). Thus fats ans oils are little oxidised and hence the most concentrated energy source (providing over twice as much energy per gram as carbohydrates).

Page 360 B5 Micro- and macro-nutrients

23. A micro-nutrient is substance that is required in very small amounts (mg or µg) and that mainly functions as a co-factor of enzymes. Examples include vitamins and trace minerals such as Fe, Cu, and Cr amongst others).

24. A macro-nutrient is a chemical substance that is required in relatively large amounts for example proteins, fats, carbohydrates and minerals (Na, Mg, K, Ca, P, S, Cl).

25. The two functional groups in vitamin D are alcohol (hydroxyl group, -OH) and C=C double bond alkene. Although it contains one –OH group, it also contains a large non-polar hydrocarbon component, making it fat soluble (note: vitamin A is also fat soluble for a similar reason).

26. The two functional groups in vitamin C are alcohol (hydroxyl group, -OH) and C=O carbonyl group (it also contains C-O-C group). The presence of four polar –OH groups which are capable of hydrogen bonding with water makes vitamin C water soluble.

Page 360 B6 Hormones

27. Hormones are secreted by the endocrine glands directly into the blood and transported by the blood stream. Hormones are chemical messengers that regulate functions such as growth and metabolism.

28. Oestradiol (an –ol) contains the hydroxyl group, and the benzene ring. The testosterone (-one) contains the carbonyl group (as part of a ketone), an alkene and an extra methyl group. The alkene in the testosterone can be identified by reaction with orange bromine water or pink iodine water which will decolorize (turns “clear” is not the right answer as both bromine and iodine water are clear, but colored).

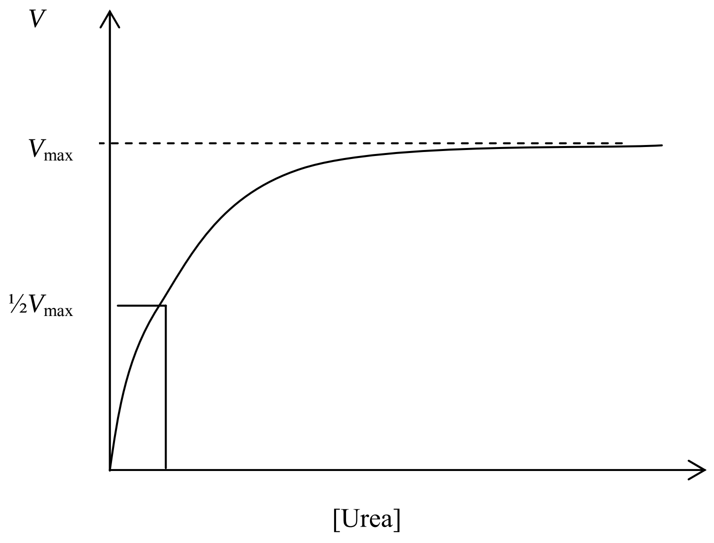
Page 361 B7 Enzymes [HL]

29. An enzyme speeds up reactions in living systems. Enzymes are proteins whose activity depends on tertiary and quaternary structure and on the specificity of enzyme action.

30. (i) Fast step: Formation of the complex ES: $E + S \leftrightarrows ES$

Slow step: Decompositon to form products : $ES \rightarrow E + P$

(ii)



(iii) At low substrate concentration, more free active sites on the enzyme molecules can react, and the rate of reaction increases as more E-S complex is formed. As the enzyme becomes saturated, the rate becomes constant regardless of how much the substrate concentrated is increased as all active sites are being used. This is the highest velocity of the reaction, called V_{max}. when all enzyme has been converted to enzyme-substrate complex.

(iv) K_m is equal to the substrate concentration when the velocity (rate) is equal to half the maximum value as shown on the graph.

(v) K_m value is inversely proportional to enzyme activity: a lower value of K_m means a more efficient enzyme because, with the same substrate concentration, there is a higher reaction rate.

31. Enzymes and substrates are only effective if they have the specific 3-D shapes which complement each other (that is, the lock and key model). If there is any change in enzyme shape or arrangement, the enzyme is denatured and the substrate is no longer able to bind to the active site.

32. (i) Heavy metal ions can bind or chelate with enzyme disulfide bridges in proteins (often irreversibly). Thus these can act as inhibitors by changing protein shapes which stops a substrate from binding to the active site. Note that enzymes and substrates are only effective if they have the specific 3-D shapes which complement each other (that is, the lock and key model).

(ii) An increase in temperature increase the number of particles with energy, $E \geq E_a$. Above a certain temperature, the thermal agitation of the enzyme disrupts the bonds (such a hydrogen bonds, ionic bonds and other non-covalent interactions) that stabilize its active structure. As the enzyme denatures, the rate of the reaction drops sharply and stops. In humans, the optimum temperature is about 37°C, the same as internal body temperature.

(iii) Basic $–NH_2$ and acidic –COOH groups lead to ionic charges on amino acids that give rise to 3D protein structure which are thus susceptible to pH changes. pH changes can alter and denature such ionizable enzymes rendering them ineffective. However, if an enzyme is acting on an electrically neutral substrate molecule, or where the charge plays no role in the catalyzed reaction, change in pH will have little effect on the rate of reaction (such as the catalysis of the hydrolysis of neutral sucrose by the enzyme invertase has a constant rate in the pH range 3.3 to 7.5).

Page 361 B8 Nucleic acids [HL]

33. (i) A nucleotide consists an ionized phosphate group bonded to a pentose sugar which is bonded to an organic nitrogenous base such as adenine (A), cytosine (C), guanine (G), thymine (T) and uracil (U).

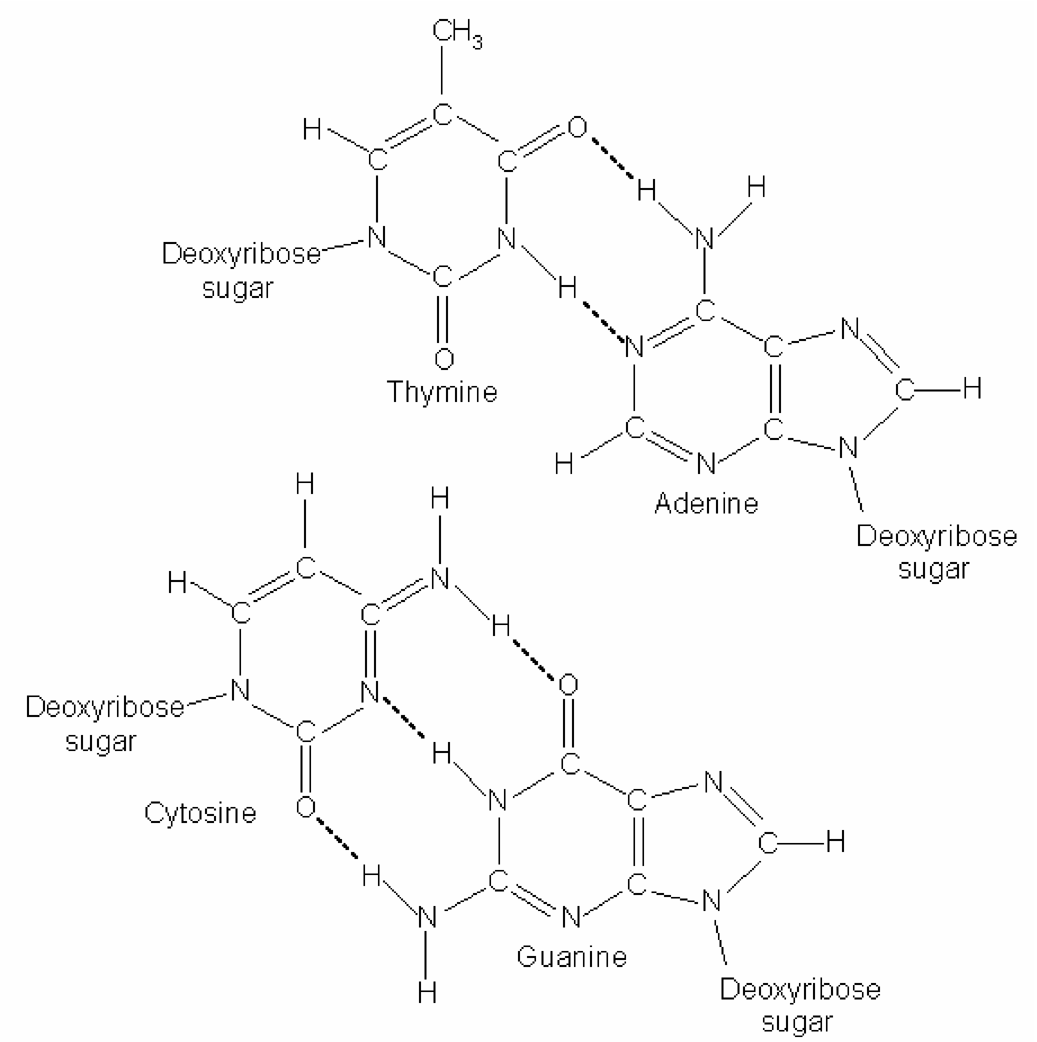
(ii) Condensation or esterification reaction.

(iii) Nucleotides are joined by the phosphodiester covalent bond or linkage that joins the sugar of one nucleotide and the phosphate of the other to form the polynucleotides, resulting in a backbone with a repeating pattern of sugar–phosphate–sugar–phosphate. Nitrogenous bases are attached to the sugar of the backbone.

(iv) Hydrogen bonding between specific pairs of nucleotide bases gives rise to the double helix structure of polynucloetides. In DNA, hydrogen bonds occur between A and T, and C and G.

(v) DNA contains the sugar deoxyribose where as RNA contains ribose, the pentose sugar. These sugars differ only in that the hydroxyl group on the C–2 of ribose is replaced by a hydrogen atom in deoxyribose and lacks an oxygen atom on C–2. Another difference is that DNA contains the base thymine; RNA contains the base uracil.

34. The combination of a purine and a pyrimidine give a similar distance between the two backbones of DNA, since a purine is double ringed and a pyrimidine is single ringed leading to intermolecular hydrogen bonding that occurs between them. Adenine forms two hydrogen bonds with thymine because of their molecular geometry and cytosine and guanine form three hydrogen bonds. The pairing of adenine with cytosine and thymine and guanine do not form hydrogen bonds strong enough to hold DNA together (*refer to next page*).



35. (i) The key to DNA profiling is that all cells from an organism must create the same DNA profile. If the process is carried out extensively enough it is possible to produce a profile of sufficient detail that would make it almost impossible for any other organisms to have the same profile.

(ii) DNA profiling involves the production of a genetic ‘fingerprint’. A DNA profile requires a small amount of cellular material and involve observing the number of different pieces a molecule of DNA can be split into and the sizes of these pieces.

(iii) The use of restriction enzymes, which have the ability to find a certain sequence of usually four to eight base-pairs and to cut the molecule of DNA at or near to those sequences can be used. If a section of DNA is chosen that varies considerably from person to person, then each person will have this section of DNA cut into different lengths as the restriction sequences will occur at different points in each person’s DNA.. Once a unique combination of DNA fragments of different sizes is created, gel electrophoresis is used to make an observable DNA profile. A thin plate of electrically conducting gel is set up, a negative potential is applied at one end of the plate and a positive potential at the other. A solution of the various DNA fragments is placed on the plate near to the negative end. Since DNA has negatively charged phosphate groups it is attracted to the positively charged end. As the fragments of DNA move, the smaller fragments moving more quickly through the gel than the larger ones. A fluorescent dye is added which makes the DNA glow in UV light. A photograph can then be taken of the number and position of the bands of DNA that appear in the gel.

(iv) DNA profiling is mainly used to identify people. This is especially useful in helping to solve crimes, as any cells left behind at the scene of a crime in the form of blood, semen, saliva or hair roots can be used to provide a DNA sample. DNA profiles can be made from the suspect's DNA and compared to the DNA profile connected with the scene of the crime. DNA profiling can also be used in paternity cases.

Page 362 B9 Respiration [HL]

36. (a) Aerobic (also called oxidative) respiration requires air; anaerobic (the opposite of aerobic) respiration occurs in the absence of air, meaning without oxygen.

(b) Molecular oxygen is the oxidizing agent (electron acceptor) and a glucose molecule is the reducing agent (the electron donor).

(c) In aerobic oxidation, the carbon atoms in glucose are oxidized to form CO_2 and oxygen is reduced to form water. The two redox half equations for the reactions are:

Oxidation ½-reaction (ox. # of C increases): $C_6H_{12}O_6 + 6H_2O + 24\ e^- \rightarrow 6CO_2 + 24H^+ + 24\ e^-$

Reduction ½-reaction (ox. # of O decreases): $6O_2 + 24H^+ + 24e^- \rightarrow 12H_2O$

Overall redox reaction: $C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O$

(d) Glucose, $C_6H_{12}O_6$ contains a larger number of C–C and C–H bonds which are not as strong (bond enthalpies respectively of 348 and 412 kJ mol^{-1} in the gaseous state) compared to C=O and O–H bonds (743 and 463 kJ mol^{-1} respectively) in the products. Thus less energy is required to break the weaker reactant bonds and more energy is produced in making stronger product bonds; the net result is an exothermic reaction.

(e) Anaerobic respiration takes place during strenuous exercise, which requires oxygen faster than it can be delivered by the blood stream. Anaerobic respiration occurs causing the build up of lactic acid in muscle cells. This happens for a limited time only in the human body as the increase in lactic acid decreases the pH in the muscle causing pain. If oxygen is again available, lactic acid can be oxidized to carbon dioxide and water.

37. (i) Electron transport: Cytochrome containing the iron and copper ions; Fe undergo one–electron oxidation–reduction reactions during aerobic respiration between iron(II) and iron(III) oxidation states and the copper between copper(I) and copper(II)

$Fe^{2+} \rightarrow Fe^{3+} + e^-$

$Cu^+ \rightarrow Cu^{2+} + e^-$

Carbon is glucose is oxidized and oxygen is reduced to water.

(ii) Haemoglobin containing iron ion is the best–known oxygen transport protein. Coordinate covalent bonding occurs between the lone electron pairs on the nitrogen containing bases and the iron ion, Iron bonds reversibly to the oxygen in the lungs in order to transport it via the blood to tissues throughout the body.

CHAPTER 14 (OPTION C)

CHEMISTRY IN INDUSTRY AND TECHNOLOGY

Page 401   C1 Iron, steel and aluminium

1. (a) Aluminium is extracted by electrolytic reduction of its ore where as iron is extracted by chemical reduction of its ore.

Al: Electrolytic cell used; oxidation occurs at the positive electrode; reduction at the negative cathode and the cell uses large amounts of electrical energy.

Aluminium is a reactive metal; iron is not as reactive. Al has a more negative $E°$ value; it is more reactive than carbon (namely, it has a higher affinity for oxygen than for carbon), thus it is not extracted from its oxide by reduction with carbon (or CO) and requires electricity.

Fe: Pre-heated oxygen is introduced into the blast furnace at high pressure. Coke converted to the reducing agent (Impurities are oxidised that reduces to iron oxide to iron.

(b) (i) the main source of iron are the mineral ores: haematite (Fe_2O_3), magnetite (mixed oxides) and pyrites (FeS_2).

(ii) Oxidation of coke (C) is an exothermic process and produces the high temperatures for the reaction: $C + O_2 \rightarrow 2CO_2 + \text{heat}$

It is converted to carbon monoxide ($2C + O_2 \rightarrow 2CO$; $CO_2 + C + \text{heat} \rightarrow 2CO$), the reducing agent that converts iron oxide to iron.

(iii) Oxygen and limestone, $CaCO_3$

Oxygen reacts with coke to form CO (see equations in (ii) above.

$$Fe_2O_3\,(s) + 3CO\,(g) \rightarrow 2Fe\,(l) + 3CO_2\,(g) + \text{heat}$$

$$Fe_3O_4\,(s) + 4CO\,(g) \rightarrow 3Fe\,(l) + 4CO_2\,(g) + \text{heat}$$

Heat decomposes limestone to lime, CaO

$$\text{heat} + CaCO_3\,(s) \rightarrow CaO\,(s) + CO_2\,(g)$$

The highly basic calcium oxide combines with the acidic silicon(IV) oxide present as sand in the impure ore and the amphoteric aluminium oxide (which can behave as an acid or a base). These impurities in the ore form a molten slag of calcium silicate(IV) and calcium aluminate(III):

$$CaO\,(s) + SiO_2\,(s) \rightarrow CaSiO_3\,(l)$$

$$CaO\,(s) + Al_2O_3\,(s) \rightarrow CaAl_2O_4\,(l)$$

Slag can be used for road making, as land fill and re-landscaping and for manufacture of cement.

(iv)

$$2CH_4\,(g) + O_2\,(g) \rightarrow 2CO\,(g) + 4H_2\,(g)$$

Hydrogen gas is the reducing agent:

$$Fe_3O_4\,(s) + 4H_2\,(g) \rightarrow 3Fe\,(l) + 4H_2O\,(g)$$

(v) Any release of carbon monoxide as it is a metabolic poison.

2. (a) (i) aluminium oxide, Al_2O_3 (alumina)

(ii) Na_3AlF_6. The Al_2O_3 is dissolved in molten cryolite which reduces the melting point and improves the conductivity, at about 900°C. The reaction is thus carried out at a lower temperature saying energy.

(iii) Iron(III) oxide, Fe_2O_3 and silicon(IV) oxide, SiO_2.

The impure bauxite is treated with hot concentrated sodium hydroxide. Silicon(IV) oxide and aluminum oxide dissolve:

$SiO_2\ (aq) + 2NaOH\ (aq) \rightarrow H_2O\ (l) + Na_2SiO_3\ (aq)$

$Al_2O_3\ (s) + 2NaOH\ (aq) \rightarrow 2NaAlO_2\ (aq) + H_2O\ (l)$

Iron oxide other basic materials remain insoluble and are removed by filtration. The solution is diluted and seeded with solid sodium hydroxide to reverse the reaction and precipitate aluminium hydroxide; sodium silicate stays in solution:

$2H_2O(l) + NaAlO_2(aq) \rightarrow Al(OH)_3(s) + NaOH(aq)$

Finally, the aluminium hydroxide is heated to obtain pure Al2O3:

$2Al(OH)_3\ (s) \rightarrow Al_2O_3(s) + 3H_2O\ (g)$

(iv) Oxidation occurs at the positive anode to form oxygen gas:

$2\ O^{2-}\ (l) \rightarrow O_2\ (g) + 4\ e–$

Reduction occurs at the negative cathode to form liquid aluminium:

$Al^{3+}\ (l) + 3e^- \rightarrow Al\ (l)$

Over all reaction:

$4\ Al^{3+}\ (l) + 6O^{2-}\ (l) \rightarrow 4Al\ (l) + 3O_2\ (g)$

(b) The oxygen gas produced reacts with the graphite positive electrodes (anodes) to form oxides of carbon:

$C\ (s) + O_2\ (g) \rightarrow CO_2\ (g)$

Thus the anodes gradually burn away and are replaced regularly.

3. (a) (i) Pig iron.

(ii) carbon and silicon

(b) To remove the impurities pure oxygen and powered calcium oxide (lime) are blown through the molten liquid high pressure to convert these to the oxides. The volatile ones such as CO_2 escape as gases, the non-volatile ones such as SiO_2 react with the calcium oxide to form slag. The slag forms a layer above the crude steel and remains behind as liquid steel which is poured off.

(c) (i) An alloy is a mixture of two or more elements at least one of which is a metal; it is a homogeneous mixture of metals or a mixture of a metal and non-metal in which the metal, called the base metal, is in the much larger amount resulting in metallic properties.

