

FOR USE WITH IB DIPLOMA SCIENCE

# Chemistry

Version 1.0 August 2014

# Preface



This resource supplements the text:

Chemistry 4th Edition by Green & Damji.

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published in print form by IBID Press.

It is not intended to be a stand alone resource for the IB Diploma Course.

We have produced this resource to provide a few of the things that are difficult to include in print media:

- 3D material.
- Additional photographs.
- Enlargements of the more detailed diagrams from the text.
- Internet links.

The main intention of this resource is to support the cross-curricular objectives of the IB Diploma courses. Students will be challenged to address the historical aspects of science, the mathematical background of the sciences and the over-arching principle that the pursuit of knowledge is a powerful human drive.



Chapter 1

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# Stoichiometry

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Chemical changes are evident in the camp-fire.



# Chemical Compounds

## KEY UNDERSTANDING

1. Atoms of different elements combine in fixed ratios to form compounds

## Compounds and Mixtures

If you mix soil and water, you get mud. You can mix these components in any proportion to get wet mud...



## Additional Material

or dry(ish) mud



The two components (soil and water) are easy to separate - the water often just evaporates.

Compounds are different.

For example, carbon (a solid) burns in oxygen (a gas) to form carbon dioxide (a gas).

Separating these components is difficult.

Most importantly, however, the components combine in fixed ratio (by weight).

### Interactive 1.1 Carbon Dioxide

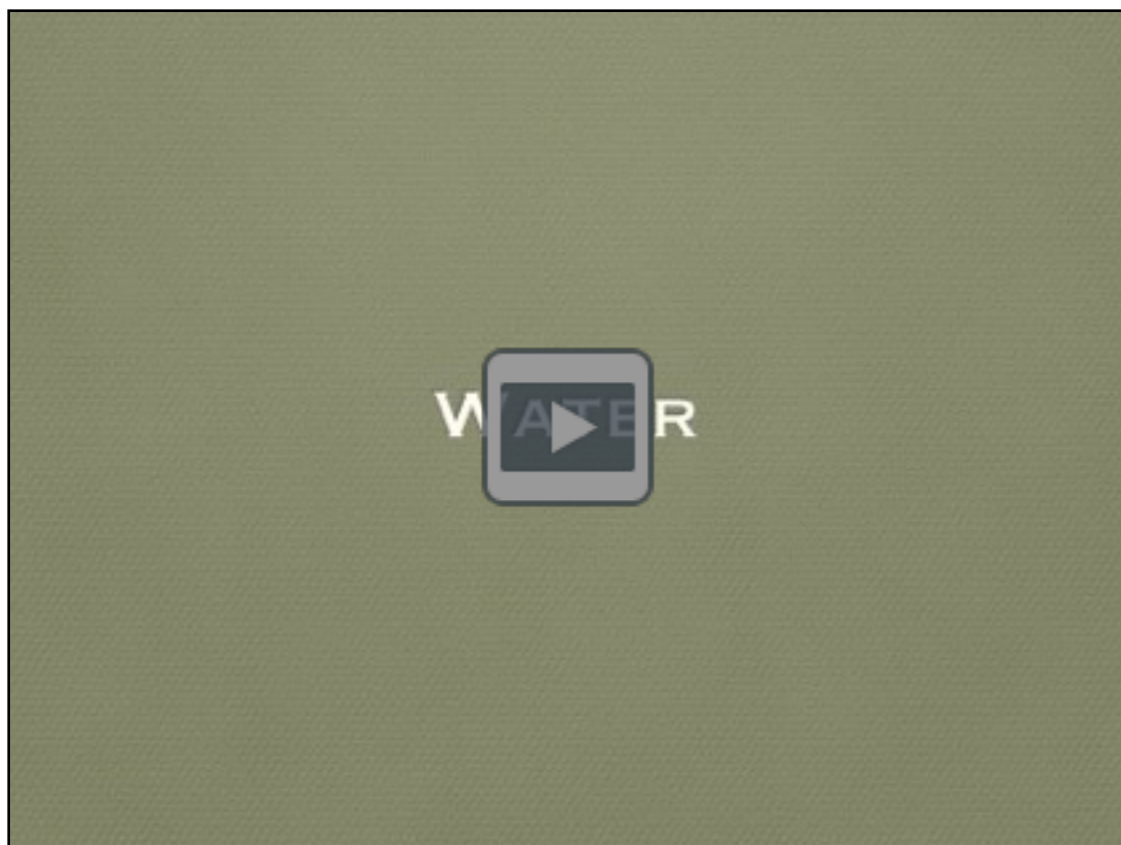


*The chemical reaction between carbon and oxygen.*

What happens if hydrogen combines with oxygen?

We get the sinister sounding dihydrogen monoxide - otherwise known as water.

## Interactive 1.2 Water



*The chemical reaction between hydrogen and oxygen*

So the ratios are:

When carbon reacts with oxygen:

By number of atoms:

carbon:oxygen

1:2

By weight:

carbon:oxygen

3:8

When hydrogen reacts with oxygen:

By number of atoms:

hydrogen:oxygen

2:1

By weight:

hydrogen:oxygen

1:8

What should happen when carbon reacts with hydrogen?

As far as numbers of atoms are concerned:

carbon:oxygen : 1 : 2

hydrogen:oxygen : 2 : 1 = 4 : 2

We have made the ratio number for oxygen 2 in both so that you can see that the carbon hydrogen ratio should be 1 : 4 in terms of atoms.

By weight:

carbon:oxygen : 3 : 8

hydrogen:oxygen : 1 : 8

Thus the compound of carbon and hydrogen should be  $\text{CH}_4$  and its weight proportion C:H should be 3:1

This compound is methane and it has the properties predicted.

These conclusions were originally arrived at in the reverse direction.

The simple ratios were observed experimentally and the conclusion was reached must be that:

Matter is atomic.

Atoms combine in simple ratios.

We are simplifying a complex subject.

The details are in the text.

Now read on...

One of the pioneers of these studies was Henry Cavendish FRS (1731 – 1810).

The Cavendish family were (and are!) wealthy and built the splendid Chatsworth House in England. In addition to direct contributions to science, they founded the Cavendish Laboratory at Cambridge University. This has been one of the most significant centres of scientific research in the World.

**Gallery 1.1** Chatsworth House



*Worth a visit!*





# Answers to exercises

## EXERCISE 1-A

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.

## EXERCISE 1-B

1. A 2. C 3. D

4. a)  $\text{H}_2\text{SO}_4$ , b)  $\text{NaOH}$ , c)  $\text{HNO}_3$ , d)  $\text{NH}_3$ , e)  $\text{HCl}$ ,

f)  $\text{CH}_3\text{COOH}$ , g)  $\text{CuSO}_4$ , h)  $\text{CO}$ , i)  $\text{SO}_2$ , j)  $\text{NaHCO}_3$

5. a)  $\text{NaCl}$  b)  $\text{CuS}$  c)  $\text{ZnSO}_4$  d)  $\text{Al}_2\text{O}_3$  e)  $\text{Mg}(\text{NO}_3)_2$

f)  $\text{Ca}_3(\text{PO}_4)_2$  g)  $\text{HI}$  h)  $(\text{NH}_4)_2\text{CO}_3$  i)  $\text{CH}_4$  j)  $\text{PCl}_5$

## EXERCISE 1-C

1. C 2. B 3. A

4. a)  $\text{CaO} + 2 \text{HNO}_3 \rightarrow \text{Ca}(\text{NO}_3)_2 + \text{H}_2\text{O}$  b)  $2 \text{NH}_3 + \text{H}_2\text{SO}_4 \rightarrow (\text{NH}_4)_2\text{SO}_4$

c)  $2 \text{HCl} + \text{ZnCO}_3 \rightarrow \text{ZnCl}_2 + \text{H}_2\text{O} + \text{CO}_2$  d)  $\text{SO}_2 + 2 \text{Mg} \rightarrow \text{S} + 2\text{MgO}$

e)  $\text{Fe}_3\text{O}_4 + 4 \text{H}_2 \rightarrow 3 \text{Fe} + 4\text{H}_2\text{O}$  f)  $2 \text{K} + 2 \text{C}_2\text{H}_5\text{OH} \rightarrow 2 \text{KC}_2\text{H}_5\text{O} + \text{H}_2$

g)  $2 \text{Fe}(\text{OH})_3 \rightarrow \text{Fe}_2\text{O}_3 + 3 \text{H}_2\text{O}$  h)  $\text{CH}_3\text{CO}_2\text{H} + 2 \text{O}_2 \rightarrow 2 \text{CO}_2 + 2 \text{H}_2\text{O}$

i)  $2 \text{Pb}(\text{NO}_3)_2 \rightarrow 2 \text{PbO} + 4 \text{NO}_2 + \text{O}_2$

j)  $2 \text{NaMnO}_4 + 16 \text{HCl} \rightarrow 2 \text{NaCl} + 2 \text{MnCl}_2 + 5 \text{Cl}_2 + 8 \text{H}_2\text{O}$

5. a)  $\text{CuCO}_3 \rightarrow \text{CuO} + \text{CO}_2$  b)  $\text{NiO} + \text{H}_2\text{SO}_4 \rightarrow \text{NiSO}_4 + \text{H}_2\text{O}$

c)  $2 \text{Fe} + 3 \text{Br}_2 \rightarrow 2 \text{FeBr}_3$  d)  $\text{PbO}_2 + 2 \text{CO} \rightarrow \text{Pb} + 2 \text{CO}_2$

e)  $2 \text{FeCl}_2 + \text{Cl}_2 \rightarrow 2 \text{FeCl}_3$  f)  $\text{C}_2\text{H}_5\text{OH} + 3 \text{O}_2 \rightarrow 2 \text{CO}_2 + 3 \text{H}_2\text{O}$

g)  $\text{Ag} + 2 \text{HNO}_3 \rightarrow \text{AgNO}_3 + \text{NO}_2 + \text{H}_2\text{O}$

h)  $\text{MnO}_2 + 4\text{HCl} \rightarrow \text{MnCl}_2 + \text{Cl}_2 + 2\text{H}_2\text{O}$

i)  $\text{SO}_2 + 2\text{H}_2\text{S} \rightarrow 3\text{S} + 2\text{H}_2\text{O}$  j)  $4\text{NH}_3 + 5\text{O}_2 \rightarrow 4\text{NO} + 6\text{H}_2\text{O}$

## EXERCISE 1-D

1. D 2. C 3. C 4. D 5. C 6. D x

7. a) 0.20 b)  $1.2 \times 10^{23}$  c)  $3.6 \times 10^{23}$  8. a)  $3.61 \times 10^{24}$  b)  $5.4 \times 10^{23}$

### EXERCISE 1-E

1. D 2. A 3. B 4. D 5. A 6. B 7. A

8 a) 127.9 b) 106.4 c) 132.1 d) 126.1 e) 152.0 f) 233.3

9. a) 51.1 g, b) 7.47 g, c) 10.7 g, d) 68.7 g, e) 1.90 g

10. a) 1.00, b) 3.00, c) 25.8, d) 5.44

11. a) 150 g mol<sup>-1</sup>, b) 128 g mol<sup>-1</sup>

12. 1.245x10<sup>23</sup> molecules

13. a) 3.41x10<sup>-4</sup>, b) 5.68x10<sup>-3</sup> mol c) 2.05x10<sup>22</sup>

### EXERCISE 1-F

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<sub>2</sub>O<sub>3</sub> b) SiF<sub>4</sub> c) C<sub>2</sub>H<sub>2</sub>O<sub>4</sub> 13. SnO<sub>2</sub> 14. CuSO<sub>4</sub>.5H<sub>2</sub>O

15. 66700 g mol<sup>-1</sup> 16. K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>

17. 354.5; 47.4% carbon, 2.56% hydrogen, 50.0% chlorine 18. 56.7%

### EXERCISE 1-G

1. C 2. B 3. a) 2 KClO<sub>3(s)</sub> → 2 KCl<sub>(s)</sub> + 3 O<sub>2(g)</sub> b) 0.4 mol c) 2.45 g

4. 37.69 g 5. a) MnO<sub>2</sub> ; Mn<sub>3</sub>O<sub>4</sub>, b) 3 MnO<sub>2</sub> → Mn<sub>3</sub>O<sub>4</sub> + O<sub>2</sub>, c) 0.353 g

### EXERCISE 1-H

1. a) Limiting reagent is Al, yield is 1.2 mol,

b) Limiting reagent is I<sub>2</sub>, yield is 2.57 g c) 1.03 g excess aluminium

2. a) Limiting reagent is SbF<sub>3</sub>, CCl<sub>4</sub> 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%

### EXERCISE 1-J

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

6. 30 cm<sup>3</sup> of oxygen remains unreacted 7. 1.20 x 10<sup>23</sup> 8. 47.4 g mol<sup>-1</sup>

9. 0.749 g dm<sup>-3</sup> 10. 2.27 x 10<sup>5</sup> dm<sup>3</sup> (224 m<sup>3</sup>)

### EXERCISE 1-K

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

7. a) 0.0139 mol, b) 83.2%

8. a) 1120 dm<sup>3</sup> b) 100 g (n.b. H<sub>2</sub>)

9. Mass of gas in flask = 4.685 + 0.924 = 5.609 g; (allowing for buoyancy)

Volume of flask (assuming density of water = 1 kg dm<sup>-3</sup>) = 0.8043 dm<sup>3</sup>;

The flask contains 0.03195 mol at this T & P,

Molar mass = 175.6 g mol<sup>-1</sup>.

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.

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

### EXERCISE 1-L

1. A 2. D 3. B

4. a) 0.75 mol dm<sup>-3</sup> b) 0.0250 mol dm<sup>-3</sup> c) 0.0811 mol dm<sup>-3</sup>

5. a) 2.1 mol, b) 0.0020 mol, c) 2.55x10<sup>-3</sup> mol

6. a) 0.4 dm<sup>-3</sup> b) 2.94 dm<sup>-3</sup> c) 0.720 dm<sup>-3</sup> (=720 cm<sup>-3</sup>)

7. Weigh out precisely 2.922 g of solid sodium chloride (0.0500 mol) and make it up to 500 cm<sup>3</sup> of solution in a 500 cm<sup>3</sup> volumetric flask.

8. Measure out 240 cm<sup>3</sup> of 2.0 mol dm<sup>-3</sup> hydrochloric acid (0.48 mol) and make this up to 1.2 dm<sup>3</sup> of solution.

9. 1.25 mol dm<sup>-3</sup>

10. [NO<sub>3</sub><sup>-</sup>] = 0.8 mol dm<sup>-3</sup>, [Cl<sup>-</sup>] = 0 mol dm<sup>-3</sup>, [H<sup>+</sup>] = 0.4 mol dm<sup>-3</sup>, [Pb<sup>2+</sup>] = 0.2 mol dm<sup>-3</sup>

### EXERCISE 1-M

1. C 2. A 3. D

4. a) 0.0125 mol, b) 0.0125 mol, c) 0.630 mol dm<sup>-3</sup>

5. a) 3.75x10<sup>-4</sup> mol, b) 1.875x10<sup>-4</sup> mol, c) 0.556 g dm<sup>-3</sup>

6. a) Ag<sup>+</sup>(aq) + Cl<sup>-</sup>(aq) → AgCl(s), b) 4.00x10<sup>-3</sup> mol, c) 2.00·10<sup>-3</sup> mol, d) 90.66%

7 a) 5.01x10<sup>-4</sup> mol, b) 2.51x10<sup>-3</sup> mol, c) 0.711 g, d) 0.268 g, x = 6

8 a) 9.46 mol dm<sup>-3</sup>, b) 105.7 cm<sup>3</sup>

9 a) 6 Fe<sup>2+</sup>(aq) + Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup>(aq) + 14 H<sup>+</sup>(aq) → 6 Fe<sup>3+</sup>(aq) + 2 Cr<sup>3+</sup>(aq) + 7 H<sub>2</sub>O(l),

b)  $3.74 \times 10^{-4}$  mol, c)  $2.24 \cdot 10^{-3}$  mol, d) 96.4%

10.  $122 \text{ g mol}^{-1}$ , possibly benzoic acid ( $\text{C}_6\text{H}_5\text{COOH}$ )

### EXERCISE 1-N

1. a) 0.0050 mol, b) 0.010 mol, c) 0.005 mol, 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)  $12.0 \text{ g mol}^{-1}$  b)  $24.0 \text{ g mol}^{-1}$  c)  $36.0 \text{ g mol}^{-1}$ .

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

### EXERCISE 1-P

1. C 2. C 3. A

4. a)  $4.376 \times 10^5$ , b)  $2.3 \times 10^{-7}$ , c)  $4.15 \times 10^8$ , d)  $3.72 \times 10^{-2}$ , e)  $4.768 \times 10^2$ , f)  $3.26 \times 10^0$

5. a) 820000, b) 0.00629, c) 271 380 000 000, d) 0.0000002, e) 42, f) 0.589

### EXERCISE 1-Q

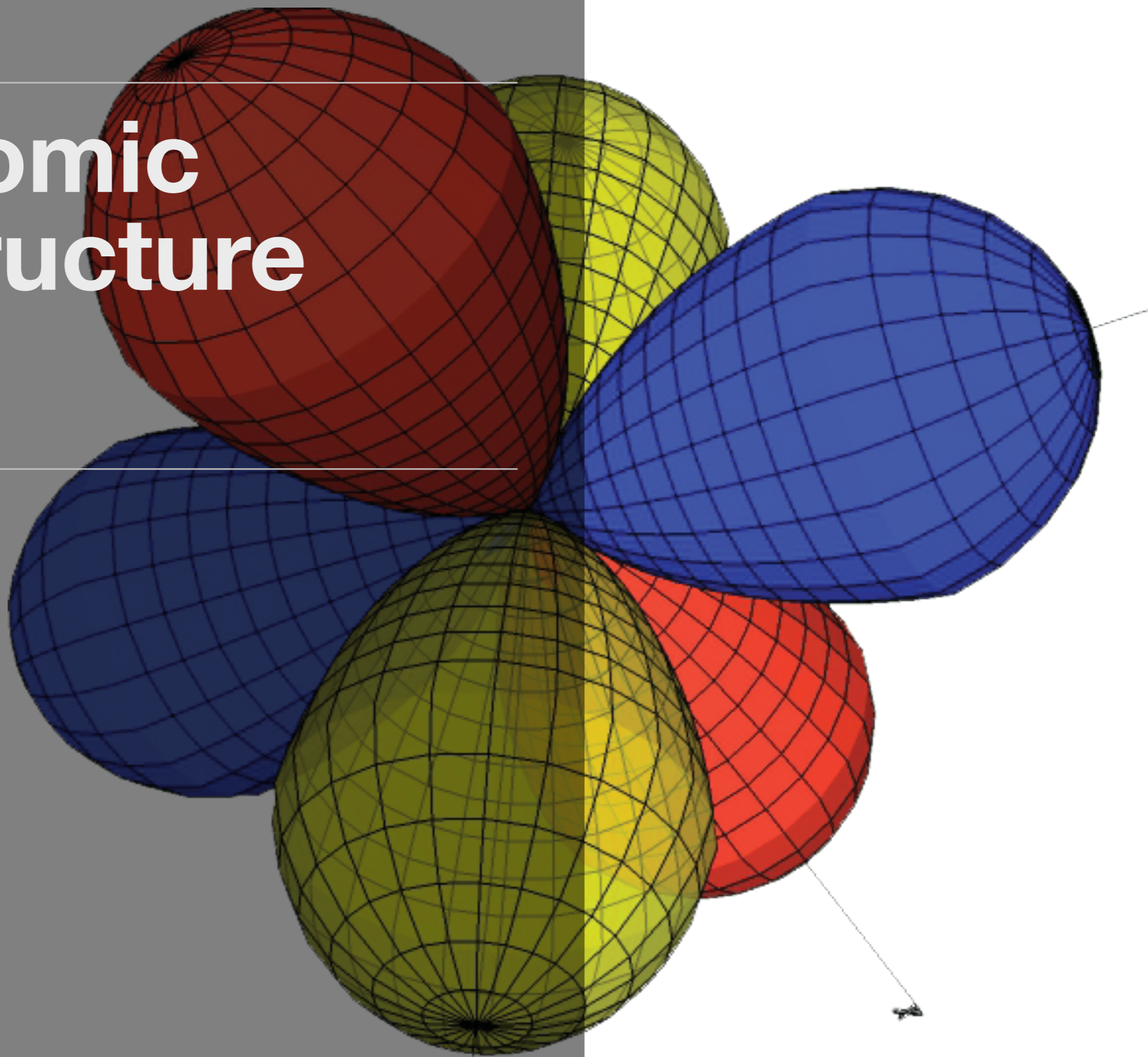
1. B 2. D 3. B 4. B

5 a) 0.028, b) 28, c)  $3.76 \cdot 10^5$ , d) 0.00175, e)  $2 \times 10^9$

Chapter 2

# Atomic Structure

p-orbitals



# Atomic Structure

## CONTENTS

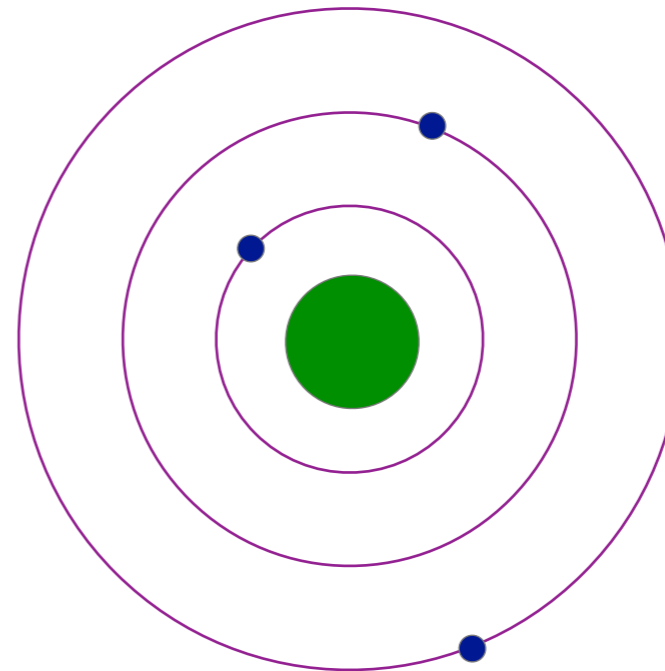
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1. 2.1 The Nuclear Atom
2. 2.2 Electron configuration
3. 12.1 Electrons in atoms

## Electron orbitals

The atom cannot be 'seen'. All our models are visualisations.

One of the simplest is the planetary model in which the nucleus is seen as a 'sun' and the electrons as 'planets' moving in orbits:



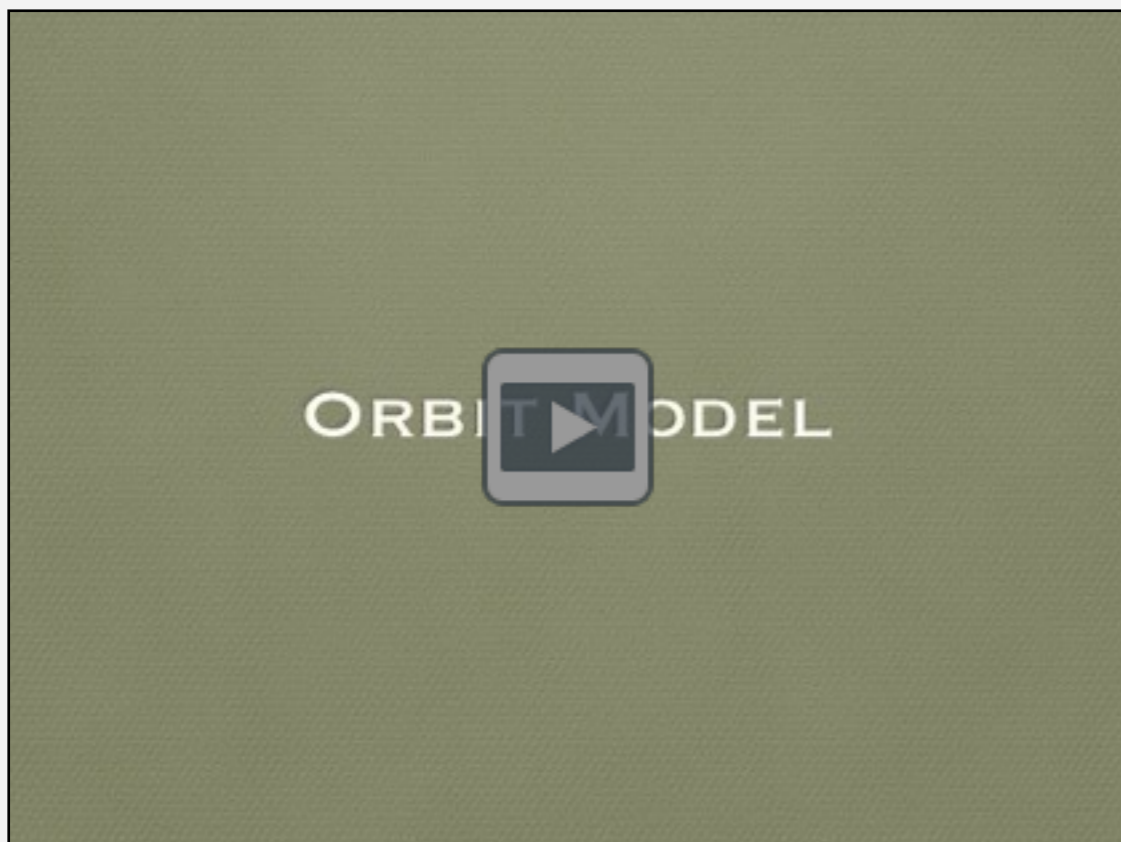
This model does not represent reality for a variety of reasons. Chief amongst these is that the particles do not really behave like minute balls.

## Additional Material

However, as a preliminary view, it does allow an explanation of line spectra.

It runs a bit like this...

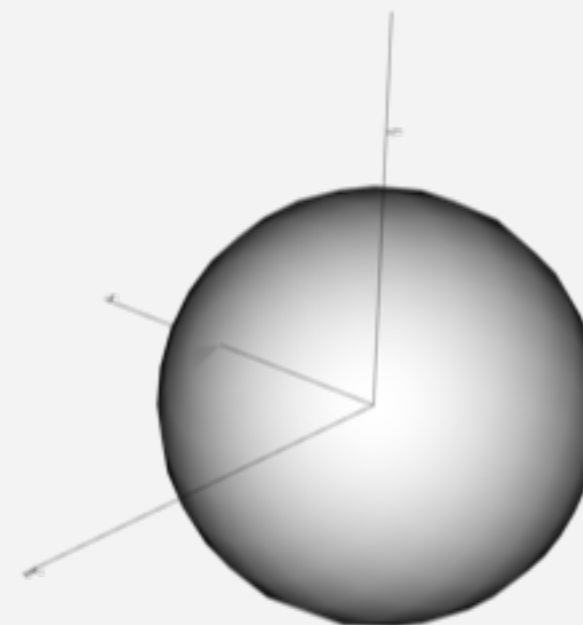
### Interactive 2.1 The orbital model.



A somewhat more sophisticated visualisation is the 'orbital model'. Here, the electrons are visualised as clouds - if you can see a single object as a 'cloud'!

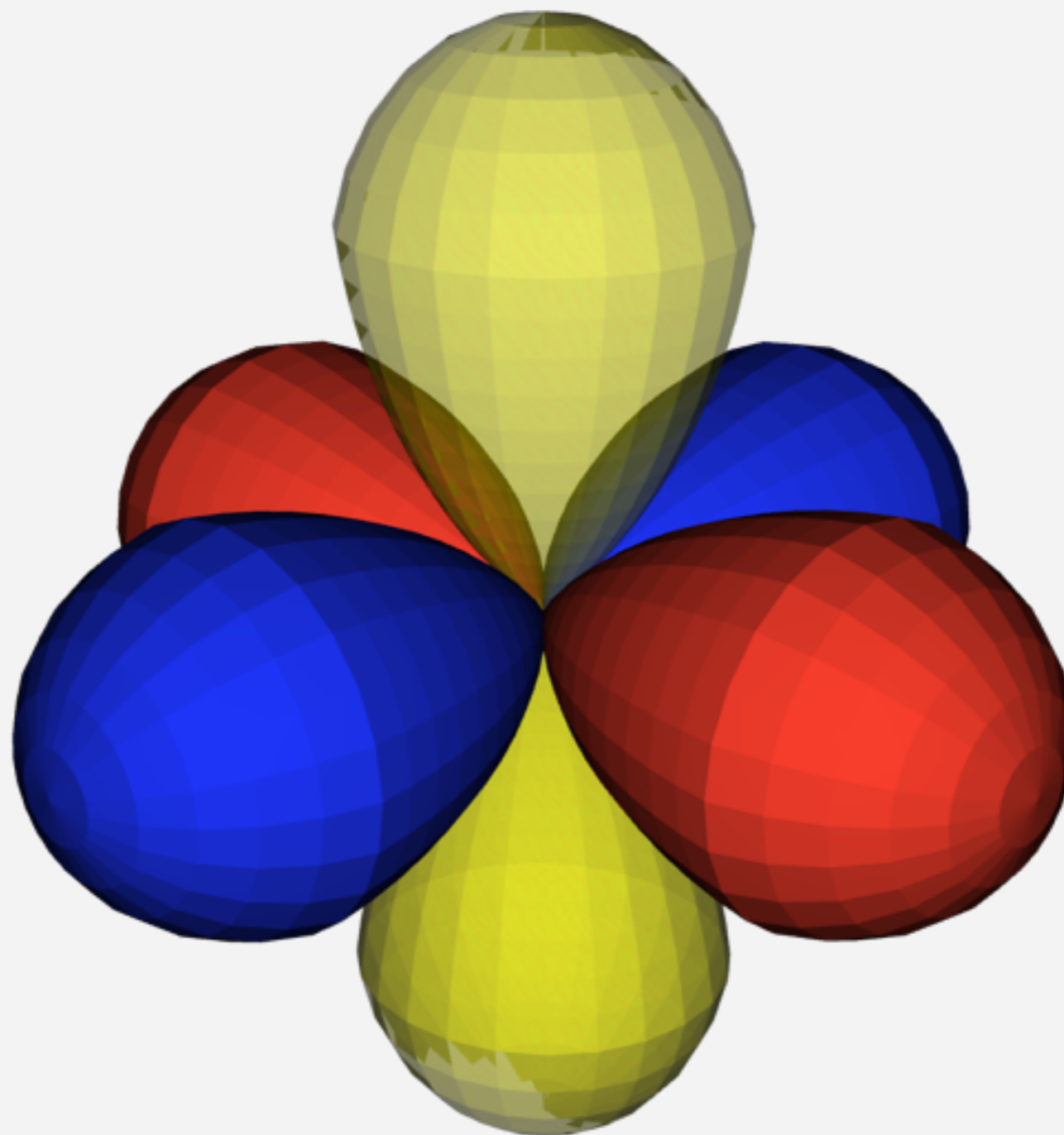
The simplest orbital is the spherical s-orbital.

### Interactive 2.2 The s-orbital



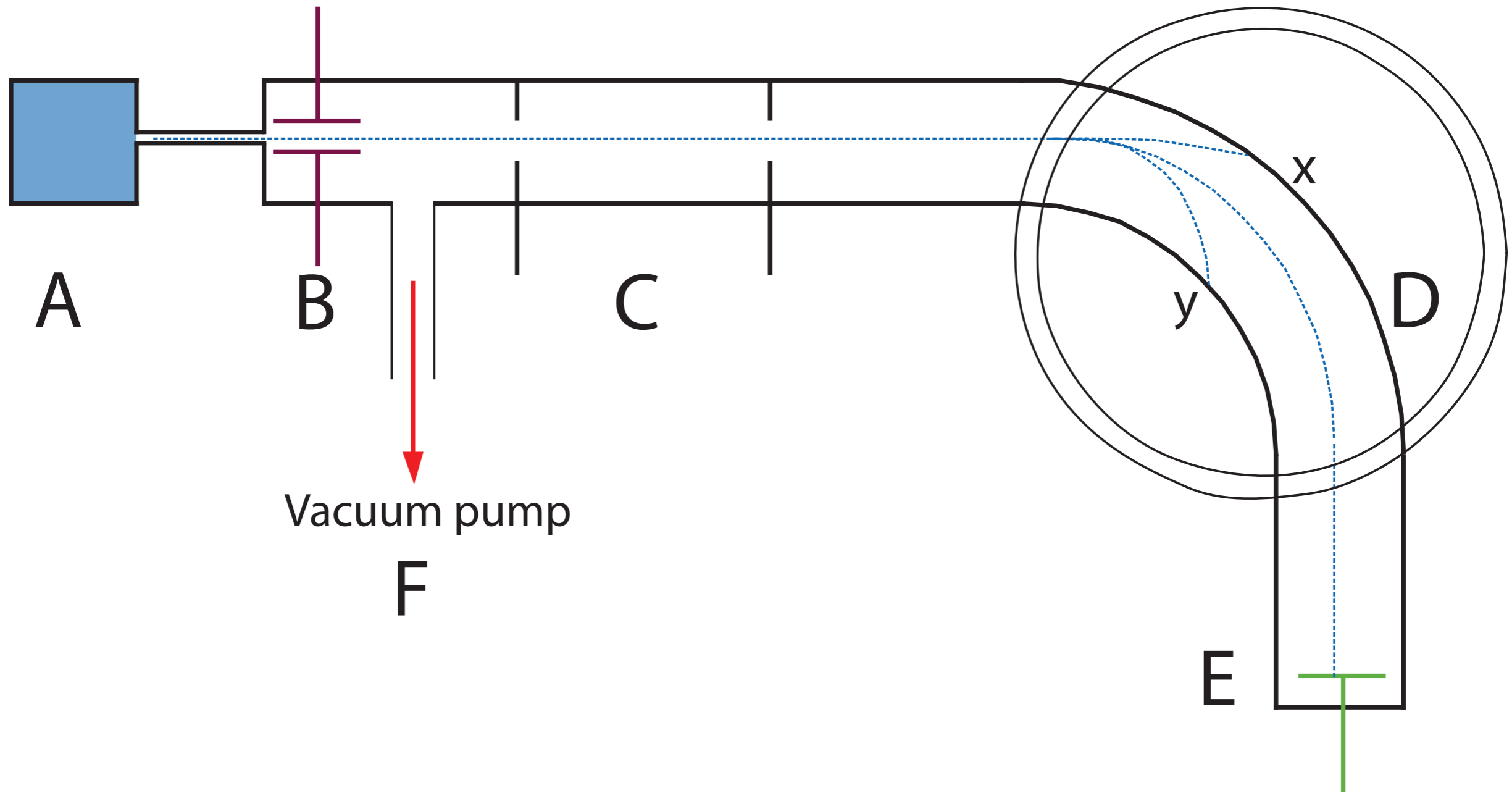
The p-orbitals are visualised as these barbell shapes.

**Interactive 2.3** The p-orbitals





Schematic of a mass spectrometer.



# Answers to exercises

## EXERCISE 2-A

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

6. a) electron; b) neutron; c) electron; d) proton; e) electron

7.

Element	Mass No.	Protons	Neutrons	Electrons
Helium	4	<b>2</b>	<b>2</b>	<b>2</b>
Nitrogen	14	<b>7</b>	<b>7</b>	<b>7</b>
Aluminium	27	<b>13</b>	<b>14</b>	<b>13</b>
Manganese	55	<b>25</b>	<b>30</b>	<b>25</b>
Iodine	127	<b>53</b>	<b>74</b>	<b>53</b>

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  $^{10}_5\text{B}$  and  $^{11}_5\text{B}$

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	<b>29</b>	<b>29</b>	<b>63</b>
Isotope 2	<b>29</b>	<b>36</b>	<b>29</b>	<b>29</b>	<b>65</b>

therefore 72.5%  $^{63}\text{Cu}$  and 27.5%  $^{65}\text{Cu}$

11.

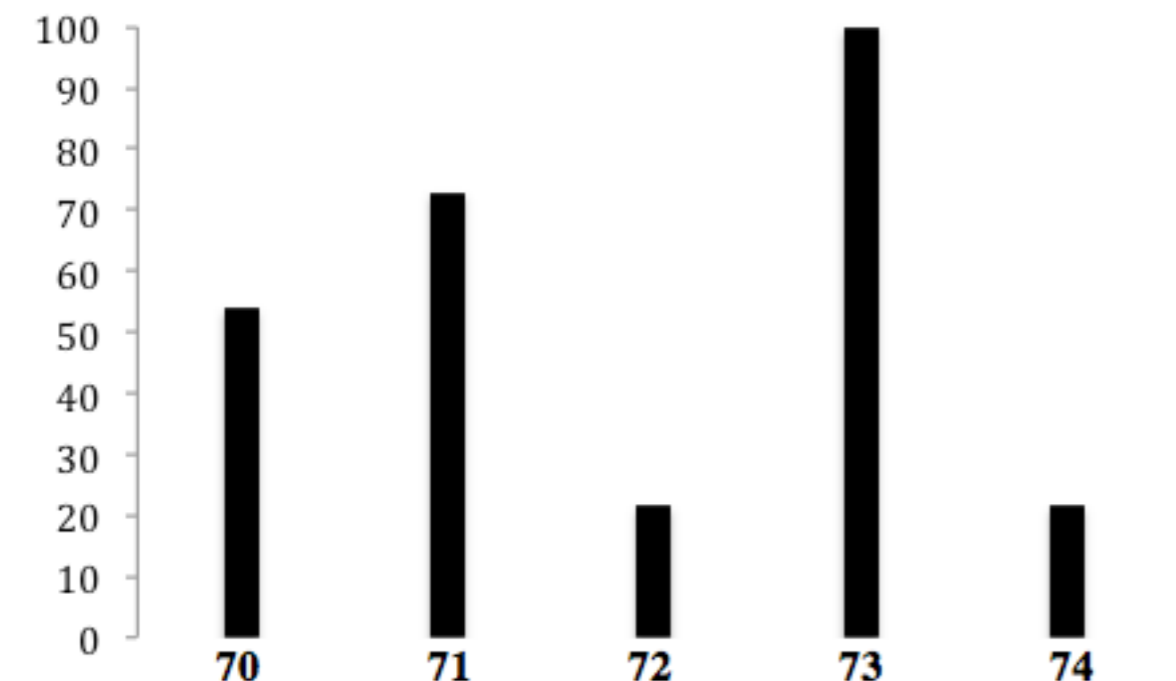
Isotope	Number of		
	protons	neutrons	electrons
	<b>1</b>	<b>2</b>	<b>1</b>
	<b>7</b>	<b>8</b>	<b>7</b>
	<b>26</b>	<b>31</b>	<b>26</b>
	<b>38</b>	<b>52</b>	<b>38</b>
	<b>92</b>	<b>143</b>	<b>92</b>

12.

Species	Number of		
	protons	neutrons	electrons
-	<b>1</b>	<b>2</b>	<b>1</b>
2+	<b>12</b>	<b>12</b>	<b>10</b>
3+	13	14	10
2-	16	18	18
<b>Ti</b> 4+	22	26	<b>18</b>

## EXERCISE 2-B

1.



2. a)

${}_{76}^{188}\text{Os}$	14%
${}_{76}^{189}\text{Os}$	17%
${}_{76}^{190}\text{Os}$	27%
${}_{76}^{192}\text{Os}$	42%

$$\text{b) } (188 \times 0.14) + (189 \times 0.17) + (190 \times 0.27) + (192 \times 0.42) = 190.39$$

$$3. (70 \times 0.20) + (71 \times 0.27) + (72 \times 0.080) + (73 \times 0.37) + (74 \times 0.080) = 71.86$$

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

$$206(100 - 2y) + 207y + 208y = 207.2 \times 100$$

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

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

5. Bromine is composed of two stable isotopes,  ${}^{79}\text{Br}$  and  ${}^{81}\text{Br}$ , but these are present in almost exactly equal proportions, so that its relative atomic mass is almost exactly 80.

## EXERCISE 2-C

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

6. 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.

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.