An alloy is made by mixing the alloying element(s) with the base metal when molten and allowing the mixture to cool to form the alloy.

(ii) A pure metal has an orderly arrangement of atom or cations (in a sea of electrons) with no directional or rigid bonds. As a result, metal layers are able to slide over each other when a stress is applied to it and are soft, ductile and malleable – properties typical of metals. The presence of another element with differently sized atoms/cations size modifies the micro-structure of the base metal by disrupting the regular, repeating lattice. This now makes it difficult for one layer to slide over another.

Alloying can modify physical properties such as hardness and malleability, as well as engineering properties such as tensile strength and chemical properties such as resistance to corrosion.

(iii) In **annealing**, the metal is allowed to cool slowly to produce a soft malleable steel.

In **quenching**, very hot metal is rapidly cooled so that the high-temperature crystal structure is retained, giving a hard, brittle steel.

In **tempering**, the quenched steel is reheated to achieve a hardness intermediate between that achieved by annealing and quenching.

(iv) Aluminium has a very low density and, owing to a thin impervious layer of its oxide, it is corrosion resistant with good electrical and thermal conductivity. Though quite soft it can be made harder by alloying with other metals such as magnesium. Many of its alloys are very strong. Hence, aluminium is an excellent choice when a strong, but lightweight, metal is required. It is used both as a structural and decorative metal and as an electrical conductor in high voltage transmission lines. Most of the uses of aluminium such as saucepans, aircraft and vehicle bodywork are possible because of the protective oxide coating.

(d) (i) The production of both steel and aluminium consume large amounts of energy and use great volumes of water. They both generate CO2, a greenhouse gas, and produce solid waste (slag and Fe2O3 respectively) which requires disposal. In both cases recycling waste metal can greatly reduce the environmental impact.

(ii) To preserve natural resources and to save energy as production of aluminium form its ore is very energy intensive compared to recycling the metal.

Page 401 C2 The oil industry

4. (a) (i) Currently about 90% of oil is used as a fuel and about 10% for petrochemicals. It is probably easier and, because of the production of greenhouse gases, such as CO2, better for the environment to search for new energy sources to conserve more oil for petrochemical production.

(ii) Cracking is the breaking up of larger, less useful, hydrocarbon fractions into shorter chain, more useful alkanes and alkenes which are used as fuels and petrochemical feedstock.

(iii) catalytic cracking: Cracking of gas oil fractions at lower temperatures of about 500°C, moderately low pressures; powdered zeolite (aluminum silicate)*; historically silica (SiO_2) and alumina (Al_2O_3) used; short contact time.

$C_{16}H_{34} \rightarrow C_8H_{18} + C_8H_{16}$

Branched alkanes and alkenes

Uses: High grade gasoline (branched chain alkanes increase fuel octane rating)

Thermal cracking: Lower molar mass alkane reactants from kerosene. Moderate temperature range: 500 – 750°C; high pressure of about 70 atm., no catalyst, longer contact time.

$C_{12}H_{26} \rightarrow C_8H_{18} + C_4H_8$

Branched alkanes and alkenes

Lighter fractions used as fuel; alkenes, specially ethane used in making polymers.

Steam cracking: Higher temperature range: 800 – 900°C, moderately low pressures, no catalyst, very short contact time:

$C_6H_{14} \rightarrow C_3H_6 + C_3H_8$

$C_4H_8 \rightarrow 2C_2H_4 + H_2$

Alkanes and alkenes (+ hydrogen)

Low molar mass alkenes used in polymer manufacture; hydrogen used in hydrocracking.

Page 401,402 C3 Addition polymers

5. (a) (i) Polymers are long chain macromolecules made by joining together many smaller repeating units (called monomers).

(ii) All the monomer's atoms are present in the polymer, a double bond is converted to a single bond and two extra single bonds are formed.

Any of: chloroethene, CH_2=CHX or propene, CH_3CH=CH_2 or tetrafluoroethene, CF_2=CF_2, etc.

(b) (i) Branching: branch chain polymers cannot form a regular lattice - hence lower density (hence LDPE), weaker intermolecular forces (van del Waals' forces) and lower melting point. These are softer, weaker, more flexible with low tensile strength. On the other hand, polymers with no branching form a regular lattice (hence HDPE), have greater van der Waals' forces, have higher melting point, are more rigid and harder with higher tensile strength.

(ii) Orientation: The hydrogen atom and the methyl side chain (—CH3) can appear on either side of the backbone. If the methyl groups are all on the same side and the H atoms on the opposite side, that is the methyl groups are ordered with the same orientation (isotactic). Polymers with regular isotactic arrangements can pack more closely with stronger intermolecular forces. Thus these polymers are tough (and are used to make fibres, ropes, carpets and automobile bumpers). If the arrangement is random, that is without any order to the orientation of the methyl groups (which is the more likely), the polymer is called atactic. Polymer chains in atactic polypropylene cannot pack as closely and are not held very tightly making it soft and flexible, with a low melting point and not very strong.

(iii) LDPE (Low Density Polyethene): carried out at high temperature and very high pressure in the presence of a free-radical initiator (trace of O2 or peroxides).

HDPE (High Density Polyethene): carried out at much lower P and T in presence of complex catalysts ($Al(C_2H_5)_3$ & $TiCl_4$).

(c) Polymers are light, impermeable to water and can be pigmented, giving rise to articles with a wide variety of attractive colors. Since weak van der Waals' forces exist between polymer chains, most polymers become soft and melt on heating so they can be molded to form thin films and sheets as well as rods and tubes. Polymers contain strong covalent bonds within the polymer chains making them resistant to chemical reactions and they also generally have good electrical insulation properties.

Disadvantages of plastics: The source of most synthetic polymers is petroleum, a non–renewable resource so using plastics further depletes this. Other disadvantages include the volume occupied by plastics in landfills which can be substantial, environmental impact of non-degradable materials and release of toxic fumes caused by the burning plastics. Some other disadvantages appear under disposal of plastics.

Page 402 C4 Catalysts

6. (a) (i) A catalyst is a substance that increases the rate of a chemical reaction without being chemically changed. It is usually required in small amounts and is not used up in the reaction. A catalyst speeds up a reaction by lowering the activation energy of a reaction involving different transition state(s) and providing an alternate path for it to occur. With lower activation energy, a larger number of particles can now react successfully. However, ΔH of the reaction is not affected (it remains the same); neither is the position of equilibrium; a catalyst increases the rate of both the forward and reverse reactions equally.

(ii) Most industrial processes involve catalysts because they speed up the reaction (greater efficiency) and can also increase the yield of the desired product rather than by-products (greater selectivity). Some disadvantages are the way conditions can reduce the activity of catalysts (denaturing of enzymes, surfaces deactivated by “poisons”) and the environmental impact of the escape of toxic catalysts.

(b) **Homogeneous** catalysts (such as an concentrated sulfuric acid in the reaction of an carboxylic acid with an alcohol to form an ester, esterification) are in the same phase as the reactants. They react with one of the reactants to produce an intermediate, which is consumed at a later stage to regenerate the catalyst. These stages have lower activation energies than the uncatalysed process.

$$CH3COOH\ (aq) + C2H5OH\ (aq) \leftrightarrows CH3COOC2H5\ (aq) + H2O\ (l)$$

Heterogeneous catalysts are in a different phase to the reactants (typically a solid catalyst with the reactants being in the gas or liquid phase) and hence are easy to separate. They provide an active surface on which the reaction can take place with a reduced activation energy. It is important that the product does not bond to the surface so the surface is freed for other reactants. Example: production of sulfur trioxide for the manufacture of sulfuric acid using vanadium(V) oxide solid as the catalyst. $V2O5\ (s)$

$$2SO_2\ (g) + O_2\ (g) \leftrightarrows 2SO_3\ (g)$$

(c) **Homogeneous catalysts:**

Advantages: High activity as all the catalyst is exposed to the reactants; high selectivity for single product as the catalyst has unique active sites.

Disadvantage: Difficult to recover from reaction mixture for reuse

Heterogeneous catalysts:

Advantages: Solid catalysts are easy to remove and recover from products by filtration; have long catalytic life

Disadvantages: Only effective on the surface – hence most of the solid is not used; also, any coating on surface reduces activity.

7. (a) Like homogeneous catalysts most enzymes occur in the same phase as the reactants, but like heterogeneous catalysts the reactants bind to an active site on the surface of the enzyme molecule.

Enzymes are unique in that these are very specific, efficient and work best at body temperature.

Enzymes can catalyse only one particular reaction unlike inorganic catalysts such as alumina, which catalyses many reactions. Enzymes differ from inorganic catalysts in their incredibly higher catalytic activity.

(b) (i) Ability to form a range of oxidation states by transition metal compounds: Transition metal ions exhibit relatively stable multiple oxidation states by gaining or losing electrons in redox reactions. An example of a heterogeneous catalyst involving change in oxidation number of the transition metal ion catalyst is the use of vanadium(V) oxide in the Contact process. In the first step, sulphur dioxide is oxidised to sulphur trioxide and the vanadium(V) is reduced to V(IV); subsequently, V(IV) is oxidised by oxygen to regenerate the catalyst.

(ii) The shape of the catalyst: The three dimensional shape of the globular protein molecules is crucial to the catalytic activity of enzymes. Enzymes and substrates are only effective if they have specific three–dimensional shapes which complement one another (the lock and key model). If the enzyme changes its shape or arrangement, the substrate will no longer be able to bind to the active site and the enzyme is rendered non-functional.

(iii) Availability of active sites: The region of the catalyst which binds to one or more reactants is called the active site (as in the case of enzymes). Heterogeneous catalysts contain active sites that are able to adsorb one or more reactants onto it to facilitate the reaction and reduce the activation energy.

8. **Selectivity**: Good selectivity means only the desired product is produced and unwanted by-products are not formed. If a catalyst leads to unwanted products, it exhibits poor selectivity. Enzymes are highly selective and catalyse only one type of reaction.
Efficacy (or effectiveness): This tells us how rapidly the catalyst forms the desired product. For example, in the alkylation of methylbenzene, zeolites expose a much larger surface area to reactants producing greater efficacy than $AlCl_3$.
Ability to work under mild/severe conditions: For example, heterogeneous catalysts such as iron are effective under vastly different conditions of temperature and pressure, for example in the Haber process (on the other hand, enzymes work under narrow temperature and pH ranges and are easily denatured beyond these ranges).
Environmental impact: For example, the demand for platinum group elements (platinum, rhodium, palladium) used in catalytic converters has increased greatly. Some of these metals are lost to the environment and raise the issue of potential health risks as these exhibit severe side effects and toxicity to living cells. Disposal of spent catalysts is a concern though the cost of the platinum group of elements makes a convincing argument for recycling.
Catalyst poisoning: A catalyst can be poisoned or rendered ineffective. Efficiency of a catalyst usually decreases with time as it becomes inactive due to impurities in the reaction mixture, side reactions, or if its active surface becomes coated and unavailable for activity such as the coke coating on alumina or silica in catalytic cracking. Enzymes denature by the effect of temperature, pH and heavy metal ions such as Hg^{2+} and Pb^{2+} if their structures are altered.

Page 402 C5 Fuel cells and rechargeable batteries

9. (a) A fuel cell is a device that converts the chemical energy of fuels directly into electrical energy. Normally fuels are burnt converting chemical energy to heat which can be converted to electricity by generating steam to turn turbines. This is a highly inefficient method; fuel cells lead to a much more efficient conversion of chemical energy directly into electrical energy to generate power.

(b) In a hydrogen-oxygen fuel cell, the negative electrode (anode) is made of porous carbon impregnated with the catalyst Pd or Pt; the positive electrode (cathode) is also made of porous carbon containing the catalyst Pt. These electrodes are separated by aqueous hydroxide electrolyte (KOH or NaOH) and the oxidation of hydrogen gas by oxygen gas takes place in a controlled manner.

(i) In **acidic** solution:

(–) anode oxidation half reaction:

$$2H_2\text{ (g)} \rightarrow 4\,H^+\text{ (aq)} + 4e^-$$

(+) cathode reduction half reaction:

$$O_2\text{ (g)} + 4H^+\text{ (aq)} + 4e^- \rightarrow 2H_2O\text{ (l)}$$

(ii) In **basic** solution:

(**–**) anode oxidation half reaction:

$$2H_2\text{ (g)} + 4OH^-\text{ (aq)} \rightarrow 4H_2O\text{ (l)} + 4e^-$$

(**+**) cathode reduction half reaction:

$$O_2\text{ (g)} + 2H_2O\text{ (l)} + 4e^- \rightarrow 4OH^-\text{ (aq)}$$

(c) Advantages and disadvantages of fuel cells: Fuel cells are highly efficient (70-80%) since they convert the chemical energy of the fuels directly to electrical energy. Thus these greatly reduce thermal pollution, as well as being less polluting in general as water is the product, so there is no release of greenhouse gases from the combustion of fossil fuels (although if electrolysis of water is used as a source of hydrogen gas for the fuel cell, the power for the electrolysis may well have come from fossil fuel plants). Fuel cells also tend to be light weight. However, fuel cells can experience technical problems ranging from leaks to corrosion and catalytic failures. The dangers of storing and transporting hydrogen gas also have to be considered.

10. (a) (i) **Lead-acid** battery:

Negative electrode $Pb\text{ (s)} + SO_4^{2-}\text{ (aq)} \rightarrow PbSO_4\text{ (s)} + 2e^-$

Positive electrode

$PbO_2\text{ (s)} + 4H^+\text{ (aq)} + SO_4^{2-}\text{ (aq)} + 2e^- \rightarrow PbSO_4\text{ (s)} + 2H_2O\text{ (l)}$

(ii) **NiCad** battery:

Negative electrode $Cd\text{ (s)} + 2OH^-\text{ (aq)} \rightarrow Cd(OH)_2\text{ (s)} + 2e^-$

Positive electrode $NiO(OH)\text{ (s)} + H_2O\text{ (l)} + e^- \rightarrow Ni(OH)_2\text{ (s)} + OH^-\text{ (aq)}$

(iii) **Lithium ion** battery

Negative electrode $LiC_6 \rightarrow Li^+ + 6C + e^-$

Positive electrode $Li^+ + e^- + MnO_2 \rightarrow LiMnO_2$

(b) **Similarities**: Both devices convert chemical energy directly into electrical energy using spontaneous redox reactions. Both have similar modes of operation, namely, negative anode electrodes where an oxidation half-reaction takes place and positive cathode electrodes where a reduction half-reaction takes place.

Differences: Fuel cells are energy conversion devices whereas rechargeable batteries are energy storage devices. Fuel cells require a constant supply of reactants and produce electrical energy only as long as fuel is made available to the cell. Batteries on the other hand have stored chemical energy in a closed system and provide power until the stored chemicals are used up (batteries can be recharged).

Page 402 C6 Liquid crystals

11. (a) Liquid crystals are fluids that have anisotropic physical properties (electrical, optical and elasticity), if the molecules of the fluid all have the same orientation.

(b) Thermotropic liquid-crystals are pure substances, such as biphenyl nitriles, that show liquid-crystal behaviour over a temperature range between the solid and liquid states.

Lyotropic liquid crystals are solutions, such as soap and water that show the liquid crystal state at certain concentrations.

(c) Thermotropic behaviour: At the temperature below the range, the substance forms a solid crystal; above the temperature range, it turns into the liquid phase. The biphenyl nitriles (cyanobiphenyls) are common examples of thermotropic LCs, for example 5CB, which is crystalline below 18 °C, isotropic liquid above 36 °C and LC between the two temperatures. Biphenyl nitriles produce an effective liquid crystal state because the biphenyl group makes the molecule more rigid and rod-shaped, whilst the nitrile group makes the molecule polar, so that the intermolecular forces are strong enough to make the molecules align.

In the crystalline solid, the rod-shaped molecules are fixed in position and direction: these are parallel, arranged in layers and the layers positioned one over the other in a three-dimentional arrangement. The intermolecular forces present in solid lattice of a LC are different in various directions. As the solid crystal is heated, first the weak forces are overcome; the heating disturbs the precise order of molecules giving rise to random arrangement in some direction, but the stronger forces are still at play and this provides regular arrangement in other directions.

In smectic LCs, layers still exist (the molecules centred are still arranged in layers) with movement within layers so that the molecules are roughly parallel.
In the nematic phase rod-shaped molecules are distributed randomly but tend to align themselves giving rise to anisotropic properties.
If the temperature is raised, the increased thermal agitation disrupts this directional order until it is lost at the temperature at which the normal liquid phase is formed.

12. a) In liquid-crystal displays (LCDs) the orientation of the polar molecules can be controlled by the application of a small voltage across a thin film of the material. The ordered areas of the display have anisotropic optical properties, hence the light and dark areas can be controlled by the applied voltage to a grid of electrodes.

b) In order to be useful, a liquid crystal must be stable, maintain the liquid crystal state over a large temperature range, be polar so the orientation can be controlled by an electrical field and be capable of rapidly changing orientation.

Page 403 C7 Nanotechnology

13. (a) Nanotechnology involves research and technology development at the 1 nm to 100 nm range. It creates and uses structures that have novel properties because of their small size and builds on the ability to control or manipulate at atomic scale.

(b) Scanning probe microscopes are able to move individual atoms on a surface one atom at a time, whereas chemical reactions allow atoms to be positioned at a particular site in a molecule.

(c) Nanotubes are cylinders made only from carbon hexagons (like a looped round graphite sheet). The closed ends of the tube also involve pentagons to produce the curvature (as in fullerenes). Nanotubes can be either single or multiple, comprising a series of concentric single nanotubes. Nanotubes have anisotropic properties with high tensile strength along their axes. As the surface of nanotubes allow the flow of electrons (like graphite), the electrical conductivity of nanotubes increases with their length.

(d) Possible applications: Current applications include invisible suncreens comprising titanium or zinc oxides, bacteriocidal bandages with silver nanoparticles, production of spill-proof, water repellent and wrinkle free garments (requiring cold water cleaning that is not that frequent), heterogeneous catalysis and microcircuits, amongst many others.

Potential uses range from development of vaccines and drugs to faster, cheaper and more powerful electronics with much higher storage capacities, to light weight, longer lasting materials for construction, transportation and everyday uses that require less energy and resources and cause less pollution. Nanomedicine and bionanotechnology are examples of new multidisciplinary fields with developments in, for example, drug delivery methods.

Heath and environment effects and concerns: It is possible that the combination of small size and distinctive properties may pose environmental and or health risks. The small size means it is easy to inhale nanoparticles. For example, the ultra thin soot particles from industrial activity are known to have adverse effects on the respiratory system of humans . Nanoparticles have been found to be harmful to animals. If these can enter the lymphatic system, the body's immune system, by passing through the skin's top layer, there could be health concerns.

Toxicity concerns: The field of nanotoxicology is concerned with various apsects of the toxicity of nanoparticles, since such materials have properties quite different from their macro counterparts.

Ethical and political issues: The implications of nanotechnology are many and these have give rise to new interdisciplinary areas of study ranging from nanoethics (for example the military uses such as cheaper, more powerful weapons) to nanopolitics, (such as need for public education, for informed debate and for public involvement in policy discussions).

The threat to health of nanoscale particles is largely unknown, hence there are people who have significant concerns in this regard. It is an issue that requires industrial responsibility and strong political leadership.

Page 403 C8 Condensation polymers [HL]

14. (a) In addition polymerization, monomers are unsaturated organic compounds. Monomer units add together without the elimination of any atoms to form the polymer. Addition takes place across the double bond. After polymerization, the double bond is converted to a single bond. Typically, a single monomer is involved.

In condensation polymerization, the monomer units have two reacting sites on them for polymerization to take place (called bi-functional monomers). These undergo condensation reactions to produce a larger molecule with the elimination of a smaller molecule such as water.

(b) Chain length: The greater the average chain length, the greater are the intermolecular forces and hence the higher the strength and melting point.

Different properties can arise from different stereochemistries of polymers. In Kevlar the trans orientation of the chain allows it to be a straight chain polymer with close approach between chains, allowing strong hydrogen bonding between them, which gives it great strength. The cis-orientation however produces bent chains and does not allow close approach for strong bonding between chains.

The phenol-methanal plastic is an example of a polymer where the benzene ring is bonded to CH_2 in three positions with extensive 3-D cross-links that produce very rigid polymer owing to the extensive cross-linking between the chains and in Kevlar, used for bullet-proof vests, there is strong hydrogen bonding between the polymer chains.

(c) A 'blowing agent' such as air can modify the properties of polyurethane foam to produce onr that is soft and has a low density. More often, in the case of polyurethane, water is used to produce the foaming agent carbon dioxide since the isocyanate group reacts with water to produce CO_2.

$$-NCO + H_2O \rightarrow NH_2 + CO_2$$

The feel of fibres made from some polyesters can be rather harsh and they are not easy to dye. Blending with other fibres, either natural (like cotton) or synthetic (like polyamides) can improve these properties.

(d) Thermoplastics such as polyurethanes become soft and melt on heating; they can be moulded, are excellent insulators and are unreactive. Rigid polyurethanes have high tensile strength and are used as insulators in building panels. Polyurethane can be made flexible and used as foam material for furniture. Polyurethane is used to make fabric that stretches for use in exercise clothing. Phenol-methanal plastics are cross-linked by covalent bonding, hence they are chemically inert, act as electrical and thermal insulators, are non- flammable. Also, the have high density and high strength with numerous applications including use as electric switches, electronic casings, utensil handles, etc. Some plastics such as PET can be recycled. Plastics are durable and can stand up to a variety of environmental conditions without falling apart (the lack of degradability is also a disadvantage).

Page 403 C9 Mechanisms in the organic chemicals industry [HL]

15. (i) LDPE is manufactured at a temperature of about 500K and at very high pressures. An organic peroxide (R-O-O-R) or as trace of oxygen gas (O_2) is used as a catalyst.

(ii) **Initiation** step which involves the formation of free radicals;: Peroxides decompose to form alkoxy free radicals as the O—O covalent bond in the peroxide is weak and the bond is broken such that each oxygen gets an electron from the bonding pair (hemolytic fission):

$$R—O—O—R \rightarrow 2R—O\bullet \text{ (if oxygen is used, then: } R\text{-}H + O{=}O\ R\bullet + HO\text{-}O\bullet)$$

Propagation step in which one free radical is replaced by another one; the lone electron on the free radical attacks the alkene carbon atom and uses an electron from the pi bond to form the bond. The C=C double bond is converted to a single bond as the other pi electron moves the second carbon atom to form a free radical, that is, the alkoxy free radicals react with the alkene to produce a longer alkyl free radical:

$$RO\bullet + CH_2{=}CH_2 \rightarrow R—O—CH_2—CH_2\bullet$$

The chains add successive ethene units to produce longer free radicals:

$$R—O—CH_2—CH_2\bullet + CH_2{=}CH_2 \rightarrow R—O—CH_2—CH_2—CH_2—CH_2\bullet$$

The free radicals can also remove hydrogen atoms in the middle of a chain, giving rise to branching of the chains.

Termination step: The free radicals either combine to form a longer chain molecule or the transfer of a hydrogen atom occurs to form a combination of an alkane and alkene:

$$2\ R—O—CH_2—CH_2—CH_2—CH_2\bullet \rightarrow (R—O—CH_2—CH_2—CH_2—CH_2)_2—$$

or

$$2\ R—O—CH_2—CH_2—CH_2—CH_2\bullet \rightarrow R—O—CH_2—CH{=}CH—CH_3 + R—O—CH_2—CH_2—CH_2—CH_3$$

(iii) A temperature of about 350K (75°C), pressure of about 5 – 7 atmospheres, and Ziegler–Natta catalysts (triethylaluminum and titanium(IV) chloride.

(iv) Production of HDPE involves an ionic mechanism with the formation of a complex with the catalyst in which the titanium atom can utilize its empty d-orbitals. Ethene molecules then insert themselves into this very polar ($C^{\delta}—Ti^{\delta+}$) bond resulting in polymer chains without any branching. The following equation is an oversimplification of this:

$$TiCl_4 + Al(C_2H_5)_3 \rightarrow C_2H_5\text{-}TiCl_3 + Cl\text{-}Al(C_2H_5)_2$$

$$CH_2{=}CH_2 + C2H5\text{-}TiCl_3 \rightarrow C_2H_5\text{-}CH_2\text{-}CH_2\text{-}TiCl_3 \text{ etc.}$$

Page 403 C10 Silicon and photovoltaic cells [HL]

16. (a) Silicon, a semiconductor, has four electrons in its valence shell, meaning that the lowest electron band in the lattice structure is totally filled. It therefore cannot conduct except when electrons gain enough energy to jump into the next unfilled band.

(b) If traces of atoms with one more electron (e.g. As, Sb) are added to the structure (doping) then the extra electrons have to go in the unfilled band, increasing conductivity (n-type semiconductors). Similarly if traces of atoms with one less electron (e.g. Ga, In) are added to the structure then this creates a space ("hole") in the filled band, again increasing conductivity (p-type semiconductors).

(c) If p-type and n-type conductors are placed next to each other electrons flow from the surface of the n-type conductor to the p-type conductor, producing an electric field. This allows a p-n flow, but not a n-p flow, because the extra electrons just inside the p-type repel other electrons. If solar energy excites electrons in silicon into the conducting band then they canmove p-n, but not the other way, hence the n-type semiconductor becomes the negative terminal of a solar cell. Electrons can flow through the external circuit back to the p-type (which acts as the positive terminal because it has lost electrons).

17. (a) Cyanobiphenyls (biphenyl nitriles) show liquid crystal. These molecules have three key chemical/structural features:

(i) The polar cyano (nitrile) group allows an electric field to control the orientation of the molecules as well as create strong intermolecular forces for the molecules to be oriented in the same direction.
(ii) The biphenyl groups contain two planar benzene rings bonded by a single covalent bond. These are chemically stable, make the molecule rod-like and rigid.
(iii) The long hydrocarbon chain affects the melting point as the molecules cannot pack together as closely and can maintain the LC phase. The size and shape of the alkyl group can be changed to alter the melting range.

(b) In a LCD display, each pixel contains a liquid crystal sandwiched between two scratched glass plates, which have a polarising film aligned with the direction of the scratches. The liquid crystal molecules in contact with the glass line up with the scratches, and because the scratches in the two plates are at 90˚ to each other, the molecules form a twisted arrangement between the plates, stabilised by intermolecular forces between the chains. These molecules rotate the plane of polarisation of plane-polarized light so that light will pass through the film and the pixel will appear bright (called the 'off' position). If a voltage is applied across the film, the polar molecules will align with the field, rather than the scratches, so the twisted structure is lost and the plane of the plane-polarized light is no longer rotated. As a result, the crossed polarising films cause the pixel to appear dark (on the 'on' position).

(c) Kevlar is a rod-like polyaromatic amide having rigid rod-shaped molecules with strong intermolecular hydrogen bonds between the chains. If concentrated sulfuric acid is added to Kevlar, then the O and N atoms are protonated, destroying the hydrogen bonded structure between the chains. Hydrolysis of the amide linkage takes place to form a lyotropic liquid crystal solution in moderate concentration of the acid containing rigid rod-shaped molecules due to the linked benzene rings. The long range order (the alignment of the molecules) is maintained depending on the concentration of LC molecules in the concentrated acid solution.

Page 404 C12 The chlor-alkali industry [HL]

18. The electrolysis of aqueous sodium chloride produces chlorine, hydrogen and sodium hydroxide:

At (–) cathode $2H_2O\ (l) + 2e^- \rightarrow 2OH^-\ (aq) + H_2\ (g)$

At (+) anode $2\ Cl^- \rightarrow Cl_2\ (aq) + 2e^-$ (but at low $[Cl^-]$: $4OH^-\ (aq) \rightarrow 2H_2O\ (l) + O_2\ (g) + 4e^-$)

As a result Na+ and OH^- remain in the solution as sodium hydroxide.

It is important to keep the products apart, otherwise they react to form bleach:

$Cl_2\ (aq) + 2OH^-\ (aq) \rightarrow Cl^-\ (aq) + ClO^-\ (aq) + H_2O\ (l)$

19. Brine solution (aqueous sodium chloride) is continuously passed into the mercury-cell in which mercury is used as the (–) cathode; this results in the formation of a sodium amalgam rather than hydrogen. This amalgam is then pumped to a separate vessel where it is allowed to react with water to give the sodium hydroxide; This is catalysed by the presence of steel grids. The mercury is then recycled to the electrolysis cell:

$Na^+\ (aq) + e^- \rightarrow Na/Hg$

$2\ Na/Hg + 2H_2O\ (l) \rightarrow 2Na^+\ (aq) + 2OH^-\ (aq) + H_2\ (g)$

Oxidation takes place at the positive graphite electrode, the anode to form chlorine gas:

$2Cl^- \rightarrow Cl_2\ (aq) + 2e^-$

The overall equation for the reactions taking place is:

$2NaCl\ (aq) + 2H_2O\ (l) \rightarrow 2NaOH\ (aq) + H_2\ (g) + Cl_2\ (g)$

Though it produces purer products (than the diaphragm cell), the mercury-cell is being phased because of concerns of brain damage that can result from the escape of mercury in to the environment and its concentration in the food chain.

20. In the diaphragm cell, the positive electrode, the anode is made of titanium, the negative electrode, the cathode is made of steel and the diaphragm is made of fluorinated polymer (asbestos is no longer in use). The electrodes are in two compartments separated by a diaphragm. The brine solution (aqueous sodium chloride) is placed in the cell.

In the (+) anode compartment, chlorine is given off by the oxidation of chloride ions:

$2\ Cl^- (aq) \rightarrow Cl_2 (g) + 2\ e^-$

At the (–) cathode compartment, water is reduced to hydrogen gas and hydroxide ions are formed:

$2H_2O (l) + 2e^- \rightarrow 2OH^- (aq) + H_2 (g)$

Sodium ions move through the diaphragm towards the negative electrode. The overall result is that the brine loses its chloride ions and becomes richer in hydroxide ions as a result of electrolysis:

$2NaCl (aq) + 2\ H_2O (l) \rightarrow Cl_2 (g) + H_2 (g) + 2NaOH (aq)$

The diaphragm cell is relatively cheap and produces less pollution (compared to the mercury cell), but the product is of lower purity and the diaphragm needs frequent replacement.

21. Electrolysis of an aqueous solution of sodium chloride produces three very important chemicals, chlorine gas, hydrogen gas and sodium hydroxide.

Some uses of chlorine: Manufacture of solvents, PVC manufacture, bleaching paper products, disinfecting drinking and swimming pool water, production of inorganic and organic chemicals.

Some uses of sodium hydroxide: Manufacture of inorganic and organic chemicals, production of paper products (converting wood to pulp), aluminium industry, soap manufacture.

Some uses of hydrogen: Hydrogenation of unsaturated oils – margarine; manufacture of ammonia, HCl and methanol, refinery processes (reforming), future potential use in fuel cells.

CHAPTER 15 (OPTION D) MEDICINES AND DRUGS

Page 434 D1 Pharmaceutical products

1 (a) A drug or medicine is any chemical which does one or more of the following:

alters incoming sensory sensations, alters mood or emotions, alters physiological state, including consciousness, activity level or co-ordination.

(b) A placebo is an inert substance used as a control in an experiment, or given to patients for its probable beneficial effects (i.e. a ‘fake’ therapy without any side effects). The placebo effect refers to a pharmacologically inert substance that produces a significant reaction because of what an individual expects, desires or is told will happen.

(c) The testing of new drugs is a lengthy process and the stages involved usually include: tests on microbes or tissue cultures, animal tests to establish the *LD*50 (the dose lethal to half the population) and double-blind clinical trials.

(d) **Orally**: by mouth; very convenient. However the effect is variable since the rate of absorption is influenced by drug concentration and stomach content.

Parenteral (by injection): (i) Beneath the skin (subcutaneous route): Drug absorption is slower than intravenous (directly into a vein) (ii) into muscles (intra-muscular): This method is used if immediate response is not required or when a large volume of drug needs to be injected. The method is relatively safe and easy provided a blood vessel is not accidentally penetrated (iii) directly into the blood stream (intravenous): the drug is introduced by injection into a vein and distributed around the body within about a minute, so the effect is virtually instantaneous. An advantage is that it is possible to administer precise amounts of drug since concentration is not affected by stomach acid or content. However, once administered, the drug cannot be retrieved as it can be (to some extent) with oral administration.

Inhalation (by breathing in): administration is rapid because of the extensive network of blood vessels in the lungs.

Rectal (via the rectum): is very effective when patients experience nausea or vomiting or are unable to take medicine orally before or after surgery. Drugs that are pH sensitive and which may be destroyed by the stomach’s acidity may be delivered rectally.

2. (a) **Therapeutic window** is a measure of the relative margin of safety of the drug for a particular treatment (for a typical population). Quantitatively, it is given as a ratio of the lethal dose (*LD50*) to the therapeutic dose of the drug (*ED50*) where *LD50* is the lethal dose for 50% of the population and *ED50* is the effective dose for 50% of the population.

Tolerance means that, over time and with regular use, a user needs increasing amounts of a drug to get the same physiological effect. Tolerance increases the health hazards of any drug simply because the amount taken increases over time.

Side effects refer to the unwanted responses to a drug are considered side effects (the desired effect of a drug is considered to be the main effect). This happens because no drug exerts a single effect; usually several different body functions are altered. To achieve the main effect, the side effects must be tolerated which is possible if they are minor but may be limiting if they are more serious. The distinction between main and side effects is relative and depends on the purpose of the drug, e.g. morphine. If pain relieving properties are sought, the intestinal constipation induced is an undesirable side effect. However, it may also be used to treat diarrhoea, so constipation induced is the main effect and any relief of pain is a side effect.

(b) **Physical** dependence occurs when a drug user's body becomes so accustomed to a drug that it can only function normally if the drug is present. Without the drug, the user may experience a variety of physical symptoms ranging from mild discomfort to convulsions.

Psychological dependence exists when a drug is so central to a person's thoughts, emotions, and activities that it is extremely difficult to stop using it, or even stop thinking about it. Psychological dependence is marked by an intense craving for the drug and its effects. Like physical dependence, psychological dependence is a form of drug addiction.

Page 434 D2 Antacids

3. (a) To suppress growth of harmful bacteria, and to help in digestion by hydrolysing proteins to amino acids. Heart burn is caused by stomach acid rising up the esophagus.

(b) An antacid is a base, usually, metal oxides, hydroxides, carbonates or hydrogen carbonates (bicarbonates) that neutralizes excess acid in the stomach to adjust the stomach pH to the desired level. It relieves indigestion and allows damage done by excess acid to the stomach lining to repair itself.

(c) (i) sodium carbonate/sodium hydrogen carbonate; magnesium oxide/hydroxide; calcium carbonate, aluminium hydroxide

(ii) $NaHCO_3\ (aq) + HCl\ (aq) \rightarrow NaCl\ (aq) + H_2O\ (l) + CO_2\ (g)$

$Mg(OH)_2\ (aq) + 2HCl\ (aq) \rightarrow MgCl_2\ (aq) + 2\ H_2O\ (l)$

$CaCO_3\ (s) + 2HCl\ (aq) \rightarrow CaCl_2\ (aq) + H_2O\ (l) + CO_2\ (g)$

$Al(OH)_3\ (s) + 3\ HCl\ (aq) \rightarrow AlCl_3\ (aq) + 3\ H_2O\ (l)$

(iii) Dimethicone is an anti-foaming agent that is added to some antacids to reduce the surface tension of gas bubbles, causing them to coalesce (come together) and prevents acid from rising up the oesophagus.

(d) Both ingredients neutralise 2 mol H^+ per mol

$M(CaCO_3) > M(Mg(OH)_2)$

$n = \dfrac{m}{M}$; higher molar mass means less amount in moles of $CaCO_3$; thus it will neutralise less H^+ and $Mg(OH)_2$ is a better buy.

Page 434 D3 Analgesics

4. (a) Analgesics are drugs that relieve pain (without causing loss of consciousness). Mild analgesics used for relief of mild pain (and frequently fever). Strong analgesics used for the relief of very severe pain include the narcotics morphine, heroin (also called diacetylmorphine or diamorphine) and codeine.

(b) Mild analgesics function by intercepting the pain stimulus at the source, for example by interfering with the production of substances (such as prostaglandins) that cause pain, swelling or fever. Strong analgesics work by temporarily bonding to receptor sites in the brain, preventing the transmission of pain impulses without depressing the central nervous system.

(c) Examples of mild analgesics: aspirin, acetaminophen

Examples of strong analgesics include the narcotics morphine, heroin (and codeine).

5. (a) (i) benzoic acid/carboxylic acid and the ester group (Ar-$COOCH_3$).

(ii) Amide group (-NHCO-)

(iii) Tertiary amine/amine

(iv) Replace the two –OH groups on morphine by two ester (CH3COO-) groups

6. (a) As an antipyretic to reduce fever, as an anti-inflammatory agent when there is swelling from injuries and as an anti-platelet agent in the prevention of abnormal blood clotting and as an anti clotting agent after heart surgery.

(b) Aspirin can cause stomach upset and internal bleeding (due to its acidic nature in aqueous solution,); it can cause ulceration and aggravate existing peptic ulcers.

Allergic reaction leading to skin rashes, respiratory difficulty, and even shock, development of Reye's syndrome in children (a potentially fatal liver and brain disorder).

(c) In the relief of severe pain caused by injury, chronic disease such as cancer, prior to and recovery from surgery; in the treatment of diarrhoea by producing a constipating effect; to relieve coughing by suppressing the 'cough centre' situated in the brain stem.

Disadvantages: Opiates produce drowsiness, mood changes and mental clouding (psychological effects). Users develop tolerance to the drug (need more for the same effect), as well as physical dependence, a state in which users do not function properly without a drug. Withdrawal is experienced when the drug is not regularly administered; symptoms include restlessness, sweating, fever, chills, vomiting, increased rate of respiration, cramping, diarrhoea, unbearable aches and pains..

Page 435 D4 Depressants

7. (a) (i) Depressants calm and relax (that is depress) the central nervous system ` by interfering with nerve impulse transmission.

(ii) Depressants slow down the activity of the brain and other organs such as the heart. They reduce the rate of breathing and in general dull emotional responses.

(iii) Depressants are described as anti-depressants because they relieve depression.

(b) (i) At low doses a depressant may exert little or no effect. At moderate doses the compound may induce sedation (soothing, reduction of anxiety). At higher doses it may induce sleep and at extremely high doses it may cause death. Depressants are often described as anti-depressants because they relieve depression.

(ii) Tranquilizers reduce nervous tension and anxiety but do not produce sleep in normal doses. Sedatives are stronger than tranquilizers and can cause soothing of distress, again without producing sleep in normal doses. The main difference between a tranquilizer and a sedative is one of degree of action. Hypnotics are a class of drug that produces sleep.

8 (a) **Social** effects aride from sickness and death associated with drinking. These costs consist of hospital treatment as well as lost productivity due to ill health and death; also increased crime, motor traffic related costs and the pain and suffering felt by crime and accident victims and their families.