## EXERCISE 2-D

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

6. a)  $1s^2 2s^2$  b)  $1s^2 2s^2 2p^1$  c)  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^1 4s^2$  or  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^1$  d)  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^1$  or  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1 3d^{10}$

e)  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^3$

7. 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.

8. 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)  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^1$

9. 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.

10. a) It has two s-electrons in its valence shell, like the other elements in group 2.

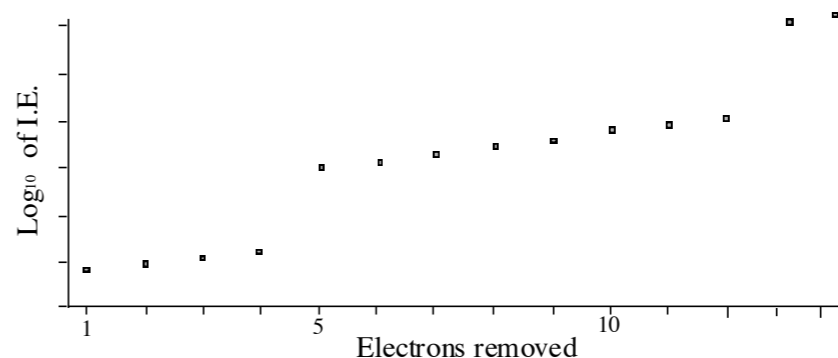
b) It has a complete valence shell like all the other elements in group 18.

## EXERCISE 2-E

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

6.  $\text{Na} < \text{Li} < \text{O} < \text{N} < \text{Ne}$

7. 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.

8. 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.

9. 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.

10. 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

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# Periodic Table

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Making sense of a complex world.



# Periodicity

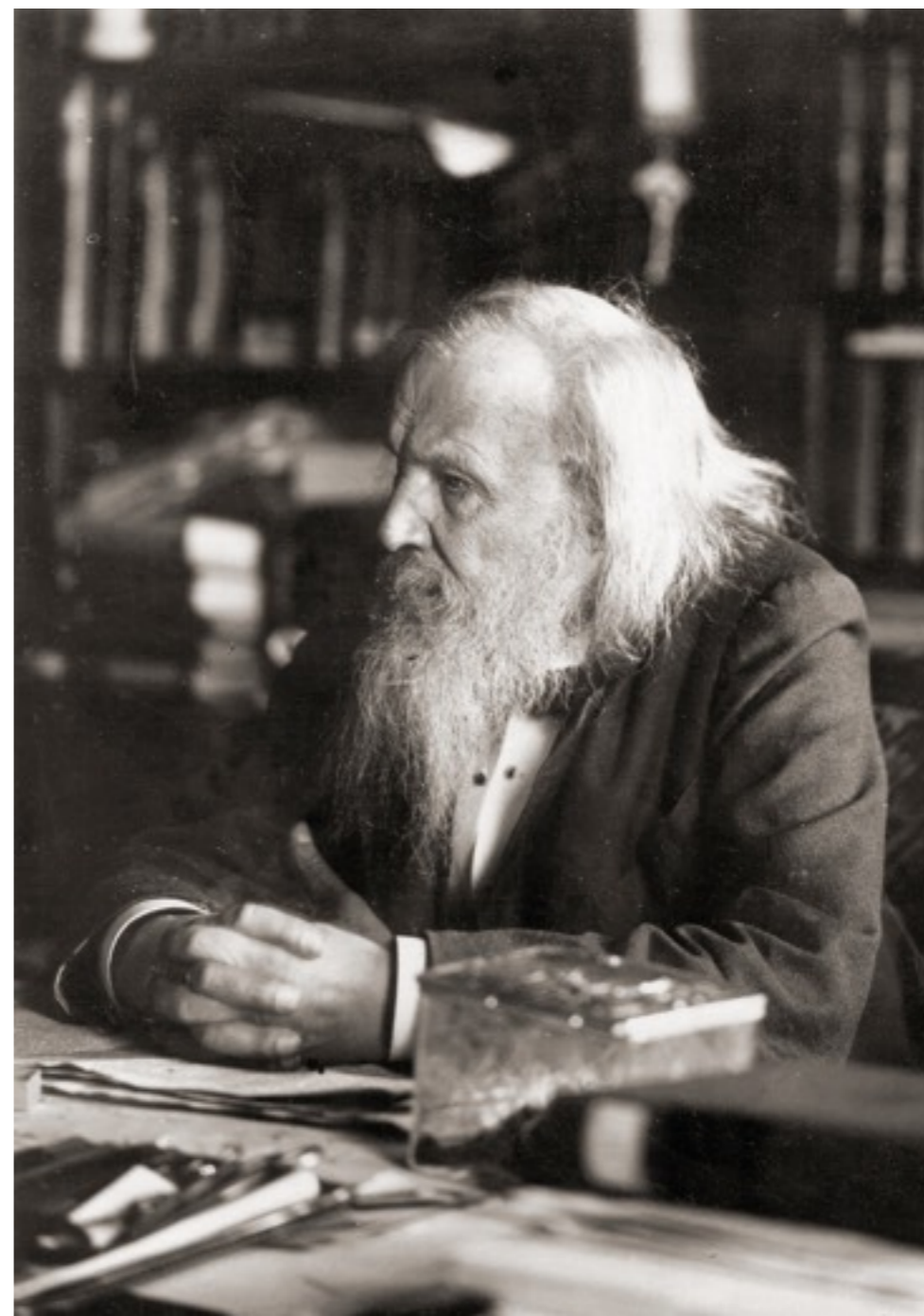
## CONTENTS

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1. 3.1 Periodic Table
2. 3.2 Periodic Trends
3. 13.1 First-row d-block elements
4. 13.2 Coloured complexes

This section begins with enlarged versions of some of the most important diagrams in Chapter 3 of the text.

**Dmitri Mendeleev**  
(1834 – 1907)



# Additional Material

## The Periodic Table - Modern Version

### THE PERIODIC TABLE

KEY																	
atomic number																	
atomic symbol																	
name																	
relative atomic mass																	
1 H hydrogen 1.0																	2 He helium 4.0
3 Li lithium 6.9	4 Be beryllium 9.0											5 B boron 10.8	6 C carbon 12.0	7 N nitrogen 14.0	8 O oxygen 16.0	9 F fluorine 19.0	10 Ne neon 20.2
11 Na sodium 23.0	12 Mg magnesium 24.3											13 Al aluminium 27.0	14 Si silicon 28.1	15 P phosphorus 31.0	16 S sulfur 32.1	17 Cl chlorine 35.5	18 Ar argon 39.9
19 K potassium 39.1	20 Ca calcium 40.1	21 Sc scandium 45.0	22 Ti titanium 47.9	23 V vanadium 50.9	24 Cr chromium 52.0	25 Mn manganese 54.9	26 Fe iron 55.8	27 Co cobalt 58.9	28 Ni nickel 58.7	29 Cu copper 63.5	30 Zn zinc 65.4	31 Ga gallium 69.7	32 Ge germanium 72.6	33 As arsenic 74.9	34 Se selenium 79.0	35 Br bromine 79.9	36 Kr krypton 83.8
37 Rb rubidium 85.5	38 Sr strontium 87.6	39 Y yttrium 88.9	40 Zr zirconium 91.2	41 Nb niobium 92.9	42 Mo molybdenum 95.9	43 Tc technetium -	44 Ru ruthenium 101	45 Rh rhodium 103	46 Pd palladium 106	47 Ag silver 108	48 Cd cadmium 112	49 In indium 115	50 Sn tin 119	51 Sb antimony 122	52 Te tellurium 128	53 I iodine 127	54 Xe xenon 131
55 Cs caesium 133	56 Ba barium 137	57 La lanthanum 139	72 Hf hafnium 178	73 Ta tantalum 181	74 W tungsten 184	75 Re rhenium 186	76 Os osmium 190	77 Ir iridium 192	78 Pt platinum 195	79 Au gold 197	80 Hg mercury 201	81 Tl thallium 204	82 Pb lead 207	83 Bi bismuth 209	84 Po polonium -	85 At astatine -	86 Rn radon -
87 Fr francium -	88 Ra radium -	89 Ac actinium -															
		lanthanides	6	58 Ce cerium 140	59 Pr praseodymium 141	60 Nd neodymium 144	61 Pm promethium -	62 Sm samarium 150	63 Eu europium 152	64 Gd gadolinium 157	65 Tb terbium 159	66 Dy dysprosium 163	67 Ho holmium 165	68 Er erbium 167	69 Tm thulium 169	70 Yb ytterbium 173	71 Lu lutetium 175
		actinides	7	90 Th thorium -	91 Pa protactinium -	92 U uranium -	93 Np neptunium -	94 Pu plutonium -	95 Am americium -	96 Cm curium -	97 Bk berkelium -	98 Cf californium -	99 Es einsteinium -	100 Fm fermium -	101 Md mendelevium -	102 No nobelium -	103 Lr lawrencium -



Figure 3-03a

(a) The trend in atomic radius going down Group 1

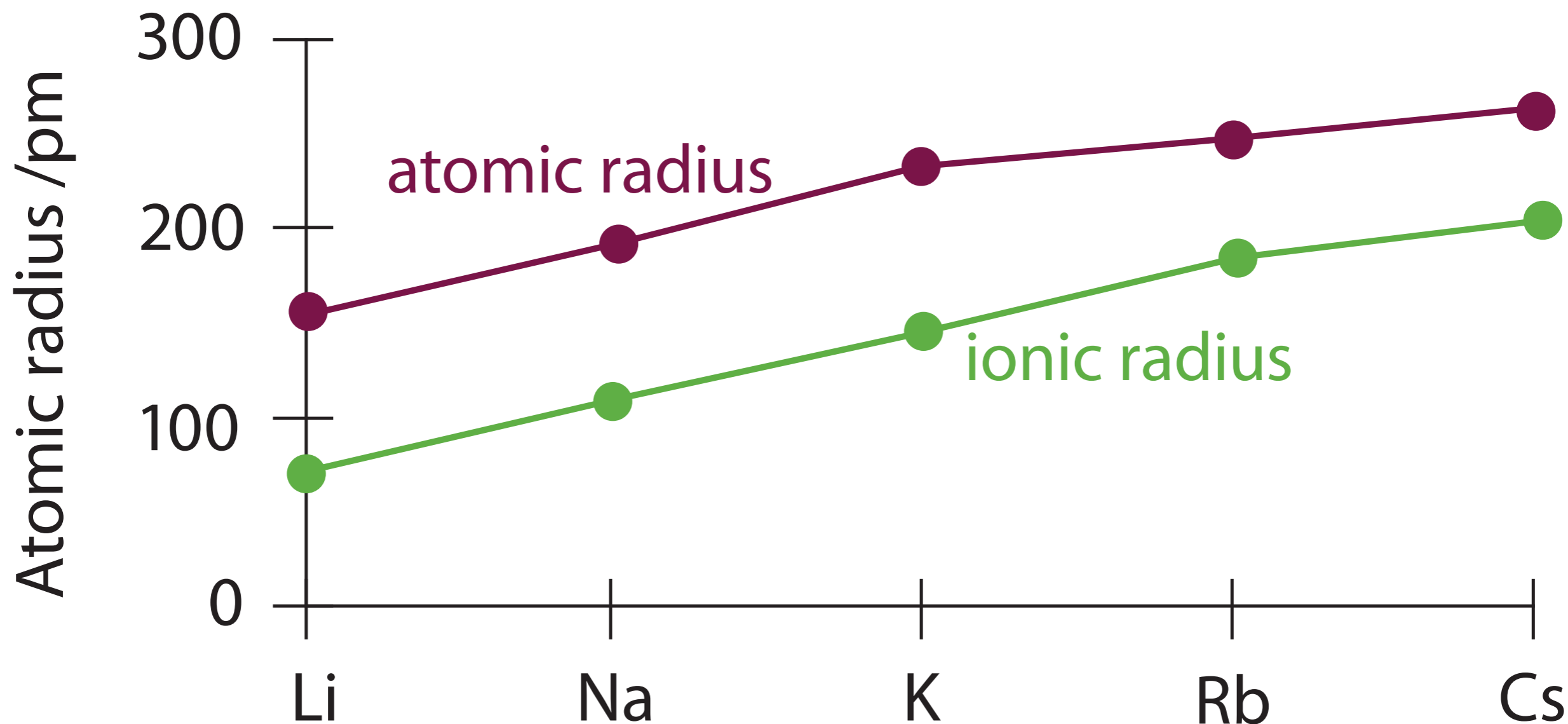


Figure 3-03b

(b) The trend in ionization energy going down Group 18

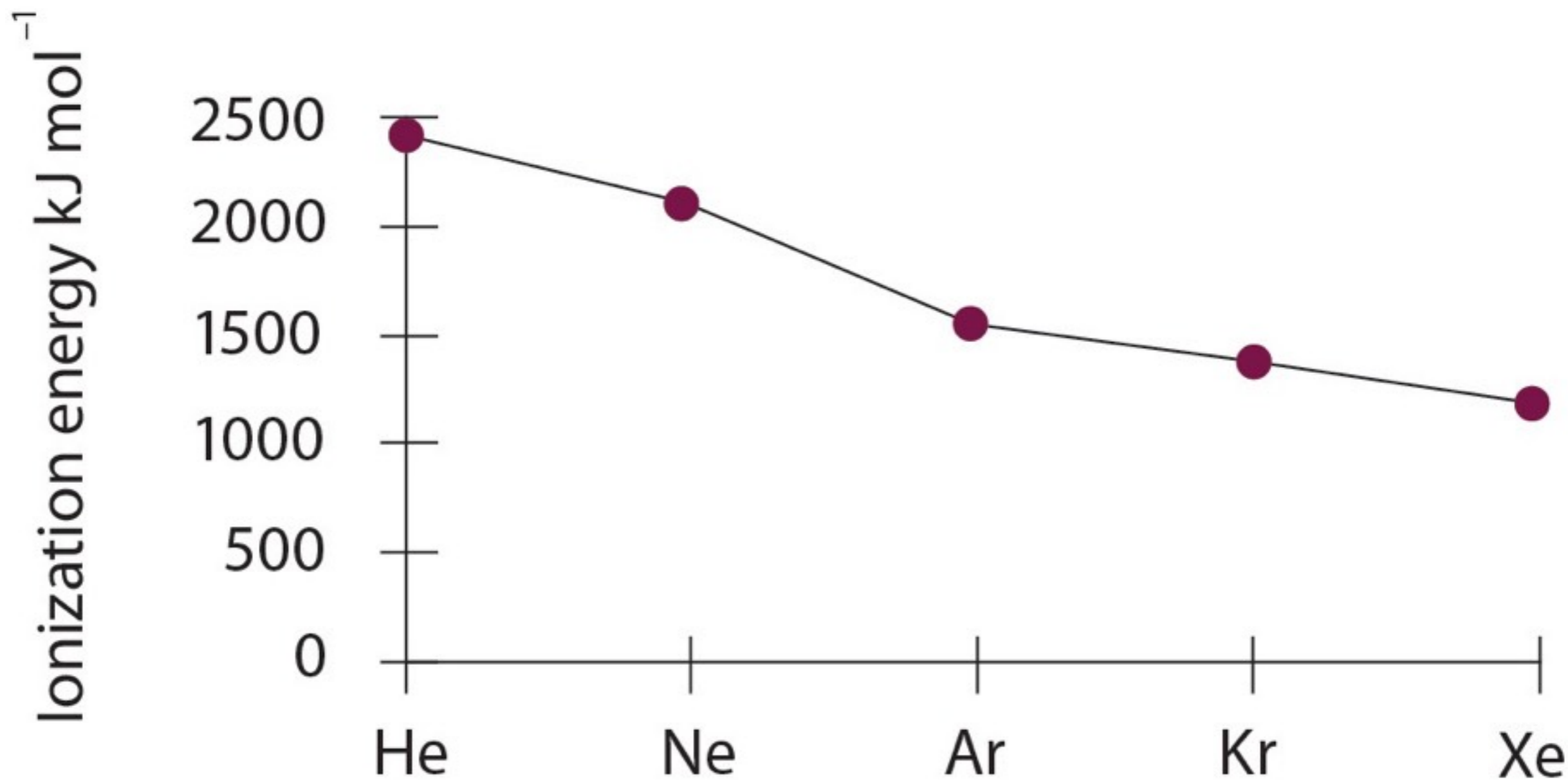


Figure 3-03c

(c) The trend in electronegativity going down Group 17

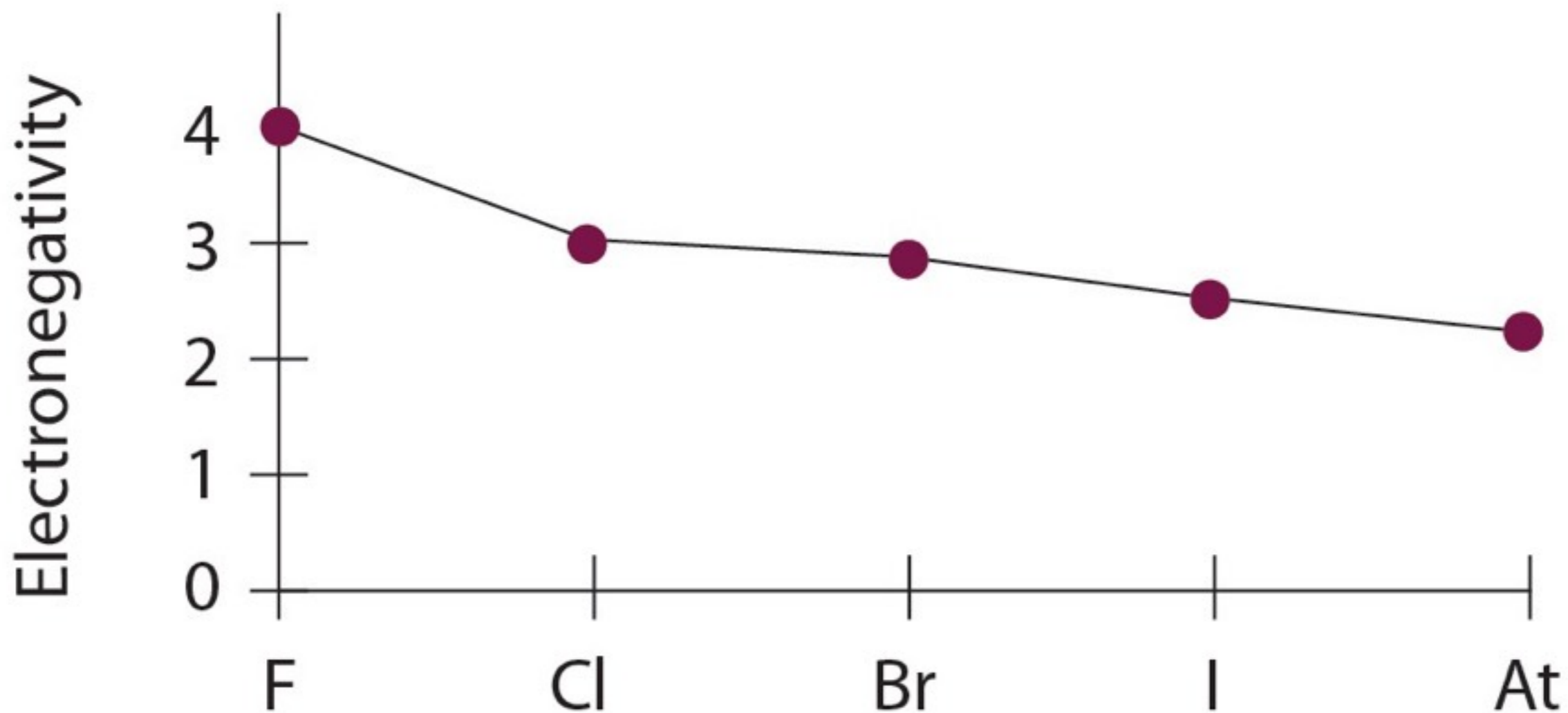


Figure 3-04a

(a) Variation in atomic radius across the third period

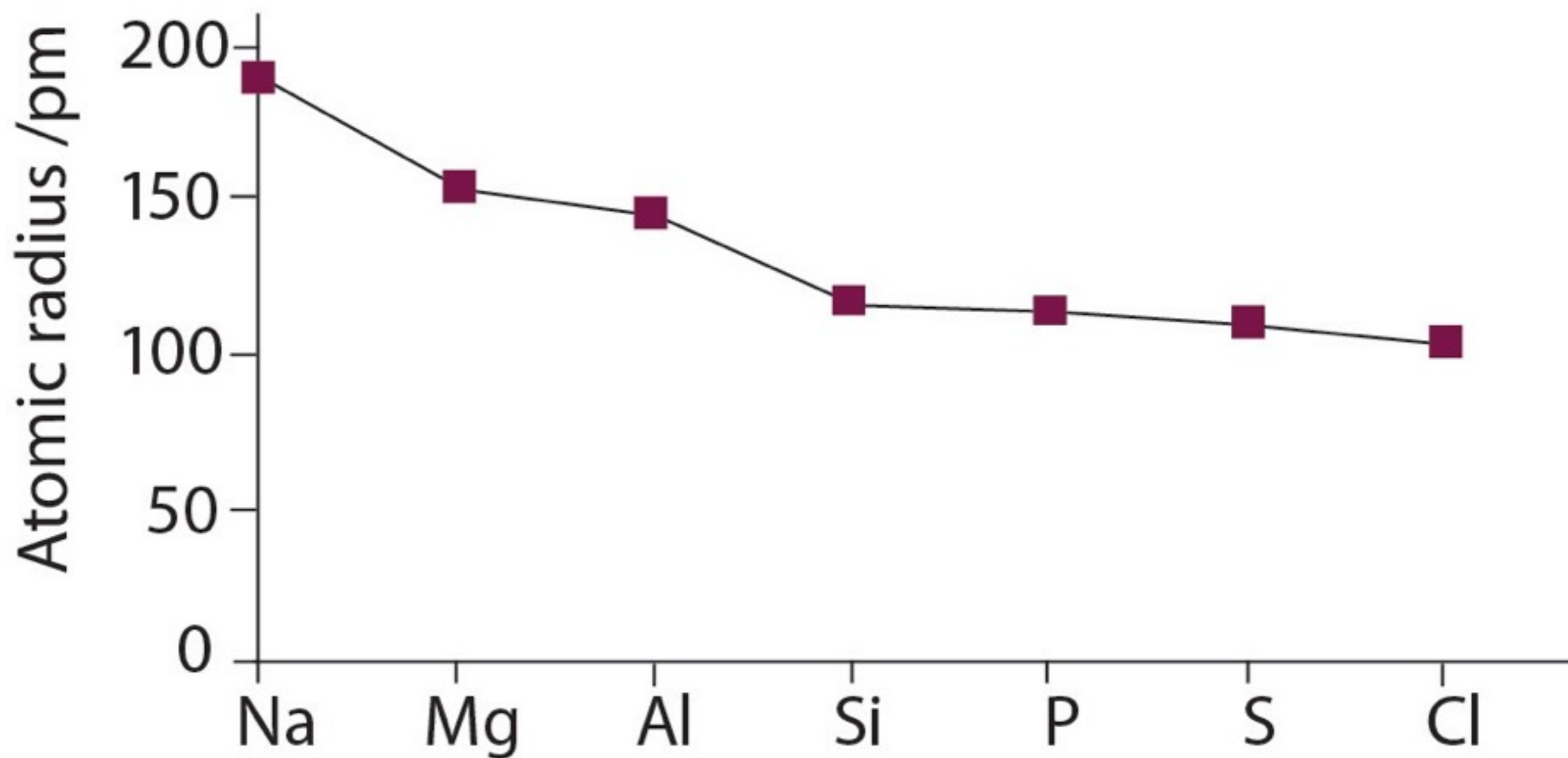


Figure 3-04b

(b) Variation in ionization energy across the third period

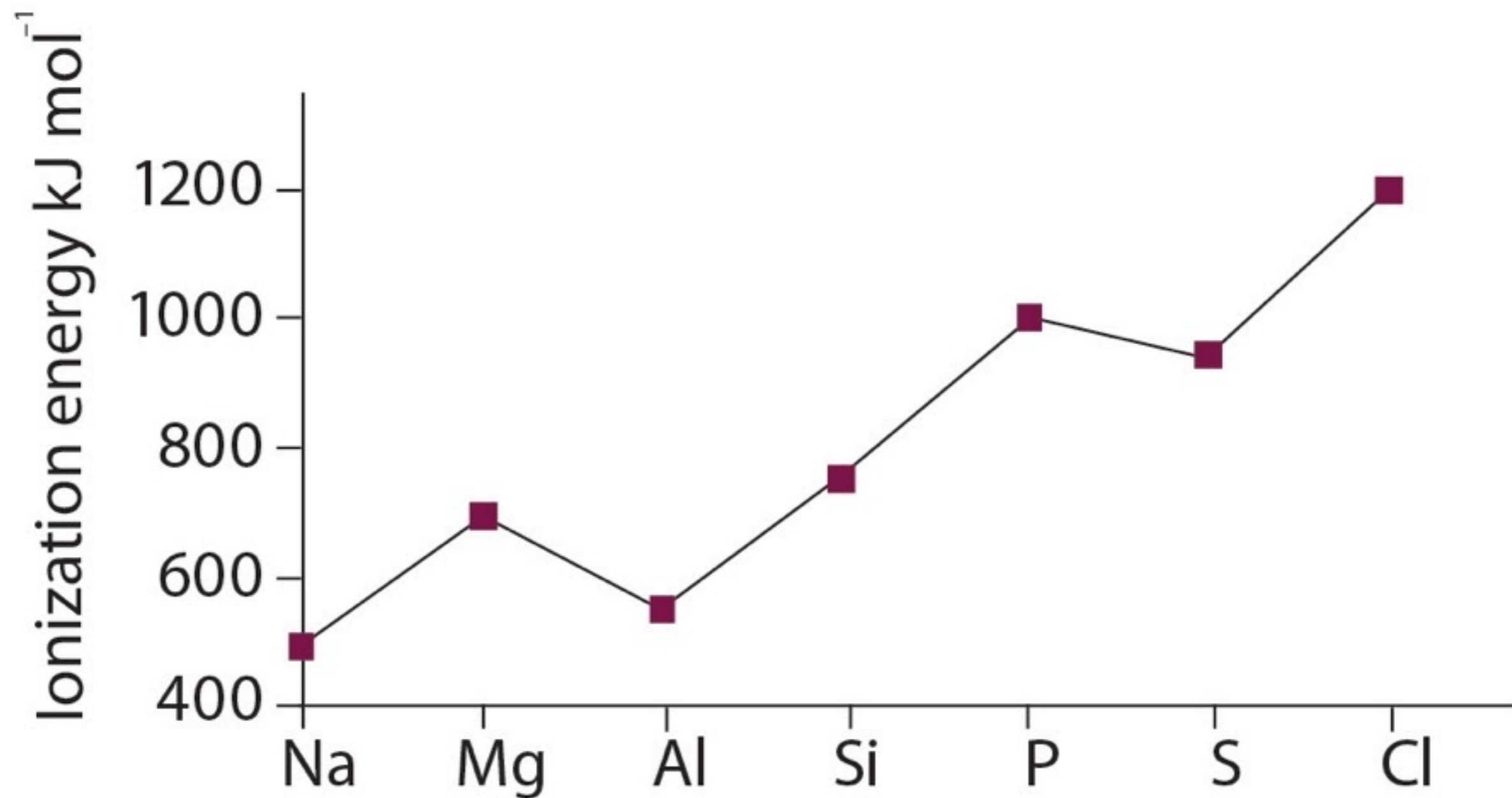


Figure 3-04c

(c) Variation in electronegativity across the third period

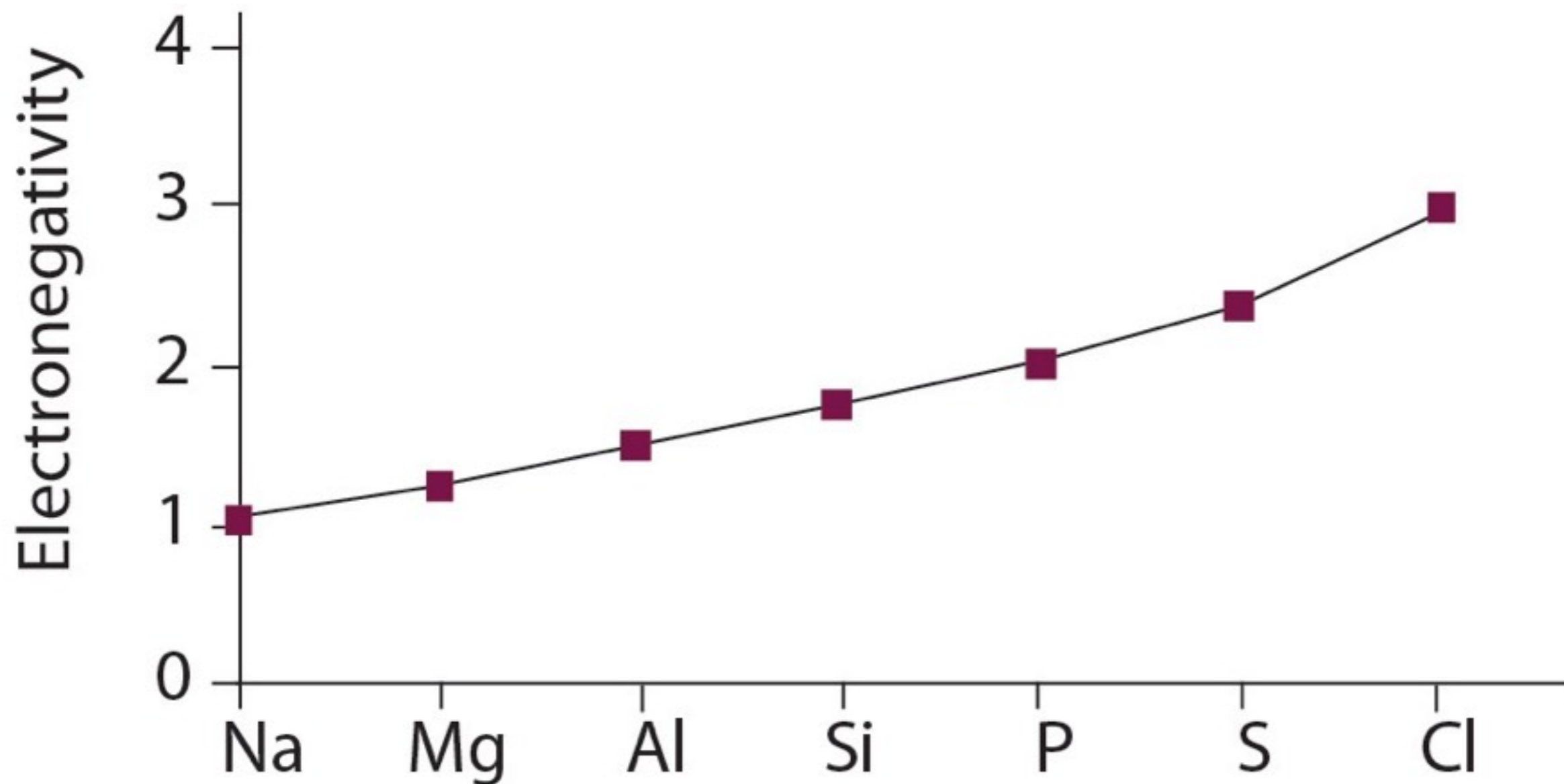
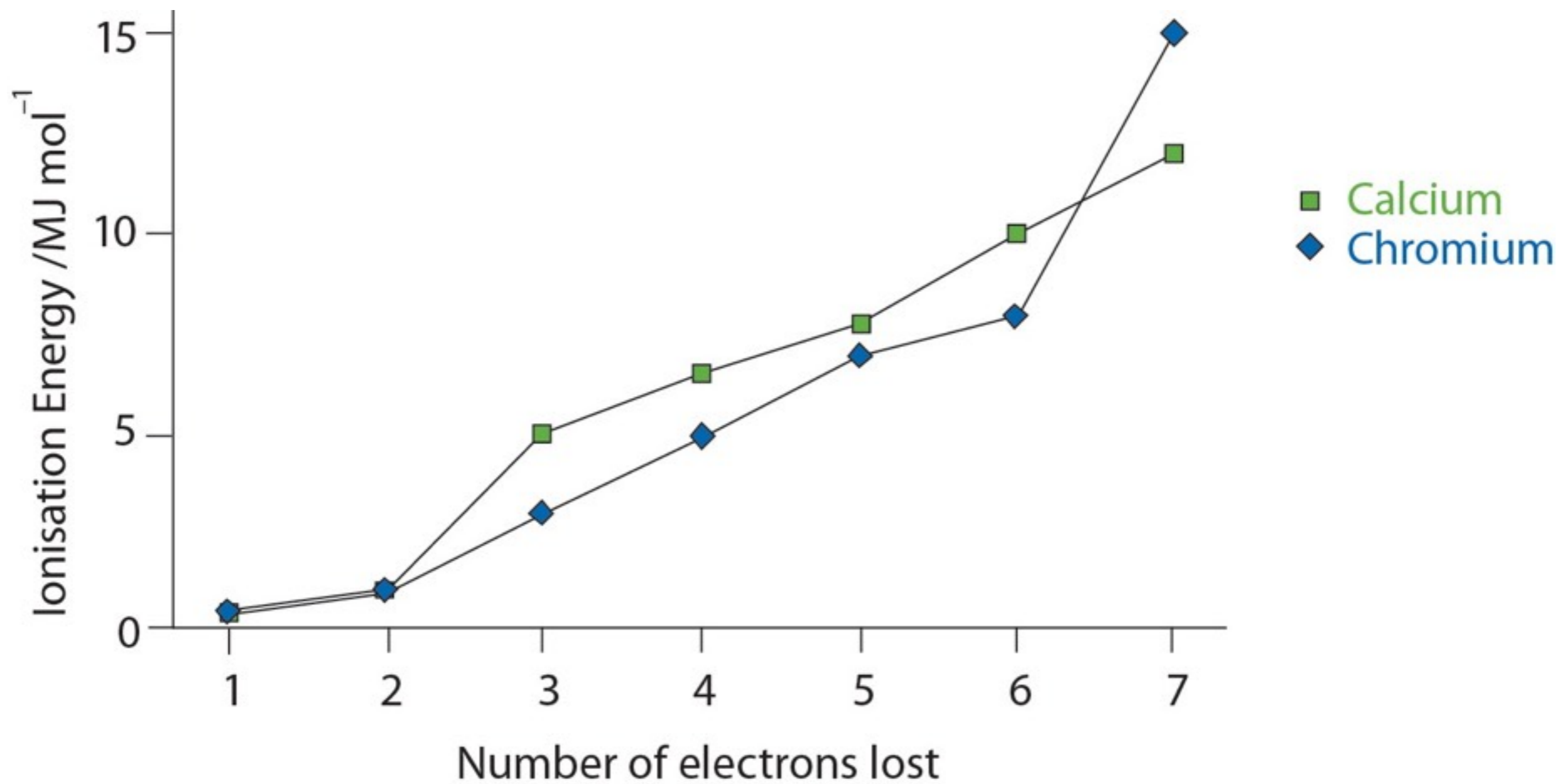
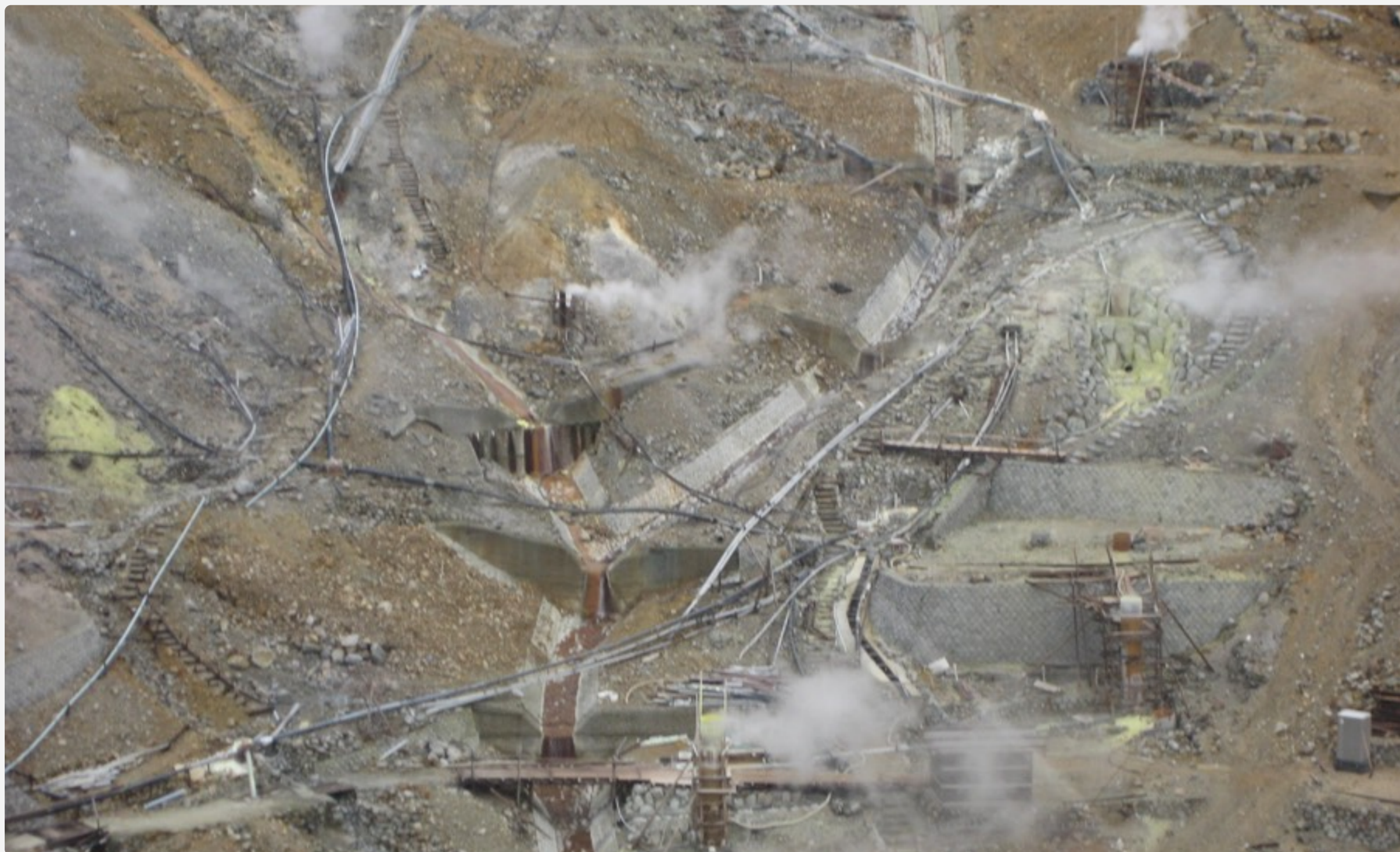


Figure 3-08



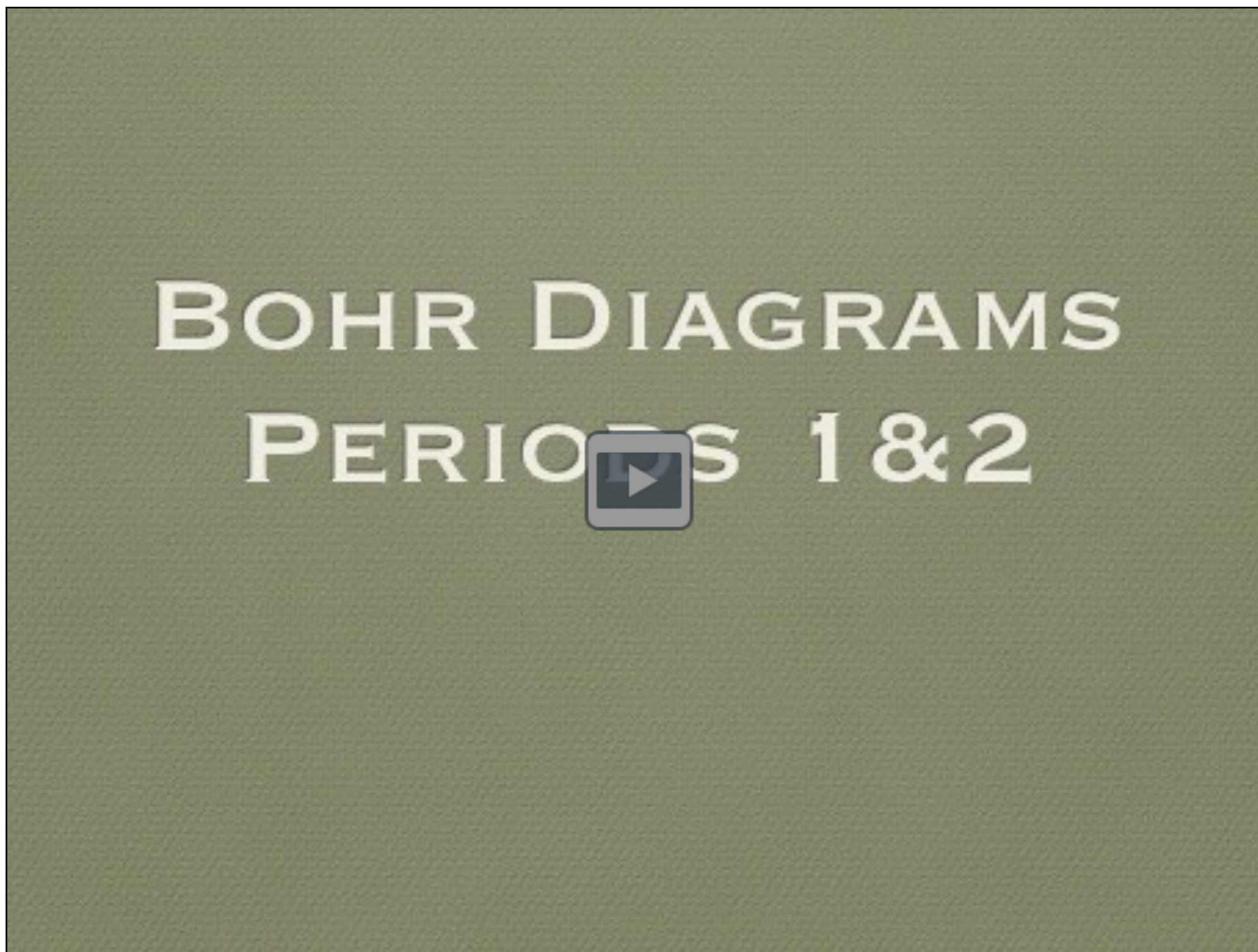
**Gallery 3.1** The search for the riches of the Periodic Table.