Physiological addiction characterized by an inability to control intake, that is a craving or compulsion to drink and inability to stop drinking, as well as physical addiction.

(b) **Synergetic** effect takes place when if the combination of two drugs is more harmful than either drug taken alone. Alcohol taken with sleeping pills that affect the central nervous system can produce increased risk of heavy sedation even leading to coma and death. Alcohol taken with aspirin increases the risk of stomach bleeding.

9. (a) Reactant: ethanol C_2H_5OH; product: ethanoic/acetic acid. CH_3COOH

(b) From orange to green.

(c) Reduction half-reaction: $Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$

Oxidation half-reaction: $C_2H_5OH + H_2O \rightarrow CH_3COOH + 4^{e^-} + 4\ H+$

Over all reaction: $2Cr_2O_7^{2-} + 3C_2H_5OH + 16H+ \rightarrow 4Cr^{3+} + 3CH_3COOH + 11H_2O$

(d) (i) 0.080% means 0.080 g in 100 cm^3 blood sample = 80 mg alcohol per 100 cm^3 of blood.

(ii) $$n(C_2H_5OH) = \frac{0.080\,g}{[(2x12)+6(1)+16]\,g\ mol^{-1}} = \frac{0.080\,g}{46\,g\ mol^{-1}}$$

$= 1.7(4) \text{ x } 10^{-3}$ mol

$$[C_2H_5OH] = \frac{1.74\,x10^{-3}\ mol}{0.100\,dm^3} = 1.7(4) \text{ x } 10^{-2}\ mol\ dm^{-3}$$

10. GLC uses a stationary phase (a non-volatile liquid or solid support) and a mobile phase, an inert carrier gas such as N2. The components of the breath including alcohol vapour are partitioned between the mobile and stationary phases depending on their boiling points. Thus the components move through a column of the solid phase at differing speeds and exit after intervals of time depending on the substance. These can then be detected and recorded by a detector that can identify the changes in the composition of the carrier gas as it comes out of the column. It displays the time taken for each component to pass through the column, called the retention time. A standard ethanol sample is first passed through the column as the same carrier gas to determine its retention time. The sample of breadth is then introduced under all the same conditions (same flow rate, same stationary phase and a constant temperature) and the ethanol is identified by comparing the retention times. Glc not only identifies the compound, but the area under the peak represents the amount of the compound, thus allowing accurate determination of the blood alcohol concentration (BAC).

Intoximeter is an IR spectrophotometer in which the IR radiation is passed through the breath sample. If alcohol is present, the frequencies are absorbed by the sample depending on the bands present (such as C–H and O–H) and the rest of the radiation is transmitted. The detector compares the intensity of IR radiation through the sample with the intensity through air. The recorder then produces the IR spectrum as % transmittance (the amount of radiation through the sample) against wavenumber. However, the Intoximeter does not distinguish between ethanol and propanone which is often present in the breadth of a diabetic patient.

CHAPTER 15 (OPTION D) MEDICINES AND DRUGS

Page 435 D5 Stimulants

11. (a) A stimulant is a chemical that stimulates the brain and the central nervous system by increasing the state of mental alertness. It causes increased alertness and wakefulness.

Amphetamines, nicotine and caffeine.

(b) All three contain the phenylethylamine structure which contains a benzene ring attached to two carbon atoms attached to an amine.

(c) Amphetamine contains a primary amine (N is bonded to two hydrogen atoms and an R group) where as adrenaline or "Speed" contains a secondary amine in which the N atom is bonded to one H and two R groups.

(d) Drugs whose actions resemble that of the stimulated sympathetic nerves (mimic the effect of adrenaline). They constrict the arteries, speed up the heart rate, increase rate of breathing and increasing sweat production.

12. (a) Heterocyclic in which one or more carbon atoms in the ring are replaced by nitrogen; contain five- and six-membered rings; tertiary amine (N atom bonded to three R groups); CH_3 on N.

(b) Short term effects of nicotine: increases heart rate and blood pressure and constricts the blood vessels.

Long term effects of nicotine: produces psychological dependence and builds up tolerance. Many experience physical dependence as well; increased risk of heart disease and coronary thrombosis (formation of blood clots); bronchitis, emphysema, mouth/throat/lung cancer.

Page 435 D6 Antibacterials

13. (a) Antibacterials (antibiotics) are drugs that inhibit the growth of, or kill, microorganisms that cause infectious diseases.

(b) In the 1890s scientists found that certain fungi killed bacteria; these results were however largely ignored. In late 1920s similar observations were made by Alexander Fleming in one of the cultures in a petri dish whose lid had been left off, he found mold growing, but no bacteria around the mold. He concluded that the mold (*penicillium notatum*) must have inhibited bacterial growth by producing a compound that he called penicillin. However Fleming gave up the project after he found it difficult to isolate and purify the active ingredient in the mould. Florey and Chain renewed the research some years later. They injected mice with deadly bacteria; some mice received penicillin and survived. First large scale production possible made penicillin widely used antibacterials.

(c) The cell wall in the bacteria are reinforced by a series of three dimensional chemical cross-links connecting one layer to another which protects and supports the delicate cell structure and components enclosed within it. Penicillins work by interfering with bacterial cell wall formation thus weaking the cell walls (cells of animals do not have cell walls and thus not affected by penicillins). The cells can burst easily, water enters the cell and the bacteria die.

Penicillins all have a similar structure with a four-membered heterocyclic ring fused to a five-membered one. The side chains attached to these can be altered to enhance their resistance to hydrolysis both in the stomach and by enzymes produced by penicillin-resistant bacteria.

(d) Penicillins have had great value in controlling a large number of infectious diseases. However, over prescription can produce disadvantages. Penicillins are usually safe except for a small percentage of the population who experience allergic reactions. Repeated use can sometimes lead to allergic reaction. Antibiotics, if used repeatedly, may wipe-out harmless bacteria and helpful ones in the alimentary canal (this is the food canal, or gut, including the esophagus stomach and intestines). Also, the destroyed bacteria may be replaced by more harmful bacteria. Also, as antibiotics are used extensively, a few organisms survive and pass on their resistance to succeeding generations.

Page 435 D7 Antivirals

14 (a) Bacteria are cellular (single cell microorganisms), measuring about 1 μm, that are capable of independent existence by cell division whereas viruses, which basically comprise only genetic material in a protective protein coat are non-cellular, are about a tenth of this size (smaller than bacteria) and cannot exist separate from other living organisms, because they rely on invading cells to reproduce, namely, viruses insert DNA/RNA into cells and reply on the host cells to multiply.

(b) One class of antiviral drugs depends on altering the cell's ribosomes (protein production organelles) so that the virus cannot use them to produce its own proteins. Some other antiviral drugs block specific enzymes that only the virus produces.

(c) AIDS has been found to be closely associated with the HIV virus. The HIV virus can bind to T cells (a type of white blood cell) rendering it ineffective. This greatly weakens the immune response system that protects the body from infections, rendering the individual much more susceptible to many diseases.

The HIV virus has the ability to mutate rapidly, making it difficult to develop a drug or vaccine that will remain effective against it. As with other viruses, the fact that their metabolism is linked closely to that of the cell, makes it difficult to destroy viruses without affecting healthy cells.

Drugs that have been developed to combat AIDS are expensive, whilst the disease is very prevalent in developing countries where the cost of this treatment is prohibitive. The stigma associated with AIDS also often prevents infected people seeking diagnosis and treatment.

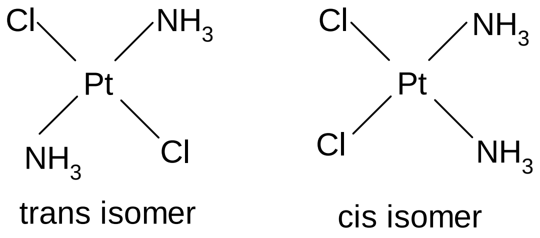
Page 436 D8 Drug action [HL]

15. (a) Stereoisomers are isomers with the same molecular formula and the same structural formula, but a different arrangement of atoms in space. If a pair of stereoisomers contains a double bond, then it is possible to obtain cis (on the same side) and trans (across/opposite) arrangements of substituents at each end of the double bond. These are referred to as geometric or cis-trans isomers.

(b) Geometric isomers have different physical properties such as polarity (dipole moment) and boiling point: For example, if two electronegative groups are on the same side the molecule (cis arrangement) will be polar, have greater inter-particle forces and experience higher boiling point. The trans-arrangement with the two EN groups on the opposite side will be non-polar and have a lower boiling point.

Geometric isomers can undergo different chemical reactions. Since they contain the same functional groups, they do show some similar chemical properties but not all their chemical properties are identical, and the two different isomers can have different pharmacological effects.

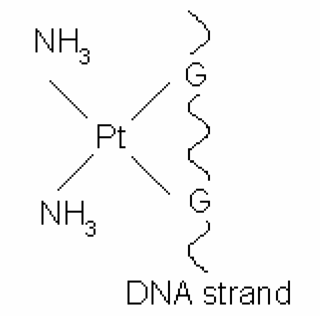
(c)



Square planar complexes; covalent bonding between N and H; dative (coordinate covalent bonding) between Cl and Pt and the lone electron pair on N and Pt.

This is a Lewis acid-base reaction

(d) The cis- arrangement gives rise to the anticancer activity from its ability to enter the nucleus of a cancerous cell in which the two Cl atoms are replaced by bonds that are eventually formed with guanine bases of the same DNA strand; as a result this prevents replication.



(e) The different enantiomers may have differenct chemotherapeutically activity in which one may be active and the other one either non-active or harmful.

An example is the thalidomide tragedy. Thalidomide was designed as a mild non-addictive sedative. It was prescribed to alleviate morning sickness in pregnant women and marketed as a racemic mixture of the two enantiomers. One enantiomer alleviates morning sickness, but the other entantiomer causes deformities in the limbs of fetuses and hence birth defects.

16. (a) Both are stereoisomers (with the same molecular formula and the same structural formula, but a different arrangement of atoms in space). Optical isomers differ from geometric isomers in two ways – the molecules are chiral (asymmetric, containing, for example, 4 different groups on a carbon atom). Optical isomers are non-superimposable mirror images of each other (called a pair of enantiomers). These isomers differ in their optical activity; optical activity is the ability to rotate the plane of polarised light. One optical isomer will rotate plane polarised light clockwise, and its non-superimpossable mirror image will rotate it anti-clockwise by the same amount.

(b) Racimic mixture is an equi-molar mixture of the two enantiomers will not rotate the plane of polarised light and is said to be optically inactive.

(c) Separating recimic mictures can be an expensive process – if one of the enantiomers is inactive and the other pharmacologically active, it is cheaper to sell it as a mixture.

(d) Chiral auxiliary is an enantiomer that assists in converting a non-chiral molecule into the desired enantiomer, thus avoiding the need to resolve enantiomers from a racemic mixture. It works by attaching itself chemically to the non-chiral molecule to create the stereochemical conditions necessary to force the reaction to follow a certain stereo-specific path. Once the new molecule has been formed, the auxiliary can be removed (and recycled) to leave the desired enantiomer. An example is the synthesis of Taxol, an anti-cancer drug, effective against breast cancer.

17. (a) Presence of the R group, the carboxylic acid group and the beta-lactam ring. The four-membered beta-lactam ring structure has a lot of steric strain owing to its small bond angles. This enhances the reactivity of the amide group within it, allowing it to bond to the enzyme transpeptidase, responsible for the construction of the cell wall of bacteria, inhibiting its action.

    (b) Heroin is much more active than morphine. This is because, in diamorphine, the polar hydroxyl groups in morphine are replaced by the far less polar ester group, increasing its solubility in the lipids of the central nervous system.

Page 436 D9 Drug design [HL]

18. (a) (i) **Combinatorial chemistry** involves a variety of techniques and technologies for creating a large number of molecules and testing them quickly for desirable biological properties.

    Combi-chem basically involves reacting a set of starting materials in all possible combinations.

    Pharmacophore is a receptor site that represents the essential molecular structure features based on the functional groups and geometry, that is responsible for a drug's activity.

    (ii) The term **compound library** is used to describe a collection of compounds that are screened to determine their pharmacological activity. Libraries of a very large number of related compounds have been produced by the combi-chem technique. This involves the use of robotics to carry out identical chemical processes between chemicals to produce smaller, more focused libraries. The products of such reactions (called 'libraries') are then tested *en masse* for their potential pharmacological activities.

    (iii) Carboxylic acids react with an alcohol in the presence of an acid catalyst to produce an ester:

    $R1\text{-}COOH + HO\text{-}R2 \rightarrow R1COOR2$

    Eight different carboxylic acids can be reacted with each of eight different alcohols in the presence of acid catalyst in 64 separate test tubes by computer controlled addition of fixed volumes of each reactant using syringes. Each test tube then contains a particular ester after the parallel synthesis.

    (b) Chiral auxiliary is an enantiomer that assists in converting a non-chiral molecule into the desired enantiomer, thus avoiding the need to resolve enantiomers from a racemic mixture. It works by attaching itself chemically to the non-chiral molecule to create the stereochemical conditions necessary to force the reaction to follow a certain stereo-specific path. Once the new molecule has been formed, the auxiliary can be removed (and recycled) to leave the desired enantiomer. An example is the synthesis of Taxol, an anti-cancer drug, effective against breast cancer.

19. (a) **Rational Drug Design** (RDD) is the use of molecular modelling software to discover safe drugs in as short a time as possible.

    (b) The mode of action of many drugs involves some form of interaction with biological molecules such as enzymes. The presence of functional groups and the orientation of the drug molecule may make it possible for it to interact with the enzyme protein structure active site, thus interfering with its biological action. Computer programs that can convert two dimensional diagrams into their 3-D equivalent structures have been instrumental in drug research. Three dimensional molecular models can be created *in silico* (that is, performed on a computer or via computer simulation). The 3-D structure of the target biological enzyme molecules together with those of the drug molecules are stored on the computer for retrieval purposes. Computer modelling can then be used to design smaller molecules that are capable of binding or interfering with the active site of the protein.

20. Acetyl alicylic acid is virtually insoluble in water due to the presence of the aromatic ring and no ionic bonding. On the other hand, salt of ASA which is ionic and water soluble. Insoluble aspirin takes longer to dissolve; the longer it takes, the less effective it is. In the case of aspirin, the ability of the acidic (carboxylic acid) group to form an ionic salt makes it possible for the insoluble ASA to form a soluble salt which is more effective.

    Prozac contains a basic group, an amine, which can form an ionic salt by reaction with hydrochloric acid. This makes it water soluble, easier to distribute in the body and more effective.

Page 436 D10 Mind-altering drugs [HL]

21. (a) **Hallucinogen** is a mid altering drug that causes a mistaken notion, that is a perception or feeling that has no external cause (produces a qualitative change in thought, perception or mood and can cause vivid illusions and fantasies).

(b) LSD, mescaline and psilocybin all have quite similar structures, involving an indole ring, or in the case of mescaline a side chain that can take on a similar conformation to such a ring.

(c) Effects of **LSD**: a powerful hallucinogen, produces a highly personal effect and one that varies with the dose, physiological condition (state of vital processes) and psychological condition (state of mind) of the user, and the user's expectations. Perception is magnified many fold. It can destroy the sense of judgement (i.e. jumping from a high building). LSD can cause strong opposite emotions at the same time e.g. relaxation and tension. The physical effects of a 'trip' on LSD are dilation of the pupils, an increase in heart rate, blood pressure and body temperature, as well as sweating, sleeplessness and tremors. It can produce frightening 'bad' trips as well as flash backs without taking LSD.

Effects of **mescaline**: Like LSD it produces visual colour hallucinations, that is, it produces vivid colour perceptions. although its potency is considerably less than that of LSD. A mescaline trip usually lasts about 12 hours, and often leads to a decrease in appetite.

Psilocybin is a mild hallucinogen; effects of psilocybin are similar to LSD; perception is magnified although the drug is less potent. In low doses it produces feelings of relaxation similar to those of cannabis. At high doses the effect is closer to that of LSD. Users experience an intensification of colour, hallucinations and a sense of well-being. A 'magic mushroom' trip tends to last about 4 hours (as opposed to 8 or more with LSD).

Tetrahydrocannabinol (THC) is a mild hallucinogen and has some effects similar to alcohol. At low doses users feel excited and silly. As the dose is increased, it produces changes in perception - the user sees bright colours and has a keener sense of hearing. Still higher doses produce visual hallucinations (objects in odd shapes). The initial feeling of joy can turn to extreme anxiety, depression, uneasiness, panic attack and fearfulness. Decisions become harder to make, and a person is more likely to follow the suggestions of others. Tasks like driving that require clear thinking and good reflexes become difficult.

22.

For	**Against**
Better control of the product	Can have negative long term health effects such as respiratory diseases, increased risk of lung cancer, decreased fertility
Separation from 'hard drug' environments	May lead to other more dangerous drugs
Some legitimate uses, e.g., cancer, glaucoma, terminal illnesses	May lead to antisocial behaviour
Frees up police and legal resources	Linked with genetic and brain damage

CHAPTER 16 (OPTION E) ENVIRONMENTAL CHEMISTRY

Page 472 E1 Air pollution

1.

Primary Pollutant	Human source	Natural source	Method of control
Carbon monoxide (CO)	Incomplete combustion of fossil fuels used for transportation and industry; forest fires. Localized, high emissions produced. $C_7H_{16} + 7\frac{1}{2}O_2 \rightarrow 7CO + 8H_2O$	From atmospheric oxidation of CH_4 (from anaerobic decomposition of organic matter). $2CH_4 + 3O_3 \rightarrow 2CO + 4H_2O$	1. Catalytic converter $2CO + 2NO \rightarrow 2CO_2 + N_2$ 2. Lean burn engine (less fuel present with higher air/fuel ratio) 3. Thermal exhaust reactor
Oxides of Nitrogen oxides (NO_x): N_2O, NO and NO_2	High temperature combustion in automobiles produces mostly NO, nitric oxide: $N_2 + O_2 \rightarrow 2NO$ This is oxidised to NO_2 in the atmosphere: $2NO + O_2 \rightarrow 2NO_2$	Decomposition of N-containing compounds by bacterial action produces N_2O, and NO. (Nearly all NO_2 is man made).	1. Catalytic converter. 2 Lean burning engines. 3. Recirculation of exhaust gases.
Oxides of sulfur (SOx): SO_2 and SO_3	Combustion of sulfur containing coal, smelting plants, sulfuric acid plants: $S + O_2 \rightarrow SO_2$ $2SO_2 + O_2 \rightleftharpoons 2SO_3$	No major direct sources of SOx in nature, but oxidation of H_2S gas from decay of organic matter and volcanic activity.	1. Alkaline scrubbing. $CaO + SO_2 \rightarrow CaSO_3$ 2. Limestone-based fluidized beds 3. Sulfur removed from fossil fuels before burning
Particulates	Combustion of fossil fuel use by industry, transportation, e.g.: $CH_4 + O_2 \rightarrow C + 2H_2O$ Breakup of solid matter, industrial plants which produce smoke, soot, ash, dust	Blowing dust, volcanic activity, forest fires, biological sources such as pollen.	1. Electrostatic precipitators. 2. Gravity settling chambers. 3. Cyclone separators.
Volatile organic compounds (VOCs)	Petroleum extracting, refining, transporting and use; solvents, incomplete combustion of gasoline, coal and wood.	CH_4 from biological anaerobic bacterial decomposition of organic matter; trees and plants produce terpenes.	1. Catalytic converters. $2C_8H_{18} + 25O_2 \rightarrow 16CO_2 + 18H_2O$

2. (a) A very high voltage is applied between oppositely charged plates which ionizes the gas molecules present ($G + e^- \rightarrow G^-$). The negatively charged particles are attracted to the positively charged collector plates. The collector plates have to be periodically shaken to remove the collected solid particles.

(b) Washing the coal removes some sulfur and injecting lime into the fluidised-bed combustion chamber converts a lot of sulfur dioxide into calcium sulfite:

$CaO + SO_2 \rightarrow CaSO_3$

Wet alkaline scrubbing can remove sulfur dioxide from the waste gases:

$SO_2 + OH^- \rightarrow HSO_3^-$.

Page 472 E2 & E11(HL) Acid deposition

3 (a) A process by which acidic particles, gases and precipitation leave the atmosphere; includes both wet deposition such as acid rain, fog and snow and dry deposition such as acidic gases and particles.

(b) pH 5.6 / 5.7. The carbon dioxide present in air is the acidic anhydride of carbonic acid, a weak acid:

$CO_2(g) + H_2O(l) \rightleftarrows H_2CO_3(aq) \rightleftarrows H^+(aq) + HCO_3^-(aq)$

(c) pH = 6, $[H^+] = 1.0 \times 10^{-6}$ mol dm^{-3}. pH = 4, $[H^+] = 1.0 \times 10^{-4}$ mol dm^{-3}. Thus 100 times more concentrated.

4. (a) SO_2: from the industrial combustion of fossil fuels/ sulfur containing coal

$S + O_2 \rightarrow SO_2$; $SO_2 + H_2O \rightarrow H_2SO_3$; a weak acid

$2\ SO_2 + O_2 \rightleftarrows SO_3$; $SO_3 + H_2O \rightarrow H_2SO_4$; a strong acid

NO_x, nitrogen oxides from internal combustion engine; nitrogen monoxide formed as a primary pollutant is rapidly oxidised in the air to nitrogen dioxide:

$N_2(g) + O_2(g) \rightarrow 2\ NO(g)$

$N_2(g) + 2\ O_2(g) \rightarrow 2\ NO_2(g)$

$2\ NO_2(g) + H_2O(l) \rightarrow HNO_2(aq) + HNO_3(aq)$

$4NO_2 + 2H_2O + O_2 \rightarrow 4HNO_3(aq)$

(b) Marble is made of calcium carbonate, a base. Thus acid rain corrodes marble objects:

$CaCO_3 + H_2SO_4 \rightarrow CaSO_4 + CO_2 + H_2O$

Acid rain removes important nutrients from the soil such as Ca^{2+} and Mg^{2+}; for example lowering Mg^{2+} concentration reduces chlorophyll production. It also removed Al^{3+} from rocks and affects roots.

(c) SO_x reduction: Sulfur can be removed before burning (pre-combustion method). Coal is finely ground, and washed with water. FeS_2 has high density, settles rapidly and is removed. However, even in finely ground coal, a lot of sulfur is trapped below the surfaces of the particles and is therefore not removed. Organic sulfur, chemically bonded to carbon atoms in coal cannot be removed by this physical process.

Post-combustion method: Remove sulfur after burning, for example a wet alkaline scrubber, usually water based, to remove contaminants. This uses a counter-flow method in which the alkaline liquid is sprayed downward while the gas stream moves upwards. The effectiveness depends on the contact between the alkaline liquid and the acidic sulfur dioxide:

$CaO(s) + H_2O(l) \rightarrow Ca(OH)_2(aq)$

$Ca(OH)_2\ (aq) + SO_2\ (g) \rightarrow CaSO_3\ (aq) + H_2O(l)$

$CaCO_3(s) + SO_2(g) \rightarrow CaSO_3(aq) + CO_2(g)$

NO_x: Use catalytic converter: converts NO to N_2

$2NO + 2CO \rightarrow N_2 + 2CO_2$

Rich fuel to air ratio or modify internal combustion engine to reduce formation of NO by operating at lower temperatures or alternate fuel sources such as battery powered or hydrogen as fuel.

Page 473 E3 Greenhouse effect

5. (i) **Greenhouse effect** is the natural process of trapping of the heat in the atmosphere thus maintaining the average temperature of the Earth's surface nearly constant (at about 16°C).

Short wavelength radiation form the sun enters the atmosphere. Some of the radiation is absorbed by vibration of the bond molecules of the gases in the atmosphere and thus loner wavelength infrared radiation leaves the Earth's surface. Effectively, some of the heat from the sun is trapped in the atmosphere (like the greenhouse effect).

(ii) The major greenhouse gases include methane CH_4, water vapour, H_2O (g), carbon dioxide, CO_2, dintrogen monoxide, N_2O, ozone, O_3 and chlorfluorocarbons, CFCs. Their effects depend on their abundance and their ability to absorb heat radiation.

Main Sources:

H_2O: Evaporation from bodies of water; product of hydrocarbon combustion

CO_2: Combustion of fossil fuels, forest fires, decay of plants and animals

CH_4: Anaerobic decomposition of organic matter; from ruminant animals (cows and sheep by bacterial breakdown of cellulose), rice paddies, oil and gas fields

N_2O: Bacterial action, use of nitrogen-based fertilizers

O_3: Photo-chemical smog

CFCs: In spray can propellants, old refrigerators and air conditioners, as solvents, production of plastic foams (no natural sources of CFCs).

(iii) CFCs effectiveness is far greater at absorbing energy than the other greenhouse gases.

(iv) The climate change will impact on health, agriculture, forests, melting of polar ice caps, water resources, thermal expansion of oceans and its impact on coastal areas/raising sea levels, coastal flooding, species diversity, species numbers/increased insect populations, increased rain falls in certain areas, droughts in others, etc.

Page 473 E4 & E 9(HL) Ozone depletion

6. (a) The photo–dissociation of molecular oxygen into oxygen atoms (which are extremely reactive free radicals containing unpaired electrons) by shorter wavelength ultraviolet (uv) light represents the principle mechanism of ozone's formation in the upper atmosphere.

$O_2(g) + \text{uv light} \rightarrow 2\ {\bullet}O$

The oxygen atoms react with other oxygen molecules, O_2 to form O_3:

$O_2(g) + {\bullet}O(g) \rightarrow O3(g)$

The reverse reaction takes place when O_3 absorbs rather longer wavelength uv light of less energy (since it has weaker bonds than the double bonds in O_2):

$O_3(g) \rightarrow O_2(g) + {\bullet}O(g)$

The oxygen free radicals react with ozone to form O_2 gas:

$O_3(g) + {\bullet}O(g) \rightarrow 2O_2(g)$

Thus O_3 is constantly being formed and broken down. The ozone layer acts as a shield by absorbing 99% of the sun's harmful uv light of longer wavelength than that absorbed by O_2 and N_2.

(b) Look at the Lewis structures of di-molecular oxygen (oxygen gas, O_2) and tri-molecular oxygen, O_3, ozone:

O_2 contains the stronger O=O double bond (bond order of 2), needs more energy and thus radiation of lower wavelength to dissociate it into oxygen atoms.

Ozone on the other hand is a resonance hybrid showing a single and a double bond in its Lewis structure. It therefore has a bond order of 1.5. This is a weaker bond than in O_2, requires less energy and thus a radiation of higher wavelength to dissociate ozone.

(c) (i) Sources of CFCs: aerosols/propellants/ spray cans, air conditioners/refrigerators, solvents, fire extinguishers.

(ii) UV light from the sun decomposes CCl_2F_2 to form chlorine free radicals (C-F bond is too strong to be broken) by homolytic fission:

$CCl_2F_2 \rightarrow CClF_2 + {\bullet}Cl$

In the ozone layer the chlorine free radicals react to form other free radicals (propagating step) such as ClO• and decompose ozone in which chlorine atoms are regenerated:

$O_3 + {\bullet}Cl \rightarrow ClO{\bullet} + O_2$

$ClO{\bullet} + O_3 \rightarrow Cl{\bullet} + 2O_2$

ClO• also reacts with any oxygen free atoms to regenerate •Cl:

$ClO{\bullet} + {\bullet}O \rightarrow Cl{\bullet} + O_2$

N.B. This also explains why such a small amount of CFCs has such a large impact on the ozone layer since the chlorine free radical is generated and thus one Cl• can decompose many ozone molecules.

(iii) The extremely low temperatures in the artic winters freezes any water vapour into ice crystals which behave as surface catalysts and provide the surface area over which pollutants present in the polar atmosphere combine to produce reactive chemicals such as chlorine molecules. As the spring approaches, the uv light from the sun decomposes Cl_2 to form chlorine free radicals which catalyze the destruction of ozone over Antarctica to produce the ozone hole.

(iv) Skin cancer, genetic mutation, cataracts.

(v) 1. Hydrocarbons, such as propane, C_3H_8 and 2–methylpropane, $CH_3CH(CH_3)_2$, are used as refrigerant coolants. Although these do not lead to ozone depletion, they are flammable as well as being greenhouse gases (able to absorb infrared radiation) and would lead to global warming.

2. Hydrochlorofluorocarbons, HClFCs contain hydrogen, chlorine, fluorine and carbon atoms in their molecules, for example: CHF_2Cl, Chlorodifluoromethane. The presence of a hydrogen atom makes the compound decompose less easily since the C–H bond is stronger (412 kJ mol^{-1}) than the C–Cl bond. Nonetheless, these do reduce the ozone layer because of the presence of a C–Cl bond in the molecule and can only be considered a temporary solution.

3. Fluorocarbons: For example, CF_4, tetrafluoromethane; C_2F_6, hexafluoroethane. These have low reactivity, are neither toxic nor flammable and the very strong C–F bond makes them stable to uv radiation so they cannot catalyze ozone depletion. However, these are greenhouse gases, absorb infrared radiation and would eventually lead to an increase in the global temperature.

4. HFCs hydrofluorocarbons: For example, CF_3CH_2F, 1,1,1,2-tetraflouroethane, without any chlorine atoms, are considered good alternatives to CFCs as no chlorine atoms, which are primarily responsible for ozone depletion, are involved . These also have low reactivity, low toxicity and low flammability, but do contribute to global warming.

Page 473 E5 Dissolved oxygen in water

7 (a) (i) For animals to survive in aquatic systems, water must contain a minimum concentration of dissolved oxygen.

(ii) Temperature, organic waste and inorganic ions such as nitrates and phosphates.

Increase in temperature decreases the concentration of dissolved oxygen and thus reduces the quality of water.

Increase in organic waste uses oxygen and its concentration decreases as organic waste is decomposed, thus decreasing the quality of water.

Nitrates and phosphates are nutrients for algae growth. Decomposition of these decrease DO and decrease the quality of water.

(b) BOD is the measure of the quantity of oxygen gas required for the decomposition of biodegradable organic waste matter in a given volume of water over a set period of time (5 days) at a given temperature (20°C).

(c) The process of eutrophication decreases the concentration of water dissolved in a body of water. Nitrates act as nutrients that lead to excessive growth of aquatic plant life, often in the form of algal blooms; their decay uses up dissolved oxygen in the water. Consequently, fish die of asphyxiation (lack of oxygen);

anaerobic processes produce toxic substances such as hydrogen sulfide and phospine and that part of the water becomes lifeless.

(d) Aerobic decomposition of organic matter in water in the presence of oxygen is a natural biological process in which bacteria that thrive in oxygen-rich environments break down and digest the organic matter. This is an oxidation process where the organic matter is broken down into carbon dioxide and water. Any organic nitrogen is converted into nitrates, NO_3^-, organic sulfur to sulfates, SO_4^{2-} and organic phosphorus to phosphates, PO_4^{3-}.

Anaerobic decomposition of organic matter in water takes place in the absence of oxygen. The reduction of organic matter in the presence of water include:

- methane (biogas or marsh gas), from the carbon and hydrogen
- ammonia and amines (with a strong fishy smell) from nitrogen and hydrogen
- hydrogen sulfide, H_2S (foul rotten egg smell) from organic sulfur
- phosphine, PH_3 from phosphorus.

Page 473 E6 Water treatment

8. Water is a unique, highly polar substance capable of hydrogen bonding and dipole-dipole interaction and this property allows it to dissolve many chemicals.

9. (i) The purpose of sewage treatment is to remove hazardous materials, reduce the BOD (Biological Oxygen Demand) of the sewage and kill micro-organisms prior to discharge.

(ii) **Primary** treatment: filters out large objects such as trash and debris and removes floating objects including grease (which has a high BOD). Smaller heavier objects such as rocks, stones and sludge settle and can be removed from the bottom. Removes 30 – 40% of BOD waste.

Secondary: Microbial activity oxidizes and breaks down most organic matter; can remove most (about 90%) organic oxygen-demanding wastes and suspended particles.

Tertiary: removes the remaining organic materials, nutrients and substances not taken out by the biological processes in secondary treatment, such as toxic metal ions as well as nitrate and phosphate ions.

(iii) Allows suspended particles to join together to form large clumps.

(iv) This involves microbial activity and requires aeration in which air, or air enriched with oxygen, is bubbled, using large blowers, through sewage mixed with bacteria–laden sludge. This allows aerobic bacteria to thoroughly mix with the sewage in order to oxidize and break down most of the organic matter (called activated sludge process).

10. (a) Distillation and reverse osmosis

Distillation: Sea water, containing dissolved salts, is not fit for human consumption or for agricultural and industrial uses. Desalination processes remove salts from sea water and brackish water to produce fresh water. Distillation is the process that allows the separation of a volatile liquid from non-volatile materials. Heating the solution allows for the volatile water to be converted to water vapor that can be separated and collected as fresh water leaving behind the non-volatile salts in solution. Large scale desalination by distillation is made more efficient by using a multistage process to maximize the use of heat so that when condensation of vapor produces heat in one stage, it is used to heat water in the second stage and so on.

Reverse osmosis: A semi-permeable membrane allows water, but not ions or large molecules, to pass through it. If pure water and salt water are separated by a semi-permeable membrane then, due to osmosis, pure water (of higher solvent concentration) will move into the salt water thus diluting it. This flow of water can in fact be stopped if a pressure equal to the osmotic pressure of the solution is applied. Indeed, if the pressure applied is greater, then the flow of the solvent takes place in the opposite direction and the process is called reverse osmosis.

(b) Nitrates and phosphates are water soluble. Cadmium ions can be precipitated as sulfide salt since its solubility in water is very little. Similarly, the presence of phosphate ions can be reduced to very low levels by the addition of calcium ions since the solubility product constant of calcium phosphate is very small.

$M^{2+}(aq) + S^{2-}(aq) \rightarrow CdS(s)$

$3Ca^{2+}(aq) + 2PO_4^{3-}(aq) \rightarrow Ca_3(PO_4)_2(s)$

Page 474 E7 & 12(HL) Soil

11. (a) (i) Larger amounts of: Oxygen, silicon and aluminium; smaller amounts of calcium, iron, potassium (magnesium and sodium).

(ii) Inorganic matter, the largest component in soil due to weathering of rocks, water, air and smaller amounts of organic matter.

(iii) Bacteria and fungi convert the organic matter into a typically water insoluble mixture called humus containing about half its mass as carbon and about 5% nitrogen.

(iv) SiO_2, is a tetrahedron with silicon covalently bonded to four oxygen atoms in which each oxygen atom is shared between two Si atoms to form a giant covalent structure. The consequence of replacing one in every four tetrahedrons contain Al^{3+} instead of Si^{4+} in the silica structure is that it will be short one electron, making it an anion with a one negative charge and an empirical formula $AlSi_3O_8^-$ instead of SiO_2.

The existence of these ions in inorganic matter and the presence of the highly electronegative oxygen explains its ability to hold on to plant nutrient cations such as K^+, NH_4^+, Ca^{2+}, Mg^{2+} and to form salts such as $NaAlSi_3O_8$.

12. Salinization is the accumulation of water soluble ions or salts in the soil due to continual irrigation to grow crops. Water for irrigation contains small amounts of dissolved salts such as calcium chloride, magnesium sulfate and sodium chloride. As the water is used by plants or evaporates due to high atmospheric temperature, and where salts are not washed away due to poor drainage or low rainfall, the salts accumulate over time, leading to salinization of the soil. Salinization reduces plant growth as the increased concentrations of ions reduce the ability of the roots to take up water. This is due to the phenomenon of osmosis which is the movement of water from a region of low ion concentration in the roots to high ion concentration in the soil (to eventually reach infinite dilution).

Nutrition depletion is the removal of essential nutrients and minerals from the soil food web by crops that grow and are continually harvested due to agricultural practices, and leads to soil degradation. Nutrient depletion or loss results in decreased soil quality and can lead to a serious decline in the yield of crops, thus affecting food supply.

Soil pollution arises from the presence of man-made chemicals such as pesticides and herbicides. Pesticides provide better harvests by killing insect pests.

Herbicides kill unwanted plants or weeds and fungi are controlled using fungicides. Pesticides can lead to lower crop yields by destroying very small flora and fauna, and similarly to fertilizers, they leach into ground water polluting it. Soil pollution also arises from the addition of nitrate and phosphate fertilizers to replenish the soil with nitrogen and phosphorus. Soil contamination is also caused by domestic and industrial waste added directly to soil or by wastes leached from land fill sites. These may contain heavy metals such as arsenic, chromium, copper, mercury, lead and zinc and organic contaminants such as PCBs, and PAHs. Similar to leaching of fertilizers, these poisonous chemicals can pollute ground water, affect water supplies and create health risks.

13 (i) The term soil organic matter (SOM) refers to the mixture of non-living organic components present in the soil in various stages of decomposition arising from the chemical and biological action on plant matter and organisms.

(ii) Soil organic matter includes organic matter converted into a mixture by bacteria and fungi, smaller molecules such as sugars and amino acids and high molecular mass polysaccharides and proteins. It can be determined experimentally by titration with a dichromate(VI) solution.

(iii) SOM plays an important role in soil quality, and thus in producing high crop yields, in a variety of ways. In deserts, for example, organic matter added to sand can greatly improve plant growth. Soil organic matter contains a pool of mineral nutrients it can exchange with plant roots, it holds on to water, improves soil structure and reduces soil erosion.

14. **Mineralization**: This is the slow process by which organic matter containing nitrogen and phosphorus is broken down or mineralized to release nitrogen and phosphorus to roots.

Biological: Organic soil matter binds to many nutrients and is a substantial reservoir of the mineral nutrients nitrogen, phosphorus and sulfur that are made available to microbes and plants for growth. Nitrogen is used in the synthesis of proteins and chlorophyll. Phosphorus is used in the synthesis of enzymes and the storage of energy. Sulfur is used in the synthesis of some amino acids, the building blocks of proteins. Bacteria and fungi decompose the organic matter and release the nutrients to the plant roots in the soil.

Physical: Soil clusters collect together in stable forms due to the presence of organic matter. This reduces soil erosion, and increases the ability of air and water to move through the soil. As a result, like a sponge, soil organic matter can absorb several times its mass of water and thus influences soil's water retention property. It also improves soil structure since the porous soil makes it possible for roots to spread through the soil

Chemical: SOM has the ability to increase CEC (cation-exchange capacity) of the soil, behaves as a buffer and hence controls soil pH, removes heavy metals and pesticides through its chelating ability.

15. (a) $Ca^{2+}(aq) + SO_4^{2-}(aq) \rightarrow CaSO_4(s)$

(b) $CaSO_4(s) \leftrightarrows Ca^{2+}(aq) + SO_4^{2-}(aq)$

If the solubility is x mol dm^{-3}, then:

$K\text{sp} = [Ca^{2+}][SO_4^{2-}] = x^2 = 3.0 \times 10^{-5}$

$x = 5.5 \times 10^{-3}$ mol dm^{-3}

(c) $[Ca^{2+}][SO_4^{2-}] = 1.0 \times 10^{-3} \times 1.0 \times 10^{-2} = 1.0 \times 10^{-5} < K\text{sp}$. Thus there is no precipitate formed and no equilibrium present.