*Mining in Japan*



**Interactive 3.1** Periods 1 & 2 Bohr Diagrams



# Answers to exercises

## EXERCISE 3-A

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

## EXERCISE 3-B

1. C 2. D 3. D 4. B 5. C 6. A 7. B 8. A 9. A 10. C

11. Al, Mg, Ca, Ba, Cs

12. 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) Becomes more exothermic – the electron being gained is nearer to the nucleus.

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

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

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

13. a)  $2 \text{ Na} + 2 \text{ H}_2\text{O} \rightarrow 2 \text{ NaOH} + \text{ H}_2$

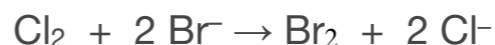
b) The sodium would fizz around on the surface as a molten blob, slowly dissolving.

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.

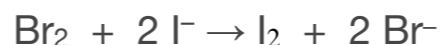
14. a) Yellow-green b) Yellow/Orange/Brown c) Purple

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



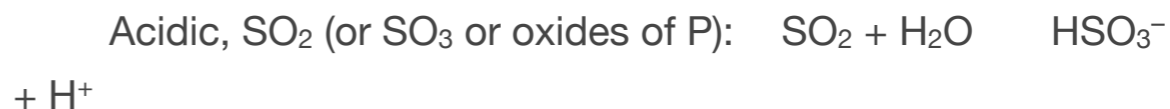
b) No reaction

c) Yes; the yellow–brown solution will turn to another yellow–brown solution and with excess bromine a black solid will form;



d) No reaction

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



Basic, Na<sub>2</sub>O (or MgO):  $\text{Na}_2\text{O} + \text{H}_2\text{O} \rightarrow 2 \text{Na}^+ + 2 \text{OH}^-$

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.

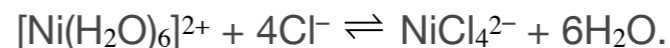
c) The reducing strength increases going down the group. Going down the group the electrons are successively further away from the nucleus and hence are more easily lost.

### EXERCISE 3-C

1. B 2. C 3. C 4. B 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:

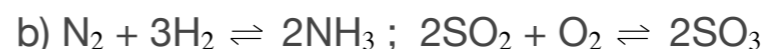


The energies of the d-orbitals in the two ions are slightly different and hence they absorb light of a different wavelengths, giving slightly different colours.

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

a) Iron metal, vanadium(V) oxide.



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.

8. 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.

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.

9. a)  $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$  changing to  $[\text{CuCl}_4]^{2-}$ . b)  $[\text{Cu}(\text{NH}_3)_4]^{2+}$ .

c)  $[\text{CoCl}_4]^{2-}$  changing to  $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ . d)  $\text{Cr}_2\text{O}_7^{2-}$  changing to  $\text{CrO}_4^{2-}$ .

e)  $\text{MnO}_4^-$  changing to  $\text{MnO}_4^{2-}$ .

10. a) Octahedral b) +2 in  $[\text{Fe}(\text{CN})_6]^{4-}$  and +3 in  $[\text{Fe}(\text{CN})_6]^{3-}$

c)  $:\text{CN}$ . 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.

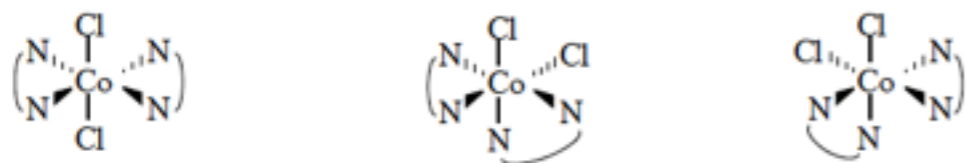
b)  $\text{V}^{3+}$  has electrons in the 3d sub-level. These electrons can move from one 3d orbital to another of higher energy and this process involves the absorption of light in the visible region of the spectrum, making the compound coloured. In the case of  $\text{Sc}^{3+}$  there are no electrons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

c)  $\text{V}^{3+}$  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.  $\text{Sc}^{3+}$  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)  $\text{Cu}^+$  has a completely filled d-orbital hence electron transitions cannot occur between these and absorb light in the visible region. In  $\text{Cu}^{2+}$  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  $90^\circ$  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 hand being the 'trans-' form and the right hand ones both 'cis-' forms.

b) The pair of right hand diagrams are non-superimposable mirror 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.

c) Vitamin B12, or cobalamin

Chapter 4

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# Chemical Bonding

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Most colour results from chemical bonding.



# Bonding

## CONTENTS

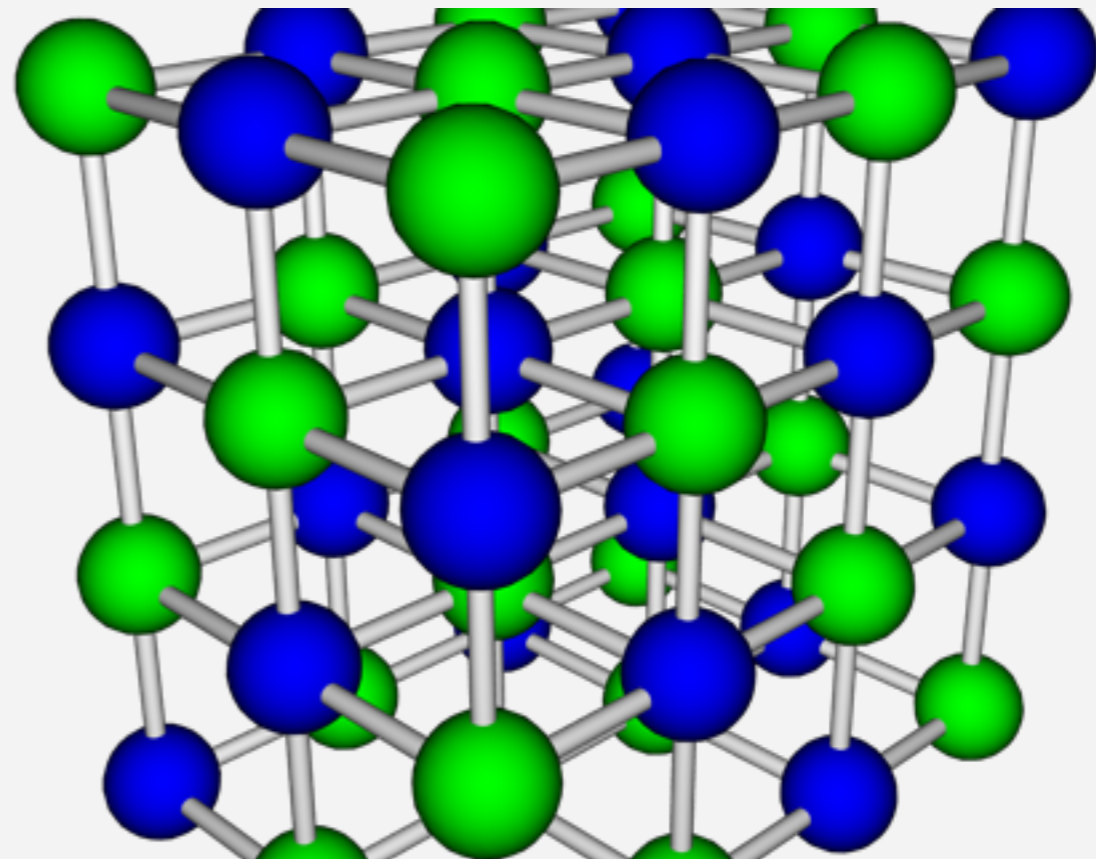
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1. 4.1 Ionic bonding and structure
2. 4.2 Covalent Bonding
3. 4.3 Covalent structures
4. 14.1 Covalent bonding and electron domain and molecular geometries
5. 14.2 Hybridization
6. 4.4 Intermolecular forces
7. 4.5 Metallic bonding

## Ionic Bonding

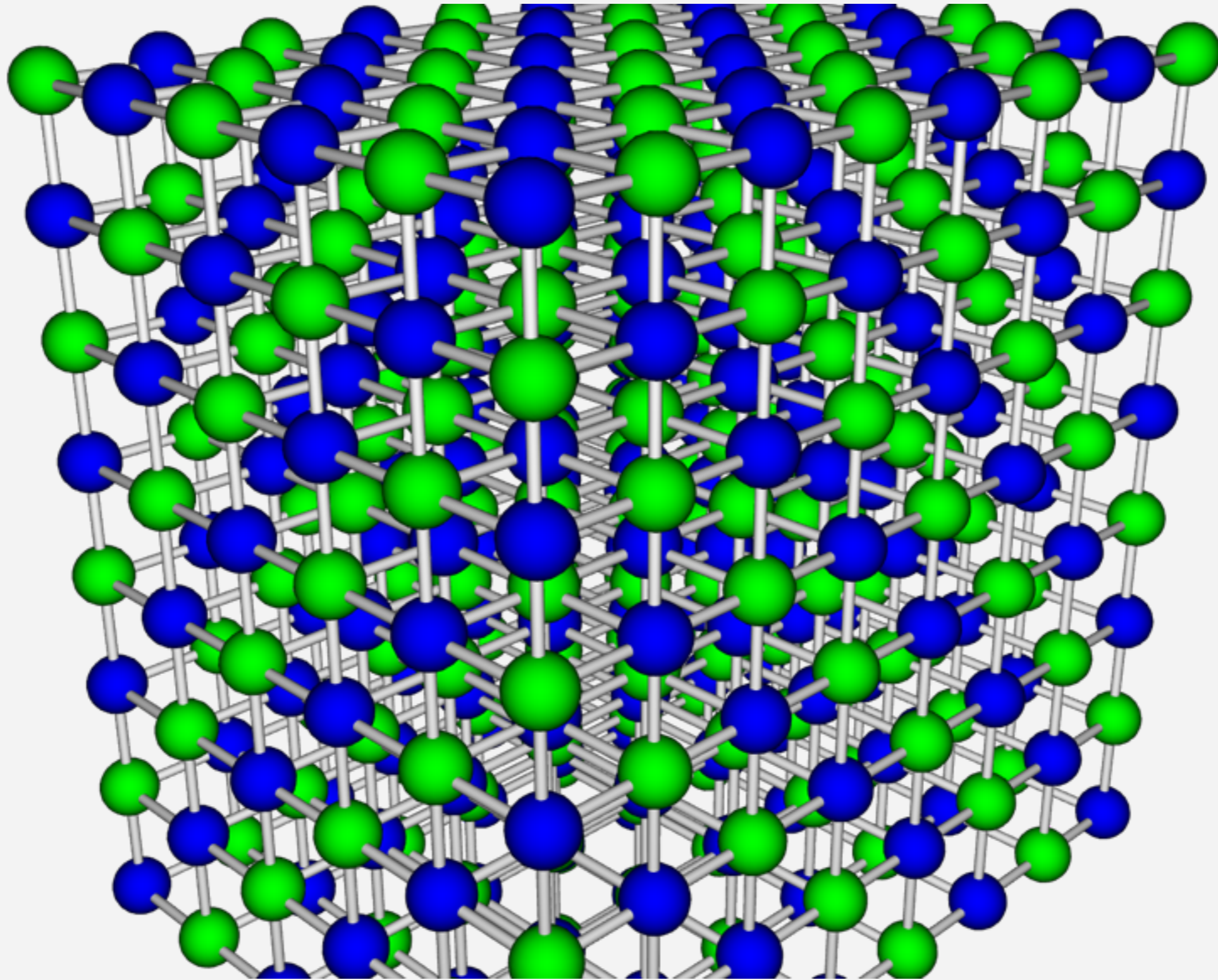
Figure 4-03

Interactive 4.1 Cubic Lattice (small)



## Additional Material

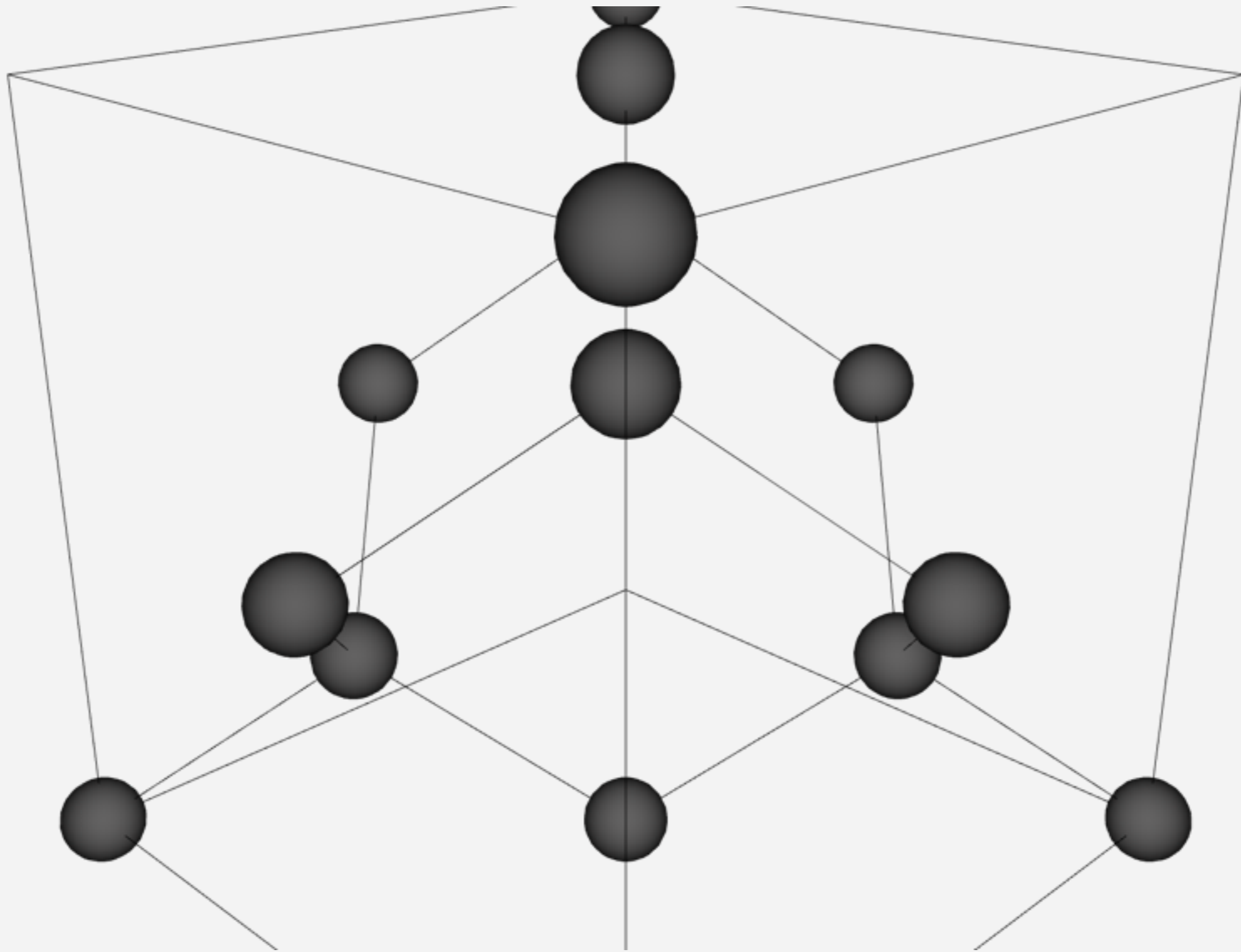
Interactive 4.2 Cubic Lattice (large)



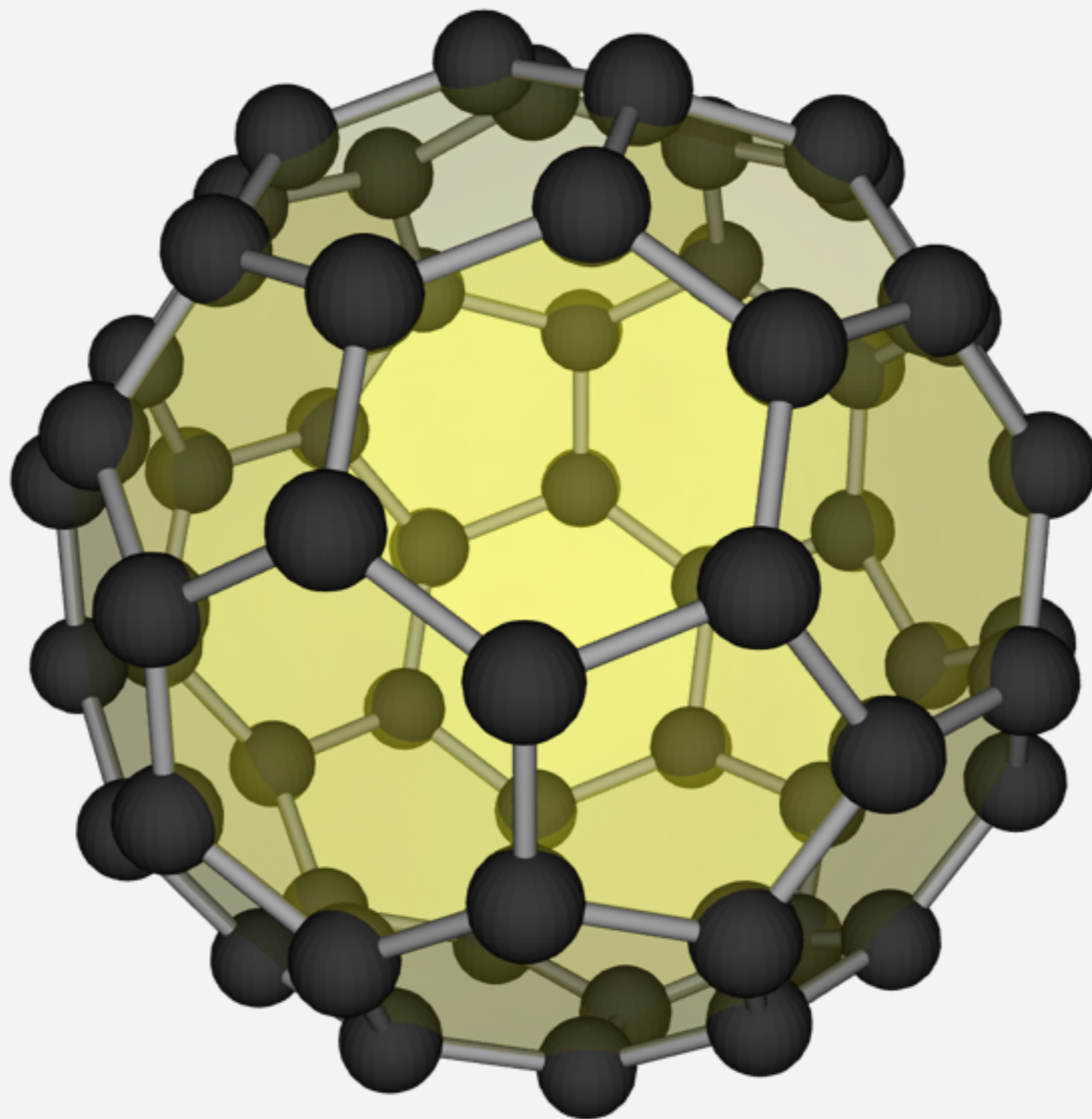
*Only for devices with big memory!*



**Interactive 4.3** Diamond Lattice



Interactive 4.4 C-60 Buckyball



# Internet resources

## Ice Lattice

<http://learnbiochemistry.wordpress.com/category/ice-lattice/>

### EXERCISE 4-A

1. D 2. D 3. B

4. a) In the crystal lattice, each ion is surrounded by ions of the opposite charge, hence the whole lattice is held together by strong electrostatic forces, making it hard. Even a slight movement however, would bring ions in one layer close to ions of a similar charge in the neighbouring layer and the resultant forces would cause the crystal to split, hence ionic substances are brittle.

b) An ionic substance is comprised of electrically charged ions. In the solid state these are held in fixed positions by the crystal lattice and hence cannot move. When molten, or in solution, the ions are free to move under the influence of an electrical field and hence can conduct an electric current.

c) In most solvents the strong forces between the oppositely charged ions prevent the ionic lattice splitting and the substance dissolving. Water molecules, because they are so polar, can form bonds to the individual ions of comparable strength to the forces

# Answers to exercises

between the ions, hence many ionic substances can dissolve in water.

5. a) AB b) BA c)  $A_2B$  d)  $AB_3$  e)  $B_3A_2$

### EXERCISE 4-B

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

7. a) No compound (He is a noble gas) b) HCl c)  $NCl_3$  d)  $SiF_4$  e)  $P_2O_3$

8. a) covalent b) covalent c) ionic d) covalent e) no compound

9. a) N b) O c) F d) neither e) O

10. The bond in  $CH_3-O-CH_3$  will be the longest as it is a single bond, that in  $H_2C=O$  will be shorter as it is a double bond and that in  $C\equiv O$  will be the shortest. Going from single, to double to triple, the number of shared electrons increases and hence the attraction of the nuclei for the shared electrons becomes greater.

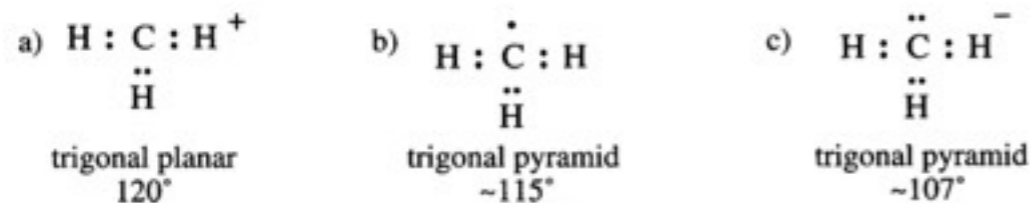
### EXERCISE 4-C

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

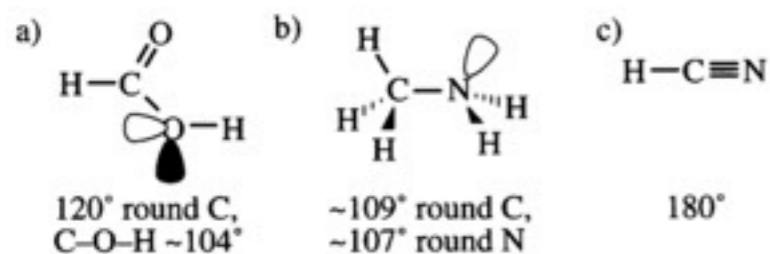
6. a) tetrahedral b) trigonal pyramid c) non-linear, bent or 'V'-shaped

d) trigonal pyramid e) tetrahedral

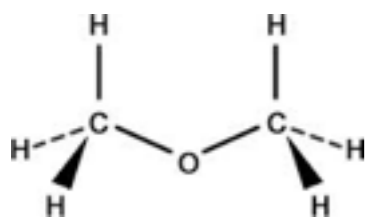
7.



8.



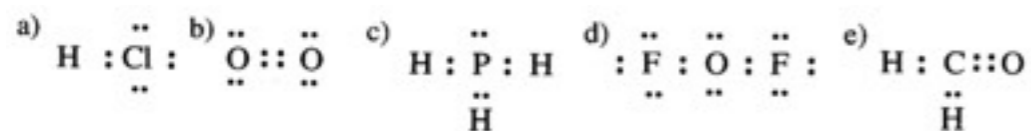
d)



$\sim 109^\circ$  round C

$\sim 104^\circ$  round O

9.



10. a) non-polar b) polar c) polar d) polar e) non-polar

11. 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.

12. Graphite as electrodes – Each layer of carbon atoms in the graphite structure has a layer of delocalized  $\pi$ -electrons above and below it. Like the electrons in a metallic structure, these electrons are mobile and hence graphite is a good conductor in two dimensions, though because of the random orientation of individual crystals most samples of graphite can conduct quite well in all three dimensions.

Graphite as a lubricant – Each layer of carbon atoms in the graphite structure has only weak dispersion forces bonding it to the layers above and below it. This allows the layers of carbon atoms to easily slide past each other, hence it can be used as a lubricant.

Diamond in cutting tools – In the diamond structure each carbon is joined to the four carbon atoms arranged tetrahedrally around it

by covalent bonds. This gives rise to a very strong, rigid three dimensional crystal structure, which requires a large force to break it down, hence diamond is very hard and will cut most other materials.

#### EXERCISE 4-D

1. C 2. D 3. B

4. 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.

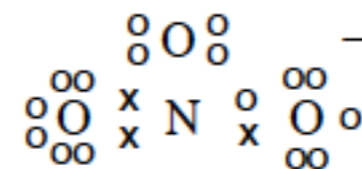
b) The shape of  $BF_3$  is trigonal planar. This is also the shape of  $sp^2$  hybrid orbitals.

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

5. a) The single bond is a  $\sigma$ -bond. The double bond is a  $\sigma$ -bond and a  $\pi$ -bond. The triple bond is a  $\sigma$ -bond and two  $\pi$ -bonds.

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

6. 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  $\sigma$ -bonds and for there also to be a delocalised  $\pi$ -bond that connects all four atoms.

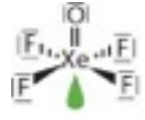
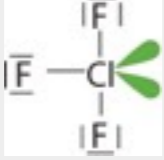
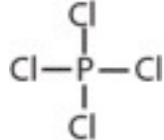
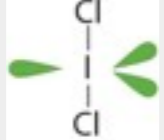
d) The  $\sigma$ -bonds would be formed between  $sp^2$  hybrid orbitals on the oxygen and nitrogen atoms. The delocalised  $\pi$ -bond would be the result of the interaction of the p-orbitals, on all of the atoms, that are at right angles to the  $sp^2$  hybrid orbitals.

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

7.

Species	Lewis Diagram	Bond Angles	Polarity
XeOF <sub>4</sub>		All ~90° Maybe just <90° Owing to lone pair	Polar
ClF <sub>3</sub>		All ~90° Maybe just <90° Owing to lone pairs	Polar
PCl <sub>4</sub> <sup>+</sup>		All 109.5°	Non-polar
ICl <sub>2</sub> <sup>-</sup>		180°	Non-polar

8. The frequency of the light absorbed by the dissociation of covalent bonds is linked to their strength (E) by the equation  $E = h\nu$ , so the stronger the bond the higher the frequency of the radiation absorbed. The bond in molecular oxygen is a double bond, whereas that in ozone contains a delocalised  $\pi$ -bond giving it an overall bond order of 1.5. The O–O bond in ozone is therefore weaker than that in the O<sub>2</sub> molecule, so ozone absorbs at a lower frequency.

### EXERCISE 4-E

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

6. a) These molecules have only dispersion 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 dispersion forces between these molecules will increase with the surface area of the molecule, hence they are weakest in the more spherical molecule and the weaker the forces, 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 dispersion forces between chlorine molecules, hence its higher boiling point, in spite of its lower molar mass.

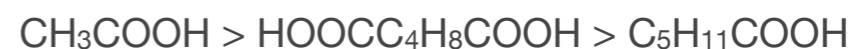
7. The hydrides of fluorine, oxygen and nitrogen (HF, H<sub>2</sub>O, H<sub>3</sub>N) can all form hydrogen bonds between their molecules, whereas the hydrides of the elements lower down in the same group (e.g. HCl, H<sub>2</sub>S and H<sub>3</sub>P) only have dispersion forces and dipole-dipole interaction between their molecules. Hydrogen bonds are much stronger than dispersion 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 include:

NH<sub>3</sub> is much more soluble in water than PH<sub>3</sub>, 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<sub>2</sub>O) 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.

8. The solubility in water would decrease in the order:



This is because, whilst organic compounds are generally insoluble in water owing to the fact that if they were to dissolve they would disrupt its strongly hydrogen bonded structure, the carboxyl group (COOH) can form its own hydrogen bonds to water. In a small molecule, like CH<sub>3</sub>COOH, this more than compensates for the disrupted bonds so the compound is miscible with water. If the hydrocarbon chain is greater, and the disruption of the water structure greater, then the hydrogen bonding of the carboxyl group cannot fully compensate and the solubility decreases. If there are more carboxyl groups, as in

HOOC<sub>4</sub>H<sub>8</sub>COOH, then the offsetting is greater and the solubility higher.

#### EXERCISE 4-F

1. C 2. B

3. 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 “sea” of delocalized electrons that surrounds them. This means that they can move relative to each other, allowing layers of metal ions to slide over each other, without the need to break bonds.

c) The delocalized 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.

d) When metals deform the layers of metal ions slide over each other. If the layers contain ions of different sizes, as is the case with alloys, then the resistance to the sliding of layers is increased making the substance harder.

#### EXERCISE 4-G

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<sub>2</sub>. 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 to compensate for the broken hydrogen bonds. 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 more than any hydrogen bonding from the ester group (-CO-O-) could compensate 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 can be described as being ionic, involving two highly charged ions ( $\text{Al}^{3+}$  &  $\text{O}^{2-}$ ) or as having a giant covalent structure similar to that of silicon dioxide. Either

would result in a very high melting point. Silicon dioxide has a giant covalent structure so that to melt it 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.

# Thermo-chemistry

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# Thermochemistry

## CONTENTS

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1. 5.1 Measuring energy changes
2. 5.2 Hess's law
3. 5.3 Bond enthalpies
4. 15.1 Energy cycles
5. 15.2 Entropy and spontaneity



# Additional Material

## TOK The Unification of Ideas

As an example of the conservation of energy, this illustrates the unification of ideas from different areas of science.

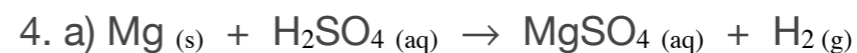
When ideas from one part of science seem to explain apparently unrelated phenomena elsewhere, then you get the feeling things are really falling in place and you are on to something fairly fundamental. Newton probably experienced this when he found he could use his theory of gravity to explain the motion of the planets. Similarly Mendeleev's periodic table, originally drawn up to show regular patterns of chemical properties seems to fit in beautifully with later evidence about electron structure, which in its turn relates amazingly to quantum mechanics through the Schrödinger wave equation.

Another interesting trick is to say, suppose this wasn't true? Suppose if when I converted reactants A into products B by a different route I found that the energy change wasn't the same as for the direct conversion, what would be the consequences? It is said that Einstein started research into his theory of relativity by saying let's assume that when a light source is moving towards us and when it is moving away from us, the speed of light from the source is just the same.

# Answers to exercises

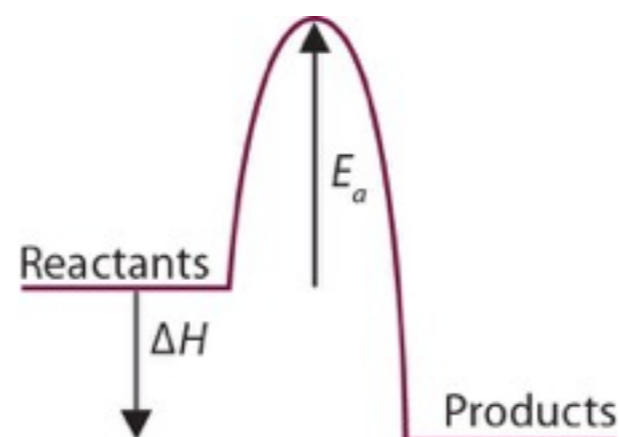
## EXERCISE 5-A

1. B 2. C 3. A



b) Exothermic

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



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 at constant pressure. d) Positive e) Endothermic

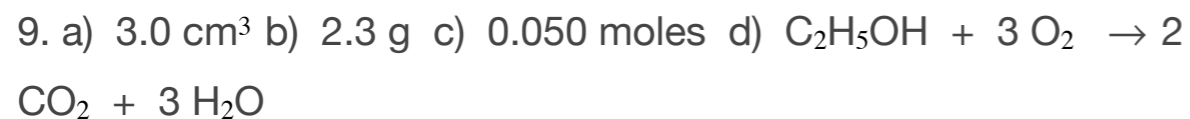
## EXERCISE 5-B

1. B 2. C 3. B 4. C 5. D 6. A 7. D

8. Heat energy absorbed =  $m.s.\Delta T = 100 \times 4.18 \times 4.5 = 1881 \text{ J}$

Amount of ammonium nitrate =  $m/M = 8.00/80.06 = 0.100 \text{ mol}$

Enthalpy of solution =  $1881/0.100 = 18810 \text{ J mol}^{-1} = 18.8 \text{ kJ mol}^{-1}$



e)  $1367 \times 0.050 = 68 \text{ kJ}$

10. a) Heat energy absorbed by the aluminium =  $m.s.\Delta T = 0.1 \times 875 \times 80 = 7000 \text{ J}$

b) Heat energy absorbed by the water =  $m.s.\Delta T = 500 \times 4.18 \times 80 = 167200 \text{ J}$

Total energy absorbed =  $167200 + 7000 = 174200 \text{ J} = 174 \text{ kJ}$

c) Amount of butane =  $m/M = 14.5 / 58.14 = 0.2494 \text{ mol}$

d) Enthalpy of reaction =  $174.2 / 0.2494 = 698 \text{ kJ mol}^{-1}$

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

### EXERCISE 5-C

1. D 2. A

3. Let required enthalpy change =  $\Delta H$

Applying Hess' law,  $2.\Delta H + (-120) = (-800)$

$\Delta H = (120-800)/2 = -340 \text{ kJ mol}^{-1}$

4.  $-(-1561) - 1411 - 286 = -136 \text{ kJ mol}^{-1}$

5. a) Weigh out a sample of  $\text{CaCO}_3$ . 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. Repeat the procedure using  $\text{CaO}$  instead of  $\text{CaCO}_3$ .

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 or carbon dioxide from the air converting it to the hydroxide or the carbonate.

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

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

## EXERCISE 5-D

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

6. a) Equation:  $\text{Zn}_{(s)} + \text{Cl}_{2(g)} \rightarrow \text{ZnCl}_{2(s)}$

$$\Delta H = \Delta H_f(\text{ZnCl}_2) - [\Delta H_f(\text{Zn}) + \Delta H_f(\text{Cl}_2)] = -416 \text{ kJ mol}^{-1}$$

b) Equation:  $2 \text{H}_2\text{S}_{(g)} + \text{SO}_{2(g)} \rightarrow 2 \text{H}_2\text{O}_{(l)} + 3 \text{S}_{(s)}$

$$\Delta H = [2\Delta H_f(\text{H}_2\text{O}) + 3\Delta H_f(\text{S})] - [2\Delta H_f(\text{H}_2\text{S}) + \Delta H_f(\text{SO}_2)] = -233 \text{ kJ mol}^{-1}$$

c) Equation:  $2 \text{Pb}(\text{NO}_3)_{2(s)} \rightarrow 2 \text{PbO}_{(s)} + 4 \text{NO}_{2(g)} + \text{O}_{2(g)}$

$$\Delta H = [2\Delta H_f(\text{PbO}) + 4\Delta H_f(\text{NO}_2) + \Delta H_f(\text{O}_2)] - [2\Delta H_f(\text{Pb}(\text{NO}_3)_2)] = +598 \text{ kJ mol}^{-1}$$

7.  $\text{C}_{12}\text{H}_{26} \rightarrow \text{C}_5\text{H}_{12} + \text{C}_3\text{H}_8 + 2 \text{C}_2\text{H}_4$

$$\Delta H = \Delta H_{\text{comb}}(\text{C}_{12}\text{H}_{26}) - [\Delta H_{\text{comb}}(\text{C}_5\text{H}_{12}) + \Delta H_{\text{comb}}(\text{C}_3\text{H}_8) + 2 \cdot$$

$$\Delta H_{\text{comb}}(\text{C}_2\text{H}_4)]$$

$$\Delta H = -7901 - [(-3509) + (-2058) + 2(-1411)] = +488 \text{ kJ mol}^{-1}$$

8. For the equation  $\text{CH}_2\text{Cl}_{2(l)} + \text{O}_{2(g)} \rightarrow \text{CO}_{2(g)} + 2 \text{HCl}_{(g)}$ ;  $\Delta H = -458 \text{ kJ mol}^{-1}$ .

For the equation  $\text{CH}_2\text{Cl}_{2(l)} + 2 \text{O}_{2(g)} \rightarrow \text{CO}_{2(g)} + \text{H}_2\text{O}_{(l)} + \text{Cl}_{2(g)}$ ;  $\Delta H = -560 \text{ kJ mol}^{-1}$  The latter is much closer to the experimental value, so this is presumably the reaction occurring.

9. a)  $4 \text{CH}_3\text{NHNH}_{2(l)} + 5 \text{N}_2\text{O}_{4(g)} \rightarrow 4 \text{CO}_{2(g)} + 12 \text{H}_2\text{O}_{(l)} + 9 \text{N}_{2(g)}$

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

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

10.

a) i  $\text{C}_6\text{H}_{10(g)} + \text{H}_2(g) \rightarrow \text{C}_6\text{H}_{12(g)}$ , ii  $\text{C}_6\text{H}_6(g) + 3 \text{H}_2(g) \rightarrow \text{C}_6\text{H}_{12(g)}$

$$\text{b) } \Delta H_i = \Delta H_{\text{comb}}(\text{C}_6\text{H}_{10}) + \Delta H_{\text{comb}}(\text{H}_2) - \Delta H_{\text{comb}}(\text{C}_6\text{H}_{12}) \\ = -3752 - 286 + 3924 = -114 \text{ kJ mol}^{-1}$$

$$\Delta H_{ii} = \Delta H_{\text{comb}}(\text{C}_6\text{H}_6) + 3 \Delta H_{\text{comb}}(\text{H}_2) - \Delta H_{\text{comb}}(\text{C}_6\text{H}_{12}) \\ = -3273 - 3 \times 286 + 3924 = -207 \text{ kJ mol}^{-1}$$

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 ( $\Delta H_{ii}$ ) might be 3 times the enthalpy change for the hydrogenation of cyclohexene ( $\Delta H_i$ ).