(d) $Ksp = [Ca^{2+}][SO_4^{2-}] = 0.001\ x = 3.0 \times 10^{-5}$

$x = 3.0 \times 10^{-2}$ mol dm^{-3}

16. Cation-exchange capacity (CEC) is the extent to which the negative charges on clay and/or humus in the soil can exchange nutrient cations at the roots of plants. CEC is an indicator of soil fertility.

17. (a) (i) Zn: H^+ from acid deposition can replace Zn^{2+} in the soil since zinc sulfide is insoluble in water, but dissolves in an acid by reacting with H^+ ions by forming H_2S:

$ZnS(s) + 2H^+(aq) \rightarrow Zn^{2+}(aq) + H_2S(g)$

Similarly, zinc hydroxide, a base, is insoluble in water but reacts with H^+ ions:

$Zn(OH)_2(s) + 2H^+(aq) \rightarrow Zn^{2+}(aq) + 2H_2O(l)$

(ii) Al: Alumina, Al_2O_3 is insoluble in water but reacts as a base with H^+ ions to form soluble Al^{3+} (aq) ions:

$Al_2O_3(s) + 6H^+(aq) \rightarrow 2Al^{3+}(aq) + 3H_2O(l)$

Al^{3+} is toxic to plants and is not a plant nutrient. Its presence in soil below pH 5 is problematic. Due to its high charge density (charge to size ratio) and thus high chelating effect of binding onto the negative surfaces in clay and humus, it is able to displace important plant nutrient cations such as Ca^{2+} and Mg^{2+} from the soil:

$3Mg^{2+}(soil) + 2Al^{3+}(aq) \rightarrow 2Al^{3+}(soil) + 3Mg^{2+}(aq)$

(b) Phosphoric(V) acid, H_3PO_4 is a weak, triprotic acid. Its first dissociation is at low pH where as the third dissociation is at high pH, both typically out of soil pH range:

$H_3PO_4(aq) \leftrightarrows H^+(aq) + H_2PO_4^-(aq)$; pH < 4

$H_2PO_4^-\ (aq) \leftrightarrows H^+(aq) + HPO_4^{2-}(aq)$; pH ~ 7

$HPO_4^{2-}\ (aq) \leftrightarrows H^+(aq) + PO_4^{3-}(aq)$; pH > 10

Thus, as plants absorb inorganic phosphorus from the soil as $H_2PO_4^-$ and HPO_4^{2-}, its supply depends on having a soil pH between about 6 and 7.5. In acidic soil below pH 5, the presence of Al^{3+} and Fe^{3+} produce insoluble phosphate compounds thus decreasing the availability of phosphorus to plants. Above pH 7, phosphates of Ca^{2+} and Mg^{2+} precipitate out.

Page 474 E8 Waste

18. **Landfill** is simple but the problems are identifying suitable sites; it takes up precious land space, leaves ugly and smelly sites, leads to the build up of potentially explosive flammable gases from anaerobic decomposition and the pollution of ground water supplies by the leaching of toxic substances, such as heavy metals.

    Incineration greatly reduces the volume of waste matter, but the plant and fuel can be costly. Also some materials can produce toxic combustion products. Emission of pollutants on burning plastics release dioxins into the environment. Incineration destroys disease causing microorganisms.

19. **Steel**: scrap steel is added to molten iron from the blast furnace, so that energy is saved in the reduction of the ore and alloying materials are re-used.

    Aluminium: the smelting of aluminium consumes vast quantities of electricity so that recycling saves 95% of the energy consumed in aluminium manufacture.

    Glass: broken glass, preferably colour sorted, is added to the raw materials in glass manufacture. It is then melted and molded into new containers. This saves raw materials and energy.

    Plastic: plastic waste has to be sorted according to the polymer present; not an easy task. The plastic can then be melted and molded. Some plastics, such as thermosetting ones, cannot be recycled.

    Paper: the waste paper is pulped, de-inked, bleached and then reformed into paper. Though it conserves raw materials, there is inevitably some degradation of quality during this processing.

20. Radioactive waste can be classified as low, medium or high level-waste according to the intensity and half-life of the radiation produced:

    Low-level: mainly materials that have been exposed to radiation around a nuclear reactor producing low levels of short-lived radioactivity. These materials are stored securely until the radioactivity has fallen to a low enough level for disposal by incineration, or dilution and releasing into the sea.

    Medium or intermediate-level waste: Contain greater amounts of radioisotopes with intermediate activity and generally of intermediate half-lives, mostly from nuclear reactor parts and processing nuclear fuel. Can either be stored securely until the radioactivity has fallen to a low enough level for disposal or dealt with as high-level waste.

    High-level: mainly from spent fuel rods that are highly radioactive, often with half-lives of thousands of years. Initially these wastes, in secure containers, have to be stored in cooling ponds because of the heat the decay generates. Then they are either converted into a glass (vitrification) or sealed in strong corrosion resistant containers and stored deep underground in stable geological strata.

Page 474 E10 Smog (HL)

21. (i) NO and VOCs from the internal combustion engine/automobile exhaust.

(ii) Increased automobile use during morning rush hours; NO is rapidly converted to NO_2, a secondary pollutant. UV light from the sunlight photo-dissociates NO_2 to produce reactive atomic oxygen free radicals leading to formation of other secondary pollutants:

$NO_2 \rightarrow NO + \bullet O$

Oxygen in the air reacts with the free radical to form ozone, another secondary pollutant:

$O_2 + O \rightarrow O_3$

Ozone reacts with moisture in the atmosphere to produce reactive hydroxyl free radicals:

$O_2 + H_2O \rightarrow 2\bullet OH$

The hydroxyl free radicals can react with volatile organic compounds to form other free radicals (via propagating steps) leading to the formation of aldehydes and peroxyacylnitrates (PANs, e.g., $CH_3CO_3NO_2$):

$RCH_3 + \bullet OH \rightarrow RCH_2\bullet + H_2O$

$RCH_2\bullet + O_2 \rightarrow RCH_2OO\bullet$

$RCH_2OO\bullet + NO \rightarrow RCH_2O\bullet + NO_2$

$ROO\bullet + \bullet NO_2 \rightarrow ROONO_2$

Increase in NO_2 concentration further increases ozone concentration and the process continues.

(iii) Irritating to the eyes/make eyes water (PANS are lacrymators); cause respiratory problems.

(iv) Catalytic converters: In the presence platinum–based catalysts, CO and NO are converted to carbon dioxide and harmless nitrogen gas:

$2\ CO(g) + 2\ NO(g) \rightarrow 2\ CO_2(g) + N_2(g)$

It also oxidizes volatile organic compounds (hydrocarbons) to carbon dioxide and water.

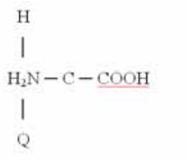
Use of air to fuel ratio: different air to fuel ratios produce different amounts of pollutants. Lower air to fuel ratios produce less NOx but more CO and VOCs due to incomplete combustion. Higher air to fuel ratios produce more complete combustion, thus less CO and VOCs but more NOx as the more complete combustion produces higher temperatures and the presence of more oxygen favors NOx production. ‘Lean burn’ engines with modification use an air:fuel ratio of approximately 18:1 by volume to minimise the production of pollutants.

Use of electric cars, better public transportation, etc.

CHAPTER 17 (OPTION F) FOOD CHEMISTRY

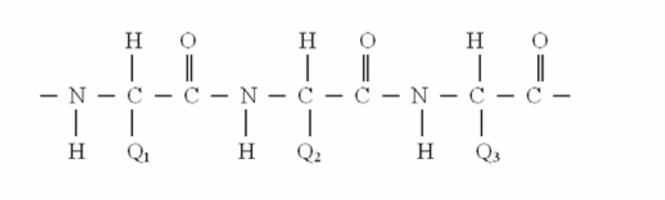
Page 490 F1 Food groups

1. A food is anything that is prepared for human consumption. A nutrient is something obtained from food that provides energy or supplies material essential for the growth, body maintenance or effective working of the metabolism.
   Some “foods” that we consume provide very little nutrition; sugar free chewing gum might be a good example. As a nutrient is defined as vital substances obtained from food, then it is not possible to have a nutrient that is not a food, though in emergency situations such substances may be introduced intravenously.
2. Oils and fats are all tri-esters of propan-1.2.3-triol (glycerol) with carboxylic acids having a long hydrocarbon chain. They differ in that oils are liquid at room temperature, whereas fats are solid at room temperature. It is found that fats are esters of fatty acids with saturated hydrocarbon chains, whereas the hydrocarbon chains in oils are unsaturated (one double bond) or poly-unsaturated (a number of double bonds). The double bonds create “kinks” in the hydrocarbon chains so that they cannot align themselves next to each other. As a result the van der Waals’ forces are much weaker when the chains are unsaturated, resulting in lower melting points.
3. The general structure of an amino acid is:

   $H_2N-\overset{\overset{H}{|}}{\underset{\underset{Q}{|}}{C}}-COOH$

   where Q represents a side-chain that varies from one amino acid to another. These can join together to form a polymer chain, a short section of which is shown below:

   $-\underset{\underset{H}{|}}{N}-\overset{\overset{H}{|}}{\underset{\underset{Q_1}{|}}{C}}-\overset{\overset{O}{\|}}{C}-\underset{\underset{H}{|}}{N}-\overset{\overset{H}{|}}{\underset{\underset{Q_2}{|}}{C}}-\overset{\overset{O}{\|}}{C}-\underset{\underset{H}{|}}{N}-\overset{\overset{H}{|}}{\underset{\underset{Q_3}{|}}{C}}-\overset{\overset{O}{\|}}{C}-$

   The bond between the CO of one amino acid and the NH of the next, formed by the loss of a water molecule, is known as a peptide bond.

4. Glucose is a carbohydrate. Starch comprises many glucose units joined together (cellulose is also a possible answer – it is a food component even if not a nutrient). Many foods such as rice, pasta, potato and bread are rich in starch.
5. Olive oil is a lipid. It is essentially an energy source.
   Flour is a complex carbohydrate. It is essentially and energy source.
   Honey is a simple carbohydrate (sugar). It is essentially and energy source.
   Eggs have protein as the major component. They are used for growth and repair.
   Rice is a complex carbohydrate. It is essentially and energy source.
   Chocolate is a lipid. It is essentially an energy source.
6. All of these minor nutrients are essential for the healthy functioning of the body:
   Minerals provide the ionic substances, such as salt, that are essential for cells to operate. Some components have more specialised uses, such as iron in haemoglobin.
   Vitamins are relatively simple organic molecules that fulfil vital roles in the body, for example without Vitamin C humans suffer from scurvy.
   Water is the medium that almost all bodily reactions take place in, hence it is vital both for this and to take away waste in the form of urine.

CHAPTER 17 (OPTION F) FOOD CHEMISTRY

Page 491 F2 Fats and oils

7. Mono-unsaturated means that on average each hydrocarbon chain of the lipid molecule contains on C-C double bond, whereas poly-unsaturated means that on average each chain has two or more. It would be expected that the melting point of sunflower oil would be lower than that of olive oil. This is because each double bond causes a kink in the hydrocarbon chain, so reducing its ability to pack close to other chains. This reduces the strength of the intermolecular van der Waals' forces causing a lower melting point.

8. *Cis*- and *trans*- isomers differ in whether the carbons in the carbon chain are joined to the same side (*cis*-) or the opposite side (*trans*-) of the C-C double bond:

Greater effect on the "straightness" of the hydrocarbon chain and hence its ability to pack close to other chains. This reduces the strength of the van der Waals' forces between molecules of the *cis*-isomer more than the *trans*-isomer, hence the *cis*-isomer will have the lower melting point. Almost all naturally occurring lipids have C-C double bonds with a *cis*- configuration, hence natural enzymes have developed to catalyse reactions of *cis*-isomer, but not the *trans*-isomer, hence the *cis*-isomer has more nutritional value.

9. In order to produce a product with a texture similar to chocolate, it is important to choose a lipid with a melting point considerably above room temperature. This means that a saturated lipid (a fat) would have to be used rather than an unsaturated lipid (an oil), because in the solid state the straightness of the saturated hydrocarbon chains leads to a greater degree of crystallinity (regular close packing), stronger van der Waals' intermolecular forces and hence a higher melting point.

10. The chemical stability of the lipid would decrease from lard through olive oil to canola oil. This is because the C-C double bond is much more reactive towards autoxidation reactions that lead to rancidity than the saturated hydrocarbon chain, so the more double bonds the lower the stability.

11. Vegetable oils are hydrogenated by heating under pressure with hydrogen gas in the presence of a catalyst, usually made of finely divide nickel. The more saturated product will often be a solid which means it useful for some cooking techniques, like rubbing in flour to make pastry, that are not possible with a liquid. The product will also last longer before becoming rancid. The disadvantages are that saturated fats are less healthy because they can give rise to atherosclerosis, increasing the risk of strokes and heart attacks. partial hydrogenation can also give rise to trans-fats, that is those that contain a C-C double bond with a trans- configuration. These have an adverse effect on the ratio of different forms of cholesterol in the blood.

CHAPTER 17 (OPTION F) FOOD CHEMISTRY

Page 491 F3 Shelf life

12. When stored beyond their shelf-life, foods might undergo undesirable changes in their colour (such as meat going a brown rather than a red colour), their texture (such as biscuits becoming soggy) and their smell/flavour (such as oils becoming rancid).

13. Fermentation – the storage time of fruit juice is extended by fermenting it to produce wine. The presence of alcohol in the liquid prevents the growth of many types of bacteria and other micro-organisms.
    Pickling is the addition of vinegar, for example onions or other small vegetables may be stored in vinegar. Many types of bacteria and other micro-organisms cannot grow at the low pH of these solutions.
    Salting can for example be used to preserve fish. If the food becomes moist the salt causes the liquid formed to have a very low osmotic pressure so any cells exposed to it die because of loss of moisture, hence it reduces the possibility of micro-organisms spoiling the food.
    Drying can be used to preserve fruits, for example turning grapes into raisins. Almost all forms of life require water for growth, hence the lack of moisture will prevent micro-organisms growing in the food.

14. Rancidity is a process by which fats and oils develop unpleasant odours and flavours. Rancidity requires the presence of either moisture or oxygen, so excluding these, for example by vacuum packing will prevent rancidity. Storing food at lower temperatures and in the dark will also help delay its onset.

15. An antioxidant is a substance that delays or prevents the onset of oxidative degradation in foods, in particular oxidative rancidity in lipids. A commonly natural antioxidant is Vitamin C. A widely used synthetic antioxidant is propyl gallate (PG).

16. (i) Hydrolytic rancidity can affect all types of lipids. In this the ester bond joining the fatty acid to the glycerol is broken by the action of water, often catalysed by enzymes:

    $$\text{C-O-CO-C}_x\text{H}_y + \text{H}_2\text{O} \rightarrow \text{C-OH} + \text{HO-CO- C}_x\text{H}_y$$

    (ii) Oxidative rancidity is mainly a problem with unsaturated lipids. The C-C double bonds in the hydrocarbon chain of the lipid react with oxygen, causing the chain to break at this point.

    $$\text{-C=C-} + \text{O}_2 \rightarrow \text{-CO-H} + \text{H-CO-}$$

    Obviously this requires the presence of oxygen, but it is greatly accelerated by the presence of light, high temperatures and traces of transition metal ions.

17. Eating large quantities of citrus fruits, kiwi fruit or indeed almost any green vegetable will provide Vitamin C, an active antioxidant. Eating carrots and tomatoes will provide β-carotene another naturally occurring antioxidant.

18. (i) Moisture is vital for the growth of almost all living organisms, hence excluding moisture limits the growth of undesirable micro-organisms on food.

    (ii) Excluding air would reduce the onset of oxidative rancidity in any unsaturated fats present in the food, as this requires oxygen gas.
    iii Oxidative rancidity requires the breaking of a covalent bond to produce free radicals in the initiation step. Often this comes from the interaction of light, especially UV-light with the food, so keeping the food in an opaque container prevents this occurring.
    iv The rate of chemical reactions increases rapidly with temperature, hence storing food at a lower temperature reduces the rate of the chemical reactions responsible for its degradation.

19. Benzoic acid, or its sodium salt, are often added to fruit juice to delay the onset of microbial growth. The nitrates and nitrites of both sodium and potassium are used to preserve "cured" meats such as ham.

20. A free radical chain reaction is a chain reaction (that is one in which the major reaction regenerates the reactive species) which occurs through the generation of free radicals as the reactive intermediate. Chain reactions have three stages – Initiation in which the reactive species (in this case the free radicals) are generated; Propagation which produces the major products and regenerates the active species; Termination which are reactions that consume the reactive species. In this case alkyl radicals (R•) are formed in the initiation and these then react with oxygen

$$R\bullet + O_2 \rightarrow R\text{-}O\text{-}O\bullet$$

The peroxy radical then reacts with another hydrocarbon chain to form a hydroperoxide, a reactive species which goes on to give the final products, and regenerates the alkyl radical:

$$R\text{-}O\text{-}O\bullet + R\text{-}H \rightarrow R\bullet + R\text{-}O\text{-}O\text{-}H$$

21. Antioxidants may work by:

- Functioning as free radical scavengers, so providing additional termination reactions for the auto-oxidation reaction, hence reducing the chain length of the reaction and the amount of oxidation product. Most synthetic antioxidants, such as TBHQ (*tert*-butylhydroquinone) act in this way.
- Functioning as chelating agents for transition metal ions so that they cannot react with organic hydroperoxides to produce free radicals. EDTA (ethylenediamine tetraacetic acid) and its salts act in this way.
- Acting as reducing agents to remove oxygen from the food or reacting with undesirable oxidation products. Many natural antioxidants, such as Vitamin C, are reducing agents.

22. Even though the initiation step of auto-oxidation occurs infrequently the free radical it produces can be quite long lived because its removal would usually involve an encounter with another free radical (termination reaction), also a rare event. In the meantime the free radical can convert many molecules of the lipid and oxygen into the products that lead to rancidity through the propagation stages of the chain reaction.

23. The initial products of auto-oxidation are organic hydroperoxides. These molecules can oxidise transition metal ions to a higher oxidation state and in the process generate free radicals, for example:

$$Fe^{2+} + R\text{-}O\text{-}O\text{-}H \rightarrow Fe^{3+} + R\text{-}O\bullet + OH^-$$

These free radicals can then undergo propagation reactions to produce further oxidative degradation.

Page492 F4 Colour

24. The major groups of compounds responsible for the colour of foodstuffs are anthocyanins (responsible for the red colour of beetroot and berries such as strawberries), carotenoids (responsible for the colour of carrots and of butter) and compounds containing a porphyrin ring (such as chlorophyll responsible for the green colour of plant leaves and haemoglobin responsible for the red colour of blood and meat).

25. The carotenoids have a structure similar to Vitamin A and indeed are a precursor for the biosynthesis of this vitamin. Carotenoids have a long hydrocarbon chain containing conjugated double bonds (that is alternate single and double bonds), usually with a ring at either end of the chain.

26. The colour of red cabbage comes principally from anthocyanins. The colour of these is very pH dependent, they are also affected by hydrolysis equilibria, the position of which will depend on temperature, finally they can form coloured complex ions with the ions of metals such as iron and aluminium, which are often used for containers for the storage or cooking of foods.

27. Chlorophyll is found in all green plants, whilst heme is found in the blood of mammals and hence in meat. Both contain a porphyrin ring structure, but in chlorophyll the metal ion at the centre of this is Mg^{2+}, whilst in haemoglobin it is Fe^{2+}. When heme is converted to myoglobin a heme porphyrin ring becomes bonded to a globin protein molecule.

28. Many synthetic dyes are quite reactive organic molecules and a few have well documented carcinogenic activity. Concerns relating to the use of synthetic dyes in foods relate to the difficulty of proving the safety of consumption of small concentrations of dyes over an extended period. Concerns are exacerbated by the fact that the use of certain dyes in foods is permitted in one country, but not in another country. A major advance would be the drawing up of internationally agreed regulations relating to the use of synthetic dyes in foods, which could potentially also reduce the amount of duplicated research. In the shorter term, requiring all synthetic dyes used with foods to be clearly labelled on the packaging, coupled with checking of this in relation to local regulations as part of import/export formalities, would help allay some worries.

29. When heated on their own simple carbohydrates, such as sucrose, undergo a process of caramelization. This involves the loss of water molecules causing the polymerisation of the sugar to give brown coloured products.

    When proteins are present with reducing sugars a different type of browning reaction, known as Maillard reactions occurs. In these a condensation reaction takes place between the carbonyl group of the reducing sugar and the free amino group of the amino acid:

$$\underset{\text{(Reducing sugar)}}{HO\text{-}CH_2\text{-}[CH(OH)]_4\text{-}CH{=}O} + \underset{\text{(Amino acid)}}{H_2N\text{-}CHQ\text{-}COOH} \longrightarrow \underset{\text{(Initial condensation product)}}{HO\text{-}CH_2\text{-}[CH(OH)]_4\text{-}CH{=}N\text{-}CHQ\text{-}COOH + H_2O}$$

This initial product then undergoes polymerisation reactions to form brown coloured products.

30. Heme usually contains iron in a +2 oxidation state. It is however slowly oxidised by atmospheric oxygen to the +3 state. In the case of myoglobin, this slow oxidation is accompanied by a colour change from purple-red to the brown colour of metmyoglobin, as the oxidised product is known. The rate of this reaction can be reduced by storage in a refrigerator and by ensuring that the meat does not come into contact with oxygen by, for example, vacuum packing.

31. Whilst having rather different chemical structures anthocyanins, carotenoids and chlorophyll all have extensive systems of conjugated double bonds (alternate single and double bonds). This leads to a large delocalised π-bond, for which the difference in energy between the highest filled and lowest unfilled electron energy level will correspond to a quanta of light in the visible region of the spectrum. These molecules therefore absorb light of a particular colour and hence appear the complementary colour.

32. The colouring matter in beetroot is an anthocyanin. Anthocyanins have an oxygen in one ring and have many hydroxy groups attached to the other rings. These can hydrogen bond to water. Hence anthocyanins tend to be water soluble and some colour is taken up with the liquid when boiling. Carrots are coloured as a result of carotenoids. These are essentially hydrocarbons and so cannot hydrogen bond to water, hence they are not water soluble and so that the water remains almost colourless on boiling. Oil however is non-polar and the intermolecular forces are essentially van der Waals' forces, similar to those between carotenoid molecules, hence orange coloured carotenoids will dissolve in oils.

33. The colour of the β-carotene results from the extended system of conjugated double bonds (alternate single and double bonds). This leads to a large delocalised π-bond, for which the difference in energy between the highest filled and lowest unfilled electron energy level will correspond to a quanta of light in the visible region of the spectrum. If hydrogenation occurred some, or all, of the double bonds would be converted to single bonds, disrupting the delocalised π-bond. As a result the molecule would no longer absorb light in the visible region and hence it would be colourless.

34. In genetically modified species sequences of DNA from a different organism are introduced into the DNA of the species being modified, altering its characteristics in accordance with the introduced sequence. This may confer greater drought tolerance, it may allow it to produce chemicals making it resistant to pests or it may enable it to synthesise biologically active chemicals that can be extracted and used for human medication.

CHAPTER 17 (OPTION F) FOOD CHEMISTRY

Page 493 F5 Genetically modified foods

35. Three ways in which genetic modification can improve the yield would be simply producing a larger plant, or a plant with larger fruit. It could also enable the plant to mature more rapidly so that more crops may be grown each year, or it may cause the plant to synthesise chemicals making it resistant to a particular disease or infestation.

36. Examples of genetic modification to yield novel products include the genetic modification of rice to produce Vitamin A and of chickens to lay eggs containing human interferon.

37. Some of the major concerns relating to genetic modification are that the effects of a given modification may not always be predictable, hence the process may produce species that present dangers that we may be unaware of until it is too late. Although GT crops are usually grown under controlled farm conditions, it is possible for some seeds to escape into the wild and contaminate closely related wild populations. The process genetic modification could also affect the nutritional content of the foods produce affecting the balance of the food intake of those consuming them. There are also suspicions that unusual proteins produced by GM species are responsible for the increasing number of allergies found in recent times.

Page 493 F6 Texture

38. The texture of a food depends on properties such as hardness, density and elasticity as well as the way these change at the temperature of the mouth and in the moist environment it provides. A disperse system is a stable, macroscopically homogenous mixture of one phase in another with which it would normally be immiscible.

39. A suspension is a stable mixture of solid particles in a liquid medium.

    An emulsion is a stable mixture of one liquid in a second immiscible liquid.

    A foam is a stable mixture of a gas in a liquid medium.

40. An emulsifier is a surfactant that orientates itself at a boundary between the two liquids involved, usually an aqueous and a non-aqueous phase. Emulsifiers have one part of the molecule that is hydrophilic and bonds to the aqueous phase, whereas another part of the molecule is hydrophobic and bonds to the non-aqueous liquid. Polyoxyethylene stearate would be an example of a synthetic emulsifier. The hydrophilic (polyoxyethylene) end of the molecule has many oxygen atoms that can hydrogen bond to water, and attached to this is the hydrophobic (stearate) part comprising a long hydrocarbon chain.

    A stabiliser is a substance that enhances the action of an emulsifier by delaying the separation of an emulsion. The sodium and potassium salts of hydroxycarboxylic acids such as gluconic acid [$HOCH_2$-$(CHOH)_4$-$COOH$] are often used as stabilisers.

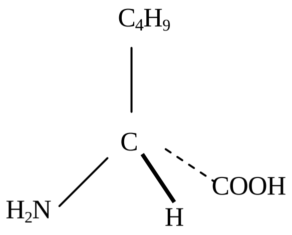
41. All emulsifiers have a hydrophilic section, one that can bond to water either because it is ionic or it has groups that can form hydrogen bonds, and a hydrophobic section that cannot bond to water and therefore prefers a non-polar environment, usually comprising a long hydrocarbon chain. Because they have these two different parts emulsifiers locate themselves at the boundary between the two phases, so that each part can be in its preferred environment. The greater the area of such surfaces, that is the more small droplets of one phase in the other, then the more sites there are where the emulsifier can bond. In a water based

emulsion the hydrophilic parts of the emulsifier will often repel each other reducing the tendency of the droplets to coalesce.

42. In order for an emulsifier to stabilise an emulsion, the mixture of very small droplets of one phase in the other has to be created. This can be done by vigorous beating of the mixture. Once these very small droplets of one immiscible component have been created, then the emulsifier and stabiliser can prevent the mixture separating, but beating is necessary to initially produce the dispersion.

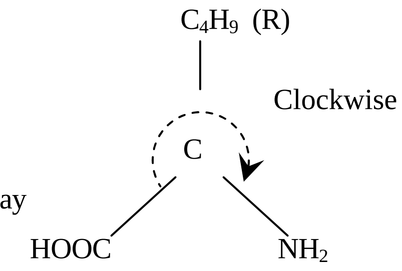
43. The absolute configuration of a chiral molecule gives the actual positions of the atoms in the molecule. For many years it was known how a pair of enantiomeric molecules differed, but which enantiomer corresponded to which possible configuration was uncertain. The absolute configuration states which enantiomer corresponds to which three dimensional structure.
The R-S system works in order of increasing mass of the substituents at the chiral centre. Therefore for the first atom the order is [-CO-CH_3; -CH_2-CH_3; -C=CH_2; -CO-OH] < -OH < -F. For the carbon substituents it is therefore necessary to go to the highest ranking second atom, remembering that atoms joined by a double bond count double their mass, hence the order is
-CH_2-CH_3 < -C=CH_2 < -CO-CH_3 < -CO-OH < -OH < -F.

44. Consider applying the CORN law to the enantiomer of leucine given:



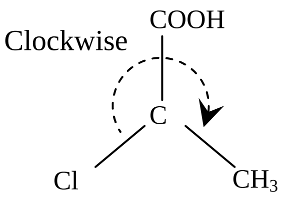
Looking along the C-H

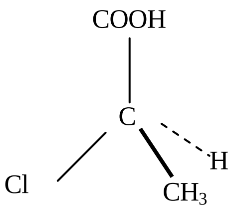
with the H-pointing away



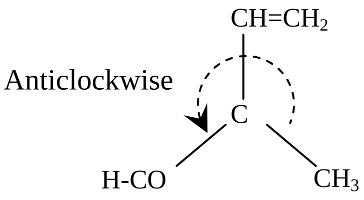
It can therefore be seen, applying the “CORN” rule, that this is D- leucine (COOH -> R -> NH_2 clockwise).

45. The substituents around the chiral carbon are, in increasing mass order H < CH_3 < COOH < Cl. If it is the R-isomer then looking along the C-H bond, with the H pointing away, the masses should decrease in a clockwise direction. This, and a 3D representation of the resulting enantiomer, are shown below:

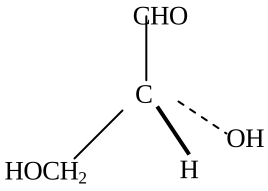


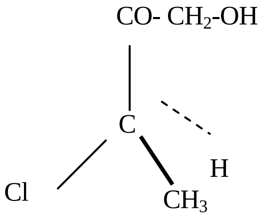


46. Consider looking at the molecule along the C-H bond with the H pointing away:
Consideration of the illustration shows that the groups decrease
(CH_3 < CH=CH_2 < CO-H)
in an anticlockwise direction hence it is the L-isomer.



47. D-glyceraldehyde is shown below and, alongside it, by analogy, is the D-isomer of erythrulose.





48. It is dextrorotatory because it’s specific rotation has a “+” sign. Its enantiomer would have a specific rotation of -66.5^{o}. (laevorotatory , ∴ “-“, by the same amount)

49. A sample of the food colouring should be placed in a polarimeter to see whether it was optically active (that is whether it rotated the plane of polarisation of plane polarised light). If it turned out to be optically active then it would probably have came from a natural source as biosynthetic reactions tend to produce just one enantiomer of a substance capable of exxisting in two enantiomeric forms. If was optically inactive, it would most likely be synthetic as chemical synthesis usually produces a racemic mixture.

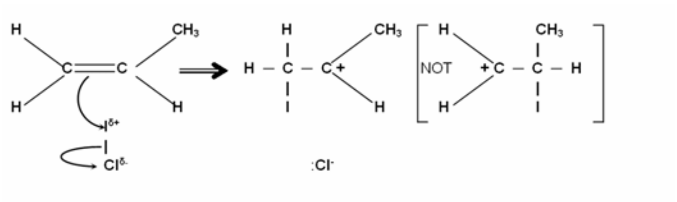
50. +(d)-carvone has the smell and taste of caraway; -(l)-carvone has the smell and taste of spearmint.

Page 497 Ex G1

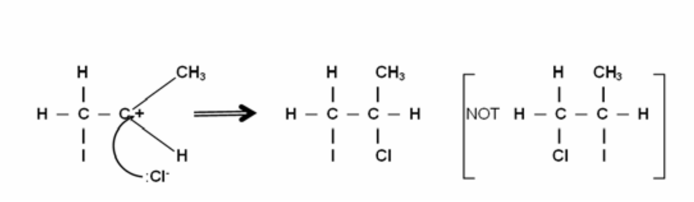
1. B

2. C

3. Iodine is less electronegative than chlorine and so it will have a partial positive charge as a result of the polarity of the chlorine-iodine bond. This means that the iodine atom is the one that attacks the double bond and the carbocation formed is the more stable secondary one rather than the less stable primary one:

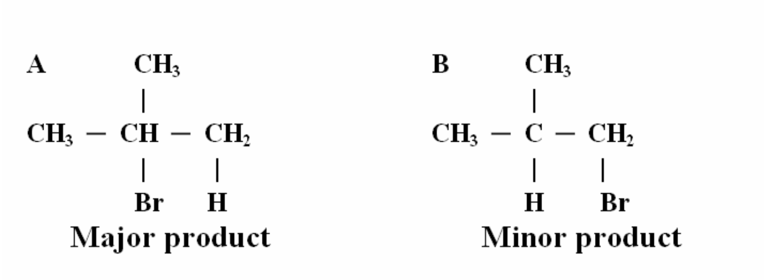


Then in the second stage, this carbocation will react with an anion present to complete the addition process:



Therefore the major product is CH_3-CHI-CH_2Cl not CH_3-CHCl-CH_2I.

4 (a)



(b) (i) Warm with aqueous sodium hydroxide

(ii) From A, methylpropan-2-ol, a tertiary alcohol will be formed.

From B, methylpropan-1-ol, a primary alcohol will be formed.

5. The reaction is:

$$CH_3\text{-}CH{=}CH_{2(g)} + H_2O_{(g)} \rightleftharpoons CH_3\text{-}CH(OH)\text{-}CH_{3(g)} \qquad \Delta H \text{ negative}$$

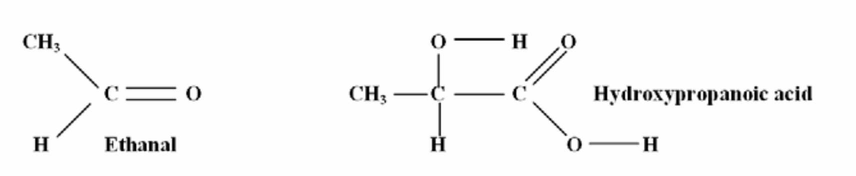
In the equilibrium two moles of gas are converted into one mole of gas, therefore a high pressure would favour a high yield of product, as Le Chatelier's principle predicts that an increase in pressure will shift the equilibrium to the side with the least moles of gas. Le Chatelier's principle also predicts that a decrease in temperature will shift the equilibrium in the exothermic direction, therefore a low temperature will produce a higher yield of product (but at a slower rate!).
In the initial step of the reaction a hydrogen ion adds on to the double bond. This can produce two possible carbocations:

$$CH_3\text{-}C^{+}H\text{-}CH_3 \text{ and } CH_3\text{-}CH_2\text{-}CH_2^{+}$$

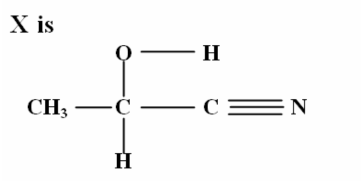
The former is a secondary carbocation and is therefore more stable than the latter which is a primary carbocation since the electron releasing inductive effect of the two methyl groups stabilises the positive charge more in the secondary carbocation. Propan-2-ol, the product from the reaction of the secondary carbocation with water, will therefore predominate.

Page 499 Ex G4

1. D
2. D
3. C
4 (a)

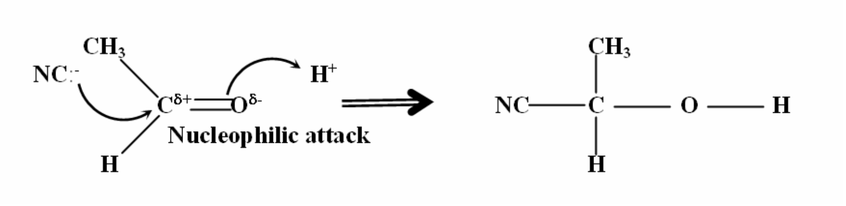


(b)



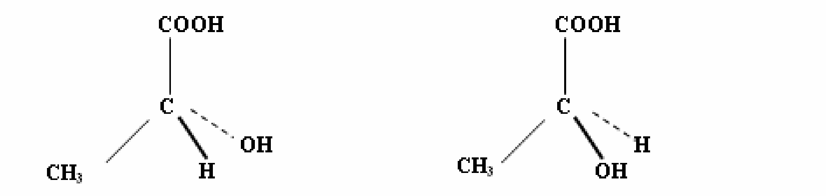
(c) Reflux ethanal with hydrocyanic acid (HCN) and a strong base catayst.

(d)



(e) Warm with dilute aqueous acid

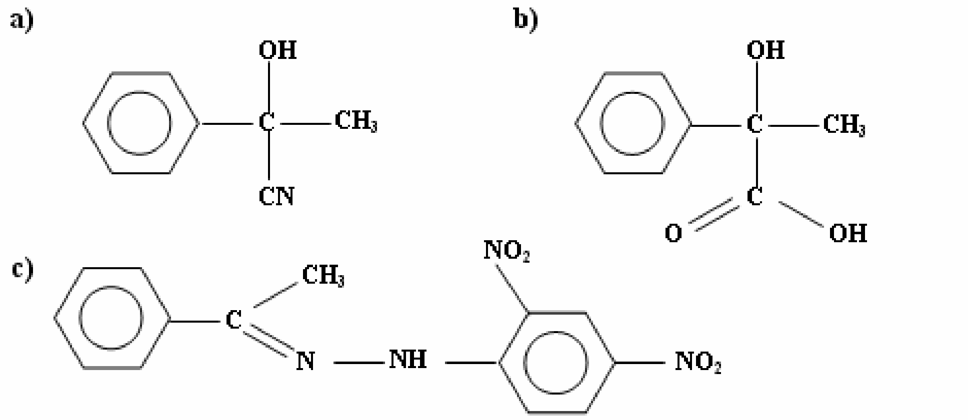
(f) Hydroxypropanoic acid contains an asymmetric carbon atom (one that is bonded to four different groups):



(g) Optical activity is the ability of a substance to rotate the plane of polarisation of plane polarised light. One of the two enantiomers above will rotate the light clockwise, the other anticlockwise.

(h) Which enantiomer is produced depends on whether the nucleophilic attack occurs from above or below the plane of the carbonyl group. As there are equal probabilities of the two attacks, equal amounts of the two products are produced (a racemic mixture). This has no effect on polarised light as the rotations of the two enantiomers cancel each other out.

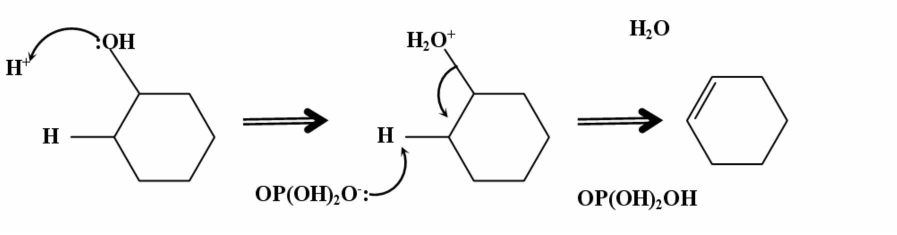
5.



Historically the melting points of these crystalline derivatives were used to identify aldehydes and ketones.

Page 500 Ex G3

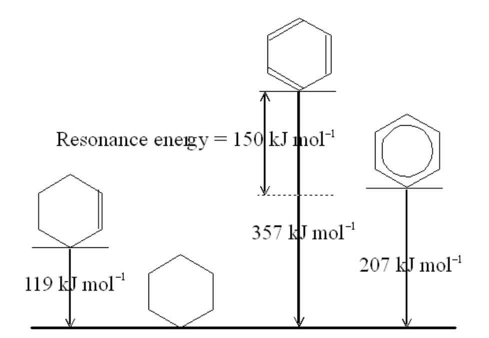
1. D
2. A
3.