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

## EXERCISE 5-E

1. A 2. A 3. A

4. Equation:  $2 \text{CO}_{(g)} + \text{O}_{2(g)} \rightarrow 2 \text{CO}_{2(g)}$

Bonds broken  $2 \cdot (\text{C}\equiv\text{O}) + \text{O}=\text{O} = (2 \times 1073) + 498 = 2644 \text{ kJ mol}^{-1}$ .

Bonds made  $4 \times 804 = 3216 \text{ kJ mol}^{-1}$ .

Overall enthalpy change =  $2644 - 3216 = -572 \text{ kJ mol}^{-1}$  for 2 moles of CO, so for 1 mole =  $-286 \text{ kJ mol}^{-1}$

5. Enthalpy change in breaking bonds =  $(944) + (3 \times 242) = 1670 \text{ kJ mol}^{-1}$

Overall enthalpy change =  $1670 - (6 \times \text{N-Cl}) = +688 \text{ kJ mol}^{-1}$

Enthalpy of N-Cl bond =  $\frac{1}{6} (1670 - 688) = 164 \text{ kJ mol}^{-1}$

6. Equation:  $\text{C}_3\text{H}_6(\text{g}) + \text{H}_2(\text{g}) \rightarrow \text{C}_3\text{H}_8(\text{g})$

Bonds broken C-C + H-H =  $346 + 436$

=  $782 \text{ kJ mol}^{-1}$

Bonds made  $2 \cdot (\text{C-H}) = 2 \times 414 = 828 \text{ kJ mol}^{-1}$ .

Enthalpy change =  $782 - 828 = -46 \text{ kJ mol}^{-1}$

The actual value is much more exothermic than this value. The reason for this is that the bond angle in cyclopropane is  $60^\circ$ , much less than the normal tetrahedral angle of  $109^\circ$ . 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.

7. 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  $42 \text{ kJ mol}^{-1}$  and between Br-Br and Cl-Cl it is  $49 \text{ kJ mol}^{-1}$ , hence continuing this trend the difference between Cl-Cl and F-F would be expected to be  $56 \text{ kJ mol}^{-1}$ . This would give a F-F bond enthalpy of  $298 \text{ kJ mol}^{-1}$ .

The F-F bond enthalpy is  $159 \text{ kJ mol}^{-1}$ , which is much less. The reason for this is the repulsion between the inner electron shells is greater and the strong attractive force of the nucleus draws electrons away from the central region between the atoms.

8.  $2 \text{ P}_{(\text{s})} + 5 \text{ H}_{2(\text{g})} \rightarrow 2 \text{ P}_{(\text{g})} + 10 \text{ H}_{(\text{g})} \quad \Delta H_1$

$2 \text{ P}_{(\text{g})} + 10 \text{ H}_{(\text{g})} \rightarrow 2 \text{ PH}_{5(\text{g})} \quad \Delta H_2$

$\Delta H_1 = (2 \times +354) + (10 \times +218) = +2888 \text{ kJ mol}^{-1}$

$$\Delta H_2 = 10 \times -322 = -3220 \text{ kJ mol}^{-1}$$

$$\text{Enthalpy of formation} = \frac{1}{2} (2888 - 3220) = -166 \text{ kJ mol}^{-1}$$

9. 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.

$$\text{b) Bonds broken} = \text{C-C} + \text{O-H} = 346 + 463 = 809 \text{ kJ mol}^{-1}$$

$$\text{Bonds made} = \text{C-O} + \text{C-H} = 358 + 414 = 772 \text{ kJ mol}^{-1}.$$

$$\text{Enthalpy change} = +37 \text{ kJ mol}^{-1}$$

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

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.

10. The H-S bond enthalpy [E(H-S)] could be calculated from:

Enthalpy of atomization of hydrogen;  $\Delta H_{\text{at}}(\text{H})$

Enthalpy of atomization of sulfur;  $\Delta H_{\text{at}}(\text{S})$

Enthalpy of formation of hydrogen sulphide;  $\Delta H_{\text{f}}(\text{H}_2\text{S})$

(The enthalpy of formation of hydrogen sulphide could be calculated from the enthalpies of combustion of hydrogen, sulfur and hydrogen sulphide)

They could be combined according to the equation:

$$\Delta H_{\text{f}}(\text{H}_2\text{S}) = 2.\Delta H_{\text{at}}(\text{H}) + \Delta H_{\text{at}}(\text{S}) - 2. E(\text{H-S})$$

so

$$E(\text{H-S}) = \frac{1}{2} [2.\Delta H_{\text{at}}(\text{H}) + \Delta H_{\text{at}}(\text{S}) - \Delta H_{\text{f}}(\text{H}_2\text{S})]$$

### EXERCISE 5-F

$$1. \text{ C } \quad 2. \text{ C } \quad 3. \text{ B } \quad 4. \text{ A } \quad 5. \text{ B}$$

$$6. -860 = +175 + 2 \times 121 + 503 + 966 + 2 \times \text{EA}(\text{Cl}) - 2069$$

$$\text{EA}(\text{Cl}) = \frac{1}{2} (-860 - 175 - 242 - 503 - 966 + 2069) = -338.5 \text{ kJ mol}^{-1}$$

$$7. \Delta H_{\text{f}} = +193 + \frac{1}{2} \times 159 + 590 - 328 - 930 = -395.5 \text{ kJ mol}^{-1}$$

If two moles of calcium were reacted with one mole of fluorine, then the formation of two moles of CaF would release 791 kJ mol<sup>-1</sup>, but 1214 kJ mol<sup>-1</sup> would be released if only one mole of CaF<sub>2</sub> was formed and the excess calcium remained unreacted so this is the reaction that occurs.

$$8. \text{ a) } -100 = +285 + 112 + 731 - 325 + \text{LE}(\text{AgBr})$$



$$LE(\text{AgBr}) = -100 - 285 - 112 - 731 + 325 = +903 \text{ kJ mol}^{-1}$$

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

9. Theoretical  $\Delta H_{\text{sol}} = +833 - 464 - 359 = +10 \text{ kJ mol}^{-1}$

Experimental  $\Delta H_{\text{sol}} = +905 - 464 - 359 = +82 \text{ kJ mol}^{-1}$

In sodium chloride, which has an enthalpy of solution similar to the theoretical value for silver chloride, the positive entropy 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.

10.  $S^{2-} > Cl^- > I^-$

$S^{2-}$  has a double negative charge making the hydration enthalpy considerably greater than that of the singly charged ions.  $Cl^-$  is greater than  $I^-$  because it is a smaller size.

## EXERCISE 5-G

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)  $\Delta S = 109 + 5 \times 70 - 300 = +159 \text{ J K}^{-1} \text{ mol}^{-1}$

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

b)  $\Delta S = (2 \times 142) - (2 \times 118) - 223 = -175 \text{ J K}^{-1} \text{ mol}^{-1}$

Negative as a decrease in the number of moles of gas

c)  $\Delta S = 132 - 80 - 90 = -38 \text{ J K}^{-1} \text{ mol}^{-1}$

Negative as a solid is formed from aqueous ions

## EXERCISE 5-H

1. C 2. B

3. a)  $-430 \text{ J mol}^{-1}\text{K}^{-1}$  ( $= 3 \times 201 - 173$ ) b)  $-635 \text{ kJ mol}^{-1}$  ( $= 49 - 3 \times 228$ )

c)  $2131 \text{ J mol}^{-1}\text{K}^{-1}$  ( $= 635000/298$ )

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.

$$= 2131 - 430 = 1701 \text{ J mol}^{-1}\text{K}^{-1}$$

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,  $\Delta G = 64.1 - 67.1 = -3.0 \text{ kJ mol}^{-1}$

This is negative, therefore the product, the *trans*- isomer is the more stable. For "perfect equilibrium"  $\Delta G$  is zero:

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

$$T = 4400/5 = 880 \text{ K.}$$

The temperature at which there would be perfect equilibrium is 880 K / 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 monoxide is a more powerful reductant than carbon, but above this temperature the reverse is true.

c) Hydrogen will not reduce  $\text{Al}_2\text{O}_3$  at any temperature. It will reduce PbO at almost all temperatures shown on the graph. It will only reduce ZnO at temperatures below ~1500K.

6. a)  $+214 \text{ J mol}^{-1}$ , b) Ice is the stable form as  $\Delta G$  for melting is positive,

c)  $-226 \text{ J mol}^{-1}$ ;

d) 273 K (actual value using the data given is 272.7) – this is the melting point of ice, when it is in equilibrium with water.

e)  $\Delta S$  for melting will be larger, therefore the temperature required for  $\Delta G$  to be equal to zero (assuming  $\Delta H$  unchanged) will be smaller. This corresponds to the lowering of the freezing point of ice caused by a solute.

Chapter 6

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# Chemical Kinetics

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# Kinetics

## CONTENTS

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1. 6.1 Collision theory and rates
2. 16.1 Rate expression and reaction mechanism
3. 16.2 Activation energy



# Additional Material

## Rate Model

The spreadsheet Ch6.xlsx is a basic simulation of a rate process in which the change in 'concentration' is proportional to concentration (and time interval).

The main parts are:

The times. These start at zero (cell A6) and are incremented by an amount in cell B3.

The entry in cell A7 is the sum of the cell above it and the increment. The '\$' sign ensures absolute cell addressing when the formula is copied to the cells below.

	A	B
1	Rate simulation	
2		
3	Time Increment	5
4		
5	Time	
6	0	
7	5	
8	10	

Formula bar: A7 =A6+\$B\$3

The initial concentration is in cell D6.

Subsequent concentrations are calculated by the formulas:

In column E, we calculate the product of the current concentration, the time interval and the 'rate constant'.

	A	B	C	D	E
1	Rate simulation				
2					
3	Time Increment	5		Rate Constant	-0.03
4					
5	Time			Concentration	
6	0			100	-15

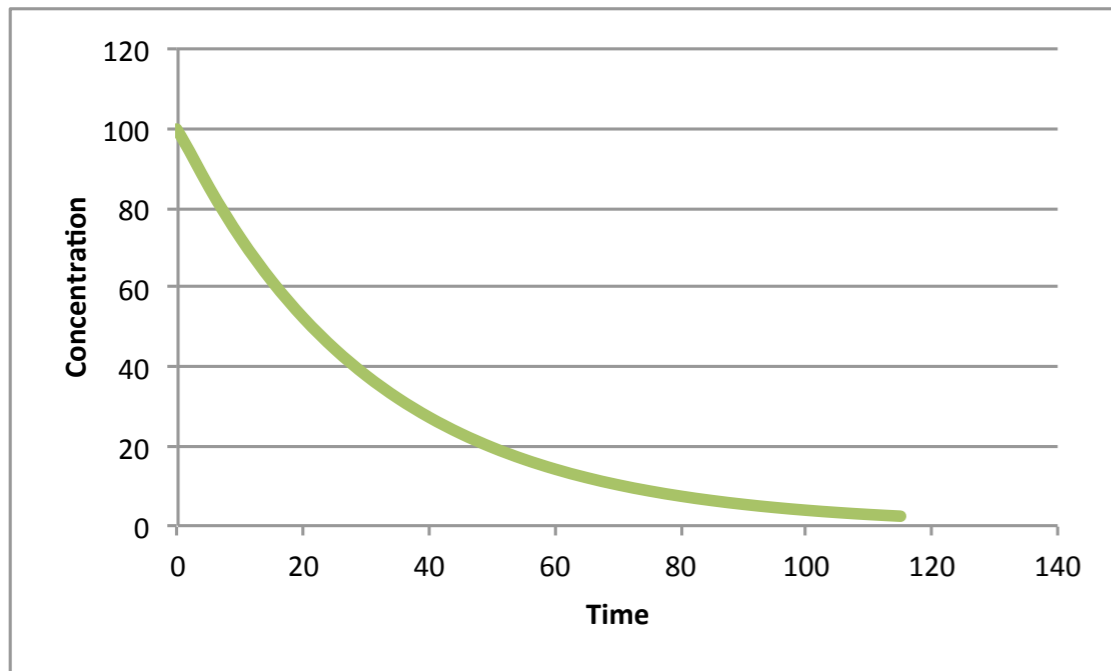
Formula bar: E6 =D6\*\$B\$3\*\$E\$3

The new concentration in cell D7 is the old concentration plus the change (cell E6).

	A	B	C	D	E
1	Rate simulation				
2					
3	Time Increment	5		Rate Constant	-0.03
4					
5	Time			Concentration	
6	0			100	-15
7	5			85	-12.75

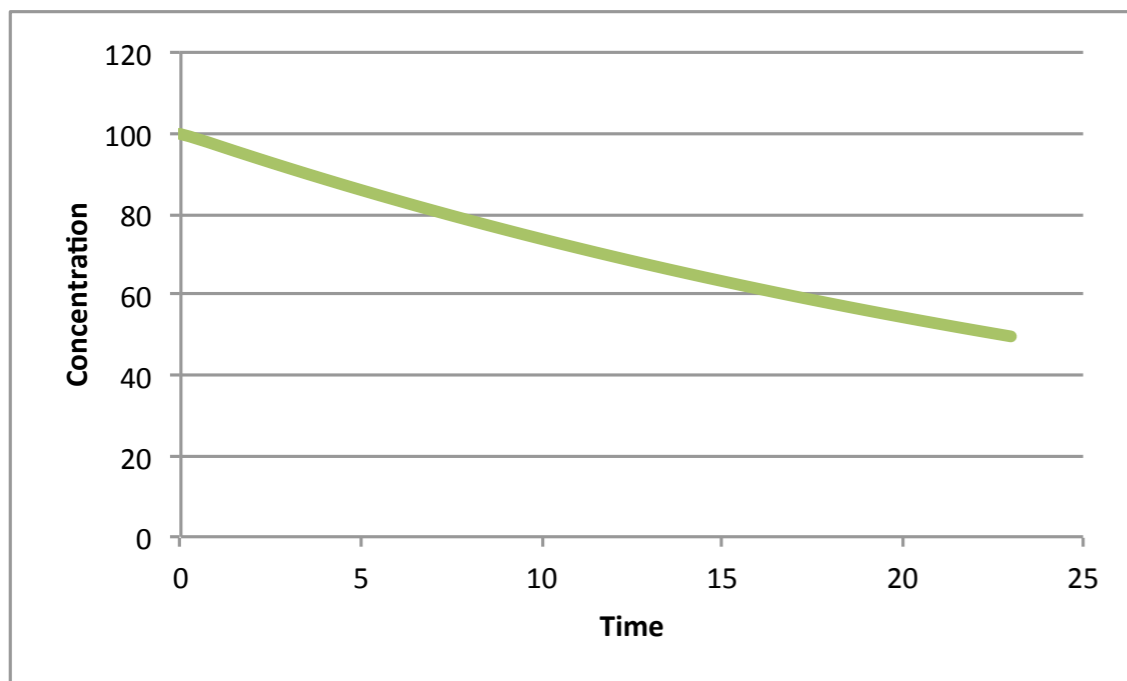
Formula bar: D7 =D6+E6

Columns A & D can now be displayed as a graph.



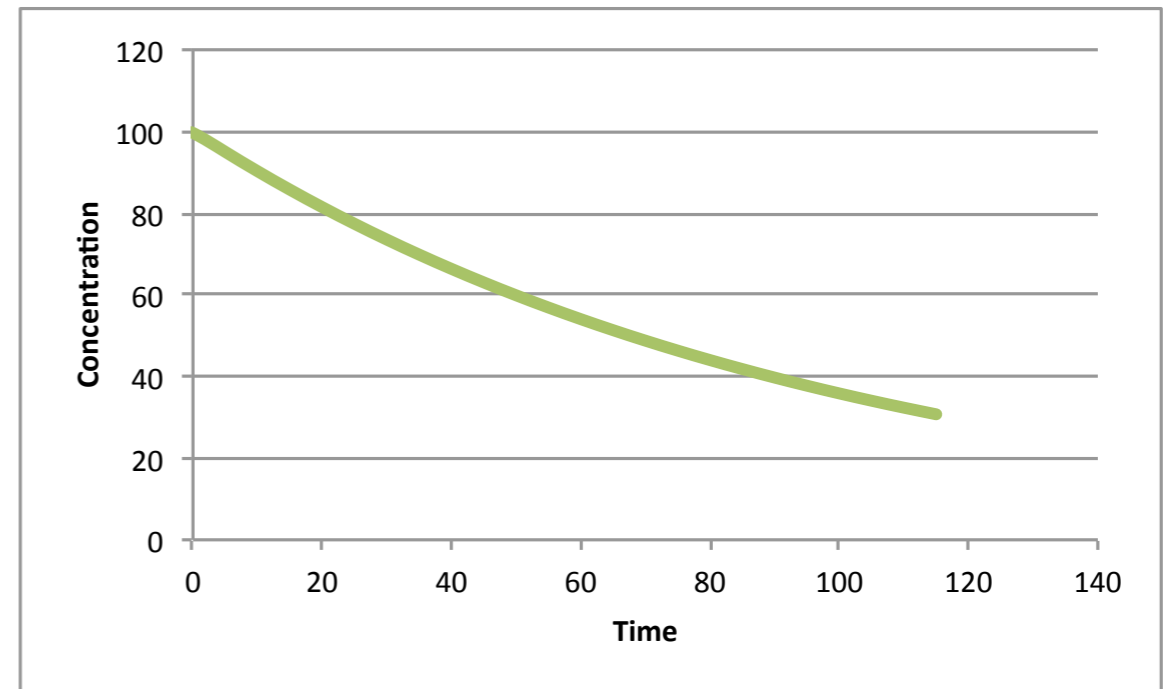
What order of reaction are we modelling?

The time period that is being modelled is controlled by cell B3. If this is changed to 1, the graph is:



Cell E3 controls the rate.

Returning the time increment (B3) to 5 and entering -0.01 in E3 gives:



This is a slower reaction.

Can you model reactions of other orders?

**Gallery 6.1** Some 'devices' are dependent on the rate of chemical reactions. Some are not.



*The power output of a steam engine is controlled by a valve (a physical process) and the heat of the fire is controlled by altering the air supply (chemical).*





# Answers to exercises

## EXERCISE 6-A

1. B 2. C 3. A

4. a) Rate =  $0.005/120 = 4.17 \times 10^{-5} \text{ mol dm}^{-3} \text{ s}^{-1}$

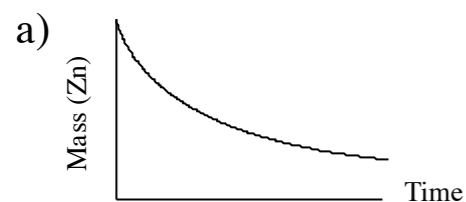
b) i.  $\text{H}_2\text{O}_2$  is consumed at a rate of  $4.17 \times 10^{-5} \text{ mol dm}^{-3} \text{ s}^{-1}$

ii.  $\text{I}^-$  ions are consumed at a rate of  $8.34 \times 10^{-5} \text{ mol dm}^{-3} \text{ s}^{-1}$

2 moles of  $\text{I}^-$  are consumed for every mole of  $\text{H}_2\text{O}_2$ , so ii is double

i

5



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.

Titration samples from the reaction mixture with an aqueous alkali of known concentration.

## EXERCISE 6-B

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.

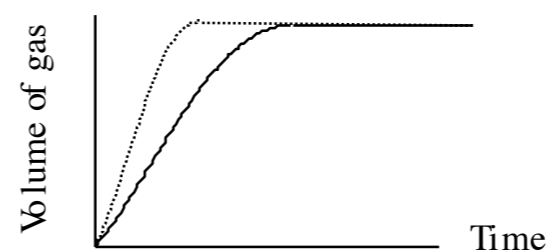
- a) The reaction of marble (calcium carbonate) chips with hydrochloric acid.
- b) The variation of the total mass of the reaction system with time. As a gas with quite a high molar mass is evolved there is a significant change in total mass during the reaction. This technique is relatively easy to carry 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.

### EXERCISE 6-C

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.
- d) Chemical reactions usually require an input of energy to overcome the activation energy of the reaction. Usually this comes from the kinetic energy of the particles, but in some cases light energy can be absorbed to produce a very reactive excited state of one of the reactants, or it results in the breaking of a covalent bond in one of the reactant molecules to form reactive free radicals.



- c) The lead dioxide is acting as a catalyst. d) By increasing the temperature.

## EXERCISE 6-D

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

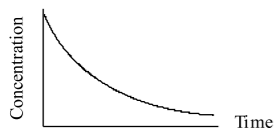
6. a) Comparing 1 and 2, doubling  $[\text{CH}_3\text{COCH}_3]$  doubles the rate of reaction. Comparing 2 and 4, halving  $[\text{I}_2]$  has no effect on the rate of reaction. Comparing 1 and 6, doubling  $[\text{H}^+]$  doubles the rate of reaction.

The rate expression is:  $\text{Rate} = k.[\text{CH}_3\text{COCH}_3].[\text{H}^+]$

b) The reaction is first order in  $\text{CH}_3\text{-CO-CH}_3$ . The reaction is zero order in  $\text{I}_2$ . The reaction is first order in  $\text{H}^+$ . The reaction is second order overall.

c)  $\text{Rate} = k.[\text{CH}_3\text{-CO-CH}_3].[\text{H}^+] = 4 \times 10^{-6} \text{ mol dm}^{-3}\text{s}^{-1}$ ,  $\therefore k = 2 \times 10^{-5} \text{ mol}^{-1}\text{dm}^3\text{s}^{-1}$ .

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,  $\therefore k_1 = 4.95 \times 10^{-3} \text{ s}^{-1}$

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)  $\text{Rate} = k_2.[\text{ester}].[OH^-]$

If  $[OH^-]$  is virtually constant because it is present in excess, then

$\text{Rate} = (k_2.[OH^-]).[\text{ester}]$ .

This gives first order kinetics with an apparent rate constant ( $k_2.[OH^-]$ )  $= 0.2.k_2 = 4.95 \times 10^{-3} \text{ s}^{-1}$ .

$\therefore k_2 = 2.475 \times 10^{-2} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$

The two values are related by the concentration of the reagent present in large excess.

## EXERCISE 6-E

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

6. a) The reaction is second order in A and zero order in B, therefore  $\text{Rate} = k.[A]^2$

b) Substituting:  $3.2 \times 10^{-4} = k.(0.2)^2$ ;  $k = 3.2 \times 10^{-4} / 0.04 = 8 \times 10^{-3} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$

c)  $\text{Rate} = k.[A]^2 = 8 \times 10^{-3} \cdot (0.1)^2 = 8 \times 10^{-5} \text{ mol dm}^{-3} \text{ s}^{-1}$

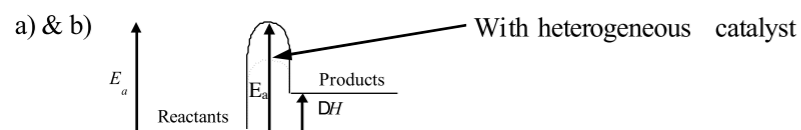
d) i  $A+A \rightarrow X$  (slow RDS) then  $X+B \rightarrow C+D+A$  (fast)

ii  $A+B \rightarrow C+D$  (slow RDS) or other possibilities.

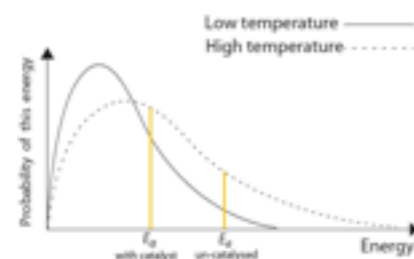
### EXERCISE 6-F

1. A 2. A 3. D

4.



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



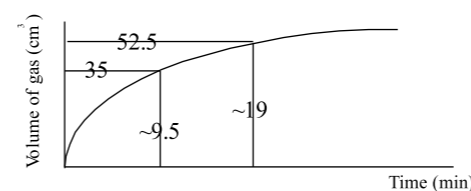
d) This would increase the rate of reaction. The reason for this is that the shape of the distribution of kinetic energies amongst the molecules will change so that a greater proportion of the molecules, and hence of the collisions, will have the required activation energy. There will also be a slight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

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

f) The rate of reaction with the catalyst could be measured at about 5 different temperatures, keeping all other conditions constant. A graph could be drawn of  $\ln(\text{rate})$  vs  $1/T$ , where  $T$  is the absolute temperature. Multiplying the gradient of the best fit line through the data points by  $R$  (the gas constant) would give the activation energy of the reaction in J.

g) 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.

7. 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) Half life at  $60^\circ\text{C} = \sim 28$  min and at  $70^\circ\text{C} = \sim 9\frac{1}{2}$  min, so rates in ratio  $\sim 1:3$ .

$$= -1.099$$

$$E_a = 104276 \text{ J mol}^{-1} = \sim 100 \text{ kJ mol}^{-1}$$

Chapter 7

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# Equilibrium

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A fine point of balance.



# Equilibrium

## CONTENTS

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1. 7.1 Equilibrium

2. 17.1 The equilibrium law



# Additional Material

## Swimming Pools



This very inviting swimming pool has a number of equilibria that the managers must monitor:

1. There is a need to include an anti-septic agent (for health reasons)

There are two common ways of achieving this:

A: adding chemicals.

B: adding sodium chloride and circulating the water through an electrolytic cell

What equilibria are involved in the two techniques.

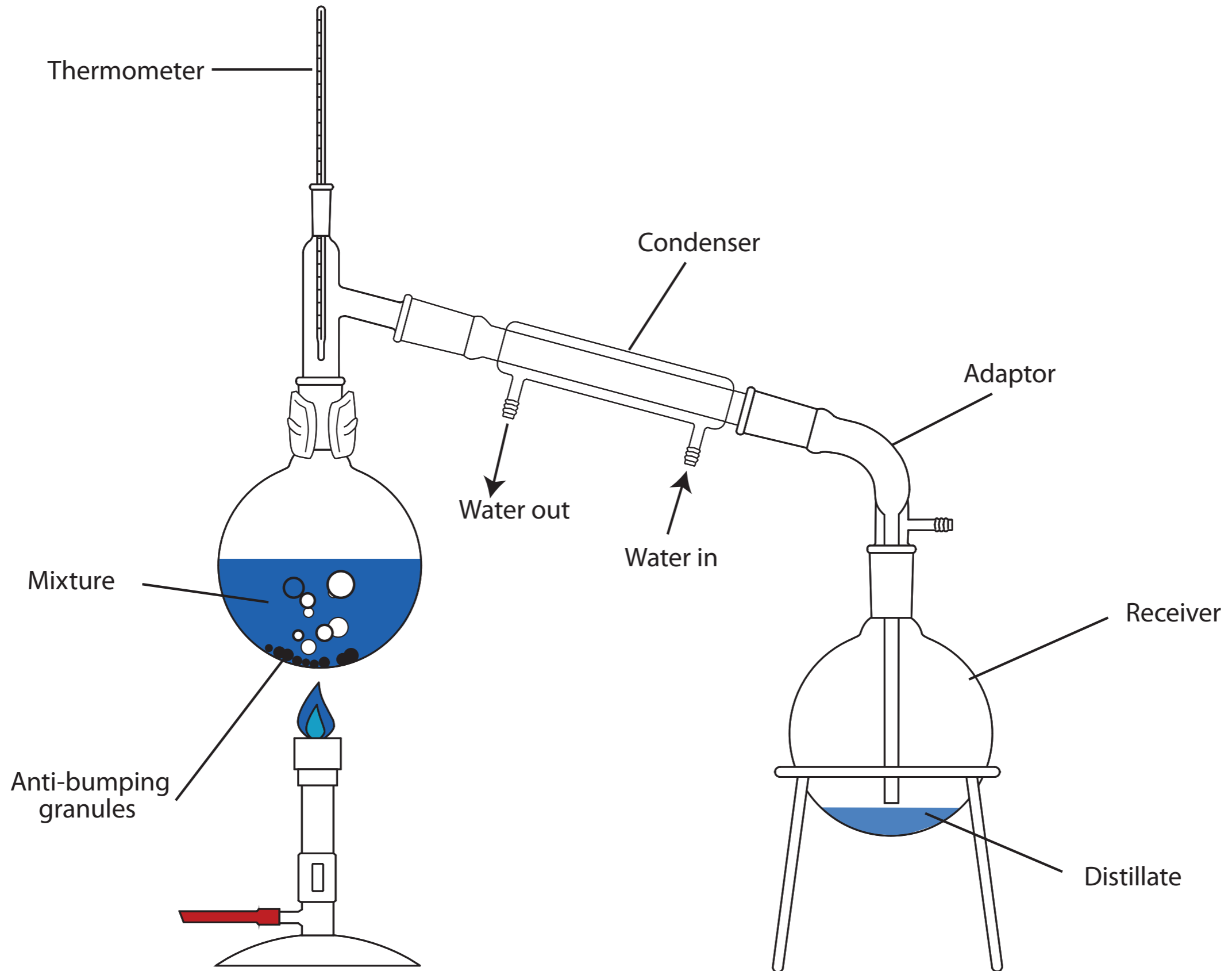
2. The pH of the pool must be maintained near neutral or swimmers will suffer eye and skin irritation. This is done by use of basic and acidic additives and a pH buffer.

What chemicals are commonly used?

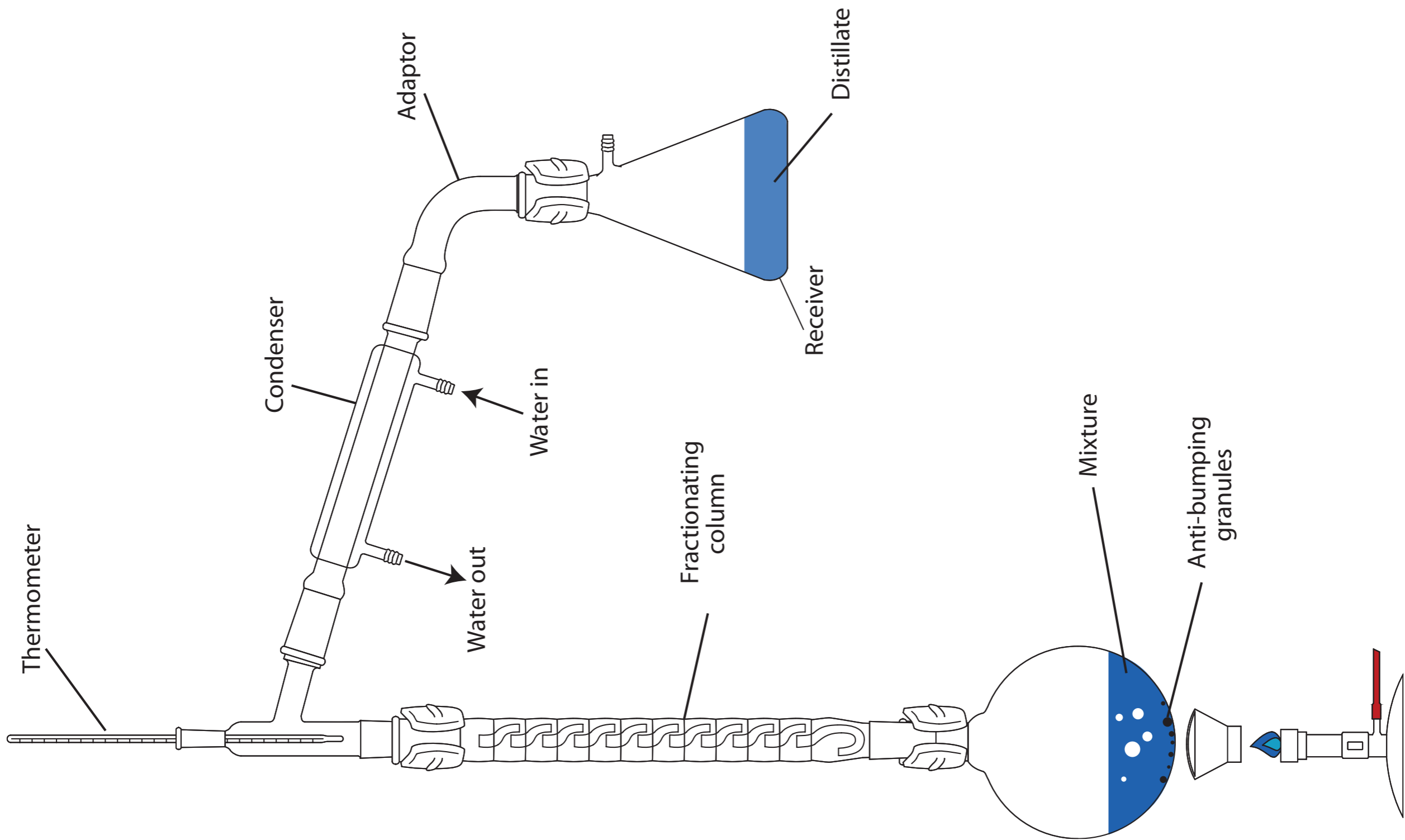
3. Tiled swimming pools use a basic mortar between the tiles. The tiles are usually fired ceramic and are inert.

How is the mortar/grout protected from acidic erosion?

# Enlarged diagrams







# Answers to exercises

## EXERCISE 7-A

1. C 2. C 3. D 4. C 5. A 6. D 7. B 8. C

9. a)  $\text{PCl}_5(\text{s}) \rightleftharpoons \text{PCl}_3(\text{s}) + \text{Cl}_2(\text{g})$

b) i It will start to dissociate.

ii The rate will decrease as its surface area 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) Yes. 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.

10. a)  $\text{N}_2(\text{g}) + 3 \text{H}_2(\text{g}) \rightleftharpoons 2 \text{NH}_3(\text{g})$   $K_c = \frac{[\text{NH}_3]^2}{[\text{N}_2] \cdot [\text{H}_2]^3}$

b)  $2 \text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2 \text{SO}_3(\text{g})$   $K_c = \frac{[\text{SO}_3]^2}{[\text{SO}_2]^2 \cdot [\text{O}_2]}$

c)  $\text{NH}_3(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{NH}_4^+(\text{aq}) + \text{OH}^-(\text{aq})$   
 $K_c = \frac{[\text{NH}_4^+] \cdot [\text{OH}^-]}{[\text{NH}_3]}$

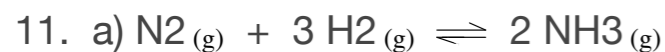
d)  $\text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}^+(\text{aq}) + \text{OH}^-(\text{aq})$   $K_c = [\text{H}^+] \cdot [\text{OH}^-]$

e)  $2 \text{NO}(\text{g}) + \text{Cl}_2(\text{g}) \rightleftharpoons 2 \text{NOCl}(\text{g})$   $K_c = \frac{[\text{NOCl}]^2}{[\text{NO}]^2 \cdot [\text{Cl}_2]}$

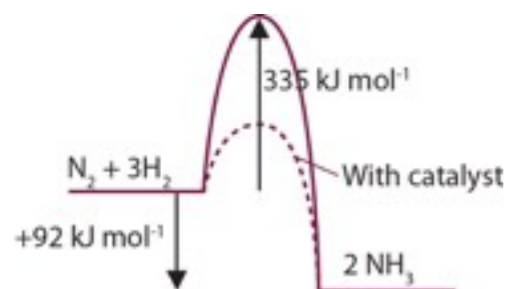
f)  $4 \text{NH}_3(\text{g}) + 5 \text{O}_2(\text{g}) \rightleftharpoons 6 \text{H}_2\text{O}(\text{g}) + 4 \text{NO}(\text{g})$   
 $K_c = \frac{[\text{H}_2\text{O}]^6 \cdot [\text{NO}]^4}{[\text{NH}_3]^4 \cdot [\text{O}_2]^5}$

g)  $\text{CH}_3\text{NH}_2(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{CH}_3\text{NH}_3^+(\text{aq}) + \text{OH}^-(\text{aq})$   
 $K_c = \frac{[\text{CH}_3\text{NH}_3^+] \cdot [\text{OH}^-]}{[\text{CH}_3\text{NH}_2]}$

h)  $\text{CH}_3\text{OH}(\text{l}) + \text{CH}_3\text{COOH}(\text{l}) \rightleftharpoons \text{CH}_3\text{COOCH}_3(\text{l}) + \text{H}_2\text{O}(\text{l})$   
 $K_c = \frac{[\text{CH}_3\text{COOCH}_3] \cdot [\text{H}_2\text{O}]}{[\text{CH}_3\text{OH}] \cdot [\text{CH}_3\text{COOH}]}$



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.

12. 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.



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  $\text{NO}_2$ , producing a lighter colour.

13.

Equilibrium	Effect of change	Balance by
a	Shifts to the left	Increasing the temperature
b	Shifts to the left	Increasing the pH (reducing $[\text{H}^+]$ )
c	Shifts to the left	Decreasing the pressure
d	Shifts to the right	Increasing the temperature
e	Shifts to the right	Increasing $[\text{NH}_3]$

14. 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 pressure 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.

15. 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  $\text{ICl}_3$  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.



b) i Increase the rate of the forward reaction.

ii Increases the rate of the reverse reaction.

iii The proportions of the two oxides 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.

## EXERCISE 7-B

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

5. a)  $\text{NH}_4\text{HS}$  is a solid so that its concentration cannot vary, therefore it is omitted from the equilibrium constant expression, so that the units are just  $[\text{NH}_3] \times [\text{H}_2\text{S}]$ , i.e.  $\text{mol}^2 \text{dm}^{-6}$ .

b)  $K_c = [\text{NH}_3] \times [\text{H}_2\text{S}] = 0.00001$ ,  $[\text{NH}_3] = [\text{H}_2\text{S}] = 3.16 \cdot 10^{-3} \text{ mol dm}^{-3}$ .

c) i Increases the mass of solid.

ii Decreases  $[\text{H}_2\text{S}]$ .

iii Does not affect the value of  $K_c$ .

6. 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 and that the reaction results in a reduction in the number of moles of gas as an increase in pressure causes an increase in the amount of product.

b)  $0.600 \text{ mol}^{-2} \text{dm}^6$ .

7. a)

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

c)  $[\text{CO}] = 1.60$ ;  $[\text{Cl}_2] = 1.20$ ;  $[\text{COCl}_2] = 0.400 \text{ mol dm}^{-3}$

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  $Q$  until its value is equal to the equilibrium constant.

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, as was concluded above.

8. a) As the temperature increases the equilibrium constant decreases, indicating the equilibrium shifts to the left, hence the reverse reaction must be endothermic, making the forward reaction exothermic.

b)  $\Delta G = -R.T. \ln K = -21.1 \text{ kJ mol}^{-1}$  at 500K and  $-29.4 \text{ kJ mol}^{-1}$  at 1100K

c)  $\Delta G = \Delta H - T.\Delta S$ , so  $\Delta H = T.\Delta S + \Delta G$ , hence assuming  $\Delta H$  is constant:

$500\Delta S - 21100 = 1100\Delta S - 29400$ , so  $\Delta S = +13.8 \text{ J mol}^{-1} \text{ K}^{-1}$

## EXERCISE 7-C

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

7. a) The temperature at which the total vapour pressure equals the external pressure.

b) The lower the boiling point, the weaker the intermolecular forces, so the intermolecular forces in cyclohexane are stronger than those in hexane.

c) Between  $69^\circ\text{C}$  and  $81^\circ\text{C}$ . 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 atmospheric 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.

$$8. \Delta T = K \times \frac{n \times m_{st}}{M_{st}} \times \frac{1000}{m_{sv}}$$

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

$$9. K = \Delta T \times \frac{1}{n_{st}} \times \frac{m_{sv}}{1000} = 1.2 \times \frac{1}{0.0135} \times \frac{20}{1000} = 1.78 \text{ K mol}^{-1}\text{kg}$$

$$10. PV = RT$$

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

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

11. 1 g of NaCl is equal to 0.0171 mol and of CaCl<sub>2</sub> is equal to 0.00901 mol. Because NaCl splits into 2 particles then it will produce 0.0342 mol of particles and as CaCl<sub>2</sub> splits into 3 particles, then it will produce 0.0270 mol of particles. As depression of freezing point is dependent on the number of moles of solute particles, 1 g of NaCl will, because of its lower molar mass, have a greater effect on the freezing point of water than 1 g of CaCl<sub>2</sub>.

$$12. \text{Initially: } p(\text{O}_2) = 20 \text{ kPa; } p(\text{N}_2) = 80 \text{ kPa; } p(\text{NO}) = 0$$

$$\text{At equilibrium } p(\text{O}_2) = 20 \times 0.97 = 19.4 \text{ kPa; } p(\text{N}_2) = 79.4 \text{ kPa; } p(\text{NO}) = 1.2 \text{ kPa}$$

Chapter 8

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# Acids and Bases

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Gargoyle at Canterbury Cathedral.

Partly a victim of acid rain and partly a victim of old age.



# Acids and Bases

## CONTENTS

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1. 8.1 Theories of acids and bases
2. 18.1 Lewis acids and bases
3. 8.2 Properties of acids and bases
4. 8.3 The pH scale
5. 8.4 Strong and weak acids and bases
6. 18.2 Calculations involving acids and bases
7. 18.3 pH curves
8. 8.5 Acid deposition



A volcanic 'beach-scape' in Hawaii. Volcanoes emit acidic gases and basic rocks in huge quantities. Are they environmentally neutral?



# Additional Material

Gallery 8.1 Classify these common items as acidic, basic or neutral.



*The sea*

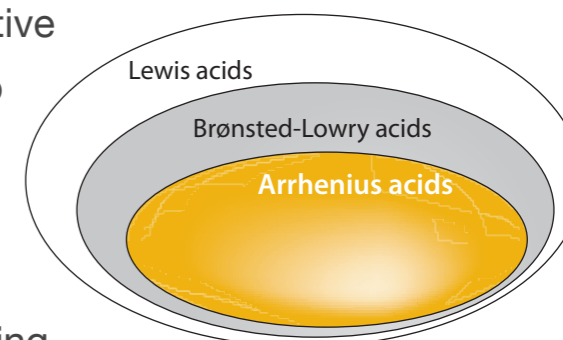


## TOK What is the relationship between depth and simplicity?

There is nothing that imparts energy quite like rivalry - if at a party last weekend your boy/girlfriend had been looking in an interested way at a member of the opposite sex, you might be taking a little more trouble over things this week. It's the same in science - if there is a rival theory on the block then people will start putting a lot more effort into research in this area, devising ingenious experiments that will support their pet theory or, more scientifically (you can never prove anything, only disprove it) undermine the alternative theory. In other words having differences of opinion raises interest and sharpens the focus on just what the differences are between the two approaches, maybe a little bit like the approach of a general election prompts you to look at the policy differences between the parties. Sometimes rival theories turn out to be complementary rather than in opposition to each other, as with the particle and wave theories of light where each describes a different aspect of the phenomena.

In the case of acid-base theories the relationship is one of generalisation, best indicated by the diagram shown. All Arrhenius acids are Brønsted-Lowry acids, and all of these are Lewis acids. Why don't we just have the Lewis definition; aren't the other ones obsolete? The answer is, not really. Almost all the acids we deal with are Arrhenius ones, because we work most of the time in aqueous solution. It is therefore a lot easier to

interpret these reactions in terms of the reactions of  $H^+$  (aq), rather than to spend time considering how electron-pair acceptance fits in to the picture. That is not to say that the other developments were a waste of time. The Brønsted-Lowry theory is the one that people most often use unless they specify otherwise. It has the advantages of focussing our attention on the reciprocity of the interaction (conjugates), as well as being nice and snappy ("proton donor" & "proton acceptor") – an aspect not to be underestimated. Lewis just pointed out that this is a subset of a much wider range of interactions that involve the formation of a dative bond. It can be useful at times to reflect on generalities, like there a variety of activities that you can only partake of above a certain age (drinking alcohol, driving, joining the army etc.), but it is sometimes more useful to have more specific knowledge, like knowing what the drinking age is before going into a bar.



# Answers to exercises

## Gallery 8.1

The sea is slightly basic.

Wood ash is strongly basic. Mixed with water it forms lye. When boiled with fats, lye forms soap.

Vinegar and oranges are acidic.

Household cleaners are typically basic.

New Zealand waterfall. Hmmm!! Probably close to neutral. There is the dissolved carbon dioxide (acidic), but those rocks are basic.

## EXERCISE 8-A

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

6 a) HCl;  $\text{HPO}_4^{2-}$ ;  $\text{C}_5\text{H}_5\text{NH}^+$  or  $\text{C}_5\text{H}_6\text{N}^+$ ;  $\text{H}_3\text{N}-\text{NH}_3^{2+}$ ;  $^- \text{OOC}-\text{COOH}$ .

b)  $\text{NO}_3^-$ ;  $\text{I}^-$ ;  $\text{SO}_4^{2-}$ ;  $\text{NH}_3$ ;  $\text{HONH}_2$

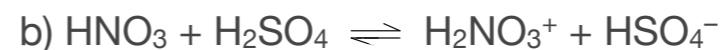
c)  $\text{HSO}_4^-$  and  $\text{N}_2\text{H}_5^+$ .

d) e.g.  $\text{H}_2\text{O}$  Conjugate base  $\text{OH}^-$  Conjugate acid  $\text{H}_3\text{O}^+$

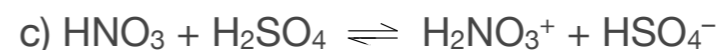
or  $\text{HCO}_3^-$  Conjugate base  $\text{CO}_3^{2-}$  Conjugate acid  $\text{H}_2\text{CO}_3$

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

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



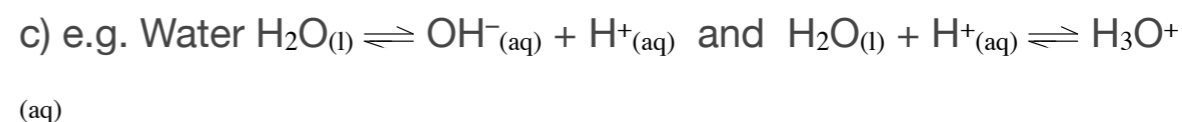
Sulfuric acid donates a proton to nitric acid, and thus behaves as an acid.



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

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 ( $\text{CO}_3^{2-}$ ), or it can act as a base and form carbonic acid ( $\text{H}_2\text{CO}_3$ ).

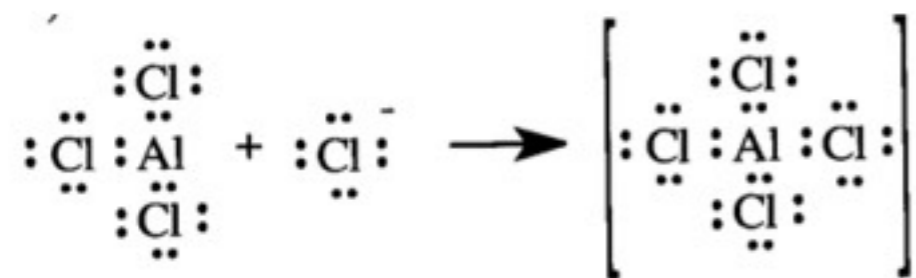


### EXERCISE 8-B

1. C

2. 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

3. a) Lewis base – the P in the  $\text{PH}_3$  has a lone pair of electrons that it can donate.

b) Lewis acid – the B in the  $\text{BCl}_3$  has an incomplete valence shell, so can accept a pair of electrons.

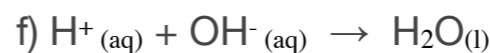
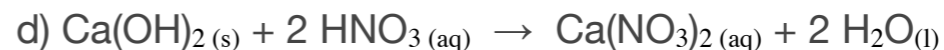
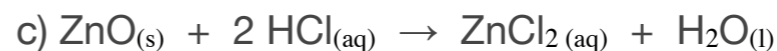
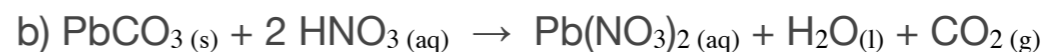
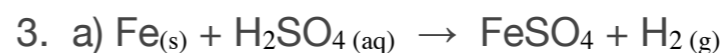
c) Lewis base – the S in the  $\text{H}_2\text{S}$  has a lone pair of electrons that it can donate.

d) Lewis base – the S in the  $\text{SF}_4$  has a lone pair of electrons that it can donate.

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

### EXERCISE 8-C

1. D 2. B



### EXERCISE 8-D

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

6. a)  $10^{-3} \text{ mol dm}^{-3}$  b)  $10^{-11} \text{ mol dm}^{-3}$  c)  $1 \text{ mol dm}^{-3}$

d)  $4.27 \times 10^{-5} \text{ mol dm}^{-3}$  e)  $7.41 \times 10^{-16} \text{ mol dm}^{-3}$

7. a) 4 b) 12 c) 7 (not 9, as adding acid to water cannot give an alkaline solution with pH greater than 7!) d) -0.26 e) 10.7

8. a) 1.14 b) 8.34 c)  $1.48 \times 10^{-6} \text{ mol dm}^{-3}$  d)  $0.00437 \text{ mol dm}^{-3}$   
e) 13.13

9. a)  $0.00250 \text{ mol dm}^{-3}$  b)  $4.00 \times 10^{-12} \text{ mol dm}^{-3}$   
c) Greater as each  $\text{Ba}(\text{OH})_2$  forms two  $\text{OH}^-$  ions.

10. a)  $3.16 \times 10^{-7} \text{ mol dm}^{-3}$  b)  $3.16 \times 10^{-8} \text{ mol dm}^{-3}$  c) Both would increase as more water dissociates producing more  $\text{H}^+$  and  $\text{OH}^-$ .

### EXERCISE 8-E

1. C 2. A 3. A

4. a)  $\text{NH}_3(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{NH}_4^+(\text{aq}) + \text{OH}^-(\text{aq})$ .

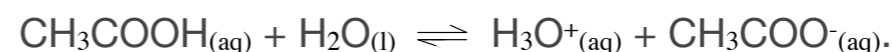
The presence of hydroxide ions make the solution alkaline or  $\text{NH}_4^+$  is a weak acid and  $\text{OH}^-$  is a strong base, thus the solution is basic.

b) A base is a species that accepts a hydrogen ion, for example  $\text{NH}_3$  accepts a hydrogen ion to form  $\text{NH}_4^+$ . 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  $[\text{OH}^-] = 0.1 \text{ mol dm}^{-3}$  whereas in ammonia the ammonia is in equilibrium with the ammonium and

hydroxide ions, so  $[\text{OH}^-]$  is much less than  $0.1 \text{ mol dm}^{-3}$ . This means that the pH is lower in the ammonia solution.

5. a)  $\text{HCl}(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightarrow \text{H}_3\text{O}^+(\text{aq}) + \text{Cl}^-(\text{aq})$ . The acid is fully dissociated.



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.

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 at pH 7, whereas with the weak acid, it will be greater than pH 7 (approximately pH 9).x

6. The hydrochloric acid is full dissociated and so  $[\text{H}^+] = 5 \times 10^{-4} \text{ mol dm}^{-3}$ , 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)

$$n = \frac{m}{M} = \frac{0.63}{63} = 0.01, c = \frac{n}{v} = \frac{0.01}{0.1} = 0.1 \text{ mol dm}^{-3}$$

b) 1 c)  $1 \times 10^{-13} \text{ mol dm}^{-3}$  d)  $\text{HNO}_2 \rightleftharpoons \text{H}^+ + \text{NO}_2^-$

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 ( $\text{HCl} \rightarrow \text{H}^+ + \text{Cl}^-$ ),

hence the  $[\text{H}^+] = 0.01 \text{ mol dm}^{-3}$  and the pH is 2. Sulfuric acid is a strong dibasic acid ( $\text{H}_2\text{SO}_4 \rightarrow 2\text{H}^+ + \text{SO}_4^{2-}$ ), hence the  $[\text{H}^+] = 0.02 \text{ mol dm}^{-3}$  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 ( $\text{CH}_3\text{COOH} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{CH}_3\text{COO}^-$ ). This means that  $[\text{H}^+]$  is much less than  $0.01 \text{ mol dm}^{-3}$  and hence the pH is much greater than 2.

### EXERCISE 8-F

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

6. a) 7.21 b)  $[\text{H}^+] = \sqrt{(0.02 \times 6.17 \times 10^{-8})} = 3.51 \times 10^{-5} \text{ mol dm}^{-3}$ , therefore pH = 4.45

c)  $1.62 \times 10^{-7} \text{ mol dm}^{-3}$

7. a)  $4.57 \times 10^{-4} \text{ mol dm}^{-3}$

b)  $[\text{OH}^-] = \sqrt{(0.003 \times 4.57 \times 10^{-4})} = 1.17 \times 10^{-3} \text{ mol dm}^{-3}$ , so pOH = 2.93 and pH =  $14 - 2.93 = 11.07$

c) Concentration dissociated =  $1.17 \times 10^{-3} \text{ mol dm}^{-3}$

Original concentration = 0.003, so % dissociated = 39%, % undissociated = 61% (so approximation used in b not valid!)

$$8. \text{ a) } K_a = \frac{(10^{-4.67})^2}{0.28} = 1.63 \times 10^{-9} \text{ mol dm}^{-3}$$

b) Weaker, as  $pK_a = 8.79$  and the greater  $pK_a$ , the weaker the acid.

$$\text{c) } K_a = \frac{(10^{-5})^2}{[\text{acid}]} = 1.63 \times 10^{-9} \text{ mol dm}^{-3}$$

$$[\text{acid}] = \frac{1 \times 10^{-10}}{1.63 \times 10^{-9}} = 0.0613$$

9.  $pK_a = 14 - pK_b = 9.25$

$$\text{So } K_a = 10^{-9.25} = \frac{(10^{-6})^2}{[\text{NH}_4^+]}$$

$$[\text{NH}_4^+] = 10^{9.25-12} = 10^{-2.75} = 1.78 \times 10^{-3}$$

10. a)  $\text{HCN}_{(\text{aq})} \rightleftharpoons \text{H}^+_{(\text{aq})} + \text{CN}^-_{(\text{aq})}$  or  $\text{HCN}_{(\text{aq})} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+_{(\text{aq})} + \text{CN}^-_{(\text{aq})}$

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

c) Percentage =  $100 \times \frac{2.24 \times 10^{-6}}{0.01} = 0.0224 \%$

If diluted, the percentage increases.

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

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

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

### EXERCISE 8-G

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

6. a) Amount of HCl =  $c \cdot V = 0.2 \times 0.015 = 3 \times 10^{-3} \text{ mol}$

$c = \frac{n}{V} = \frac{3 \times 10^{-3}}{0.02} = 0.15 \text{ mol dm}^{-3}$

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

$0.15 \text{ mol dm}^{-3}$

b) i  $pK_b = 14 - pK_a = 14 - 9.3 = 4.7$

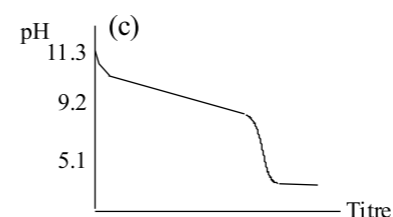
$[OH^-] = \sqrt{(K_b \cdot [B])} = \sqrt{(10^{-4.7} \cdot 0.15)} = 1.73 \times 10^{-3}$ ;

$pOH = 2.76$ , 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  $[H^+] = \sqrt{(K_a \cdot [HA])} = \sqrt{(10^{-9.3} \times 0.15)} = 8.67 \times 10^{-6}$ , 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.

6. 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 colour change will be at about pH 4, which is within the expected pH change at the equivalence point.

8. 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  $14 - pK_b$  of ammonia.

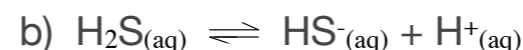
9. a) i. The sudden drop in pH would occur at  $\sim 12.5 \text{ cm}^3$  as  $H_2SO_4$  is dibasic.

ii. The sudden drop in pH at  $\sim 25 \text{ cm}^3$  would only go to  $\sim \text{pH} = 6$  and would decrease only very gradually 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.

10. a)  $HS^-$



$$c) \text{ As volume} = 1 \text{ dm}^3, c = \frac{m}{M} = \frac{3.41}{34.1} = 0.100 \text{ mol dm}^{-3}$$

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

therefore  $\text{pH} = 4.01$

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.

$$g) c = \frac{m}{M} = \frac{11.0}{56.07} = 0.196 \text{ mol dm}^{-3}$$

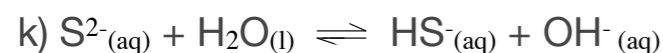
h) The solution has a pH of 4.01 (see d), so with bromothymol blue it will be yellow (the "acid" colour), and with methyl yellow it will also be yellow (the 'alkali' colour).

i) Indicators are weak acids/bases in which the colours of the acidic and basic forms ( $HIn$  and  $In^-$  in the equilibrium  $HIn_{(aq)} \rightleftharpoons H$



$^{+}(\text{aq}) + \text{In}^{-}(\text{aq})$  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  $\text{p}K_a$  value of the acid.

j) 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.



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

m)  $= 0.0891 \text{ mol dm}^{-3}$

n) 
$$K_b = \frac{[\text{HS}^{-}] \cdot [\text{OH}^{-}]}{[\text{S}^{2-}]} = \frac{0.0891^2}{0.100} = 0.0794$$

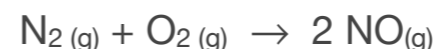
$$K_a = \frac{K_w}{K_b} = \frac{1 \times 10^{-14}}{0.0794} = 1.26 \times 10^{-13} \text{ mol dm}^{-3}$$

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

## EXERCISE 8-H

1. A 2. C 3. B

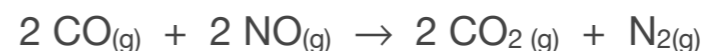
4. a) The combination of atmospheric nitrogen and oxygen in high temperature flames:



b) Chemically, marble is calcium carbonate. It dissolves in acidic solutions because of the reaction:



c) The valuable metals are elements like platinum and palladium. These are used as catalysts in catalytic converters fitted to car exhausts. In the catalytic converter carbon monoxide and nitrogen monoxide in the exhaust gases react to form carbon dioxide and water according to the equation:



5. Fish are seriously affected by acid deposition, which reduces the pH of the rivers and lakes that they live in. They are unable to breed if the pH falls too low and acid deposition causes leaching of the soil and the resulting increase in  $[\text{Al}^{3+}]$  can affect the functioning of the gills, causing oxygen deprivation that can lead to death.

Trees may be directly affected by acid deposition causing damage to their leaves. They are also indirectly affected because the leaching of the soil by acid deposition can lead to a deficiency of vital trace elements such as calcium and magnesium.

### EXERCISE 8-1

1. B 2. D 3. B 4. C 5. C 6. B 7. C

8. a)  $\text{pOH} = 14 - \text{pH} = 14 - 9.3 = 4.7$

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

b) The solution must be more acidic, so more of the acidic component ( $\text{NH}_4^+$ ) is required, so more ammonium chloride is needed.

c) At  $\text{pH} = 9$ ,  $[\text{OH}^-] = 10^{-5}$ , so

$$[\text{BH}^+] = \frac{K_b \cdot [\text{B}]}{[\text{OH}^-]} = \frac{2.00 \times 10^{-5} \times 0.1}{10^{-5}} = 0.200 \text{ mol dm}^{-3}$$

d) Ethanoic acid and sodium ethanoate (or any similar strength weak acid and conjugate base) or sodium hydroxide and excess ethanoic acid (or any similar strength weak acid partially neutralised by a strong base).

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



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.

10. 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.

# Redox Processes

Solar Power plants often require large lead-acid cells to store energy during the day for use at night.

Detail of the system on Lady Elliot Island, Great Barrier Reef.

The system also has a diesel generator backup.



# Redox Processes

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1. 9.1 Oxidation and reduction
2. 9.2a Electrochemical cells
3. 19.1a Electrolysis of aqueous solutions
4. 19.1b Quantitative aspects of electrolysis
5. 9.2b Voltaic cells
6. 19.1c Standard electrode potentials

**Gallery 9.1** A medium sized solar power station (see chapter header).



*Cells*



## Additional Material

### TOK Are Oxidation Numbers Real?

I remember contemplating on the nature of reality back in Chapters 2 and 4, with regard to electrons and hybridization respectively. The implication always seems to be that reality is in some way desirable. Maybe my bank account might be a useful analogy to oxidation numbers? At the end of every month there is a number assigned to it, but as the month progresses this number gets smaller and the numbers assigned to the local supermarket, the petrol station, the government etc. all go up. Hardly any of it gets turned into bank notes for me to carry around and even then is a bank note any more real than the number printed on my bank statement. Isn't the fact that this piece of paper is worth \$20 just another, very convenient, shared fiction? Along as we are all happy to share the belief that the figures on my bank statement and the number on my bank notes mean something then real or not these numbers, like oxidation numbers, are very useful and certainly a lot easier than pushing around wheelbarrows full of gold, or wearing a necklace of sea-shells with holes drilled in them. The whole thing is perhaps closely related to the philosophy of Charles Sanders Peirce, who developed the concept of "pragmatic truth" - that in which it was convenient for society to believe; in other words truth is more an attribute of a society than an attribute of the physical world. Are oxidation numbers useful? Certainly they are capable of giving us a definitive answer as to whether in a chemical change, a

particular atom is oxidised, reduced, or neither, but is the change any more than "electron accounting" that helps us balance equations? F going to F<sup>-</sup> is just a change of -1 whereas N going to N<sup>3-</sup> is a change of -3, but the former is far more energetically favourable.

### Minerals

Crocoite is a monoclinic crystalline mineral containing of lead chromate, PbCrO<sub>4</sub>



Geologists have a general principle that the colour of a mineral reflects the redox conditions in which it was formed. Oxidising conditions lead to red colours. Reducing conditions lead to green or white.

How does this principle explain the colour of crocoite?

Here are some other examples.

Quartz



# Answers to exercises

## EXERCISE 9-A

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  $\text{Fe}^{2+}$  e.g.  $\text{FeSO}_4$ ,  $\text{FeCl}_2$  etc.

b)  $\text{NH}_3$ ,  $\text{NH}_4^+$  c)  $\text{MnO}_4^-$  d)  $\text{CH}_2\text{Cl}_2$ ,  $\text{CH}_2\text{O}$  e)  $\text{PCl}_5$ ,  $\text{POCl}_3$ ,  $\text{P}_4\text{O}_{10}$  ( $\text{P}_2\text{O}_5$ )

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)  $2\text{N}_2\text{H}_4 + \text{N}_2\text{O}_4 \rightarrow 3\text{N}_2 + 4\text{H}_2\text{O}$

c) The products are both common, stable, inert, non-toxic species and hence cannot be considered pollutants.

10. a)  $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$

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)  $\text{N}_2$ ; h) Orange to green; i) The reaction is exothermic.

## EXERCISE 9-B

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.

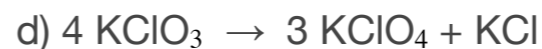
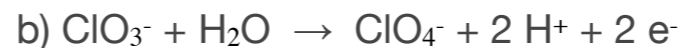
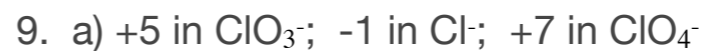
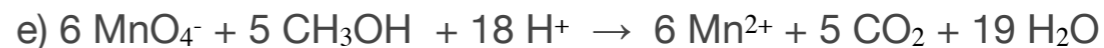
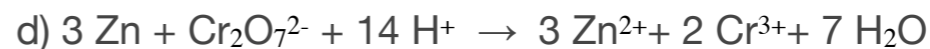
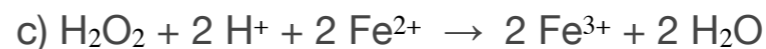
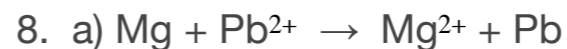
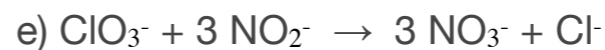
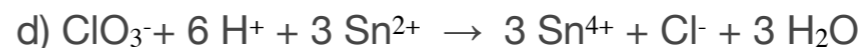
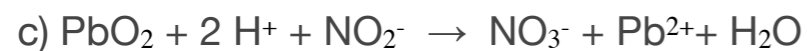
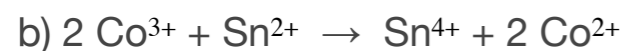
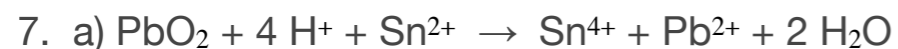
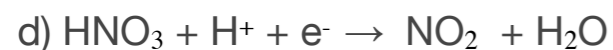
5. You could put strips of the metal M into aqueous solutions of salts of metals such as copper sulfate, zinc chloride and

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  $\text{MSO}_4$ . 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.

### EXERCISE 9-C

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



e) When combining the half equations the water and hydrogen ion terms cancel out, so no other reagent is needed.

10.

	Initial	Final
Mol $\text{S}_2\text{O}_3^{2-}$	$2.13 \times 10^{-4}$	$1.36 \times 10^{-4}$
Mol $\text{I}_2$	$1.065 \times 10^{-4}$	$6.8 \times 10^{-5}$
Mol $\text{Mn}^{3+}$	$2.13 \times 10^{-4}$	$1.36 \times 10^{-4}$
Mol $\text{O}_2$	$5.325 \times 10^{-5}$	$3.4 \times 10^{-5}$



Mol O<sub>2</sub> consumed = (5.325 – 3.400) x 10<sup>-5</sup> = 1.925 x 10<sup>-5</sup> in  
200 cm<sup>3</sup>

[O<sub>2</sub>] consumed = 5 x 1.925 x 10<sup>-5</sup> = 9.625 x 10<sup>-5</sup> mol dm<sup>-3</sup>

BOD = 32.00 x 1.925 x 10<sup>-5</sup> = 6.16 x 10<sup>-4</sup> g dm<sup>-3</sup> = 0.616  
mg dm<sup>-3</sup>

### EXERCISE 9-D

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<sub>2</sub> + 2 S<sub>2</sub>O<sub>3</sub><sup>2-</sup> → 2 I<sup>-</sup> + S<sub>4</sub>O<sub>6</sub><sup>2-</sup>

d) +2 to +2½

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

f) Mol S<sub>2</sub>O<sub>3</sub><sup>2-</sup> = c x V = 0.2 x 0.015 = 3 x 10<sup>-3</sup>

Mol of Cu<sup>2+</sup> = 2 x mol I<sub>2</sub> = mol S<sub>2</sub>O<sub>3</sub><sup>2-</sup> = 3x10<sup>-3</sup>

[Cu<sup>2+</sup>] = n/V = 3x10<sup>-3</sup>/0.02 = 0.15 mol dm<sup>-3</sup>

5. a) From colourless to purple (from excess MnO<sub>4</sub><sup>-</sup>).

b) Mol Fe = m/M<sub>r</sub> = 2.00/55.85 = 0.0358

MnO<sub>4</sub><sup>-</sup> + 8 H<sup>+</sup> + 5 Fe<sup>2+</sup> → Mn<sup>2+</sup> + 4 H<sub>2</sub>O + 5 Fe<sup>3+</sup>

Mol MnO<sub>4</sub><sup>-</sup> = 1/5 mol Fe<sup>2+</sup> = 0.0358/5 = 7.16 x 10<sup>-3</sup>

Volume required = n/V = 7.16x10<sup>-3</sup>/0.2 = 0.0358 dm<sup>3</sup> = 35.8  
cm<sup>3</sup>

### EXERCISE 9-E

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<sup>-</sup> → Cl<sub>2</sub> + 2 e<sup>-</sup>

d) Bubbles of yellow-green gas.

e) Cu<sup>2+</sup> + 2 e<sup>-</sup> → Cu

- f) A layer of a red-brown solid
- g) Reduction, because the copper ions are gaining electrons.

### EXERCISE 9-F

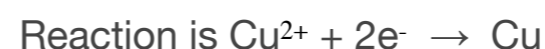
1. D 2. A 3. D
4. a) The chloride ion.
- b) Oxidation.
- c) The ion from the calcium chloride.
- d)  $2 \text{Cl}^- \rightarrow \text{Cl}_2 + 2 \text{e}^-$
- e) Bubbles of yellow-green gas would be evolved.
- f) If the chloride ion concentration was quite low, then the water might be oxidised to oxygen, rather than the chloride ions to chlorine.
- g) The calcium ion.
- h) The water will be changed most easily.
- i)  $2 \text{H}_2\text{O} + 2 \text{e}^- \rightarrow \text{H}_2 + 2 \text{OH}^-$  or  $2 \text{H}^+ + 2 \text{e}^- \rightarrow \text{H}_2$
- j) Bubbles of colourless gas would be evolved.
- k) The solution would eventually become calcium hydroxide.

l)  $\Delta G$  is probably positive because the process is non-spontaneous and electrolysis is required for the change to occur.

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

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

c) Amount of electrons passed = 0.0373 mol



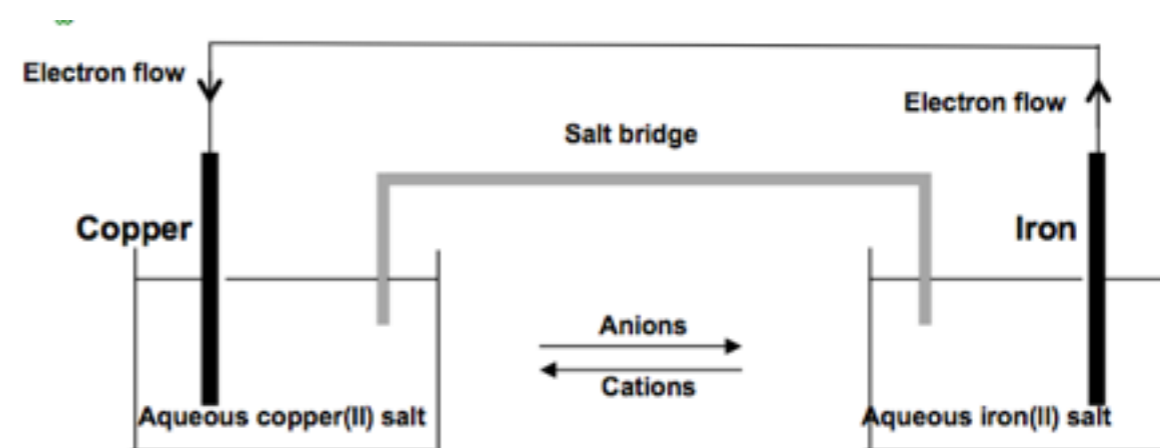
Amount of Cu =  $\frac{1}{2}$  amount of electrons = 0.01865 mol

Mass of Cu =  $n \times M = 0.01865 \times 63.55 = 1.19 \text{ g}$

### EXERCISE 9.G

1. A 2. D 3. B

4. a)



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

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

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.

f)  $\text{Fe(s)} \mid \text{Fe}^{2+}(\text{aq}) \parallel \text{Cu}^{2+}(\text{aq}) \mid \text{Cu(s)}$

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.

### EXERCISE 9-H

1. D 2. C 3. A

4. a) A temperature of 298K, all concentrations 1 mol dm<sup>-3</sup>, (pressure of 100 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)  $\text{Ag(s)} \mid \text{Ag}^+(\text{aq}) \parallel \text{Mn}^{2+}(\text{aq}) \mid \text{Mn(s)}$

g) -1.98 V

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

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

5. a)

$$E = E^\ominus + \frac{R.T}{n.F} \ln \frac{[\text{Ox}]}{[\text{Red}]} = +1.36 + \frac{8.31 \times 298}{6 \times 96500} \ln \frac{[\text{Cr}_2\text{O}_7^{2-}] \cdot [\text{H}^+]^{14}}{[\text{Cr}^{3+}]^2}$$
$$= +1.36 + 4.277 \times 10^{-3} \times \ln \frac{2 \times 5^{14}}{(1 \times 10^{-4})^2}$$

$$= + 1.36 + 4.277 \times 10^{-3} \times \ln(1.22 \times 10^{18})$$

$$= + 1.36 + 4.277 \times 10^{-3} \times 41.65$$

$$= 1.54 \text{ V}$$

b) The electrode potential is now significantly greater than that of the chloride ion/chlorine under standard conditions (+1.36 V) and so the reaction would become spontaneous and the fact that chlorine gas is evolved would drive the equilibrium to the right resulting in complete reaction.

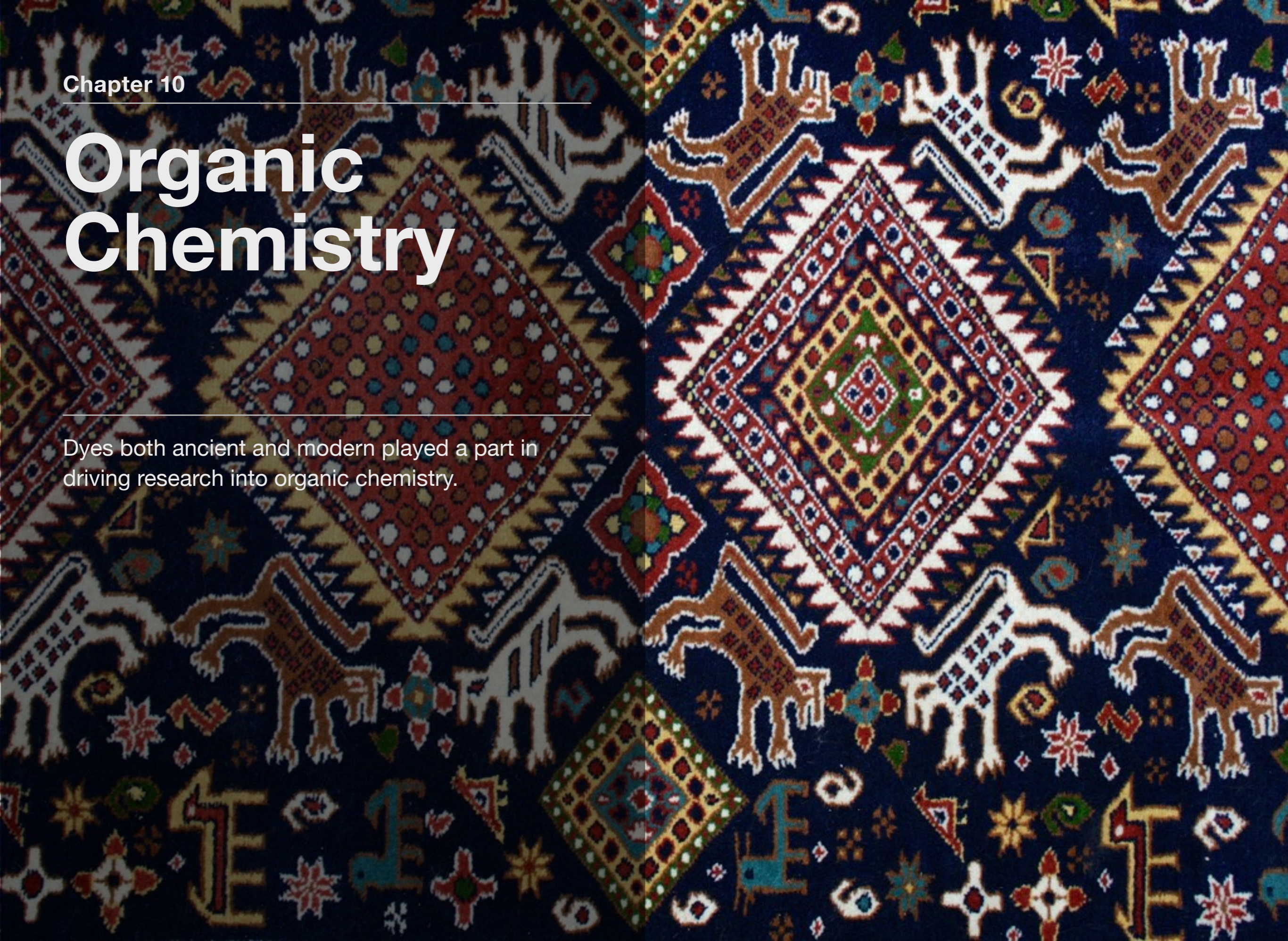
Chapter 10

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# Organic Chemistry

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Dyes both ancient and modern played a part in driving research into organic chemistry.



## Section 1

# Organic chemistry

### CONTENTS

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1. 10.1 Fundamentals of organic chemistry
2. 10.2 Functional group chemistry
3. 20.1 Types of organic reactions
4. 20.2 Synthetic routes
5. 20.3 Stereoisomerism



Hexagons in the roof of the Eden Project, UK.

# Additional Material

## TOK The importance of chemical models

The different types of formulas referred to in this chapter are certainly employed for different purposes. “Empirical” means “by experiment” and that’s exactly what the empirical formula is – the result of a microanalysis experiment in which all of the carbon in the compound is converted into carbon dioxide and all the hydrogen into water, so the relative amounts of carbon, hydrogen and oxygen can be calculated, but on its own it is not of much further use. Combine it however with some information about how heavy each molecule is and we can then deduce some much more interesting information; how many atoms of each element are present in every molecule. That then allows us to test our theories of chemical bonding to work out the structural formulae showing how atoms can join together. Sometimes this can really stretch the mind and require creative thought, like Kekulé’s dream.

This question also started me thinking about the words “formula” and “model” – do they mean the same thing and if not how do they differ? Both transfer information, but models (like the Bohr model of the atom) are also used to help with our “understanding” (whatever exactly that is) of the world and maybe that is a facet we do not seek in a formula. When I look, even at a full structural formula, I do not think that it helps my “understanding”, it just conveys “information” about how the atoms are joined in the

molecule and hence its probable shape. Now that leads us back to “models”, though perhaps a slightly different use of the word – I’ll leave you to judge. We get an even better idea of the shape using molecular models of different types. These are rather like different maps, each show some things clearly and other things less well, “Ball and stick” models for example give a clear idea of shape and what bonds are present, but the atoms always seem to be a long way apart. “Space filling” models more accurately reflect bond lengths as well as the different sizes of the atoms involved. Actually the concept of atomic size is an interesting one considering that we envisage the outer regions of an atom as just a cloud of electron density. How do we know where it ends? It’s a bit like asking where does the Earth’s atmosphere end; it doesn’t really it just sort of fades away to nothing.

TOK The use of conventions in representing three-dimensional molecules in two dimensions

Conventions, and the extent that they are a result of cultural conditioning, is a fascinating subject. The diagrams in this book have to attempt to represent three-dimensional molecules through the two-dimensional medium of the page of the book. This is a problem that graphic artists also have to contend with and as a result they developed the technique of perspective. Our drawings have attempted to draw on some of these techniques, but added a few other little conventions, such as things with

dotted lines being below the plane of the book and wedge shaped lines coming out of the page. Like so many things, the concept of perspective was well known to the Greeks, but was then lost to be rediscovered and thoroughly developed in the Renaissance period. It depends on the apparent diminution of size with distance and the resulting convergence of lines. If we show two human figures in a drawing, but one is much smaller than the other we can either assume the smaller one is further away from us, or that it represents a leprechaun or some other kind of diminutive human. Usually for us the former explanation is more convincing. A consequence of this is that the constant width of a road appears to be smaller the further away from us it goes, hence as it disappears towards the horizon the sides of the road appear to get closer together, meeting at the horizon (in theory an infinite distance away!). We have grown up with these tricks of the graphic artist and find it difficult when viewing a scene drawn using perspective, to imagine in any other way.

It is reported that when drawings incorporating perspective are shown to people of more 'primitive' cultures, they do not realise that some of the objects are supposed to be further away than others, in other words the appreciation of perspective is something that we develop by growing up in a culture where it is widely employed. Others however contest this say that the appreciation of perspective, even though not developed by all societies, is innate to humans rather than something that is culturally developed. Anyway I hope that you have all been

exposed to enough Escher "impossible geometries" to be able to pick up the three-dimensional shapes that we are trying to represent.

## **TOK The use of conventions in representing three-dimensional molecules in two dimensions**

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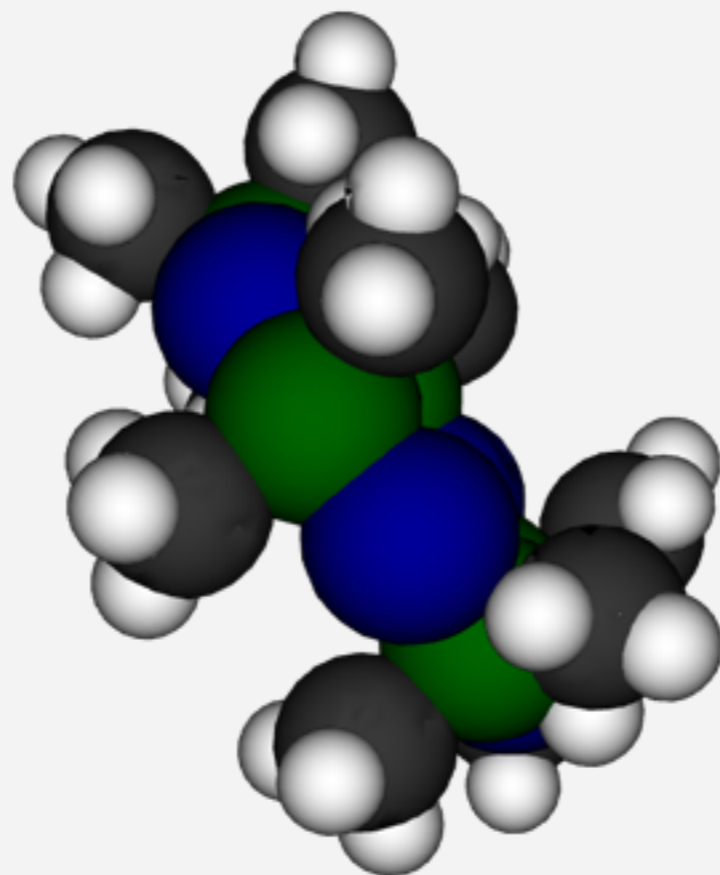
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#### PERSPECTIVES IN THE KIMBERLEY RANGES

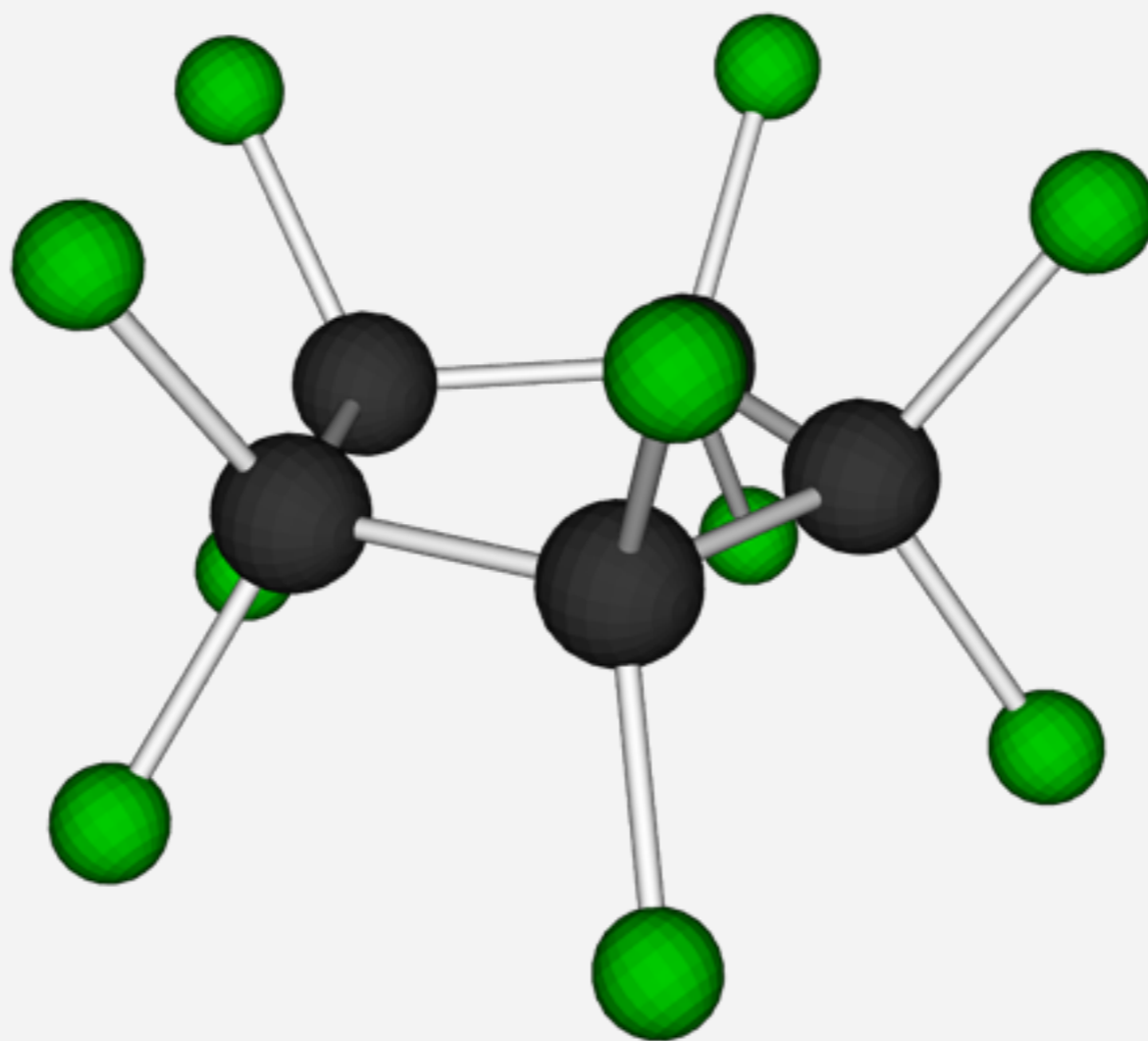


**Interactive 10.1** Types of molecular model.



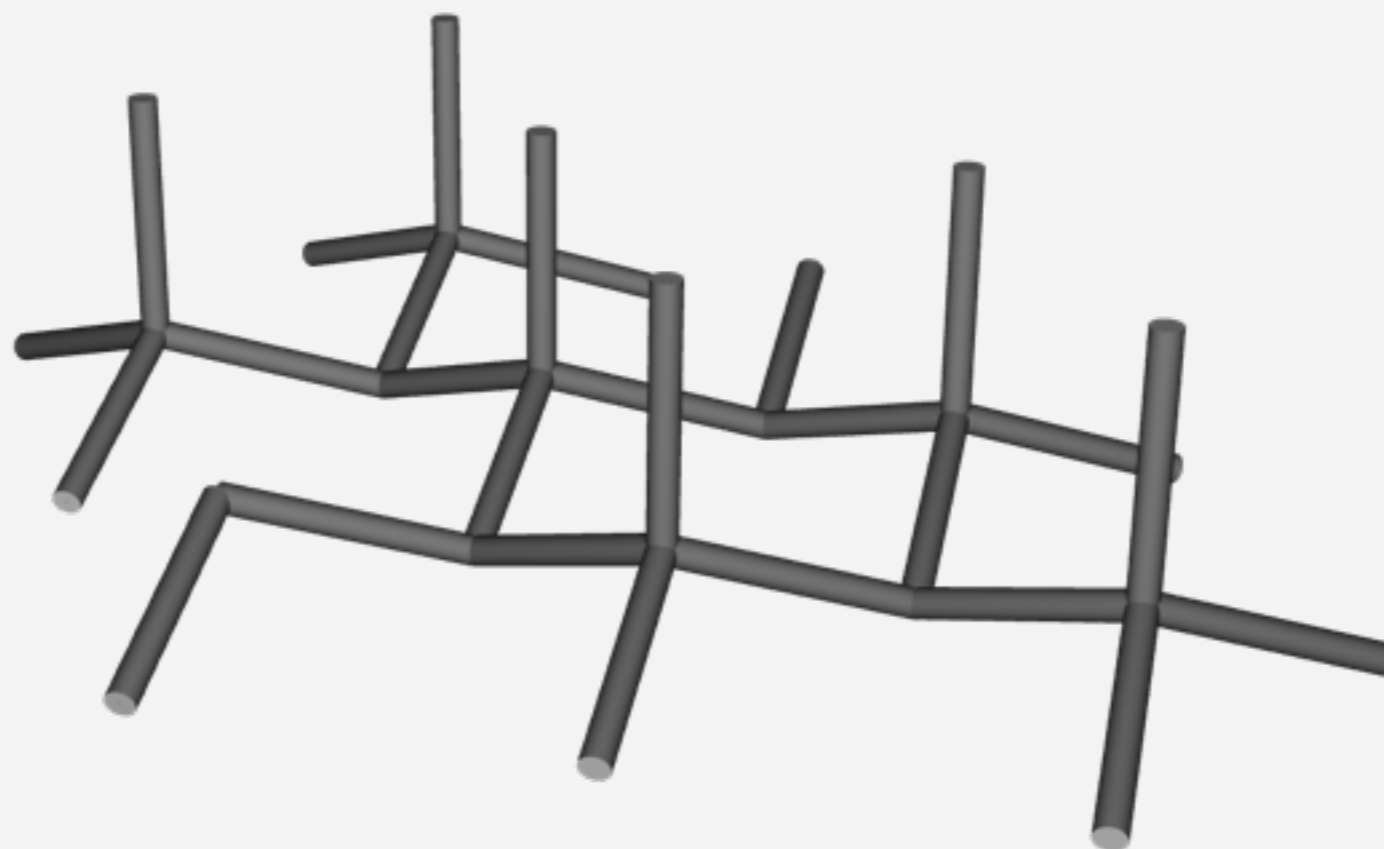
*Space filler model*

**Interactive 10.2** Types of molecular model.



*Stick and Ball Model - cyclopentane*

**Interactive 10.3** Types of molecular model.



*Stick Model - menthol*

# Answers to exercises

## EXERCISE 10 - A

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 dispersion 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 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)  $CH_3-(CH_3)CH-CH=CH_2$

e)  $CH_3-CCl_2-(CH_3)CH-COOH$

13. a)  $CH_3-(CH_3-O)CH-CH_2-CH_3$  or  $CH_3-CH_2-O-CH_2-CH_2-CH_3$

b)  $CH_3-O-CH_2-CH(CH_3)_2$

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

$CH_3-CH(CH_3)-CH(CH_3)-CH_3$  2,3-dimethylbutane

$CH_3-C(CH_3)_2-CH_2-CH_3$  2,2-dimethylbutane

15. a) Methylpropene

b) 3-chloropentane

c) 3-iodobutan-1-ol

d) 4-hydroxy-4-methylpentanoic acid

e show two human figures in a drawing, but one is much smaller than the other we can either assume the smaller one is further away from us, or that it represents a leprechaun or some other kind of diminutive human. Usually for us the former explanation is more convincing. A consequence of this is that the constant width of a road appears to be smaller the further away from us it

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### EXERCISE 10 - B

1. A 2. B 3. A 4. D 5. B 6. A 7. D 8. D 9. A 10. D

11. a)  $\text{CH}_3\text{-CH}_2\text{-CH=CH-CH}_3$

b)  $\text{C}_5\text{H}_{10(l)} + 7\frac{1}{2} \text{O}_{2(g)} \rightarrow 5 \text{CO}_{2(g)} + 5 \text{H}_2\text{O}_{(l)}$

c) Heat energy.

d) Carbon monoxide, or carbon.

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

f)  $\text{CH}_3\text{-CH}(\text{CH}_3)\text{-CH=CH}_2$ ; 3-methylbut-1-ene or

$\text{CH}_3\text{-CH}_2\text{-C}(\text{CH}_3)=\text{CH}_2$ ; 2-methylbut-1-ene.

12. a) Bromoethane;  $\text{CH}_3\text{-CH}_2\text{-Br}$

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 (or aluminium oxide) catalyst.

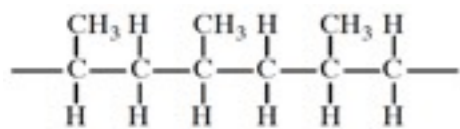
f) But-2-ene

g)  $\text{CH}_3\text{-CH}_2\text{-CH}(\text{OH})\text{-CH}_3$

13. 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)  $[-\text{CH}_2\text{CHCl}-]_n$ , formed from  $\text{CH}_2=\text{CHCl}$

c)



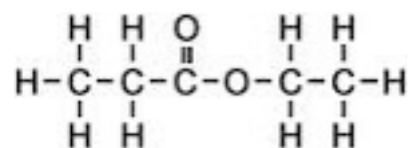
14. a) Acidified potassium dichromate(VI)

b) From orange to green.

c) Bubbles of carbon dioxide gas would be evolved.

d) Esterification or (nucleophilic) addition-elimination or condensation

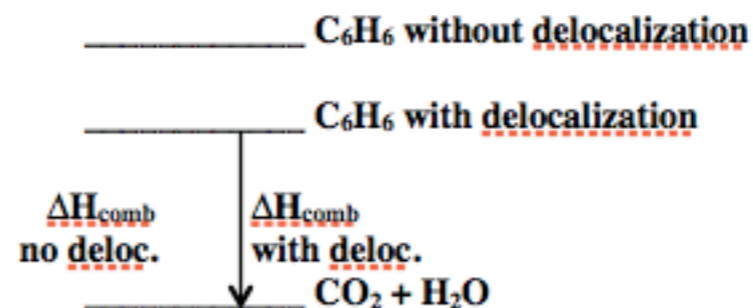
e)



Ethyl propanoate

15. Delocalization always increases thermodynamic stability.

Combustion is always an exothermic reaction so, as can be seen from the diagram below, delocalization will make the enthalpy of combustion less exothermic than it would be otherwise.

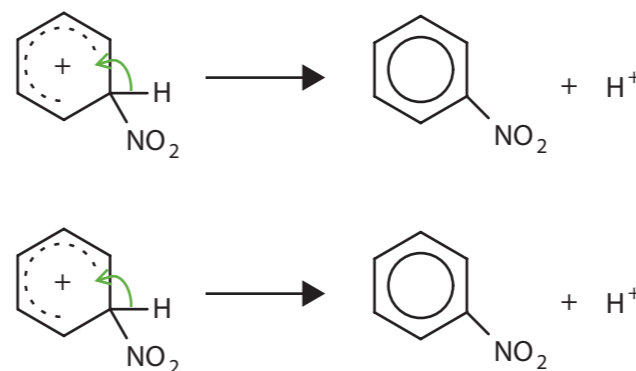
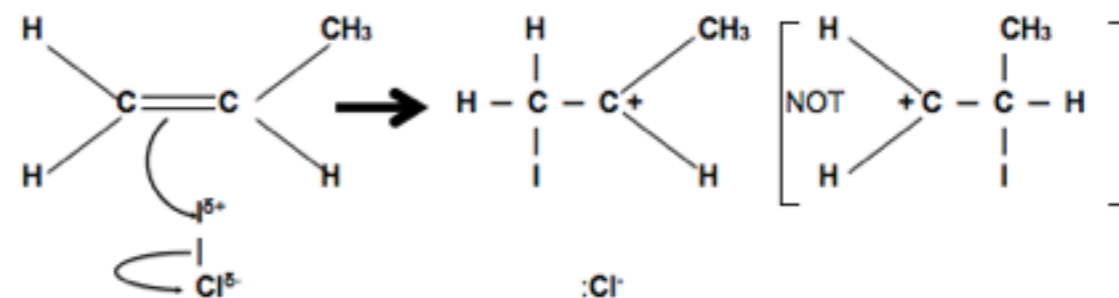


### EXERCISE 10 - C

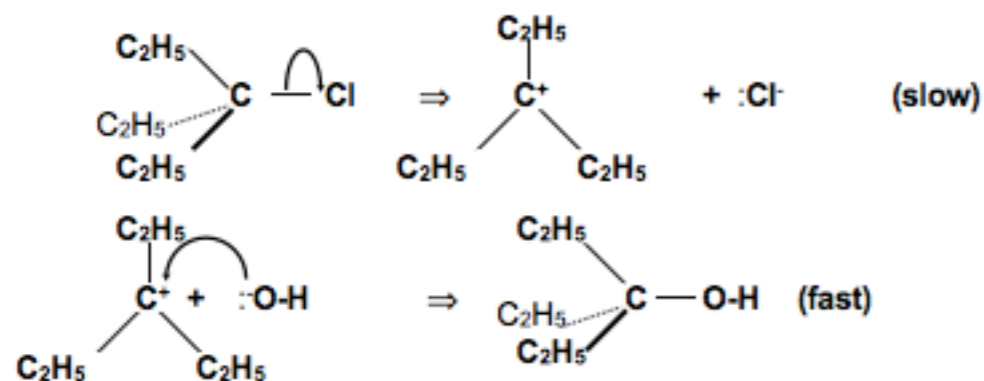
1. B 2. B 3. C 4. B 5. B 6. C 7. C 8. C 9. B 10. D

11. a) Electrophilic substitution

b) A mixture of concentrated nitric and sulfuric acids



12.

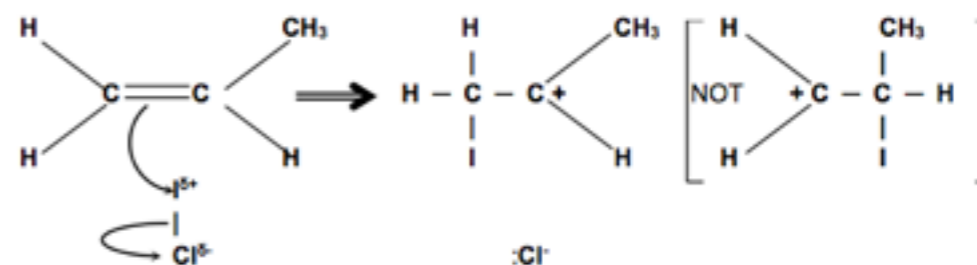


Heterolytic fission means the breaking of a covalent bond so that both of the bonding electrons go to the same atom, as for the breaking of the C-Cl bond in the first step of the mechanism.

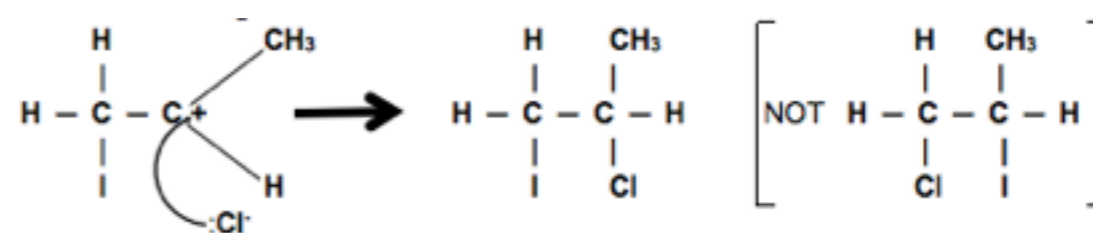
A carbocation intermediate is an intermediate, that is a species formed in one step of a reaction and consumed in a subsequent step, that involves a carbon carrying a positive charge. The  $(\text{C}_2\text{H}_5)_3\text{C}^+$  species is an example of a carbocation intermediate.

13. 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:

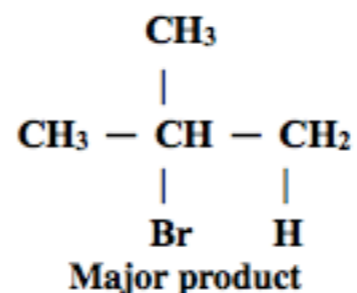


Then in the second stage, this carbocation will react with an anion present to complete the addition process:

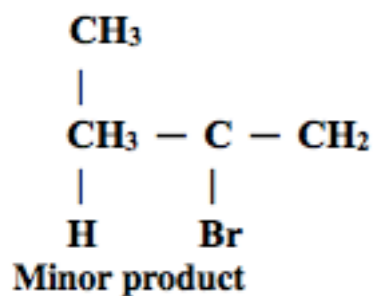


Therefore the major product is  $\text{CH}_3\text{-CHI-CH}_2\text{Cl}$  not  $\text{CH}_3\text{-CHCl-CH}_2\text{I}$ , because the secondary carbocation is a more stable intermediate than the primary carbocation.

14.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.

15. Were benzene to undergo electrophilic addition then the product would no longer have a delocalized  $\pi$ -electron system and hence it would lose the additional stability associated with this. Hence it is energetically more favourable for benzene to undergo electrophilic substitution and form a product which is energetically more favourable.

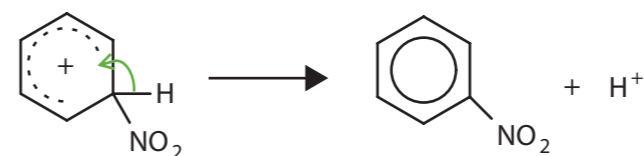
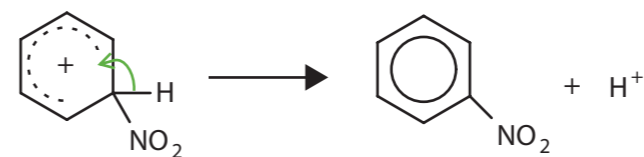
### EXERCISE 10 - D

1. D 2. D 3. C 4. A 5. D 6. D 7. A 8. C 9. A 10. B

11. 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 delocalized  $\pi$ -bond. In phenol a lone pair of electrons from the oxygen is associated with the delocalized  $\pi$ -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 delocalized  $\pi$ -bond of methylbenzene is slightly greater than that in benzene.

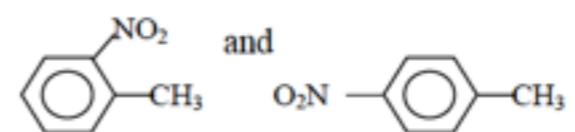
b)



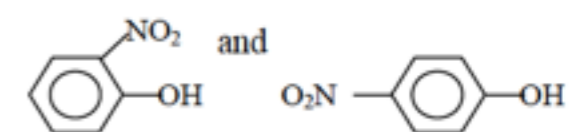
c) The replacement of a second hydrogen would take place less readily because the nitro group is electron withdrawing, reducing the electron density in the delocalized  $\pi$ -bond and hence lowering the reactivity.

d) Methylbenzene and phenol would both give mixtures of the 2- and 4- isomers:

From methylbenzene:

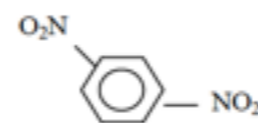


From phenol:



and

and

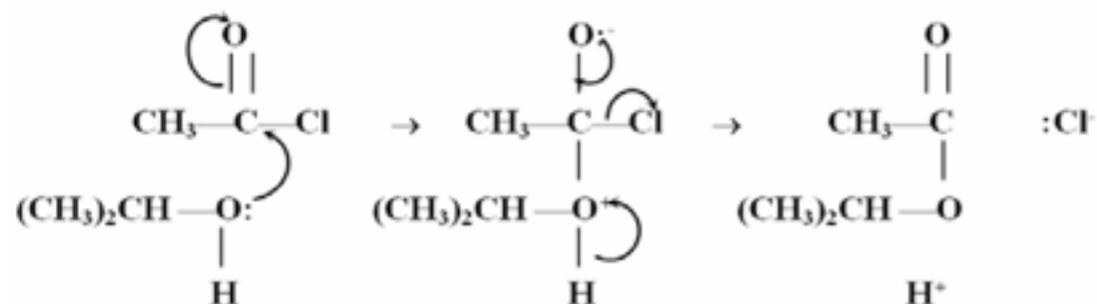


Nitrobenzene on the other hand would give 1.3-dinitrobenzene:



The product is an ester.

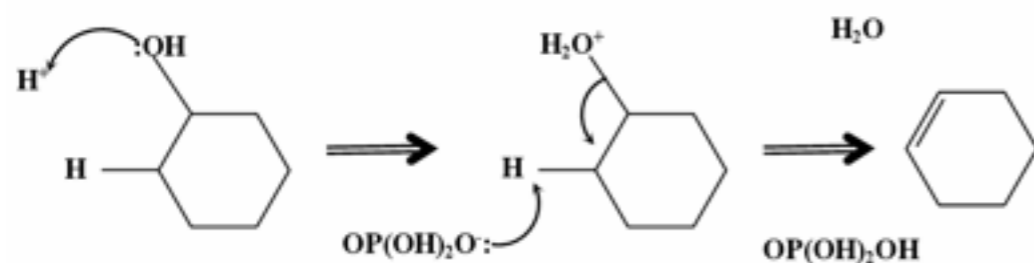
b)



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  $\text{CH}_3\text{COOH}$  rather than  $\text{HCl}$ ), but the reaction would be less vigorous.

13. a)



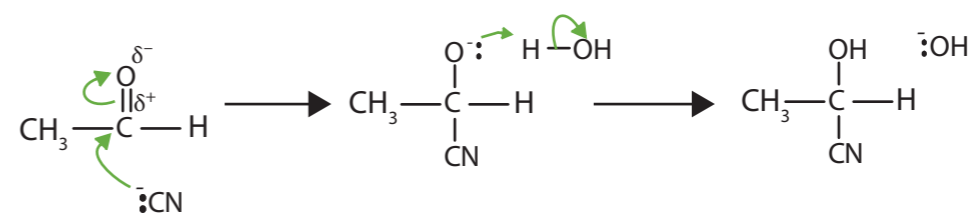
This reaction occurs when cyclohexanol is heated with concentrated phosphoric acid. It can only yield one product because if the hydrogen removed was from the carbon going clockwise around the ring (rather than the one going anticlockwise as shown) the product would be identical

14. a) Ethanal –  $\text{CH}_3\text{-CHO}$ ; 2-hydroxypropanoic acid –  $\text{CH}_3\text{-CH(OH)-COOH}$

b) X is probably  $\text{CH}_3\text{-CH(OH)-C}\equiv\text{N}$

c) React ethanal with hydrogen cyanide, in the presence of a base catalyst.

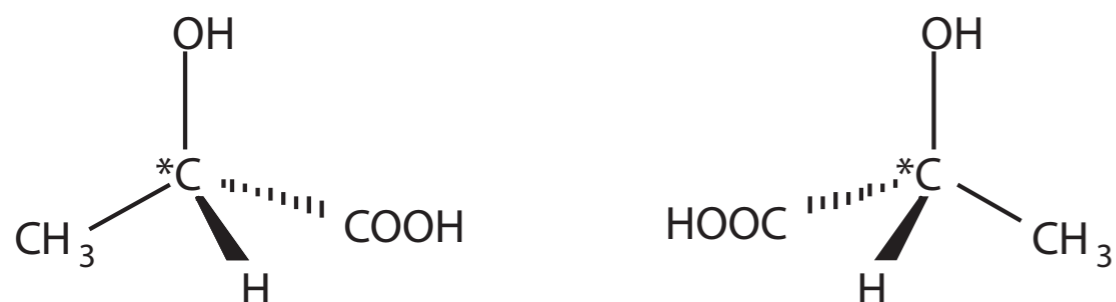
d)



e) Heat the cyanohydrin, X, with any dilute strong acid (or heat with dilute alkali, followed by acidification).

f) Enantiomers occur when four different groups are attached to the same carbon atom, so that two non-superimposable mirror image molecules are possible. The two possible molecules for 2-hydroxypropanoic acid are:

and



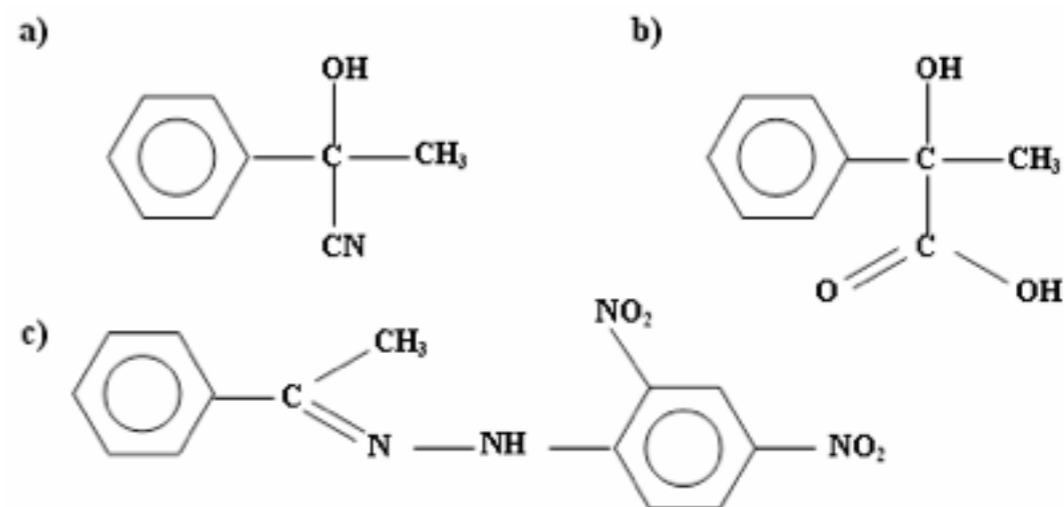
g) Optical activity is the property that some molecules have to rotate the plane of polarization of polarized light. The left-hand enantiomer would rotate the plane of polarization in one direction (say clockwise) and the right-hand enantiomer would rotate it in the opposite direction (anticlockwise).

h) When produced by a series of chemical reactions an equal amount of each enantiomer will be produced because the attack of the cyanide ion on the ethanal could be from either side giving two different products.

15. The strength of an acid is dependent on the extent to which the negative charge on the oxygen of the anion formed when it dissociates, can be decreased. 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 oxygen 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 dependent on the extent

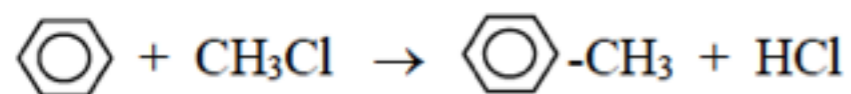
to which the positive charge on the nitrogen which accepts a hydrogen ion, can be decreased. In this case therefore an alkyl group donates electrons better than a hydrogen, reducing this charge, hence stabilising the cation making the amine a stronger base.

16.

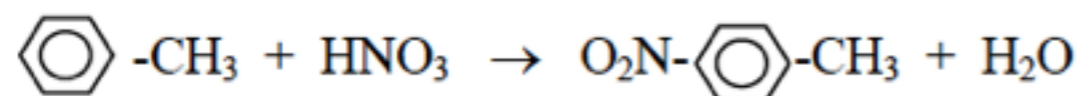


Historically the melting point of the compound in c) would be used to identify the parent carbonyl compound.

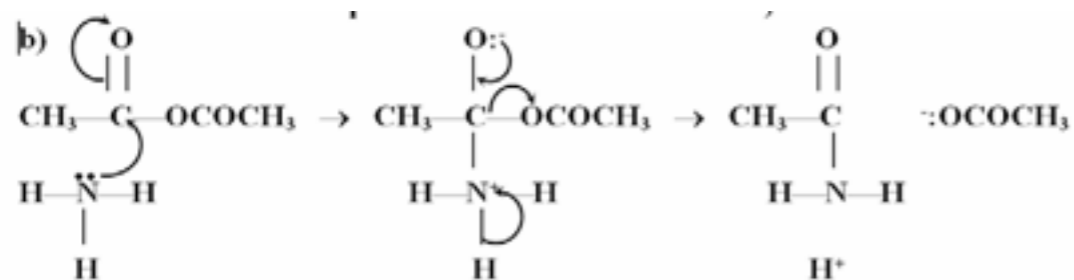
17. This conversion requires the introduction of both a methyl group and a nitro group. It is probably better to introduce the methyl group first as this activates the benzene ring for the second reaction, rather than nitrating the ring which would deactivate it. Firstly react benzene with chloromethane 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:

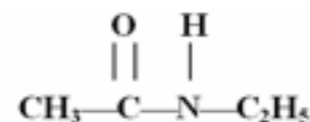


The products are ethanamide (an amide) and ethanoic acid (which will react with excess ammonia to produce ammonium ethanoate)



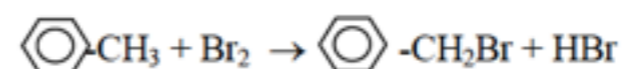
c) Two moles of ammonia would be required for each mole of ethanoic anhydride; one to give the ethanamide by the reaction above and one to neutralise the ethanoic acid that is also produced.

d) If ethylamine had been used, then the product would be N-ethylethanamide:

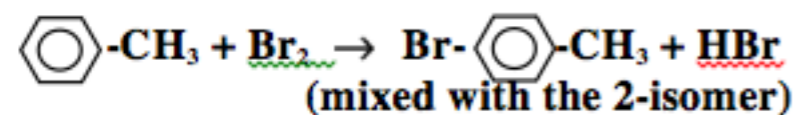


19. The strength of the acid largely depends on the extent to which the anion becomes stable by reducing the charge on the oxygen atom. In ethanol the loss of a hydrogen ion would result in the negative charge being totally localized on the oxygen atom. The resulting ethoxide ion is not very stable, hence ethanol is not acidic. In phenol, a little of the charge can be distributed on to the benzene ring through the delocalized  $\pi$ -bond system, making phenol very weakly acidic. In ethanoic acid there is complete delocalization 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.

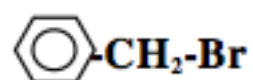
20. a) In the presence of UV light:



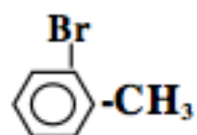
In the dark with a FeBr<sub>3</sub> catalyst:



b) The product of the first reaction is (bromomethyl)benzene:



That of the second reaction a mixture of 2-bromomethylbenzene:



and 4-bromomethylbenzene:



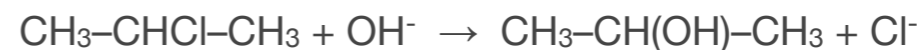
c) The first reaction is a free radical chain substitution reaction.

The second reaction is an electrophilic substitution reaction.

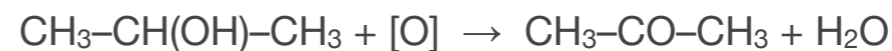
## Exercise 10 - E

1. A 2. B 3. D

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



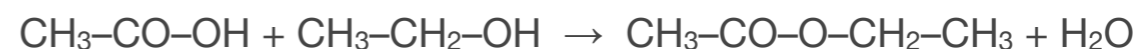
Then heat the secondary alcohol with acidified potassium dichromate(VI) solution to oxidise it to the ketone:



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



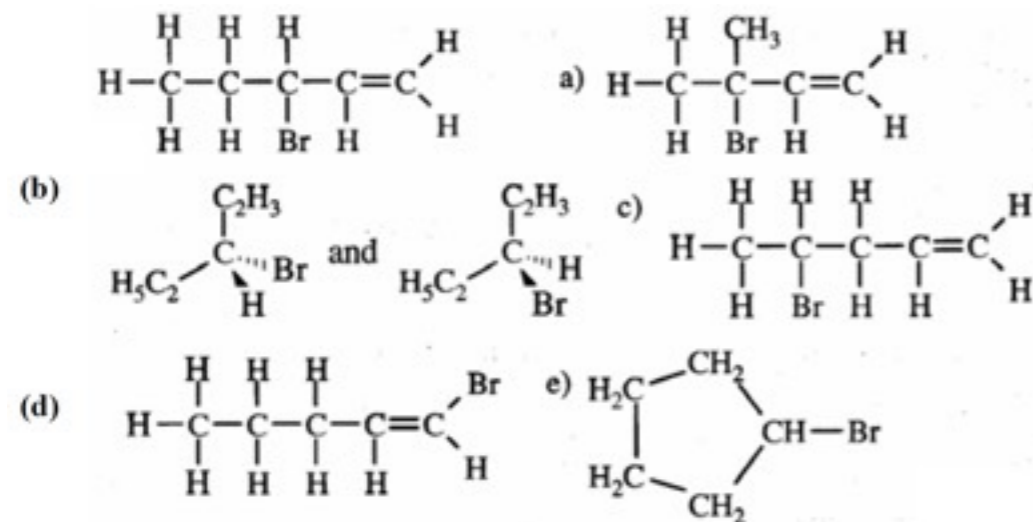
Then heat the ethanoic acid produced with some more ethanol, in the presence of a trace of concentrated sulphuric acid to produce an ester.



The ester in this case is ethyl ethanoate.

## Exercise 10 - F

1. C 2. C 3. C



4.

5. a) *Optically active* means that the substance will rotate the plane of polarization of polarized 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 polarized 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 polarization of the light.

## Exercise 10 - G

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

6. Add bromine water and the hexene would immediately decolourize it from orange-brown. With hexane two distinct layers would form with the upper one being orange-brown, and this would slowly decolourise in UV light. With ethanol and ethanoic acid the solution would be a homogenous orange-brown colour. Ethanol and ethanoic acid could be told apart using litmus paper because the latter would turn moist blue litmus paper red whereas ethanol would not have any effect on its colour.

7. a)  $\text{Br-CH}_2\text{-CH}_2\text{-Br}$

b)  $\text{CH}_3\text{-COO}^- \text{Na}^+$

c)  $\text{CH}_3\text{-CO-H}$

d)  $\text{CH}_3\text{-CH}_2\text{-OH}$

e)  $\text{CH}_3\text{-CO-O-CH}_2\text{-CH}_3$

8. a) A propanoic acid

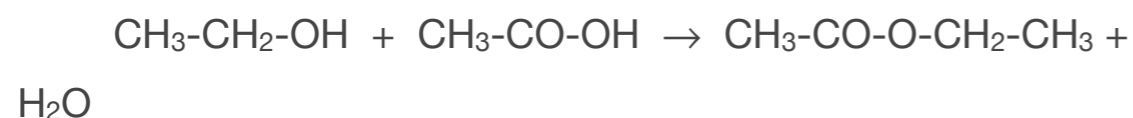
B methylpropane

C butane

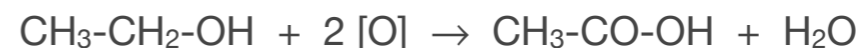
D propene

- b) C and G
- c) B and D are both C<sub>4</sub>H<sub>10</sub>
- d) E would give Br-CH<sub>2</sub>-CHBr-CH<sub>3</sub>
- e) A is a weak acid and can dissociate to give CH<sub>3</sub>-CH<sub>2</sub>-COO<sup>-</sup> + H<sup>+</sup>, making the solution acidic
- f) i Compound A
- ii Methanol (CH<sub>3</sub>OH)
- iii Concentrated sulfuric acid
- iv Methyl propanoate
- v A sweet smell
- g) CH<sub>3</sub>-CH<sub>2</sub>-CH(OH)-CH<sub>3</sub>, butan-2-ol;  
 or (CH<sub>3</sub>)<sub>2</sub>CH-CH<sub>2</sub>-OH, 2-methylpropan-1-ol  
 or (CH<sub>3</sub>)<sub>3</sub>C-OH, 2-methylpropan-2-ol (or an ether)

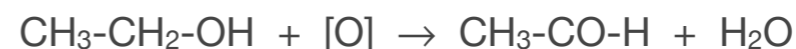
9. a) Heat ethanol with ethanoic acid and a trace of concentrated sulfuric acid:



b) Reflux ethanol with excess acidified potassium dichromate(VI):



b) Distil ethanol with acidified potassium dichromate(VI):



10 a) CH<sub>3</sub>-CH<sub>2</sub>-CO-CH<sub>3</sub>

b) (CH<sub>3</sub>)<sub>2</sub>CH-O-CO-CH<sub>3</sub>

c) CO<sub>2</sub> and H<sub>2</sub>O (there are 3 easily oxidised H-atoms; methanoic acid is itself easily oxidized to carbon dioxide and water)

11. a) Add bromine water and the hexene would immediately decolourize it from orange-brown. With hexane two distinct layers would form with the upper one being orange-brown, and this would slowly decolourise in UV light.

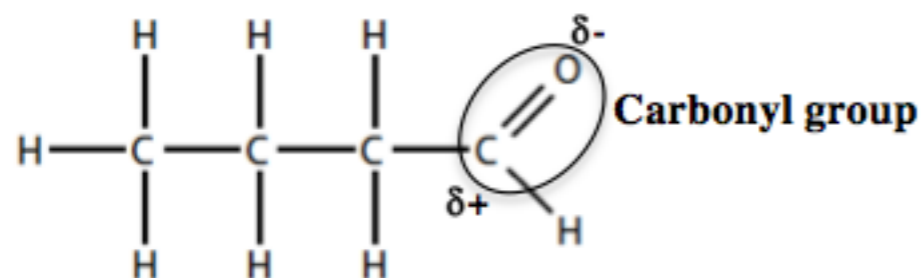
b) Test both with moist red litmus paper. With butylamine the litmus paper would change colour from red to blue, but with ethanamide the litmus paper would remain red.

c) Add samples of the two alcohols to acidified potassium dichromate(VI). With 2-methylpropan-1-ol the reagent would change colour from orange to green, but with 2-methylpropan-2-ol the reagent remain orange.

12. a) 2-bromobutane contains a chiral carbon atom, as the carbon attached to the bromine has four different groups attached to it (H-, CH<sub>3</sub>- and C<sub>2</sub>H<sub>5</sub>- as well as the Br-). This means the molecule can exist as two different enantiomers which are mirror images of each other.

b) When HBr reacts with the double bond of but-2-ene the attack will randomly occur from either side of the double bond yielding a racemic mixture. Because this contains equal amounts of the two enantiomers their effects on polarized light cancel each other out so it is optically inactive.

13. a)

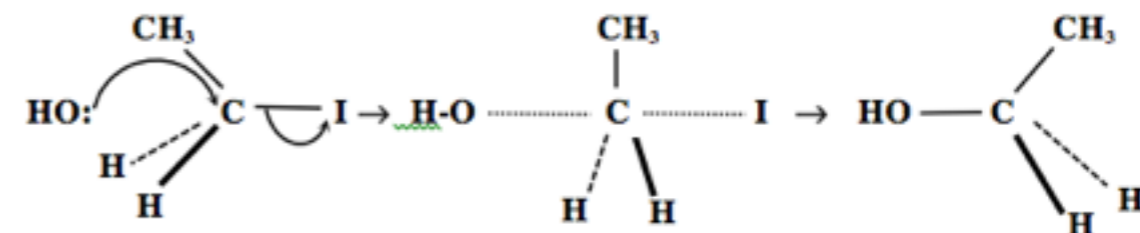


b) Easily oxidized: (CH<sub>3</sub>)<sub>2</sub>CH-CO-H

Not easily oxidized: C<sub>2</sub>H<sub>5</sub>-CO-CH<sub>3</sub>

c) i. Compound Y would turn moist blue litmus paper red, whereas Compound X would not affect the colour of the litmus paper.

ii. Reflux Compound X with excess acidified potassium dichromate(VI).



15. a) The white magnesium hydroxide powder would dissolve in the colourless liquid to yield a colourless solution.

b) When the colourless ethanol is added to the purple, aqueous manganate(VII) it would be decolourized.

c) Because the reactants are immiscible, initially the mixture would comprise two colourless layers. As the reaction proceeds the two layers would react to form only a single colourless liquid containing the products.

d) The two colourless liquids would react to produce a white precipitate of silver chloride in a colourless solution.

16. a) Ethanoic acid would turn moist blue litmus paper red, whereas ethanol would not affect it.



b) When warmed with acidified potassium dichromate(VI), the propanal would change its colour from orange to green, but with propanone the reagent would remain orange.

c) When butanone is added to 2,4-dinitrophenylhydrazine a yellow-orange precipitate would form, but with butanoic acid the reagent would remain clear yellow.

d) When orange-brown bromine water is added to cyclohexene it would immediately decolourize, whereas with hexan-1-ol it would retain its colour.

17. a) Methanoic acid behaves as a weak acid and dissociates in aqueous solution to produce hydrogen ions, hence reducing the pH.



b) Chloropropane cannot form hydrogen bonds so that if it were present inside water it would be unable to form bonds to compensate for the hydrogen bonds between water molecules that would be broken.

c) Ethanamide contains the amide group and strong hydrogen bonds can form between the  $>\text{C}=\text{O}$  group of one molecule and the hydrogens of the  $\text{NH}_2$  group on a neighbouring molecule.

d) Living systems only produce one enantiomer of chiral molecules, hence the alanine from protein will contain just one of the two possible isomers so it will be optically active.

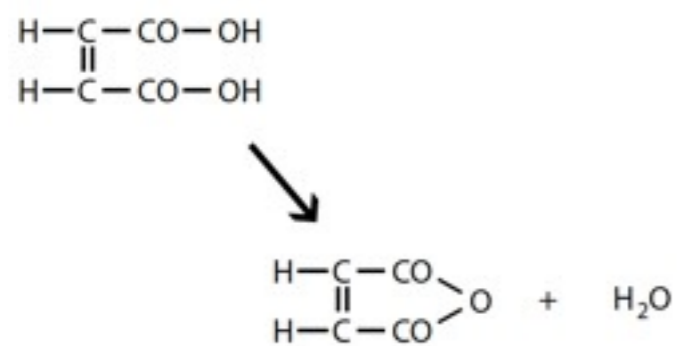
18. a) These are all reduction reactions.

- b) i. Sodium borohydride in aqueous solution.
- ii. Hydrogen in the presence of a nickel catalyst.
- iii. Tin and concentrated hydrochloric acid.
- iv. Lithium tetrahydridoaluminate in dry ether.

19. a) The molecule cannot rotate around the double bond, hence the two hydrogens can be on the same side of the molecule (*cis*-) or on opposite sides (*trans*-).

b) The polarity would be different because in the *cis*- molecule both of the electronegative carboxylate groups will be on the same side of the molecule, making it polar, whereas in the *trans*- isomer they will be on opposite sides hence their polarities will cancel.

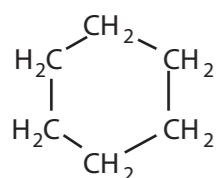
c) In the *cis*- isomer the two carboxylate groups are close to each other so that they can interact and dehydrate to form a cyclic anhydride, whereas in the *trans*- isomer this can only occur at temperatures high enough for the molecule to rotate around the double bond, converting it to the *cis*- isomer, hence giving the same product.



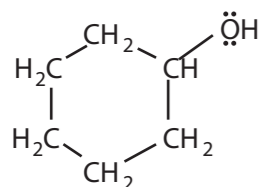
e) 84.18 g of cyclohexane (1 mol) should yield 100.17 g (1 mol) of cyclohexanol

8.42 g should therefore yield 10.02 g, so 7.00 g is a 70% yield.

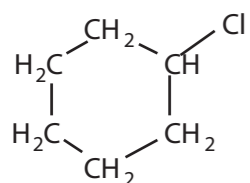
20. a) Cyclohexane



Cyclohexanol



b) Chlorocyclohexane would be a suitable intermediate:



c) Chlorine and UV light

d) Warm with dilute aqueous sodium hydroxide

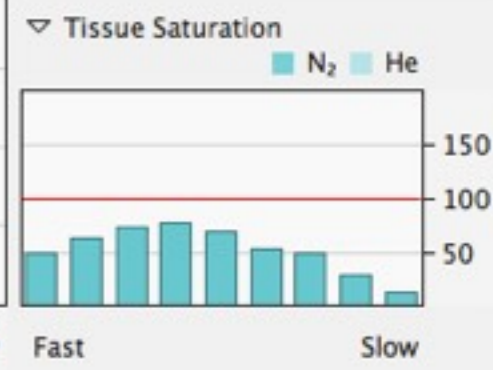
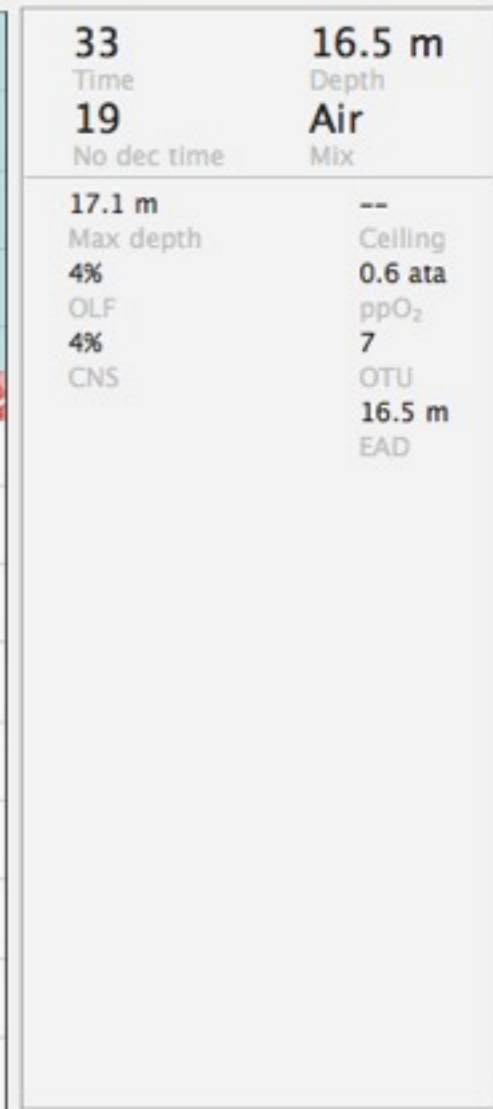
## Chapter 11

# Measurement and Data Processing

All this data exists in the 'mind' of a scuba diving computer.

There are a lot of measurements collected by the instrument during the dive - and some inferences.

Can you see which is which?



Summary | Details | Profile | Mixtures | My notes | Dive plan

ACTIVITY	DIVE MODE	DIVE TIME	MAX DEPTH	MAX DEPTH TEMP.
	Nitrox	0:48'40	17.1 m	26°C

# Measurement

## CONTENTS

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1. 11.1 Uncertainties and errors in measurement and results
2. 11.2 Graphical techniques
3. 11.3 Spectroscopic identification of organic compounds (21.1)



Precision measurement on the grand scale. Radio telescope at Parkes, NSW, Australia.

# Additional Material

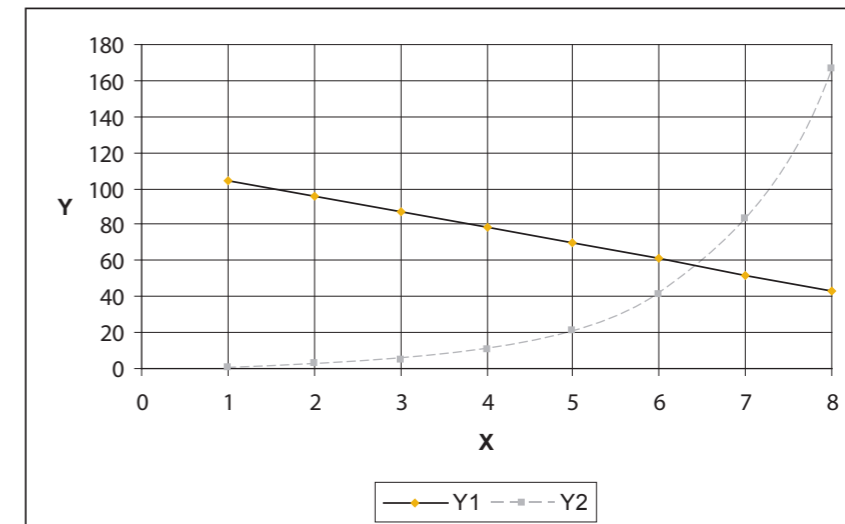
## TOK Why are graphs helpful in providing powerful interpretations of reality?

“Seeing is believing.” I suppose this sums up better than anything else the extent to which we rely on vision to interpret the world and probably that is why we find graphs, and indeed diagrams in general, such a useful way of “getting a feel” for things. I suppose another relevant quotation would be “A picture’s meaning can express 10,000 words” (apparently a more accurate literal translation than the usual one of the anonymous Chinese proverb).

Diagrams and graphs provide us with a more concrete and less abstract experience. If we had the data table:

x	Y1	Y2
1	104.3	1.3
2	95.6	2.6
3	86.9	5.2
4	78.2	10.4
5	69.5	20.8
6	60.8	41.6
7	52.1	83.2
8	43.4	166.4

Given a little time we could probably work out that the numbers represented a linear decrease (Y1) and an exponential increase (Y2), but it is immediately obvious if we look at the graph. Maybe that is because one requires the use of the logic circuits in our brain (is the difference between 104.3 and 95.6, the same as between 78.2 and 69.5?), whereas the pictorial representation seems to by-pass this - we immediately see a recognisable, familiar pattern, like the face of an old friend.



# Answers to exercises

## Exercise 11-A

1. C 2. B 3. B 4. D 5. C 6. A 7. C 8. A 9. B 10. C

11. a) 22.85 0.15 b) 939 2 c) -55.1 0.8

d) 30.2 1.3 (or maybe 30 1?) e) 13700 200

12. a) The literature value is well outside the result, even taking into account the uncertainties. It would therefore appear that there are significant systematic errors in the method being used, that result in a lower value, and the method should be examined to identify these.

b) Taking into account the uncertainties, the result is in agreement with the literature. Any improvements should test this better by reducing the uncertainty by minimising random errors, or even repeating the experiment and taking the mean of the results.

13. a) 14.72 0.005 b) 13.4 0.05 c) 12 0.5 (or maybe 12.25 0.25?)

14. a) 17.4 (1 dp) b) 940 (2 sf) c) 499 (3 sf as the top line is only to nearest digit)

15. a) Systematic b) Random c) Neither (though bad practice!)

16. a)  $100 \times (4.183 - 4.02) / 4.183 = 4\%$  (actually 3.9%, but no need for that precision)

b)  $4.02 \pm 0.2 \text{ J g}^{-1} \text{ K}^{-1}$  (or anything with a smaller value).

c)  $4.20 \pm 0.8 \text{ J g}^{-1} \text{ K}^{-1}$  (or anything nearer to 4.183 than 4.02).

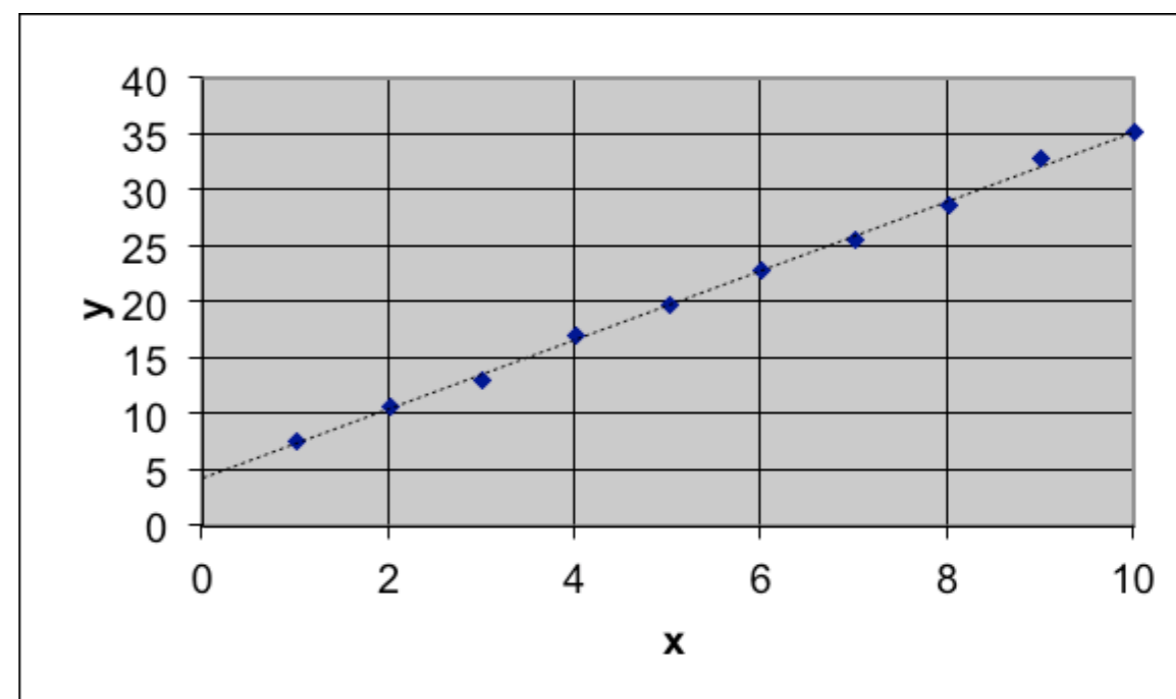
d) The uncertainty (0.8) would be reduced.

e) The value found would be closer to the literature value of 4.183.

## Exercise 11-B

1. C 2. A 3. C

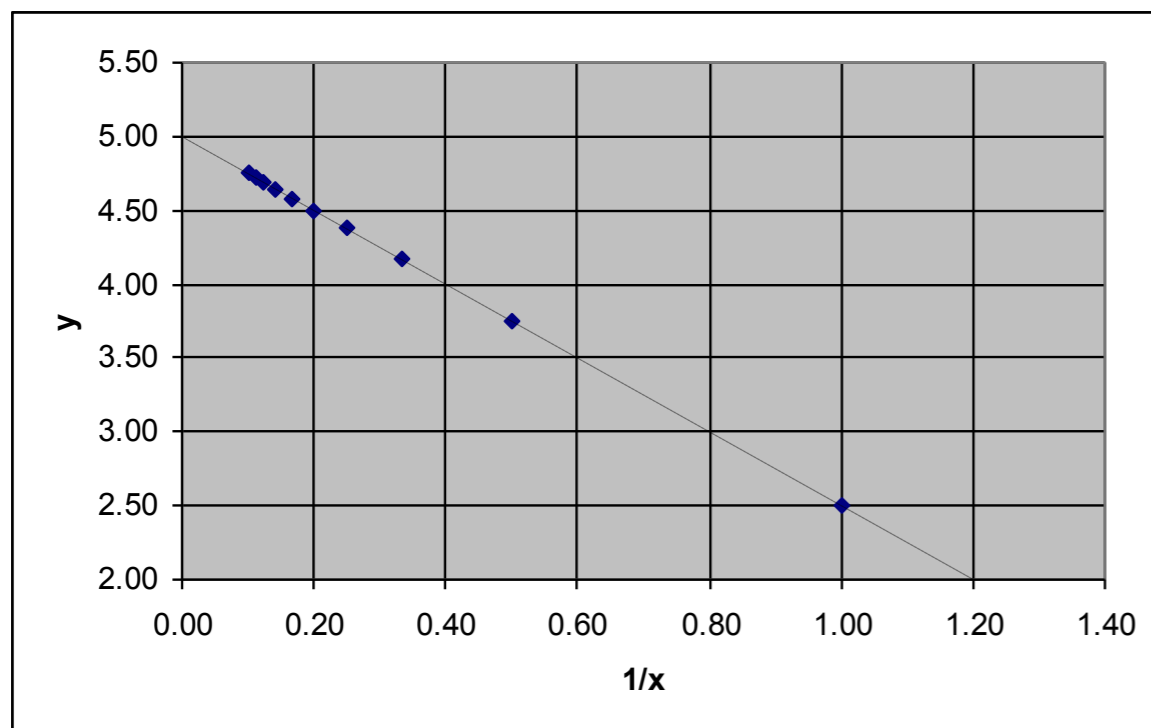
4. From the graph, the intercept is 4 and the gradient is 3.1



5) Rearrange to give  $y = T - \frac{5}{S} \dots \left( \frac{1}{x} \right)$ .

This is an inverse relationship and so requires a graph of  $\frac{1}{x}$  against  $y$ .

When  $\frac{1}{x} = 0$ ,  $y = T$ ; gradient =  $-\frac{5}{S}$ :



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

(Note how important the  $\frac{1}{x} = 1.0$  point is!)

## Exercise 11-C

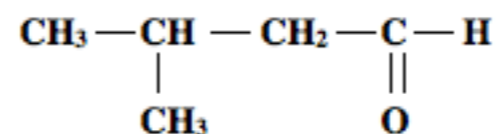
1. A 2. D 3. A 4. C 5. D

6. a)  $^1\text{H}$  NMR spectroscopy – propan-1-ol would give 4 peaks (3:2:2:1 ratio) and propan-2-ol would give 3 peaks (6:1:1 ratio).

b) Mass spectrometry – the compounds containing  $^{18}\text{O}$  would appear at  $m/z$  two greater than those containing  $^{16}\text{O}$ ; for example  $\text{H}_2^{16}\text{O}$  would be at  $m/z=18$  and  $\text{H}_2^{18}\text{O}$  would be at  $m/z=20$ .

c) IR spectroscopy – a ketone would absorb radiation at  $\sim 1700\text{-}1750\text{ cm}^{-1}$  whereas an alcohol would not, conversely an alcohol would absorb radiation  $\sim 3200\text{-}3600\text{ cm}^{-1}$  whereas a ketone would not.

7. a)



It can be seen that there are hydrogens in 4 different environments so there will be four peaks at  $\sim 0.9\text{-}1.0$  (both  $\text{CH}_3$  groups),  $\sim 1.5$  (CH),  $\sim 2.2\text{-}2.7$  ( $\text{CH}_2$  next to CO) and  $\sim 9.4\text{-}10.0$  (CO-H), with areas under the peak in the ratio of 6 : 1 : 2 : 1.

The 0.9-1.0 peak will be a doublet the 1.5 will be very fragmented (8 H-atoms on neighbouring carbons!), the 2.2-2.7 will be a doublet and the 9.4-10.0 a singlet.

8.  $\sim 1200\text{ cm}^{-1}$  due to C-O bonds and  $\sim 3000\text{ cm}^{-1}$  due to C-H bonds.

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

Given access to a library of IR spectra this spectrum, especially the  $500\text{-}1500\text{ cm}^{-1}$  region, could be matched to that of a known compound and hence it could be identified.

9. 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  $\text{C}_2\text{H}_5\text{-COOH}$ ; propanoic acid.

b) A is  $\text{C}_2\text{H}_5^+$ ; B is also  $\text{C}_2\text{H}_5^+$ , but containing one  $^{13}\text{C}$  atom; C is  $\text{COOH}^+$ ; D is  $\text{C}_3\text{H}_5\text{O}_2^+$ ; E is the molecular ion  $\text{C}_3\text{H}_6\text{O}_2^+$ ; F is the molecular ion  $\text{C}_3\text{H}_6\text{O}_2^+$ , but containing one  $^{13}\text{C}$  atom.

10. The molecule has H-atoms in 4 different environments and the 3:2:2:3 ratio implies that there are probably 10 H-atoms in total. The absorption at 4.1 ppm probably corresponds to  $-\text{CH}_2-\text{O}$  (3.7-4.8), and that at 2.1 ppm to  $\text{CH}_3-\text{CO}-$  (2.0-2.7), hence the compound is probably an ester. There are 2 other environments at lower shifts, hence the molecule is probably has two carbon atoms other than the one attached to the ester group in the hydrocarbon chain, hence  $\text{CH}_3-\text{CO}-\text{O}-\text{CH}_2-\text{CH}_2-\text{CH}_3$ , prop-1-yl ethanoate.

Going from left to right through the formula as written, the  $\text{CH}_3-\text{CO}-$  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  $-\text{CH}_2-$  with a signal around 1.8 are split by both the  $-\text{CH}_2-\text{O}$  on one side and the  $\text{CH}_3-$  on the other giving a complex pattern; finally the  $\text{CH}_3-$  at 0.9 is split into a triplet by the neighbouring  $-\text{CH}_2-$ .

11. The wavenumber is equal to  $1/\text{wavelength in cm} = 100/\text{wavelength in m } (\lambda)$ . 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  $3652\text{ cm}^{-1}$ , the wavelength will be  $0.000274\text{ cm}$  or  $2.74 \times 10^{-6}\text{ m}$  ( $= 100/3652$ ) and the frequency will be  $1.095 \times 10^{14}\text{ Hz}$  ( $= 3 \times 10^8 / 2.74 \times 10^{-6}$ ).

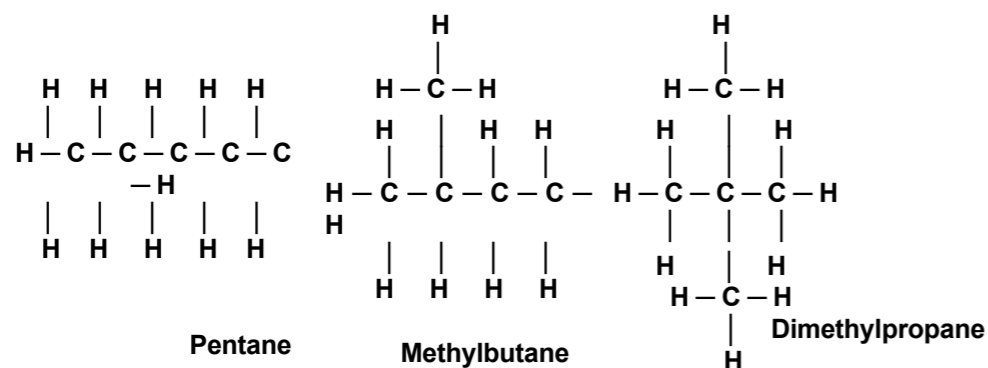
12. a) In 100 g there is 83.3 g ( $= 83.3/12 = 6.94\text{ mol}$ ) of carbon and 16.7 g ( $= (100-83.3)/1 = 16.7\text{ mol}$ ) of hydrogen. The molar C:H ratio is therefore 1:2.4 ( $= 16.7/6.94$ ) or 5:12, hence its empirical formula is  $\text{C}_5\text{H}_{12}$ .

b) If the molecular formula was  $\text{C}_5\text{H}_{12}$  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  $\text{C}_5\text{H}_{12}$ . (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<sub>4</sub> = 16.0427; N = 14.0067, CH<sub>2</sub> = 14.0269).

c) The possible isomers are:



Pentane would have regularly spaced peaks resulting from the loss of successive CH<sub>3</sub> and CH<sub>2</sub> 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<sub>3</sub> group and so would have a very large peak at 57.

13. The m/z for the molecular ion is 72, so the M<sub>r</sub> of the hydrocarbon part of the ketone must be 44 (72-28) corresponding

to a methyl group on one side and an ethyl group on the other side, hence the molecule is butanone (CH<sub>3</sub>CH<sub>2</sub>COCH<sub>3</sub>).

72 is the molecular ion peak, C<sub>4</sub>H<sub>8</sub>O<sup>+</sup>

57 (72-15) corresponds to the loss of a methyl group so C<sub>3</sub>H<sub>5</sub>O<sup>+</sup> formed when a methyl group breaks off either end of the molecule.

43 (72-29) corresponds to the loss of an ethyl group so C<sub>2</sub>H<sub>3</sub>O<sup>+</sup>, probably CH<sub>3</sub>-CO<sup>+</sup> formed when the ethyl group breaks off the carbonyl group.

29 (72-43) corresponds to the loss of the CH<sub>3</sub>-CO group leaving C<sub>2</sub>H<sub>5</sub><sup>+</sup>.

14. ~700 cm<sup>-1</sup> due to the C-Cl bond

~1100 cm<sup>-1</sup> due to the C-O bond

~2900 cm<sup>-1</sup> due to the C-H bonds

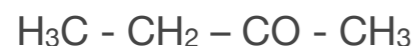
~3300 cm<sup>-1</sup> due to the OH bond

15. The molecular ion in the mass spectrum is at m/z = 72, so that this is the probable M<sub>r</sub> of the compound.

The IR spectrum has a strong peak ~1720 cm<sup>-1</sup>, corresponding to a carbonyl group and no broad peak over 3000 cm<sup>-1</sup>, so it is not a carboxylic acid or an alcohol, meaning it must be an aldehyde, ketone or ester.

Looking at the  $^1\text{H}$  NMR spectrum the absence of peaks at high chemical shifts rules out an aldehyde and absence of a peak at  $\sim 3.8$  ppm from  $-\text{CH}_x-\text{O}-\text{CO}-$  would also seem to rule out an ester, implying the compound is a ketone.

If it is a ketone with  $M_r=72$  then the hydrocarbon parts must comprise  $M_r = 44$  ( $72-28$ ) so  $\text{CH}_3$  &  $\text{C}_2\text{H}_5$ , leading to the conclusion it is butanone.



This would fit in with the notable peaks at 43 ( $M_r-29$ ;  $\text{CH}_3-\text{CO}^+$ ) and 29 ( $M_r-43$ ;  $\text{C}_2\text{H}_5^+$ ) in the mass spectrum.

In the  $^1\text{H}$  NMR spectrum there is a triplet at about 1 ppm corresponding to the  $\text{CH}_3$  of the ethyl group and two peaks in the 2.2-2.7 ppm region where  $-\text{CH}_x-\text{CO}-\text{R}$  absorbs; the singlet corresponding to the methyl group and the quartet to the  $\text{CH}_2$  of the ethyl group.

Chapter 12

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# Option A Materials

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Metal 'Eco-trees' at *Gardens by the Bay*, Singapore.



## CONTENTS

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1. A.1 Material Science Introduction
2. A.2 Metals and inductively coupled plasma (ICP) spectroscopy
3. A3 Catalysis
4. A4 Liquid crystals
5. A5 Polymers
6. A6 Nanotechnology
7. A7 Environmental Impact
8. A8 Superconductivity and X-ray crystallography
9. A9 Condensation Polymers
- 10.A10 Environmental impact – heavy metals



Part of the heat shield of the Command Module of Apollo 11 - with evidence of the extremes it survived on re-entry. The materials used had to be light, strong, have a high melting point and be non-combustible.

# Additional Material

## TOK Science versus Politics

### Who should determine priorities in the funding of research?

Can anything ever be ‘values free’? As humans we inevitably have values and cannot help regarding everything in the light of these values. These values of course are the fundamentals of moral judgements and differ from person to person. There are various moral codes such as Utilitarianism, “Might is right”, “Do unto others as you would have them do to you”, “Cultural relativism”.

I suppose, pragmatically, the basic principle guiding research has to be “He who pays the piper calls the tune”. If you don’t want any money to do it, then you can probably research into what you like – as long as it’s legal. Again I don’t think there is much question about this with regard to private research institutions; if ICI is paying for the research then nobody questions them telling their scientists what to investigate. With research that takes place in state institutions then it is not quite clear who is paying the piper. Sometimes industrial companies will sponsor a research worker and again probably they have the right to direct that research, but what about the others? Maybe there shouldn’t be any others, maybe those who are likely to profit should pay like industry does, but who then would be likely to profit? In the

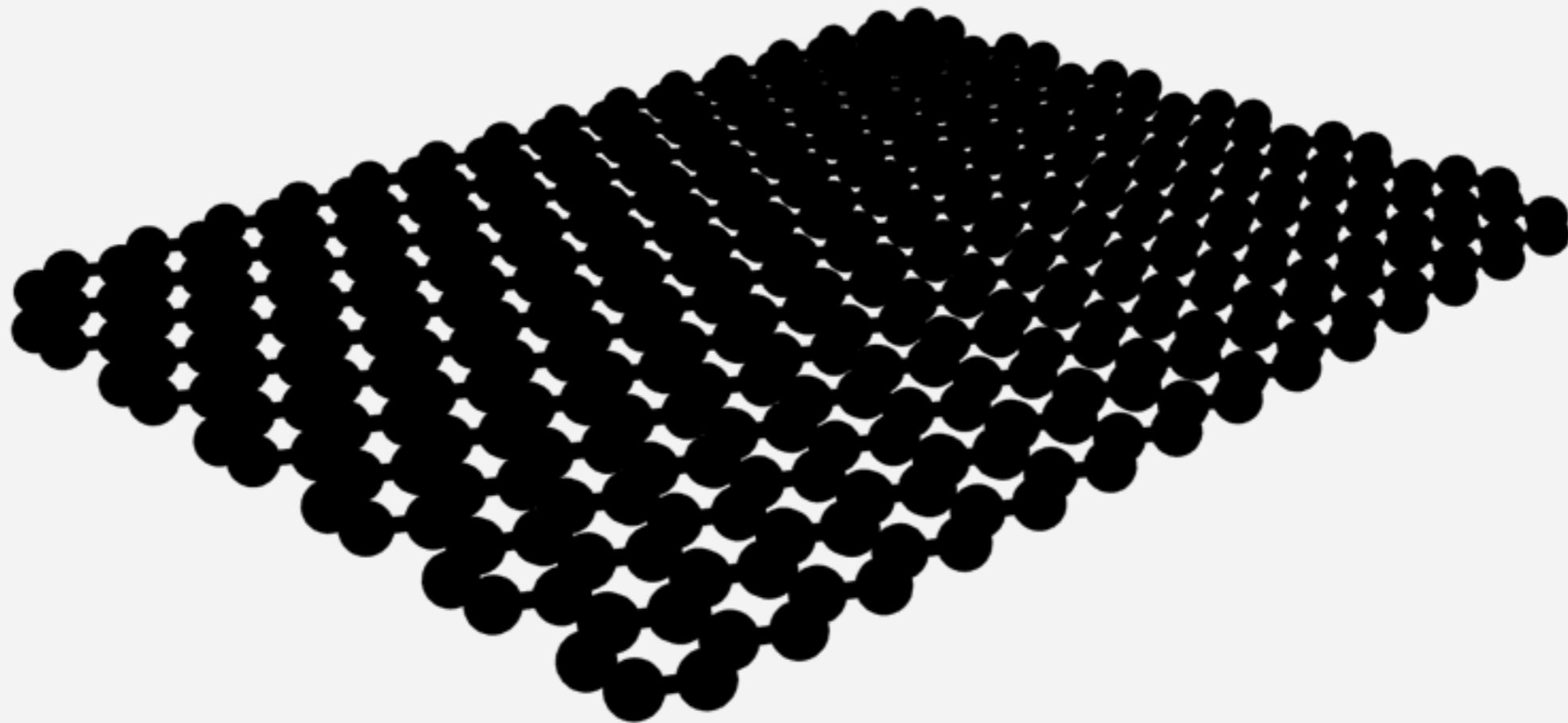
short term, shall we pay for better mapping of the Earth’s magnetic field by an expensive satellite? It might never get done even though in the long term there could be lots of benefits, generally impossible to predict at the outset. The laser is a good example of a discovery that has transformed so many things and which came out of some “blue sky” research. I suspect we (at least if you are a taxpayer) are the “payers”. Maybe I have 10 minutes of a scientist’s time as a result of what I pay in taxes – I wonder what I’m going to get him/her to do? Not a problem, the government, in its wisdom, as well as taking our money away from us in taxes because it knows better how to spend it, also relieves us of the burden of research decisions. Once upon a time academics were trusted just to research into whatever they found interesting. Nowadays money is a little tighter, so that usually they have to submit proposals to research councils who award funding. Unfortunately that means that many spend as much time writing research proposals and going through all the involved “follow up”, as they do actually carrying out any research! Who are on these research councils anyway? Usually it is other scientists in a similar field who, supposedly, have the expertise to decide which projects deserve support and which do not. But what should their decisions rest on – something that looks likely to “pay off” in 5-years or something that, just possibly, might revolutionise everything 50 years down the track? Somebody who is working in a prestigious university, somebody who has published a lot of academic papers (though maybe of dubious interest) recently, the guy who bought you a beer in the

bar at the last conference? Lack of funding might even be a stimulus; I think it was Ernest Rutherford who said “Our request for funding hasn’t been granted, so we’ll have to think instead”.

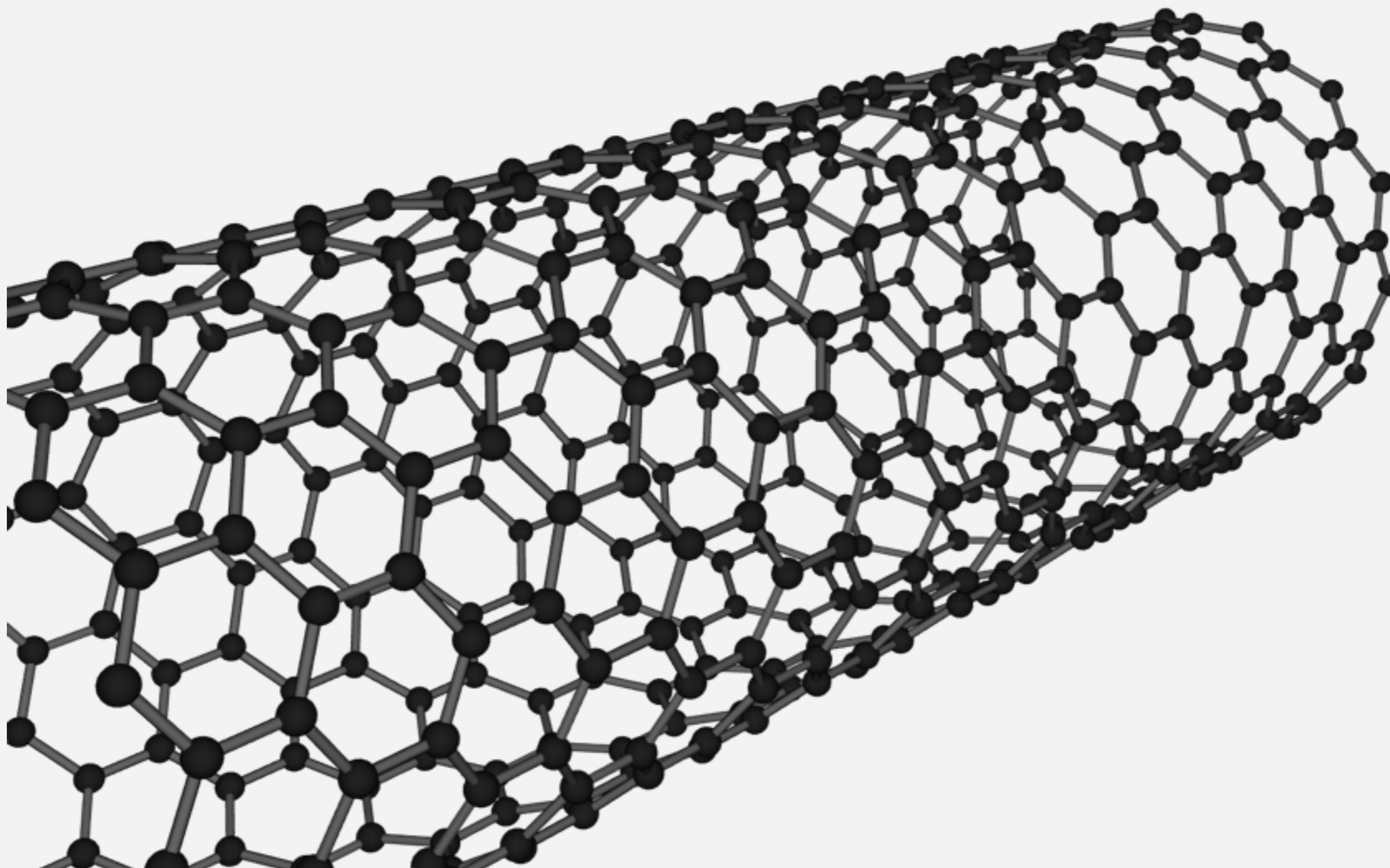
How are places on space missions allocated?



## Interactive 12.1 Graphene



Interactive 12.2 A Simple Nanotube





# Internet resources

Samson Jenekhe

[http://academic.research.microsoft.com/Author/13258598/  
samson-a-jenekhe](http://academic.research.microsoft.com/Author/13258598/samson-a-jenekhe)

Nanotubes

<http://www.pa.msu.edu/cmp/csc/nanotube.html>

Advancements in biotechnology allow scientists across continents to collaborate to synthesize new enzymes and to control desired reactions (i.e. waste control) and the computational organic chemistry work at University of Oxford is one such example: ([http://paton.chem.ox.ac.uk/common\\_files/  
PatonGroupPoster\\_2010-11.pdf](http://paton.chem.ox.ac.uk/common_files/PatonGroupPoster_2010-11.pdf))

# Answers to exercises

## Answers

8.(a)(iii) (Ratio of 3 : 5)

9. 15.9 g)

10. amount = 17.9(1) mol; volume at STP = 407 dm<sup>3</sup>

23. (c) (iii) 89.4%

36. 0.315 nm

42. (b)  $[\text{AgCl}] = 1.34 \times 10^{-5} \text{ g mol}^{-1}$ ;  $K_{\text{sp}} = 1.80 \times 10^{-10}$

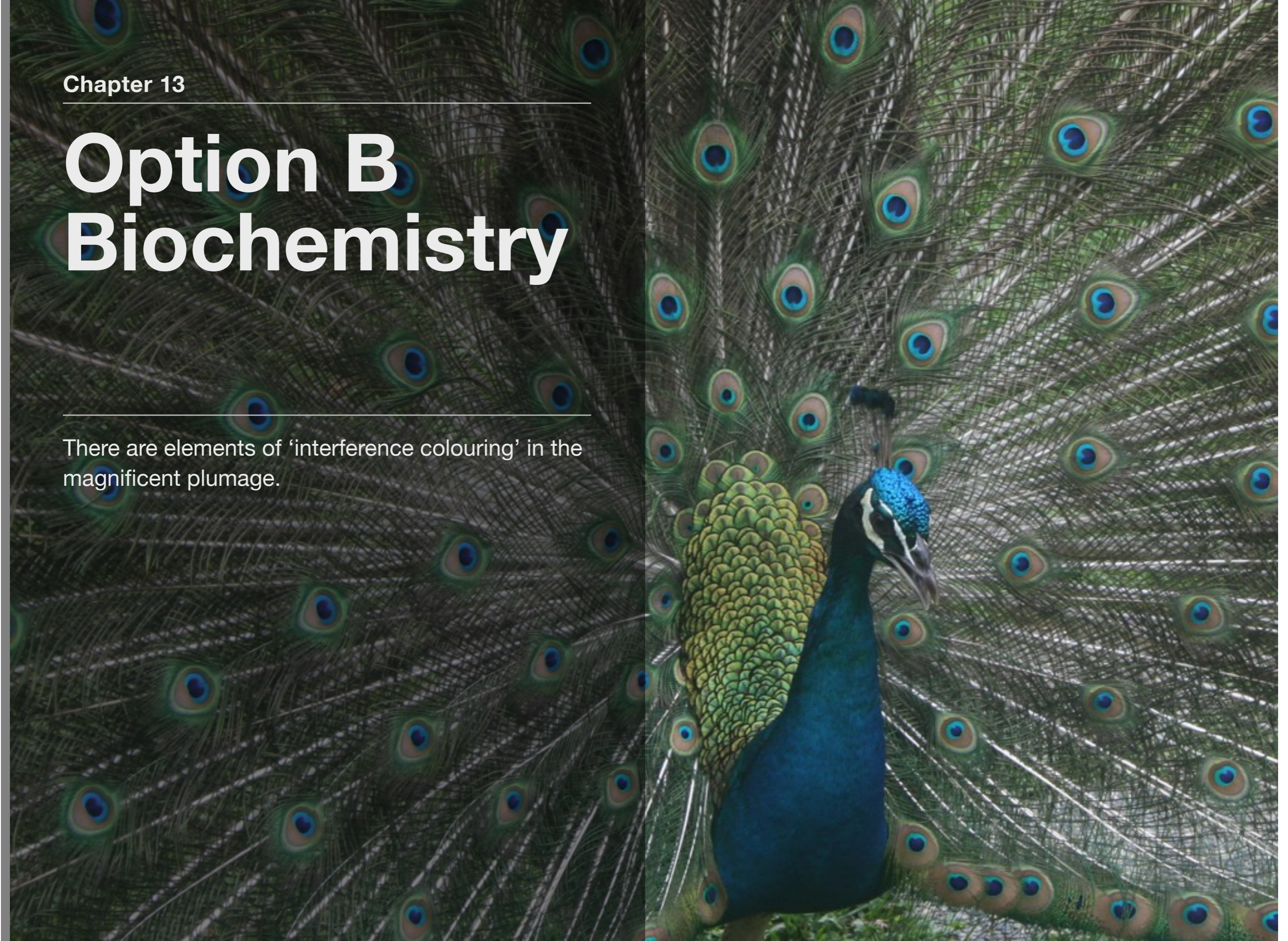
Chapter 13

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# Option B Biochemistry

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There are elements of 'interference colouring' in the magnificent plumage.



# Biochemistry

## CONTENTS

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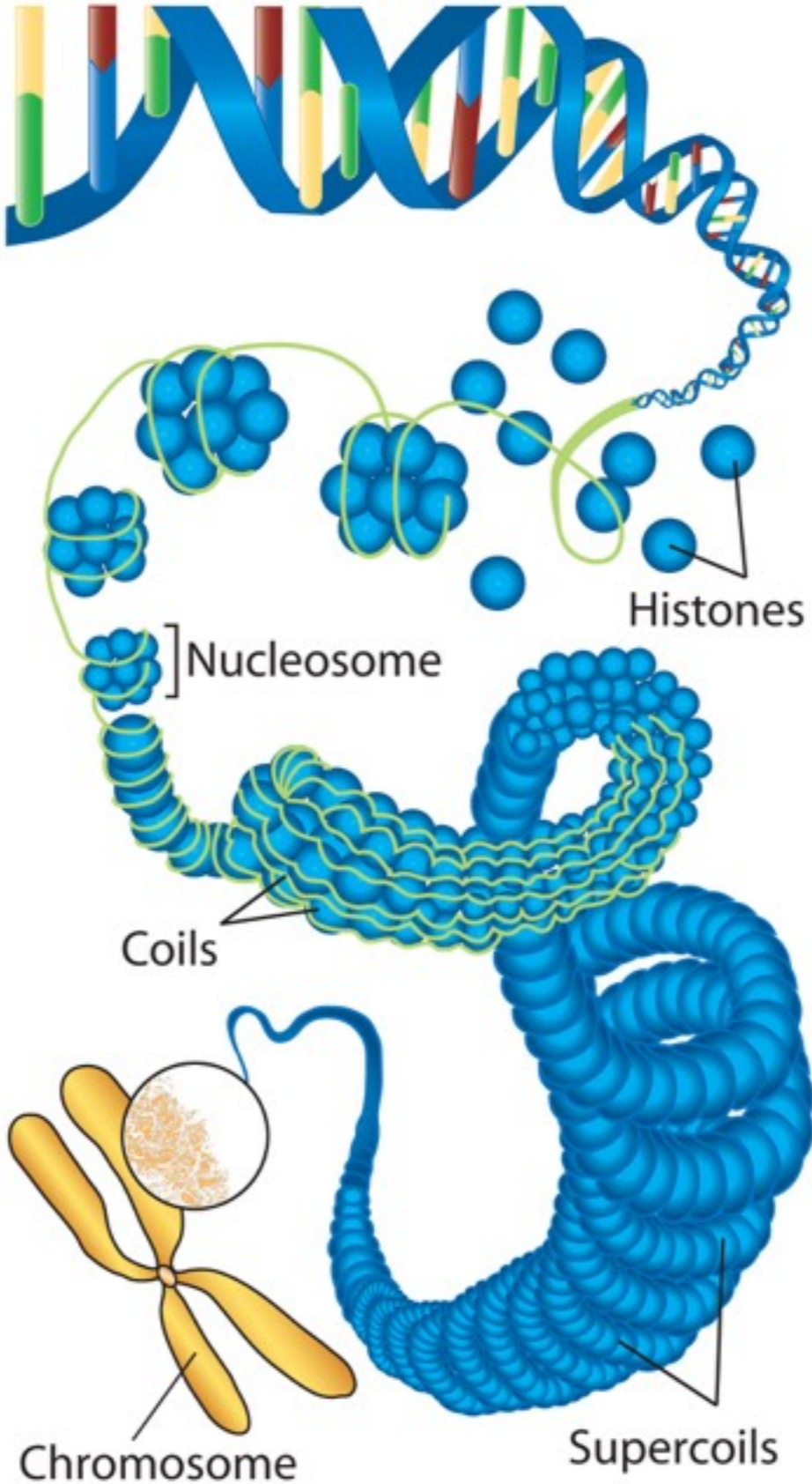
1. B.1 Introduction to biochemistry
2. B2 Proteins and enzymes
3. B3 Lipids
4. B4 Carbohydrates
5. B5 Vitamins
6. B6 Biochemistry and the environment
7. B7 Proteins and enzymes
8. B8 Nucleic acids
9. B8 Nucleic acids
10. B9 Biological pigments
11. B10 Stereochemistry in biomolecules



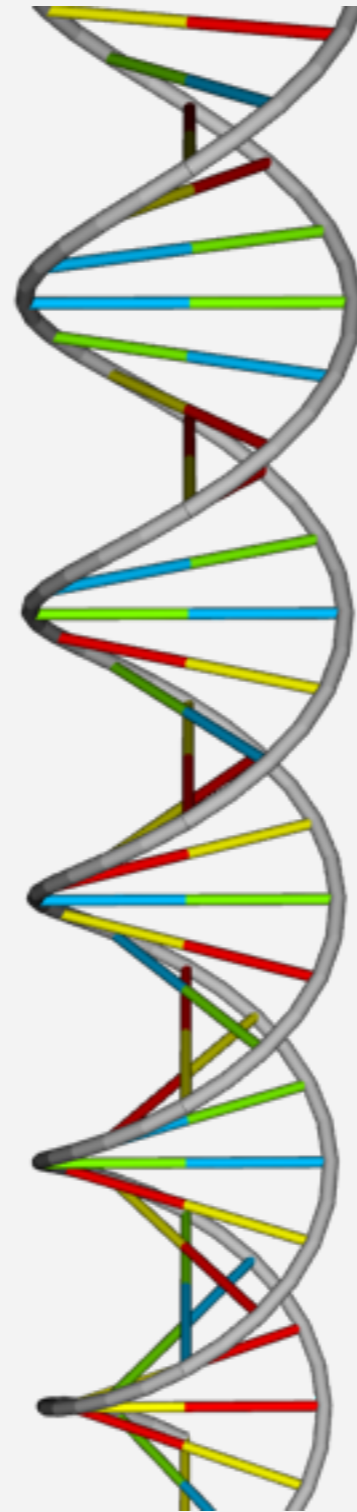
Every living creature is a biochemical machine of great complexity.

# Additional Material

Alternative to Figure 13-72 p436

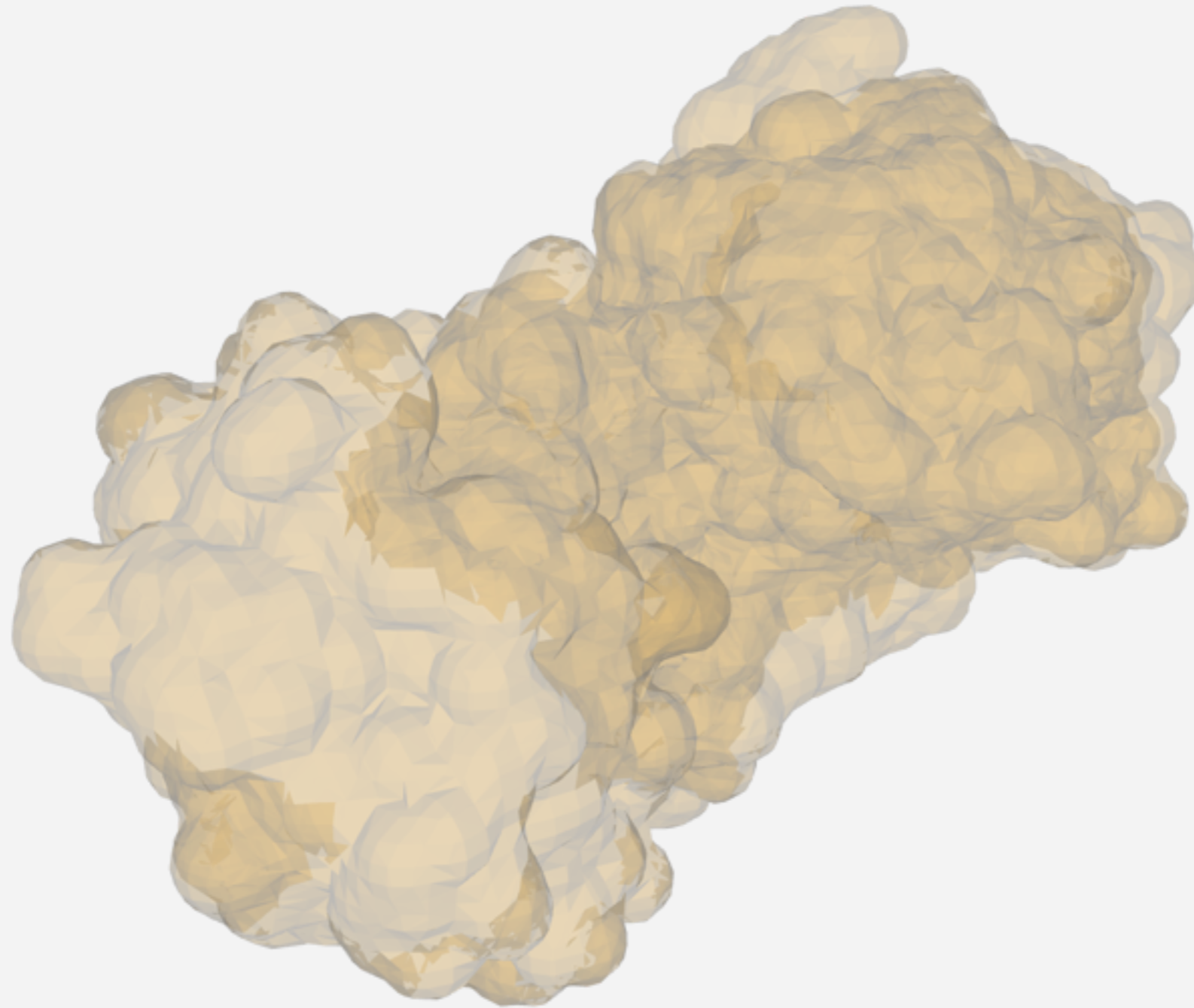


## Interactive 13.1 DNA



*The code of life*

**Interactive 13.2** This is a space filling model of a human enzyme



*Note the great complexity of geometry!*

# CODON TABLE

UUU	phe	UCU	ser	UAU	tyr	UGU	cys
UUC	phe	UCC	ser	UAC	tyr	UGC	cys
UUA	leu	UCA	ser	UAA	stop	UGA	stop
UUG	leu	UCG	ser	UAG	stop	UGG	trp
CUU	leu	CCU	pro	CAU	his	CGU	arg
CUC	leu	CCC	pro	CAC	his	CGC	arg
CUA	leu	CCA	pro	CAA	gln	CGA	arg
CUG	leu	CCG	pro	CAG	gln	CGG	arg
AUU	ile	ACU	thr	AAU	asn	AGU	ser
AUC	ile	ACC	thr	AAC	asn	AGC	ser
AUA	ile	ACA	thr	AAA	lys	AGA	arg
AUG	start/met	ACG	thr	AAG	lys	AGG	arg
GUU	val	GCU	ala	GAU	asp	GGU	gly
GUC	val	GCC	ala	GAC	asp	GGC	gly
GUA	val	GCA	ala	GAA	glu	GGA	gly
GUG	val	GCG	ala	GAG	glu	GGG	gly



## TOK What are the implications of the molecular basis of life?

Now this one probably deserves a book, or even a series of books, with one volume devoted to each field of knowledge. About the best I can do in the confines of this tiny box that I've been given is generate a few random thoughts, mainly related to our mental pre-programming, assuming that our brains are as different as our bodies and that this affects the way we think about things (are these both fair assumptions?).

- Suppose we know somebody has a genetic tendency to violence or criminal acts, will we keep that person under extra surveillance? If your answer is "No", then what are your reasons? What if you could detect this during the first weeks of pregnancy?
- Should we allow people to choose their own jobs? If I have an excellent mind for a teacher, wouldn't it be a waste to allow me to work as a check-out operative at a supermarket (and vice-versa - equally culpable). Does this mean that we would get paid different amounts on the basis of our mental construction?
- Suppose two artists produce equally brilliant work, but we know one has the perfect brain for artistic creativity (are either of these two assumptions possible?), whereas the other has a

brain totally unsuited to this, but ideal for flipping burgers. Would knowing this affect the way in which we viewed their work?

- What about religions that postulate a soul or reincarnation? Do they assume that there is a part of DNA responsible for this (maybe divine influence affects which bits come from each parent and hence constructs the required physical/mental incarnation) or do they assume that it is passed on in some other way?

# Internet resources

P 389 (<http://www.hsph.harvard.edu/nutritionsource/what-should-you-eat/fats-and-cholesterol/>).

P404

(<http://www.scientificamerican.com/article.cfm?id=just-thinking-about-science-triggers-moral-behavior&page=2>)

The 12 Principle of green chemistry can be summarised with the following diagram taken from: <http://nas-sites.org/emergingscience/files/2011/05/green-chem-nl-25.pdf>

Health effects: Tests on a vast majority of women tested in a hospital in Quebec were found to contain Bt toxin in the blood of non-pregnant and pregnant women as well as in the umbilical blood in the babies. If this affects the microorganisms in the intestinal track, it could lead to superbugs and possibly causing abdominal problems and food allergies as well as other health issues. According to the American Academy of Environmental Medicine, AAEM, <http://www.aaemonline.org/gmopost.html>: “

Problem set:

1. Deduce and explain the complementary base pair arrangement for the DNA strand ACGATCATA.

Answer: The DNA base pairs are A & T and G & C. Thus the complementary base pair arrangement must be: TGCTAGTAT.

2. Deduce and explain the complementary base pair arrangement for the RNA strand UUCAUCGCGAGA.

Answer: The RNA base pairs are A & U and G & C. Thus the complementary base pair arrangement must be: AAGUAGCGCUCU.

3. Calculate the percentage of thymine, T in a nucleotide that contains 21% guanine, G.

Answer: If G is 21%, then its complementary base cytosine, C, must also be 21%.

Thus the total of T and A must be  $(100\% - 21\% - 21\%) = 58\%$ .

Since A and T are complimentary base pairs, these must be in equal amounts.

Thus there must be 29% T in the nucleotide; OR the percentage of thymine from one base pair and guanine from the other base pair must equal 50%. Thus, there must be 29% T in the nucleotide.

4. Deduce the nucleic acid that contains the bases A, C, U and G and explain your reasoning.

Answer: Since uracil is one of the bases, it must be RNA (not DNA).

5. Determine whether a viral polynucleotide is a single or double stranded DNA or RNA if it contains 20% adenine, 20% guanine, 24% cytosine and 36% thymine and explain your reasoning.

Answer: Since thymine is present only in DNA, not RNA, this rules out RNA.

Since base pairs A & T and C & G are not in equal amounts, it cannot be a double stranded DNA. Thus it must be a single stranded DNA.

# Answers to exercises

## Answers

18. (b) (3 C=C)

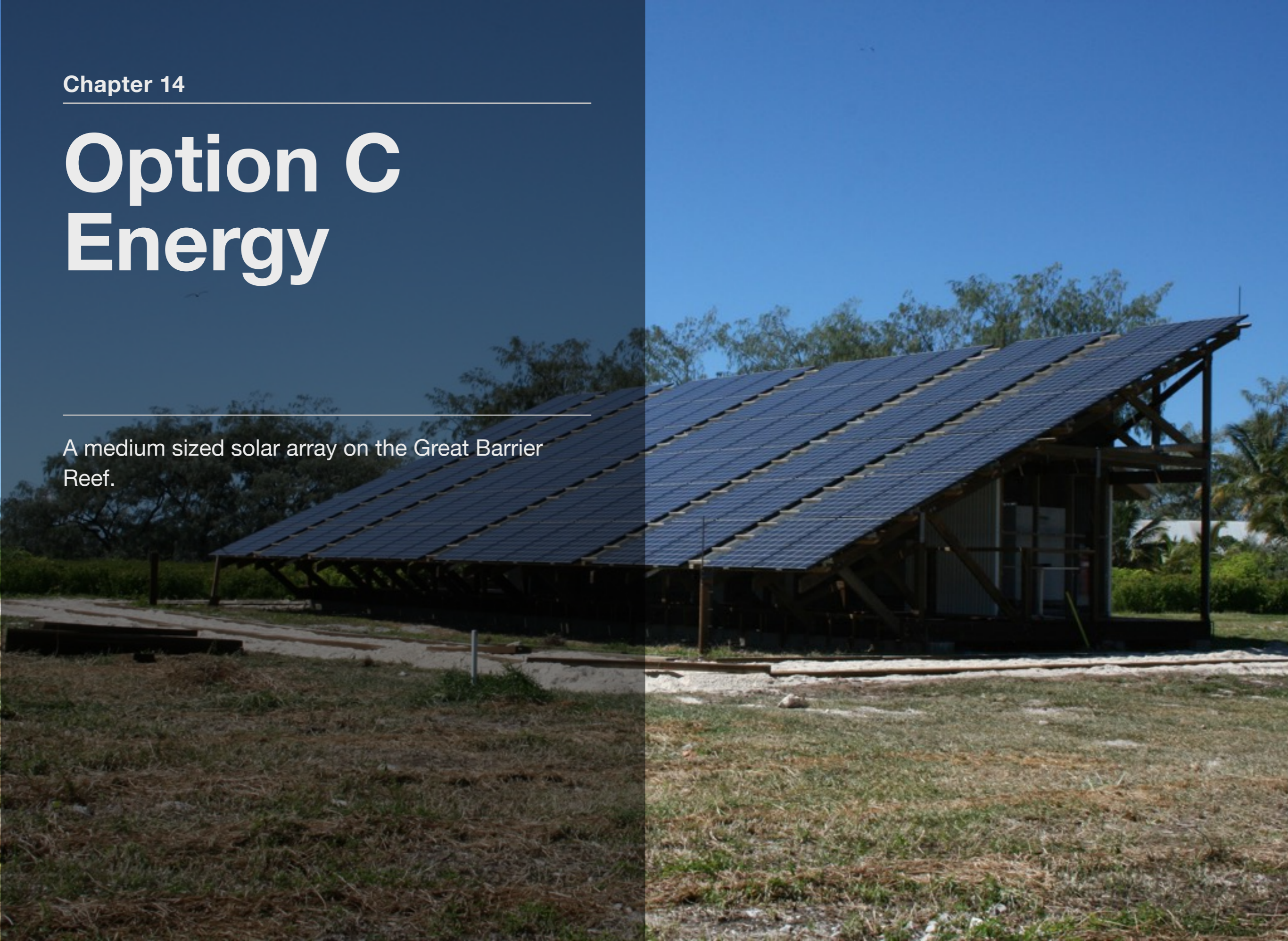
45. (b) pH = 2.57

46. (b) 0.617 mol dm<sup>-3</sup>

# Option C Energy

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A medium sized solar array on the Great Barrier Reef.



# Energy

## CONTENTS

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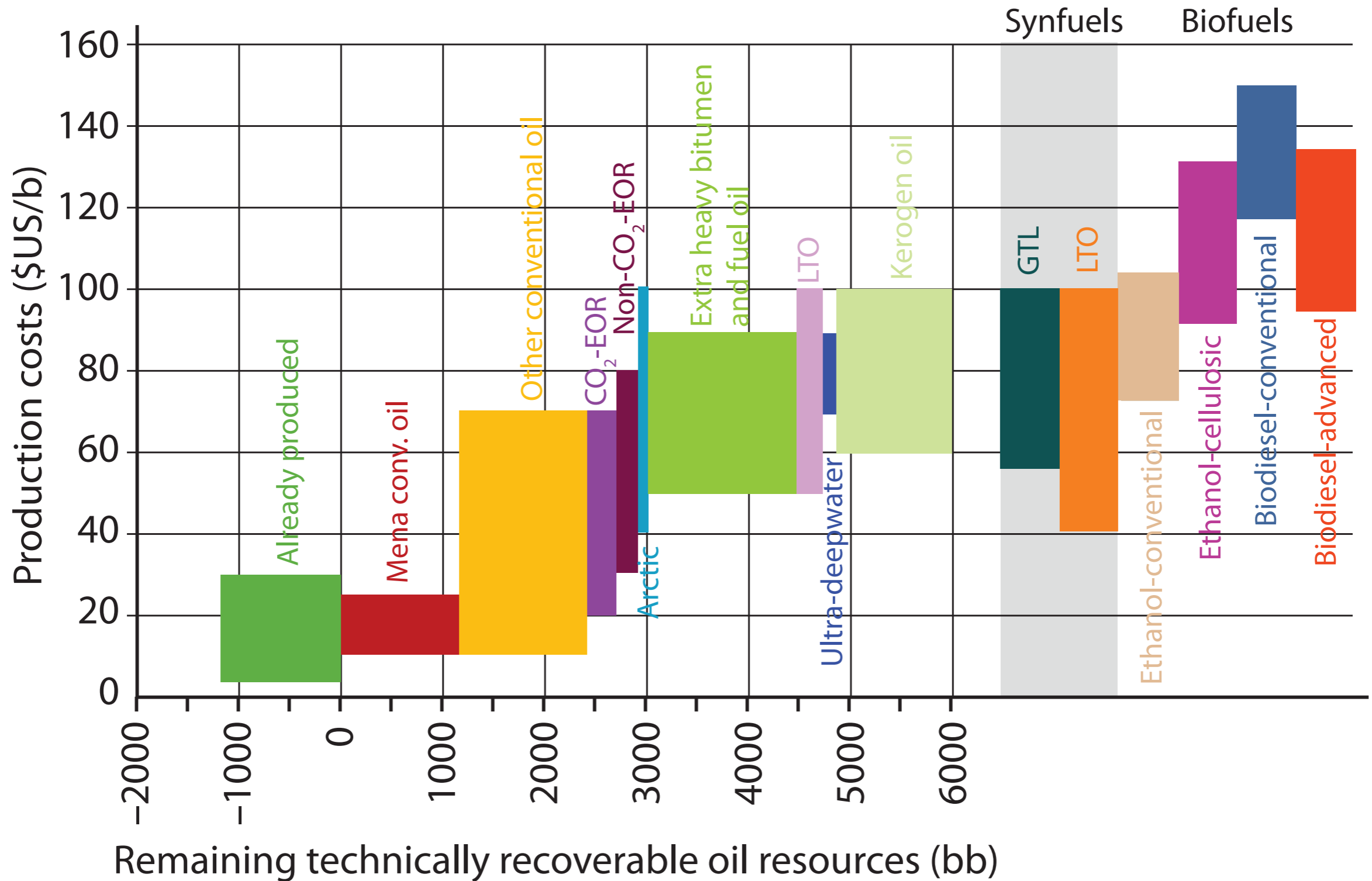
1. C1 Energy Sources
2. C.2 Fossil Fuels
3. C.3 Nuclear fusion and fission
4. C.4 Solar Energy
5. C.5 Environmental impact—global warming
6. C.6 Electrochemistry, rechargeable batteries and fuel cells
7. C.7 Nuclear fusion and fission
8. C.8 Photovoltaic cells and dye-sensitized solar cells (DSSC)



New Zealand hydro-electric dam

# Enlarged diagram

## Oil production costs for various resource categories

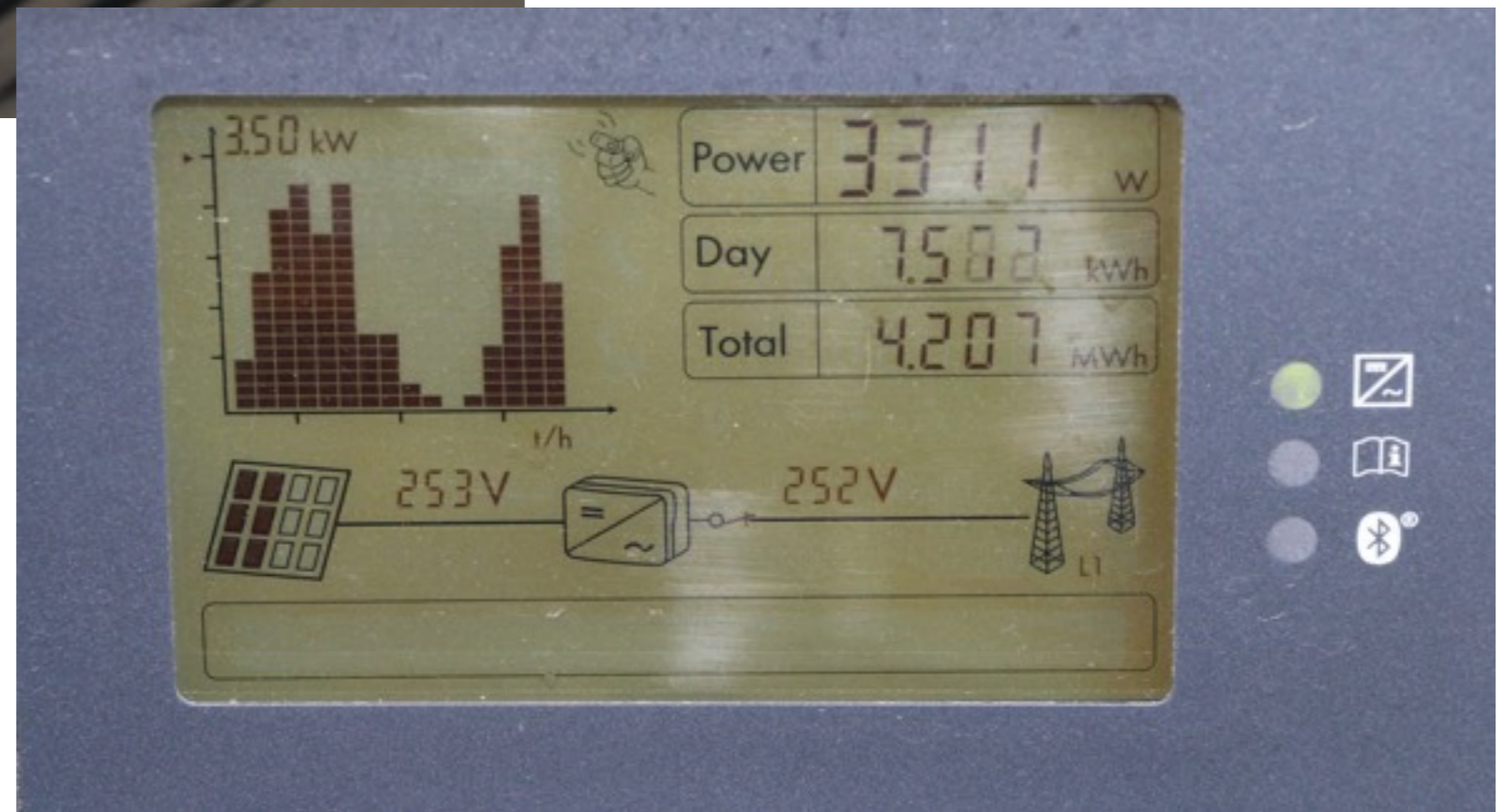


## Additional Material



IBID Press runs two 5 kW solar generating installations. Part of one of them is shown.

At noon on a sunny day in mid-winter it is shown generating 3.3 kW.





One of the biggest tidal flows in the world is at King Sound in Western Australia. The maximum tidal range is an amazing 11.8 metres. Twice a day an amount of water larger than that contained in Sydney Harbour passes in and out of it.



Unfortunately the region is very remote and not a candidate for a tidal power station.



## **TOK Is climate change real or is there 'reasonable doubt'?**

“There are lies, damned lies and statistics” (variously attributed to Benjamin Disraeli and Mark Twain) - probably nowadays that is starting to apply just as much to some fields of science as it is to the social sciences for which it was originally coined. How much evidence is required to prove something beyond reasonable doubt? The old question of inductive logic, though slightly tainted by hints that the person who is paying the piper might just influence the ‘reasonable doubt’ judgement. There were many studies on the effects of tobacco funded by cigarette manufacturers and on acid-rain funded by power generating companies, whose conclusions differed from more independent researchers.

With regard to climate change, there is little doubt that there have previously been tremendous differences in climate and not just on a geological timeframe. In the 18th century there were regular winter fairs held on the frozen River Thames, whereas even 50 years ago, before the current global warming scare really began, just a frost in London was unusual, let alone the whole river freezing. Another factor is the fact that the connection between mean global temperature and industrial pollution is a complex one for which we do not have models accepted by all scientists. When people differ it is human nature to speculate on the reasons underlying the fact that people do not agree with you, and then

probably use these to impugn their scientific impartiality. It is not only in science that ‘reasonable doubt’ is a factor – it is interesting to speculate on what kind of world we might now be living in if different recent political leaders had been elected.

# Internet resources

Oil reserves

(<http://theenergycollective.com/schalk-cloete/286196/understanding-continued-dominance-fossil-fuels>

<http://www.eia.gov/tools/faqs/faq.cfm?id=367&t=6>

<http://recipes.howstuffworks.com/vegetarian-diet-carbon-footprint.htm>

Nature of Science C3

(Environ. Sci. Technol., DOI: 10.1021/es3051197).

<http://www.nei.org/Issues-Policy/Protecting-the-Environment/Life-Cycle-Emissions-Analyses>

The 1990 NCI report (<http://www.cancer.gov/cancertopics/factsheet/Risk/nuclear-facilities>)

Energy Justice Network (<http://www.energyjustice.net/nuclear/#1>

p443

[http://www.climatechange2013.org/images/uploads/WGI\\_AR5\\_SPM\\_brochure.pdf](http://www.climatechange2013.org/images/uploads/WGI_AR5_SPM_brochure.pdf)

IBID press and carbon emissions.

Charlottes diag of battery

# Answers to exercises

## Answers

4. (a) Energy density =  $34.0 \text{ MJ dm}^{-3}$   
(b) Specific energy =  $48.3 \text{ MJ kg}^{-1}$
23. (c) 3.35 days
43. (a)  $E^\circ_{\text{cell}} = +0.93 \text{ V}$
44. (a)  $E^\circ_{\text{cell}} = +0.78 \text{ V}$  (b)  $E^\circ_{\text{cell}} = +0.76 \text{ V}$
45. (a)  $6.695098 \times 10^{-27} \text{ kg}$   
(b)  $0.050441 \times 10^{-27} \text{ kg}$   
(c)  $4.53 \times 10^{-12} \text{ J}$
48.  $1.41 \times 10^{+3} \text{ years}$

# Option D Medicinal Chemistry

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A first world 'senior's breakfast' will probably include cholesterol and blood pressure control drugs.



# Medicines

## CONTENTS

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1. D.1 Pharmaceutical products and drug action
2. D.2 Aspirin and penicillin
3. D.3 Opiates
4. D.4 pH regulation of the stomach
5. D.5 Antiviral medications
6. D6 Environmental impact of some medications
7. D.7 Taxol — a chiral auxiliary case study
8. D.8 Nuclear medicine
9. D.9 Drug detection and analysis



Many modern medicines are derived from substances found in plants.

## Additional Material

### Should Scientists be held responsible when drugs have adverse effects?

Firstly is this the same question about scientists being morally responsible for anything they discover that, like the invention of gunpowder, has brought misfortune to some people. Scientists always have the option of not telling anybody about a discovery they have made. On the plus side nobody will be harmed, but equally nobody will benefit and they will not get the kudos for the discovery. Also, somebody else, more unscrupulous, might come up with the same idea in a few month's time. Initially at any rate, the direction in which it is developed might be controlled. I don't know of any instances where people have not told us of their discoveries (think about it.). Actually that is clever, not quite accurate – I seem to recall that after his death, somebody sorting through Gauss' papers found that he had developed a lot of the theory of non-Euclidean geometry, but had not published it for fear of ridicule.

Whilst in the case of drugs the above is obviously true, perhaps in some ways they are a little different. Let's assume that this refers to drugs developed with the intention of fighting disease, rather than the replacement for Ecstasy, so that the underlying motivation is a worthy one. (I will leave you to discuss whether developing a successor to Ecstasy could display positive motives). In building a new road bridge we know there is a distinct possibility that somebody will die whilst building it, and an

even higher possibility that some day there will be a fatal crash on it. Nevertheless, provided we take reasonable precautions to guard against both we go ahead because the potential good well outweighs the potential ill.

The Supreme Court of the USA where such issues are decided.



## TOK How does perception affect our way of knowing?

Why is it that when I have a headache I usually ignore it, but my wife will usually pop a couple of Paracetamols and get rid of it? Probably, if you asked her, she would tell you that it's because I'm a stupid masochist and maybe she has a point. In all kinds of perception we differ in our sensitivities, but to what point? Do I have less pain cells? Do my cells generate lower output voltages? Do my nerves conduct the signal less efficiently? Is the part of my brain where they end up less responsive? Have I got so many things whizzing round my mind that I don't notice? Was I brought up by people telling me "big boy's don't cry if they're hurt" and that eventually led to conditioning? There are so many points on the chain where things could differ – it's not just like the needle on a light meter.

How does this affect perception as a way of knowing? Well it would be unwise to rely on absolutes. My "loud noise" might not be a loud noise to somebody else, depending on where they spend their Saturday nights, but we would most likely agree that the plane currently going overhead is louder than the music coming from my stereo – it's a lot safer to stick to comparatives. I remember being told that women have a greater ability than men to differentiate between shades of colour. I wonder if that is because they have different eyes, different brains, or have just developed this ability more as they grew up?

The 'sound of progress' or 'noise'?





## TOK What part does serendipity play in scientific discoveries?

There's a saying, (at least in my part of the world), that people make their own luck and that is probably true with regard to serendipity, the art of making fortunate discoveries by chance, in science. Take the discovery of the nucleus of the atom. Marsden was a very junior research assistant and only 1 in 2000  $\alpha$ -particles were being deflected through an angle of more than 180° by the gold foil. How easy would it have been to have ignored these ("Detector seems to be playing up.") and to have produced the expected result? How many times have we done exactly that. In some circumstances it is not just enough to have the courage to double check whether unexpected results that challenge the paradigm are genuine. It also probably needs a little bit of lateral thinking to realise the significance of the interesting observation.

Probably that is what differentiated Fleming from Florey and Chain. Fleming revived his observation after over a decade; the latter pair could see the possibility that this discovery could lead to drugs to fight bacterial infections. Even though they did not make a fortune through their discovery, they got the Nobel prize. Actually, just by coincidence, I'm writing this in the suburb of Florey, in Canberra, Australia, named after the great man. Nowadays a degree of business acumen helps as well – I remember a professor telling me how one of his students showed him a compound that was yellow, but went purple when air was

let into the apparatus, then went yellow again as the pressure was reduced. There is now a piece of apparatus for the small scale extraction of pure oxygen from air based on this principle, patented in the name of the professor.

The legendary 'Isle of Serendip' - from which we get the word 'serendipity' is real. Where is it?



## Internet resources

\*<http://www.forbes.com/sites/matthewherper/2012/02/10/the-truly-staggering-cost-of-inventing-new-drugs/>

CADET-Hp study (<http://www.bmj.com/content/324/7344/1012>)

The battle against viral infections is long, arduous and expensive which will continue to require global action plan.

1: [http://www3.imperial.ac.uk/newsandeventspggrp/imperialcollege/newssummary/news\\_18-12-2012-13-34-31](http://www3.imperial.ac.uk/newsandeventspggrp/imperialcollege/newssummary/news_18-12-2012-13-34-31)

2: <http://m.livescience.com/10510-viruses-invade.html>

3: <http://www.sciencedaily.com/releases/2013/11/131128103951.htm>

Novel stem-cell based approach “to produce cells that are either resistant to infection ...or cells that specifically target the immune response against the virus” (<http://www.ncbi.nlm.nih.gov/pubmed/21242896>).

## Answers to exercises

### Answers

26.(c) ( $[A^-] : [HA]$  ratio = 1: 1000;  $1000 [A^-] = 1 [HA]$ ).

For every one  $[A^-]$ , 1000  $[HA]$  present; thus, HA will form a precipitate.

48. 0.979 or 97.9%

Serendip is Sri Lanka.

# Errata

## WHAT CROSS WINDS CAN DO

This propeller was retrieved from a Cessna C340 charter flight which came to grief 5 km's from the departure end of the runway on 21<sup>st</sup> April 1988. The pilot and three passengers were on their way to Kalgoorlie at night when a sudden wind shift during a critical phase of takeoff resulted in a severe loss of altitude. The plane touched down with gear up and slid to a stop in flat marshy country. No injuries were suffered to those on board. The plane, however, was not so lucky.

*See exhibit for details.*

On page 477 of the IB Chemistry Textbook, under F2 Fats and Oils in Chapter 17 Food Chemistry, the third bullet point in the right-hand column says "the texture (hardness and plasticity) of the product can the controlled." It seem that last "the" should be "be."