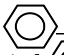
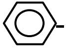
This reaction ocurs when cyclohexanol is heated with concentrated phosphoric acid. It can only yield on product because if the hydrogen removed was from the carbon going clockwise around the ring (rather than the one going anticlockwise as shown) the product would be identical.

Page 501,502 Ex G5

1. D
2. C
3. B
4.



As can be seen from the diagram, the enthalpy change for the hydrogenation of hexene is –119 kJ mol^{-1}. If benzene did indeed contain three separate double bonds, then the enthalpy of hydrogenation might be expected to be ~–357 kJ mol^{-1}. In fact experimentally it is found to be only –207 kJ mol^{-1}. This is taken as strong evidence for the delocalisation of π-bonds round the benzene ring and the fact that this leads to the molecule having much more thermodynamic stability (~150 kJ mol^{-1} more stable on this calculation) as a result.

5. It is found that halogens attached directly to a benzene ring are far more resistant to hydrolysis reactions than those attached to a hydrocarbon chain. This means that the –CH_2–Cl chlorinewill hydrolse far more easily than the –Cl chlorine. As a result warming 4-chloro(chloromethyl)benzene (Cl- -CH_2Cl) with aqueous sodium hydroxide would readily yield 4-chlorophenylmethanol (Cl- -CH_2OH), but a much more elborate synthesis would be required to produce 4-hydroxy(chloromethyl)benzene (HO- -CH_2Cl).

Page 503 Ex G6

1. B
2. C
3. A
4. The 1-bromobutane would be dissolved in ethoxyethane that had been dried by being stored over metallic sodium for a few days (this reacts with any traces of water) in a flask fitted with a reflux condenser. The magnesium turnings, dried by gently warming to ~100°C (Caution, magnesium burns!), are then added. If the reaction does not start within a few minutes, add a single small crystal of iodine, which can catalyse the reaction. Have an ice bath on hand to cool down the reaction, because once started it can become very vigorous. After the initial vigorous reaction has subsided, reflux gently on a water bath for about 30 minutes.
5. The starting material for this reaction would be pentan-3-one (C_2H_5-CO-C_2H_5), because this has ethyl groups on either side of the carbonyl (>C=O) group. If pentan-3-one is reacted with ethylmagnesium bromide then the ethyl group will add to the carbon of the carbonyl group and when the initial product is hydrolysed, 3-ethylpentan-3-ol will be the major product:

$$C_2H_5\text{-}MgX + C_2H_5\text{-}CO\text{-} C_2H_5 \ (+ \ H^+) \rightarrow C_2H_5\text{-}C(C_2H_5)_2\text{-}OH + Mg^{2+} + X^-$$

Page 504 Ex

1. To produce 2-hydroxypropanoic acid ($CH_3CH(OH)COOH$) from ethanal (CH_3CHO) requires the addition of an extra carbon. This can be done via a Grignard reagent (with carbon dioxide or ethanal) or through the formation of a nitrile, which is then hydrolysed. In this case as the starting material is a carbonyl compound rather than a halogenoalkane, the latter seems more appropriate and reaction with hydrogen cyanide, in the presence of a base catalyst, followed by hydrolysis of the cyanohydrin formed by heating with dilute sulfuric acid, should produce the required product:

$$CH_3CHO + HCN \rightarrow CH_3CH(OH)\text{-}CN$$

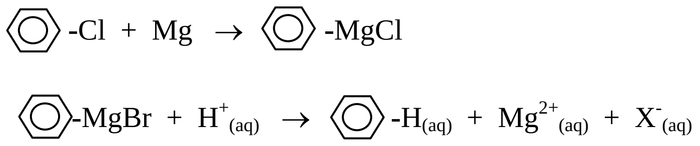
$$CH_3CH(OH)\text{-}CN + 2\ H_2O + H^+ \rightarrow CH_3CH(OH)\text{-}COOH + NH_4^+$$

2. To convert propanone (CH_3COCH_3) to methylpropan-2-ol ($CH_3C(CH_3)OHCH_3$) involves adding a methyl group to the carbonyl group. This could best be done by recting the propanone with methylmagnesium bromide and hydrolysing the product by warming with dilute acid:

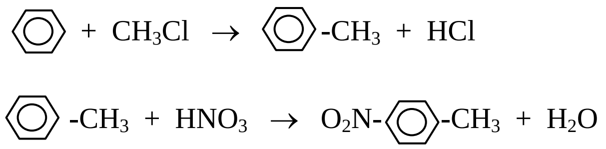
$$CH_3MgBr + (CH_3)_2C{=}O \rightarrow CH_3\text{-}C(CH_3)_2OMgBr$$

$$CH_3\text{-}C(CH_3)_2OMgBr + H^+_{(aq)} \rightarrow (CH_3)_3COH_{(aq)} + Mg^{2+}_{(aq)} + X^-_{(aq)}$$

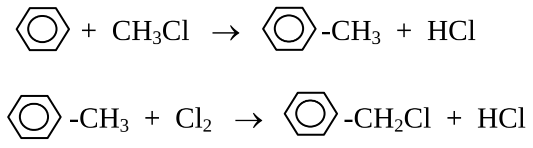
3. Hydrolysis of a halogen attached directly to a benzene ring is difficult, so therefore the only route accessible for the removal of these atoms is via a Grignard reagent, which they form readily when reacted with magnesium under anhydrous conditions. The hydrolysis of a Grignard reagent by warming with dilute acid will replace the magnesium by a hydrogen to give the required product:



4. This conversion requires the introduction of both a methyl group and a nitro group. It is probably better to introduce the methyl group first as this activates the benzene ring for the second reaction, rather than nitrating the ring which would deactivate it. Firstly react benzene with chloromethane with in the presence of an anhydrous aluminium chloride catalyst, to form methylbenzene. Then warm this with a mixture of concentrated nitric and sulfuric acids to nitrate the ring. This gives a mixture of the required product (4-nitromethylbenzene) and 2-nitromethylbenzene, which will therefore be the major impurity:



5. Initially the methyl group needs attaching to the benzene ring by reacting benzene with chloromethane with in the presence of an anhydrous aluminium chloride catalyst. There are two sets of conditions under which this may be chlorinated. The one that results in the desired sunbstitution of the side chain is th react the methylbenzene with chlorine in the presence of UV light to initiate a free radical chain reaction:



CHAPTER 18 (OPTION G) FURTHER ORGANIC CHEMISTRY

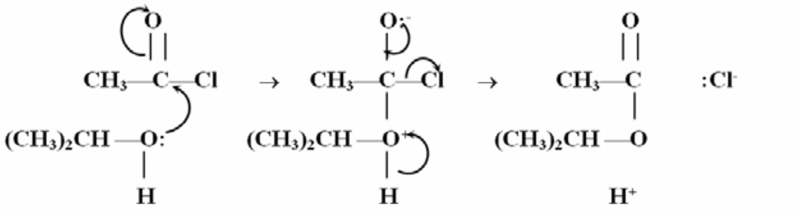
Page 505,506 Ex

1. D
2. D
3. A
4. The strength of the acid largely depends on the extent to which the anion becomes stable by reducing the charge on the oxygen atom. In ethanol the loss of a hydrogen ion would result in the negative charge being totally localised on the oxygen atom. The resulting ethoxide ion is not very stable, hence ethanol is not acidic. In phenol, a little of the charge can be distributed on to the benzene ring through the delocalised π–bond system, making phenol very weakly acidic. In ethanoic acid there is complete delocalisation of the charge between the two equivalent oxygen atoms of the ethanoate ion, hence it is a weak acid. In trichloroethanoic acid, the electron attracting inductive effect of the chlorine atoms further reduces the electrical charge on the oxygens with the result that it is quite a strong acid.
5. The strength of an acid is very dependent on the extent to which the negative charge on the carboxylate ion, formed when it dissociates, can be distributed away from the oxygen of the hydroxy group. Compared to a hydrogen atom, an alkyl group joined to a carbon donates electrons making the carbon slightly more negative. Therefore having an alkyl group, rather than a hydrogen, joined to the same carbon as the charged oxygens actually increases the negative charge on the carboxylate oxygens, making the ion less stable and hence the acid weaker. Conversely the strength of an amine is very dependent on the extent to which the positive charge on the nitrogen, which accepts a hydrogen ion, can be distributed away. In this case therefore an alkyl group donates electrons better than a hydrogen, reducing this charge, hence making the amine a stronger base.

Page 507 Ex G9

1. A
2. B
3. D (HCl is a product)
4. a) $(CH_3)_2CHOH + CH_3COCl \rightarrow (CH_3)_2CHOCOCH_3 + HCl$

   b)

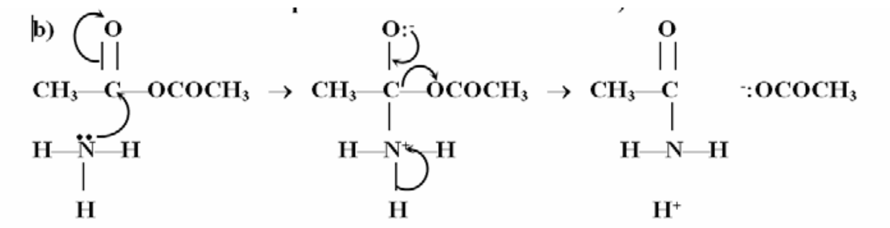


   c) Water would react with the ethanoyl chloride, even more vigorously than the alcohol, to produce ethanoic acid and hydrogen chloride

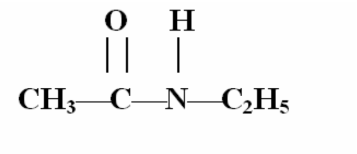
   d) Ethanoic anhydride would react in an almost identical manner giving CH_3COOH rather than HCl), but the reaction would be less vigorous.

5. a) $(CH_3CO)_2O + NH_3 \rightarrow CH_3CONH_2 + CH_3COOH$
The products are ethanamide (an amide) and ethanoic acid (which will react with excess ammonia to produce ammonium ethanoate)

b)



c) Two moles of ammonia would be required for each mole of ethanoic anhydride; one to give the ethanamide by the reaction above and one to neutralise the ethanoic acid that is also produced.
d) If ethylamine had been used, then the product would be N-ethylethanamide:

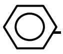


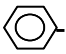
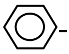
$CH_3—C(=O)—N(H)—C_2H_5$

Page 511 Ex

1. C

2. D

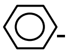
3. a) In the presence of UV light: $-CH_3 + Br_2 \rightarrow$  $-CH_2Br + HBr$

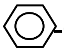
In the dark with a $FeBr_3$ catalyst: $-CH_3 + Br_2 \rightarrow$ Br- $-CH_3 + HBr$

(mixed with the 2-isomer)

b) The product of the first reaction is (bromomethyl)benzene  $-CH_2-Br$

Br

That of the second reaction a mixture of 2-bromomethylbenzene: $-CH_3$

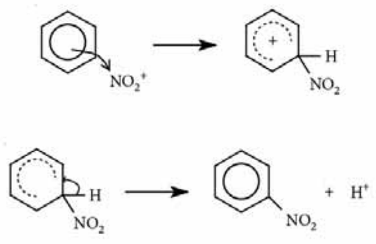
and 4-bromomethylbenzene: Br- $-CH_3$

c) The first reaction is a free radical chain substitution reaction. The second reaction is an electrophilic substitution reaction.

4. a) It is an electrophilic substitution reaction.

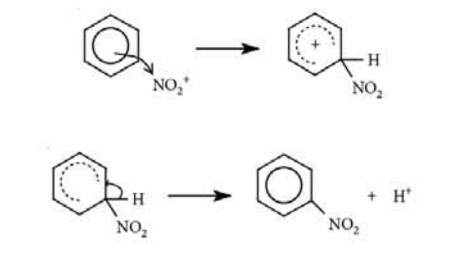
b) The reagent required is a mixture of concentrated sulphuric acid and concentrated nitric acid.

c)



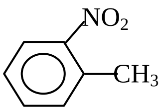
5. a) Phenol would be the most reactive, followed by methylbenzene, with benzene the least reactive. The reactivity of the benzene ring depends on the electron density in the delocalised π-bond. In phenol a lone pair of electrons from the oxygen is associated with the delocalised π-bond (mesomeric effect) and this greatly increases the electron density. An alkyl group is a better electron donor than a hydrogen atom (inductive effect), hence the electron density in the delocalised π-bond of methylbenzene is slightly greater than that in benzene.

b)

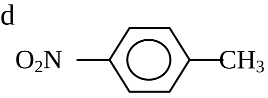


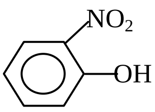
c) The replacement of a second hydrogen would take place less readily because the nitro group is electron withdrawing, reducing the electron density in the delocalised π-bond and hence the reactivity.

d) Methylbenzene and phenol would both give mixtures of the 2- and 4- isomers:
From methylbenzene: From phenol:

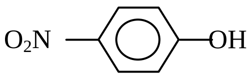


and

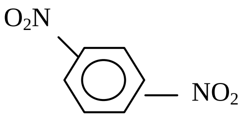




and

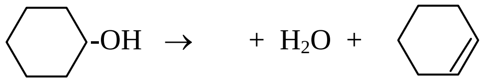


Nitrobenzene on the other hand would give 1.3-dinitrobenzene:

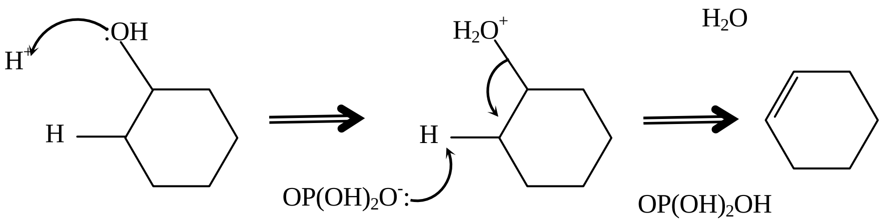


Page 511,512 General Exercises

1. An example of an elimination reaction would be the dehydration of cyclohexanol to form cyclohexene, catalysed by concentrated phosphoric acid:



The mechanism is:

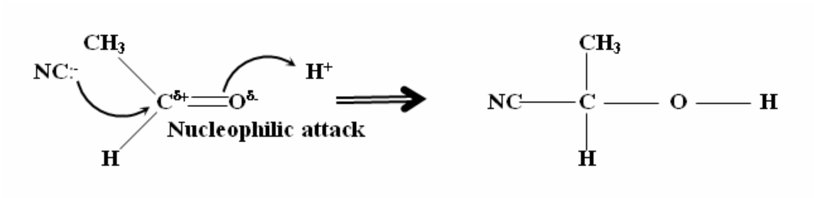


An example of a nucleophilic addition reaction would be the reaction of hydrogen cyanide with ethanal in the presence of a base catalyst ($:B^-$):

$$CH_3CHO + HCN \rightarrow CH_3CH(OH)CN$$

The mechanism is:

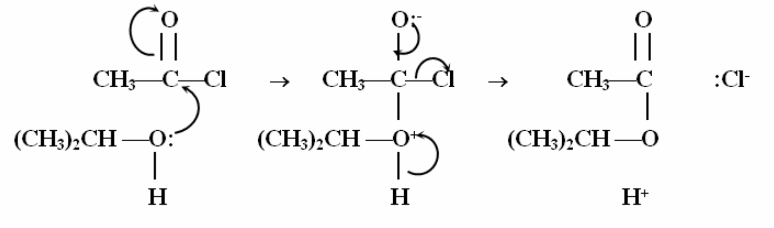
$$N{\equiv}C\text{-}H + :B^- \rightleftharpoons N{\equiv}C^-: + H\text{-}B$$



An example of an addition elimination reaction would be that of ethanoyl chloride with propan-2-ol:

$$(CH_3)_2CHOH + CH_3COCl \rightarrow (CH_3)_2CHOCOCH_3 + HCl$$

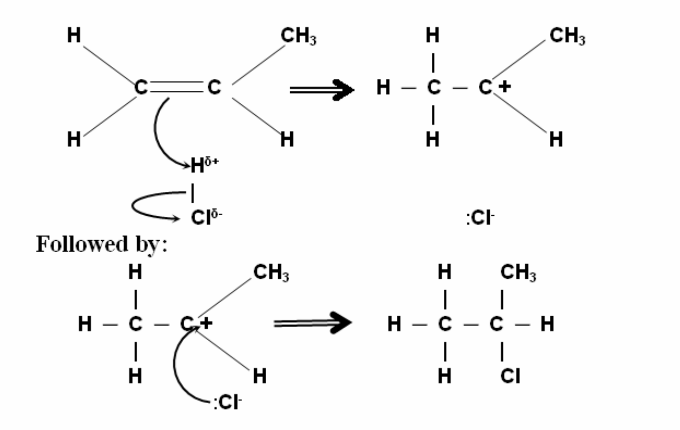
The mechanism is:



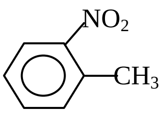
An example of an electrophilic addition reaction would be that of propene with hydrogen chloride:

$$CH_3\text{-}CH{=}CH_2 + HCl \rightarrow CH_3\text{-}CHCl\text{-}CH_3$$

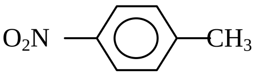
The mechanism is:



2. a) $C_3H_7\text{-}CH(OH)\text{-}C_2H_5$
   b) $C_2H_5\text{–}C{=}N\text{-}NH\text{-}C_6H_3(NO_2)_2$
   c) $C_3H_7\text{-}C(CH_3)OH\text{-}C_2H_5$
   (assuming that it should have read butan-2-one, not butan-2-ol!)
   d) CH_3CONH_2
   e)



and



3. a) There would be an evolution of bubbles of gas. (methane is a product)
   b) A bright orange-yellow crystalline product would form.
   c) Again bubbles of gas would be evolved. (propene is formed)

4. a) Methylamine acts as a weak base and forms an alkaline aqueous solution:

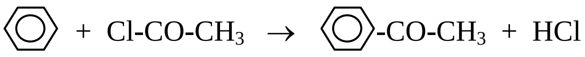
   $CH_3\text{-}NH_2 + H_2O \rightleftharpoons CH_3\text{-}NH_3^+ + OH^-$

   b) The methylammonium ion in the salt reacts with the hydroxide ions to release free methylamine, which has a fishy smell:

   $CH_3\text{-}NH_3^+ + OH^- \rightarrow R\text{-}NH_2 + H_2O$

   c) In ethanamide (CH_3CONH_2) there is hydrogen bonding between the hydrogens of the NH_2 group and the lone pairs on the carbonyl oxygen (>C=O:) leading to strong intermolecular forces.
   d) The strength of an amine is very dependent on the extent to which the positive charge on the nitrogen, which accepts a hydrogen ion, can be distributed away. An alkyl group donates electrons better than a hydrogen, reducing this charge, therefore the more alkyl groups there are attached to the nitrogen atom, the stronger the resulting base. Hence trimethylamine is a stronger base than methylamine.
   In ethanamide, the lone pair of the $-NH_2$ group is involved with the π-bond between the carbon and the oxygen to give a delocalised π-bond. This it means it is not available for donation so amides do not behave as bases.

5. a) Phenylethanone can be prepared by refluxing benzene with ethanoyl chloride in the presence of an anhydrous aluminium chloride catalyst:



   b) By adding a solution of 2.4-dinitrophenylhydrazine. Aldehydes and ketones both give an orange-yellow precipitate with this reagent. Showing that it is not oxidised by potassium dichromate(VI), as the colour would remain orange rather than going green, would show that it was not an aldehyde.
   c) The product would be a tertiary alcohol as shown: