Exam-style questions and sample answers have been written by the author. In examinations, the way marks are awarded may be different.

Coursebook answers

Chapter 1

Test your understanding

1 a compound

b element

c compound

d element

e compound

f mixture

g compound

h compound

2 a compound – two or more different atoms chemically bonded together

b element – all atoms are the same

c mixture of a compound and an element

d mixture of elements

e mixture (an alloy)

3 a homogeneous

b heterogeneous

c homogeneous

d heterogeneous

4 a Filtration: sand is filtered off (residue) and water passes through the filter paper (filtrate).

b Evaporation: heat the solution and water will evaporate off, leaving solid potassium chloride. Distillation could also be used.

c paper chromatography

d Distillation (the difference between boiling points is sufficiently high to give good separation).

5 Add (distilled/deionised) (warm) water to the mixture and stir thoroughly. Potassium bromide will dissolve but calcium carbonate will not.

Filter off calcium carbonate. The filtrate is a potassium bromide solution.

Evaporate off water to produce solid potassium bromide.

6 Put the aqueous iodine solution in a separatory funnel and add some hexane.

Shake the mixture and let the layers settle out again.

Separate the layers.

Evaporate off hexane to leave solid iodine.

7 a 35.00 + 273.15 = 308.15 K

b 500.00 + 273.15 = 773.15 K

c −100.00 + 273.15 = 173.15 K

d −145.00 + 273.15 = 128.15 K

8 a 323.15 − 273.15 = 50.00 °C

b 100.85 − 273.15 = −172.30 °C

c 50.00 − 273.15 = −223.15 °C

d 500.20 − 273.15 = 227.05 °C

9 Both temperatures are below absolute zero (0 K/−273.15 °C); absolute zero is the lowest possible temperature – it is not possible to have temperatures lower than this.

10 a melting

b sublimation

c condensation

d deposition

Chemistry for the IB Diploma – Owen © Cambridge University Press & Assessment 2023

11 a solid as 100 °C is below its melting point

b liquid as −200 °C is above its melting point but a lower temperature than its boiling point

c gas as 1000 °C is above its boiling point

d liquid as 25 °C is above its melting point but a lower temperature than its boiling point

Exam-style questions

1 B

2 B

3 C

4 A

5 C

6 B

7 A

8 B

9 D

10 D

11 a ethyl benzoate and propanone; 25 °C is 298 K and 298 K is between the melting and boiling points for both ethyl benzoate and propanone (therefore, these will be liquid at 298 K); **[2]**

b Distillation;

And any two further points for 1 mark each:

Mixture heated in a flask fitted with a condenser;

Propanone is more volatile, so it boils over and is condensed;

Sufficiently high difference in boiling points; **[3]**

c Filter off undissolved anthracene;

Evaporation *and* heat the mixture to boil off propanone and leave anthracene that had dissolved *OR* propanone has a much lower boiling point than anthracene (so can be boiled off); **[2]**

d This is true – ethene has the lowest boiling point and boils (becomes a gas) at a lower temperature than that at which any of the other substances melt (so they are still solids at a temperature at which ethene is a gas). **[1]**

12 a Zn(s): element

H_2SO_4(aq): mixture. **[1]**

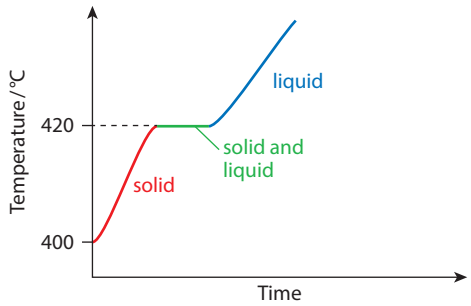
b Filter off the zinc; evaporation – boil the solution to remove water, to leave solid $ZnSO_4$/heat to boil off some water and allow to crystallise;

Allow distillation **[2]**

c Zinc – a solid – particles vibrate around mean positions;

Hydrogen – a gas – the particles move randomly at high speed in all directions; **[2]**

d



general form of curve including axes labelled [1]; correct labels [1] **[2]**

13 a Solid sodium chloride will also be formed, and so, the caffeine will not be pure. **[1]**

b i Caffeine is more soluble in trichloromethane than in water but less soluble in propanone than in water;

Trichloromethane is not miscible with water, and so, will form a separate layer into which caffeine will dissolve, but propanone is miscible in water and will dissolve in the mixture; **[2]**

ii Trichloromethane added to the mixture and stirred/shaken;

Trichloromethane layer collected;

Trichloromethane evaporated off; **[3]**

Chemistry for the IB Diploma – Owen © Cambridge University Press & Assessment 2023

Chapter 2

Test your understanding

1 Atoms contain a POSITIVELY charged nucleus composed of PROTONS and NEUTRONS.

2 Electrons have a NEGATIVE charge and are found IN THE SPACE AROUND THE NUCLEUS/IN SHELLS/ORBITS AROUND THE NUCLEUS.

Virtually all the mass of an atom is due to the NUCLEUS/PROTONS AND NEUTRONS.

3 a false – atomic number has the symbol *Z*, mass number has the symbol *A*

b true

c true

d false – a neutron has no charge

e true

f true

4 a $^{23}_{11}Na$: 11 protons, 12 neutrons, 11 electrons

b $^{15}_{7}N$: 7 protons, 8 neutrons, 7 electrons

c $^{35}_{17}Cl$: 17 protons, 18 neutrons, 17 electrons

d $^{239}_{92}U$: 92 protons, 147 neutrons, 92 electrons

e $^{75}_{33}As$: 33 protons, 42 neutrons, 33 electrons

f $^{81}_{35}Br$: 35 protons, 46 neutrons, 35 electrons

5 a $^{7}_{3}Li^{+}$: 3 protons, 4 neutrons, 2 electrons

b $^{2}_{1}H^{+}$: 1 proton, 1 neutron, 0 electrons

c $^{31}_{15}P^{3-}$: 15 protons, 16 neutrons, 18 electrons

d $^{33}_{16}S^{2-}$: 16 protons, 17 neutrons, 18 electrons

e $^{1}_{1}H^{-}$: 1 proton, 0 neutrons, 2 electrons

f $^{40}_{20}Ca^{2+}$: 20 protons, 20 neutrons, 18 electrons

g $^{127}_{53}I^{-}$: 53 protons, 74 neutrons, 54 electrons

h $^{140}_{58}Ce^{3+}$: 58 protons, 82 neutrons, 55 electrons

6 a more electrons than neutrons

$^{18}_{9}F^{-}$ $^{32}_{16}S^{2-}$

b same number of electrons and neutrons

$^{18}_{8}O^{2-}$ $^{3}_{1}H^{-}$

c more neutrons than electrons

$^{24}_{11}Na^{+}$ $^{29}_{14}Si^{+}$ $^{52}_{24}Cr$

$^{59}_{27}Co^{3+}$ $^{76}_{35}Br^{-}$ $^{26}_{13}Al^{3+}$ $^{71}_{33}As^{5+}$

7 17+ (17 protons in the nucleus)

8 Isotopes are different atoms of the same element (same atomic number/number of protons in the nucleus) with different mass numbers: i.e. different numbers of neutrons in the nucleus.

9 a D and L are isotopes; Q and M are isotopes; isotopes have the same number of protons.

b D, X, L (fewer electrons than protons)

10 a $^{11}_{5}B$: 5 protons, 6 neutrons, 5 electrons

$^{10}_{5}B$: 5 protons, 5 neutrons, 5 electrons

b $^{28}_{14}Si$: 14 protons, 14 neutrons, 14 electrons

$^{29}_{14}Si$: 14 protons, 15 neutrons, 14 electrons

$^{30}_{14}Si$: 14 protons, 16 neutrons, 14 electrons

c $^{32}_{16}S$: 16 protons, 16 neutrons, 16 electrons

$^{33}_{16}S$: 16 protons, 17 neutrons, 16 electrons

$^{36}_{16}S$: 16 protons, 20 neutrons, 16 electrons

11 46 is the atomic number of palladium – all palladium atoms have an atomic number of 46, so there is no need to use the name and the atomic number. If a number follows the name, it should be the mass number in order to identify the particular isotope being discussed.

12 Isotopes have the same CHEMICAL properties because they have THE SAME NUMBER OF ELECTRONS but different PHYSICAL properties because they have DIFFERENT MASSES.

13 $[(50.69\times79)+(49.31\times81)]\div100=79.99$

14 $[(4.35\times50)+(83.79\times52)+(9.50\times53)+(2.36\times54)]\div100=52.06$

15 $[(92.2\times28)+(4.7\times29)+(3.1\times30)]\div100=28.11$

16 $[(0.35\times78)+(2.25\times80)+(11.6\times82)+(11.5\times83)+(57.0\times84)+(17.3\times86)]\div100=83.89$

Chemistry for the IB Diploma – Owen © Cambridge University Press & Assessment 2023

17 a Let % ^{113}In be x, then the % ^{115}In is $(100 - x)$

$$114.82 = \frac{113x + 115(100 - x)}{100}$$

$x = 9$, therefore 91% indium-115; 9% indium-113

b Let % ^{69}Ga be x, then the % ^{71}Ga is $(100 - x)$

$$69.723 = \frac{69x + 71(100 - x)}{100}$$

$x = 63.85$, therefore 63.85% gallium-69; 36.15% gallium-71

c Let % ^{63}Cu be x, then the % ^{65}Cu is $(100 - x)$

$$63.546 = \frac{63x + 65(100 - x)}{100}$$

$x = 72.7$, therefore 72.7 % copper-63; 27.3 % copper-65

d ^{84}Sr and ^{88}Sr have a total abundance of 0.56 + 82.58 = 83.14 %. This means that the total abundance of ^{86}Sr and ^{87}Sr together is 100 − 83.14 = 16.86 %

Let % ^{86}Sr be s, then the % ^{87}Sr is (16.86 − s)

$$87.71 = \frac{\left[84 \times 0.56 + 86s + 87(16.86 - s) + 88 \times 82.58\right]}{100}$$

s = 9.90, therefore 9.90% ^{86}Sr; 6.96% ^{87}Sr

18 Rb: $\frac{[(72.17 \times 85) + (27.83 \times 87)]}{100} = 85.56$

Nd: $[(27.13 \times 142) + (12.18 \times 143) + (23.80 \times 144) + (8.30 \times 145) + (17.19 \times 146) + (5.76 \times 148) + (5.64 \times 150)]$ / 100 = 144.33

Exam-style questions

1 B

2 C

3 B

4 D (you need to refer to the periodic table)

5 C (you need to refer to the periodic table)

6 A (you need to refer to the periodic table)

7 B

8 B

9 C

10 A

11 a *Atomic number*: the number of protons in the nucleus of an atom;

isotopes: atoms of the same element/ same atomic number/same number of protons; with different mass numbers/ different numbers of neutrons in the nucleus; **[3]**

b number of protons = 26 and number of electrons = 26;

number of neutrons = 31; **[2]**

(The number of protons is given by the atomic number, 26. The number of neutrons is the mass number minus the atomic number, i.e., 57 − 26 = 31
This is an atom, so the number of electrons equals the number of protons: 26.)

c relative atomic mass =

$$\frac{[(5.80 \times 54) + (91.16 \times 56) + (3.04 \times 57)]}{100};$$

= 55.91;

max [1] if answer not given to 2 decimal places. **[2]**

d They would be different – isotopes have different physical properties due to different masses of atoms. **[1]**

e $^{56}FeI_2$ and $^{54}FeCl_3$;

Isotopes have the same chemical properties because they have the same number of electrons, therefore, the formulas of the products are the same; **[2]**

12 a i mass spectrum and mass spectrometer **[1]**

ii $\frac{[(0.73 \times 235) + (99.27 \times 238)]}{100}$;

= 237.98; **[2]**

max [1] if answer not given to 2 decimal places.

b $\frac{[235x + 238(100 - x)]}{100}$; = 235.24

92.0% ^{235}U and 8.0% ^{238}U; **[2]**

Chemistry for the IB Diploma – Owen © Cambridge University Press & Assessment 2023

Chapter 3

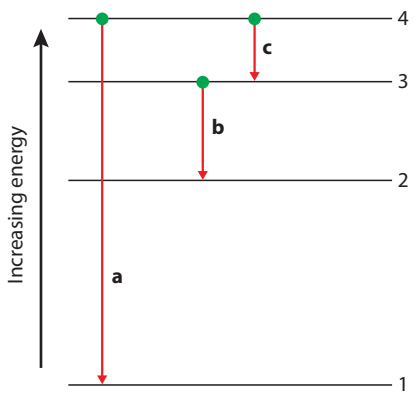
Test your understanding

1 **a** microwaves < infrared radiation < orange light < green light < ultraviolet radiation

b microwaves > infrared radiation > orange light > green light > ultraviolet radiation

2 An electron in a hydrogen atom that has been promoted to a higher energy level falls down to energy level 1. As it does so, it gives out energy in the form of a photon of light in the ultraviolet region of the electromagnetic spectrum.

3



a any transition to level 1

b any transition to level 2

c any transition to level 3

4 **a** $1s^2\ 2s^2\ 2p^3$

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

c $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$

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

e $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^3$

f $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^1\ 3d^5$

5 **a** $[He]\ 2s^2\ 2p^4$

b $[Ne]\ 3s^2\ 3p^5$

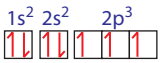
c $[Ar]\ 4s^2\ 3d^5$

d $[Ar]\ 4s^2\ 3d^{10}\ 4p^1$

e $[Ar]\ 4s^2\ 3d^{10}\ 4p^5$

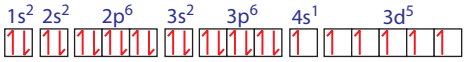
f $[Ar]\ 4s^1\ 3d^{10}$

6 **a**

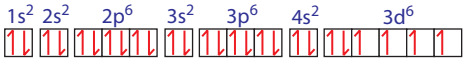


b

c



d



7 **a** 1 $2p^1$

b 3 $3p^3$ one electron in each p orbital

c 0 $4s^2$

d 5 $4s^2\ 3d^5$ one electron in each d orbital

e 3 $4p^3$ one electron in each p orbital

8 **a** $1s^2\ 2s^2\ 2p^6$

b $1s^2\ 2s^2\ 2p^6$

c $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$

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

e $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^6$

9 **a** $[Ne]\ 3s^2\ 3p^6$

b $[Ar]\ 3d^{10}$

c $[Ar]\ 3d^{10}$

d $[Ar]\ 3d^2$

e $[Ar]\ 3d^8$

10 $E = hf = 6.63 \times 10^{-34} \times 3.29 \times 10^{15}$
$= 2.18 \times 10^{-18}$ J

$$\frac{2.18 \times 10^{-18} \times 6.02 \times 10^{23}}{1000} = 1310 \text{ kJ mol}^{-1}$$

11 $f = c/\lambda = \dfrac{3.00 \times 10^8}{2.281 \times 10^{-8}} = 1.32 \times 10^{16}$ Hz

$E = hf = 6.63 \times 10^{-34} \times 1.32 \times 10^{16}$
$= 8.72 \times 10^{-18}$ J

$$\frac{8.72 \times 10^{-18} \times 6.02 \times 10^{23}}{1000} = 5250 \text{ kJ mol}^{-1}$$

12 **a** **i** $Ca(g) \rightarrow Ca^+(g) + e^-$

ii $Cl^+(g) \rightarrow Cl^{2+}(g) + e^-$

iii $Fe^{9+}(g) \rightarrow Fe^{10+}(g) + e^-$

iv $Cu^{28+}(g) \rightarrow Cu^{29+}(g) + e^-$

b The 29th ionisation of copper – the electron is removed from the shell closest to the nucleus (no shielding) and the nuclear charge is the highest.

13 X is in Group 14 (large jump after the 4th ionisation energy); Z is in Group 2 (large jump after the 2nd ionisation energy); Q is in Group 15 (large jump after the 5th ionisation energy).

Chemistry for the IB Diploma – Owen © Cambridge University Press & Assessment 2023

14 A = Mg

T = Al

For A, there is a large jump in ionisation energy between the 10th and the 11th, so the 10th and 11th electrons are from different shells. The values for the 11th and 12th ionisation energies are extremely high, suggesting that the electrons are removed from the shell closest to the nucleus.

For T, there is a large jump in ionisation energy between the 11th and the 12th, so the 11th and 12th electrons are from different shells. The value for the 12th ionisation energy is extremely high, suggesting that the electron is removed from the shell closest to the nucleus.

The elements could also be e.g. Ca/Sc, Ni/Cu etc., but the ionisation energies are unlikely to be that high for removal of the 11th/12th electrons.

Exam-style questions

1 C

2 B

3 A

4 D

5 B

6 C

7 C

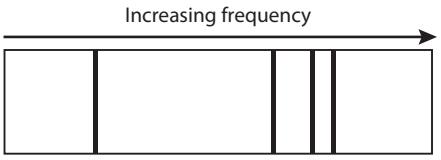
8 A

9 C

10 C

11 a *Continuous spectrum*: all frequencies/wavelengths of light present; *line spectrum*: only certain frequencies/wavelengths of light present; **[2]**

b



Series of lines; **[2]**

Getting closer together at higher frequency;

c An electron (which has been promoted) falls from a higher energy level to a lower energy level; the excess energy is given out as a photon of light; **[2]**

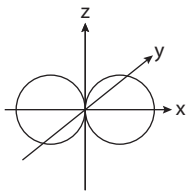
d Electrons fall to different energy levels to give different series of lines;

Any transition to $n = 1$ results in a line in the UV region of the spectrum, e.g., $n = 2 \rightarrow n = 1$; **[2]**

12 a A region of space where there is a high probability of finding an electron. **[1]**

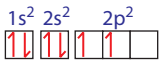
b This is not correct – the energy of an orbital depends on the nuclear charge, the electron configuration and the chemical environment. **[1]**

c **[1]**



d A p sub-level is made up of three p orbitals/a p sub-level can contain up to six electrons, but a p orbital can hold a maximum of two electrons. **[1]**

e **[1]**

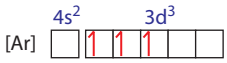


13 a The highest-energy occupied sub-level (subshell) is a p sub-level (subshell). **[1]**

b $1s^2\ 2s^2\ 2p^6$ **[1]**

c The full electron configuration is $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}$ – all sub-levels are full, so there are no unpaired electrons. **[1]**

d **[1]**



14 a $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^1$ **[1]**

b $K^+(g) \rightarrow K^{2+}(g) + e^-$

for equation [1]

for state symbols [1]

Chemistry for the IB Diploma – Owen © Cambridge University Press & Assessment 2023

c The first electron is removed from the fourth shell (main energy level), but the second electron is removed from the third shell;

an electron in the third shell is closer to the nucleus and, therefore, more strongly attracted;

1 mark each for each of the above points then 1 mark for one of the following points:

the first electron is removed from a neutral atom, but the second is removed from a positive ion – it is more difficult to remove a negatively charged electron from a positive ion than from a neutral atom;

an electron in the third shell is shielded by fewer shells of electrons, therefore more strongly attracted by the nucleus; **[3]**

d Large jump in ionisation energy between the 5th and 6th ionisation energies, so 5 electrons in outer shell and in Group 15;

Sixth electron is in a shell closer to the nucleus and less shielded, therefore, more strongly attracted to the nucleus;

1 *mark each for each of the above points then* 1 *mark for one of the following points:*

Also a jump between third and fourth ionisation energies: electrons are removed from different sub-shells;

Also a jump between third and fourth ionisation energies, so p subshell is higher in energy than s subshell, therefore, less energy required to remove an electron;

Also a jump between third and fourth ionisation energies: three p electrons removed first then two s electrons; **[3]**

Chemistry for the IB Diploma – Owen © Cambridge University Press & Assessment 2023

Chapter 4

Test your understanding

1

Compound	Relative molecular mass
SO_2	64.07
NH_3	17.04
C_2H_5OH	46.08
$MgCl_2$	95.21
$Ca(NO_3)_2$	164.10
$CH_3(CH_2)_5CH_3$	100.23
PCl_5	208.22
$Mg_3(PO_4)_2$	262.87
$Na_2S_2O_3$	158.12
$CH_3CH_2CH_2COOCH_2CH_3$	116.18

2

Compound	Molar mass/g mol^{-1}	Mass/g	Amount of substance /mol
H_2O	18.02	9.01	0.500
CO_2	44.01	5.00	0.114
H_2S	34.09	3.41	0.100
NH_3	17.04	59.6	3.50
Q	28.6	1.00	0.0350
Z	51.61	0.0578	1.12×10^{-3}
$Mg(NO_3)_2$	148.33	1.75	0.0118
C_3H_7OH	60.11	2500	41.59
Fe_2O_3	159.70	9.07×10^{-3}	5.68×10^{-5}
nitrogen gas	28.02	10.00	0.3569
chlorine gas	70.90	0.3545	5.000×10^{-3}

3 a $\frac{10}{134.45} = 0.0744$ mol

b $\frac{10.0}{28.06} = 0.356$ mol

c $\frac{10.0}{32.07} = 0.312$ mol

d $\frac{10.0}{48.00} = 0.208$ mol

e $\frac{10.0}{123.12} = 0.0812$ mol

4 a $0.155 \times 74.10 = 11.5$ g

b $1.78 \times 10^{-3} \times 101.96 = 0.181$ g

c $2.50 \times 80.06 = 200$ g

d $400 \times 4.00 = 1600$ g

e $0.245 \times 2.02 = 0.495$ g

5 a $\frac{10\,000}{16.05} = 623$ mol

b $\frac{25\,000}{58.44} = 428$ mol

c $\frac{10\,000\,000}{44.01} = 2.27 \times 10^5$ mol

d $\frac{50\,000\,000}{100.09} = 5.00 \times 10^5$ mol

e $\frac{1200}{158.12} = 7.59$ mol

Chemistry for the IB Diploma – Owen © Cambridge University Press & Assessment 2023

6 **a** $\frac{18.02}{(6.02 \times 10^{23})} = 2.99 \times 10^{-23}$ g

b $\frac{17.04}{(6.02 \times 10^{23})} = 2.83 \times 10^{-23}$ g

c $\frac{44.01}{(6.02 \times 10^{23})} = 7.31 \times 10^{-23}$ g

7 Note: the word *average* is used in the question because the relative atomic mass is being used, which is the average mass of an atom taking into account isotopes.

a $\frac{1.01}{(6.02 \times 10^{23})} = 1.68 \times 10^{-24}$ g

b $\frac{63.55}{(6.02 \times 10^{23})} = 1.06 \times 10^{-22}$ g

c $\frac{20.18}{(6.02 \times 10^{23})} = 3.35 \times 10^{-23}$ g

8 **a** $0.100 \times 6.02 \times 10^{23} = 6.02 \times 10^{22}$

b $2.00 \times 10^{-3} \times 6.02 \times 10^{23} = 1.20 \times 10^{21}$

c $0.280 \times 6.02 \times 10^{23} = 1.69 \times 10^{23}$

9 **a** Amount of Ar $= \frac{1.00}{39.95} = 0.0250$ mol

There are 6.02×10^{23} atoms in 1 mol Ar, therefore in 0.0250 mol, the number of atoms is:

$0.0250 \times 6.02 \times 10^{23} = 1.51 \times 10^{22}$

b $\left(\frac{1.00}{65.38}\right) \times 6.02 \times 10^{23} = 9.21 \times 10^{21}$

c $\left(\frac{1.00}{196.97}\right) \times 6.02 \times 10^{23} = 3.06 \times 10^{21}$

10 **a** Amount of $H_2O = \frac{10.00}{18.02} = 0.555$ mol

There are 6.02×10^{23} molecules in 1 mol H_2O, therefore in 0.555 mol, the number of molecules is:

$0.555 \times 6.02 \times 10^{23} = 3.34 \times 10^{23}$

b $\frac{10.00}{32.00} \times 6.02 \times 10^{23} = 1.88 \times 10^{23}$

c $\frac{10.00}{44.01} \times 6.02 \times 10^{23} = 1.37 \times 10^{23}$

11 **a** There are 6.02×10^{23} molecules in 1 mol NH_3, therefore in 0.0100 mol, the number of molecules is:

$0.0100 \times 6.02 \times 10^{23} = 6.02 \times 10^{21}$

There are 4 atoms (1 N and 3 H) per molecule, therefore the total number of atoms is $4 \times 6.02 \times 10^{21} = 2.41 \times 10^{22}$

b $0.200 \times 6.02 \times 10^{23} \times 8 = 9.63 \times 10^{23}$

c $0.0400 \times 6.02 \times 10^{23} \times 9 = 2.17 \times 10^{23}$

12 **a** $0.2 \times 4 = 0.8$ mol

b $0.1 \times 7 = 0.7$ mol

c $0.03 \times 4 = 0.12$ mol

13 **a** $1.00 \times 6.02 \times 10^{23} \times 2 = 1.20 \times 10^{24}$

b $0.200 \times 6.02 \times 10^{23} \times 4 = 4.82 \times 10^{23}$

c $0.0500 \times 6.02 \times 10^{23} \times 3 = 9.03 \times 10^{22}$

14 **a** $\frac{16.00}{46.08} \times 100 = 34.72\%$

b $\frac{(2 \times 16.00)}{74.09} \times 100 = 43.19\%$

c $\frac{(7 \times 16.00)}{182.90} \times 100 = 61.24\%$

15 **a** Na: $\frac{22.99}{58.44} \times 100 = 39.3\%$

Cl: $\frac{35.45}{58.44} \times 100 = 60.7\%$

b K: $\frac{39.10}{214.00} \times 100 = 18.3\%$

I: $\frac{126.90}{214.00} \times 100 = 59.3\%$

O: $\frac{48.00}{214.00} \times 100 = 22.4\%$

c C: $\frac{72.06}{213.12} \times 100 = 33.8\%$

H: $\frac{3.03}{213.12} \times 100 = 1.42\%$

N: $\frac{42.03}{213.12} \times 100 = 19.7\%$

O: $\frac{96.00}{213.12} \times 100 = 45.0\%$

16 **a** $\frac{16.00}{60.11} \times 6.00 = 1.60$ g

b $\frac{(16.00 \times 2)}{64.07} \times 5.00 = 2.50$ g

c $\frac{(16.00 \times 10)}{283.88} \times 10.00 = 5.64$ g

17 **a** $\frac{32.05}{16.00} \times 1.00 = 2.00$ g

b $\frac{80.07}{(3 \times 16.00)} \times 1.00 = 1.67$ g

c $\frac{219.88}{(6 \times 16.00)} \times 1.00 = 2.29$ g

18 CO_2, CH, HO, C_3H_8, H_2O, PCl_5, $C_6H_5CH_3$

Chemistry for the IB Diploma – Owen © Cambridge University Press & Assessment 2023

19

Empirical formula	Relative molecular mass	Molecular formula
HO	34.02	H_2O_2
ClO_3	166.90	Cl_2O_6
CH_2	84.18	C_6H_{12}
BNH_2	80.52	$B_3N_3H_6$

20 a C: $\frac{0.399}{12.01} = 0.0332$ mol

H: $\frac{0.101}{1.01} = 0.100$ mol

C: $\frac{0.0332}{0.0332} = 1.00$

H: $\frac{0.100}{0.0332} = 3.01$

Empirical formula is CH_3

b $\frac{30.08}{15.04} = 2$

$(CH_3)_2$, therefore C_2H_6

21 %O = 100 – 81.6 = 18.4%

Cl: $\frac{81.6}{35.45} = 2.30$

O: $\frac{18.4}{16.00} = 1.15$

$\frac{2.30}{1.15} = 2$

therefore Cl_2O

22 I: $\frac{76.0}{126.90} = 0.600$ mol

O: $\frac{24.0}{16.00} = 1.50$ mol

I: $\frac{0.600}{0.600} = 1.00$

O: $\frac{1.50}{0.600} = 2.50$

Ratio I:O is 1:2.5

Multiply by 2 to get whole numbers

therefore I_2O_5

23 a %O = 100 − 77.7 = 22.3%

Fe: $\frac{77.7}{55.85} = 1.39$ mol

O: $\frac{22.3}{16.00} = 1.39$ mol

$\frac{1.39}{1.39} = 1$; therefore, FeO

b %O = 100 − 72.4 = 27.6%

Fe: $\frac{72.4}{55.85} = 1.30$ mol

O: $\frac{27.6}{16.00} = 1.73$ mol

Fe: $\frac{1.30}{1.30} = 1.00$

O: $\frac{1.73}{1.30} = 1.33$

Ratio Fe:O is 1:1.33

Multiply by 3 to get whole numbers

Therefore, Fe_3O_4

24 a Na: $\frac{28.4}{22.99} = 1.24$

Cr: $\frac{32.1}{52.00} = 0.617$

O: $\frac{39.5}{16.00} = 2.47$

Na: $\frac{1.24}{0.617} = 2$

Cr: $\frac{0.617}{0.617} = 1$

O: $\frac{2.47}{0.617} = 4$

Na_2CrO_4

b Na: $\frac{17.55}{22.99} = 0.763$

Cr: $\frac{39.70}{52.00} = 0.763$

O: $\frac{42.75}{16.00} = 2.67$

Na: $\frac{0.763}{0.763} = 1$

Cr: $\frac{0.763}{0.763} = 1$

O: $\frac{2.67}{0.763} = 3.5$

multiply by 2 to get whole numbers

$Na_2Cr_2O_7$

25 a C: $\frac{74.83}{12.01} = 6.23$ mol

H: $\frac{25.17}{1.01} = 24.92$ mol

C: $\frac{6.23}{6.23} = 1.00$

H: $\frac{24.92}{6.23} = 4.00$

CH_4

Chemistry for the IB Diploma – Owen © Cambridge University Press & Assessment 2023

b C: $\frac{79.85}{12.01} = 6.65$ mol

H: $\frac{20.15}{1.01} = 19.95$ mol

C: $\frac{6.65}{6.65} = 1.00$

H: $\frac{19.95}{6.65} = 3.00$

CH_3

c C: $\frac{85.60}{12.01} = 7.127$ mol

H: $\frac{14.40}{1.01} = 14.257$ mol

C: $\frac{7.127}{7.127} = 1.00$

H: $\frac{14.257}{7.127} = 2.00$

CH_2

d C: $\frac{81.68}{12.01} = 6.801$ mol

H: $\frac{18.32}{1.01} = 18.139$ mol

C: $\frac{6.801}{6.801} = 1.00$

H: $\frac{18.139}{6.801} = 2.67$

$C_1H_{2.67}$

Multiply by 3 to get whole numbers: C_3H_8

e C: $\frac{83.21}{12.01} = 6.928$ mol

H: $\frac{16.79}{1.01} = 16.624$ mol

C: $\frac{6.928}{6.928} = 1.00$

H: $\frac{16.624}{6.928} = 2.40$

$C_1H_{2.40}$

Multiply by 5 to get whole numbers: C_5H_{12}

26 Mass of O = 5.60 – 3.92 = 1.68 g

O: $\frac{1.68}{16.00} = 0.105$ mol

Fe: $\frac{3.92}{55.85} = 0.0702$ mol

$\frac{0.105}{0.0702} = 1.5$

Fe_2O_3

27 a $\frac{0.100}{2.00} = 0.0500$ mol dm^{-3}

b $\frac{1.20 \times 10^{-3}}{(10.0/1000)} = 0.120$ mol dm^{-3}

c $\frac{0.0560}{(250.0/1000)} = 0.224$ mol dm^{-3}

28 a $\frac{50.0}{10.00} = 5.00$ g dm^{-3}

b $\frac{2.00}{\left(\frac{100.0}{1000}\right)} = 20.0$ g dm^{-3}

c $\frac{0.780}{\left(\frac{25.0}{1000}\right)} = 31.2$ g dm^{-3}

29 a $\left(\frac{20.0}{1000}\right) \times 0.220 = 4.40 \times 10^{-3}$ mol

b $\left(\frac{27.8}{1000}\right) \times 0.0840 = 2.34 \times 10^{-3}$ mol

c $\left(\frac{540}{1000}\right) \times 0.0200 = 0.0108$ mol

d $2.50 \times 0.140 = 0.350$ mol

30 a $\frac{20.0}{40.00} = 0.500$ mol dm^{-3}

b $\frac{10.00}{101.11} = 0.0989$ mol dm^{-3}

c $\frac{2.50}{159.62} = 0.0157$ mol dm^{-3}

31 a $0.0200 \times 58.44 = 1.17$ g dm^{-3}

b $0.150 \times 105.99 = 15.9$ g dm^{-3}

c $0.500 \times 98.09 = 49.0$ g dm^{-3}

32 a Amount of NaOH = $\frac{50.0}{1000} \times 0.100$ = 5.00×10^{-3} mol

Mass of NaOH = $5.00 \times 10^{-3} \times 40.00$ = 0.200 g

b Amount of $Na_2Cr_2O_7$ = $\frac{75.0}{1000} \times 0.0100$ = 7.50×10^{-4} mol

Mass of $Na_2Cr_2O_7$ = $7.50 \times 10^{-4} \times 261.98$ = 0.196 g

c Amount of $Na_2S_2O_3{\cdot}5H_2O$ = $\frac{50.0}{1000} \times 0.200 = 1.00 \times 10^{-2}$ mol

Mass of $Na_2S_2O_3{\cdot}5H_2O$ = $1.00 \times 10^{-2} \times 248.22 = 2.48$ g

Chemistry for the IB Diploma – Owen © Cambridge University Press & Assessment 2023

33 $\dfrac{\left(\dfrac{12.50}{286.19}\right)}{\left(\dfrac{100.0}{1000}\right)} = 0.437 \text{ mol dm}^{-3}$

34 a $0.100 \times 2 = 0.200 \text{ mol dm}^{-3}$

b $0.200 \times 3 = 0.600 \text{ mol dm}^{-3}$

c $0.125 \times 4 = 0.500 \text{ mol dm}^{-3}$

35 a Amount of NaOH = 2.00/40.00 = 0.0500 mol

1 Na^+ ion per unit, therefore, amount of Na^+ ions = 0.0500 mol

Concentration of ions = $\dfrac{0.0500}{\left(\dfrac{100.0}{1000}\right)}$

$= 0.500 \text{ mol dm}^{-3}$

b Amount of $Na_2CO_3 = \dfrac{4.50}{105.99} = 0.04246$ mol

2 Na^+ ions per unit, therefore, amount of Na^+ ions = 0.04246 × 2 = 0.08491 mol

Concentration of ions = $\dfrac{0.08491}{\left(\dfrac{250.0}{1000}\right)}$

$= 0.340 \text{ mol dm}^{-3}$

c $\dfrac{\left(\dfrac{5.00}{248.22}\right)}{\left(\dfrac{500.0}{1000}\right)} \times 2 = 0.0806 \text{ mol dm}^{-3}$

d $\dfrac{\left(\dfrac{1.00}{163.94}\right)}{\left(\dfrac{50.0}{1000}\right)} \times 3 = 0.366 \text{ mol dm}^{-3}$

36 a Amount of $FeSO_4 = \dfrac{1.64}{151.92} = 0.0108$ mol

Mass of water = 3.00 − 1.64 = 1.36 g

Amount of water = $\dfrac{1.36}{18.02} = 0.0755$ mol

Ratio of water to $FeSO_4$ = 0.0755/0.0108 = 7

Therefore $x = 7$

b Amount of $Na_2SO_4 = \dfrac{1.10}{142.05} = 7.74 \times 10^{-3}$ mol

Mass of water = 2.50 − 1.10 = 1.40 g

Amount of water = $\dfrac{1.40}{18.02} = 0.0777$ mol

Ratio of water to $Na_2SO_4 = \dfrac{0.0777}{(7.74 \times 10^{-3})}$

= 10

Therefore $x = 10$

c Amount of $BaCl_2$ = 1.02/208.23 = 4.90×10^{-3} mol

Mass of water = 1.20 − 1.02 = 0.18 g

Amount of water = $\dfrac{0.18}{18.02} = 9.99 \times 10^{-3}$ mol

Ratio of water to $BaCl_2 = \dfrac{9.99 \times 10^{-3}}{(4.90 \times 10^{-3})}$ = 2.04

Therefore $x = 2$

d Amount of $CuSO_4{\bullet}5H_2O = \dfrac{3.76}{249.72}$ = 0.01506 mol

There is 1 $CuSO_4$ in every $CuSO_4{\bullet}5H_2O$ unit, therefore the amount of $CuSO_4$ in 3.76 g $CuSO_4{\bullet}5H_2O$ = 0.01506 mol

Mass of $CuSO_4$ = 0.01506 × 159.62 = 2.404 g

Mass of water in $CuSO_4{\bullet}xH_2O$ = 3.33 − 2.404 = 0.926 g

Amount of water = 0.926/18.02 = 0.0514 mol

Ratio of water to $CuSO_4 = \dfrac{0.0514}{0.01506} = 3.41$

Therefore $x = 3.41$

37 a **A** $\dfrac{100}{5} = 20.0 \text{ cm}^3$

B $\dfrac{100}{8} = 12.5 \text{ cm}^3$

C $\dfrac{100}{\left(\dfrac{13}{2}\right)} = 15.4 \text{ cm}^3$

D $\dfrac{100}{\left(\dfrac{17}{2}\right)} = 11.8 \text{ cm}^3$

b **A** $3 \times 100 = 300 \text{ cm}^3$

B $5 \times 100 = 500 \text{ cm}^3$

C $\left(\dfrac{8}{2}\right) \times 100 = 400 \text{ cm}^3$

D $\left(\dfrac{12}{2}\right) \times 100 = 600 \text{ cm}^3$

c **A** $\left(\dfrac{3}{5}\right) \times 1.00 = 0.600 \text{ dm}^3/600 \text{ cm}^3$

B $\left(\dfrac{5}{8}\right) \times 1.00 = 0.625 \text{ dm}^3/625 \text{ cm}^3$

C $\left(\dfrac{8}{13}\right) \times 1.00 = 0.615 \text{ dm}^3/615 \text{ cm}^3$

D $\left(\dfrac{12}{17}\right) \times 1.00 = 0.706 \text{ dm}^3/706 \text{ cm}^3$

Chemistry for the IB Diploma – Owen © Cambridge University Press & Assessment 2023

d **A** 20.0 cm^3 of the hydrocarbon reacts with $20.0 \times 5 = 100.0$ cm^3 of O_2

Volume of O_2 remaining = 200.0 − 100.0 = 100.0 cm^3

B $200.0 - (8 \times 20.0) = 40.0$ cm^3

C $200.0 - \left[\left(\frac{13}{2}\right) \times 20.0\right] = 70.0$ cm^3

D $200.0 - \left[\left(\frac{17}{2}\right) \times 20.0\right] = 30.0$ cm^3

Exam-style questions

1 C

2 D

3 B

4 C

5 C

6 A

7 B

8 B

9 C

10 D

11 C

12 a

	Carbon	Hydrogen
	$\frac{89.47}{12.01}$	$\frac{10.53}{1.01}$
amount/mol	7.450	10.43;
	$\frac{7.450}{7.450}$	$\frac{10.43}{7.450}$
ratio	1	1.4;

Multiply by 5 to get whole numbers.
Empirical formula is C_5H_7; **[3]**

b $\frac{536.96}{67.12} = 8$, therefore, $C_{40}H_{56}$ **[1]**

13 a $3.72 - 3.45 = 0.27$ g O

$\frac{3.45}{207.20} = 0.0167$, $\frac{0.27}{16.00} = 0.0169$;

1 : 1, therefore, PbO; **[2]**

b i $\frac{1.80}{80.06} = 0.0225$ mol NH_4NO_3

$C = \frac{n}{V} = \frac{0.0225}{\left(\frac{500.00}{1000}\right)} = 0.0450$ mol dm^{-3} **[1]**

c i $\frac{1.236}{200.59} = 6.16 \times 10^{-3}$ mol Hg,

$\frac{0.567}{46.01} = 0.0123$ mol NO_2,

$\frac{0.197}{32.00} = 6.16 \times 10^{-3}$ mol O_2 **[1]**

ii The oxygen in 0.0123 mol NO_2 was originally in the mercury nitrate.

Amount of O in 0.00123 mol NO_2 is $2 \times 0.0123 = 0.0246$ mol

The mass of O in 0.0246 mol NO_2 is $0.0246 \times 16.00 = 0.394$ g;

Alternatively: $\frac{32.00}{46.01} \times 0.567 = 0.394$ g

There was also 0.197 g oxygen gas produced - this was also from oxygen in the mercury nitrate.

Total mass of O in the mercury nitrate = 0.394 + 0.197 = 0.591 g;

Percentage O in the mercury nitrate = $\frac{0.591}{2.000} \times 100 = 29.6$ %; **[3]**

iii Amount of O in the mercury nitrate = $\frac{0.591}{16.00} = 0.0369$ mol O

0.0123 mol N in the mercury nitrate (since 1 N in each NO_2);

Hg: $\frac{6.16 \times 10^{-3}}{(6.16 \times 10^{-3})} = 1$,

N: $\frac{0.0123}{(6.16 \times 10^{-3})} = 2$,

O: $\frac{0.0369}{(6.16 \times 10^{-3})} = 6$,

therefore, HgN_2O_6 [or $Hg(NO_3)_2$]; **[2]**

d $300 \times \left(\frac{80}{100}\right) = 240$ cm^3 of the NO_2 dimerises which produces 120 cm^3 N_2O_4; so volume decreases by 120 cm^3

$300 + 150 - 120 = 330$ cm^3; **[2]**

Chemistry for the IB Diploma – Owen © Cambridge University Press & Assessment 2023

14 a i molar mass of $Na_2CO_3 \cdot 10H_2O$ is 286.19 g mol^{-1}

$\frac{20.00}{286.19} = 0.0699$ mol $Na_2CO_3 \cdot 10H_2O$;

Concentration of $Na_2CO_3 \cdot 10H_2O$ =

$\frac{0.0699}{\left(\frac{250.0}{1000}\right)} = 0.2795$ mol dm^{-3}

2 Na^+ ions per unit

Concentration of $Na^+(aq)$ = $2 \times 0.2795 = 0.5591$ mol dm^{-3} **[2]**

b i molar mass of Na_2CO_3 is 105.99 g mol^{-1}

Mass of Na_2CO_3 in 1.20 g of $Na_2CO_3 \cdot 10H_2O$ is $\frac{105.99}{286.19} \times 1.20$ = 0.444 g

This is also the mass of Na_2CO_3 in the white powder.

mass of water in the white powder = 0.520 − 0.444 = 0.076 g;

$\frac{0.076}{18.02} = 4.22 \times 10^{-3}$ mol H_2O in white powder

$\frac{0.444}{105.99} = 4.19 \times 10^{-3}$ mol Na_2CO_3 in white powder;

1 : 1; therefore, $Na_2CO_3 \cdot H_2O$ **[3]**

all figures were carried through on the calculator to obtain this answer, but if you work out $\frac{0.076}{18.02}$, *you get the answer* 4.22×10^{-3}.

Alternative method:

molar mass of $Na_2CO_3 \cdot 10H_2O$ is 286.19 g mol^{-1}

amount of $Na_2CO_3 \cdot 10H_2O = \frac{1.20}{286.19} = 4.19 \times 10^{-3}$ mol

1 $Na_2CO_3 \cdot 10H_2O$ decomposes to form 1 $Na_2CO_3 \cdot xH_2O$

therefore amount of $Na_2CO_3 \cdot xH_2O$ is 4.19×10^{-3} mol.

Molar mass of $Na_2CO_3 \cdot xH_2O$ is $\frac{0.520}{(4.19 \times 10^{-3})}$ = 124.02 g mol^{-1}

Of this 105.99 is due to the Na_2CO_3

124.02 – 105.99 = 18.03

$\frac{18.03}{18.02} = 1$

ii mass of water lost = 1.20 − 0.520 = 0.68 g

amount of water = $\frac{0.68}{18.02} = 0.0377$ mol;

$0.0377 \times 6.02 \times 10^{23} = 2.3 \times 10^{22}$ molecules; **[2]**

Chemistry for the IB Diploma – Owen © Cambridge University Press & Assessment 2023

Chapter 5

Test your understanding

1 $\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$

$\frac{1.01 \times 10^5 \times 20.0}{273} = \frac{1.06 \times 10^5 \times V_2}{311}$

Therefore:

$V_2 = \frac{(1.01 \times 10^5 \times 20.0 \times 311)}{(273 \times 1.06 \times 10^5)} = 21.7\ cm^3$

2 $\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$

$\frac{9.8900 \times 10^4 \times 250.00}{(20.00 + 273.15)} = \frac{9.8900 \times 10^4 \times 400.00}{(T_2 + 273.15)}$

$(T_2 + 273.15) = \frac{400.00 \times 293.15}{250.00}$

$(T_2 + 273.15) = 469.04$

$T_2 = 195.89\ °C$

3 $\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$

$\frac{120 \times 8.90}{(50.00 + 273.15)} = \frac{P \times 5.00}{(100.00 + 273.15)}$

Therefore:

$P = \frac{(120 \times 8.90 \times 373.15)}{(5.00 \times 323.15)} = 247\ kPa$

4 $\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$

$\frac{1.56 \times 10^5 \times 1.50}{(249.85 + 273.15)} = \frac{2.45 \times 10^5 \times V}{(119.85 + 273.15)}$

Therefore:

$\frac{V = (1.56 \times 10^5 \times 1.50 \times 393.00)}{(523.00 \times 2.45 \times 10^5)} = 0.718\ dm^3$

5 $\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$

If P is constant we can rearrange this to

$\frac{V_2}{V_1} = \frac{T_2}{T_1}$

Therefore the volume and the temperatures are in the same ratio. This is just the same as realising that volume is proportional to temperature. Temperature must be in K, so $T_1 = 298.15$ K and $T_2 = 323.15$ K

$\frac{323.15}{298.15} = 1.0839$, so 1.0839: 1

6 V is constant, so:

$\frac{P_2}{P_1} = \frac{T_2}{T_1}$

Temperature must be in K, so $T_1 = 373.15$ K and $T_2 = 773.15$ K

Pressure increases by a factor of 773.15/373.15 = 2.07

7 **a** Doubling the pressure causes the volume to halve $\left(\frac{P \propto 1}{V}\right)$ Halving the temperature halves the volume ($V \propto T$). So V changes by a factor of $\frac{1}{2} \times \frac{1}{2} = \frac{1}{4}$. So, volume decreases by a factor of 4.

b 10 × pressure causes the volume to be $\times \frac{1}{10}$. 5 × temperature causes volume to be × 5. $5 \times \frac{1}{10} = \frac{1}{4}$. So, volume is halved.

8 $PV = nRT$

$1.00 \times 10^5 \times 0.0500 = n \times 8.31 \times 300$

$n = 2.01$ mol

9 $PV = nRT$

$P = 1.10 \times 10^5$ Pa

$V = 1.50\ dm^3$ convert to $m^3 \Rightarrow 1.50 \times 10^{-3}\ m^3$

$T = 30\ °C$ convert to K ⇒ 30.00 + 273.15 = 303.15 K

$1.10 \times 10^5 \times 1.50 \times 10^{-3} = n \times 8.31 \times 303.15$

$n = 0.0655$ mol

10 $PV = nRT$

$1.20 \times 10^5 \times V = 0.600 \times 8.31 \times 250$

$V = \frac{(0.600 \times 8.31 \times 250)}{(1.20 \times 10^5)} = 0.0104\ m^3$

× 1000 to convert to dm^3, so $V = 10.4\ dm^3$

11 P = 98 kPa convert to Pa ⇒ 98 × 1000 = 98 000 Pa

$n = 2.50 \times 10^{-3}$ mol

T = 15.00 °C convert to K ⇒ 15.00 + 273.15 = 288.15 K

$V = n\frac{RT}{P} = \frac{(2.50 \times 10^{-3} \times 8.31 \times 288.15)}{(98000)}$

$= 6.11 \times 10^{-5}\ m^3$

$\times 10^6$ to convert to cm^3, so $V = 61.1\ cm^3$

Chemistry for the IB Diploma – Owen © Cambridge University Press & Assessment 2023

12 V = 128 cm^3 convert to m^3 ⇒ 128×10^{-6} m^3 ⇒ 1.28×10^{-4} m^3

T = 25.00 °C convert to K ⇒ 25.00 + 273.15 = 298.15 K

n = 1.25×10^{-3} mol

$$P = \frac{nRT}{V}$$

$$P = \frac{(1.25 \times 10^{-3} \times 8.31 \times 298.15)}{(1.28 \times 10^{-4})} = 2.42 \times 10^4 \text{ Pa}$$

13 **a** $\frac{0.240}{22.7} = 0.0106$ mol

b $\frac{2.00}{22.7} = 0.0881$ mol

c $\frac{0.100}{22.7} = 0.00441$ mol

d $\frac{\left(\frac{400.0}{1000}\right)}{22.7} = 0.0176$ mol

e $\frac{\left(\frac{250.0}{1000}\right)}{22.7} = 0.0110$ mol

14 **a** $0.100 \times 22.7 = 2.27$ dm^3

b $100.0 \times 22.7 = 2270$ dm^3

c $0.270 \times 22.7 = 6.13$ dm^3

15 P = 1.01×10^5 Pa

V = ?

T = 25.00 °C convert to K ⇒ 25.00 + 273.15 = 298.15 K

n = 1.00 mol

$$V = \frac{nRT}{P} = \frac{(1.00 \times 8.31 \times 298.15)}{(1.01 \times 10^5)} = 0.0245 \text{ m}^3$$

$\times 10^3$ to convert to dm^3, so molar volume = 24.5 dm^3 mol^{-1}

16 P = 9.97×10^5 Pa

V = ?

T = 22 °C convert to K ⇒ 21.85 + 273.15 = 295.00 K

n = 1.00 mol

$$V = \frac{nRT}{P} = \frac{(1.00 \times 8.31 \times 295.00)}{(9.97 \times 10^5)} = 0.00246 \text{ m}^3$$

$\times 10^3$ to convert to dm^3, so molar volume = 2.46 dm^3 mol^{-1}

17 Amount of He = $\frac{1.00}{4.00} = 0.250$ mol

amount of Ne = $\frac{1.00}{20.18} = 0.0496$ mol

$n = 0.250 + 0.0496 = 0.300$ mol

P = 103 kPa × 10^3 to convert to Pa ⇒ 1.03×10^5 Pa

V = ?

T = 9.85 °C convert to K ⇒ 9.85 + 273.15 = 283.00 K

n = 0.300 mol

$$V = \frac{nRT}{P} = \frac{(0.300 \times 8.31 \times 283)}{(1.03 \times 10^5)} = 6.85 \times 10^{-3} \text{ m}^3$$

$\times 10^3$ to convert to dm^3, so volume = 6.85 dm^3

If we had left the pressure in kPa, the volume would have come out directly in dm^3:

$$V = \frac{nRT}{P} = \frac{(0.300 \times 8.31 \times 283)}{103} = 6.85 \text{ dm}^3$$

18 Amount of H_2 = $\frac{2.20}{2.02} = 1.089$ mol

Amount of Ar = $\frac{10.00}{39.95} = 0.2503$ mol

Amount of N_2 = $\frac{25.60}{28.02} = 0.9136$ mol

$n = 1.089 + 0.2503 + 0.9136 = 2.253$ mol

P = 99 kPa Leave pressure in kPa to give volume in dm^3

V = ?

T = 19.85 °C convert to K ⇒ 19.85 + 273.15 = 293.00 K

n = 2.253 mol

$$V = \frac{nRT}{P} = \frac{(2.253 \times 8.31 \times 293)}{99} = 55.4 \text{ dm}^3$$

19 $$M = \frac{mRT}{PV} = \frac{(0.197 \times 8.31 \times 292)}{(1.01 \times 10^5 \times 1.58 \times 10^{-4})}$$

= 30.0 g mol^{-1}

Alternatively, use $PV = nRT$ to find n and then use $M = m/n$.

Chemistry for the IB Diploma – Owen © Cambridge University Press & Assessment 2023

20 P = 1.02×10^5 Pa

V = 282 $cm^3 \times 10^{-6}$ to convert to $m^3 \Rightarrow$ 2.82×10^{-4} m^3

T = −18.15 °C convert to K ⇒ −18.15 + 273.15 = 255.00 K

$$M = \frac{mRT}{PV} = \frac{(0.586 \times 8.31 \times 255)}{(1.02 \times 10^5 \times 2.82 \times 10^{-4})}$$

= 43.2 g mol^{-1}

21 P = 9.88×10^4 Pa

V = 1.75 $dm^3 \times 10^{-3}$ to convert to $m^3 \Rightarrow$ 1.75×10^{-3} m^3

T = 39.85 °C convert to K ⇒ 39.85 + 273.15 = 313.00 K

$$M = \frac{mRT}{PV} = \frac{(0.201 \times 8.31 \times 313)}{(9.88 \times 10^4 \times 1.75 \times 10^{-3})}$$

= 3.02 g mol^{-1}

It could be an isotope of helium, ^3He, or $^1H^2H$ (HD)

Exam-style questions

1 B

2 C

3 A

4 D

5 B

6 C

7 D

8 C

9 A

10 C

11 a P = 101000 Pa

$V = 4.20 \times 10^{-3}$ m^3

T = 293.15 K;

$$n = \frac{PV}{RT} = \frac{101000 \times 4.20 \times 10^{-3}}{8.31 \times 293.15} = 0.174 \text{ mol;}$$

Molar mass of SF_6 is 146.07 g mol^{-1}

mass = 0.174 × 146.07 = 25.4 g; **[3]**

b The volume is halved, so pressure must be doubled.

2 × 101 = 202 kPa **[1]**

12 a $$n = \frac{PV}{RT} = \frac{1.00 \times 10^5 \times 98.9 \times 10^{-6}}{8.31 \times 320}$$

$= 3.72 \times 10^{-3}$ mol;

$$\frac{0.201}{3.72 \times 10^{-3}} = 54.0 \text{ g mol}^{-1}\text{;}$$ **[2]**

b The gas behaves ideally under these conditions. **[1]**

c C: $\frac{88.8}{12.01}$ = 7.39 mol

H: $\frac{11.2}{1.01}$ = 11.1 mol;

$\frac{11.1}{7.39}$ = 1.5, therefore, C_2H_3; **[2]**

d $\frac{54.0}{27.05}$ = 2, therefore, C_4H_6 **[1]**

13 a The particles have no volume/are point masses;

All collisions (between particles and between particles and the wall of the container) are perfectly elastic (there is no change in the total kinetic energy of the colliding particles)/particles in constant, random motion; **[2]**

b High pressure and low temperature. **[1]**

c i $P \propto \frac{1}{V}$ or $P = \frac{k}{V}$ or pressure is inversely proportional to volume **[1]**

ii $\frac{600}{120}$ = 5, therefore, the volume at 600 kPa is $\frac{1}{5}$ the volume at 120 kPa **[1]**

d total amount in mol = $\frac{1.00}{4.00} + \frac{10.00}{28.02}$ = 0.607 mol;

total volume = 3.10 dm^3, i.e., 3.10×10^{-3} m^3;

$$P = \frac{nRT}{V} = \frac{0.607 \times 8.31 \times 298.15}{3.10 \times 10^{-3}}$$

$= 4.85 \times 10^5$ Pa; **[3]**

14 a $$n = \frac{PV}{RT} = \frac{1.02 \times 10^5 \times 2.500 \times 10^{-4}}{8.31 \times 294.00}$$

= 0.0104 mol;

$$\frac{0.300}{0.0104} = 28.8 \text{ g mol}^{-1}$$ **[2]**

b If we assume that the mixture contains x % nitrogen (molar mass 28.02 g mol^{-1}), then the percentage oxygen (molar mass 32.00 g mol^{-1}) will be 100 − x.

$$\frac{x \times 28.02 + (100 - x) \times 32.00}{100} = 28.8;$$

80.4% nitrogen; **[2]**

Chemistry for the IB Diploma – Owen © Cambridge University Press & Assessment 2023

Chapter 6

Test your understanding

1 a ionic (metal and non-metal)

b covalent (both non-metals)

c ionic (metal and non-metal)

d covalent (both non-metals)

e covalent (both non-metals)

f ionic (metal and non-metal)

2 a KCl

b $BaSO_4$

c $Ca(OH)_2$

d $NaHCO_3$

e SrS

f $Mg(NO_3)_2$

g Li_3N

h $Mg_3(PO_4)_2$

i MgF_2

j K_2SO_4

k $(NH_4)_2CO_3$

l Ag_2S

m $AgNO_3$

n NH_4Cl

o $Cu(NO_3)_2$

p Rb_2CO_3

3 a true

b false – they only conduct when molten or when in aqueous solution

c false – *ions* are free to move

d true – higher charge on the Ca^{2+} ion compared to K^+, therefore stronger electrostatic attraction (Ca^{2+} also smaller than K^+)

e false – ionic compounds tend to be soluble in water but insoluble in organic/non-polar solvents

4 $KCl < LiF < CaCl_2 < CaS < CaO$

In general, stronger electrostatic attraction between ions = higher lattice enthalpy.

CaO and CaS contain 2+/2− ions

$CaCl_2$ contains 2+/1− ions

KCl and LiF contain 1+/1− ions

Strongest attraction between 2+/2−, then 2+/1−, then 1+/1−

O^{2-} smaller than S^{2-} (fewer shells of electrons) − stronger attraction between smaller ions.

Li^+ smaller than K^+ (fewer shells of electrons)

F^- smaller than Cl^- (fewer shells of electrons)

Exam-style questions

1 D

2 B

3 C

4 C

5 D

6 D

7 C

8 A

9 B

10 C

11 a Li^+: $1s^2$;

F^-: $1s^2\ 2s^2\ 2p^6$; **[2]**

If neither electron configuration is correct, then Li^+ and F^- scores [1]

b Giant (lattice) structure; strong electrostatic forces of attraction between oppositely charged ions require a lot of energy to break; **[2]**

c When molten or in aqueous solution; ions are free to move. **[2]**

d Caesium chloride is CsCl, whereas barium chloride is $BaCl_2$. Higher charge on the Ba^{2+} ion compared to Cs^+;

Stronger electrostatic forces in the lattice in $BaCl_2$, therefore, higher lattice enthalpy; **[2]**

Chemistry for the IB Diploma – Owen © Cambridge University Press & Assessment 2023

e Both have the same charges on ions, but Li^+ is smaller than K^+;

Stronger electrostatic forces of attraction in the LiF lattice because of the smaller Li^+ ion. therefore LiF has higher lattice enthalpy; **[2]**

12 a Cl^-/P^{3-} **[1]**

b $Na^+/Mg^{2+}/Al^{3+}/H_3O^+$ **[1]**

c Ge **[1]**

d This is true for ions formed by elements in Groups 1, 2, 15, 16, and 17/examples of at least three ions for which it is true, e.g. Na^+, Mg^{2+}, Cl^-etc.;

[1] for the first point – cases where it is true;

[1] for any one of the following points – cases where it is not true;

It is true for Al^{3+} but not for other elements below it in Group 13.

or

It is not true for ions formed by most transition metals/lanthanoids/actinoids.

or

Not true for positive ions formed by elements in Groups 14/15.

or

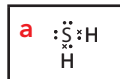
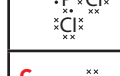
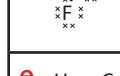
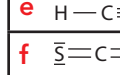
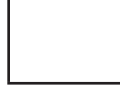
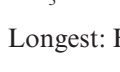
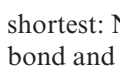
Not generally true for positive ions formed by atoms that have d/f electrons. **[2]**

Chemistry for the IB Diploma – Owen © Cambridge University Press & Assessment 2023

Chapter 7

Test your understanding

1

a		**g**	
b		**h**	
c		**i**	
d		**j**	
e		**k**	
f		**l**	or 

2 shortest: CO (triple bond)

HCHO and CO_2 have double bonds and CH_3OH has a single bond

3 Longest: H_3CCH_3 (single bond)

H_2CCH_2 has a double bond and HCCH has a triple bond

4 shortest: N_2 (triple bond) – N_2H_2 has a double bond and N_2H_4 a single bond

5 H_3O^+, CO, O_3, NH_4^+

Whenever O forms 3 bonds/N forms 4 bonds, you can assume that one of the bonds is a coordination bond.

6 CH_3^+, BF_3, $BeCl_2$

C has $6e^-$ in its outer shell;

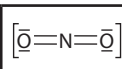
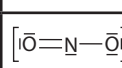
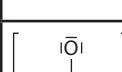
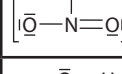
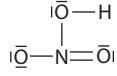
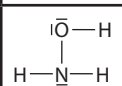
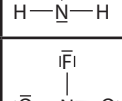
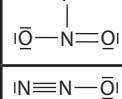
B has $6e^-$ in its outer shell;

Be has $4e^-$ in its outer shell;

7

H_2O	2
OF_2	8 (2 on O and 3 on each F)
CH_3Cl	3 (on Cl)
NH_4^+	0
Br_2	6
$SiCl_4$	12 (all on Cl)
PH_3	1

8

NO_2^+	
NO_2^-	
NO_3^-	
HNO_3	
NH_2OH	
FNO_2	
NNO	 or 

9 **a** 4 electron domains (2 single bonds and 2 lone pairs)

Electron domain geometry: tetrahedral (109.5°)

Shape: bent/V-shaped/angular; predict 100–108° (actual value 92°)

b 4 electron domains (3 single bonds and 1 lone pair);
Electron domain geometry: tetrahedral (109.5°)

Shape: trigonal pyramidal; predict 100–108° (actual value 101°)

c 4 electron domains (4 single bonds);
Electron domain geometry: tetrahedral (109.5°)

Shape: tetrahedral; 109.5°

d 2 electron domains (1 single bond and 1 triple bond)

Chemistry for the IB Diploma – Owen © Cambridge University Press & Assessment 2023

Electron domain geometry: linear (180°)

Shape: linear; 180°

e 3 electron domains (2 single bonds and 1 double bond)

Electron domain geometry: trigonal planar (120°)

Shape: trigonal planar; predict F—C—F bond angle of about 118–120° (greater repulsion due to double bond) and O—C—F bond angle of about 120–122° (actual values: F—C—F bond angle = 108°, O—C—F bond angle = 126°)

f 2 electron domains (2 double bonds) Electron domain geometry: linear (180°)

Shape: linear; 180°

g 3 electron domains (1 single bond, 1 double bond, 1 lone pair)

Electron domain geometry: trigonal planar (120°)

Shape: bent/V-shaped/angular; predict about 118° (actual value 110°)

h 4 electron domains (4 single bonds)

Electron domain geometry = tetrahedral (109.5°)

Shape: tetrahedral; 109.5°

i 2 electron domains (2 double bonds or 1 single bond and 1 triple bond) Electron domain geometry: linear (180°)

Shape: linear; 180°

j 2 electron domains (2 double bonds or 1 single bond and 1 triple bond) Electron domain geometry: linear (180°)

Shape: linear; 180°

k Around each C: 3 electron domains (2 single bonds and 1 double bond)

Electron domain geometry = trigonal planar (120°)

Shape: trigonal planar about each C; predict Cl—C—Cl bond angle of about 118° (actual value 116°) and Cl—C—C bond angle of about 121° (actual value for F—C—C bond angle about 122°)

l 2 electron domains (2 double bonds) Electron domain geometry: linear (180°)

Shape: linear; 180°

10 a H_2O; H_2O has 2 lone pairs, H_3O^+ has 1. More lone pairs = greater repulsion, so bond angle closed up.

b NH_3; NH_3 has 1 lone pair, NH_4^+ has 0

c NH_3; NH_3 electron domain geometry is tetrahedral (based on 109.5°) but for HNNH (double bond between N atoms) it is trigonal planar (based on 120°) around each N.

d H_3CCH_3; H_3CCH_3 electron domain geometry is tetrahedral (based on 109.5°) but for H_2CCH_2 (C═C) it is trigonal planar (based on 120°) around each C.

e H_3COH; H_3COH electron domain geometry is tetrahedral (based on 109.5°) but for H_2CO (contains C═O) it is trigonal planar (based on 120°) around C.

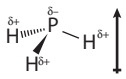
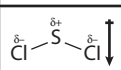
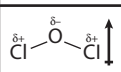
f CH_4; CH_4 electron domain geometry is tetrahedral (based on 109.5°) but for CH_3^+ it is trigonal planar (based on 120°).

g NH_2^-; NH_2^- has 2 lone pairs, NH_3 has 1

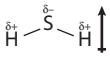
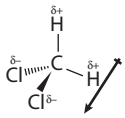
11 O_3, BCl_3, NO_2^-, CO_3^{2-}; CO_2 and NO_2^+ are linear (they are isoelectronic); NH_2^- has 4 electron domains and is bent; NF_3 has 4 electron domains and is trigonal pyramidal;

12 Na < H < Br < Cl < O

13

HBr	polar	
HCN	polar	
PH_3	polar	
SCl_2	polar	
CF_4	non-polar	polar bonds, but bond dipoles cancel due to tetrahedral shape
N_2	non-polar	both atoms have same electronegativity
OCl_2	polar	
BCl_3	non-polar	polar bonds, but bond dipoles cancel due to trigonal planar shape

Chemistry for the IB Diploma – Owen © Cambridge University Press & Assessment 2023

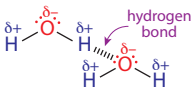
C_2Cl_2	non-polar	polar bonds, but bond dipoles cancel due to linear shape
H_2S	polar	
CH_2Cl_2	polar	

14 **a** Br_2 (higher M_r/more electrons – stronger London forces between molecules)

b CH_3Br (higher M_r/more electrons – stronger London forces between molecules)

c similar M_r but CO polar and N_2 non-polar. CO has dipole-dipole interactions as well as London forces between molecules.

d similar M_r but NO polar and O_2 non-polar. NO has dipole-dipole interactions as well as London forces between molecules, so stronger forces between molecules.

15 

16 HF, CH_3OH, N_2H_4 H bonded directly to N/O/F

17 **a** $CH_4 < CF_4 < CCl_4$ All non-polar; increasing M_r – stronger London forces between molecules

b HCl < HF; HF has hydrogen bonding between molecules (as well as dipole-dipole + London forces) but HCl does not (only dipole-dipole + London forces)

Hydrogen bonding is a particularly strong intermolecular force; overall, the intermolecular forces are stronger between molecules of HF.

c $CH_4 < NH_3 < N_2H_4$; CH_4 non-polar (just London forces); NH_3 and N_2H_4 hydrogen bonding between molecules; N_2H_4 higher M_r (stronger London forces)

d $C_2H_4 < CH_3F < CH_3OH$; C_2H_4 non-polar (just London forces); CH_3F polar (dipole-dipole + London forces); CH_3OH hydrogen bonding between molecules (as well as dipole-dipole + London forces)

e $H_2S < H_2O < H_2O_2$ H_2S polar but no hydrogen bonding; H_2O and H_2O_2 hydrogen bonding between molecules; H_2O_2 higher M_r (stronger London forces)

f $CH_3CH_2CH_2CH_2CH_3$ < $CH_3CH_2OCH_2CH_3$ < $CH_3CH_2CH_2CH_2OH$
$CH_3CH_2CH_2CH_2CH_3$ non-polar (just London forces between molecules)
$CH_3CH_2OCH_2CH_3$ polar (dipole-dipole + London forces)
$CH_3CH_2CH_2CH_2OH$ hydrogen bonding between molecules (as well as dipole-dipole + London forces)

g Ne < N_2 < F_2 < HF increasing M_r/number of electrons (stronger London forces) from Ne to N_2 to F_2; all non-polar (only London forces between molecules) except HF; HF has hydrogen bonding between molecules (as well as dipole-dipole + London forces)

18 **a** NaCl – ionic, but CCl_4 is covalent molecular.

b CH_3OH – can hydrogen bond to water but CH_3Cl cannot.

c CH_3CH_2OH – shorter non-polar chain

d $CH_2(OH)CH_2CH_2CH_2CH_2CH_2OH$ – more – OH groups that can hydrogen bond to water.

19 *Accept +/−0.03 on each one.*

a 0.23

b 0.37

c 0.85

d 0.65

20 **c, d, b, a**
c; is least polar – it has the greatest affinity for the non-polar solvent (mobile phase), so spends most time dissolved in the solvent and least time adsorbed on the plate, therefore travels furthest up the plate. **a** is most polar - it has the greatest affinity for polar groups on the surface of the plate (stationary phase), so spends more time adsorbed on the plate and less time dissolved in the non-polar solvent.

Chemistry for the IB Diploma – Owen © Cambridge University Press & Assessment 2023

21 a $HCl < CCl_4 < SiCl_4 < NaCl$; Increasing M_r from HCl to CCl_4 to $SiCl_4$ (stronger London forces between molecules). NaCl has ionic bonding (strong electrostatic forces of attraction between oppositely charged ions) – the others are covalent molecular (forces between molecules much weaker than the forces in the NaCl lattice).

b $HBr < Br_2 < PBr_3 < CaBr_2$ Increasing M_r from HBr to Br_2 to PBr_3 (stronger London forces between molecules). $CaBr_2$ has ionic bonding – the others are covalent molecular.

c $C_3H_8 < C_4H_{10} < C_3H_7OH < C_4H_9OH$ C_4H_{10} has higher M_r than C_3H_8. C_3H_7OH and C_4H_9OH have hydrogen bonding between molecules. C_4H_9OH has higher M_r.

d $CO_2 < SO_2 < SiO_2$ Increasing M_r from CO_2 to SO_2. SiO_2 has a covalent network structure, so covalent bonds (very strong) must be broken rather than intermolecular forces (much weaker).

22 a C_6H_{12} (non-polar) < $C_5H_{11}OH$ (hydrogen bonds to water) < NaCl (ionic)

b CH_4 (non-polar) < CH_3Cl (polar) < $CaCl_2$ (ionic)

23 a $5 - \frac{6}{2} - 2 = 0$

b $5 - \frac{8}{2} - 0 = +1$

c $5 - \frac{8}{2} - 0 = +1$

d $5 - \frac{6}{2} - 2 = 0$

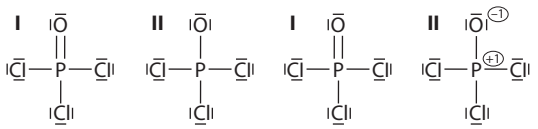
e $5 - \frac{8}{2} - 0 = +1$

f $5 - \frac{6}{2} - 2 = 0$

g $5 - \frac{8}{2} - 0 = +1$

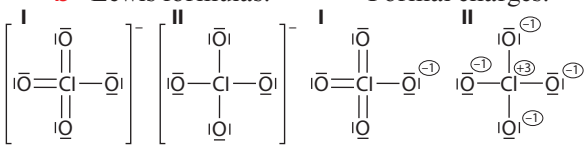
24 The first structure (with S═O) is a better representation – the formal charge on all atoms is zero and, therefore, closer to zero than the formal charge values in the second structure (+1 on S and −1 on O).

25 a Lewis formulas: Formal charges:



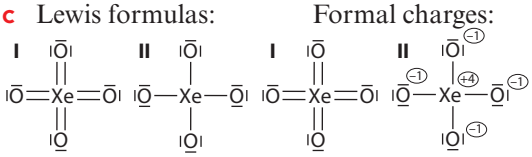
Only non-zero formal charges are shown.
I preferred - all formal charges zero

b Lewis formulas: Formal charges:



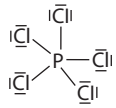
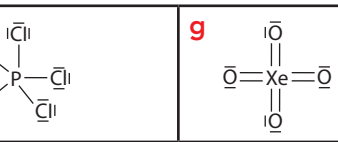
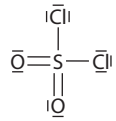
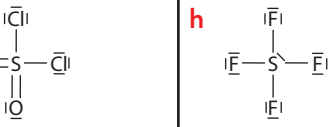
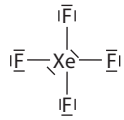
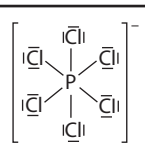
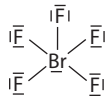
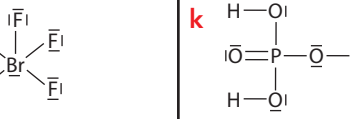
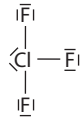
I preferred - all formal charges except the one shown are zero.
Lower formal charges, therefore the preferred structure.

c Lewis formulas: Formal charges:



I preferred - all formal charges are zero

26

a 	**g** 
b 	**h** 
c 	**i**
d 	**j**
e 	**k** 
f 	**l**

27 a 5 electron domains (3 single bonds, 2 lone pairs). Electron domain geometry: trigonal bipyramidal (120°/90°). Lone pairs go around the middle.

Shape: T-shaped/arrow-shaped; predict bond angles of about 88° (actual value 86°)

b 6 electron domains (5 single bonds, 1 lone pair). Electron domain geometry: octahedral (90°).

Shape: square-based pyramid; predict bond angle of about 88°

Chemistry for the IB Diploma – Owen © Cambridge University Press & Assessment 2023

c 4 electron domains (2 single bonds, 2 double bonds). Electron domain geometry: tetrahedral (109.5°).

Shape: (distorted) tetrahedral; predict bond angles O—S—O of about 112° and Cl—S—Cl of about 107° (angles of 109° are fine!) (actual values: O—S—O = 120° and Cl—S—Cl = 111°)

d 5 electron domains (4 single bonds, 1 lone pair). Electron domain geometry: trigonal bipyramidal (120°/90°). Lone pairs go around the middle.

Shape: see-saw shaped; predict bond angles of about 88° and 118° (actual values 85° and 101°)

e 5 electron domains (2 single bonds, 3 lone pairs). Electron domain geometry: trigonal bipyramidal (120°/90°). Lone pairs go around the middle.

Shape: linear; 180°

f 6 electron domains (6 single bonds). Electron domain geometry: octahedral (90°).

Shape: octahedral; 90°

g 6 electron domains (5 single bonds, 1 lone pair). Electron domain geometry: octahedral (90°).

Shape: square-based pyramid; predict bond angle of about 88° (actual value 79°)

h 5 electron domains (3 single bonds, 1 double bond, 1 lone pair). Electron domain geometry: trigonal bipyramidal (120°/90°). Lone pairs go around the middle.

Shape: see-saw shaped; predict bond angles of about 88° and 118°

i 4 electron domains (2 single bonds and 2 lone pairs). Electron domain geometry: tetrahedral (109.5°)

Shape: bent/V-shaped/angular; predict bond angles of about 105° (actual value 102°)

j 5 electron domains (2 single bonds, 3 lone pairs). Electron domain geometry: trigonal bipyramidal (120°/90°). Lone pairs go around the middle.

Shape: linear; 180°

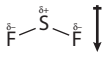
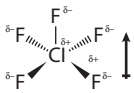
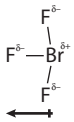
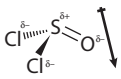
k 6 electron domains (5 single bonds, 1 lone pair). Electron domain geometry: octahedral 90°.

Shape: square-based pyramid; predict bond angle of about 88°

l 4 electron domains (1 single bonds and 3 double bonds). Electron domain geometry: tetrahedral (109.5°)

Shape: (distorted) tetrahedral; predict bond angles O—Br—O of about 112° and F—Br—O of about 107° (angles of 109° are fine!) (actual values: O—Br—O = 115° and F—Br—O = 103°)

28

XeF_6	non-polar	polar bonds, but bond dipoles cancel due to shape
XeF_4	non-polar	polar bonds, but bond dipoles cancel due to shape
SF_4	polar	
PCl_5	non-polar	polar bonds, but bond dipoles cancel due to shape
SF_2	polar	
SF_6	non-polar	polar bonds, but bond dipoles cancel due to shape
ClF_5	polar	
BrF_3	polar	
$SOCl_2$	polar	

29 **a** sp^2 3 electron domains

b sp^3 4 electron domains

c sp^3 4 electron domains

d sp^3 4 electron domains

e sp 2 electron domains

f sp^3 4 electron domains

Chemistry for the IB Diploma – Owen © Cambridge University Press & Assessment 2023

g sp^3 4 electron domains

h sp 2 electron domains

i sp^2 3 electron domains

j sp^2 3 electron domains

30 a sp^3 N—N single bond – 4 electron domains

b sp^2 N═N double bond – 3 electron domains

31 a sp^2 C═C double bond – 3 electron domains

b sp C≡C triple bond – 2 electron domains

c sp^3 C—C single bond – 4 electron domains

d sp^2 C═O double bond – 3 electron domains

32 a 9 C atoms just forming single bonds (don't forget those in the CH_3 groups)

b 6 All those that are part of a double bond, either C═C or C═O

c 3 All those that are part of a triple bond, either C≡C or C≡N

33 a 1 σ 1 π; O═O – a double bond consists of a σ bond and a π bond.

b 1 σ 2π; N≡N – a triple bond consists of 1 σ bond and 2 π bonds.

c 3 σ; 3 single bonds

d 2 σ 2π; 2 C═O – a double bond consists of a σ bond and a π bond.

e 3 σ 1 π; 2 C—H and 1 C═O – a double bond consists of a σ bond and a π bond.

f 2 σ 2 π; 1 C—H and 1 C≡N – a triple bond consists of 1 σ bond and 2 π bonds.

g 3 σ 1 π; 2 N—F and 1 N═N – a double bond consists of a σ bond and a π bond.

h 1 σ 2 π; C≡O – a triple bond consists of 1 σ bond and 2 π bonds.

i 8 σ 1 π; 6 C—H, 1 C—C and 1 C═C – a double bond consists of a σ bond and a π bond.

j 3 σ 1 π; 2 S—Cl and 1 S═O – a double bond consists of a σ bond and a π bond.

k 6 σ 2 π; 4 C—H, 1 C—C and 1 C≡C – a triple bond consists of 1 σ bond and 2 π bonds.

l 6 σ 2 π; 2 S—O, 2 O—H and 2 S═O – a double bond consists of a σ bond and a π; bond.

m 54 σ 9 π; don't forget the σ bonds in the CH_3 and OH groups.

34 IO_3^-, HNO_3, AsO_4^-, $HCOO^-$

35 SO_4^{2-}, CH_3COO^-, PO_4^{3-}

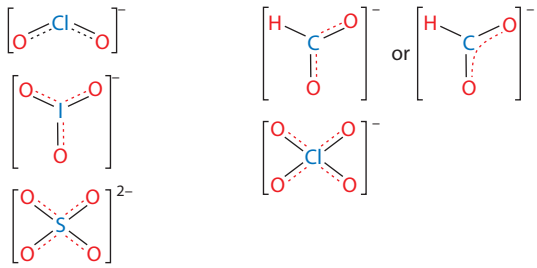
36 a $1\frac{1}{3}$ 2 S—O and 1 S═O

b $1\frac{2}{3}$ 1 Cl—O and 2 Cl═O

c The S—O bond from the S to the OH group has bond order 1; the bond order for the other bonds is $1\frac{2}{3}$.

37 ClO_4^- (Bond order $1\frac{3}{4}$) < ClO_3^- (bond order $\frac{2}{3}$) < ClO_2^- (Bond order $1\frac{1}{2}$)

38



Exam-style questions

1 B

2 C

3 C

4 B

5 A

6 A

7 D

8 A

9 C

10 D

11 B

12 B

13 C

14 D

15 D

16 D

Chemistry for the IB Diploma – Owen © Cambridge University Press & Assessment 2023

17 C

18 C

19 B

20 C

21 a ;

4 electron domains, so electron domain geometry is tetrahedral. 2 lone pairs cause the bond angle to close up from 109.5°

Accept bond angles in range: 90–108°; **[2]**

b H_2O because there is the biggest difference in electronegativity between H and X **[1]**

c H_2O has hydrogen bonding between molecules but H_2S does not;

Must be some sort of comparison/implication that H_2S does not have hydrogen bonding.

Hydrogen bonding (+London forces + dipole-dipole interactions) between water molecules is stronger than dipole–dipole interactions (+ London forces) / van der Waals forces/London forces (+ dipole-dipole interactions) between molecules in H_2S; **[2]**

22 a Pairs of electrons/electron domains in the outer shell of the central atom repel each other;

they take up positions in space to be as far away from each other as possible to minimise these repulsions;

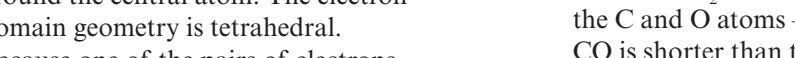
Electron domains may be bonding pairs or lone pairs/lone pairs cause greater repulsion than bonding pairs of electrons/multiple bonds act as a single electron domain; **[3]**

b i The Lewis formula is

There are four pairs of electrons around the central atom. The electron domain geometry is tetrahedral. Because one of the pairs of electrons is a lone pair, the molecular geometry/shape is trigonal pyramidal;

The bond angle will be slightly less than that in a tetrahedron (109.5°), due to extra repulsion from lone pair – *predictions in the range 100–108° will generally be accepted (the actual bond angle is 100°)*; **[2]**

ii The Lewis structure for CO_2 is

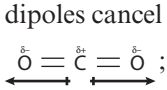


The four electrons in each double bond are constrained to be in the same region of space, so there are two electron domains around carbon. The electron domain geometry is linear and, with no lone pairs, the molecular geometry/shape is linear;

The bond angle is 180°; **[2]**

c Both contain polar bonds due to the difference in electronegativity between the atoms;

CO_2 is a linear molecule, and so, although each individual C═O bond is polar, the dipoles cancel out.

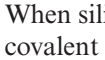
 ;

The trigonal pyramidal shape of PCl_3 means that the dipoles do not cancel – one end of the molecule is δ+ and the other is δ−; **[3]**

d Both have covalent bonding. Silicon dioxide has a covalent network structure, but carbon dioxide is covalent molecular/has a molecular structure/simple molecular structure;

When silicon dioxide is melted, strong covalent bonds between the atoms must be broken. This requires a lot of energy, so SiO_2 has a high melting point;

When carbon dioxide is melted, only the weak London forces between molecules must be overcome. This requires relatively little energy, and CO_2 has a lower melting point; **[3]**

e  ;

CO has a triple bond between C and O, whereas CO_2 has double bonds between the C and O atoms – the C—O bond in CO is shorter than that in CO_2; there are six electrons between the atoms in a triple bond, but only four electrons between the atoms in a double bond. With more electrons between the atoms, there is greater attraction between the nuclei and bonding electrons; **[3]**

Chemistry for the IB Diploma – Owen © Cambridge University Press & Assessment 2023

f London forces similar strength due to the same relative molecular mass but CO is polar whereas N_2 is non-polar;

CO has permanent dipole-permanent dipole interactions between molecules, in addition to London forces, but N_2 only has London forces. CO has stronger forces between molecules, (therefore, more energy is required to break them) – CO has the higher boiling point; **[2]**

23 a **[1]**

b Three electron domains around B, therefore, the electron domain geometry is trigonal planar. No lone pairs, therefore, the molecular geometry/shape is trigonal planar; and bond angle is 120°; **[2]**

c Non-polar; each B—F bond is polar but, because of the symmetry of the shape, the bond dipoles cancel; **[2]**

d BF_4^- and $F_3B—NH_3$ contain coordination bonds;

In both cases, B forms four bonds. In BF_4^-, there is a coordination bond, with a pair of electrons being donated from F^- to B. In $F_3B—NH_3$, a pair of electrons is donated from N to B; **[2]**

e The Lewis formula is

Four electron domains with no lone pairs, therefore, the molecular geometry/shape is tetrahedral and the bond angle is 109.5°. **[1]**

24 a i ;

; **[2]**

ii NH_3: four electron domains, so the electron domain geometry is tetrahedral. One lone pair, so the molecular geometry/shape is trigonal pyramidal;

NH_4^+: four electron domains, so the electron domain geometry is tetrahedral. Zero lone pairs, so the molecular geometry/shape is also tetrahedral;

lone pair of electrons in NH_3 repels the bonding pairs of the N—H bonds more strongly, so NH_3 has the smaller bond angle; **[3]**

b i **[1]**

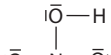
ii Hydrazine has an N—N single bond between atoms, but N_2 has an N≡N triple bond, therefore, the N—N bond length is shorter in N_2;

greater electrostatic attraction between N nuclei and six electrons in the bond in N_2 than that between N nuclei and two electrons in the bond in N_2H_4; **[2]**

iii Similar relative molecular masses, so London forces of similar strength, but hydrazine is polar, with hydrogen bonding between molecules, whereas ethane is non-polar, with no hydrogen bonding;

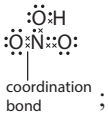
London forces + dipole–dipole interactions + hydrogen bonding between molecules of hydrazine are stronger than just London forces between ethane molecules, therefore, these require more energy to break, and so, hydrazine has a higher boiling point; **[2]**

iv Hydrazine is more soluble because it is polar and can hydrogen bond to water molecules, whereas ethane is non-polar and cannot hydrogen bond to water molecules. **[1]**

c i  or **[1]**

ii A coordination bond is a covalent bond formed when both electrons making up the bond come from the same atom;

The bond from N to the left-hand oxygen is a coordination bond – both electrons in the bond come from the nitrogen:



; **[2]**

Chemistry for the IB Diploma – Owen © Cambridge University Press & Assessment 2023

25 a The technique requires a stationary phase and a mobile phase;

The components are separated due to different affinities for the stationary and mobile phases;

Affinities/attractions to stationary/mobile phase depends on intermolecular forces;

Separation due to adsorption or partition;

The component that has greater affinity for the mobile phase travels further up the paper/plate/the component that has greater affinity for the stationary phase travels less far up the paper/plate;

Any 3 points **[3]**

b i $R_F = \frac{\textit{distance to centre of spot from pencil line}}{\textit{distance to solvent front from pencil line}}$

Actual distance measured will depend on the degree of magnification on your screen.

X: $R_F = 0.27 +/-0.01$

Y: $R_F = 0.50 +/-0.01$

Z: $R_F = 0.81 +/-0.01$

for 1/2 correct **[1]**

for all three correct **[2]**

ii X is glycine

Y is arginine

Z is tyrosine **[1]**

26 AlF_3 ionic bonding and giant structure, but $AlBr_3$ and AlI_3 are covalent molecular;

AlF_3: high melting point because strong electrostatic forces of attraction between oppositely charged ions require a lot of energy to break;

$AlBr_3$/AlI_3: Low melting point because not much energy is required to break dipole–dipole/van der Waals forces/London forces between molecules;

AlI_3 has a higher melting point than $AlBr_3$ due to higher molecular mass/more electrons and, therefore, stronger London forces between molecules;

AlF_3 conducts electricity because mobile ions are present in the liquid state, but $AlBr_3$/AlI_3 do not because no ions/only neutral molecules are present; **[5]**

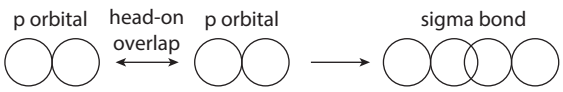
27 a Hybridisation is the mixing of atomic orbitals; to form a new set of orbitals that are better arranged in space for bonding/the number of hybrid orbitals formed is the same as the initial number of atomic orbitals/the hybrid orbitals have both s and p character; **[2]**

b There are three electron domains around each C in C_2H_4. The electron domains are arranged in a trigonal planar array around each C. The type of hybridisation that gives a trigonal planar array of orbitals is sp^2. Therefore, the C atoms in C_2H_4 are sp^2 hybridised;

There are two electron domains around each C in C_2H_2. The electron domains are arranged in a linear array around each C. The type of hybridisation that gives a linear arrangement of orbitals is sp. Therefore, the C atoms in C_2H_2 are sp hybridised; **[2]**

c A sigma bond is a head-on overlap/combination of atomic orbitals that results in the electron density lying along the internuclear axis;

Mark can be scored with a suitable diagram:

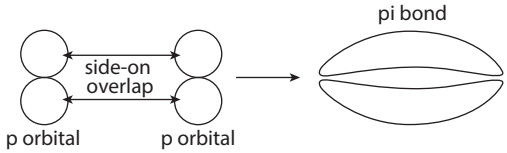


There is one sigma bond between the two C atoms in ethene and ethyne, and there are sigma bonds between the C and H atoms in ethene and ethyne;

A pi bond is a side-on overlap/combination of two parallel p orbitals. This results in the electron density in the pi bond lying above and below the internuclear axis;

Chemistry for the IB Diploma – Owen © Cambridge University Press & Assessment 2023

Mark can be scored with a suitable diagram:



The double bond in ethene is made up of a sigma bond and a pi bond. The triple bond in ethyne is made up of one sigma bond and two pi bonds; **[4]**

d i 12 – the C atoms that are part of the phenyl group (ring) or part of a C═C. **[1]**

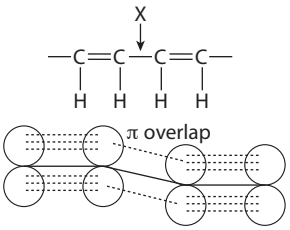
ii The ring represents a π system of delocalised electrons;

Side-on overlap/combination of six parallel p orbitals, with six delocalised electrons; **[2]**

iii W is longer than Z;

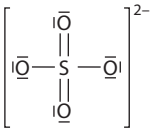
The bond order of W is 1.5 due to delocalisation, whereas, for Z, the bond order is 2; **[2]**

iv Y is a single bond, but X is part of a π delocalised system;



There is extra electron density between the C atoms in bond X/the bond order is higher and, therefore, the bond is shorter; **[2]**

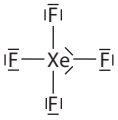
28 a i The Lewis formula of the SO_4^{2-} ion is:



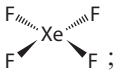
There are four electron domains around S (a double bond counts as one electron domain) and, therefore, the electron domain geometry is tetrahedral. There are no lone pairs, and so, the molecular geometry is also tetrahedral;

The bond angle is 109.5°, although two of the bonds in the Lewis structure are shown as double bonds and may be expected to repel single bonds more strongly, the structure is delocalised and all bonds are equivalent; **[2]**

ii The Lewis formula of XeF_4 is:

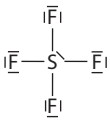


There are six electron domains around Xe and, therefore, the electron domain geometry is octahedral. The two lone pairs are opposite each other to minimise repulsion, and the molecular geometry is square planar/



The lone pairs repel equally from above and below, and so, the bond angles are the same as those in an octahedron: i.e., 90°; **[2]**

iii The Lewis formula for SF_4 is



There are five electron domains around the S atom. The electron domain geometry is trigonal bipyramidal. The lone pair in a trigonal bipyramid always goes around the middle, so the molecular geometry is 'see-saw shaped'/

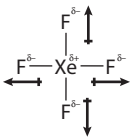
The bond angles in a trigonal bipyramid are 90° and 120°. The extra repulsion from the lone pair causes these bond angles to close up slightly, and so, predict bond angles of about 88° and 118°; **[2]**

The bond angle around the middle (102°) is actually a lot smaller than expected from this simple approach and a larger range would be accepted to allow for that – accept bond angles 80–90° and 100–119°.

Chemistry for the IB Diploma – Owen © Cambridge University Press & Assessment 2023

b XeF_4 is non-polar;

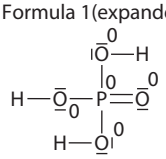
Each individual Xe—F bond is polar due to the difference in electronegativity between the atoms, but the dipoles cancel due to the square planar shape (*accept suitable diagram*); **[2]**



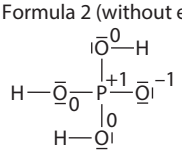
c The bond order in SO_2 is 2, but that in SO_4^{2-} is 1.5/SO_2 has two double bonds between the S and O atoms, but SO_4^{2-} has a delocalised structure in which the π components of the double bonds are shared equally between all four sulfur–oxygen bonds;

The sulfur–oxygen bond length in SO_2 would be expected to be shorter than that in SO_4^{2-} due to more electron density between the S and O atoms; **[2]**

29 a Formula 1(expanded octet):



Formula 2 (without expanded octet):



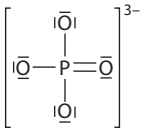
Formula 1 is a better representation of the actual structure because the formal charges are closer to 0. **[3]**

[1] for the two Lewis formulas;

[1] for all formal charges on P and O correct;

[1] for explanation;

b Lewis formula:



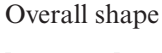
There are four electron domains around the central P and no lone pairs so the shape is tetrahedral;

The structure has delocalised electrons/exhibits resonance so all O-P-O bond angles are equal at 109.5°; **[2]**

c All bond angles are equal in PO_4^{3-} at 109.5°, but there are two different bond angles in H_3PO_4;

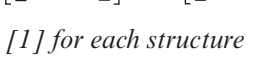
Both shapes have tetrahedral electron domain geometry, but there is no delocalisation/resonance in H_3PO_4; P═O (more electrons) in H_3PO_4 repels the P—O bonds more than they repel each other, causing the angle between the P—O bonds to close up and be smaller than 109.5°;

Any 2 points **[2]**

30 a i  **[1]**

ii Two electron domains on each C atom, so linear about each C atom.

Overall shape is also linear. **[1]**

b i 

[1] for each structure

A third formula is possible, but it is highly unlikely, as it involves coordination bonds from O to C and from C to N. The formal charges in this structure are higher than those in the others:

[2]

ii C—N bond is longer in OCN^-;

Triple bond in CN^- but resonance structures/delocalization in OCN^- (where only one of the resonance structures has a triple bond between C and N); **[2]**

If only first and third Lewis structures are drawn, accept an explanation based on the fact that only C—N and C═N are present, therefore the bond order will be between 1 and 2.

Chemistry for the IB Diploma – Owen © Cambridge University Press & Assessment 2023

Chapter 8

Test your understanding

1 a false – they are at the left and bottom

b true

c false – they also conduct when solid

d false – delocalised electrons are free to move

e false – they are malleable because layers of atoms/ions can slide over each other without changing the bonding

f true

2 a K < Na < Li decreasing size of positive ion

b Na < Mg < Al increasing charge on ion and decreasing size of ion

3 a false – transition metals have higher melting points than metals in Group 1

b true

c true

Exam-style questions

1 C

2 B

3 B

4 A

5 C

6 a Regular lattice of positive ions;

Sea of delocalised electrons; **[2]**

b Electrostatic attraction between Na^+ ions and delocalised electrons. **[1]**

c The electrostatic attraction between a more highly charged Mg^{2+} ion and delocalised electrons is stronger than that between a Na^+ ion and delocalised electrons;

The Mg^{2+} ion is smaller than the Na^+ ion and, therefore, the delocalised electrons are closer to the nucleus of the positive ion in magnesium and are more strongly attracted;

In magnesium, there are more delocalised electrons per atom, since it forms 2+ ions, but sodium only forms a 1+ ion; **[2]**

any 2 points

d i The delocalised electrons are free to move. **[1]**

ii The delocalised electrons are able to move throughout the lattice and transfer kinetic energy quickly to other electrons and metal ions in the lattice. **[1]**

iii Metallic bonding is non-directional – the metal ions in the lattice attract the delocalised electrons in all directions and vice versa, so the layers of positive ions can slide over each other without affecting the bonding. **[1]**

e Copper is a very good conductor of electricity and is ductile (can be drawn into wires). **[1]**

f i $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^3$ **[1]**

ii 4s and 3d electrons **[1]**

iii Ca forms a 2+ ion and has two delocalised electrons per atom, but V forms a more highly charged ion, and there are more delocalised electrons per atom because the 3d electrons are also delocalised;

There is a stronger electrostatic attraction between the more highly charged ion and the delocalised electrons in vanadium than in calcium (therefore, more energy is required to overcome this electrostatic attraction and the melting point is higher); **[2]**

Chemistry for the IB Diploma – Owen © Cambridge University Press & Assessment 2023

Chapter 9

Test your understanding

1

		Average electronegativity	Difference in electronegativity	Bonding
a	GeO_2	2.7	1.4	covalent
b	$BeCl_2$	2.4	1.6	covalent
c	GaAs	1.9	0.2	metallic
d	Mg_2Si	1.6	0.6	metallic
e	CaS	1.8	1.6	ionic
f	KCl	2.0	2.4	ionic

2 **a** true

b false – they are usually harder – the introduction of a different-sized atom makes it more difficult for the planes of atom/ions to slide over each other

c true

3 **a** Branches decrease the strength – branched polymer chains are less able to pack closely together, resulting in weaker London forces between chains.

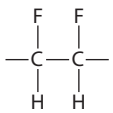
b Plastics/polymers are thermal insulators – they consist of individual molecules with only weak forces between them, and so, kinetic energy is not transmitted easily from one molecule to the next.

c Plastics are electrical insulators – the polymer chains are uncharged, and electrons are held tightly in covalent bonds – there are no charged particles free to move.

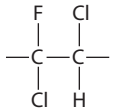
4 Plastic B will be denser – less branching allows the polymer chains to pack more closely together.

Plastic A will be more flexible – more branches mean weaker forces between the chains; therefore, the chains are more easily displaced relative to each other.

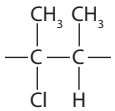
5 **a**



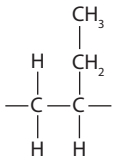
b



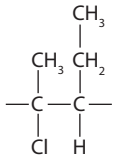
c



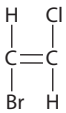
d



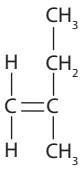
e



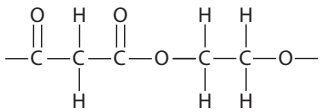
6 **a**



b

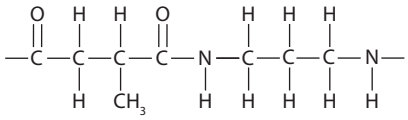


7 **a**



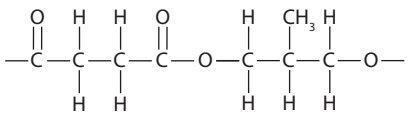
polyester

b



polyamide

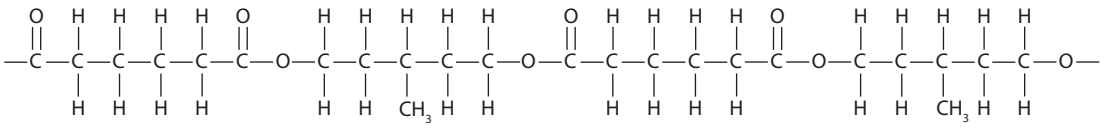
c



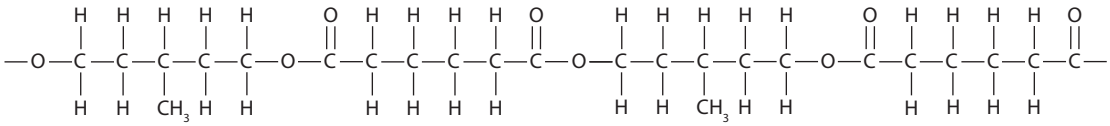
polyester

Chemistry for the IB Diploma – Owen © Cambridge University Press & Assessment 2023

8 **a**

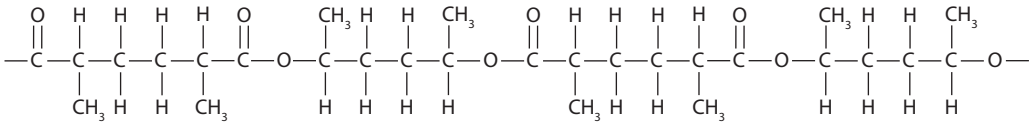


This could also be drawn the other way round:

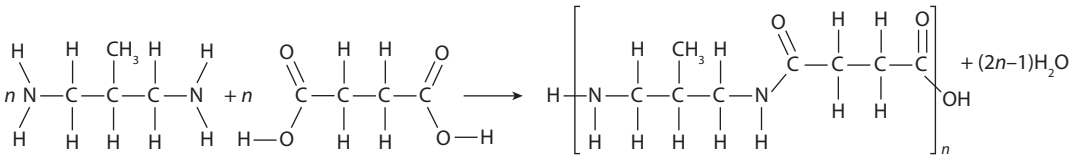


but it is exactly the same, just flipped around.

b



9



10 This is hydrolysis – the linking bond is broken and the elements of water (H one side and OH the other) are added where the linkage was.

Exam-style questions

1 B

2 B

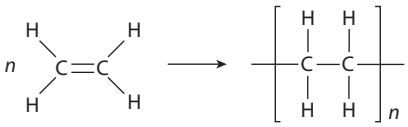
3 C

4 C

5 D

6 **a** It contains a C═C unit that can open out in the polymerisation reaction to allow the monomers to bond together. **[1]**

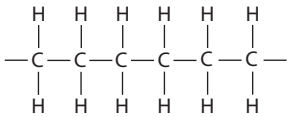
b



for C═C converted into C—C **[1]**

for continuation bonds, brackets and n **[1]**

c **[1]**



d LDPE has much more branching along the polymer chains;

With more branching, the chains cannot pack as closely together, and the density is lower; **[2]**

e As the length of the polymer chain increases, the relative molecular mass of the polymer increases and the material generally gets stronger;

This is due to stronger London forces between the chains as the relative molecular mass increases; **[2]**

Chemistry for the IB Diploma – Owen © Cambridge University Press & Assessment 2023

f Plastic advantages:

- more flexible than glass/aluminium/will not break but glass will/very low density (light)/lower density than glass/aluminium, so the water bottle is lighter and less energy required/less CO_2 generated when it is transported/can be made see-through but aluminium cannot

Plastic disadvantage:

- made from crude oil, which is a non-renewable resource and likely to run out soon/problems with disposal of plastic – non-biodegradable/not as likely to be re-used/not as easily recycled/specific statement about plastic waste in the environment – e.g. microplastics being consumed by animals/CO_2/toxic gases produced when plastics burnt **[2]**

Any [2] valid points – 1 from each section.

7 a A different-sized atom disrupts the lattice structure;

The planes of metal atoms cannot slide over each other as easily; **[2]**

b It has metallic bonding, so delocalised electrons are free to move. **[1]**

8 MgB_2: average electronegativity $= \frac{1.3+2.0}{2} = 1.65$

difference in electronegativity $= 2.0 - 1.3 = 0.7$

$MgCl_2$: average electronegativity $= \frac{1.3+3.2}{2} = 2.25$

difference in electronegativity $= 3.2 - 1.3 = 1.9$

BCl_3: average electronegativity $= \frac{3.2+2.0}{2} = 2.6$

difference in electronegativity $= 3.2 - 2.0 = 1.2$

average electronegativities correctly calculated for each one = [1]

difference in electronegativities correctly calculated for each one = [1]

MgB_2 bonding will be predominantly metallic/borderline metallic–covalent

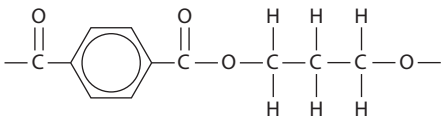
AND

$MgCl_2$ bonding will be predominantly ionic

AND

BCl_3 bonding will be predominantly covalent; **[1]**

9 a



for correct ester linkage **[1]**

for whole unit correct including continuation bonds **[1]**

b *Advantages*: renewable/does not use up crude oil;

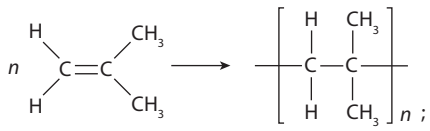
Disadvantages: corn starch could be used for food manufacture; **[2]**

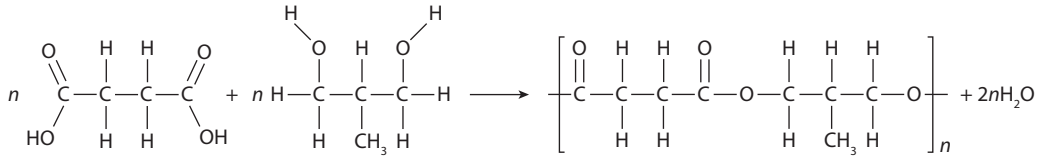
Chemistry for the IB Diploma – Owen © Cambridge University Press & Assessment 2023

10 In addition polymerisation, the monomers are alkenes/have C═C, but, in condensation polymerisation, monomers are a dicarboxylic acid and a diol (using the molecules here);

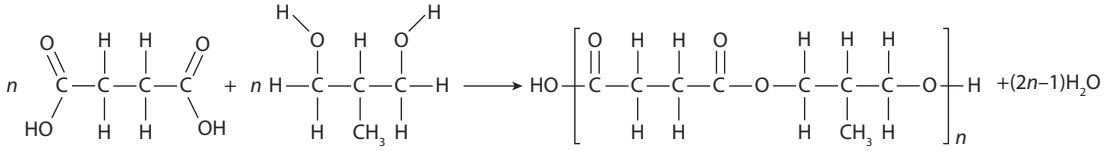
In addition polymerisation, monomers joined together to form a long chain and no other products are formed, but in condensation polymerisation water is also formed each time two molecules joined together;

In addition polymerisation, monomers joined by C—C but in condensation polymerisation joined by an ester group;





or

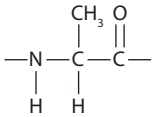


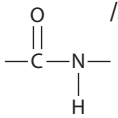
two equations = 2 marks then any 2 other points **[4]**

11 a condensation (reaction) **[1]**

b water **[1]**

c hydrolysis **[1]**

d  **[1]**

e Polyamide, as it will contain a  /amide group. **[1]**

Chemistry for the IB Diploma – Owen © Cambridge University Press & Assessment 2023

Chapter 10

Test your understanding

1 a silicon

b tellurium

c polonium

d iodine

e arsenic

2

	Alkali metal	Halogen	Noble gas	Transition element	Lanthanoid	Actinoid
Cl		✓				
Tb					✓	
Kr			✓			
W				✓		
U						✓
Os				✓		
Rb	✓					

3

	Metal	Non-metal	Metalloid
Ir	✓		
Se		✓	
Ge			✓
Ru	✓		
Ho	✓		
Si			✓

4

Ca	V	Eu	As	Ar	Pu	Fe	K
s block	d block	f block	p block	p block	f block	d block	s block

5 a increase

b decrease

6 a Mg < Ca < Sr < Ba

b $Na^+ < F^- < O^{2-}$ same number of electrons but Na has highest nuclear charge

c $Al^{3+} < Na^+ < Na < K$; Al^{3+} and Na^+ have same number of electrons but Al has higher nuclear charge. Positive ions are smaller than the parent atom, also Na^+ has 1 fewer shell than Na. K has more shells of electrons than Na.

d $Cl < Cl^- < S^{2-} < Te^{2-}$; Negative ions bigger than neutral atoms – more electron-electron repulsion. S^{2-} has same number of electrons as Cl^- but lower nuclear charge. Te^{2-} has more shells than S^{2-} but is in the same group.

7 a false – Ge has an extra shell of electrons, so larger than Si.

Chemistry for the IB Diploma – Owen © Cambridge University Press & Assessment 2023

b false – Se has more shells of electrons and so first ionisation energy is lower. Electronegativities are the same (although, in general, you would expect electronegativity to decrease down a group).

c true – Sb has one more proton than Sn, but the same number of shells, so shielding is approximately the same.

d false – Negative ions bigger than neutral atoms – s more electron-electron repulsion.

e true – electronegativity increases across a period but decreases down a group.

f false – F is smaller than Cl – so greater electron-electron repulsion when an electron is brought into outer shell of F.

8 $2Rb(s) + 2H_2O(l) \rightarrow 2RbOH(aq) + H_2(g)$

9 Cs > Rb > K > Na

10 a K – metallic bonding – smaller atom/ion – stronger attraction to delocalised electrons.

b I_2 – covalent molecular – greater M_r/more electrons – stronger London forces between molecules.

c Na – metallic bonding here is stronger than the London forces between Cl_2 molecules.

11 $Cl_2(s) + 2I^-(aq) \rightarrow 2Cl^-(aq) + I_2(aq)$

$I_2(s)$ would also be acceptable

12 a yes, bromine is more reactive and displaces iodine

b no reaction – chlorine is more reactive than iodine and so cannot be displaced by it

c no reaction, an element cannot displace itself

13 a same, decreases

b different, increases down Group 1 but decreases down Group 17

c different, decreases down Group 1 but increases down Group 17

d same, decreases down both groups

14 a $CO_2(g) \rightleftharpoons CO_2(aq)$ and

$CO_2(aq) + H_2O(l) \rightleftharpoons H_2CO_3(aq)$

or

$CO_2(g) + H_2O(l) \rightleftharpoons H_2CO_3(aq)$

b $Na_2O(s) + H_2O(l) \rightarrow 2NaOH(aq)$

c $SO_3(l) + H_2O(l) \rightarrow H_2SO_4(aq)$

d $CaO(s) + H_2O(l) \rightarrow Ca(OH)_2(aq)$

State symbols are not essential.

15

Acidic	Basic	Amphoteric
SiO_2	Na_2O	Al_2O_3
P_4O_6	MgO	
P_4O_{10}		
SO_2		
SO_3		
Cl_2O		
Cl_2O_7		

16 a acidic $H_2SO_4(aq)$

b alkaline $Mg(OH)_2(aq)$

c alkaline NaOH(aq)

d acidic $H_2CO_3(aq)$

Chemistry for the IB Diploma – Owen © Cambridge University Press & Assessment 2023

17

P_4	SO_2	SO_3	SO_4^{2-}	SO_3^{2-}	C_2H_5Cl	O_2	CO	C_2H_4
P 0	S +4 O −2	S +6 O −2	S +6 O −2	S +4 O −2	C −2 H +1 Cl −1	O 0	C +2 O −2	C −2 H +1
Ba	CrO_4^{2-}	$Cr_2O_7^{2-}$	H_2O_2	BaO_2	CaH_2	$KMnO_4$	$Na_2S_2O_3$	$S_4O_6^{2-}$
Ba 0	Cr +6 O −2	Cr +6 O −2	H +1 O −1	Ba +2 O −1	Ca +2 H −1	K +1 Mn +7 O −2	Na +1 S +2 O −2	S +2.5 O −2

18 **a** +3
b +2
c +1
d +4
e −2
f +3

19 **a** +1
b −1
c +7
d +3
e +5

20 **a** +1
b +5
c +4
d +6
e −3 (NH_4^+ NO_3^-)
f –1

21 **a** nitrogen(II) oxide
b chlorine(VII) oxide
c selenium(IV) oxide
d potassium iodate(V)
e chromium(III) oxide
f phosphoric(V) acid
g sodium nitrate(V)
h chloric(I) acid
i sodium bromate(V)
j ammonium chlorate(VII)

22 **a** Na – same group but smaller atom – the outer electron is closer to the nucleus
b N – more protons in the nucleus but similar shielding, as same number of shells
c He – same group but smaller atom – the outer electron is closer to the nucleus
d Mg – electron removed from 3s subshell but from 3p subshell in Al
e Cl – more protons in the nucleus but similar shielding, as same number of shells
f P – all p electrons in separate orbitals but S has two electrons in same p orbital

23 **a** Na^+ – electron removed from second shell rather than third
b Al^{3+} – electron removed from second shell in each case – both have the same number of electrons, but Al has the higher nuclear charge
c O^+ – all p electrons in separate orbitals, but F_+ has two electrons in same p orbital
d B^+ – electron removed from 2s subshell but from 2p subshell in C_+
e Mg^{11+} – both have 1 electron, but Mg has the higher nuclear charge

24 **a** $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^8$
b $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^6$
c $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^2$
d $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^3$

25 **a** +2
b +2
c +2
d +3

Chemistry for the IB Diploma – Owen © Cambridge University Press & Assessment 2023

e +3

f +3

g +6

h 0

26 a 3−

b 2−

c 1+/+

d 2+

27 MnF_3, CoF_2, $[Ni(H_2O)_6]^{2+}$ are coloured. They have partially filled 3d subshells.

TiF_4, VF_5 have $3d^0$, so colourless

CuI, $[Zn(H_2O)_6]^{2+}$ have $3d^{10}$, so colourless

28 $[Fe(H_2O)_6]^{2+}$ because H_2O causes less splitting of the d orbitals

29 $625 \times 10^{12} = 6.25 \times 10^{14}$ Hz
$660 \times 10^{12} = 6.60 \times 10^{14}$ Hz

$$\lambda = \frac{c}{f} = \frac{3.00 \times 10^8}{(6.25 \times 10^{14})} = 4.80 \times 10^{-7} \text{ m i.e. 480 nm}$$

$$\lambda = c/f = \frac{3.00 \times 10^8}{(6.60 \times 10^{14})} = 4.55 \times 10^{-7} \text{ m i.e. 455 nm}$$

Looking at the colour wheel in Figure 10.41, the wavelength range absorbed is in the blue part of the spectrum, so blue light is absorbed and orange light transmitted - the complex ion will appear orange.

Exam-style questions

1 B

2 A

3 D

4 B

5 B

6 A

7 C

8 A

9 D

10 D

11 C

12 B

13 a i Aluminium and sodium are in the same period in the periodic table and, therefore, have the same number of shells of electrons/the shielding from inner shells of electrons is approximately the same in both;

Aluminium has a higher nuclear charge (more protons) than sodium and, therefore, the outer electrons are attracted more strongly; **[2]**

ii An Al atom forms a 3+ ion by losing its three outer-shell electrons and a Cl atom forms a 1− ion by gaining one electron;

If the Al atom and the Al^{3+} ion are compared, the Al^{3+} ion has one fewer shell of electrons. The Al^{3+} ion is, therefore, smaller than the Al atom;

If the Cl atom and the Cl^- ion are compared, Cl^- has one extra electron, so there is greater electron–electron repulsion for the same nuclear charge pulling in the electrons. The electron cloud expands, and the ion is larger than the atom; **[3]**

iii K forms the K^+ ion, but Cl forms the Cl^- ion. These have the same number of electrons so electron-electron repulsion similar; K^+ has a higher nuclear charge (19+) than Cl^- (17+), so the electrons are pulled in more strongly and the K^+ ion is smaller; **[2]**

b i First electron affinity:

$Cl(g) + e^- \rightarrow Cl^-(g)$;

First ionisation energy:

$Mg(g) \rightarrow Mg^+(g) + e^-$; **[2]**

ii A chlorine atom is smaller than a bromine atom; so, when an electron is accepted into the outer shell of Cl, it is closer to the nucleus – and so more strongly attracted to it; **[2]**

iii A chlorine atom is smaller and has a higher nuclear charge than a magnesium atom; However, Cl and Mg have the same number of electron shells, and so, approximately the same amount of shielding from inner shells. (so, the outer electron is held more tightly in Cl and is more difficult to remove.); **[2]**

Chemistry for the IB Diploma – Owen © Cambridge University Press & Assessment 2023

12 a Sodium has the electron configuration [Ne] $3s^1$, so the highest energy subshell (sub-level) occupied by electrons is an s subshell. **[1]**

b i *Any 2 from:*

the piece of sodium floats;

the piece of sodium melts into a ball;

the reaction is (very) exothermic;

there is fizzing where sodium is in contact with water/hydrogen gas is produced;

the piece of sodium moves around on the surface of the water;

the piece of sodium gets smaller and eventually disappears; **[2]**

ii $2Na(s) + 2H_2O(l) \rightarrow 2NaOH(aq) + H_2(g)$

for all formulas correct **[1]**

for balancing and state symbol correct **[1]**

c A potassium atom is larger than a sodium atom so its outer electron is further from the nucleus, AND the reactions involve the loss of the outer-shell electron to form a positive ion, M^+;

As the size of the atom increases the ionisation energy decreases /the outer electron is less strongly attracted by the nucleus (so potassium loses its outer electron to form a positive ion much more easily than sodium and will react more vigorously); **[2]**

d i Contains the NO^{3-} ion.

The oxidation state of N in NO^{3-} is +5, therefore: sodium nitrate(V) **[1]**

ii decreases from +5 to +3 **[1]**

13 a From left to right across the period, the acid–base behaviour changes from basic through amphoteric to acidic; Magnesium forms a basic oxide, aluminium forms an amphoteric oxide and sulfur forms an acidic oxide;

b i O has an oxidation state of −2, so 2 × −2 = −4 and the oxidation state of C must be +4, as the charge is zero overall. **[1]**

ii $CO_2(g) \rightleftharpoons CO_2(aq)$ **[1]**

and

$CO_2(aq) + H_2O(l) \rightleftharpoons H_2CO_3(aq)$

or

$CO_2(g) + H_2O(l) \rightleftharpoons H_2CO_3(aq)$

iii More CO_2 dissolves in water/ [CO_2 (aq)] higher AND position of equilibrium shifts to right producing higher [H^+(aq)];

CO_2 (aq) + $H_2O(l) \rightleftharpoons HCO_3^-(aq) + H^+$ (aq);

OR

More CO_2 dissolves in water to form carbonic acid AND more carbonic acid dissociates producing higher [H^+(aq)];

CO_2 (aq) + $H_2O(l) \rightleftharpoons H_2CO_3(aq)$;

$H_2CO_3(aq) \rightleftharpoons HCO_3^-(aq) + H^+(aq)$; **[2]**

14 a i $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1 3d^{10}$ **[1]**

ii $1s^2 2s^2 2p^6 3s^2 3p^6 3d^9$ **[1]**

b Ligands are negative ions or neutral molecules that possess at least one lone pair of electrons; a lone pair is used to form a coordination bond between the ligand and the transition metal ion to form a complex ion; **[2]**

c Cl^- is a negatively charged ligand and four Cl^- ions have a total charge of 4− and the overall charge on the complex ion is 2−, therefore the oxidation state of Cu must be +2. **[1]**

2+ scores 0

Chemistry for the IB Diploma – Owen © Cambridge University Press & Assessment 2023

d i The $[Cu(H_2O)_6]^{2+}$ complex ion contains the Cu^{2+} ion, which has a partially filled 3d subshell;

The d orbitals are split into two groups at different energies;

Energy in the form of a certain frequencies of *visible* light is absorbed; to promote an electron from the lower set of d orbitals to the upper set;

The light transmitted has the complementary colour to the light absorbed;

Any 3 points **[3]**

ii $[Cu(NH_3)_2]^+$ contains the Cu^+ ion, which has a full 3d subshell. There is no space available in the upper set of d orbitals to promote an electron to, so light in the visible region of the spectrum cannot be absorbed. **[1]**

Chemistry for the IB Diploma – Owen © Cambridge University Press & Assessment 2023

Chapter 11

Test your understanding

1 a C_5H_{12}

b $C_{10}H_{20}$

c $C_6H_{12}O_2$

d $C_{10}H_{14}O$

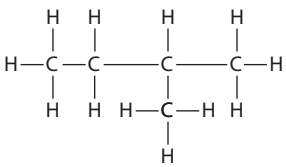
2 a $CH_3CH_2CH_2CH_2CH_2CH_3/CH_3(CH_2)_4CH_3$

b $C(CH_3)_4$

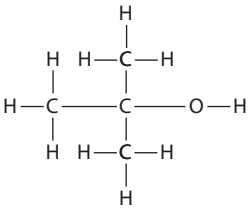
c $CH_3CH_2CH_2CH_2CH_2OH$

d $(CH_3)_2CBrCH_2OH$

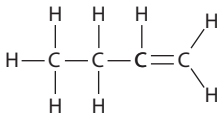
3 a



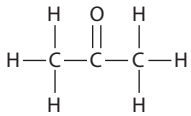
b



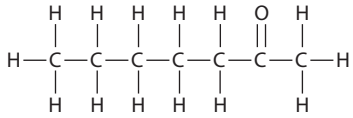
c



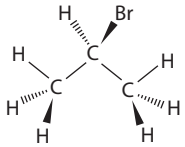
d



e



4



5 a alcohol

b ketone

c ester

6 a carbonyl, carbon–carbon double bond, hydroxyl

b carboxyl, carbonyl, amino

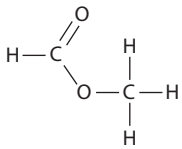
c phenyl, ester

d carbonyl, alkoxy

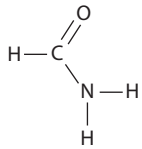
e amido

f phenyl, hydroxyl, ester, carbon–carbon double bond, chloro/halogeno

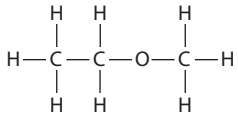
7 a



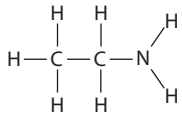
b

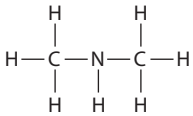


c



d





8 a 2-methylpentane

b 2,2,3-trimethylbutane

c 2,2-dimethylpentane

d 2-methylpentane

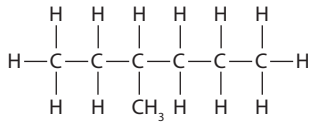
9 a 1-bromobutane

b 2-bromo-2-methylbutane

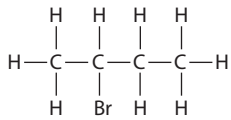
c 2-chloropropane

d 1-iodo-3-methylbutane

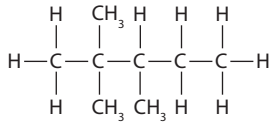
10 a



b

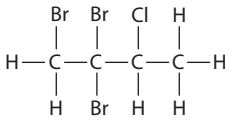


c

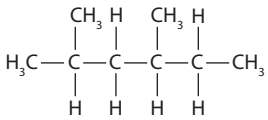


Chemistry for the IB Diploma – Owen © Cambridge University Press & Assessment 2023

d



e



11 a 2-chloro-3-methylpentane

b 3-bromo-2-methylpentane

c 2-bromo-3-chlorobutane

d 2-chloro-4-methylpentane

e 1,1,1,2-tetrachloropropane

f 2-bromo-1,1-dichloropropane

12 a 3-methylpentane

b 3-methylpentane

c 2,2-dimethylbutane

13 a 1,2-dichloropentane

b 2,2,3-trimethylhexane

c 2,2,5-trimethylhexane

d 2-bromo-3,4-dimethylhexane

e 4-chloro-2,3-dimethylhexane

f 2-chloro-3-methylpentane

14 a but-2-ene

b 2-methylbut-1-ene

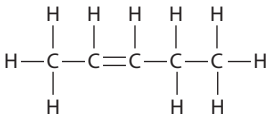
c 3-methylpent-2-ene

d 2,3-dimethylbut-2-ene

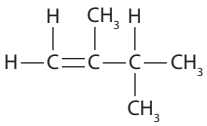
e 2-methylhex-3-ene

f 5-methylhex-2-ene

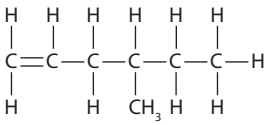
15 a



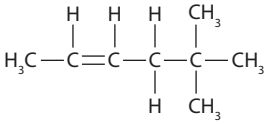
b



c



d



16 a hexan-3-ol

b 2-methylpropan-2-ol

c 3-methylbutan-1-ol

d 2,3-dimethylbutan-1-ol

e 5-methylhexan-1-ol

f 2-methylpentan-3-ol

g ethane-1,2-diol

h 2-methylhexan-3-ol

i 2-methylpentan-3-ol

17 a butanone

b pentanal

c hexanoic acid

d 3-methylbutanal

e 2-methylpentanoic acid

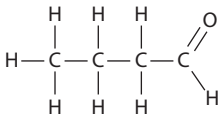
f 5-methylhexan-2-one

g 3-methylbutanoic acid

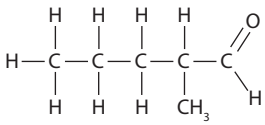
h ethanedioic acid

i 3,4-dimethylpentan-2-one

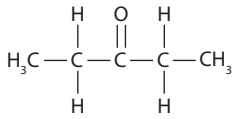
18 a



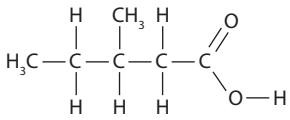
b



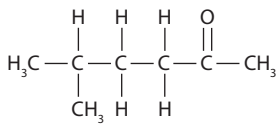
c



d



e



Chemistry for the IB Diploma – Owen © Cambridge University Press & Assessment 2023

19 **a** but-3-en-1-ol

b 2-chlorobut-1-ene

c but-3-en-2-one

d 3,4-dibromobut-1-ene

e pent-3-en-1-ol

f pent-4-enal; the aldehyde group must be on carbon 1, as otherwise it would be a ketone, so the '1' is not necessary in the name

g hex-4-en-2-one

h hex-3-enoic acid

i 3,4,5-trimethylhex-5-en-2-ol

20 **a** 1-bromobutane; primary halogenoalkane;
1 C atom joined to the C atom with the Br

b 2-bromo-2-methylbutane; tertiary halogenoalkane; 3 C atoms joined to the C atom with the Br

c 2-chloropropane; secondary halogenoalkane; 2 C atoms joined to the C atom with the Cl

d 1-iodo-3-methylbutane; primary halogenoalkane; 1 C atom joined to the C atom with the I

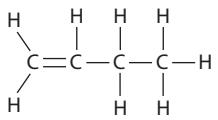
e 3,3-dimethylbutan-2-ol; secondary alcohol; 2 C atoms joined to the C atom with the OH

f 2-methylbutan-2-ol; tertiary alcohol; 3 C atoms joined to the C atom with the OH

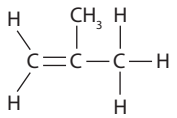
g secondary amine; here we are looking at the number of C atoms joined to the N – 2 in this case

h primary amine; 1 C atom joined to the N.

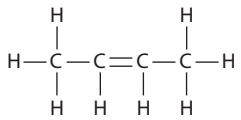
21



but-1-ene



2-methylpropene

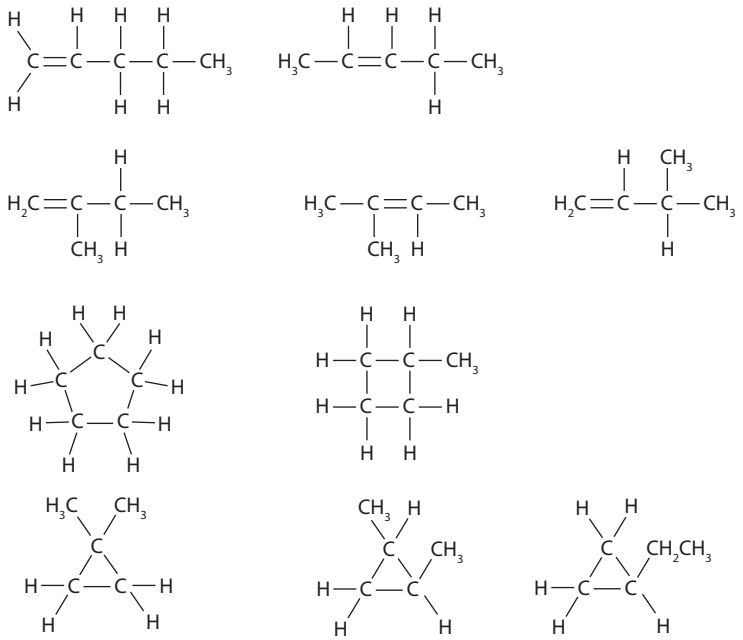


but-2-ene

Note: *cis–trans* isomers are also possible for but-2-ene – see HL section on stereoisomerism.

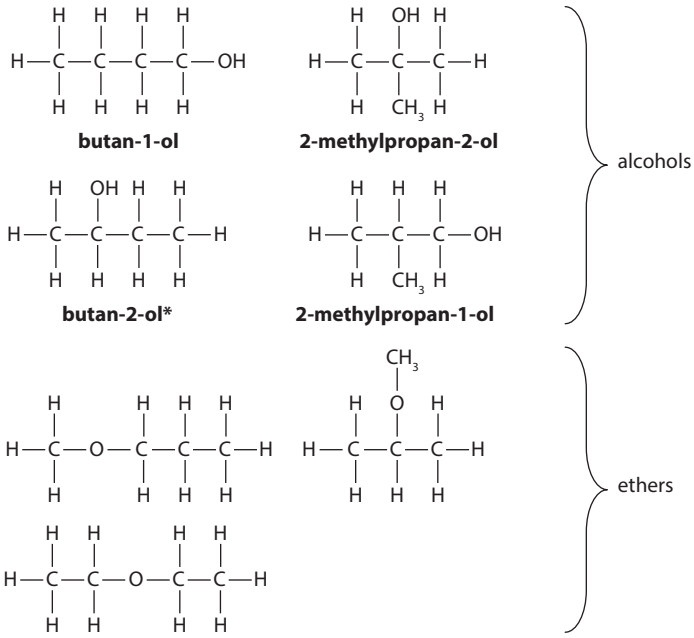
Chemistry for the IB Diploma – Owen © Cambridge University Press & Assessment 2023

22



Note: stereoisomers also exist for some of these (see HL section on stereoisomerism).

23 a,b

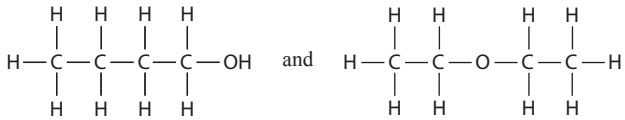


*Note: butan-2-ol also has optical isomers – see later in the Higher Level section on stereoisomerism.

c butan-1-ol and 2-methylpropan-1-ol are chain isomers

position isomers: butan-1-ol butan-2-ol; and 2-methylpropan-1-ol and 2-methylpropan-2-ol; first two ethers are also position isomers of each other – the $-OCH_3$ group in different positions

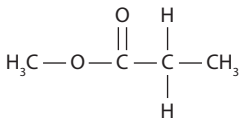
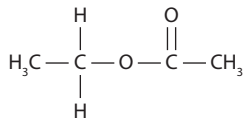
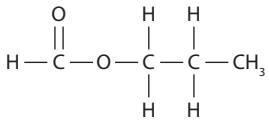
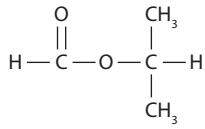
any of the alcohols are functional group isomers of any of the ethers, e.g.



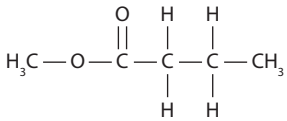
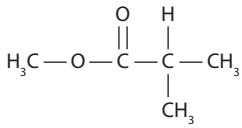
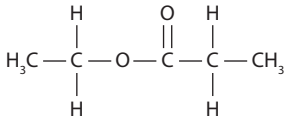
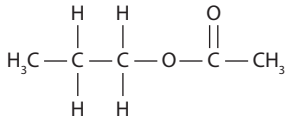
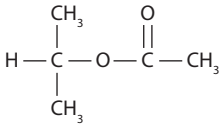
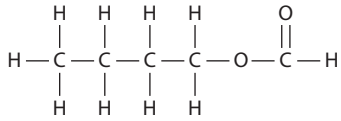
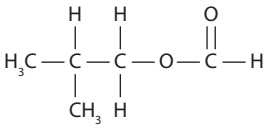
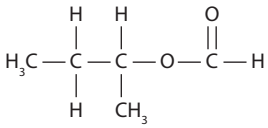
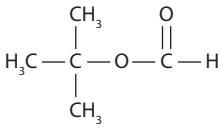
are functional group isomers

Chemistry for the IB Diploma – Owen © Cambridge University Press & Assessment 2023

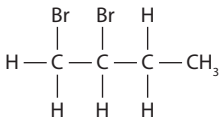
24 a

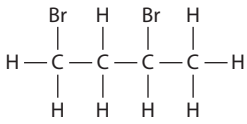





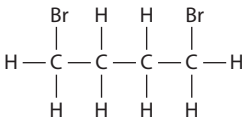
b

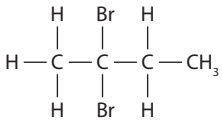










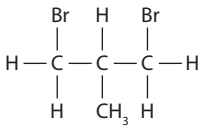
25

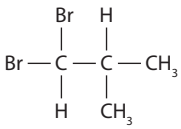

Position

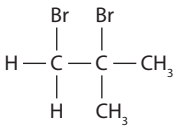

Position


Position

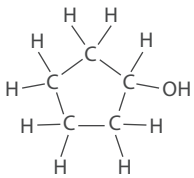
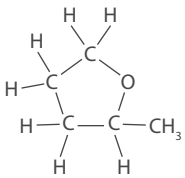
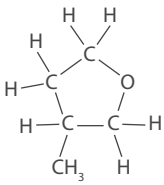

Position


Chain


Chain


Chain

26

Chemistry for the IB Diploma – Owen © Cambridge University Press & Assessment 2023

27 B and C

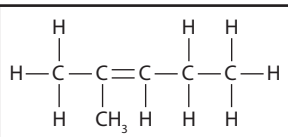
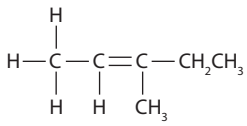
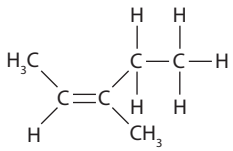
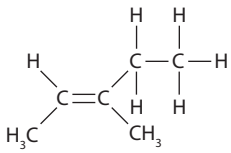
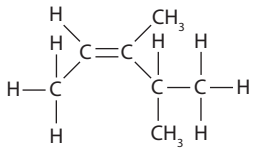
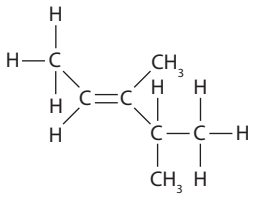
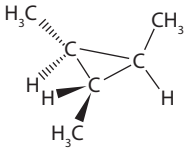
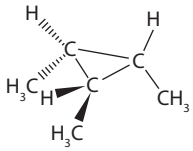
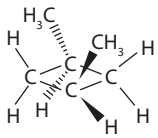
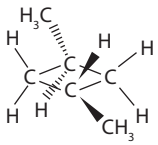
28 **a** neither, they have different molecular formulas

b isomers

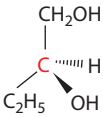
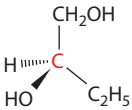
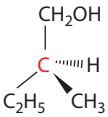
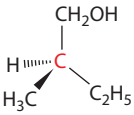
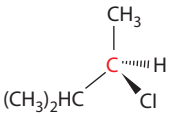
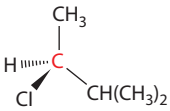
c identical

d isomers

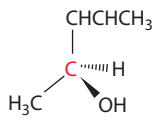
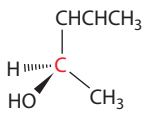
29 For a molecule to exhibit *cis-trans* isomerism it must have 2 different groups on each side of the C=C.

a		no	two CH_3 groups on one of the C atoms of the C=C	
b		yes		
c	2,3-dimethylpent-2-ene	no	two CH_3 groups on one of the C atoms of the C=C	
d	3,4-dimethylpent-2-ene	yes		
e	1,2,3-trimethylcyclopropane	yes		
f	1,3-dimethylcyclobutane	yes		

30 We are looking for molecules with a chirality centre, i.e. a C atom that have 4 different groups attached.

a	chiral		
b	achiral		
c	chiral		
d	chiral		

Chemistry for the IB Diploma – Owen © Cambridge University Press & Assessment 2023

e	achiral		
f	chiral		

Note: chirality centres are shown in red.

31 We are looking for molecules with a chirality centre, i.e. a C atom that have 4 different groups attached.

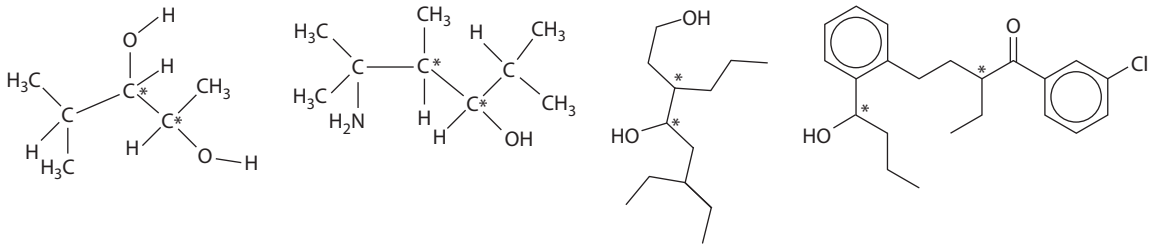
a achiral

b chiral Chirality centre is the second C, the one joined to the Br.

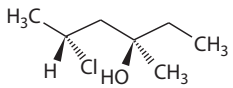
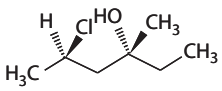
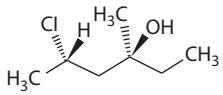
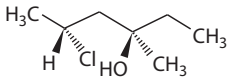
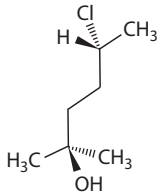
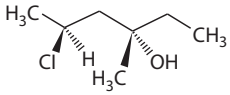
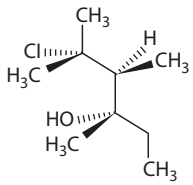
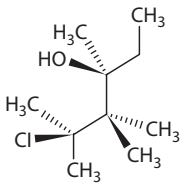
c chiral Chirality centre is the C joined to the OH.

d achiral

32 We are looking for C atoms that have 4 different groups attached.



33

a			identical – turn one molecule upside down to see this
b			enantiomers The molecules are non-superimposible mirror images of each other. Put the second molecule on top of the first one.
c			structural isomers In the first structure, there are 2 C atoms between the C atoms with the Cl and the C atom with the OH, but in the second structure, there is only 1 C atom between them
d			not isomers – different molecular formulas

Chemistry for the IB Diploma – Owen © Cambridge University Press & Assessment 2023

34 We are looking for molecules containing C═O, which absorb in this frequency range:

B propanal,

C CH_3COCH_3,

E CH_3COCH_3,

G CH_3CH_2COOH

35 a C—H 2840–3100 cm^{-1}

b C—H 2840–3100 cm^{-1}

O—H 3200–3600 cm^{-1}

c C═C 1610–1680 cm^{-1}

C—H 2840–3100 cm^{-1}

d C═O 1700–1750 cm^{-1}

O—H 2400–3400 cm^{-1}

C—H 2840–3100 cm^{-1}

36 HCN, HF, CO, CO_2, H_2S, $CFCl_3$, N_2O

O_2, H_2 and N_2 are all non-polar and can only vibrate in one way, so there can be no change in dipole moment as they vibrate.

37 a C_2H_4O

b $C_3H_8O/C_2H_4O_2$

c $C_4H_8O/C_3H_4O_2$

d $C_5H_{12}O/C_4H_8O_2/C_3H_4O_3$

38 a CH_3^+

b CO^+, $C_2H_4^+$

c $C_2H_5^+$, HCO^+

d OCH_3^+, CH_2OH^+

e $C_3H_7^+$, $C_2H_3O^+$

f $COOH^+$, $C_2H_5O^+$

g $C_3H_7O^+$, CH_2COOH^+, $HCOOCH_2^+$

h $C_6H_5^+$

39 a 3 signals; 1 : 2 : 3

b 4 signals; 3 : 2 : 2 : 1

c 3 signals; 9 : 2 : 1

d 5 signals; 1 : 3 : 1 : 2 : 3

e 3 signals; 3 : 1 : 6

f 5 signals; 6 : 1 : 2 : 2 : 1 (the second C atom has two identical CH_3 groups attached)

g 5 signals; 3 : 2 : 2 : 1 : 3

h 2 signals; 9 : 1

All the H atoms that are in the CH_3 groups are in the same chemical environment (the molecule is symmetrical) – there are 18 H in this environment and 2 other H atoms, so 18:2 simplifies to 9:1.

i 5 signals; 3 : 1 : 2 : 2 : 3

j 7 signals; 6 : 1 : 2 : 1 : 1: 1: 6

k 3 signals; 6 : 1 : 3

40 a triplet, multiplicity = 3 2 H on adjacent C

b singlet, multiplicity = 1 no H on adjacent C

c triplet, multiplicity = 3 2 H on adjacent C

d doublet, multiplicity = 2 1 H on adjacent C

e triplet, multiplicity = 3 2 equivalent H on adjacent C atoms – 1 on each

41 a two doublets The H atoms on each C have 1 H on the adjacent C

b two triplets: The signal due to the H atoms on carbons 1 and 3 is split by the 2 H atoms on the middle C into a triplet. The signal due to the H atoms on the middle C atom is split by the 2 equivalent H atoms on carbons 1 and 3 into a triplet.

c one triplet, one quartet, one singlet The triplet is the signal for the H of the CH_3 group – there are 2 H atoms on the adjacent C.

The quartet is the signal for the H of the CH_2 – there are 3 H atoms on the adjacent C.

The singlet is the signal for the H of the COOH – there are 0 H atoms on the adjacent C (and an H atom in an OH group does not generally show splitting).

d one triplet, one quartet, one singlet; The triplet is the signal for the H of the left-hand CH_3 group – there are 2 H atoms on the adjacent C.

The quartet is the signal for the H of the CH_2 – there are 3 H atoms on the adjacent C.

The singlet is the signal for the H of the right-hand CH_3 there are 0 H atoms on the adjacent atom - an O atom.

Chemistry for the IB Diploma – Owen © Cambridge University Press & Assessment 2023

42 a The singlet is the H of the OH group. 0.5–5.0 ppm

b The singlet is due to the H atoms of the left-hand CH_3 group. 2.0–2.5 ppm

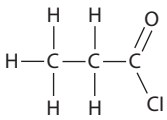
c The singlet is due to the H atoms of the left-hand CH_3 group. 3.7–4.8 ppm

d The singlet is due to the H atoms of the CH_3 group on carbon 1 – next to the C=O. 2.1–2.7 ppm

e The first singlet is due to the H of the CHO group; all the H atoms in the 3 equivalent CH_3 groups give rise to the second singlet. 9.4–10.0 ppm and 0.9–1.7 ppm

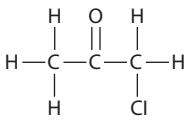
f The singlet is due to the H of the COOH group. 9.0–13.0 ppm

43 a



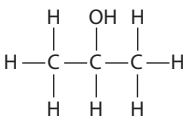
2 signals, therefore 2 different chemical environments for H. 2 protons, signal is a quartet, indicating 3 H on the adjacent C. 3 protons signal is a triplet, indicating 2 H on the adjacent C. 2 H next to 3 and 3 H next to 2 indicates an ethyl group.

b



2 signals, therefore 2 different chemical environments for H. Both signals are singlets, indicating 0 H on the adjacent C (the C═O group).

44



3 signals, therefore 3 different different chemical environments for H. 6 H in one environment suggests 2 CH_3 groups in the same environment. The 6H signal is split into a doublet, indicating 1 H on the adjacent atom; so there are 2 CH_3 groups next to a C atom that has 1 H on it.

Multiplicity of signal at $\delta = 4.0$ ppm is 7; this is the H on the central C, which has 6 H on adjacent C atoms (the H of the OH group does not cause splitting).

Exam-style questions

1 B

2 D

3 C

4 A

5 B

6 A

7 C

8 B

9 B

10 D

11 B

12 D

13 C

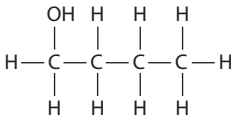
14 B

15 A

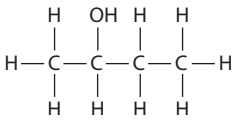
16 B

17 a hydroxyl group **[1]**

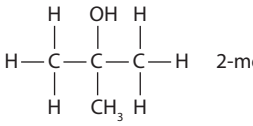
b i



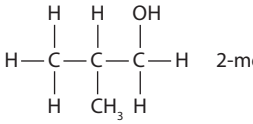
butan-1-ol



butan-2-ol



2-methylpropan-2-ol



2-methylpropan-1-ol **[4]**

[1] each for structure and name. 4 correct structures/names with no names/structures scores [2] max.

Chemistry for the IB Diploma – Owen © Cambridge University Press & Assessment 2023

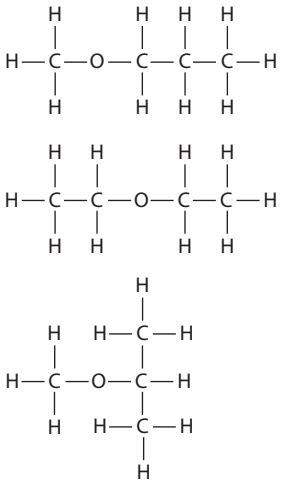
ii

butan-1-ol	primary
butan-2-ol	secondary
2-methylpropan-2-ol	tertiary
2-methylpropan-1-ol	primary

all correct [2]

2/3 correct [1] **[2]**

iii



any one structure; **[2]**

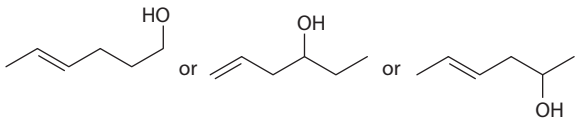
these all contain the ether (C—O—C) functional group;

c i unsaturated because it contains C═C **[1]**

ii $C_nH_{2n}O$ **[1]**

iii hex-5-en-1-ol **[1]**

iv e.g.



the carbon skeleton must stay the same, but C═C and/or —OH groups are moved. **[1]**

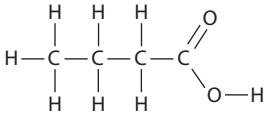
v **A** will have a higher boiling point;

A has higher relative molecular mass/ more electrons and, therefore, stronger London forces between molecules; **[2]**

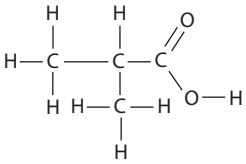
d i carbonyl (group) **[1]**

ii 4,4-dimethylpentanal **[1]**

e i



butanoic acid



2-methylpropanoic acid

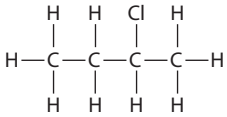
[1] each for each structure and [1] for both names. **[3]**

accept methylpropanoic acid

ii The general molecular formula of carboxylic acids and esters is the same/$C_nH_{2n}O_2$, so this is true for most carboxylic acids;

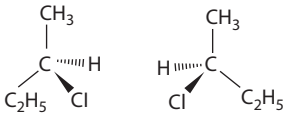
However, methanoic acid does not have an isomer that is an ester because esters must contain a minimum of two C atoms; **[2]**

18 a



[1]

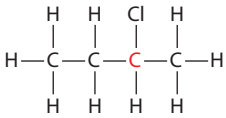
b i



[2]

[1] for each structure showing wedges and dashed bonds, second structure must be a clear mirror image of the first.

ii 2-chlorobutane has a carbon atom (shown in red below) with *four different* groups attached – this is the chirality centre. **[1]**



iii The two enantiomers of 2-chlorobutane rotate the plane of polarisation of plane-polarised light;

in opposite directions by the same amount; **[2]**

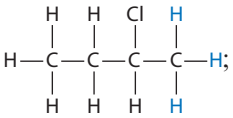
Chemistry for the IB Diploma – Owen © Cambridge University Press & Assessment 2023

iv A racemic mixture is an equimolar mixture of the two enantiomers of a chiral compound;

A racemic mixture has no effect on plane-polarised light – it is not optically active – because the rotation effects of the two enantiomers cancel each other out; **[2]**

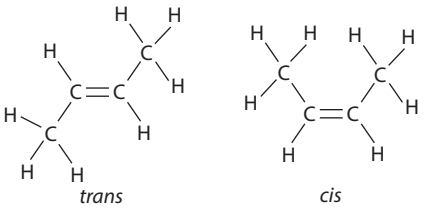
c Four because there are four different chemical environments for protons/H atoms/nuclei. **[1]**

d This is the signal for the hydrogen atoms/nuclei/protons on the CH_3 next to the CHCl group/shown in blue:



There is one H on the adjacent C therefore, the signal is split into a doublet; **[2]**

19 a



[1]

b *cis–trans* isomerism arises because there are two different groups on both sides of C═C;

the π component of the C═C bond restricts rotation of groups around the bond; **[2]**

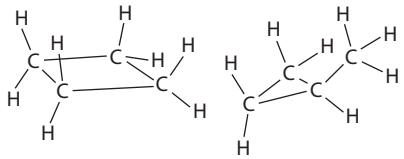
c The groups of both sides of C═C are the same – there are two CH_3 groups on one side of C═C and two H atoms on the other side of C═C. **[1]**

d Two signals because there are two different chemical environments for protons/H atoms/nuclei; **[2]**

There are 6 H atoms in one chemical environment and 2 in the other, therefore the ratio of the areas under the signals is 6:2, i.e. 3:1;

e It is only the alkene with the formula C_4H_{10} that exhibits *cis–trans* isomerism because but-1-ene and 2-methylpropene have two identical groups on at least one of the C atoms making up the C═C;

There are two cyclic isomers of C_4H_{10} – these do not exhibit *cis–trans* isomerism, as they do not have at least two carbon atoms that have two different groups attached, therefore, the statement is correct; **[2]**



20 a There is an absorption band in the range 1700–1750 cm^{-1}, which suggests the presence of a C═O group, so molecule I can be eliminated (also there is no O—H absorption in the IR spectrum);

There is no very broad band absorption in the range 2400–3400 cm^{-1}, which is characteristic of carboxylic acids, so molecule III can be eliminated;

There is no absorption band in the range 1000–1300 cm^{-1}, indicating that no C—O bond is present, so molecule IV (and III and I) can be eliminated;

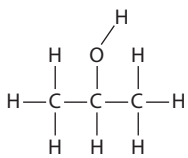
So, this must be the spectrum of molecule II – there is an absorption band in the range 1700–1750 cm^{-1}, corresponding to the C═O group, and the only other absorption above 1500 cm^{-1} is the C—H absorption around 3000 cm^{-1}. **[4]**

b Both propanal and propanone contain the same bonds and will have very similar absorption bands in the region above 1500 cm^{-1}, therefore, they cannot be easily distinguished using IR spectroscopy looking at the region above 1500 cm^{-1};

They could, however, be distinguished by looking at the fingerprint region and if the spectra of propanal and propanone are available for comparison;

Propanal has three signals in its NMR spectrum but propanone has only one. So, they can be distinguished easily using NMR; **[3]**

21 a i

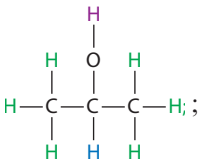


[1]

Chemistry for the IB Diploma – Owen © Cambridge University Press & Assessment 2023

ii The three signals arise because there are three different chemical environments for the protons/H atoms/nuclei in propan-2-ol;

The different chemical environments for H are:

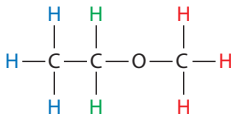


[2]

[1] for correct statement about different chemical environments and [1] for identification of the different environments for H, either as a description or by a diagram.

iii The integration trace gives the relative numbers of protons (hydrogen atoms) in each environment. **[1]**

b i



H atoms/protons in blue: triplet because there are two H atoms on the adjacent atom;

H atoms/protons in green: quartet because there are three H atoms on the adjacent atom;

H atoms/protons in red: singlet because there are no H atoms on the adjacent atom (the O atom); **[3]**

ii Propan-2-ol will have an absorption band in the range 3200–3600 cm^{-1} but methoxyethane will not. **[1]**

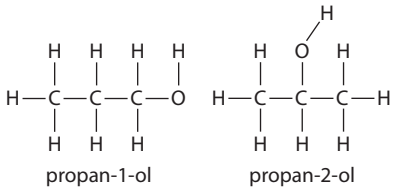
22 a 60 from the molecular ion peak (furthest right peak) **[1]**

b **Z** contains C, H and O and the only two possible combinations of these that add up to a relative molecular mass of 60 are C_3H_8O and $C_2H_4O_2$. **[1]**

c *m/z* 31 could be due to CH_3O^+ / CH_2OH^+; *m/z* 29 could be due to $C_2H_5^+$ / CHO^+; **[2]**

d The absorption band at about 3350 cm^{-1} suggests the presence of an O—H bond; No absorptions in the range 1600−1800 cm^{-1} suggest that there is no C═C or C═O present; **[2]**

e **Z** cannot have the formula $C_2H_4O_2$ because this requires the presence of a double bond (a three-membered ring including O would not have an O—H bond); So, **Z** has the molecular formula C_3H_8O and possible structural formulas that contain an O—H group are



[2]

f There are four signals in the NMR spectrum, indicating four different chemical environments for hydrogen atoms;

There are four different chemical environments for hydrogen atoms in propan-1-ol but only three in propan-2-ol because it is symmetrical, so **Z** must be propan-1-ol; **[2]**

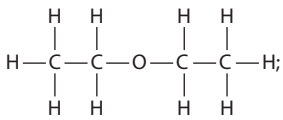
(We could also measure the vertical heights of the steps on the integration trace – this works out to be 1 : 2 : 2 : 3, which corresponds with the numbers of hydrogen atoms in each environment in propan-1-ol.)

23 a There is one hydrogen atom on the adjacent carbon atom;

so the signal due to the bold proton is split into a 1 : 1 doublet; **[2]**

(The signal due to the proton (hydrogen atom) in bold type is not split by the protons on the same carbon atom because they are chemically equivalent.)

b The compound is **[4]**

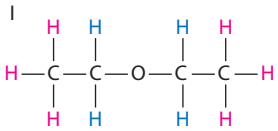


Chemistry for the IB Diploma – Owen © Cambridge University Press & Assessment 2023

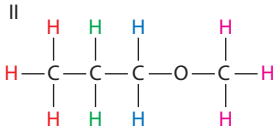
Reasoning:

The isomers of $C_4H_{10}O$ are

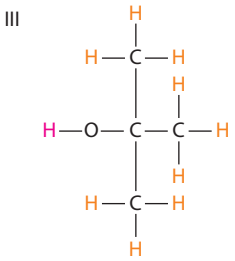
I



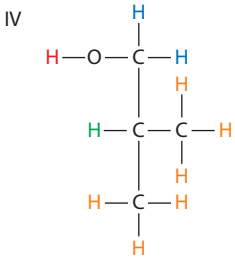
II



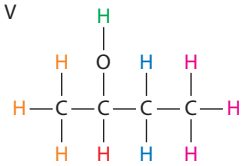
III



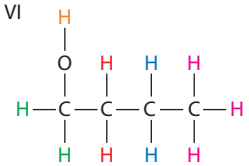
IV



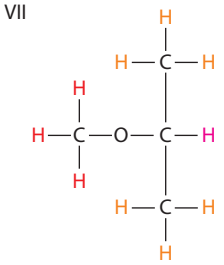
V



VI



VII



;

There are two sets of signals in the NMR spectrum, corresponding to two different chemical environments for H;

Only two of these isomers (I and III) have two different chemical environments for hydrogen;

The ratio of the heights of the steps in the integration trace is 1 : 1.5 or 2 : 3;

There are 10 protons (hydrogen atoms) in this molecule and, if they are divided in the ratio 2 : 3, there are 4 protons in 1 chemical environment and 6 in the other. Only structure 1 has protons in this ratio;

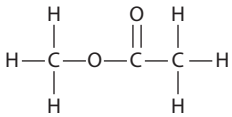
The splitting pattern is a quartet and a triplet – the quartet indicates three hydrogen atoms on the adjacent carbon atom, and the triplet indicates two hydrogen atoms on the other adjacent carbon atom.

These two signals together are characteristic of an ethyl group, CH_3CH_2. So, with ten protons, there must be two ethyl groups, and the compound is isomer I;

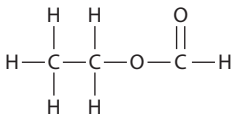
correct structure **[1]**

any three further points **[3]**

c **i** I



II



[1]

ii Isomer I has two different chemical environments for hydrogen atoms, so there will be two sets of signals in its NMR spectrum. Isomer II has three different chemical environments for hydrogen atoms, so there will be three sets of signals in its NMR spectrum;

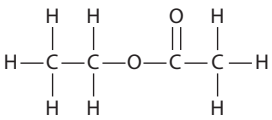
The ratio of the areas under the signals for isomer I will be 1 : 1. The ratio of the areas under the signals for isomer II will be 3 : 2: 1;

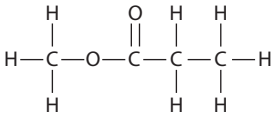
Chemistry for the IB Diploma – Owen © Cambridge University Press & Assessment 2023

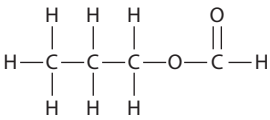
There are no hydrogen atoms on adjacent carbon atoms for isomer I, so the spectrum will consist of two singlets. For isomer II, there are three hydrogen atoms on one carbon atom and two on the adjacent carbon atom, so the signal with area 3 will be a triplet and the signal with area 2 will be a quartet – the third signal will be a singlet;

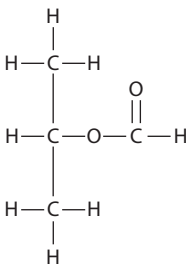
The triplet in the spectrum of isomer II will have a chemical shift in a different range (0.9–1.7 ppm) to any of the protons in isomer I because the protons (hydrogen atoms) are in a type of environment not found in isomer I; **[4]**

d i

I


II


III


IV


[2]

4 correct = [2]

2/3 correct = [1]

1 correct = 0 **[1]**

ii They will all contain an absorption band in the region 1700–1750 cm^{-1}, corresponding to C═O;

They will all contain an absorption band in the region 2840–3100 cm^{-1}, corresponding to C—H;

They will all contain an absorption band in the region 1000–1300 cm^{-1}, corresponding to C—O;

any two points **[2]**

iii The ester is isomer II – methyl propanoate; **[1]**

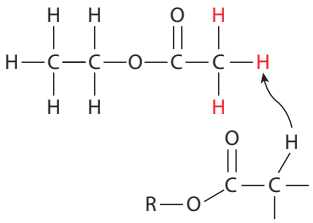
Reasoning – any three points for [1] each:

The NMR spectrum shows three sets of signals, and so, there are three different chemical environments for hydrogen atoms/protons. This means that isomer III can be eliminated because it has four different environments;

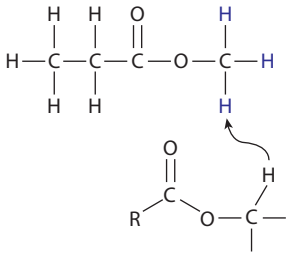
The ratio of the heights of the vertical steps in the integration trace is 3 : 2 : 3. There is a total of eight hydrogen atoms in one molecule, so this ratio indicates the numbers in each environment. Isomer IV can be eliminated because its ratio of hydrogen atoms in different environments is 6 : 1 : 1;

The splitting pattern is singlet, quartet, triplet. There are three H atoms with no H atoms on an adjacent carbon atom, two H atoms with three H atoms on an adjacent carbon atom, three H atoms with two H atoms on an adjacent carbon atom. Both isomers I and II have the splitting pattern shown in the spectrum (and so, have to be distinguished using chemical shifts);

If we consider the singlet in the spectra of isomers I and II, we can predict the following chemical shifts using Table 11.20:



δ = 2.0–2.5 ppm



δ = 3.7–4.8 ppm

The singlet in the spectrum occurs at 3.7 ppm;

An argument based on the quartet in the spectrum could also score this last mark. **[4]**

Chemistry for the IB Diploma – Owen © Cambridge University Press & Assessment 2023

Chapter 12

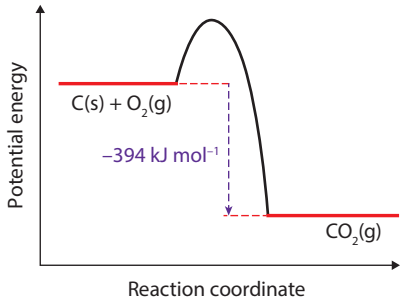
Test your understanding

1 **a** ΔH is negative, therefore exothermic, temperature goes up

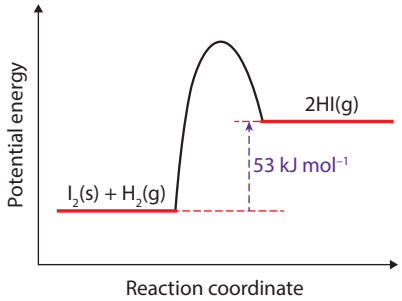
b ΔH is positive, therefore endothermic, temperature goes down

c ΔH is negative, therefore exothermic, temperature goes up

2 **a** ΔH is negative, therefore products more stable than the reactants.



b ΔH is positive, therefore products are less stable than the reactants.



3 **a** $Q = mc\Delta T$

$$\frac{3.00}{(2.00 \times 11.7)} = 0.128 \text{ J g}^{-1}\,°\text{C}^{-1}$$

b $Q = mc\Delta T$

$$\frac{50.0}{(100.0 \times 2.12)} = 0.236 \text{ J g}^{-1}\,°\text{C}^{-1}$$

4 **a** $\dfrac{10\,000}{4.18 \times 100} = 23.9°\text{C}$

b $\dfrac{40\,000}{4.18 \times 250} = 38.3°\text{C}$

c $\dfrac{10\,000\,000}{4.18 \times 10\,000} = 23.9°\text{C}$

5 $\Delta H = \dfrac{-Q}{n}$

divide by 1000 to convert to kJ.

Negative sign since all these are combustion reactions, so ΔH is negative.

a $\dfrac{-105\,000}{0.100 \times 1000} = \Delta H = -1050 \text{ kJ mol}^{-1}$

b $\dfrac{-84\,000}{0.042 \times 1000} = \Delta H = -2000 \text{ kJ mol}^{-1}$

c convert mass to amount in mol by dividing by molar mass.

$$\frac{-11000}{(0.500 \div 32.05) \times 1000} = \Delta H$$

$$\Delta H = -705 \text{ kJ mol}^{-1}$$

d $\dfrac{-6000}{(0.150 \div 78.12) \times 1000} = \Delta H$

$$\Delta H = -3120 \text{ kJ mol}^{-1}$$

e Convert volume to dm^3 before dividing by the molar volume (22.7 dm^3 mol^{-1}) to give the amount in mol.

$$\frac{-13000}{(0.200 \div 22.7) \times 1000} = \Delta H$$

$$\Delta H = -1480 \text{ kJ mol}^{-1}$$

6 **a** $Q = mc\Delta T$

$Q = 250.0 \times 4.18 \times 56.0 = 58\,520$ J

$n = \dfrac{1.20}{86.20} = 0.0139$ mol

$\Delta H = -\dfrac{Q}{n} = -\dfrac{58\,520}{0.0139}$

$= -4200000$ J mol^{-1}, so $\Delta H = -4200$ kJ mol^{-1}

b $Q = mc\Delta T$

$Q = 180.0 \times 4.18 \times 38.0 = 28\,591$ J

$n = \dfrac{0.870}{88.17} = 9.867 \times 10^{-3}$ mol

$\Delta H = -\dfrac{Q}{n} = -\dfrac{28\,591}{(9.867 \times 10^{-3})}$

$= -2\,900\,000$ J mol^{-1}, so

$\Delta H = -2900$ kJ mol^{-1}

c $Q = mc\Delta T$

$Q = 320.0 \times 4.18 \times 12.2 = 16\,329$ J

$n = \dfrac{0.521}{78.12} = 6.669 \times 10^{-3}$ mol

$\Delta H = -\dfrac{Q}{n} = -\dfrac{16\,329}{(6.669 \times 10^{-3})}$

$= -2\,450\,000$ J mol^{-1}, so $\Delta H = -2450$ kJ mol^{-1}

Chemistry for the IB Diploma – Owen © Cambridge University Press & Assessment 2023

d $Q = mc\Delta T$

$Q = 500\,000 \times 4.18 \times 46.0 = 96\,140\,000$ J

$n = \frac{2000}{114.26} = 17.50$ mol

$\Delta H = -\frac{Q}{n} = -\frac{96\,140\,000}{17.50}$

$= -5490000$ J mol^{-1}, so $\Delta H = -5490$ kJ mol^{-1}

7 a $Q = mc\Delta T$

$Q = 200.0 \times 4.18 \times (38.6 - 18.2) = 17\,054$ J

$n = \frac{(185.51 - 184.56)}{60.11} = 1.580 \times 10^{-2}$ mol

$\Delta H = -\frac{Q}{n} = -\frac{17\,054}{(1.580 \times 10^{-2})} = -1\,080\,000$ J mol^{-1}, so $\Delta H = -1080$ kJ mol^{-1}

b Heat energy loss to the surroundings; incomplete combustion; (other, more minor, factors include evaporation of water and/or propan-1-ol)

8 $Q = mc\Delta T$

$Q = 150.00 \times 4.18 \times (37.7 - 19.5) = 11\,411$ J

$n = \frac{(154.23 - 153.42)}{32.05} = 2.527 \times 10^{-2}$ mol

$\Delta H = -\frac{Q}{n} = -\frac{11411}{(2.527 \times 10^{-2})} -452000$ J mol^{-1}, so $\Delta H = -452$ kJ mol^{-1}

9 a $\frac{25.0 \times 4.18 \times 4.20}{\left(\frac{2.00}{85.00}\right) \times 1000} = \Delta H = +18.7$ kJ mol^{-1}

b $\frac{-50.0 \times 4.18 \times 1.80}{\left(\frac{1.20}{138.55}\right) \times 1000} = \Delta H = -43.4$ kJ mol^{-1}

c $\frac{-30.0 \times 4.18 \times 2.10}{\left(\frac{2.50}{138.93}\right) \times 1000} = \Delta H = +14.6$ kJ mol^{-1}

10 a $Q = mc\Delta T$

$Q = (200.0 + 100.0) \times 4.18 \times 1.36 = 1705$ J

amount of HCl $= \frac{200.0}{1000 \times 0.150} = 0.0300$ mol

amount of NaOH $= \frac{100.0}{1000 \times 0.300}$

$= 0.0300$ mol

Equivalent numbers of moles, therefore 0.0300 mol H_2O formed

$n = 0.0300$ mol

$\Delta H = -\frac{Q}{n} = -\frac{1705}{0.0300} = -56800$ J mol^{-1}, so

$\Delta H = -56.8$ kJ mol^{-1}

b i Double the number of moles, so twice as much heat energy given out. But twice the mass of solution to heat, therefore the temperature change is the same, 1.36°C

ii Double the number of moles, so twice as much heat energy given out, but the mass of solution stays the same, therefore the temperature change is double, 2.72°C

iii Half the number of moles, so half as much heat energy given out, but quarter the mass of solution to heat up, therefore the temperature change is double, 2.72°C

11 a $Q = mc\Delta T$

$Q = 50.0 \times 4.18 \times (29.1 - 21.5) = 1588$ J

$n = \frac{1.00}{95.21} = 1.050 \times 10^{-2}$ mol

$\Delta H = -\frac{Q}{n} = -\frac{1588}{(1.050 \times 10^{-2})}$

$= -151000$ J mol^{-1}, so

$\Delta H = -151$ kJ mol^{-1}

b Double the number of moles of $MgCl_2$, so twice as much heat energy given out, but twice the mass of water to heat up, therefore the temperature change stays the same, 7.6°C

c Double the number of moles of $MgCl_2$, so twice as much heat energy given out, but the same mass of water to heat up, therefore the temperature change is double, 15.2°C

Exam-style questions

1 B

2 C

3 A

4 D

5 B

6 a i $Q = 200 \times 4.18 \times 22.0 = 18392$ J;

amount of butan-1-ol $= \frac{0.75}{74.14}$

$= 0.0101$ mol;

$\frac{18392 / 0.0101}{1000} = 1818$ kJ mol^{-1}

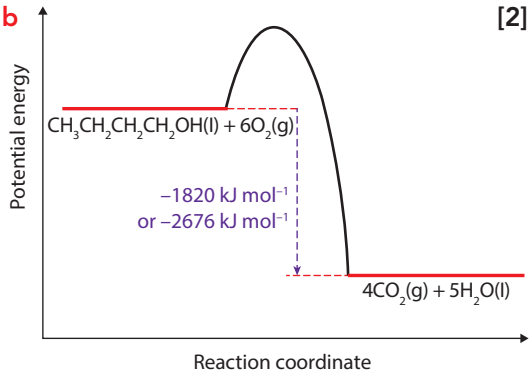
$\Delta H = -1820$ kJ mol^{-1}; **[3]**

Chemistry for the IB Diploma – Owen © Cambridge University Press & Assessment 2023

ii Heat loss to the surroundings – not all the heat energy from the combustion reaction goes to heating the water;

Incomplete combustion – insufficient oxygen supply for complete combustion – this gives out less energy than complete combustion; **[2]**

b **[2]**



for products lower than reactants and ΔH marked **[1]**

for everything else correct **[1]**

7 a To get the salts to dissolve as quickly as possible. If the salts dissolve slowly, there is more time for heat to be absorbed from/given out to the surroundings and the temperature rise/drop is not as large as it should be. **[1]**

b It is a good insulator – reduces heat loss to/heat gain from the surroundings. **[1]**

c $Q = mc\Delta T$

$Q = 50.0 \times 4.18 \times 4.05 = 846.45$ J;

amount of LiCl $= \frac{1.00}{42.39} = 0.02359$ mol;

$\frac{846.45 / 0.02359}{1000} = 35.88$ kJ mol^{-1}

$\Delta H = -35.9$ kJ mol^{-1}; **[4]**

Assumptions: the density of the solution is the same as that of water/the specific heat capacity of the solution is the same as that of water; **[4]**

d The first part of the conclusion is correct – the temperature goes up when lithium chloride dissolves but goes down when the other solids dissolve, therefore, the enthalpy change of solution of LiCl is exothermic, but those for the other salts are endothermic;

Because the temperature change for potassium chloride is much larger than that for sodium chloride, it can be deduced that potassium chloride has a more endothermic enthalpy of solution than sodium chloride.

This is also correct – the same mass was added in each experiment and, because the relative formula mass of KCl is larger than that of NaCl, fewer moles were added of KCl – if this caused a greater temperature change, the enthalpy change per mole must also have been larger;

From potassium chloride to caesium chloride, because the temperature change decreases, I can conclude that the enthalpy change of solution becomes less endothermic.

This is not correct – the same mass has been added in each experiment and not the same number of moles. The temperature change is smaller for CsCl than that for RbCl, but the number of moles of CsCl was smaller/the values of the enthalpy change of solution are RbCl +14.6 kJ mol^{-1} and CsCl +16.9 kJ mol^{-1}; **[3]**

8 a Lines cross at a maximum temperature of 23.6 °C. The maximum temperature change is 23.6 − 19.80 = 3.8 °C **[1]**

b $\frac{20.0}{1000} \times 0.400 = 8.00 \times 10^{-3}$ mol **[1]**

c 20.00 cm^3 of acid is neutralised by 5.50 cm^3 of alkali (where lines cross), so total volume is 25.50 cm^3. We make the assumption that this has the same density and specific heat capacity as water, so mass of water = 25.50 g;

$Q = 25.50 \times 4.18 \times 3.8 = 405.0$ J;

$\frac{405.0 / 8.00 \times 10^{-3}}{1000} = 50.6$ kJ mol^{-1}

$\Delta H = -51$ kJ mol^{-1} **[3]**

d All the acid has been neutralised when more than 5.50 cm^3 of NaOH is added, so the amount of heat energy given out is the same for 7 and 10 cm^3;

A greater mass of water/solution is being heated when 10 cm^3 is added; therefore, the temperature change is smaller; **[2]**

Chemistry for the IB Diploma – Owen © Cambridge University Press & Assessment 2023

Chapter 13

Test your understanding

1 a $Cl_2(g) \rightarrow 2Cl(g)$

b $HBr(g) \rightarrow H(g) + Br(g)$

2 a (2 × 436 + 498) – (4 × 463) = −482 kJ mol^{-1}

b (4 × 414 + 242) – (3 × 414 + 324 + 431) = −99 kJ mol^{-1}

c (2 × 346 + 614 + 8 × 414 + 436) – (3 × 346 + 10 × 414) = −124 kJ mol^{-1}

d (2 × 414 + 839 + 2 × 436) – (6 × 414 + 346) = −291 kJ mol^{-1}

e (346 + 614 + 6 × 414 + 431) – (2 × 346 + 7 × 414 + 324) = −39 kJ mol^{-1}

f (1070 + 242) – (804 + 2 × 324) = −140 kJ mol^{-1}

3 a (2 × 346 + 8 × 414 + 5 × 498) – (6 × 804 + 8 × 463) = −2034 kJ mol^{-1}

b (2 × 346 + 12 × 414 + 7 × 498) – (8 × 804 + 12 × 463) = −2842 kJ mol^{-1}

c (6 × 346 + 20 × 414 + 9 × 498) – (8 × 1070 + 20 × 463) = −2982 kJ mol^{-1}

d (1 × 614 + 4 × 414 + 3 × 498) – (4 × 804 + 4 × 463) = −1304 kJ mol^{-1}

e (2 × 839 + 4 × 414 + 3 × 498) – (4 × 1070 + 4 × 463) = −1304 kJ mol^{-1}

f (2 × 346 + 7 × 414 + 358 + 463 + 4.5 × 498) – (6 × 804 + 8 × 463) = −1876 kJ mol^{-1}

4 $\Delta H = \Sigma(\text{bonds broken}) - \Sigma(\text{bonds made})$

$-164 = (242 + 3 \times 159) - 6x$

Cl—F bond enthalpy = 147 kJ mol^{-1}

5 $\Delta H = \Sigma(\text{bonds broken}) - \Sigma(\text{bonds made})$

$-91 = (3x + 159) - 5x$

Cl—F bond enthalpy = 125 kJ mol^{-1}

6 a Reverse second equation to get $C_2H_5OH(g)$ on the right-hand side ⇒ +1415

$-1371 + 1415 = 44$ kJ mol^{-1}

b Divide first equation by 2.

Reverse second equation and divide by 2.

$\left[\frac{1}{2} \times -6544\right] + \left[\frac{1}{2} \times 6606\right] = 31$ kJ mol^{-1}

7 a Add the two equations together and cancel terms that are the same on each side to give the target equation.
−242 − 158 = −400 kJ mol^{-1}

b Reverse first equation and divide by 2 ⇒ $ClF_3(g)$ on left

Divide second equation by 2 ⇒ 1 $ClF_5(g)$ on right

$\left[\frac{1}{2} \times 328\right] + \left[\frac{1}{2} \times (-510)\right] = -91$ kJ mol^{-1}

8 a Reverse first equation and multiply by 2 ⇒ $4NH_3(g)$ on left.

Multiply second equation by 3 ⇒ $6H_2O(g)$ on right.

$[2 \times 92] + [3 \times -484] = -1268$ kJ mol^{-1}

b Reverse first equation and multiply by 3.

Multiply second equation by 2.

$[3 \times 1387] + [2 \times -1669] = 823$ kJ mol^{-1}

c Multiply first equation by 2

Leave second equation unchanged.

Multiply third equation by 2.

$[2 \times -297] + [-196] + [2 \times -130]$

$= -1050$ kJ mol^{-1}

9 Leave first equation unchanged.

Multiply second equation by 2

Reverse third equation ⇒ $C_2H_6(g)$ on right

$[-1300] + [2 \times -286] + [1560] = -312$ kJ mol^{-1}

10 Reverse first equation and multiply by 2 ⇒ $2C_6H_{14}(g)$ on left.

Multiply second equation by 2 to give correct number of $CO_2(g)$

Multiply third equation 14 to give correct number of $H_2O(g)$

$[2 \times -32] + [2 \times -4163] + [14 \times 44] = -7774$ kJ mol^{-1}

11 a $C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(l)$

b $C_2H_5OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l)$

12 $\Delta H = \Sigma\Delta H_c(\text{reactants}) - \Sigma\Delta H_c(\text{products})$

= (−2717 − 286) − (−2877) = −126 kJ mol^{-1}

Chemistry for the IB Diploma – Owen © Cambridge University Press & Assessment 2023

13 $\Delta H = \Sigma\Delta H_c(\text{reactants}) - \Sigma\Delta H_c(\text{products})$

$= (-1301 + 2 \times -286) - (-1561) = -312 \text{ kJ mol}^{-1}$

14 $\Delta H = \Sigma\Delta H_c(\text{reactants}) - \Sigma\Delta H_c(\text{products})$

$= (3 \times -394 + 3 \times -286) - (-1817)$

$= -223 \text{ kJ mol}^{-1}$

15 $\Delta H = \Sigma\Delta H_c(\text{reactants}) - \Sigma\Delta H_c(\text{products})$

$= (6 \times -394 + 6 \times -286) - (-2803)$

$= -1277 \text{ kJ mol}^{-1}$

16 **a** $\frac{1}{2}H_2(g) + \frac{1}{2}F_2(g) \rightarrow HF(g)$

b $\frac{3}{2}H_2(g) + C(s) + \frac{1}{2}Cl_2(g) \rightarrow CH_3Cl(g)$

c $H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l)$

d $6H_2(g) + 5C(s) + \frac{1}{2}O_2(g) \rightarrow C_5H_{11}OH(l)$

17 $\Delta H^\ominus = \Sigma\Delta H_f^\ominus(\text{products}) - \Sigma\Delta H_f^\ominus(\text{reactants})$

$= (2 \times -19.7) - (-59.4 + 0) = +20 \text{ kJ mol}^{-1}$

18 $(4 \times -1137 + 3 \times -19.7) - (4 \times -427 + 3 \times -775) =$
$-574.1 \text{ kJ mol}^{-1}$

19 **a** $[(-246 + (-597)] - [(-297 + (-444)] =$
-102 kJ mol^{-1}

b $(6 \times -314 + 3 \times -242) - (3 \times 80 + 10 \times -46)$
$= -2390 \text{ kJ mol}^{-1}$

c $\Delta H^\ominus = \Sigma\Delta H_f^\ominus(\text{products}) - \Sigma\Delta H_f^\ominus(\text{reactants})$

$-124 = (-444) - (\Delta H_f^\ominus + 0)$

$\Delta H_f^\ominus = -444 + 124 = -320 \text{ kJ mol}^{-1}$

enthalpy change of formation of $PCl_3(l)$
$= -320 \text{ kJ mol}^{-1}$

20 $\Delta H^\ominus = \Sigma\Delta H_f^\ominus(\text{products}) - \Sigma\Delta H_f^\ominus(\text{reactants})$

$602 = (4\Delta H_f^\ominus + 2 \times -217 + 0) - (2 \times -452)$

$4\Delta H_f^\ominus = 602 + 434 - 904 = 132 \text{ kJ mol}^{-1}$

$\Delta H_f^\ominus = +33 \text{ kJ mol}^{-1}$

21 $CH_3OH(l) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$

$\Delta H^\ominus = \Sigma\Delta H_f^\ominus(\text{products}) - \Sigma\Delta H_f^\ominus(\text{reactants})$

$\Delta H^\ominus = [-394 + 2 \times (-286)] - (-239 + 0)$
$= -727 \text{ kJ mol}^{-1}$

22 $5C(g) + 6H_2(g) \rightarrow C_5H_{12}(l)$

$\Delta H^\ominus = \Sigma\Delta H_c^\ominus(\text{reactants}) - \Sigma\Delta H_c^\ominus(\text{products})$

$\Delta H^\ominus = [5 \times (-394) + 6 \times (-286)] - (-3509)$
$= -177 \text{ kJ mol}^{-1}$

23 The equation for the enthalpy change of combustion of $H_2(g)$ is
$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l)$

This is the same as the equation for the enthalpy of formation of $H_2O(l)$, so we know $\Delta H_f^\ominus$ of $H_2O(l)$ is -286 kJ mol^{-1} and we can use

$\Delta H^\ominus = \Sigma\Delta H_f^\ominus(\text{products}) - \Sigma\Delta H_f^\ominus(\text{reactants})$

$\Delta H^\ominus = (-242) - (-286) = 44 \text{ kJ mol}^{-1}$

24 **a** $Ca(g) \rightarrow Ca^+(g) + e^-$

b $MgO(s) \rightarrow Mg^{2+}(g) + O^{2-}(g)$

c $N^-(g) + e^- \rightarrow N^{2-}(g)$

d $Br_2(g) \rightarrow 2Br(g)$

e $\frac{1}{2}I_2(s) \rightarrow I(g)$

f $Al^+(g) \rightarrow Al^{2+}(g) + e^-$

25 **a** always endothermic

b always endothermic

c always endothermic

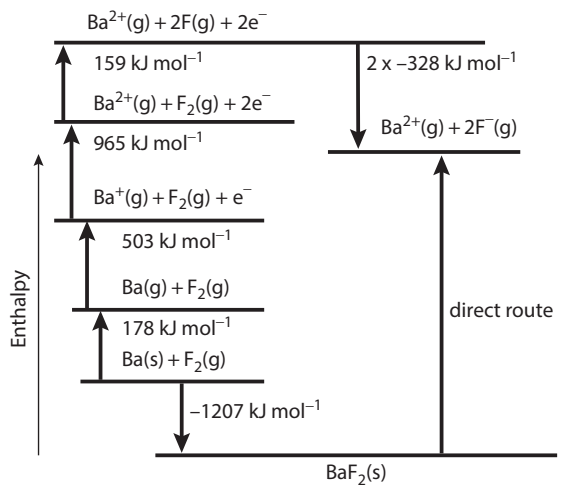
d sometimes exothermic and sometimes endothermic

e always exothermic

f always endothermic

26 $-112 - 418 - 90 - 394 + 670 = -344 \text{ kJ mol}^{-1}$

27



$1207 + 178 + 503 + 965 + 159 + (2 \times -328)$
$= 2356 \text{ kJ mol}^{-1}$

Chemistry for the IB Diploma – Owen © Cambridge University Press & Assessment 2023

Exam-style questions

1 C

2 A

3 C

4 A

5 B

6 A

7 C

8 B

9 C

10 B

11 D

12 B

13 a The average amount of energy required to break one mole of covalent bonds in a gaseous molecule under standard conditions;

'Average' refers to the fact that the bond enthalpy is different in different molecules and, therefore, the value quoted is the average amount of energy to break a particular bond in a range of typical molecules; **[2]**

b bonds broken = 346 + (5 × 414) +

+ 358 + 463 + (3 × 498) = 4731 kJ mol^{-1};

bonds made = 4 × 804 + 6 × 463 = 5994 kJ mol^{-1};

$\Delta H = \Sigma(\text{bonds broken}) - \Sigma(\text{bonds made})$

$\Delta H = 4731 - 5994 = -1263$ kJ mol^{-1} ; **[3]**

c i Two of the substances involved are in the liquid state, but bond enthalpies can be used only when all substances are in the gaseous state. (When substances are not in the liquid state, energy must also be supplied to overcome intermolecular forces, or energy is released when intermolecular forces are formed.) **[1]**

ii Rearrange the equations to produce the target equation:

$2CO_2(g) + 3H_2O(g) \rightarrow C_2H_5OH(g) + 3O_2(g)$ +1263 kJ mol^{-1}

$C_2H_5OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l)$ −1367 kJ mol^{-1}

$3H_2O(l) \rightarrow 3H_2O(g)$ 3 × 44 kJ mol^{-1}

$C_2H_5OH(l) \rightarrow C_2H_5OH(g)$

$\Delta H = 1263 - 1367 + (3 \times 44) = 28$ kJ mol^{-1} **[3]**

[1] for reversing first equation;

[1] for multiplying third equation by 3;

[1] for adding appropriate values to get final answer;

Correct final answer with no working scores **[3]**

14 bonds broken = (4 × 414) + (2 × 242) + (2 × 159) = 2458 kJ mol^{-1};

bonds made = (2 × 324) + (2 × 485) + (2 × 431) + (2 × 567) = 3614 kJ mol^{-1};

$\Delta H = \Sigma(\text{bonds broken}) - \Sigma(\text{bonds made})$

$\Delta H = 2458 - 3614 = -1156$ kJ mol^{-1}; **[3]**

15 a $q = mc\Delta T = 30.0 \times 4.18 \times (23.1 - 19.2)$

= 489.06 J;

amount of $LiClO_4 = \frac{2.00}{106.39} = 0.0188$ mol;

$\frac{489.06}{0.0188} = 26016$ J mol^{-1}

$\Delta H = -26.0$ kJ mol^{-1}; **[3]**

b $LiClO_4(s) \rightarrow LiClO_4(aq)$ −26.0 kJ mol^{-1}

$LiClO_4(aq) + 3H_2O(l) \rightarrow LiClO_4{\bullet}3H_2O(s)$ −32.6 kJ mol^{-1}

$LiClO_4(s) + 3H_2O(l) \rightarrow LiClO_4{\bullet}3H_2O(s)$

$\Delta H = -26.0 - 32.6 = -58.6$ kJ mol^{-1}

If −20.0 is used, the answer is −52.6 kJ mol^{-1}

[1] for reversing the equation

[1] for adding appropriate values to get final answer;

Correct final answer with no working scores **[2]**

Chemistry for the IB Diploma – Owen © Cambridge University Press & Assessment 2023

16 a $4H_2(g) + 3C(s) + \frac{1}{2}O_2(g) \rightarrow C_3H_7OH(l)$ **[1]**

b $\Delta H = \sum \Delta H_c(\text{reactants}) - \sum \Delta H_c(\text{products})$

$4 \times -286 + 3 \times -394 = -2326$ kJ mol^{-1};

$-2326 + 2021 = -305$ kJ mol^{-1}; **[2]**

17 a **[1]**

b $N_2(g) + 2H_2(g) \rightarrow N_2H_4(g)$ **[1]**

c bonds broken = 945 + 2 × 436
= 1817 kJ mol^{-1};

bonds made = 158 + 4 × 391
= 1722 kJ mol^{-1};

$\Delta H = \Sigma(\text{bonds broken}) - \Sigma(\text{bonds made})$

$\Delta H = 1817 - 1722 = 95$ kJ mol^{-1}; **[3]**

d $\Delta H_r = \sum \Delta H_f(\text{products}) - \sum \Delta H_f$

(reactants) $-622 = 2 \times -286 - \Delta H$; **[2]**

$\Delta H = +50$ kJ mol^{-1}

e $\Delta H_r = \sum \Delta H_f(\text{products}) - \sum \Delta H_f$

(reactants) $\Delta H = 95 - 50 = 45$ kJ mol^{-1} **[1]**

18 a $\Delta H_r = \sum \Delta H_f(\text{products}) - \sum \Delta H_f(\text{reactants})$

$\Delta H = 6 \times -111 + 8 \times -286 - (2 \times -105)$;

$= -2744$ kJ mol^{-1} **[2]**

b $C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(l)$ -2219 kJ mol^{-1}

$3CO(g) + 4H_2O(l) \rightarrow C_3H_8(g) + 3.5O_2(g)$ $+2744/2$ kJ mol^{-1}

$3CO(g) + 1.5O_2(g) \rightarrow 3CO_2(g)$ -847 kJ mol^{-1};

$\frac{-847}{3} = -282$ kJ mol^{-1}; **[3]**

[1] for reversing equation and dividing by 2

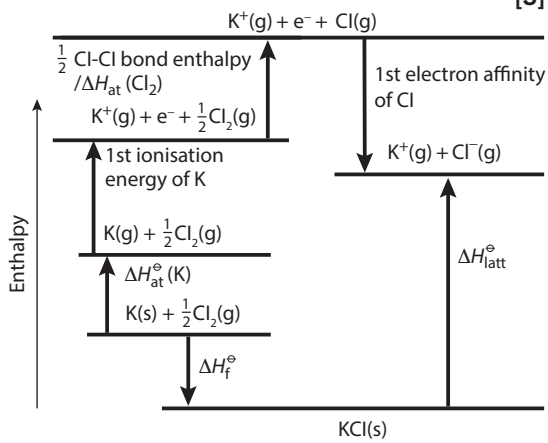
Correct final answer with no working scores **[3]**

19 a i $KCl(s) \rightarrow K^+(g) + Cl^-(g)$

ii $Cl(g) + e^- \rightarrow Cl^-(g)$

iii $K(g) \rightarrow K^+(g) + e^-$ **[3]**

b i **[3]**



All upward arrows represent endothermic processes and all downward arrows represent exothermic processes.

for the species present at each step **[1]**

for the labels for the enthalpy changes **[1]**

for statement/description about which enthalpy changes are exothermic and which endothermic **[1]**

ii $\Delta H_{latt}^{\ominus} = -(-436) + 90 + 418 + \frac{242}{2} - 364$;

$= 701$ kJ mol^{-1}; **[2]**

Chemistry for the IB Diploma – Owen © Cambridge University Press & Assessment 2023

Chapter 14

Test your understanding

1 a S gains O/increase in oxidation state from 0 to +4

b Na gains O/increase in oxidation state from 0 to +1

c $(CH_3)_2CO$ gains O/increase in average oxidation state of C from −1.33 to +4

2

	Substance that gets oxidised	Substance that gets reduced	Oxidising agent	Reducing agent
a	C	O_2	O_2	C
b	C_3H_8	O_2	O_2	C_3H_8
c	C	CuO	CuO	C
d	Mg	NO	NO	Mg
e	Ca	H_2O	H_2O	Ca

3 a $C_2H_4(g) + 3O_2(g) \rightarrow 2CO_2(g) + 2H_2O(l)$

b $C_5H_{12}(l) + 8O_2(g) \rightarrow 5CO_2(g) + 6H_2O(l)$

c $2C_8H_{18}(l) + 25O_2(g) \rightarrow 16CO_2(g) + 18H_2O(l)$

d $2CH_3OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 4H_2O(l)$

e $CH_3CH_2CH_2CH_2OH(l) + 6O_2(g) \rightarrow 4CO_2(g) + 5H_2O(l)$

4 a $C_2H_4(g) + 2O_2(g) \rightarrow 2CO(g) + 2H_2O(l)$

b $2C_2H_2(g) + O_2(g) \rightarrow 4C(s) + 2H_2O(l)$

c $2C_6H_{14}(l) + 13O_2(g) \rightarrow 12CO(g) + 14H_2O(l)$

d $C_3H_7OH(l) + 3O_2(g) \rightarrow 3CO(g) + 4H_2O(l)$

e $2C_5H_{11}OH(l) + 5O_2(g) \rightarrow 10C(g) + 12H_2O(l)$

5 Energy released per g $= \dfrac{-\Delta H_c}{\text{molar mass}}$

a $\dfrac{726}{32.05} = 22.7\ \text{kJ g}^{-1}$

b $\dfrac{4163}{86.20} = 48.3\ \text{kJ g}^{-1}$

c $\dfrac{1367}{46.08} = 29.7\ \text{kJ g}^{-1}$

d $\dfrac{2219}{44.11} = 50.3\ \text{kJ g}^{-1}$

6 a $\dfrac{50.8}{2.62} = 19.4\ \text{kJ g}^{-1}$

b Energy released in kJ is $\dfrac{8570}{1000} = 8.57$ kJ

$\dfrac{8.57}{0.180} = 47.6\ \text{kJ g}^{-1}$

c Energy released in kJ is $\dfrac{2800}{1000} = 2.80$ kJ

$\dfrac{2.80}{0.0560} = 50.0\ \text{kJ g}^{-1}$

Chemistry for the IB Diploma – Owen © Cambridge University Press & Assessment 2023

7

		Mass of CO_2 produced per gram of fuel burned	Mass of CO_2 produced per kJ of energy released
a	$CH_3OH(l)+\frac{3}{2}O_2(g)\rightarrow CO_2(g)+2H_2O(l)$	$\frac{44.01}{32.05}=1.37$ g	$\frac{44.01}{726}=0.0606$ g
b	$C_6H_{14}(l)+\frac{19}{2}O_2(g)\rightarrow 6CO_2(g)+7H_2O(l)$	$\frac{6\times44.01}{86.20}=3.06$ g	$\frac{6\times44.01}{4163}=0.0634$ g
c	$C_2H_5OH(l)+3O_2(g)\rightarrow 2CO_2(g)+3H_2O(l)$	$\frac{2\times44.01}{46.08}=1.91$ g	$\frac{2\times44.01}{1367}=0.0644$ g
d	$C_2H_6(g)+\frac{7}{2}O_2(g)\rightarrow 2CO_2(g)+3H_2O(l)$	$\frac{2\times44.01}{30.08}=2.93$ g	$\frac{2\times44.01}{1561}=0.0564$ g
e	$C_2H_4(g)+3O_2(g)\rightarrow 2CO_2(g)+2H_2O(l)$	$\frac{2\times44.01}{28.06}=3.14$ g	$\frac{2\times44.01}{1411}=0.0624$ g
f	$C_2H_2(g)+\frac{5}{2}O_2(g)\rightarrow 2CO_2(g)+H_2O(l)$	$\frac{2\times44.01}{26.04}=3.38$ g	$\frac{2\times44.01}{1300}=0.0677$ g
g	$C_6H_6(l)+\frac{15}{2}O_2(g)\rightarrow 6CO_2(g)+3H_2O(l)$	$\frac{6\times44.01}{78.12}=3.38$ g	$\frac{6\times44.01}{3268}=0.0808$ g

8 a mass of CO_2 produced per gram of fuel burned:

ethanol < ethane < ethene < ethyne

Ethanol has the lowest value, so the lowest mass of CO_2 produced per gram of fuel burnt. For the hydrocarbons, the mass of CO_2 produced per gram of fuel burnt increases as the C:H ratio increases.

b mass of CO_2 produced per kJ of energy released:

ethane < ethene < ethanol < ethyne

Ethane has the lowest value, so the lowest mass of CO_2 produced per kJ of energy released. For the hydrocarbons, the mass of CO_2 produced per kJ of energy released increases as the C : H ratio increases.

From the data of both parts, ethane and ethanol are the best fuels in terms of mass of CO_2 produced per gram of fuel burnt and per kJ of energy released.

9 a $H_2(g)+2OH^-(aq)\rightarrow 2H_2O(l)+2e^-$

b $2H^+(aq)+\frac{1}{2}O_2(g)+2e^-\rightarrow H_2O(l)$

c $CH_3OH(aq) + H_2O(l) \rightarrow CO_2(g) + 6H^+(aq) + 6e^-$

10 a oxidation (loss of electrons)

b reduction (gain of electrons)

c oxidation (loss of electrons)

11 a $H_2(g)+\frac{1}{2}O_2(g)\rightarrow H_2O(l)$

b $CH_3OH(aq)+\frac{3}{2}O_2(g)\rightarrow CO_2(g)+2H_2O(l)$

Exam-style questions

1 D

2 C

3 A

4 A

5 B

6 a i $2H_2(g)+O_2(g)\rightarrow 2H_2O(l)$ [1]

ii H_2 – it reduces the oxygen – the oxidation state of H increases and that of oxygen decreases. [1]

b H_2: $\frac{286}{2.02}=142$ kJ g^{-1};

CH_4: $\frac{891}{16.05}=55.5$ kJ g^{-1}; [2]

c Only water (and not CO_2) is produced when it burns/supplies essentially unlimited as it can be made from water. [1]

Chemistry for the IB Diploma – Owen © Cambridge University Press & Assessment 2023

d anode: $H_2(g) \rightarrow 2H^+(aq) + 2e^-$;

cathode:

$2H^+(aq) + \frac{1}{2}O_2(g) + 2e^- \rightarrow H_2O(l)$

[1] max if anode and cathode not specified **[2]**

e Explosive gas/difficult to store/production of hydrogen uses large amounts of energy/fossil fuels/ production can generate large amount of greenhouse gases. **[1]**

7 a Renewable energy sources are naturally replenished – they will not run out, but non-renewable energy sources are finite – they will eventually run out. **[1]**

b

Advantages – any 2 – [1] each	Disadvantages – any 1 for [1]
A cleaner fuel – undergoes more complete combustion than coal;	Methane is a powerful greenhouse gas, and leaks during production and transportation of natural gas contribute to climate change;
Produces less particulates/soot (C) or gases that contribute to acid rain when it burns;	Risk of explosions due to leaks;
Easily transported in pipelines and tankers;	More diffcult to store than coal because it is a gas – must be stored under pressure or cooled to liquefy it;
Releases a higher quantity of energy per kg than coal or oil;	
Produces less CO_2 per kJ of energy released than coal or oil;	

[3]

c $2C_8H_{18} + 17O_2 \rightarrow 16CO + 18H_2O$ **[2]**

for all formulas correct **[1]**

for correct balancing **[1]**

d $\frac{3203}{114.26} = 28.03$ kJ **[1]**

e Incomplete combustion releases less energy than complete combustion;

Incomplete combustion produces carbon monoxide, which is toxic/incomplete combustion produces particulates, which can be harmful to health and the environment/contribute to climate change; **[2]**

8 a A biofuel is a fuel derived from biomass/ material of plant or animal origin. **[1]**

b $6CO_2 + 6H_2O \rightarrow C_6H_{12}O_6 + 6O_2$ **[1]**

c $C_2H_5OH + 3O_2 \rightarrow 2CO_2 + 3H_2O$ **[1]**

d i ethanol: $\frac{1367}{46.08} = 29.67$ kJ

octane: $\frac{5470}{114.26} = 47.87$ kJ;

octane releases more energy per gram of fuel burnt; **[2]**

ii $2C_8H_{18} + 25O_2 \rightarrow 16CO_2 + 18H_2O$;

O_2 is the oxidizing agent – O is reduced/the oxidation state of O decreases (from 0 to −2); **[2]**

iii octane: $C_8H_{18} + \frac{25}{2}O_2 \rightarrow 8CO_2 + 9H_2O$

$8 \times 44.01 = 352.08$ g of CO_2 produced when 5470 kJ produced

$\frac{352.08}{5470} = 0.0644$ g per kJ;

Ethanol: $C_2H_5OH + 3O_2 \rightarrow 2CO_2 + 3H_2O$

$2 \times 44.01 = 88.02$ g of CO_2 produced when 1367 kJ produced

$\frac{88.02}{1367} = 0.0644$ g per kJ and they both release the same mass of CO_2 per kJ of energy released; **[2]**

e Advantages – *any one*

Biofuels are renewable but liquid fossil fuels are not – more sugar cane/corn can be grown to make more ethanol, etc., but fossil fuels will eventually run out;

Biofuels can be produced locally and reduce reliance on expensive oil imports from other countries/only some countries have reserves of crude oil, but biofuel crops can be grown much more widely;

Chemistry for the IB Diploma – Owen © Cambridge University Press & Assessment 2023

Biofuels can be produced from waste materials, e.g., biodiesel from waste plant oils;

Biofuels are biodegradable, and so, the potential environmental impact of spillages of biofuels is considerably lower than that of a spillage of fossil fuels;

Disadvantages – *any one*

Growing biofuel crops requires large areas of land that could be used for growing crops for food;

Clearing land for growing crops for biofuels could destroy animal habitats/deforestation contributes to climate change; **[2]**

9

Fuel	Equation	Mass of CO_2 produced per mole of fuel burned	Mass of CO_2 produced per gram of fuel burned	Mass of CO_2 produced per kJ of energy released
methane	$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$	$1 \times 44.01 = 44.01$ g	$\frac{44.01}{16.05} = 2.74$ g	$\frac{44.01}{891} = 0.0494$ g
but-1-ene	$C_4H_8(g) + 6O_2(g) \rightarrow 4CO_2(g) + 4H_2O(l)$	4×44.01 176.0 g	$\frac{4 \times 44.01}{56.12} = 3.14$ g	$\frac{4 \times 44.01}{2718} = 0.0648$ g
benzene	$C_6H_6(l) + \frac{15}{2}O_2(g) \rightarrow 6CO_2(g) + 3H_2O(l)$	$6 \times 44.01 = 2905$ g	$\frac{6 \times 44.01}{78.12} = 3.38$ g	$\frac{6 \times 44.01}{3268} = 0.0808$ g

for all three equations **[1]**

for each correct row in the table **[1]**

Methane has the highest ratio of H : C and benzene has the lowest ratio so this statement is correct for the three substances here – methane produces the lowest mass of CO_2 in each category and benzene the highest mass;

For this statement to be proved more generally true, other compounds would have to be investigated/all the compounds here are hydrocarbons; **[6]**

Chemistry for the IB Diploma – Owen © Cambridge University Press & Assessment 2023

Chapter 15

Test your understanding

1 **a** decrease; decrease in the number of moles of gas

b decrease; decrease in the number of moles of gas

c increase; increase in the number of moles of gas

d increase; increase in the number of moles of gas

e decrease; decrease in the number of moles of gas

2 All of these questions use the equation:

$\Delta S^{\ominus} = \Sigma S^{\ominus}(\text{products}) - \Sigma S^{\ominus}(\text{reactants})$

a $(2\times70)-(2\times131+205)=-327\ \text{J K}^{-1}\ \text{mol}^{-1}$

b $189-(131+0.5\times205)=-44.5\ \text{J K}^{-1}\ \text{mol}^{-1}$

c $(214+2\times70)-(186+2\times205)$
$=-242\ \text{J K}^{-1}\ \text{mol}^{-1}$

d $(4\times214+5\times70)-(226+6\times205)$
$=-250\ \text{J K}^{-1}\ \text{mol}^{-1}$

e $(2\times43+4\times240+205)-(2\times193)$
$=865\ \text{J K}^{-1}\ \text{mol}^{-1}$

f $(4\times254+3\times282+3\times223)$
$-(4\times206+3\times292)=831\ \text{J K}^{-1}\ \text{mol}^{-1}$

3 All of these questions use the equation:

$\Delta G^{\ominus} = \Delta H^{\ominus} - T\Delta S^{\ominus}$

T must be in K. $\Delta S^{\ominus}$ is in J but $\Delta H^{\ominus}$ is in kJ, therefore $\Delta S^{\ominus}$ must be divided by 1000.

a $\Delta G^{\ominus}=-891-298.15\times\frac{-243}{1000}=-819\ \text{kJ mol}^{-1}$

Spontaneous because $\Delta G^{\ominus}$ is negative

b $\Delta G^{\ominus}=572-298.15\times\frac{327}{1000}=+475\ \text{kJ mol}^{-1}$

Not spontaneous because $\Delta G^{\ominus}$ is positive

c $\Delta G^{\ominus}=-137-298.15\times\frac{-55}{1000}=-121\ \text{kJ mol}^{-1}$

Spontaneous because $\Delta G^{\ominus}$ is negative

d $\Delta G^{\ominus} = -2219 - 298.15\times\frac{-373}{1000}$
$= -2108\ \text{kJ mol}^{-1}$

Spontaneous because $\Delta G^{\ominus}$ is negative

4 All of these questions use the equation:

$\Delta G^{\ominus} = \Delta H^{\ominus} - T\Delta S^{\ominus}$

T must be in K. $\Delta S^{\ominus}$ is in J but $\Delta H^{\ominus}$ is in kJ, therefore $\Delta S^{\ominus}$ must be divided by 1000.

a $\Delta G^{\ominus} = -1170 - 310.15\times\frac{-534}{1000}$
$= -1000\ \text{kJ mol}^{-1}$

Spontaneous because $\Delta G^{\ominus}$ is negative

b $\Delta G^{\ominus}=178-373.15\times\frac{161}{1000}=+118\ \text{kJ mol}^{-1}$

Not spontaneous because $\Delta G^{\ominus}$ is positive

c $\Delta G^{\ominus}=-25-773.15\times\frac{16}{1000}=-37\ \text{kJ mol}^{-1}$

Spontaneous because $\Delta G^{\ominus}$ is negative

d $\Delta G^{\ominus}=251-1273.15\times\frac{7.8}{1000}=241\ \text{kJ mol}^{-1}$

Not spontaneous because $\Delta G^{\ominus}$ is positive

5 **a** Rearranging $\Delta G^{\ominus} = \Delta H^{\ominus} - T\Delta S^{\ominus}$ we get

$\Delta S^{\ominus} = \frac{\Delta H^{\ominus} - \Delta G^{\ominus}}{T}$

The values of $\Delta H^{\ominus}$ and $\Delta G^{\ominus}$ are multiplied by 1000 to convert to J, which is required for the units of $\Delta S^{\ominus}$.

$\Delta S^{\ominus} = \frac{-144000-(-133000)}{298.15}$
$=-36.9\ \text{J K}^{-1}\ \text{mol}^{-1}$

b Rearranging $\Delta G^{\ominus} = \Delta H^{\ominus} - T\Delta S^{\ominus}$ we get

$\Delta H^{\ominus} = \Delta G^{\ominus} + T\Delta S^{\ominus}$

$\Delta H^{\ominus} = -1139+298.15\times\frac{-184}{1000}=-1194\ \text{kJ mol}^{-1}$

6 Rearranging $\Delta G^{\ominus} = \Delta H^{\ominus} - T\Delta S^{\ominus}$ we get

$T = \frac{\Delta H^{\ominus} - \Delta G^{\ominus}}{\Delta S^{\ominus}}$

The temperature at which the reaction becomes spontaneous is that when $\Delta G^{\ominus} = 0$, so $T = \frac{\Delta H^{\ominus}}{\Delta S^{\ominus}}$

$\Delta H^{\ominus}$ and $\Delta S^{\ominus}$ must be in the same units, so $\Delta H^{\ominus}$ is multiplied by 1000 to convert it to J.

$T = \frac{179000}{160} = 1119\ \text{K}$

7 $T = \frac{82000}{108} = 759\ \text{K}$

8 $T = \frac{250000}{243} = 1029\ \text{K}$

Chemistry for the IB Diploma – Owen © Cambridge University Press & Assessment 2023

9 a Rearranging $\Delta G^{\ominus} = \Delta H^{\ominus} - T\Delta S^{\ominus}$ we get

$$\Delta S^{\ominus} = \frac{\Delta H^{\ominus} - \Delta G^{\ominus}}{T}$$

The values of $\Delta H^{\ominus}$ and $\Delta G^{\ominus}$ are multiplied by 1000 to convert to J, which is required for the units of $\Delta S^{\ominus}$.

$$\Delta S^{\ominus} = \frac{598000 - 333000}{298} = 889 \text{ J K}^{-1} \text{ mol}^{-1}$$

b $\Delta G^{\ominus} = 0$, so

$$T = \frac{\Delta H^{\ominus}}{\Delta S^{\ominus}}$$

$\Delta H^{\ominus}$ and $\Delta S^{\ominus}$ must be in the same units, so $\Delta H^{\ominus}$ is multiplied by 1000 to convert it to J.

$$T = \frac{598000}{889} = 673 \text{ K}$$

$$673 - 273.15 = 400\,°\text{C}$$

The temperature in K was to 3 significant figures with no decimal places and when we subtract numbers we keep the lower number of decimal places, that is zero.

10 The boiling point is the temperature at which liquid → gas becomes spontaneous. At this point, $\Delta G^{\ominus} = 0$, so

$$T = \frac{\Delta H^{\ominus}}{\Delta S^{\ominus}}$$

$$T = \frac{30900}{93.3} = 331 \text{ K}$$

$$331 - 273.15 = 58\ °\text{C}$$

11 Using $\Delta G^{\ominus} = \Delta H^{\ominus} - T\Delta S^{\ominus}$, if $\Delta S^{\ominus}$ is positive then $-T\Delta S^{\ominus}$ is negative and, as T (always positive) increases, $-T\Delta S^{\ominus}$ becomes more negative, so $\Delta G^{\ominus}$ becomes more negative, i.e., more spontaneous. So, in general, if $\Delta S^{\ominus}$ is positive, the reaction becomes more spontaneous as temperature increases and if $\Delta S^{\ominus}$ is negative, it becomes less spontaneous.

a more spontaneous because ΔS is positive (increase in the number of moles of gas from left to right)

b less spontaneous because ΔS is negative (decrease in the number of moles of gas)

c more spontaneous because ΔS is positive (increase in the number of moles of gas)

d more spontaneous because ΔS is positive (increase in the number of moles of gas)

12 a i $Q = \frac{[Z]}{[X]} = \frac{1.0}{2.0} = 0.50$

$\ln Q = \ln\ 0.50 = -0.69$

$\Delta G = \Delta G^{\ominus} + RT \ln Q$

$= -3000 + (8.31 \times 298.15 \times -0.69)$

$= -4700 \text{ J mol}^{-1}$

or -4.7 kJ mol^{-1}

Will move to right towards equilibrium because ΔG is negative

ii $Q = \frac{[Z]}{[X]} = \frac{2.0}{1.0} = 2.0$

$\ln Q = \ln 2.0 = 0.69$

$\Delta G = \Delta G^{\ominus} + RT \ln Q$

$= -3000 + (8.31 \times 298.15 \times 0.69)$

$= -1300 \text{ J mol}^{-1}$

or -1.3 kJ mol^{-1}

Will move to right towards equilibrium because ΔG is negative

b i $Q = \frac{[B]}{[A]} = \frac{10.0}{0.50} = 20$

$\ln Q = \ln 20 = 3.0$

$\Delta G = \Delta G^{\ominus} + RT \ln Q$

$= 2000 + (8.31 \times 300.15 \times 3.0)$

$= 9500 \text{ J mol}^{-1}$

or 9.5 kJ mol^{-1}

Will move to left towards equilibrium because ΔG is positive

ii $Q = \frac{[B]}{[A]} = \frac{0.010}{0.10} = 0.10$

$\ln Q = \ln 0.10 = -2.3$

$\Delta G = \Delta G^{\ominus} + RT \ln Q$

$= 2000 + (8.31 \times 323.15 \times -2.3)$

$= -4200 \text{ J mol}^{-1}$

or -4.2 kJ mol^{-1}

Will move to right towards equilibrium because ΔG is negative

c i $Q = \frac{[D]}{[C]} = \frac{4.0 \times 10^{-4}}{0.020} = 0.020$

$\ln Q = \ln 0.020 = -3.9$

$\Delta G = \Delta G^{\ominus} + RT \ln Q$

$= -5000 + (8.31 \times 298.15 \times -3.9)$

$= -15000 \text{ J mol}^{-1}$

or -15 kJ mol^{-1}

Will move to right towards equilibrium because ΔG is negative

Chemistry for the IB Diploma – Owen © Cambridge University Press & Assessment 2023

ii $Q = \frac{[D]}{[C]} = \frac{0.10}{0.050} = 2.0$

$\ln Q = \ln 2.0 = 0.693$

$\Delta G = \Delta G^{\ominus} + RT \ln Q$

$= -5000 + (8.31 \times 298.15 \times 0.693)$

$= -3300 \text{ J mol}^{-1}$

or -3.3 kJ mol^{-1}

Will move to right towards equilibrium because ΔG is negative

d i $Q = \frac{[F]}{[E]} = \frac{0.80}{5.0 \times 10^{-3}} = 160$

$\ln Q = \ln 160 = 5.1$

$\Delta G = \Delta G^{\ominus} + RT \ln Q =$

$20000 + (8.31 \times 293.15 \times 5.1) = 32000 \text{ J mol}^{-1}$

or 32 kJ mol^{-1}

Will move to left towards equilibrium because ΔG is positive

ii $Q = \frac{[F]}{[E]} = \frac{5.0 \times 10^{-4}}{0.10} = 5.0 \times 10^{-3}$

$\ln Q = \ln(5.0 \times 10^{-3}) = -5.3$

$\Delta G = \Delta G^{\ominus} + RT \ln Q$

$= 20000 + (8.31 \times 296.15 \times -5.3)$

$= 7000 \text{ J mol}^{-1}$

or 7.0 kJ mol^{-1}

Will move to left towards equilibrium because ΔG is positive

Exam-style questions

1 D

2 B

3 B

4 A

5 B

6 B

7 a $\Delta H^{\ominus} = \Sigma\Delta H_f^{\ominus}(\text{products}) - \Sigma\Delta H_f^{\ominus}(\text{reactants})$

$= [(3 \times -394) + (4 \times -286)] - (-316)$

$= -2010 \text{ kJ mol}^{-1}$ **[2]**

b $C_3H_7OH(l) + 4.5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(l)$

$\Delta S^{\ominus} = \Sigma S^{\ominus}(\text{products}) - \Sigma S^{\ominus}(\text{reactants})$

$\Delta S = [(3 \times 214) + (4 \times 69.9)] - [(1 \times 196.6) + (4.5 \times 205)]$

$\Delta S^{\ominus} = -197.5 \text{ J K}^{-1} \text{ mol}^{-1}$;

The sign of $\Delta S^{\ominus}$ is negative because the reaction involves a decrease in the number of moles of gas (4.5 on the left-hand side but only 3 on the right-hand side) therefore, a decrease in disorder/a decrease in the number of ways the available energy can be distributed among the particles; **[2]**

c For the complete combustion of propan-1-ol:

$\Delta H^{\ominus} = -2010 \text{ kJ mol}^{-1}$

$\Delta S^{\ominus} = -197.5 \text{ J K}^{-1} \text{ mol}^{-1}$

At 298.15 K:

$\Delta G^{\ominus} = \Delta H^{\ominus} - T\Delta S^{\ominus}$

$\Delta G^{\ominus} = -2010 - 298.15 \times -\frac{197.5}{1000}$

Therefore, $\Delta G^{\ominus} = -1951 \text{ kJ mol}^{-1}$;

$\Delta G^{\ominus}$ is negative, so the reaction is spontaneous at 25°C; **[2]**

8 a $\Delta H^{\ominus} = \Sigma\Delta H_f^{\ominus}(\text{products}) - \Sigma\Delta H_f(\text{reactants})$

$\Delta H^{\ominus} = -241.8 + 285.8 = 44 \text{ kJ mol}^{-1}$ **[1]**

b $\Delta S^{\ominus} = \Sigma S^{\ominus}(\text{products}) - \Sigma S^{\ominus}(\text{reactants})$

$\Delta S^{\ominus} = 188.8 - 70.0$

$\Delta S^{\ominus} = 118.8 \text{ J K}^{-1} \text{ mol}^{-1}$ **[1]**

c $\Delta G^{\ominus} = \Delta H^{\ominus} - T\Delta S^{\ominus}$

$\Delta G^{\ominus} = 44 - 298.15 \times \frac{118.8}{1000}$

Therefore, $\Delta G^{\ominus} = 8.6 \text{ kJ mol}^{-1}$;

$\Delta G^{\ominus}$ is positive, so the reaction is not spontaneous at 25.00 °C; **[2]**

d The process becomes spontaneous when $\Delta G^{\ominus} < 0$

$0 = \Delta H^{\ominus} - T\Delta S^{\ominus}$

$0 = 44 - T \times \frac{118.8}{1000}$;

Therefore T = 370 K

$370 - 273.15 = 97°C$; **[2]**

Chemistry for the IB Diploma – Owen © Cambridge University Press & Assessment 2023

e The process represents the boiling of water, so the answer should be 100 °C. The temperature is not exactly this because the values of $\Delta H^{\ominus}$ and $\Delta S^{\ominus}$ vary with temperature (and we have used the values for 298.15 K). **[1]**

9 **a** $\Delta S^{\ominus} = \Sigma S^{\ominus}(\text{products}) - \Sigma S^{\ominus}(\text{reactants})$

$\Delta S^{\ominus} = 2 \times 210.8 - (191.6 + 205.2)$

$\Delta S^{\ominus} = 24.8 \text{ J K}^{-1} \text{ mol}^{-1}$ **[1]**

b $\Delta G^{\ominus} = \Delta H^{\ominus} - T\Delta S^{\ominus}$

$\Delta G^{\ominus} = 182.6 - 298.15 \times \frac{24.8}{1000}$;

Therefore, $\Delta G^{\ominus} = 175 \text{ kJ mol}^{-1}$; **[2]**

c $0 = \Delta H^{\ominus} - T\Delta S^{\ominus}$

$0 = 182.6 - T \times \frac{24.8}{1000}$

Therefore, $T = 7362$ K;

$7362 - 273.15 = 7090°\text{C}$; **[2]**

The temperature here is very high and the oxygen, especially, will be mostly dissociated into its atoms at this temperature and so the calculation is not really valid!

Chemistry for the IB Diploma – Owen © Cambridge University Press & Assessment 2023

Chapter 16

Test your understanding

1 a $2NO + O_2 \rightarrow 2NO_2$

b $C_3H_8 + 5O_2 \rightarrow 3CO_2 + 4H_2O$

c $CaCO_3 + 2HCl \rightarrow CaCl_2 + CO_2 + H_2O$

d $C_2H_5OH + 3O_2 \rightarrow 2CO_2 + 3H_2O$

e $WO_3 + 3H_2 \rightarrow W + 3H_2O$

f $2H_2O_2 \rightarrow O_2 + 2H_2O$

g $4CrO_3 \rightarrow 2Cr_2O_3 + 3O_2$

h $Al_4C_3 + 6H_2O \rightarrow 3CH_4 + 2Al_2O_3$

i $8HI + H_2SO_4 \rightarrow H_2S + 4H_2O + 4I_2$

j $4PH_3 + 8O_2 \rightarrow P_4O_{10} + 6H_2O$

2 a $\frac{2.00}{55.85} = 0.0358 \text{ mol}$

b $\frac{0.400}{40.00} = 0.0100 \text{ mol}$

c $\frac{1200}{44.01} = 27.3 \text{ mol}$

d $\frac{5.00}{249.72} = 0.0200 \text{ mol}$

e $\frac{10.0}{22.7} = 0.441 \text{ mol}$

f $\frac{0.500}{22.7} = 0.0220 \text{ mol}$

g $\frac{0.0300}{22.7} = 1.32 \times 10^{-3} \text{ mol}$

3 a $\frac{25.0}{1000} \times 0.200 = 5.00 \times 10^{-3} \text{ mol}$

b $\frac{28.2}{1000} \times 0.100 = 2.82 \times 10^{-3} \text{ mol}$

c $\frac{32.0}{1000} \times 0.0200 = 6.40 \times 10^{-4} \text{ mol}$

d $\frac{500}{1000} \times 1.00 = 0.500 \text{ mol}$

4 a $0.600 \times 16.05 = 9.63 \text{ g}$

b $2.30 \times 18.02 = 41.4 \text{ g}$

c $0.165 \times 142.05 = 23.4 \text{ g}$

d $0.830 \times 248.22 = 206 \text{ g}$

5 a $0.100 \times 22700 = 2270 \text{ cm}^3$

b $2.40 \times 10^{-3} \times 22700 = 54.5 \text{ cm}^3$

c $0.0750 \times 22700 = 1700 \text{ cm}^3$

d $0.820 \times 22700 = 18600 \text{ cm}^3$

6 a $\frac{\left(\frac{4.00}{40.00}\right)}{\left(\frac{250}{1000}\right)} = 0.400 \text{ mol dm}^{-3}$

b $\frac{\left(\frac{10.0}{95.21}\right)}{\left(\frac{500}{1000}\right)} = 0.210 \text{ mol dm}^{-3}$

c $\frac{\left(\frac{0.800}{158.04}\right)}{\left(\frac{100.0}{1000}\right)} = 0.0506 \text{ mol dm}^{-3}$

d $\frac{\left(\frac{0.250}{249.72}\right)}{\left(\frac{10.0}{1000}\right)} = 0.100 \text{ mol dm}^{-3}$

7 a $\frac{0.4}{2} = 0.2 \text{ mol}$

b $0.01 \times 5 = 0.05 \text{ mol}$

c $\frac{0.02}{2} = 0.01 \text{ mol}$

d $0.6 \times \frac{3}{2} = 0.9 \text{ mol}$

e $0.9 \times \frac{2}{3} = 0.6 \text{ mol}$

f $2.4 \times 10^{-3} \times \frac{3}{2} = 3.6 \times 10^{-3} \text{ mol}$

8 a Amount of arsenic $= \frac{0.150}{74.92}$

From the chemical equation, 2 mol As produce 2 mol $AsCl_3$, therefore the amount of $AsCl_3$ is the same as the amount of As $= \frac{0.150}{74.92}$

Mass of $AsCl_3$ = amount × molar mass.

We can summarise this as:

$\frac{0.150}{74.92} \times 181.27 = 0.363 \text{ g}$

Chemistry for the IB Diploma – Owen © Cambridge University Press & Assessment 2023

b Amount of $Fe_2S_3 = \frac{5.78}{207.91}$

From the chemical equation, 2 mol Fe_2S_3 produce 6 mol S, therefore the amount of S is three times the amount of $Fe_2S_3 = \frac{5.78}{207.91 \times 3}$

Mass of S = amount × molar mass.

We can summarise this as:

$$\frac{5.78}{207.91} \times 3 \times 32.07 = 2.67 \text{ g}$$

c $\frac{5.00}{411.67} \times \frac{3}{2} \times 253.80 = 4.62$ g

d $\frac{2.25}{58.44} \times \frac{3}{4} \times 102.97 = 2.97$ g

9 amount of $NaNO_3 = \frac{\text{mass}}{\text{molar mass}} = \frac{0.850}{85.00}$

From the equation we get: 2 mol $NaNO_3$ forms 1 mol O_2, therefore the amount of O_2 is half of the amount of $NaNO_3$.

The volume of O_2 at STP is given by:

volume = amount × molar volume

We will use the molar volume in cm^3, i.e. 22700 cm^3 mol^{-1}

The overall calculation can be summarised as:

$$\frac{0.850}{85.00} \times \frac{1}{2} \times 22700 = 114 \text{ cm}^3$$

10 $\frac{2.50}{118.71} \times 4 \times 22700 = 1910 \text{ cm}^3$

11 $\frac{100.0}{22700} \times 105.99 = 0.467$ g

12 a Amount of HCl is

$$\frac{50.0}{1000} \times 0.500 = 0.0250 \text{ mol}$$

From the chemical equation, 1 mol $CaCO_3$ reacts with 2 mol HCl, therefore the amount of $CaCO_3$ is $\frac{0.0250}{2}$ = 0.0125 mol.

Mass of $CaCO_3$ = amount × molar mass = 0.0125 × 100.09 = 1.25 g

b Amount of CO_2 is the same as the amount of $CaCO_3$, i.e. 0.0125 mol Volume of CO_2 = amount × molar volume = 0.0125 × 22.7 = 0.284 dm^3 or 284 cm^3

13 $\frac{25.0}{1000} \times 0.200 \times \frac{1}{2} \times 22700 = 56.8 \text{ cm}^3$

14 amount of $BaSO_4 = \frac{\text{mass}}{\text{molar mass}} = \frac{0.100}{233.40}$

$= 4.28 \times 10^{-4}$ mol

From the equation we get: 1 mol $BaSO_4$ is formed from 1 mol $BaCl_2$, therefore the amount of $BaCl_2$ is the same as that of $BaSO_4$.

concentration (mol dm^{-3}) = $\frac{\text{amount}}{\text{volume (dm}^3\text{)}}$

Therefore, volume (dm^3) = $\frac{\text{amount}}{\text{concentration}}$

volume = $\frac{4.28 \times 10^{-4}}{0.0100} = 0.0428$ dm^3

The volume is multiplied by 1000 to convert to cm^3.

volume = 42.8 cm^3

15 a

Sb_4O_6		H_2SO_4
$\frac{0.1}{1}$	>	$\frac{0.5}{6}$

Therefore H_2SO_4 is limiting

b

$AsCl_3$		H_2O
$\frac{0.20}{4}$	>	$\frac{0.25}{6}$

Therefore H_2O is limiting

c

Cu		HNO_3
$\frac{0.25}{3}$	>	$\frac{0.50}{8}$

Therefore HNO_3 is limiting

d

NaCl	MnO_2	H_2SO_4
$\frac{0.10}{2}$	$\frac{0.15}{1}$	$\frac{0.20}{2}$
0.050	0.15	0.10

Smallest number for NaCl, therefore this is the limiting reactant

16 a

$CaCO_3$		HCl
$\frac{1.00}{100.09}$		$\left(\frac{25.0}{1000}\right) \times 0.200$
0.01 mol		0.005 mol
$\frac{0.1}{1}$	>	$\frac{0.005}{2}$

Therefore hydrochloric acid is limiting

Chemistry for the IB Diploma – Owen © Cambridge University Press & Assessment 2023

b S $\frac{2.00}{32.07}$ 0.0624 mol; O_2 $\frac{2.00}{22.7}$ 0.0881 mol

$\frac{0.0624}{1} < \frac{0.0881}{1}$

Therefore sulfur is limiting

c Fe_2O_3 $\frac{1000}{159.70}$ 6.26 mol; CO $\frac{500}{22.7}$ 22 mol

$\frac{6.26}{1} < \frac{22}{3}$

Therefore iron(III) oxide is limiting

d $AgNO_3$ $\left(\frac{25.0}{1000}\right) \times 0.0500$ 1.25×10^{-3} mol; NaCl $\left(\frac{30.0}{1000}\right) \times 0.0400$ 1.20×10^{-3} mol

$\frac{1.25 \times 10^{-3}}{1} > \frac{1.20 \times 10^{-3}}{1}$

Therefore sodium chloride solution is limiting

e Volume is proportional to number of moles, so we can use these directly

C_3H_8 $\frac{2.00}{1}$ > O_2 $\frac{4.00}{5}$

Therefore oxygen is limiting

17 Amount of $B_2O_3 = \frac{0.75}{69.62} = 0.0108$ mol

Amount of Mg $= \frac{0.50}{24.31} = 0.0206$ mol

$\frac{0.0206}{3} = 6.86 \times 10^{-3}$

$0.0108 > 6.86 \times 10^{-3}$ therefore Mg is limiting

We use the amount of the limiting reactant to work out the amount of B

Amount of B $= \frac{2}{3} \times 0.0206 = 0.0137$ mol

Mass of B = 0.0137 × 10.81 = 0.15 g

18 1 t is 1×10^6 g

Amount of $Fe_2O_3 = \frac{10.0 \times 10^6}{159.70} = 62617$ mol

Amount of C $= \frac{1.00 \times 10^6}{12.01} = 83263$ mol

$\frac{83263}{3} = 27755$

62617 > 27755 therefore C is limiting

We use the amount of the limiting reactant to work out the amount of Fe

Amount of Fe $= \frac{2}{3} \times 83263 = 55509$ mol

Mass of Fe = 55509 × 55.85 = 3.10×10^6 g or 3.10 tonne

19 Amount of $Pb(NO_3)_2$ =

$\frac{20.0}{1000} \times 0.100 = 2.00 \times 10^{-3}$ mol

Amount of NaI $= \frac{10.0}{1000} \times 0.150 = 1.5 \times 10^{-3}$ mol

$\frac{1.5 \times 10^{-3}}{2} = 7.5 \times 10^{-4}$

$2.00 \times 10^{-3} > 7.5 \times 10^{-4}$ therefore NaI limiting

We use the amount of the limiting reactant to work out the amount of PbI_2

Amount of $PbI_2 = \frac{1.5 \times 10^{-3}}{2} = 7.5 \times 10^{-4}$ mol

Mass of $PbI_2 = 7.5 \times 10^{-4} \times 461.00 = 0.346$ g

20 Amount of $CuSO_4 = \frac{25.00}{1000} \times 0.100 = 2.5 \times 10^{-3}$ mol

$\frac{2.5 \times 10^{-3}}{2} = 1.25 \times 10^{-3}$

Amount of KI $= \frac{30.0}{1000} \times 0.120 = 3.60 \times 10^{-3}$ mol

$\frac{3.60 \times 10^{-3}}{4} = 9.00 \times 10^{-4}$

$1.25 \times 10^{-3} > 9.00 \times 10^{-4}$ therefore KI limiting

We use the amount of the limiting reactant to work out the amount of CuI

Amount of CuI $= \frac{3.60 \times 10^{-3}}{2} = 1.80 \times 10^{-3}$ mol

Mass of CuI = $1.80 \times 10^{-3} \times 190.45 = 0.343$ g

21 Amount of Zn $= \frac{5.00}{65.38} = 0.0765$ mol

Amount of HCl = 30.0/1000 × 2.00 = 6.00×10^{-2} mol

$\frac{6.00 \times 10^{-2}}{2} = 0.0300$

0.0765 > 0.0300 therefore HCl limiting

We use the amount of the limiting reactant to work out the amount of H_2

Amount of $H_2 = \frac{6.00 \times 10^{-2}}{2} = 3.00 \times 10^{-2}$ mol

Volume of $H_2 = 3.00 \times 10^{-2} \times 22.7 = 0.681$ dm^3

Multiply by 1000 to get volume in cm^3 = 681 cm^3

Chemistry for the IB Diploma – Owen © Cambridge University Press & Assessment 2023

22 a Theoretical yield

$= \frac{10.0}{74.92} \times \frac{1}{4} \times 395.68 = 13.20$ g

Percentage yield $= \frac{\text{experimental yield}}{\text{theoretical yield}} \times 100$

$= \frac{12.5}{13.20} \times 100 = 94.7\%$

b Theoretical yield $= \frac{1.20}{28.06} \times 187.86$

$= 8.03$ g

Percentage yield $= \frac{5.23}{8.03} \times 100 = 65.1\%$

c Amount of S $= \frac{2.0}{32.07}$ = amount of SO_2

Volume of $SO_2 = \frac{2.0}{32.07} \times 22.7$ dm^3

$$\frac{1.00}{\left(\frac{2.0}{32.07} \times 22.7\right)} \times 100 = 70.6\%$$

d Amount of $BaCl_2 = \frac{20.0}{1000} \times 0.100$ = amount of $BaSO_4$

Mass of $BaSO_4 = \left(\frac{20.0}{1000} \times 0.100\right) \times 233.40$ g

$$\frac{0.362}{\left(\frac{20.0}{1000} \times 0.100 \times 233.40\right)} \times 100 = 77.5\%$$

e Amount of $H_2SO_4 = 30.0/1000 \times 0.600$ mol

This is equal to the amount of $CuSO_4$ in the first equation, which is equal to the amount of $CuSO_4.5H_2O$ in the second equation.

$$\frac{3.21}{[(30.0/1000) \times 0.600 \times 249.72]} \times 1000 = 71.4\%$$

f We can use volumes directly.

Maximum volume of ammonia $= 250 \times 2 = 500$ cm^3

Percentage yield $= \frac{124}{500} \times 100 = 24.8\%$

g $$\frac{9.01}{[(13.81/138.13) \times 180.17]} \times 100 = 50.0\%$$

23 a atom economy $= \frac{\text{molar mass of desired product}}{\text{total molar mass of all reactants}} \times 100$

$$= \frac{26.04}{(64.10 + 18.02)} \times 100 = 31.71\%$$

b $$\frac{44.06}{(28.06 + 177.32 + 18.02)} \times 100 = 19.72\%$$

c $$\frac{4 \times 200.59}{(4 \times 232.66 + 56.08)} \times 100 = 81.32\%$$

d 100% because there is only one product

e $$\frac{2 \times 180.17}{(2 \times 138.13 + 102.10)} \times 100 = 95.24\%$$

24 Amount of HCl $= \frac{22.30}{1000} \times 0.1000$

$= 2.230 \times 10^{-3}$ mol

From the chemical equation, amount of NaOH $= 2.230 \times 10^{-3}$ mol

Concentration $= \frac{\text{amount}}{\text{volume}} = \frac{2.230 \times 10^{-3}}{\left(\frac{25.00}{1000}\right)}$

$= 0.0892$ mol dm^{-3}

25 Amount of $H_2SO_4 = \frac{29.70}{1000} \times 0.2000$

$= 5.940 \times 10^{-3}$ mol

From the chemical equation, amount of KOH $= 2 \times 5.940 \times 10^{-3}$ mol

$= 0.01188$ mol

Concentration $= \frac{\text{amount}}{\text{volume}} = \frac{0.01188}{\left(\frac{25.00}{1000}\right)}$

$= 0.4752$ mol dm^{-3}

26 Amount of HCl $= \frac{25.00}{1000} \times 0.1200$

$= 3.000 \times 10^{-3}$ mol

amount of $Ba(OH)_2 = \frac{(3.000 \times 10^{-3})}{2}$ mol

$= 1.500 \times 10^{-3}$ mol

Concentration $= \frac{(1.500 \times 10^{-3})}{(28.20/1000)}$

$= 0.05319$ mol dm^{-3}

27 Amount of Na_2CO_3 in 5.30 g $= \frac{5.30}{105.99}$

$= 0.0500$ mol

Amount of Na_2CO_3 in 25.0 cm^3 $= \frac{0.0500}{10}$

$= 0.00500$ mol

amount of HCl $= 0.00500 \times 2$ mol $= 0.0100$ mol

Concentration $= \frac{0.0100}{\left(\frac{26.30}{1000}\right)} = 0.380$ mol dm^{-3}

Chemistry for the IB Diploma – Owen © Cambridge University Press & Assessment 2023

28 Amount of HCl $= \left(\frac{28.85}{1000}\right) \times 0.100$
$= 2.885 \times 10^{-3}$ mol

Amount of LiOH in 25.0 $cm^3 = 2.885 \times 10^{-3}$ mol

Amount of LiOH in 250.0 cm^3 =

$2.885 \times 10^{-3} \times 10 = 2.885 \times 10^{-2}$ mol

Amount of Li in 0.20 g $= 2.885 \times 10^{-2}$ mol

Molar mass $= \frac{0.20}{(2.885 \times 10^{-2})} = 6.9$ g mol^{-1}

29 Amount of Fe $= \frac{6720}{55.85} = 120.3$ mol

Amount of $Fe_2O_3 = \frac{120.3}{2} = 60.16$ mol

Mass of $Fe_2O_3 = 60.16 \times 159.70 = 9608$ g

Percentage Fe_2O_3 in ore $= \frac{9608}{10000} \times 100 = 96.1\%$

30 Pressure in kPa and volume in dm^3 is a consistent set of units for R=8.31 J K^{-1} mol^{-1}

Amount of $O_2 = \frac{PV}{(RT)} = \frac{(100 \times 1.00)}{(8.31 \times 293)}$
$= 0.04107$ mol

Amount of $H_2O_2 = 0.04107 \times 2 = 0.08214$ mol

Concentration of $H_2O_2 = \frac{0.08214}{(50.0/1000)}$
$= 1.64$ mol dm^{-3}

31 Amount of Zn $= \frac{5.00}{65.38} = 0.0765$ mol

Amount of HCl $= \frac{30.0}{1000} \times 2.00 = 0.0600$ mol

$\frac{0.0600}{2} = 0.0300$

$0.0300 < 0.0765$, therefore HCl is limiting

Amount of $H_2 = \frac{0.0600}{2} = 0.0300$ mol

Volume of $H_2 = \frac{nRT}{P} = \frac{0.0300 \times 8.31 \times 295}{(9.88 \times 10^4)}$
$= 7.44 \times 10^{-4}$ m^3

Volume in $cm^3 = 7.44 \times 10^{-4} \times 10^6 = 744$ cm^3

32 Amount of $KMnO_4 = \left(\frac{29.40}{1000}\right) \times 0.0200$
$= 5.88 \times 10^{-4}$ mol

Amount of Fe^{2+} in 20.0 $cm^3 = 5.88 \times 10^{-4} \times 5$
$= 2.94 \times 10^{-3}$ mol

Amount of Fe^{2+} in 100.0 $cm^3 = 2.94 \times 10^{-3} \times 5$
$= 0.0147$ mol

Amount of $FeSO_4$ in 4.09 g $FeSO_4 \cdot x\ H_2O$
$= 0.0147$ mol

Mass of $FeSO_4$ in 4.09 g $FeSO_4 \cdot x\ H_2O$
$= 0.0147 \times 151.92 = 2.23$ g

Mass of H_2O in 4.09 g $FeSO_4 \cdot x\ H_2O$
$= 4.09 - 2.23 = 1.86$ g

Amount of H_2O in 4.09 g $FeSO_4 \cdot x\ H_2O$
$= \frac{1.86}{18.02} = 0.103$ mol

Ratio of H_2O to $FeSO_4 = \frac{0.103}{0.0147} = 7 = x$

33 There are many ways to do this but probably the easiest is to use ratios. The fraction of $FeCr_2O_4$ that is chromium is $\frac{(2 \times 52.00)}{223.85}$

Therefore if we obtain 2.00 kg Cr, the mass of $FeCr_2O_4$ will be $\frac{223.85}{(2 \times 52.00)} \times 2.00 = 4.305$ kg

34 Amount of $Na_2S_2O_3 = \left(\frac{23.20}{1000}\right) \times 0.0200$
$= 4.64 \times 10^{-4}$ mol

Amount of $I_2 = \frac{(4.64 \times 10^{-4})}{2} = 2.32 \times 10^{-4}$ mol

Amount of Cu^{2+} in 25.00 $cm^3 = 2.32 \times 10^{-4} \times 2$
$= 4.64 \times 10^{-4}$ mol

Amount of Cu^{2+} in 250.0 $cm^3 = 4.64 \times 10^{-4} \times 10$
$= 4.64 \times 10^{-3}$ mol

Mass of $CuNO_3$ in 1.12 g $CuNO_3 \cdot xH_2O$
$= 4.64 \times 10^{-3} \times 187.57 = 0.870$ g

Mass of H_2O in 1.12 g $CuNO_3 \cdot xH_2O$
$= 1.12 - 0.870 = 0.250$ g

Amount of H_2O in 1.12 g $CuNO_3 \cdot xH_2O$
$= \frac{0.250}{18.02} = 0.0139$ mol

Ratio of H_2O to $CuNO_3 = \frac{0.0139}{(4.64 \times 10^{-3})}$
$= 3 = x$

35 Amount of NaOH $= \left(\frac{34.30}{1000}\right) \times 0.1120$
$= 3.8416 \times 10^{-3}$ mol

Amount of HCl in 25.00 $cm^3 = 3.8416 \times 10^{-3}$ mol

Amount of HCl in 100.0 cm^3 = amount of HCl in excess $= 3.8416 \times 10^{-3} \times 4 = 0.015366$ mol

Amount of HCl added $= \left(\frac{50.00}{1000}\right) \times 2.000$
$= 0.1000$ mol

Chemistry for the IB Diploma – Owen © Cambridge University Press & Assessment 2023

Amount of HCl that reacted with Mg = 0.1000 − 0.015366 = 0.08463 mol

Amount of Mg that reacted = $\frac{0.08463}{2}$ = 0.04232 mol

Molar mass = $\frac{1.020}{0.04232}$ = 24.10 g mol^{-1}

36 Amount of AgCl = $\frac{1.410}{143.32}$ = 9.8381 × 10^{-3} mol

Amount of Cl^- in 10.00 cm^3 = 9.8381 × 10^{-3} mol

Amount of Cl^- in 50.00 cm^3 = amount of Cl^- in 5.000 g $MCl_2{\bullet}6H_2O$ = 9.8381 × 10^{-3} × 5 = 0.04919 mol

There are 2 Cl^- per $MCl_2{\bullet}6H_2O$ unit, therefore the amount of $MCl_2{\bullet}6H_2O$ = $\frac{0.04919}{2}$

= 0.024595 mol

Molar mass of $MCl_2{\bullet}6H_2O$ = $\frac{5.000}{0.024595}$ = 203.29 g mol^{-1}

Molar mass of M = 203.29 − (2 × 35.45) − (6 × 18.02) = 24.27 g mol^{-1}

Therefore the metal is magnesium.

Exam-style questions

1 D

2 A

3 A

4 C

5 C

6 A

7 B

8 A

9 C

10 D

11 a $P_4 + 6Cl_2 \rightarrow 4PCl_3$ **[1]**

b amount in mol = $\frac{0.124}{123.88}$ = 1.00×10^{-3} mol **[1]**

c 1 mol P_4 forms 4 mol PCl_3; therefore. the amount in mol of PCl_3 is $4 \times 1.00 \times 10^{-3} = 4.00 \times 10^{-3}$ mol

mass of $PCl_3 = 4.00 \times 10^{-3} \times 137.32 = 0.549$ g; this is the theoretical yield

$\frac{\text{experimental yield}}{\text{theoretical yield}} \times 100 = \%$ yield

$\frac{0.120}{0.549} \times 100 = 21.9\%$; **[2]**

this answer is obtained if all figures are carried through on the calculator. If the theoretical yield is rounded to 0.549 g, the answer is 21.9%.

d Atom economy is a theoretical quantity based on a balanced equation and allows evaluation of how much of the starting materials are incorporated into the desired product and, therefore, how much waste product will be produced. The yield of a reaction is an experimental quantity worked out from how much of the desired product is actually made in a chemical reaction;

In this reaction there is only one product, therefore the atom economy is 100 %; **[2]**

12 a $S_8(s) + 24F_2(g) \rightarrow 8SF_6(g)$ **[1]**

accept: $S(s) + 3F_2(g) \rightarrow SF_6(g)$

b amount of fluorine = $\frac{\frac{100.0}{1000}}{22.7}$

$= 4.405 \times 10^{-3}$ mol

amount of sulfur molecules

$= \frac{1.00}{256.56} = 3.898 \times 10^{-3}$ mol

1 mol S_8 reacts with 24 mol F_2; therefore, $24 \times 3.898 \times 10^{-3} = 0.0935$ mol F_2 is required to react with this mass of sulfur. Less than this is present, so F_2 is the limiting reactant;

amount of SF_6 is $\frac{4.405 \times 10^{-3}}{3}$

$= 1.468 \times 10^{-3}$ mol;

volume of SF_6 is 1.468 × 10^{-3} × 22.7 = 0.0333 dm^3 or 33.3 cm^3;

Note, this could have been done in exactly the same way using the equation:

$S + 3F_2 \rightarrow SF_6$

We could have also just looked at the coefficients in the equation to work out that the volume of SF_6 formed is $\frac{1}{2}$ the volume of F_2. **[3]**

Chemistry for the IB Diploma – Owen © Cambridge University Press & Assessment 2023

13 a $2Cu(NO_3)_2(aq) + 4KI(aq) \rightarrow$
$2CuI(s) + I_2(aq) + 4KNO_3(aq)$ **[1]**

b amount of copper(II) nitrate is
$\frac{25.0}{1000} \times 0.100 = 2.50 \times 10^{-3}$ mol
amount of potassium iodide
$= \frac{15.0}{1000} \times 0.500 = 7.50 \times 10^{-3}$ mol;
From the equation, we can see that 2 mol of $Cu(NO_3)_2$ will react with 4 mol of KI. Therefore, 2.50×10^{-3} mol of $Cu(NO_3)_2$ will react with $2 \times 2.50 \times 10^{-3}$, i.e., 5.00×10^{-3} mol of KI. The amount of potassium iodide present is greater than this, so KI is present in excess; **[2]**

c We must use the amount of the limiting reactant, $Cu(NO_3)_2$, for subsequent calculations.

From the chemical equation, 2 mol $Cu(NO_3)_2$ react to form 1 mol I_2. Therefore, 2.50×10^{-3} mol of $Cu(NO_3)_2$ will react to form $2.50 \times 10^{-3} \div 2$, i.e., 1.25×10^{-3} mol I_2;

molar mass of I_2 = 253.80 g mol^{-1}

mass of I_2 = $1.25 \times 10^{-3} \times 253.80$, i.e., 0.317 g; **[2]**

14 From the equation, 2 mol NH_3 produces 1 mol N_2. The amount in mol is proportional to the volume of gas if all volumes are measured under the same conditions. Therefore, 228 cm^3 ammonia produces $\frac{228}{2} = 114$ cm^3 N_2;

$\frac{\text{experimental yield}}{\text{theoretical yield}} \times 100 = \%$ yield

$\frac{101}{114} \times 100 = 88.6\%$;

Alternative method for determining the theoretical yield:

amount of ammonia $= \frac{228/1000}{22.7} = 0.0100$ mol

From the equation, two moles of NH_3 produce one mole of N_2.

0.0100 mol NH_3 produce 0.00500 mol N_2

0.00500 mol of N_2 have a volume of $0.00500 \times 22.7 \times 1000 = 114$ cm^3 **[2]**

15 a amount of sodium hydroxide
$= \frac{19.70}{1000} \times 1.100 = 0.02167$ mol
amount of ethanoic acid = 0.02167 mol;

concentration of ethanoic acid
$= \frac{0.02167}{(25.00/1000)} = 0.8668$ mol dm^{-3}; **[2]**

b i $Mg + 2CH_3COOH \rightarrow$
$(CH_3COOH)_2Mg + H_2$ **[1]**

ii amount of Mg is $\frac{1.00}{24.31} = 0.0411$ mol

amount of ethanoic acid is $\frac{50.0}{1000} \times 0.8668$ = 0.04334 mol;

1 mol Mg reacts with 2 mol CH_3COOH; therefore, $2 \times 0.0411 = 0.0822$ mol ethanoic acid required to react with the Mg. We have less than this, therefore ethanoic acid is the limiting reactant;

amount of H_2 is $\frac{0.04334}{2} = 0.02167$ mol

volume of H_2 is $0.02167 \times 22.7 = 0.492$ dm^3

volume in $cm^3 = 0.492 \times 1000 = 492$ cm^3; **[3]**

c i amount of ethanoic acid is
$\frac{25.0}{1000} \times 0.8668 = 0.02167$ mol
amount of sodium carbonate is
$\frac{0.02167}{2} = 0.01084$ mol;
volume of sodium carbonate is
$\frac{0.01084}{0.750} = 0.0144$ dm^3
volume of sodium carbonate in cm^3 is $0.0144 \times 1000 = 14.4$ cm^3; **[2]**

ii From the first equation, the amount of sodium ethanoate formed is the same as the amount of ethanoic acid, i.e., 0.02167 mol. *All of this reacts in the second equation – there is no arrow from $2CH_3COONa(aq)$ [first equation] to $CH_3COONa(aq)$ [second equation], so do not divide by 2.*

Chemistry for the IB Diploma – Owen © Cambridge University Press & Assessment 2023

From the second equation, the amount of $CH_3COONa{\bullet}3H_2O$ crystals is the same as the amount of sodium ethanoate, i.e., 0.02167 mol;

mass of $CH_3COONa{\bullet}3H_2O$ is $0.02167 \times 136.10 = 2.95$ g – this is the theoretical yield;

$$\frac{\text{experimental yield}}{\text{theoretical yield}} \times 100 = \%\ \text{yield}$$

$$\frac{2.12}{2.95} \times 100 = 71.9\%;$$ **[3]**

16 a amount of Mn_3O_4 is $\frac{100000}{228.82} = 437.0$ mol

amount of Al is $\frac{100000}{26.98} = 3706$ mol;

437.0 mol of Mn_3O_4 will react with $437.0 \times \frac{8}{3}$, i.e., 1165 mol Al. The amount of Al is greater than this, so Al is present in excess and Mn_3O_4 is the limiting reactant; Mn_3O_4 must be used in all calculations.

3 mol Mn_3O_4 produces 9 mol Mn.

Therefore, 437.0 mol of Mn_3O_4 will produce 437.0 × 3, i.e., 1311, mol of Mn.

mass of Mn = 1311 × 54.94, i.e., 72 030 g, i.e., 72.03 kg; **[3]**

b $3Mn_3O_4 + 8Al \rightarrow 4Al_2O_3 + 9Mn$

200.0 kg of Mn is $\frac{200\ 000}{54.94}$, i.e., 3640 mol.

This amount is produced from $\frac{3640}{3}$ i.e.. 1213, mol Mn_3O_4;

The mass of 1213 mol Mn_3O_4 is $1213 \times 228.82 = 277661$ g

To convert to tonnes, we divide by 1 000 000 to get 0.2777 tonnes;

Therefore, the percentage Mn_3O_4 in the ore is $\frac{0.2777}{1.23} \times 100$, i.e., 22.6%; **[3]**

17 a volume of CO_2 in m^3 is

$$\frac{258}{1000000} = 2.58 \times 10^{-4}\ m^3$$

$P = 1.10 \times 10^5$ Pa

$V = 2.58 \times 10^{-4}\ m^3$

$n = ?$

$R = 8.31\ J\ K^{-1}\ mol^{-1}$

$T = 27.00 + 273.15 = 300.15$ K

$$n = \frac{PV}{RT}$$

$$n = \frac{1.10 \times 10^5 \times 2.58 \times 10^{-4}}{8.31 \times 300.15};$$

= 0.0114 mol; **[2]**

b From the chemical equation, the amount of $CaCO_3$ that must react to produce 0.0114 mol of CO_2 is 0.0114 mol.

mass of $CaCO_3 = 0.0114 \times 100.09 = 1.14$ g; percentage $CaCO_3$ in the limestone

$$= \frac{1.14}{1.20} \times 100 = 95.0\%;$$ **[2]**

18 a amount of $PbI_2 = \frac{0.1270}{461.0} = 2.755 \times 10^{-4}$ mol **[1]**

b $Pb(NO_3)_2(aq) + MI_2(aq) \rightarrow PbI_2(s) + M(NO_3)_2(aq)$ **[1]**

c From the chemical equation, we can deduce that the amount of MI_2 is the same as the amount of PbI_2. Therefore, the amount of MI_2 is 2.755×10^{-4} mol. **[1]**

d We know the mass of 2.755×10^{-4} mol of MI_2 is 0.0810 g. The molar mass of MI_2 is $\frac{0.0810}{2.755 \times 10^{-4}} = 294.0\ g\ mol^{-1}$;

Some of this mass is due to the two I^- ions in the formula – these contribute 2 × 126.90 to the mass, i.e., 253.8.

The relative atomic mass of M is 294.0 – 253.8 = 40.20;

We know that this is a Group 2 element, so from the periodic table we can see that it must be calcium; **[3]**

19 a amount of $BaSO_4$ formed

$$= \frac{3.739 \times 10^{-2}}{233.40} = 1.602 \times 10^{-4}\ mol$$ **[1]**

b From the chemical equation, we can deduce that the amount of $CuSO_4$ is the same as the amount of $BaSO_4$. Therefore, the amount of $CuSO_4$ is 1.602×10^{-4} mol. **[1]**

Chemistry for the IB Diploma – Owen © Cambridge University Press & Assessment 2023

c Only 10 cm^3 of the original solution (100 cm^3) was used in the reaction, so the amount of $CuSO_4$ that was dissolved in water was $10 \times 1.602 \times 10^{-4}$ mol, i.e., 1.602×10^{-3} mol. **[1]**

d 0.4000 g of hydrated copper (II) sulfate ($CuSO_4 \bullet xH_2O$) contains 1.602×10^{-3} mol of $CuSO_4$.

The mass of $CuSO_4$ present in the sample is $1.602 \times 10^{-3} \times 159.62$, i.e., 0.2557 g of $CuSO_4$. The rest of the hydrated copper (II) sulfate is water. Therefore, the mass of water present in the sample is 0.4000 − 0.2557, i.e., 0.1443 g;

$$\text{amount of water} = \frac{0.1443}{18.02} = 8.008 \times 10^{-3} \text{ mol;}$$

ratio of amount of water to amount of

$$CuSO_4 = \frac{8.008 \times 10^{-3}}{1.602 \times 10^{-3}} = 4.999$$

This will be a whole number in the formula.

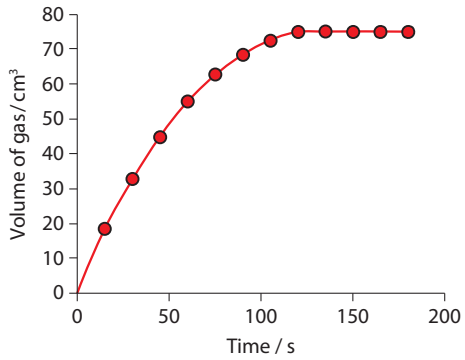
Therefore, the value of x is 5, and the formula is $CuSO_4 \bullet 5H_2O$; **[3]**

Chemistry for the IB Diploma – Owen © Cambridge University Press & Assessment 2023

Chapter 17

Test your understanding

1 a



The gradient is steepest at the beginning – the reaction is fastest; the concentration of reactants is highest at the beginning, so the collision frequency is highest.

The gradient decreases as the reaction goes on – the reaction rate decreases; reactants are being used up – there is a lower concentration of reactants, so lower collision frequency.

The graph becomes horizontal – the reaction has finished; the acid is in excess, so the reaction finishes when all the magnesium has been used up.

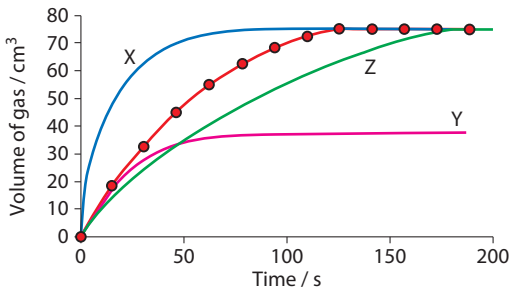
b A tangent is drawn, starting at the origin and matching the initial gradient of the curve. The gradient of the tangent is equal to the initial rate. The initial rate is approximately 1.3 $cm^3\ s^{-1}$.

c $$\text{Average rate} = \frac{\left[\text{total volume of gas produced}\right]}{\text{time}} = \frac{74.9}{120} = 0.62\ cm^3\ s^{-1}$$

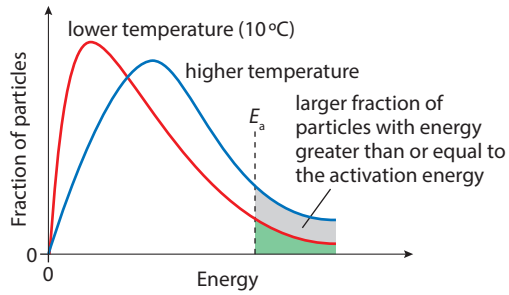
d Powdered Mg has higher surface area, therefore higher rate – higher initial gradient. Same mass of Mg used, therefore same volume of gas will be produced.

e The initial rate will be slightly lower with a lower surface area (but this will be a small difference). With half the amount of Mg (HCl is in excess), half the volume of gas will be produced.

f Lower temperature but all other conditions the same, therefore lower initial rate – the graph is less steep. Same amounts of reactants, therefore same volume of gas produced.



g



At the higher temperature, a greater proportion of particles have energy greater than or equal to the activation energy. Therefore, there is a greater chance that a collision will result in a reaction and more successful collisions per unit time. There is also a smaller effect due to the increase in collision frequency – at higher temperature the particles are moving faster and, therefore, collide more frequently.

2 a Higher concentration, therefore more frequent collisions and higher initial rate – steeper graph.

The amount of HCl is doubled (with $CaCO_3$ still in excess), therefore double the volume of gas will be produced.

b Concentration is halved, so initial rate will be lower – graph less steep. The amount of HCl is the same:

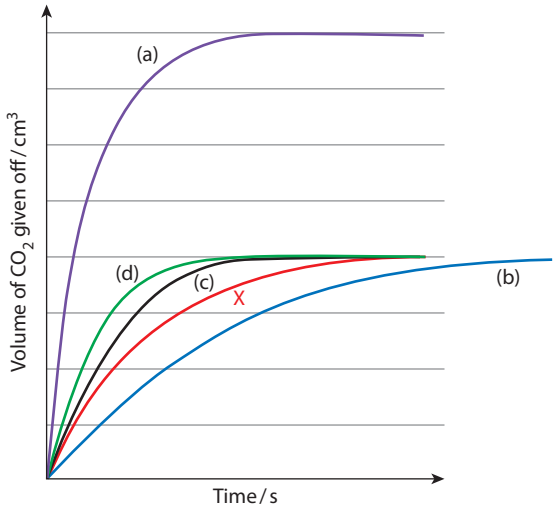
$$\left(\frac{25.0}{1000}\right) \times 1 = \left(\frac{50.0}{1000}\right) \times 0.5$$

therefore the same volume of gas will be produced.

Chemistry for the IB Diploma – Owen © Cambridge University Press & Assessment 2023

c Higher temperature, with everything else remaining constant produces a higher rate – graph steeper. Same amounts, therefore the same volume of gas is produced (we assume that only the solution is warmer, and not the gas, so there will be no effect on the volume of gas due to the higher temperature – raising the temperature would only cause a 3% increase in the volume of gas anyway).

d Higher surface area, therefore faster rate – graph is steeper. Same amounts, therefore the same volume of gas is produced. The graph for **d** may be more or less steep than that for **c**. We would have to do the experiment to see which change had the bigger effect.

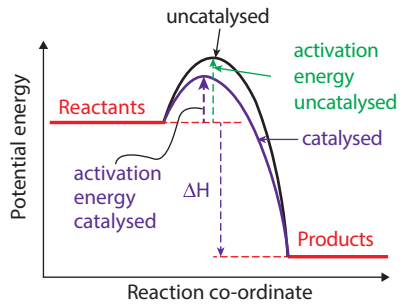


3 The average kinetic energy of the particles in a gas is proportional to its temperature in kelvin.

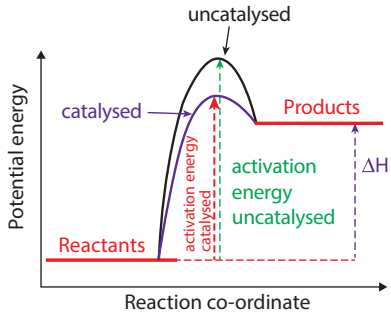
4 A catalyst is a substance that increases the rate of a chemical reaction without itself being used up in the reaction /is chemically unchanged at the end of the reaction.

5 A catalyst speeds up a reaction by allowing the reaction to proceed by an alternative pathway of lower activation energy. A larger fraction of particles has energy greater than or equal to the activation energy; therefore, a greater proportion of collisions results in reaction.

6



Exothermic



Endothermic

7 **a** In experiments 1 and 2, doubling [A] (× 2) but keeping [B] constant causes the rate to double (× 2^1), therefore, first order with respect to A.

In experiments 2 and 3, doubling [B] (× 2) but keeping [A] constant causes the rate to quadruple (× 2^2), therefore, second order with respect to B.

b 2 + 1 = 3

c Rate = $k[A][B]^2$

Using values from experiment 1:

$0.0200 = k[0.200] \times [0.100]^2$

so, $k = 10.0$

Substituting in units:

$\text{mol dm}^{-3}\ \text{s}^{-1} = k \times (\text{mol dm}^{-3}) \times (\text{mol dm}^{-3})^2$

cancelling (mol dm^{-3}) from each side and rearranging gives $k = s^{-1}/(\text{mol dm}^{-3})^2$, which can be re-written as $\text{mol}^{-2}\ \text{dm}^6\ \text{s}^{-1}$.

So, $k = 10.0\ \text{mol}^{-2}\ \text{dm}^6\ \text{s}^{-1}$

d Rate = $k[A][B]^2$

Substituting in values:

Rate = $10.0 \times [0.100] \times [0.0500]^2$

Rate = $2.50 \times 10^{-3}\ \text{mol dm}^{-3}\ \text{s}^{-1}$

Chemistry for the IB Diploma – Owen © Cambridge University Press & Assessment 2023

8 **a** In experiments 1 and 2, tripling [X] (× 3) but keeping [Y] constant causes the rate to increase by a factor of 3^1, therefore, first order with respect to X

In experiments 2 and 3, [Y] × 4, with [X] constant causes the rate to increase by a factor of 4^1, therefore, first order with respect to Y.

Therefore the rate equation is rate = k[X][Y]

b Rate = k[X][Y]

Using values from experiment 1:

$1.78 \times 10^{-3} = k[1.50 \times 10^{-2}] \times [3.00 \times 10^{-2}]$

so, $k = 3.96$

c Rate = k[X][Y]

Substituting in units:

mol dm^{-3} s^{-1} = k × (mol dm^{-3}) × (mol dm^{-3})

cancelling (mol dm^{-3}) from each side and rearranging gives k = s^{-1}/(mol dm^{-3}), which can be re-written as mol^{-1} dm^3 s^{-1}.

9 In experiments 1 and 2, doubling [A] (× 2) but keeping [B] constant causes the rate to double (× 2^1), therefore, first order with respect to A

In experiments 2 and 3, [B] × 3 (but keeping [A] constant) causes the rate to increase × 3^2, therefore, second order with respect to B

Therefore Rate = k[A][B]^2

Using values from experiment 1:

$2.0 \times 10^{-3} = k[1.0] \times [1.0]^2$ so, $k = 2.0 \times 10^{-3}$

Substituting in units:

mol dm^{-3} s^{-1} = k × (mol dm^{-3}) × (mol dm^{-3})^2

Cancelling (mol dm^{-3}) from each side and rearranging gives k = s^{-1}/(mol dm^{-3})^2, which can be re-written as mol^{-2} dm^6 s^{-1}.

So, $k = 2.0 \times 10^{-3}$ mol^{-2} dm^6 s^{-1}

10 In experiments 1 and 2, [Z] × 4 (with [Y] constant) causes the rate to increase by a factor of 16 (× 4^2), therefore, second order with respect to Z

From experiment 1 to 3, [Z] × 5 would change the rate by a factor of 5^2 = 25, but the ratio between the rates is 3.750/0.050 = 75, therefore multiplying [Y] by 3 has also caused the rate to increase by a factor of 3^1, therefore, first order with respect to Y and the rate equation is: Rate = k[Z]^2[Y]

Using values from experiment 1:

$0.050 = k[2.0 \times 10^{-3}]^2 \times [2.0 \times 10^{-3}]$, so $k = 6.25 \times 10^6$

Substituting in units:

mol dm^{-3} s^{-1} = k × (mol dm^{-3}) × (mol dm^{-3})^2

Cancelling (mol dm^{-3}) from each side and rearranging gives k = s^{-1}/(mol dm^{-3})^2, which can be re-written as mol^{-2} dm^6 s^{-1}.

So, $k = 6.25 \times 10^6$ mol^{-2} dm^6 s^{-1}

11 **a** $2^0 \times 2^2$, so the reaction rate increases by a factor of 4

b $2^1 \times \left(\frac{1}{2}\right)^2$, so the reaction rate halves

c $\left(\frac{1}{2}\right)^2 \times \left(\frac{1}{2}\right)$, so the reaction rate is $\frac{1}{8}$ of the original rate

12 **a** In experiments 1 and 2, [D] × 4 (with [E] constant, causes the rate to increase by a factor of 4^1, therefore, first order with respect to D.

b From experiment 2 to 3, [D] × 4 would change the rate by a factor of 4^1 to $4 \times 1.71 \times 10^{-3} = 6.84 \times 10^{-3}$ mol dm^{-3} s^{-1}, which is the actual rate. Therefore multiplying [E] by 4 has had no effect on the rate (factor of × 4^0) and the order with respect to E is 0.

c rate = k[D]

d Rate = k[D]

Using values from experiment 1:

$4.28 \times 10^{-4} = k[2.50 \times 10^{-3}]$, so, $k = 0.171$

Substituting in units: mol dm^{-3} s^{-1} = k × mol dm^{-3}

cancelling (mol dm^{-3}) from each side gives k = s^{-1}

So, $k = 0.171$ s^{-1}

Chemistry for the IB Diploma – Owen © Cambridge University Press & Assessment 2023

e We can ignore the concentration of E as it is zero order. 0.0600 is 6 × the concentration of D from experiment 2. The order with respect to D is 1, therefore multiplying the concentration by 6 changes the rate by the same factor.

$6 \times 1.71 \times 10^{-3} = 0.0103$ mol dm^{-3} s^{-1}

We could also just put the concentration into the rate equation to get this answer.

13 a zero order The gradient is constant, indicating that the rate is not varying as the reactant is being used up, so does not depend on concentration.

b second order Zero order would give a horizontal line; first order would be a straight line through the origin and therefore it must be second order as this is the only choice we have left. To find out whether it is actually second order and not third order etc, we would need to look at the values of rate as concentration changes.

14
- The mechanism does not agree with the stoichiometric equation (the overall equation from this mechanism is $2A + 3B \rightarrow 3C + 2D$).
- The rate-determining step contains A, but A does not appear in the rate equation.
- Step 2 involves three molecules colliding, which is extremely unlikely.
- There is only 1 molecule of B involved up to and including the RDS, but the rate equation suggests 2.

15 a rate $= k[Q]^2$ 2 Q and no other species involved up to and including the RDS

b Because it does not agree with the stoichiometric equation – the overall equation from this mechanism would be $2Q + P + Z \rightarrow Y + R + S$

c Mechanism 3 is consistent: 1 Q and 1 P involved up to and including the RDS.

Mechanism 2 would have rate = $k[P][Q]^2$ therefore not consistent.

We have already seen, in part **a**, that Mechanism 1 is not consistent with the experimental rate equation.

16 The rate equation tells us that there must be 2 NO and 1 Br_2 involved up to and including the RDS.

$NO + NO \rightleftharpoons N_2O_2$ fast

$N_2O_2 + Br_2 \rightarrow 2NOBr$ slow/RDS

or

$NO + Br_2 \rightleftharpoons NOBr_2$ fast

$NOBr_2 + NO \rightarrow 2NOBr$ slow/RDS

or

$NO + Br_2 \rightleftharpoons NOBr + Br$ fast

$Br + NO \rightarrow NOBr$ slow/RDS (this mechanism is probably unlikely as the activation energy for this step involving an atom with an unpaired electron colliding is likely to be very low)

17 The rate equation tells us that there must be 1 X and 1 Y involved up to and including the RDS.

$X + Y \rightarrow XY$ slow/rate-determining step

$XY + X \rightarrow 2Z$ fast

You could choose any other letter to represent 'XY', e.g. Q

18 A catalyst is used up then produced again, but an intermediate is produced then used up. Y is an intermediate and X is a catalyst.

19 a exothermic; C and D are the products – they are at a lower energy level than A and 2B, the reactants.

b $A + 2B \rightarrow C + D$

c The second step: $X + B \rightarrow C + D$ This is the step with higher activation energy.

d $A + B \xrightleftharpoons{\text{fast}} X$

$X + B \xrightarrow{\text{slow}} C + D$ RDS

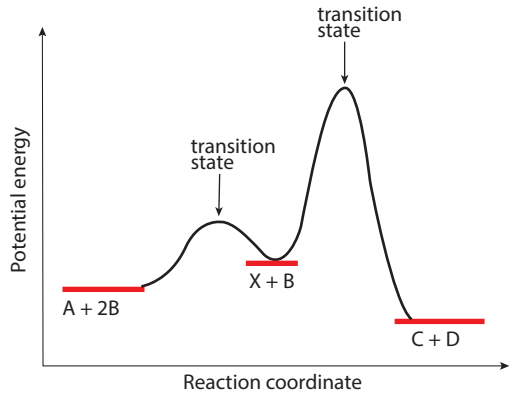
X + B present at central point, therefore 1 A and 1 B must have reacted in first stage, and not 2 B.

e Each step has of a molecularity of two because each step involves 2 particles.

f rate $= k[A][B]^2$ 1 A and 2 B involved up to and including the RDS, therefore first order with respect to A and second order with respect to B.

Chemistry for the IB Diploma – Owen © Cambridge University Press & Assessment 2023

g



Transition states occur at maximum points on the energy profile.

h X is an intermediate; Intermediates occur at local minimum points on the energy profile.

20 The first step involves A + 2X → A + Q, so A does not change and therefore the first step is X + X → Q

The second step is Q + A → E + Z.

The activation energy is higher for the first step, so this is the RDS.

Therefore the mechanism is:

$X + X \rightarrow Q$ slow/RDS

$Q + A \rightarrow E + Z$ fast

The rate equation would be: Rate = $k[X]^2$

It is zero order with respect to A because A is only involved in a fast step after the RDS.

21 In this question we will be using this equation to work out the activation energy:

$$\ln\left(\frac{k_1}{k_2}\right) = \frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

This equation can be rearranged to

$$E_a = R \times \frac{\ln\left(\frac{k_1}{k_2}\right)}{\left(\frac{1}{T_2} - \frac{1}{T_1}\right)}$$

To calculate the Arrhenius A factor, we will be using the Arrhenius equation in the form: $k = Ae^{\frac{-E_a}{RT}}$

This can be rearranged to: $A = \frac{k}{e^{\frac{-E_a}{RT}}}$

When using the equation it is important to remember that the activation energy must be in J, The equation looks complicated and it is probably easiest to work out $E_a/(RT)$ first.

The units of A are the same as those of k.

a If $k_1 = 1.20 \times 10^{-4}\ s^{-1}$ and $T_1 = 300$ K

$k_2 = 1.80 \times 10^{-3}\ s^{-1}$ and $T_2 = 500$ K

$$E_a = 8.31 \times \frac{\ln\left[\frac{1.20 \times 10^{-4}}{(1.80 \times 10^{-3})}\right]}{\left(\frac{1}{500}\right) - \left(\frac{1}{300}\right)}$$

$= 16900\ J\ mol^{-1}$ or $16.9\ kJ\ mol^{-1}$

Using the value of k at 300 K and remembering to convert E_a back to J, we get:

$$A = \frac{1.20 \times 10^{-4}}{e^{\frac{-16900}{(8.31 \times 300)}}} = 0.106\ s^{-1}$$

b $$E_a = 8.31 \times \frac{\ln[5.70 \times 10^{-6}/(2.40 \times 10^{-2})]}{\left(\frac{1}{400} - \frac{1}{300}\right)}$$

$= 83200\ J\ mol^{-1}$ or $83.2\ kJ\ mol^{-1}$

$$A = \frac{5.70 \times 10^{-6}}{e^{\frac{-83200}{(8.31 \times 300)}}} = 1.78 \times 10^{9}\ mol^{-1}\ dm^{3}\ s^{-1}$$

c Remember to convert temperatures to kelvin

$$E_a = 8.31 \times \frac{\ln(0.220/7.36)}{\left(\frac{1}{80.00 + 273.15}\right) - \left(\frac{1}{25.00 + 273.15}\right)}$$

$= 55800\ J\ mol^{-1}$

or $55.8\ kJ\ mol^{-1}$

$$A = \frac{0.220}{e^{-55800/(8.31 \times 298.15)}} = 1.33 \times 10^{9}\ min^{-1}$$

d $$E_a = 8.31 \times \frac{\ln\left[\frac{1.56 \times 10^{-3}}{(5.30 \times 10^{-3})}\right]}{\left(\frac{1}{59.00 + 273.15}\right) - \left(\frac{1}{18.00 + 273.15}\right)}$$

$= 24000\ J\ mol^{-1}$ or $24.0\ kJ\ mol^{-1}$

$$A = \frac{1.56 \times 10^{-3}}{e^{\frac{-24000}{(8.31 \times 291.15)}}} = 31.7\ s^{-1}$$

Chemistry for the IB Diploma – Owen © Cambridge University Press & Assessment 2023

22 The values can either be used to plot a graph, in which the gradient comes out as −6700 K. or any 2 points from the data can be used to work out a gradient. If we use the first and last points, we get:

$$\frac{10.7-2.27}{0.00125-0.00250}=-6744\text{ K}$$

The gradient is equal to $-E_a/R$

$E_a = 6744 \times 8.31 = 56000$ J mol^{-1}

Therefore $E_a = 56.0$ kJ mol^{-1}

From the graph, the intercept on the ln k axis occurs at 19.1. The intercept is ln A, so ln A = 19.1, therefore $A = e^{19.1} = 2.0 \times 10^8$

The units of A are the same as those of k: mol^{-1} dm^3 s^{-1}

Alternatively, a value for A can be worked out by putting the values for k into the Arrhenius equation:

$\ln k = -(E_a/R) \times \left(\frac{1}{T}\right) + \ln A$, which gives

$\ln A = \ln k + (E_a/R) \times \left(\frac{1}{T}\right)$

Taking the first row of data in the table, we get

$\ln A = 2.27 + \left(\frac{56000}{8.31}\right) \times 0.00250 = 19.1$

therefore $A = e^{19.1} = 2.0 \times 10^8$

Depending on how good the data are (how good a straight line), different rows in the table may give a slightly different value – the value from the graph should be an average value.

23 The values can either be used to plot a graph of ln k against $\frac{1}{T}$, in which the gradient comes out as −10800 K; or any 2 points from the data can be used to work out a value using the equation in question 21. Using the gradient we get:

$E_a = 8.31 \times 10800 = 89700$ J mol^{-1}, i.e. 89.7 kJ mol^{-1}

If we use the first and last rows of the data and an equation (see Question 21), we get:

$$E_a = 8.31 \times \frac{\ln\left(\frac{1.74\times10^{-2}}{1.32\times10^{4}}\right)}{\left(\frac{1}{800}-\frac{1}{400}\right)}$$

or 90.0 kJ mol^{-1}

From the graph, the intercept on the ln k axis occurs at 23.0. The intercept is ln A, so ln A = 23.0, therefore $A = e^{23.0} = 9.7 \times 10^9$

We are told the units of k, and the units of A will be the same as this, so $A = 9.7 \times 10^9$ mol^{-1} dm^3 s^{-1}.

Alternatively, a value for A can be worked out by putting the values for k into the Arrhenius equation:

$\ln k = -(E_a/R) \times \left(\frac{1}{T}\right) + \ln A$, which gives

$\ln A = \ln k + (E_a/R) \times \left(\frac{1}{T}\right)$

Taking the first row of data in the table, we get

$\ln A = \ln(1.74 \times 10^{-2}) + \left(\frac{90000}{8.31}\right) \times \left(\frac{1}{400}\right) = 23.0$

Therefore $A = 9.7 \times 10^9$ mol^{-1} dm^3 s^{-1} as calculated above.

24 a Gradient of graph $= \frac{[-4.80-(-14.80)]}{(0.00150-0.00300)}$
$= -6667$ K

The gradient $= \frac{-E_a}{R}$ so $E_a = 8.31 \times 6667$
$= 55400$ J mol^{-1}

b If the graph is extrapolated to the ln k axis, the intercept occurs at −1.4. The intercept is ln A, so ln A = −1.4, therefore $A = e^{-1.4} = 0.25$

The reaction is first order, so the units of k and, therefore, also A, will be time^{-1}, e.g. s^{-1}, min^{-1} etc,

Exam-style questions

1 C

2 A

3 B

4 C

5 C

6 C

7 A

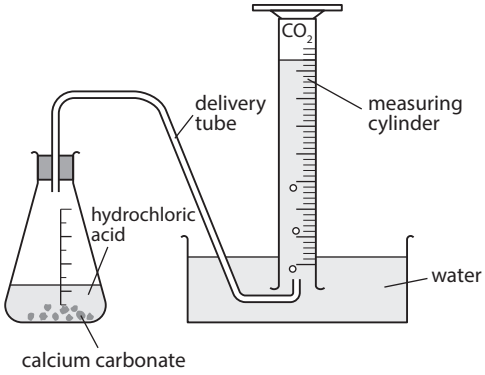
8 C

9 D

10 B

Chemistry for the IB Diploma – Owen © Cambridge University Press & Assessment 2023

11 a



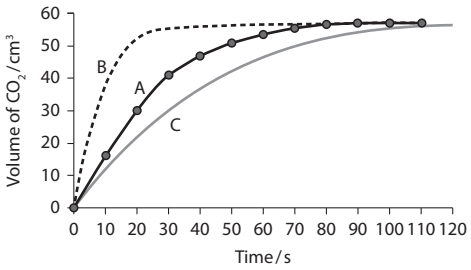
The volume of carbon dioxide produced is measured every 10 s.

for basic set-up and the volume of carbon dioxide produced is measured every 10 s. **[1]**

for apparatus sealed and some piece of apparatus with gradations to measure the volume of gas, e.g., measuring cylinder/gas burette or gas syringe **[1]**

at least three labels **[1]**

b



for all points plotted correctly **[1]**

for line of best fit **[1]**

c Rate highest at the start because the concentration of reactants is highest, therefore, most frequent collisions;

Rate decreases with time as reactants are used up, so the concentrations decrease, therefore, less frequent collisions;

Graph eventually flattens out – the reaction has stopped – all of the hydrochloric acid (the calcium carbonate was in excess) has been used up; **[3]**

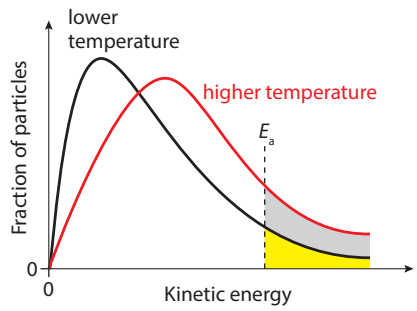
d *Line B; [1] for initial gradient steeper;*

[1] for same final volume **[2]**

e *Line C; smaller initial gradient and same final volume* **[1]**

f The most likely reason is that some gas will escape before the bung is put in the flask. *Other reasons include the concentration of the hydrochloric acid was lower than stated/some CO_2 dissolved in water, but the difference between the volume obtained and what was expected is so large that these are unlikely to account for this (CO_2 is not that soluble in water).* **[1]**

12



for axes labelled correctly and curve at one temperature **[1]**

for higher temp labelled, lower peak and to the right, activation energy marked **[1]**

As the temperature increases, the particles have more kinetic energy, and so, are moving faster and collide more often. This is only, however, a small effect; **[1]**

At higher temperature, a larger fraction of particles have energy greater than or equal to the activation energy, therefore, there is a greater chance that a collision will result in reaction and therefore more successful collisions per unit time; **[1]**

13 a From experiment 2 to 1, when the concentration of X is doubled, the rate of reaction also doubles, so the order of reaction with respect to X is 1;

From experiment 3 to 2, when the concentration of Y is doubled, the rate of reaction also doubles, so the order of reaction with respect to Y is 1;

The rate equation is: rate $= k[X][Y]$; **[3]**

b From experiment 1, [X] = 0.500 mol dm^{-3} and [Y] = 0.500 mol dm^{-3}. Substituting these values, and the value of the rate into the rate expression, we get

$3.20 \times 10^{-3} = k \times 0.500 \times 0.500$

Chemistry for the IB Diploma – Owen © Cambridge University Press & Assessment 2023

So, $k = 0.0128$;

Substituting units into the rate expression:

$\text{mol dm}^{-3}\ \text{s}^{-1} = k \times \text{mol dm}^{-3} \times \text{mol dm}^{-3}$

$\text{s}^{-1} = k \times \text{mol dm}^{-3}$

Rearranging this, we get

$$\frac{\text{s}^{-1}}{\text{mol dm}^{-3}} = k$$

$k = \text{mol}^{-1}\ \text{dm}^3\ \text{s}^{-1}$

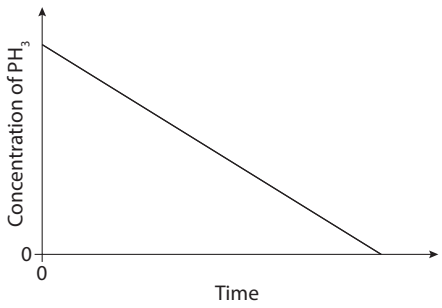
Therefore, $k = 0.0128\ \text{mol}^{-1}\ \text{dm}^3\ \text{s}^{-1}$; **[2]**

c Putting the concentrations and the value of k into the rate equation:

rate = $0.0128 \times 0.100 \times 0.100 = 1.28 \times 10^{-4}\ \text{mol dm}^{-3}\ \text{s}^{-1}$ **[1]**

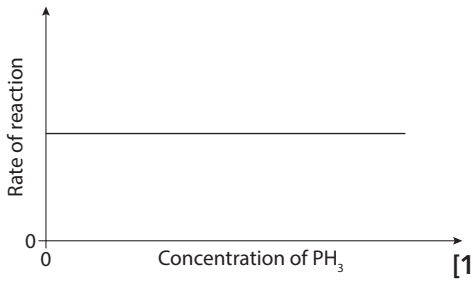
d The rate constant increases (exponentially) as the temperature increases; The main reason is that a larger fraction of particles have energy greater than or equal to the activation energy at a higher temperature, but there is also a smaller effect due to an increase in collision frequency; **[2]**

14 a



[1]

b



[1]

15 a The rate equation cannot be derived directly from the stoichiometric equation because the mechanism is unknown, and the reaction could occur in more than one step;

This reaction is unlikely to occur in one step, because that would involve three molecules all colliding at the same time, which is statistically extremely unlikely; **[2]**

b The rate-determining step is the slowest step in a reaction mechanism, that is, the step with highest activation energy. **[1]**

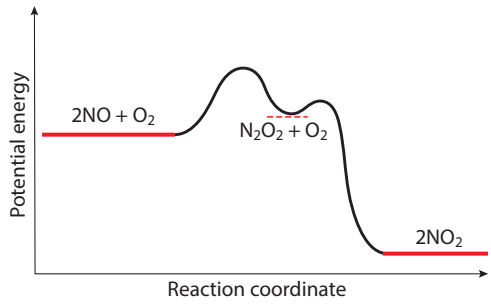
c $NO + NO \rightarrow N_2O_2$ rate-determining step

$N_2O_2 + O_2 \rightarrow 2NO_2$ fast;

The rate expression contains $[NO]^2$, which indicates that two molecules of NO are involved up to and including the rate-determining step. There is no O_2 in the rate equations, which indicates that O_2 can be involved in the mechanism only in a fast step after the rate-determining step; The molecularity of the rate-determining step is 2, because there are two reactant molecules involved; **[3]**

d The rate will be decreased by a factor of 4; All the concentrations will be decreased by a factor of 2. The rate of the reaction depends on the concentration of NO squared, so, if the concentration is halved, the rate will decrease by a factor of 2^2; **[2]**

e i



for general form and for products below reactants **[1]**

for second peak lower than first one **[1]**

ii The transition state: the highest point/maximum along the energy profile for a particular step – at the top of each peak. The species present at the highest point along the potential energy profile will have partial bonds;

N_2O_2 is an intermediate: it is at a dip/local minimum in the potential energy profile. It will exist in the reaction mixture for a finite amount of time. N_2O_2 has only fully formed bonds – there are no partially formed/broken bonds; **[2]**

Chemistry for the IB Diploma – Owen © Cambridge University Press & Assessment 2023

16 a From experiments 1 and 2, where [Y] is constant, as [X] increases by a factor of 3, the rate increases by a factor of $\frac{1.15\times10^{-4}}{1.28\times10^{-5}} = 9$, i.e., 3^2, so the order with respect to X is 2;

From experiments 1 and 3, multiplying [X] by 4, but keeping [Y] constant, would increase the rate by a factor of 4^2 to $1.28\times10^{-5}\times4^2 = 2.05\times10^{-4}$. So, doubling [Y] has no effect on the rate, so the order with respect to Y is zero;

The rate equation is rate $= k[X]^2$

Substituting in values from experiment 1:
$1.28\times10^{-5} = k\times(2.20\times10^{-3})^2$

Rearranging: k = 2.64; *accept 2.64 or 2.65*

units of k: mol dm^{-3} s^{-1} $= k\times(\text{mol dm}^{-3})^2$

rearranging: units of k are mol^{-1} dm^3 s^{-1}; **[4]**

b i $1.02\times10^{-4} = k\times(2.20\times10^{-3})^2$

Rearranging: k = 21.1 (mol^{-1} dm^3 s^{-1}) **[1]**

ii $\ln\left(\frac{k_1}{k_2}\right) = \frac{E_a}{R}\times\left(\frac{1}{T_2}-\frac{1}{T_1}\right)$

$T_1 = 20.00 + 273.15 = 293.15$ K
k_1 = 2.64 mol dm^{-3} s^{-1}
$T_2 = 50.00 + 273.15 = 323.15$ K
k_2 = 21.1 mol dm^{-3} s^{-1}

$\ln\left(\frac{2.64}{21.1}\right) = \frac{E_a}{8.31}\times\left(\frac{1}{323.15}-\frac{1}{293.15}\right)$;

$-2.08 = \frac{E_a}{8.31}\times -3.17\times10^{-4}$

E_a = 54500 J mol^{-1}

divide by 1000 to convert to kJ mol^{-1}:
54.5 kJ mol^{-1}; **[2]**

iii $k = Ae^{\left(\frac{-E_a}{RT}\right)}$

The activation energy must be in J mol^{-1}

E_a = 54500 J mol^{-1}

Taking T = 293.15 K,
k = 2.64 mol dm^{-3} s^{-1}

Substituting in values:

$A = \frac{2.64}{e^{\frac{-54500}{(8.31\times293.15)}}} = 1.37\times10^{10}$;

The units of A are the same as the units of k, so: mol^{-1} dm^3 s^{-1}

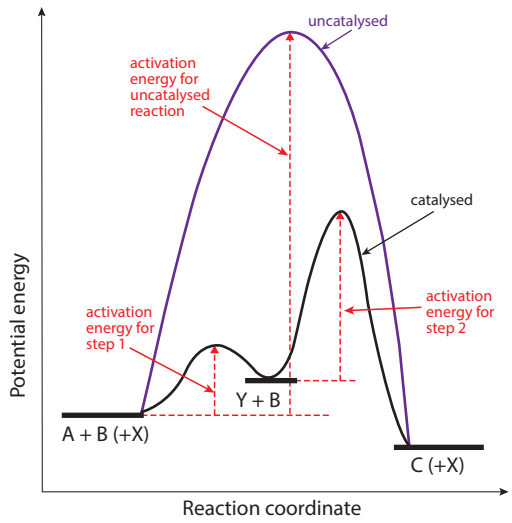
$A = 1.37\times10^{10}$ mol^{-1} dm^3 s^{-1}; **[2]**

17 a X is the catalyst – it reacts in the first step but is produced again at the end, so, overall, it has not been used up in the reaction. Y is an intermediate because it is produced in the first step but then used up again – there is no Y present at the end of the reaction. **[1]**

b A catalyst acts by allowing the reaction to proceed by an alternative pathway of lower activation energy;

A larger fraction of particles has energy greater than the activation energy, therefore, a greater proportion of collisions results in reaction and the reaction rate increases; **[2]**

c



exothermic and uncatalysed path above catalysed path **[1]**

catalysed reaction having two peaks and second peak higher **[1]**

for activation energy labels **[1]**

Chemistry for the IB Diploma – Owen © Cambridge University Press & Assessment 2023

18 a gradient of graph $= \dfrac{19.0 - 12.0}{1.60 \times 10^{-3} - 5.00 \times 10^{-3}}$

$= -2060$ (K);

$\ln k = \dfrac{-E_a}{RT} + \ln A$

gradient $= \dfrac{-E_a}{R}$

$-2060 = \dfrac{-E_a}{8.31}$;

$E_a = 17\ 100$ J mol^{-1} or 17.1 kJ mol^{-1};

allow values in the range 16.9–17.3 **[3]**

b ln A is the intercept on the ln k axis: 22.2

$A = e^{22.2} = 4.38 \times 10^9$;

The units of A are the same as those of k, so $A = 4.38 \times 10^9$ mol^{-1} dm^3 s^{-1};

allow values in the range 3.58 × 10^9 to 5.91 × 10^9 **[2]**

Chemistry for the IB Diploma – Owen © Cambridge University Press & Assessment 2023

Chapter 18

Test your understanding

1 Macroscopic properties remain constant/all concentrations are constant;

And the rate of the forward reaction = the rate of the reverse reaction

2 a shifts to left; fewer moles of gas on left (3 as opposed to 5 on right)

b shifts to left; fewer moles of gas on left (2 as opposed to 3 on right)

c shifts to right; fewer moles of gas on right (1 as opposed to 2 on left)

d shifts to right; fewer moles of gas on right (0 as opposed to 1 on left)

3 a no change; same number of moles of gas on each side

b shifts to left; more moles of gas on left (4 as opposed to 2 on right)

c shifts to left; more moles of gas on left (1.5 as opposed to 1 on right)

4 a shifts to left; reverse reaction (to the left) is endothermic

b shifts to left; reverse reaction (to the left) is endothermic

c shifts to right; forward reaction (to the right) is endothermic

d shifts to right; forward reaction (to the right) is endothermic

5 a shifts to right; forward reaction (to the right) is exothermic

b shifts to left; reverse reaction (to the left) is exothermic

c shifts to right; forward reaction (to the right) is exothermic

6 a shifts to right; to replace the CO_2 that has been removed

b shifts to left; to use up the H^+ that has been added

c shifts to right; the NaOH reacts with the H^+, so the position of equilibrium shits to the right to replace it

d shifts to right (the products formed are acids and will react with NaOH – their concentration is lowered)

7 a $K = \frac{[N_2O_3(g)]}{[NO(g)][NO_2(g)]}$

b $K = \frac{[CO(g)][H_2(g)]^3}{[CH_4(g)][H_2O(g)]}$

c $K = \frac{[H_2(g)]^2[O_2(g)]}{[H_2O(g)]^2}$

d $K = \frac{[NO(g)]^4[H_2O(g)]^6}{[NH_3(g)]^4[O_2(g)]^5}$

e $K = \frac{[NO_2(g)]^2}{[NO(g)]^2[O_2(g)]}$

8 a $K = \frac{[NO(g)][NO_2(g)]}{[N_2O_3(g)]}$

b $K = \frac{[CH_4(g)][H_2O(g)]}{[CO(g)][H_2(g)]^3}$

c $K = \frac{[H_2O(g)]}{[H_2(g)][O_2(g)]^{1/2}}$

d $K = \frac{[NO(g)]^2[H_2O(g)]^3}{[NH_3(g)]^2[O_2(g)]^{5/2}}$

e $K = \frac{[NO(g)][O_2(g)]^{1/2}}{[NO_2(g)]}$

9 Both reactions have been reversed, so K', the equilibrium constant is $\frac{1}{K}$, where K is the equilibrium constant of the original reaction. The new values are: 10^{-33} and 10^{-19}

10 a To the right, the value of K is very much greater than 1.

b i More to the left since $K << 1$. Virtually no iodine atoms are present at 298 K.

ii The position of equilibrium lies much more to the right since K is much larger than it was at the lower temperature - there will be significantly more iodine present as separate atoms than at the lower temperature. $[I(g)] > [I_2(g)]$ at the higher temperature.

Chemistry for the IB Diploma – Owen © Cambridge University Press & Assessment 2023

11 a position of equilibrium shifts to left – fewer moles of gas on left; *K* stays the same – only temperature affects *K*.

b position of equilibrium shifts to right – forward reaction endothermic-; *K* increases – at equilibrium, more products (on top of expression for *K*).

c position of equilibrium shifts to right – forward reaction exothermic; *K* increases – at equilibrium, more products (on top of expression for *K*).

d position of equilibrium shifts to right – to use up H_2; *K* stays the same – only temperature affects *K*.

e position of equilibrium shifts to right – side with fewer moles of gas; *K* stays the same – only temperature affects *K*.

f no effect on position of equilibrium; *K* stays the same; a catalyst speeds up forward and reverse reactions equally.

g no effect on position of equilibrium – same number of moles of gas on each side; *K* stays the same – only temperature affects *K*.

h position of equilibrium shifts to left – to use up H_2; *K* stays the same – only temperature affects *K*.

12 a $K = \frac{0.500}{0.150^2} = 22.2$

b $\frac{(7.86\times10^{-4})^2 \times (9.37\times10^{-5})^4}{(1.50\times10^{-3})^2 \times (2.75\times10^{-3})^3} = 1.02\times10^{-9}$

13 a Amount of *A* that reacted is 0.100 – 0.0600 = 0.0400 mol

From the equation, 2 mol *A* produce 1 mol Z

0.0400 mol *A* produce 0.0200 mol *Z*

0.500 + 0.0200 = 0.520 mol *Z*

b Amount of *Z* that has been produced = 0.400 mol

From the equation, 2 mol *A* produce 2 mol Z

Therefore 0.400 mol A must react to produce 0.400 mol *Z*.

Amount of A at equilibrium = 1.00 – 0.400 = 0.600 mol

From the equation, 1 mol X produces 2 mol Z, therefore 0.200 mol X must react to produce 0.400 mol Z.

Amount of X at equilibrium = 2.00 – 0.200 = 1.80 mol

c Amount of X that reacted = 0.200 – 0.0600 = 0.140 mol

From the equation, 0.140 mol X reacts with 0.0700 mol A

Amount of A at equilibrium = 0.200 – 0.0700 = 0.130 mol

0.140 mol X produce 0.0700 mol R – this is the amount at equilibrium

0.140 mol X produce 0.0700 mol Z – this is the amount at equilibrium

d Amount of Z that reacted = 0.600 – 0.580 = 0.020 mol

From the equation, 0.020 mol Z produce 0.010 mol A

Amount of A at equilibrium = 0.100 + 0.010 = 0.110 mol

0.020 mol Z produce 0.020 mol X

Amount of X at equilibrium = 0.400 + 0.020 = 0.420 mol

0.020 mol Z reacts with 0.010 mol R

Amount of R at equilibrium = 0.100 – 0.010 = 0.090 mol

14 a $K = \frac{[Z(g)]}{[A(g)][X(g)]}$

b i Amount of A that reacted = 0.200 – 0.100 = 0.100 mol

0.100 mol A reacts with 0.100 mol X; amount of X at equilibrium = 0.300 mol

0.100 mol A produces 0.100 mol Z

Volume of container is 1.00 dm^3, therefore all equilibrium concentrations numerically equal to equilibrium amounts.

$K = \frac{0.100}{0.100\times0.300} = 3.33$

Chemistry for the IB Diploma – Owen © Cambridge University Press & Assessment 2023

ii Amount of A that reacted = 0.200 – 0.150 = 0.050 mol

0.050 mol A reacts with 0.050 mol X; amount of X at equilibrium = 0.050 mol

0.050 mol A produces 0.050 mol Z; amount of Z at equilibrium = 0.150 mol

Volume of container is 10.0 dm^3, therefore divide amounts by 10.0 to get equilibrium concentrations.

$$K = \frac{\left(\frac{0.150}{10.0}\right)}{\left(\frac{0.150}{10.0}\right)\times\left(\frac{0.050}{10.0}\right)} = 200$$

c Forward reaction is endothermic because the value of K is higher at 400 K than at 300 K; therefore, the position of equilibrium must have shifted to the right (endothermic direction) as the temperature increased.

15 a $K = \frac{[R(g)]^4[Z(g)]}{[A(g)]^2[X(g)]}$

b i 0.200 mol A reacted to produce 0.100 mol Z

Amount of A at equilibrium = 0.800 – 0.200 = 0.600 mol

0.100 mol X reacted to produce 0.100 mol Z

Amount of X at equilibrium = 0.400 – 0.100 = 0.300 mol

From the equation, the amount of R produced will be 4 times the amount of Z produced, i.e. 0.400 mol

Volume of container is 10.0 dm^3, therefore divide amounts by 10.0 to get equilibrium concentrations.

$$K = \frac{\left(\frac{0.400}{10.0}\right)^4\left(\frac{0.100}{10.0}\right)}{\left(\frac{0.600}{10.0}\right)^2\left(\frac{0.300}{10.0}\right)} = 2.37\times10^{-4}$$

ii 0.100 mol Z reacted to produce 0.200 mol A

Amount of Z at equilibrium = 2.000 – 0.100 = 1.900 mol

If 0.200 mol A is produced, 0.100 mol of X also produced

0.400 mol R reacted to produce 0.200 mol A

Amount of R at equilibrium = 1.000 – 0.400 = 0.600 mol

Volume of container is 20.0 dm^3, therefore divide amounts by 20.0 to get equilibrium concentrations.

$$K = \frac{\left(\frac{0.600}{20.0}\right)^4\left(\frac{1.900}{20.0}\right)}{\left(\frac{0.200}{20.0}\right)^2\left(\frac{0.100}{20.0}\right)} = 0.154$$

c Forward reaction is exothermic because the value of K is higher at 500 K than at 800 K; therefore, the position of equilibrium must have shifted to the left (the endothermic direction) as the temperature increased.

16 a $Q = \frac{[N_2O_3(g)]}{[NO(g)][NO_2(g)]}$

b $Q = \frac{[CO(g)][H_2(g)]^3}{[CH_4(g)][H_2O(g)]}$

c $Q = \frac{[H_2(g)]^2[O_2(g)]}{[H_2O(g)]^2}$

d $Q = \frac{[NO(g)]^4[H_2O(g)]^6}{[NH_3(g)]^4[O_2(g)]^5}$

e $Q = \frac{[NO_2(g)]^2}{[NO(g)]^2[O_2(g)]}$

17 a i $Q = \frac{[Z(g)]}{[A(g)]^2} = \frac{0.200}{0.100^2} = 20.0$

ii not at equilibrium because $Q \neq K$

iii must move to the right to get to equilibrium because Q is smaller than K. More of the substances on the top of the expression must be produced to increase the value until $Q = K$.

Chemistry for the IB Diploma – Owen © Cambridge University Press & Assessment 2023

b i $Q = \frac{[Z(g)]^2}{[A(g)]} = \frac{0.0800^2}{0.320} = 0.0200$

ii at equilibrium, because $Q = K$

iii at equilibrium

c i $Q = \frac{[Z(g)][E(g)]^2}{[R(g)][X(g)]^2}$

$= \frac{(7.40\times10^{-3})(9.30\times10^{-3})^2}{(1.20\times10^{-3})(2.50\times10^{-3})^2} = 85.3$

ii not at equilibrium because $Q \neq K$

iii must move to left to get to equilibrium because $Q > K$; more of the substances on the bottom of the expression must be produced to reduce the value until $Q = K$.

d i $Q = \frac{[E(g)][Z(g)]^2}{[X(g)]^3[R(g)]^2}$

$= \frac{(7.40\times10^{-1})(3.65\times10^{-1})^2}{(8.20\times10^{-2})^3(5.70\times10^{-2})^2} = 55000$

ii not at equilibrium because $Q \neq K$

iii must move to left to get to equilibrium because $Q > K$; more of the substances on the bottom of the expression must be produced to reduce the value until $Q = K$.

e i $Q = \frac{[Z(g)]^3[E(g)]^2}{[R(g)]^2[X(g)]}$

$= \frac{(9.86\times10^{-2})^3(2.47\times10^{-3})^2}{(1.56\times10^{-3})^2(4.78\times10^{-2})} = 0.0503$

ii not at equilibrium because $Q \neq K$

iii must move to right to get to equilibrium because $Q < K$; more of the substances on the top of the expression must be produced to increase the value until $Q = K$.

18 a i $Q = \frac{[X(g)]}{[Z(g)]} = \frac{(0.200/1.00)}{(0.100/1.00)} = 2.00$

$Q < K$, therefore the system must move to the right towards equilibrium. Q must increase until it equals K.

ii Z must react to form X to reach equilibrium.

Assume that y mol Z react, then equilibrium amounts are:

Z: 0.100 – y

X: 0.200 + y

The volumes will cancel out, therefore, at equilibrium

$\frac{0.200 + y}{0.100 - y} = 20.0$; $y = 0.0857$

0.286 mol X

b i $Q = \frac{[X(g)]}{[Z(g)]} = \frac{\left(\frac{8.24\times10^{-3}}{5.00}\right)}{\left(\frac{1.56\times10^{-3}}{5.00}\right)} = 5.28$

$Q > K$, therefore the system must move to the left towards equilibrium. Q must decrease until it equals K.

ii X must react to form Z to reach equilibrium.

Assume that y mol X react, then equilibrium amounts are:

X: $8.24 \times 10^{-3} - y$

Z: $1.56 \times 10^{-3} + y$

The voulmes will cancel out, therefore, at equilibrium

$\frac{8.24\times10^{-3} - y}{1.56\times10^{-3} + y} = 4.20$; $y = 3.25 \times 10^{-4}$

1.88×10^{-3} mol Z

19 a Assume that y mol A reacts with y mol Z to get to equilibrium. Volume of container is 1.00 dm^3 so we can ignore this. Equilibrium concentrations are:

[X(g)] = y mol dm^{-3}

[B(g)] = y mol dm^{-3}

[A(g)] = 0.100 – y mol dm^{-3}

[Z(g)] = 0.100 – y mol dm^{-3}

$K = \frac{[X(g)][B(g)]}{[A(g)][Z(g)]} = 9.00 = \frac{y^2}{(0.100 - y)^2}$

$y = 0.075$

Chemistry for the IB Diploma – Owen © Cambridge University Press & Assessment 2023

Therefore equilibrium concentration of X is 0.075 mol dm^{-3}

Amount of X at equilibrium is 0.075 mol – the volume is 1.00 dm^3, therefore the amount is equal to the concentration.

b i All the concentrations are the same (and there are no coefficients in the chemical equation), therefore Q = 1.00; 1.00 < 16.0, therefore, moves system to right towards equilibrium

ii Assume that y mol A reacts with y mol Z to get to equilibrium. Volume of container is 2.00 dm^3. Equilibrium concentrations are:

$$[X(g)] = \frac{(0.200 + y)}{2} \text{ mol dm}^{-3}$$

$$[B(g)] = \frac{(0.200 + y)}{2} \text{ mol dm}^{-3}$$

$$[A(g)] = \frac{(0.200 - y)}{2} \text{ mol dm}^{-3}$$

$$[Z(g)] = \frac{(0.200 + y)}{2} \text{ mol dm}^{-3}$$

$$K = \frac{[X(g)][B(g)]}{[A(g)][Z(g)]} = 16.00$$

$$= \frac{(0.200 + y)^2}{(0.200 - y)^2}$$

$$y = 0.12$$

At equilibrium [A(g)] = (0.200 – y)/2 i.e.

$$[A(g)] = (0.200 - 0.12)/2$$
$$= 0.040 \text{ mol dm}^{-3}$$

20 When A reacts it produces equal numbers of moles of B and C and since there was initially none of either of these present, at equilibrium [B] = [C]

The expression for the equilibrium constant is:

$$1.58 \times 10^{-9} = \frac{[B]^2}{0.100}$$

since K is small we assume that $[A]_{equilibrium} \simeq [A]_{initial}$

[B] = 1.26 × 10^{-5} mol dm^{-3}

21 When A reacts it produces equal numbers of moles of B, C and D, and since there was initially none of any of these present, at equilibrium

[B] = [C] = [D]

$$6.23 \times 10^{-18} = \frac{[C]^3}{0.0200}$$

K is small, so we assume that:

$$[A]_{equilibrium} \simeq [A]_{initial}$$

[C] = 4.99 × 10^{-7} mol dm^{-3}

22 a $\Delta G = \Delta G^{\ominus} + RT\ln Q$

$$Q = \frac{[Z]}{[A]} = \frac{0.100}{0.100} = 1.00 \qquad \ln Q = 0$$

$$\Delta G = -10000 + (8.31 \times 500 \times 0)$$
$$= -10\,000 \text{ J mol}^{-1}$$

$$\Delta G = -10 \text{ kJ mol}^{-1}$$

b $\Delta G = \Delta G^{\ominus} + RT\ln Q$

$$Q = \frac{[Z]}{[A]} = \frac{0.110}{0.0900} = (1.22 \quad \ln Q = 0.201)$$

$$\Delta G = -10000 + (8.31 \times 500 \times 0.201)$$
$$= -9170 \text{ J mol}^{-1}$$

$$\Delta G = -9.17 \text{ kJ mol}^{-1}$$

c $\Delta G = \Delta G^{\ominus} + RT\ln Q$

$$Q = \frac{[Z]}{[A]} = \frac{0.150}{0.0500} = (3.00 \quad \ln Q = 1.099)$$

$$\Delta G = -10000 + (8.31 \times 500 \times 1.099)$$
$$= -5440 \text{ J mol}^{-1}$$

$$\Delta G = -5.44 \text{ kJ mol}^{-1}$$

The values are getting closer to zero – the system is moving towards equilibrium.

23 a $\Delta G = \Delta G^{\ominus} + RT\ln Q$

$$Q = \frac{[A][D]}{[X]^2} = \frac{0.0250 \times 0.0150}{0.120^2}$$

$$= 0.02604 \qquad \ln Q = -3.648$$

$$\Delta G = 25000 + [8.31 \times 1000 \times (-3.648)]$$
$$= -5320 \text{ J mol}^{-1}$$

$$\Delta G = -5.32 \text{ kJ mol}^{-1}$$

Value is negative, therefore the system moves to the right towards equilibrium.

Chemistry for the IB Diploma – Owen © Cambridge University Press & Assessment 2023

b $\Delta G = \Delta G^{\ominus} + RT\ln Q$

$$Q = \frac{[A][D]}{[X]^2} = \frac{0.200 \times 0.100}{0.100^2}$$

$= 2.00 \qquad \ln Q = 0.693$

$\Delta G = 25000 + (8.31 \times 1000 \times 0.693)$
$= 30800 \text{ J mol}^{-1}$

$\Delta G = 30.8 \text{ kJ mol}^{-1}$

Value is positive, therefore the system moves to the left towards equilibrium.

24 a $\Delta G^{\ominus} = -RT\ln K$

$\Delta G^{\ominus} = -8.31 \times 298 \times \ln 2.78 = -2530 \text{ J mol}^{-1}$

$\Delta G = -2.53 \text{ kJ mol}^{-1}$

b $\Delta G^{\ominus} = -RT\ln K$

$\Delta G^{\ominus} = -8.31 \times 333 \times \ln(3.58 \times 10^5)$
$= -35400 \text{ J mol}^{-1}$

$\Delta G = -35.4 \text{ kJ mol}^{-1}$

c $\Delta G^{\ominus} = -RT\ln K$

$\Delta G^{\ominus} = -8.31 \times (454.85 + 273.15) \times \ln(7.56 \times 10^{-4})$
$= 43500 \text{ J mol}^{-1}$

$\Delta G = 43.5 \text{ kJ mol}^{-1}$

25 a i $\Delta G^{\ominus} = -RT\ln K$

$50000 = -8.31 \times 298 \times \ln K$

$\ln K = -20.19$

$K = e^{-20.19} = 1.70 \times 10^{-9}$

ii $\Delta G^{\ominus} = -RT\ln K$

$-25200 = -8.31 \times 350 \times \ln K$

$\ln K = 8.664$

$K = e^{8.664} = 5790$

iii $\Delta G^{\ominus} = -RT\ln K$

$-154000 = -8.31 \times 300 \times \ln K$

$\ln K = 61.77$

$K = e^{61.77} = 6.72 \times 10^{26}$

b i towards left; because $K < 1$

ii towards right; because $K > 1$

iii towards right; because $K > 1$

Exam-style questions

1 C

2 B

3 A

4 A

5 C

6 D

7 B

8 C

9 D

10 C

11 a In dynamic equilibrium, macroscopic properties are constant/the concentrations of all reactants and products remain constant;

The rate of the forward reaction is equal to the rate of the reverse reaction; **[2]**

b i The position of equilibrium shifts to the right because the forward reaction is endothermic;

The expression for the equilibrium constant is:

$$K = \frac{[H_2O][CO]}{[H_2][CO_2]}$$

The value of the equilibrium constant increases because more H_2O and CO are present at equilibrium. (The concentrations of H_2O and CO are on the top of this expression.); **[2]**

ii The position of equilibrium does not change because there are the same number of moles of gas on both sides of the equation;

The value of the equilibrium constant does not change – only a change in temperature affects the value of the equilibrium constant; **[2]**

iii The position of equilibrium and the value of the equilibrium constant do not change;

A catalyst speeds up the forward and reverse reactions equally; **[2]**

Chemistry for the IB Diploma – Owen © Cambridge University Press & Assessment 2023

12 a $K = \frac{[NO(g)]^2}{[N_2(g)][O_2(g)]}$ **[1]**

b As the temperature increases, the value of the equilibrium constant increases. This means that the position of equilibrium has shifted to the right (more NO present at equilibrium);

When the temperature increases, the position of equilibrium shifts in the endothermic direction – the forward reaction is, therefore, endothermic; **[2]**

13 a $K = \frac{[NO_2(g)]^2}{[N_2O_4(g)]}$ **[1]**

b The forward reaction is endothermic, and, as the temperature is increased, the position of equilibrium shifts in the endothermic direction (to the right); so there will be more NO_2 (brown) in the equilibrium mixture – the reaction mixture will become browner. **[2]**

c

	$N_2O_4(g)$	$NO_2(g)$
initial amount / mol	0.200	0.00
equilibrium amount / mol	0.140	

The amount of N_2O_4 that has reacted is 0.200 − 0.140 = 0.060 mol.

From the chemical equation, we can see that 1 mol N_2O_4 reacts to form 2 mol NO_2.

Therefore, 0.060 mol N_2O_4 react to form 2 × 0.060 = 0.120 mol NO_2, so 0.120 mol NO_2 is present at equilibrium;

The volume of the container is 4.00 dm^3.

Equilibrium concentrations are worked out using the equation:

$$\text{concentration} = \frac{\text{amount}}{\text{volume}}$$

Therefore the equilibrium concentrations are

$$[N_2O_4] = \frac{0.140}{4.00} = 0.0350 \text{ mol dm}^{-3}$$

$$[NO_2] = \frac{0.120}{4.00} = 0.0300 \text{ mol dm}^{-3};$$

$$K = \frac{[NO_2(g)]^2}{[N_2O_4(g)]}$$

$$K = \frac{0.0300^2}{0.0350} = 0.0257;$$ **[3]**

14 a i $K = \frac{[SO_3(g)]^2}{[SO_2(g)]^2[O_2(g)]}$ **[1]**

ii

	$SO_2(g)$	$O_2(g)$	$SO_3(g)$
initial amount / mol	0.120	0.120	0.00
equilibrium amount / mol			0.060

From the chemical equation, we can work out that 0.030 mol O_2 must have reacted to produce 0.060 mol SO_3 (the mole ratio is 1 : 2 in the equation). Therefore, the amount of O_2 left at equilibrium is 0.120 − 0.030 = 0.090 mol

The volume of the reaction vessel is 2.00 dm^3.

Concentration of O_2 at equilibrium $= \frac{0.090}{2.00}$

$= 0.045 \text{ mol dm}^{-3}$ **[1]**

iii To work out the equilibrium constant, we need the equilibrium concentrations of all species.

	$SO_2(g)$	$O_2(g)$	$SO_3(g)$
initial amount / mol	0.120	0.120	0.00
equilibrium amount / mol		0.090	0.060

From the chemical equation, 0.060 mol SO_2 must have reacted to produce 0.060 mol SO_3 (the mole ratio is 2 : 2 in the equation). Therefore, the amount of SO_2 left at equilibrium is

0.120 − 0.060 = 0.060 mol

The volume of the reaction vessel is 2.00 dm^3.

Concentration of SO_2 at equilibrium

$$= \frac{0.060}{2.00} = 0.030 \text{ mol dm}^{-3}$$

$$K = \frac{[SO_3(g)]^2}{[SO_2(g)]^2[O_2(g)]}$$

$$K = \frac{0.030^2}{0.030^2 \times 0.045}; K = 22;$$ **[2]**

Chemistry for the IB Diploma – Owen © Cambridge University Press & Assessment 2023

b **i** $\Delta H^{\ominus} = \Sigma\Delta H_f^{\ominus}(\text{products}) - \Sigma\Delta H_f^{\ominus}(\text{reactants})$

$\Delta H_f^{\ominus}(\text{products}) = 2 \times -395 = -790 \text{ kJ mol}^{-1}$

$\Delta H_f^{\ominus}(\text{reactants}) = 2 \times -297 = -594 \text{ kJ mol}^{-1}$;

The enthalpy change of formation of $O_2(g)$ is zero, as it is an element in its standard state.

$\Delta H^{\ominus} = -790 - (-594); = -196 \text{ kJ mol}^{-1}$; **[2]**

ii The reaction is exothermic in the forward direction, so, as the temperature is increased from 1100 to 1500 K, the position of equilibrium shifts in the endothermic direction, i.e., to the left;

There will be less SO_3 present at equilibrium and because SO_3 appears on the top of the K expression, the value of K will be lower at 1500 K; **[2]**

15 **a** $K = \dfrac{[HI(g)]^2}{[H_2(g)][I_2(g)]}$ **[1]**

b The expression for the equilibrium constant for this reaction would be

$$K' = \frac{[H_2(g)][I_2(g)]}{[HI(g)]^2}$$

This is the inverse of the equilibrium constant expression in **a** so the value of the equilibrium constant is $\frac{1}{54.2} = 0.0185$ **[1]**

c **i** $[HI(g)] = \dfrac{2.20 \times 10^{-2}}{4.00}$

$= 5.50 \times 10^{-3} \text{ mol dm}^{-3}$

$[H_2(g)] = \dfrac{3.30 \times 10^{-2}}{4.00}$

$= 8.25 \times 10^{-3} \text{ mol dm}^{-3}$

$[I_2(g)] = \dfrac{3.30 \times 10^{-2}}{4.00}$

$= 8.25 \times 10^{-3} \text{mol dm}^{-3}$

$$Q = \frac{[HI(g)]^2}{[H_2(g)][I_2(g)]}$$

$$Q = \frac{[5.50 \times 10^{-3}]^2}{[8.25 \times 10^{-3}][8.25 \times 10^{-3}]} = 0.444;$$

(The volumes will actually cancel out in the expression for Q, so the same answer would be obtained using amounts rather than concentrations.)

The value of Q is less than the value of K, therefore, the system must move to the right towards equilibrium to produce more HI; **[2]**

ii

	$H_2(g)$	+	$I_2(g)$	$\rightleftharpoons$	$2HI(g)$
initial amount / mol	3.30×10^{-2}		3.30×10^{-2}		2.20×10^{-2}
equilibrium amount / mol	$3.30 \times 10^{-2} - x$		$3.30 \times 10^{-2} - x$		$2.20 \times 10^{-2} + 2x$
equilibrium concentration / mol dm^{-3}	$\dfrac{3.30 \times 10^{-2} - x}{4.00}$		$\dfrac{3.30 \times 10^{-2} - x}{4.00}$		$\dfrac{2.20 \times 10^{-2} + 2x}{4.00}$

Chemistry for the IB Diploma – Owen © Cambridge University Press & Assessment 2023

$$K = \frac{[HI(g)]^2}{[H_2(g)][I_2(g)]}$$

$$54.2 = \frac{\left[\frac{(2.20 \times 10^{-2} + 2x)}{4.00}\right]^2}{\left[\frac{(3.30 \times 10^{-2} - x)}{4.00}\right]\left[\frac{(3.30 \times 10^{-2} - x)}{4.00}\right]};$$

All the 4.00 cancel:

$$54.2 = \frac{(2.20 \times 10^{-2} + 2x)^2}{(3.30 \times 10^{-2} - x)(3.30 \times 10^{-2} - x)}$$

We can re-write as:

$$54.2 = \frac{(2.20 \times 10^{-2} + 2x)^2}{(3.30 \times 10^{-2} - x)^2}$$

take the square root of both sides:

$$7.36 = \frac{2.20 \times 10^{-2} + 2x}{3.30 \times 10^{-2} - x}$$

$x = 0.0236$;

equilibrium concentration of H_2 is $\frac{3.30 \times 10^{-2} - x}{4.00}$, i.e.

$$\frac{3.30 \times 10^{-2} - 0.0236}{4.00} = 2.35 \times 10^{-3} \text{ mol dm}^{-3};$$ **[3]**

d $\Delta G^{\ominus} = -RT\ln K$

$\Delta G^{\ominus} = -8.31 \times 700 \times \ln 54.2 = -23\,200$ J mol^{-1} or -23.2 kJ mol^{-1} **[1]**

16 a $[H_2(g)] = \frac{5.00 \times 10^{-3}}{10.0} = 5.00 \times 10^{-4}$ mol dm^{-3}

$[CO_2(g)] = \frac{5.00 \times 10^{-3}}{10.0} = 5.00 \times 10^{-4}$ mol dm^{-3}

$[H_2O(g)] = \frac{1.00 \times 10^{-3}}{10.0} = 1.00 \times 10^{-4}$ mol dm^{-3}

$[CO(g)] = \frac{1.00 \times 10^{-3}}{10.0} = 1.00 \times 10^{-4}$ mol dm^{-3}

$$Q = \frac{[H_2O(g)][CO(g)]}{[H_2(g)][CO_2(g)]} = \frac{1.00 \times 10^{-4} \times 1.00 \times 10^{-4}}{5.00 \times 10^{-4} \times 5.00 \times 10^{-4}} = 0.0400;$$

$\Delta G = \Delta G^{\ominus} + RT\ln Q$

$\Delta G = 2980 + 8.31 \times 1000 \times \ln 0.0400 = -23\,800$ J mol^{-1} or -23.8 kJ mol^{-1}; **[2]**

b The system will move to the right (towards H_2O and CO) because ΔG is negative;

ΔG will get larger/less negative until it becomes zero at equilibrium; **[2]**

c $\Delta G^{\ominus} = -RT\ln K$

$2980 = -8.31 \times 1000 \times \ln K$;

$\ln K = -0.359$

$K = e^{-0.359} = 0.699$; **[2]**

Chemistry for the IB Diploma – Owen © Cambridge University Press & Assessment 2023

d

	$H_2(g)$	+ $CO_2(g)$	$\rightleftharpoons$ $H_2O(g)$	+ $CO(g)$
initial amount / mol	5.00×10^{-3}	5.00×10^{-3}	1.00×10^{-3}	1.00×10^{-3}
equilibrium amount / mol	$5.00 \times 10^{-3} - x$	$5.00 \times 10^{-3} - x$	$1.00 \times 10^{-3} + x$	$1.00 \times 10^{-3} + x$
equilibrium concentration / mol dm^{-3}	$\frac{5.00 \times 10^{-3} - x}{10.0}$	$\frac{5.00 \times 10^{-3} - x}{10.0}$	$\frac{1.00 \times 10^{-3} - x}{10.0}$	$\frac{1.00 \times 10^{-3} - x}{10.0}$

$$K = \frac{[H_2O(g)][CO(g)]}{[H_2(g)][CO_2(g)]}$$

$$0.699 = \frac{\left[\frac{(1.00\times10^{-3}+x)}{10.0}\right]\left[\frac{(1.00\times10^{-3}+x)}{10.0}\right]}{\left[\frac{(5.00\times10^{-3}-x)}{10.0}\right]\left[\frac{(5.00\times10^{-3}-x)}{10.0}\right]};$$

All the 10.0 cancel:

$$0.699 = \frac{(1.00\times10^{-3}+x)(1.00\times10^{-3}+x)}{(5.00\times10^{-3}-x)(5.00\times10^{-3}-x)}$$

We can re-write as:

$$0.699 = \frac{(1.00\times10^{-3}+x)^2}{(5.00\times10^{-3}-x)^2}$$

take the square root of both sides

$$0.836 = \frac{1.00\times10^{-3}+x}{5.00\times10^{-3}-x}$$

$x = 1.73 \times 10^{-3}$;

equilibrium concentration of H_2 is $\frac{5.00\times10^{-3}-x}{10.0}$, i.e.,

$$\frac{5.00\times10^{-3}-1.73\times10^{-3}}{10.0} = 3.27\times10^{-4}\text{ mol dm}^{-3};$$ **[3]**

Chemistry for the IB Diploma – Owen © Cambridge University Press & Assessment 2023

Chapter 19

Test your understanding

1 a $Zn + H_2SO_4 \rightarrow ZnSO_4 + H_2$

b $CuO + 2HNO_3 \rightarrow Cu(NO_3)_2 + H_2O$

c $2NH_3 + H_2SO_4 \rightarrow (NH_4)_2SO_4$

d $Ca(HCO_3)_2 + 2HCl \rightarrow CaCl_2 + 2CO_2 + 2H_2O$

e $Mg(OH)_2 + H_2SO_4 \rightarrow MgSO_4 + 2H_2O$

f $Cu + H_2SO \rightarrow$ no reaction

g $CaO + 2HCl \rightarrow CaCl_2 + H_2O$

h $K_2CO_3 + 2CH_3COOH \rightarrow 2CH_3COOK + CO_2 + H_2O$

i $CH_3NH_2 + HCl \rightarrow CH_3NH_3Cl$

j $NH_3 + HCOOH \rightarrow HCOONH_4$

2 a calcium oxide/hydroxide and nitric acid

b cobalt(II) oxide/hydroxide and sulfuric acid

c copper(II) oxide/hydroxide and hydrochloric acid

d magnesium oxide/hydroxide and ethanoic acid

e ethylamine and sulfuric acid

3 An acid is a proton (H^+) donor; a base is a proton (H^+) acceptor.

4 a $HCN(aq) + H_2O(l) \rightleftharpoons CN^-(aq) + H_3O^+(aq)$

acid 1 base 2 base 1 acid 2

Conjugate acid-base pairs are species with the same numbers, i.e.:

HCN/CN^- and H_2O/H_3O^+

b $CH_3NH_2(aq) + H_2O(l) \rightleftharpoons CH_3NH_3^+(aq) + OH^-(aq)$

base 1 acid 2 acid 1 base 2

Conjugate acid-base pairs are species with the same numbers, i.e.:

$CH_3NH_2/CH_3NH_3^+$ and H_2O/OH^-

c $NH_4^+(aq) + OH^-(aq) \rightleftharpoons NH_3(aq) + H_2O(l)$

acid 1 base 2 base 1 acid 2

Conjugate acid-base pairs are species with the same numbers, i.e.:

NH_4^+/NH_3 and OH^-/H_2O

d $NH_3(aq) + CH_3COOH(aq) \rightleftharpoons NH_4^+(aq) + CH_3COO^-(aq)$

base 1 acid 2 acid 1 base 2

Conjugate acid-base pairs are species with the same numbers, i.e.:

NH_3/NH_4^+ and CH_3COOH/CH_3COO^-

Chemistry for the IB Diploma – Owen © Cambridge University Press & Assessment 2023

5 Add H^+ to each formula:

a NH_4^+

b H_2O

c H_2SO_4

d HBr

e $H_2PO_4^-$

6 Remove H^+ from each formula:

a CO_3^{2-}

b OH^-

c $HCOO^-$

d CH_3NH_2

7 **a** acid; proton donor – donates H^+ to H_2O

b base; proton acceptor – accepts H^+ to form H_2CO_3

c base; proton acceptor – accepts H^+ to form $CH_3COOH_2^+$

8 HCO_3^-, H_2O, $H_2PO_4^-$ can act as both Brønsted-Lowry acids and bases (are amphiprotic) because they can all accept H^+ and donate H^+

NO_3^- and OCl^- are not amphiprotic because they do not contain H, therefore cannot donate H^+

NH_4^+ is not amphiprotic because it is already positively charged and cannot accept H^+ – N also does not have a lone pair to donate to H^+ / N is already forming its maximum number of bonds

9 $pH = -\log_{10}[H^+(aq)]$

$[H^+(aq)] = 10^{-pH}$

pH	$[H^+(aq)]$ / mol dm^{-3}	acidic/alkaline/neutral?
4	1.0×10^{-4}	acidic as pH < 7
6	1.0×10^{-6}	acidic as pH < 7
7	1.0×10^{-7}	neutral as pH = 7
11	1.0×10^{-11}	alkaline as pH > 7
13	1.0×10^{-13}	alkaline as pH > 7

10 **a** $-\log_{10}(4.56 \times 10^{-3}) = 2.34$

b $-\log_{10}(9.83 \times 10^{-13}) = 12.0$

c $-\log_{10}(7.29 \times 10^{-6}) = 5.14$

d $-\log_{10}1.20 = -0.0792$

11 **a** $10^{-11.32} = 4.79 \times 10^{-12}$ mol dm^{-3}

b $10^{-8.95} = 1.12 \times 10^{-9}$ mol dm^{-3}

c $10^{-2.17} = 6.76 \times 10^{-3}$ mol dm^{-3}

d $10^{0.14} = 1.38$ mol dm^{-3}

e $10^{0.00} = 1.00$ mol dm^{-3}

12 Each time the pH goes up by 1 unit, the $[H^+(aq)]$ decreases by a factor of 10.

If pH increases by x units, $[H^+(aq)]$ decreases by a factor of 10^x.

The solution with the lower pH has the higher $[H^+(aq)]$.

a $[H^+(aq)]$ of solution X (10^{-2} mol dm^{-3}) is 10 times higher than that of solution Y (10^{-3} mol dm^{-3})

b $[H^+(aq)]$ of solution X is 10^4 times higher than that of solution Y

c $[H^+(aq)]$ of solution X is 10^9 times higher than that of solution Y

d $[H^+(aq)]$ of solution Y is 10^5 times higher than that of solution X

Chemistry for the IB Diploma – Owen © Cambridge University Press & Assessment 2023

13 When a solution is diluted by a factor of 10^x. the pH increases by x units.

a pH = 5

b pH = 3.2

c pH ≈ 7 (you cannot dilute an acid so that its pH goes above 7)

The calculations in this question hold for diluting strong acids/bases but the pH changes would be different if we were diluting solutions of weak acids/bases.

14

Strong acid	Weak acid	Strong base	Weak base	Salt
HCl	H_2CO_3	NaOH	NH_3	NH_4NO_3
H_2SO_4	HCOOH	$Ba(OH)_2$	CH_3NH_2	Na_2SO_4
HNO_3				KNO_3

15 a $CH_3COOH(aq) \rightleftharpoons CH_3COO^-(aq) + H^+(aq)$

Note: reversible arrow is essential.

b $HNO_3(aq) \rightarrow NO_3^-(aq) + H^+(aq)$

c $H_2CO_3(aq) \rightleftharpoons HCO_3^-(aq) + H^+(aq)$

$HCO_3^-(aq) \rightleftharpoons CO_3^{2-}(aq) + H^+(aq)$

Note: reversible arrows are essential.

In each case, an equation involving H_2O and H_3O^+ would also be correct, e.g. for ethanoic acid:

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

16 a $KOH(aq) \rightarrow K^+(aq) + OH^-(aq)$

b $NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$

c $CH_3NH_2(aq) + H_2O(l) \rightleftharpoons CH_3NH_3^+(aq) + OH^-(aq)$

d $HCO_3^-(aq) + H_2O(l) \rightleftharpoons H_2CO_3(aq) + OH^-(aq)$

Note: reversible arrows are essential in **b**,**c**,**d**.

17 $H_2SO_4(aq) < HCl(aq) < HCN(aq) < NH_3(aq) < NaOH(aq) < Ba(OH)_2(aq)$

$H_2SO_4(aq)$ and HCl(aq) are strong acids, but HCN(aq) is a weak acid. H_2SO_4 is a diprotic acid, so will dissociate twice to form a higher concentration of $H^+(aq)$ (lower pH) than HCl.

$NH_3(aq)$ is a weak base, but NaOH(aq) and $Ba(OH)_2(aq)$ are strong bases. $Ba(OH)_2(aq)$ ionises as:

$Ba(OH)_2(aq) \rightarrow Ba^{2+}(aq) + 2OH^-(aq)$ so has a higher concentration of $OH^-(aq)$ (higher pH) than NaOH(aq).

18 Hydrochloric acid is a strong acid and ethanoic acid is a weak acid, but HCl has the higher pH. The pH is just a measure of the concentration of H^+ ions in solution and, therefore, depends on concentration of the acid. pH is only a useful measure of acid strength when solutions of equal concentration are being compared.

19 $CH_3COO^-(aq)$ is a stronger base than NO_3^-

CH_3COO^- is the conjugate base of ethanoic acid, a weak acid, but NO_3^- is the conjugate base of HNO_3, a strong acid. The stronger the acid, the weaker the conjugate base.

Chemistry for the IB Diploma – Owen © Cambridge University Press & Assessment 2023

20 HCl(aq) is a stronger acid than NH_4^+(aq)

HCl is a strong acid. NH_4^+ is the conjugate acid of ammonia, a weak base, and will be an acid in solution, donating H^+ to H_2O:

$NH_4^+(aq) + H_2O(l) \rightleftharpoons NH_3(aq) + H_3O^+(aq)$

it, however, only dissociates partially, so is a weak acid.

21 $H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq)$

$K_w = [H^+(aq)][OH^-(aq)]$

22 1.00×10^{-14}

23 Remember that $[H^+(aq)]$ and $[OH^-(aq)]$ are not necessarily equal, but multiply together to make 1×10^{-14}.

e.g. if $[H^+(aq)] = 1.0 \times 10^{-3}$ mol dm^{-3}

$K_w = [H^+(aq)][OH^-(aq)]$

$1 \times 10^{-14} = 1.0 \times 10^{-3} \times [OH^-(aq)]$

$[OH^-(aq)] = \frac{1 \times 10^{-14}}{1.0 \times 10^{-3}} = 1.0 \times 10^{-11}$ mol dm^{-3}

$[H^+(aq)]$ / mol dm^{-3}	$[OH^-(aq)]$ / mol dm^{-3}	pH	Acidic or alkaline?
1.0×10^{-3}	1×10^{-11}	3	acidic
1.0×10^{-5}	1×10^{-9}	5	acidic
1×10^{-12}	0.01	12	basic
1×10^{-8}	1×10^{-6}	8	basic
1×10^{-2}	1×10^{-12}	2	acidic

24 **a** $\frac{1.00 \times 10^{-14}}{2.45 \times 10^{-5}} = 4.08 \times 10^{-10}$ mol dm^{-3}

b $\frac{1.00 \times 10^{-14}}{9.38 \times 10^{-10}} = 1.07 \times 10^{-5}$ mol dm^{-3}

c $\frac{1.00 \times 10^{-14}}{10^{-2.78}} = 6.03 \times 10^{-12}$ mol dm^{-3}

d $\frac{1.00 \times 10^{-14}}{10^{-12.66}} = 4.57 \times 10^{-2}$ mol dm^{-3}

e $\frac{1.00 \times 10^{-14}}{10^{-5.39}} = 2.45 \times 10^{-9}$ mol dm^{-3}

25 In pure water $[H^+(aq)] = [OH^-(aq)]$

$K_w = [H^+(aq)][OH^-(aq)]$

$2.52 \times 10^{-13} = [H^+(aq)]^2$

$[H^+(aq)] = 5.02 \times 10^{-7}$ mol dm^{-3}

$pH = -\log_{10}[H^+(aq)] = -\log_{10}[5.02 \times 10^{-7}] = 6.30$

This is the neutral pH at this temperature, so a solution with pH = 6.8 will be alkaline because the pH is greater than the neutral pH.

26 **a** pH = 11, therefore $[H^+(aq)] = 1.0 \times 10^{-11}$ mol dm^{-3}

$K_w = [H^+(aq)][OH^-(aq)]$

$1 \times 10^{-14} = 1.0 \times 10^{-11} \times [OH^-(aq)]$

$[OH^-(aq)] = \frac{1 \times 10^{-14}}{1.0 \times 10^{-11}} = 1.0 \times 10^{-3}$ mol dm^{-3}

b If the solution is diluted by a factor of 100 the $[OH^-(aq)]$ changes to 1.0×10^{-5} mol dm^{-3}

$K_w = [H^+(aq)][OH^-(aq)]$

$1 \times 10^{-14} = [H^+(aq)] \times 1.0 \times 10^{-5}$

$[H^+(aq)] = \frac{1 \times 10^{-14}}{1.0 \times 10^{-5}} = 1.0 \times 10^{-9}$ mol dm^{-3}

$pH = -\log_{10}[H^+(aq)]$
$= -\log_{10}[1.0 \times 10^{-9}] = 9.0$

Alternatively, we realise that if an alkaline solution is diluted by a factor of 10^x, the pH decreases by x units (reaching a limit of 7 at 25 °C). Technically, this only works for solutions of strong bases though.

27 **a** FALSE, the pH is 1

b FALSE, this is an alkali, the pH is 11.0

c TRUE remember that each $Ba(OH)_2$ unit ionises to produce 2 OH^- ions

d FALSE; H_2SO_4 is a diprotic acid, so dissociates twice. The $[H^+(aq)]$ will be greater than 0.010 mol dm^{-3} and the pH lower than 2.

Chemistry for the IB Diploma – Owen © Cambridge University Press & Assessment 2023

28

	pH
a solution containing 0.00100 mol dm^{-3} HNO_3(aq)	Strong acid, so dissociates completely. $[H^+(aq)] = 1.00 \times 10^{-3}$ mol dm^{-3} pH = $-\log_{10}[H^+(aq)] = -\log_{10}[1.00 \times 10^{-3}] = 3.00$
a solution of 1.00 mol dm^{-3} HCl(aq)	Strong acid, so dissociates completely. $[H^+(aq)] = 1.00$ mol dm^{-3} pH = $-\log_{10}[H^+(aq)] = -\log_{10}[1.00] = 0.00$
a solution of 2.00×10^{-4} mol dm^{-3} HNO_3(aq)	$-\log_{10}[2.00 \times 10^{-4}] = 3.70$
a solution of CH_3COOH(aq) of concentration 0.100 mol dm^{-3} assuming 1.32% dissociation of the acid	$[H^+(aq)] = \frac{1.32}{100} \times 0.100 = 1.32 \times 10^{-3}$ mol dm^{-3} pH = $-\log_{10}[H^+(aq)] = -\log_{10}[1.32 \times 10^{-3}] = 2.88$
a solution of HCN(aq) of concentration 0.100 mol dm^{-3} assuming 0.00794% of the acid dissociates	$pH = -\log_{10}\left(\frac{0.00794}{100} \times 0.100\right) = 5.10$

29 a Strong base, therefore ionises completely and

$[OH^-(aq)] = 0.0150$ mol dm^{-3}

$K_w = [H^+(aq)][OH^-(aq)]$

$1.0 \times 10^{-14} = [H^+(aq)] \times [0.0150]$

$[H^+(aq)] = 6.67 \times 10^{-13}$ mol dm^{-3}

pH = $-\log_{10}[H^+(aq)] = -\log_{10}[6.67 \times 10^{-13}]$
$= 12.2$

b Strong base, therefore ionises completely:

$Ba(OH)_2(aq) \rightarrow Ba^{2+}(aq) + 2OH^-(aq)$

$[OH^-(aq)] = 2 \times 0.0500 = 0.100$ mol dm^{-3}

$K_w = [H^+(aq)][OH^-(aq)]$

$1.0 \times 10^{-14} = [H^+(aq)] \times 0.100$

$[H^+(aq)] = 1.00 \times 10^{-13}$ mol dm^{-3}

pH = $-\log_{10}[H^+(aq)] = -\log_{10}[1.00 \times 10^{-13}]$
$= 13.0$

30 a Strong acid, therefore ionises completely and

$[H^+(aq)] = 0.020$ mol dm^{-3}

$K_w = [H^+(aq)][OH^-(aq)]$

$1.0 \times 10^{-14} = 0.020 \times [OH^-(aq)]$

$[OH^-(aq)] = 5.0 \times 10^{-13}$ mol dm^{-3}

b Strong acid, therefore ionises completely and

$[H^+(aq)] = 1.4 \times 10^{-4}$ mol dm^{-3}

$K_w = [H^+(aq)][OH^-(aq)]$

$1.0 \times 10^{-14} = 1.4 \times 10^{-4} \times [OH^-(aq)]$

$[OH^-(aq)] = 7.1 \times 10^{-11}$ mol dm^{-3}

31 a $-\log_{10}0.200$ = pH 0.70

b When a solution is diluted by a factor of 10^x. the pH increases by x units.

The original solution is diluted by a factor of 10^1 to produce solution X, therefore

solution X: pH = 1.70

Solution X is diluted by a factor of 10^2 to produce solution Y, therefore the pH goes up by 2 units:

solution Y: pH = 3.70

32 a $-\log_{10}0.200 = 0.699$

b amount of HCl $= \frac{20.0}{1000} \times 0.200$
$= 4.00 \times 10^{-3}$ mol

$NaOH + HCl \rightarrow NaCl + H_2O$

amount of NaOH $= 4.00 \times 10^{-3}$ mol

volume of NaOH in cm^3 $= \frac{4.00 \times 10^{-3}}{0.100} \times 1000$
$= 40.0$ cm^3

Chemistry for the IB Diploma – Owen © Cambridge University Press & Assessment 2023

c 7.0

d This is the pH of the 0.100 mol dm^{-3} NaOH(aq)

Strong base, therefore ionises completely and

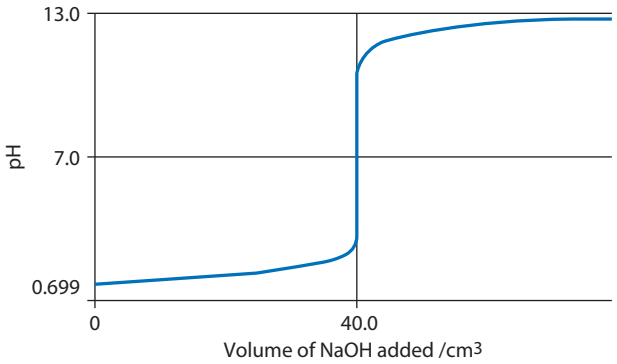
$[OH^-(aq)] = 0.100$ mol dm^{-3}

$K_w = [H^+(aq)][OH^-(aq)]$

$1.0 \times 10^{-14} = [H^+(aq)] \times 0.100$

$[H^+(aq)] = 1.00 \times 10^{-13}$ mol dm^{-3}

$pH = -\log_{10}[H^+(aq)] = -\log_{10}[1.00 \times 10^{-13}]$
$= 13.0$



33 a i $-\log_{10} 0.400 = 0.398$

ii amount of HCl $= \frac{30.0}{1000} \times 0.400 =$ 1.20×10^{-2} mol

$NaOH + HCl \rightarrow NaCl + H_2O$

amount of NaOH $= 1.20 \times 10^{-2}$ mol

volume of NaOH in cm^3 =
$\frac{1.20 \times 10^{-2}}{0.200} \times 1000 = 60.0$ cm^3

iii 7.0

iv This is the pH of the 0.200 mol dm^{-3} NaOH(aq)

Strong base, therefore ionises completely and

$[OH^-(aq)] = 0.200$ mol dm^{-3}

$K_w = [H^+(aq)][OH^-(aq)]$

$1.0 \times 10^{-14} = [H^+(aq)] \times [0.200]$

$[H^+(aq)] = 5.00 \times 10^{-14}$ mol dm^{-3}

$pH = -\log_{10}[H^+(aq)]$
$= -\log_{10}[5.00 \times 10^{-14}] = 13.3$

b i $-\log_{10} 0.0500 = 1.30$

ii amount of HCl $= \frac{40.0}{1000} \times 0.0500$
$= 2.00 \times 10^{-3}$ mol

$NaOH + HCl \rightarrow NaCl + H_2O$

amount of NaOH $= 2.00 \times 10^{-3}$ mol

volume of NaOH in cm^3 =
$\frac{2.00 \times 10^{-3}}{0.100} \times 1000 = 20.0$ cm^3

iii 7.0

iv This is the pH of the 0.100 mol dm^{-3} NaOH(aq)

Strong base, therefore ionises completely and

$[OH^-(aq)] = 0.100$ mol dm^{-3}

$K_w = [H^+(aq)][OH^-(aq)]$

$1.0 \times 10^{-14} = [H^+(aq)] \times [0.100]$

$[H^+(aq)] = 1.00 \times 10^{-13}$ mol dm^{-3}

$pH = -\log_{10}[H^+(aq)]$
$= -\log_{10}[1.00 \times 10^{-13}] = 13.0$

c i $[OH^-(aq)] = 0.400$ mol dm^{-3}

$K_w = [H^+(aq)][OH^-(aq)]$

$1.0 \times 10^{-14} = [H^+(aq)] \times [0.400]$

$[H^+(aq)] = 2.50 \times 10^{-14}$ mol dm^{-3}

$pH = -\log_{10}[H^+(aq)]$
$= -\log_{10}[2.50 \times 10^{-14}] = 13.6$

ii amount of NaOH $= \frac{20.0}{1000} \times 0.400$
$= 8.00 \times 10^{-3}$ mol

$NaOH + HCl \rightarrow NaCl + H_2O$

amount of HCl $= 8.00 \times 10^{-3}$ mol

volume of HCl in cm^3 =
$\frac{8.00 \times 10^{-3}}{0.200} \times 1000 = 40.0$ cm^3

iii 7.0

iv This is the pH of the 0.200 mol dm^{-3} HCl(aq)

Strong acid, therefore ionises completely and

$pH = -\log_{10}[0.200] = 0.700$

d i $[OH^-(aq)] = 0.125$ mol dm^{-3}

$K_w = [H^+(aq)][OH^-(aq)]$

$1.0 \times 10^{-14} = [H^+(aq)] \times [0.125]$

Chemistry for the IB Diploma – Owen © Cambridge University Press & Assessment 2023

$[H^+(aq)] = 8.00 \times 10^{-14}$ mol dm^{-3}

$pH = -\log_{10} [H^+(aq)]$
$= -\log_{10} [8.00 \times 10^{-14}] = 13.1$

ii amount of NaOH $= \frac{25.0}{1000} \times 0.125 = 3.125 \times 10^{-3}$ mol

$NaOH + HCl \rightarrow NaCl + H_2O$

amount of HCl $= 3.125 \times 10^{-3}$ mol

volume of HCl in cm^3 =
$\frac{3.125 \times 10^{-3}}{0.100} \times 1000 = 31.25$ cm^3

iii 7.0

iv This is the pH of the 0.100 mol dm^{-3} HCl(aq)

$pH = -\log_{10} [0.100] = 1.00$

34 a amount of NaOH $= \frac{20.0}{1000} \times 0.200 = 4.00 \times 10^{-3}$ mol

amount of HCl $= \frac{30.0}{1000} \times 0.200 = 6.00 \times 10^{-3}$ mol

$NaOH + HCl \rightarrow NaCl + H_2O$

amount of excess HCl =
$6.00 \times 10^{-3} - 4.00 \times 10^{-3} = 2.00 \times 10^{-3}$ mol

Total volume = 20.0 + 30.0 = 50.0 cm^3

Concentration of HCl $= \frac{2.00 \times 10^{-3}}{(50.0/1000)} = 4.00 \times 10^{-2}$ mol dm^{-3}

Strong acid, so
$[H^+(aq)] = 4.00 \times 10^{-2}$ mol dm^{-3}

$pH = -\log_{10} [4.00 \times 10^{-2}] = 1.40$

b amount of NaOH $= \frac{10.0}{1000} \times 0.150 = 1.50 \times 10^{-3}$ mol

amount of HCl $= \frac{45.0}{1000} \times 0.100 = 4.50 \times 10^{-3}$ mol

$NaOH + HCl \rightarrow NaCl + H_2O$

amount of excess HCl =
$4.50 \times 10^{-3} - 1.50 \times 10^{-3} = 3.00 \times 10^{-3}$ mol

Total volume = 10.0 + 45.0 = 55.0 cm^3

Concentration of HCl $= \frac{3.00 \times 10^{-3}}{(55.0/1000)} = 5.45 \times 10^{-2}$ mol dm^{-3}

Strong acid, so
$[H^+(aq)] = 5.45 \times 10^{-2}$ mol dm^{-3}

$pH = -\log_{10} [5.45 \times 10^{-2}] = 1.26$

c amount of NaOH $= \frac{50.0}{1000} \times 0.120 = 6.00 \times 10^{-3}$ mol

amount of HCl $= \frac{25.0}{1000} \times 0.200 = 5.00 \times 10^{-3}$ mol

$NaOH + HCl \rightarrow NaCl + H_2O$

amount of excess Na OH =
$6.00 \times 10^{-3} - 5.00 \times 10^{-3} = 1.00 \times 10^{-3}$ mol

Total volume = 50.0 + 25.0 = 75.0 cm^3

Concentration of NaOH $= \frac{1.00 \times 10^{-3}}{(75.0/1000)} = 1.33 \times 10^{-2}$ mol dm^{-3}

Strong base, so $[OH^-(aq)] = 1.33 \times 10^{-2}$ mol dm^{-3}

$[H^+(aq)] = \frac{1.0 \times 10^{-14}}{[OH^-(aq)]} = 7.50 \times 10^{-13}$ mol dm^{-3}

$pH = -\log_{10} 7.50 \times 10^{-13} = 12.1$

d amount of NaOH $= \frac{40.0}{1000} \times 0.150 = 6.00 \times 10^{-3}$ mol

amount of HCl $= \frac{15.0}{1000} \times 0.250 = 3.75 \times 10^{-3}$ mol

$NaOH + HCl \rightarrow NaCl + H_2O$

amount of excess NaOH $= 6.00 \times 10^{-3} - 3.75 \times 10^{-3} = 2.25 \times 10^{-3}$ mol

Total volume = 40.0 + 15.0 = 55.0 cm^3

Concentration of NaOH $= \frac{2.25 \times 10^{-3}}{(55.0/1000)} = 4.09 \times 10^{-2}$ mol dm^{-3}

Strong base, so $[OH^-(aq)]$
$= 4.09 \times 10^{-2}$ mol dm^{-3}

$[H^+(aq)] = \frac{1.0 \times 10^{-14}}{[OH^-(aq)]}$
$= 2.44 \times 10^{-13}$ mol dm^{-3}

$pH = -\log_{10} 2.44 \times 10^{-13} = 12.6$

Chemistry for the IB Diploma – Owen © Cambridge University Press & Assessment 2023

35 $pOH = -\log_{10}[OH^-(aq)]$

$[OH^-(aq)] = 10^{-pOH}$

pOH	$[OH^-(aq)]$ / mol dm^{-3}	Acidic/alkaline/neutral?
3	1.0×10^{-3}	alkaline since pOH < 7
5	1.0×10^{-5}	alkaline since pOH < 7
7	1.0×10^{-7}	neutral since pOH = 7
9	1.0×10^{-9}	acidic since pOH > 7
12	1.0×10^{-12}	acidic since pOH > 7

36 **a** $pOH = -\log_{10}[1.27 \times 10^{-9}] = 8.90$ $pH = 14 - 8.90 = 5.10$

b $pOH = -\log_{10}[4.91 \times 10^{-1}] = 13.69$ $pH = 14 - 1.31 = 12.69$

c $pOH = -\log_{10}[3.18 \times 10^{-5}] = 4.50$ $pH = 14 - 4.50 = 9.50$

d $pOH = -\log_{10}2.00 = -0.301$ $pH = 14 + 0.301 = 14.301$

37 **a** $[OH^-(aq)] = 10^{-9.60} = 2.51 \times 10^{-10}$ mol dm^{-3} and $[H^+(aq)] = 10^{-(14 - 9.60)} = 3.98 \times 10^{-5}$ mol dm^{-3}

b $[OH^-(aq)] = 10^{-3.78} = 1.66 \times 10^{-4}$ mol dm^{-3} and $[H^+(aq)] = 10^{-(14 - 3.78)} = 6.03 \times 10^{-11}$ mol dm^{-3}

c $[OH^-(aq)] = 10^{-6.23} = 5.89 \times 10^{-7}$ mol dm^{-3} and $[H^+(aq)] = 10^{-(14 - 6.23)} = 1.70 \times 10^{-8}$ mol dm^{-3}

d $[OH^-(aq)] = 10^{0.080} = 1.20$ mol dm^{-3} and $[H^+(aq)] = 10^{-(14 + 0.080)} = 8.32 \times 10^{-15}$ mol dm^{-3}

38 Both are strong bases, so ionise completely.

a $pOH = -\log_{10}0.0760 = 1.12$ $pH = 14 - 1.12 = 12.88$

b $Ba(OH)_2(aq) \rightarrow Ba^{2+}(aq) + 2OH^-(aq)$

$[OH^-(aq)] = 2 \times 0.0250 = 0.0500$ mol dm^{-3}

$pOH = -\log_{10}0.0500 = 1.30$ $pH = 14 - 1.30 = 12.70$

39 **a** Strong acid, therefore ionises completely

$[H^+(aq)] = 0.200$ mol dm^{-3}

$pH = -\log_{10} 0.200 = 0.699$

$pOH = 14 - pH = 14 - 0.699 = 13.30$

b Strong acid, therefore ionises completely $14 - \log_{10}[6.00 \times 10^{-2}] = 12.78$

40 **a** $K_a = \dfrac{[HCOO^-(aq)][H^+(aq)]}{[HCOOH(aq)]}$

b $K_a = \dfrac{[OBr^-(aq)][H^+(aq)]}{[HOBr(aq)]}$

c $K_a = \dfrac{[NO_2^-(aq)][H^+(aq)]}{[HNO_2(aq)]}$

d $K_a = \dfrac{[C_6H_5COO^-(aq)][H^+(aq)]}{[C_6H_5COOH(aq)]}$

Expressions of the form:

$K_a = \dfrac{[A^-(aq)][H_3O^+(aq)]}{[HA(aq)]}$ are also correct

Chemistry for the IB Diploma – Owen © Cambridge University Press & Assessment 2023

41 a

These questions require the equations:

$$K_a = \frac{[A^-(aq)][H^+(aq)]}{[HA(aq)]} = \frac{[H^+(aq)]^2}{[HA(aq)]}$$

$$pK_a = -\log_{10} K_a$$

$$pH = -\log_{10} [H^+(aq)]$$

$$[H^+(aq)] = 10^{-pH}$$

So, for HA

$$K_a = \frac{[A^-(aq)][H^+(aq)]}{[HA(aq)]} = \frac{[H^+(aq)]^2}{[HA(aq)]} = \frac{(2.00 \times 10^{-6})^2}{0.0100}$$

$$= 4.00 \times 10^{-10}$$

$$pK_a = -\log_{10} K_a = -\log_{10} [4.00 \times 10^{-10}] = 9.40$$

$$pH = -\log_{10} [H^+(aq)] = -\log_{10} [2.00 \times 10^{-6}] = 5.70$$

So, for HB

$$[H^+(aq)] = 10^{-pH} = 10^{-4.70}$$

$$= 2.00 \times 10^{-5} \text{ mol dm}^{-3}$$

$$K_a = \frac{[B^-(aq)][H^+(aq)]}{[HB(aq)]} = \frac{[H^+(aq)]^2}{[HB(aq)]}$$

$$= \frac{(2.00 \times 10^{-5})^2}{0.200} = 2.00 \times 10^{-9}$$

$$pK_a = -\log_{10} K_a$$

$$= -\log_{10} 2.00 \times 10^{-9} = 8.70$$

So, for HE

$$K_a = \frac{[E^-(aq)][H^+(aq)]}{[HE(aq)]} = 3.72 \times 10^{-8} = \frac{[H^+(aq)]^2}{0.250}$$

$$[H^+(aq)] = \sqrt{[3.72 \times 10^{-8} \times 0.250]} = 9.64 \times 10^{-5} \text{ mol dm}^{-3}$$

$$pH = -\log_{10} [H^+(aq)] = -\log_{10} [9.64 \times 10^{-5}] = 4.02$$

$$pK_a = -\log_{10} K_a = -\log_{10} 3.72 \times 10^{-8} = 7.43$$

In all calculations it is assumed that the dissociation of the acid is negligible compared to it concentration. so that $[HX(aq)]_{equilibrium} = [HX(aq)]_{initial}$.

Acid	Concentration of acid / mol dm^{-3}	$[H^+]$ / mol dm^{-3}	pH	K_a	pK_a
HA	0.0100	2.00×10^{-6}	5.70	4.00×10^{-10}	9.40
HB	0.200	2.00×10^{-5}	4.70	2.00×10^{-9}	8.70
HC	0.500	2.50×10^{-4}	3.60	1.25×10^{-7}	6.90
HD	2.20×10^{-2}	6.31×10^{-6}	5.20	1.81×10^{-9}	8.74
HE	0.250	9.64×10^{-5}	4.02	3.72×10^{-8}	7.43
HF	0.0300	4.35×10^{-4}	3.36	6.31×10^{-6}	5.20

b Higher value of K_a or lower value of pK_a = stronger acid.

HF > HC > HE > HB > HD > HA

42 Lower value of pK_a = stronger acid.

benzoic (C_6H_5COOH) > ethanoic (CH_3COOH) > ammonium ion (NH_4^+)

43 All the calculations are the same, so, for HA_1:

$$HA_1(aq) \rightleftharpoons H^+(aq) + A_1^-(aq)$$

$$K_a = 10^{-pKa} = 10^{-4.60} = 2.51 \times 10^{-5}$$

$$K_a = \frac{[A_1^-(aq)][H^+(aq)]}{[HA_1(aq)]} = 2.51 \times 10^{-5} = \frac{[H^+(aq)]^2}{0.100}$$

$$[H^+(aq)] = \sqrt{[2.51 \times 10^{-5} \times 0.100]} = 1.58 \times 10^{-3} \text{ mol dm}^{-3}$$

$$pH = -\log_{10} [H^+(aq)] = -\log_{10} [1.58 \times 10^{-3}] = 2.80$$

We can also use: $pH = \frac{1}{2}(pK_a - \log_{10} c)$

$$HA_2\text{: } pH = \frac{5.24 - \log_{10} 0.0250}{2} = 3.42$$

$$HA_3\text{: } pH = \frac{7.40 - \log_{10} 0.0640}{2} = 4.30$$

Chemistry for the IB Diploma – Owen © Cambridge University Press & Assessment 2023

Assume that the dissociation of the acid is negligible compared with the concentration of the acid – so the concentration of the acid at equilibrium is the same as its initial concentration.

44 a $CH_3CH_2COOH(aq) \rightleftharpoons H^+(aq) + CH_3CH_2COO^-(aq)$

$K_a = 10^{-pKa} = 10^{-4.87} = 1.35 \times 10^{-5}$

Assuming that dissociation of the acid is negligible compared to its concentration

$$K_a = \frac{[CH_3CH_2COO^-(aq)][H^+(aq)]}{[CH_3CH_2COOH(aq)]} = 1.35 \times 10^{-5} = \frac{[H^+(aq)]^2}{0.0200}$$

$[H^+(aq)] = \sqrt{[1.35 \times 10^{-5} \times 0.0200]} = 5.19 \times 10^{-4}$ mol dm^{-3}

$pH = -\log_{10}[H^+(aq)] = -\log_{10}[5.19 \times 10^{-4}] = 3.28$

b Using $pH = \frac{1}{2}(pK_a - \log_{10} c)$

$$pH = \frac{9.21 - \log_{10} 0.500}{2} = 4.76$$

c $$pH = \frac{9.99 - \log_{10} 0.00250}{2} = 6.30$$

45 Using: $pH = \frac{1}{2}(pK_a - \log_{10} c)$

HA_4: $pH = \frac{5.00 + 1.00}{2} = 3.00$

HA_5: $pH = \frac{7.42 + 2.00}{2} = 4.71$

HA_6: $pH = \frac{4.80 + 3.00}{2} = 3.90$

46 To compare we need everything in terms of either K_a or pK_a, so, converting to pK_a using

$pK_a = -\log_{10} K_a$

We get: HOI $pK_a = 10.5$ and HNO_2 $pK_a = 3.34$

The lower the value of pK_a, the stronger the acid, therefore the order of increasing strength is:

$HOI < HOCl < HNO_2 < HClO_2$

47 a i $NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$

ii $CH_3NH_2(aq) + H_2O(l) \rightleftharpoons CH_3NH_3^+(aq) + OH^-(aq)$

iii $(CH_3)_2NH(aq) + H_2O(l) \rightleftharpoons (CH_3)_2NH_2^+(aq) + OH^-(aq)$

b i $$K_b = \frac{[NH_4^+(aq)][OH^-(aq)]}{[NH_3(aq)]}$$

ii $$K_b = \frac{[CH_3NH_3^+(aq)][OH^-(aq)]}{[CH_3NH_2(aq)]}$$

iii $$K_b = \frac{[(CH_3)_2NH_2^+(aq)][OH^-(aq)]}{[(CH_3)_2NH(aq)]}$$

48 a These questions require the equations:

$$K_b = \frac{[HB^+(aq)][OH^-(aq)]}{[B(aq)]} = \frac{[OH^-(aq)]^2}{[B(aq)]}$$

$pK_b = -\log_{10} K_b$

Chemistry for the IB Diploma – Owen © Cambridge University Press & Assessment 2023

For B_1

$B_1(aq) + H_2O(l) \rightleftharpoons B_1H^+(aq) + OH^-(aq)$

$$K_b = \frac{[HB_1^+(aq)][OH^-(aq)]}{[B_1(aq)]} = \frac{[OH^-(aq)]^2}{[B_1(aq)]} = \frac{(1.33 \times 10^{-3})^2}{0.100} = 1.77 \times 10^{-5}$$

$pK_b = -\log_{10} 1.77 \times 10^{-5} = 4.75$

For B_2

$B_2(aq) + H_2O(l) \rightleftharpoons B_2H^+(aq) + OH^-(aq)$

$$K_b = \frac{[HB_2^+(aq)][OH^-(aq)]}{[B_2(aq)]} = \frac{[OH^-(aq)]^2}{0.250} = 5.75 \times 10^{-5}$$

$[OH^-(aq)] = \sqrt{[0.250 \times 5.75 \times 10^{-5}]} = 3.79 \times 10^{-3}$ mol dm^{-3}

$pK_b = -\log_{10} 5.75 \times 10^{-5} = 4.24$

In all calculations it is assumed that the ionisation of the base is negligible compared to it concentration. So that $[B(aq)]_{equilibrium} = [B(aq)]_{initial}$.

Base	Concentration of base / mol dm^{-3}	$[OH^-]$ / mol dm^{-3}	K_b	pK_b
B_1	0.100	1.33×10^{-3}	1.77×10^{-5}	4.75
B_2	0.250	3.79×10^{-3}	5.75×10^{-5}	4.24
B_3	0.0200	4.70×10^{-4}	1.10×10^{-5}	4.96

b Higher value of K_b or lower value of pK_b = stronger base.

$B_3 < B_1 < B_2$

49 Sample calculation, for B_4:

$B_4(aq) + H_2O(l) \rightleftharpoons B_4H^+(aq) + OH^-(aq)$

$K_b = 10^{-pK_b} = 10^{-4.20} = 6.31 \times 10^{-5}$

$$K_b = \frac{[HB_4^+(aq)][OH^-(aq)]}{[B_4(aq)]} = \frac{[OH^-(aq)]^2}{0.120} = 6.31 \times 10^{-5}$$

Assuming that ionisation of the base is negligible compared to its concentration.

$[OH^-(aq)] = \sqrt{[0.120 \times 6.31 \times 10^{-5}]} = 2.75 \times 10^{-3}$ mol dm^{-3}

$pOH = -\log_{10}[OH^-(aq)] = -\log_{10} [2.75 \times 10^{-3}] = 2.56$

$pOH + pH = 14$ assuming 25 °C

$pH = 14 - 2.56 = 11.44$

We can also use the equations:

$$pOH = \frac{1}{2}\left(pK_b - \log_{10} c\right)$$

$pH = 14 - pOH$

B_4: $pOH = \frac{1}{2}\left(4.20 - \log_{10} 0.120\right) = 2.56$

$pH = 14 - 2.56 = 11.44$

B_5: $pOH = \frac{1}{2}\left(6.46 - \log_{10} 0.0200\right) = 4.08$

$pH = 14 - 4.08 = 9.92$

B_6: $pOH = \frac{1}{2}\left(8.80 - \log_{10} 0.0400\right) = 5.10$

$pH = 14 - 5.10 = 8.90$

Chemistry for the IB Diploma – Owen © Cambridge University Press & Assessment 2023

50 Using: $pOH = \frac{1}{2}(pK_b - \log_{10} c)$ and $pH = 14 - pOH$

B_7: $pOH = \frac{1}{2}(4.00 + 1.00) = 2.50$ $\quad$ $pH = 14 - 2.50 = 11.50$

B_8: $pOH = \frac{1}{2}(7.60 + 3.00) = 5.30$ $\quad$ $pH = 14 - 5.30 = 8.70$

B_9: $pOH = \frac{1}{2}(5.86 + 2.00) = 3.93$ $\quad$ $pH = 14 - 3.93 = 10.07$

51 a $CH_3CH_2NH_2(aq) + H_2O(l) \rightleftharpoons CH_3CH_2NH_3^+(aq) + OH^-(aq)$

$$K_b = \frac{[CH_3CH_2NH_3^+(aq)][OH^-(aq)]}{[CH_3CH_2NH_2(aq)]} = \frac{[OH^-(aq)]^2}{0.0500} = 4.67 \times 10^{-4}$$

Assuming that ionisation of the base is negligible compared to its concentration.

$[OH^-(aq)] = \sqrt{[0.0500 \times 4.67 \times 10^{-4}]} = 4.83 \times 10^{-3}$ mol dm^{-3}

$pOH = -\log_{10}[OH^-(aq)] = -\log_{10}[4.83 \times 10^{-3}] = 2.32$

$pOH + pH = 14$ assuming 25 °C

$pH = 14 - 2.32 = 11.68$

b We can also use: $pOH = ½(pK_b - \log_{10} c)$

$pK_b = -\log_{10}K_b = -\log_{10}[7.41 \times 10^{-10}] = 9.13$

$pOH = \frac{1}{2}(pK_b - \log_{10} c)$

$pOH = \frac{1}{2}(9.13 - \log_{10} 0.0100) = 5.565$

$pH = 14 - pOH = 14 - 5.565 = 8.44$

c $pOH = \frac{1}{2}(pK_b - \log_{10} c)$

$pOH = \frac{1}{2}(3.34 - \log_{10} 0.0200) = 2.52$

$pH = 14 - pOH = 14 - 2.52 = 11.48$

d $pOH = \frac{1}{2}(pK_b - \log_{10} c)$

$pOH = \frac{1}{2}(3.46 - \log_{10} 0.150) = 2.14$

$pH = 14 - pOH = 14 - 2.14 = 11.86$

52 In both questions **50** and **51**, assume that ionisation of the base is negligible compared with the concentration of the base, so the concentration of the base at equilibrium is the same as its initial concentration. In question **50**, we are also making the assumption that the temperature is 25 °C, so that $pK_w = 14$.

53 a NaOH is a strong base, so fully ionised, therefore $[OH^-(aq)] = 0.1000$ mol dm^{-3}

$pOH = -\log_{10} 0.1000 = 1.000$

$pK_w = pH + pOH$

$13.53 = pH - 1.000$

$pH = 12.53$

b The increased ionisation of water at the higher temperature has negligible effect on the pH here because the $[H^+(aq)]$ from dissociation of the acid is so much larger than that from the ionisation of water.

HCl is a strong acid, therefore

$pH = -\log_{10} 0.1000 = 1.000$

Chemistry for the IB Diploma – Owen © Cambridge University Press & Assessment 2023

c KOH is a strong base, so fully ionised, therefore $[OH^-(aq)] = 0.02000$ mol dm^{-3}

$pOH = -\log_{10} 0.02000 = 1.700$

$pK_w = pH + pOH$

$13.83 = pH - 1.700$

$pH = 12.13$

54 $K_a \times K_b = K_w$

55 $pK_a + pK_b = pK_w$

56 as well as the equations in questions **55** and **56**, we will also need

$pK_a = -\log_{10} K_a \qquad K_a = 10^{-pK_a}$
$pK_b = -\log_{10} K_b \qquad K_b = 10^{-pK_b}$

e.g. for HF

$pK_a = -\log_{10} [6.31 \times 10^{-4}] = 3.20$

The conjugate base is formed by removing H^+ from the acid: F^- in this case.

$K_a \times K_b = K_w = 1.0 \times 10^{-14}$ at 25 °C

$$K_b = \frac{(1.0 \times 10^{-14})}{(6.31 \times 10^{-4})} = 1.58 \times 10^{-11}$$

$pK_b = -\log_{10} K_b = -\log_{10} [1.58 \times 10^{-11}] = 10.80$

This could also have been obtained using

$pK_a + pK_b = pK_w = 14$ at 25 °C

$pK_b = 14 - 3.20 = 10.80$

Acid	K_a	pK_a	Conjugate base	K_b	pK_b
HCN	3.98×10^{-10}	9.40	CN^-	2.51×10^{-5}	4.60
HF	6.31×10^{-4}	3.20	F^-	1.58×10^{-11}	10.80
HIO_3	0.166	0.78	IO_3^-	6.03×10^{-14}	13.22
NH_4^+	5.62×10^{-10}	9.25	NH_3	1.78×10^{-5}	4.75
CH_3COOH	1.74×10^{-5}	4.76	CH_3COO^-	5.75×10^{-10}	9.24
$CH_3NH_3^+$	2.19×10^{-11}	10.66	CH_3NH_2	4.57×10^{-4}	3.34

57 The smaller the value of pK_b the stronger the base, so HCO_3^- is the strongest base. The stronger the base, the weaker its conjugate acid, so the conjugate acid of HCO_3^- (H_2CO_3) is the weakest acid. The order of strength of the bases is

$CH_3CHClCOO^- < C_6H_5COO^- < CH_3CH_2COO^- < HCO_3^-$

so the order of strength of the conjugate acids (obtained by adding H^+) is the reverse:

$H_2CO_3 < CH_3CH_2COOH < C_6H_5COOH < CH_3CHClCOOH$

Chemistry for the IB Diploma – Owen © Cambridge University Press & Assessment 2023

58 a

	pH
0.100 mol dm^{-3} $CH_3CH_2CH_2CH_2COONa$	greater than 7; Salt of a strong base (NaOH) and a weak acid ($CH_3CH_2CH_2CH_2COOH$)
0.500 mol dm^{-3} KNO_3	7 Salt of a strong base (KOH) and a strong acid (HNO_3)
0.100 mol dm^{-3} Na_2CO_3	greater than 7; Salt of a strong base (NaOH) and a weak acid (H_2CO_3)
0.100 mol dm^{-3} $CH_3CH_2NH_3^+Cl^-$	less than 7; Salt of a strong acid (HCl) and a weak base ($CH_3CH_2NH_2$)

b $CH_3CH_2CH_2CH_2COO^-(aq) + H_2O(l) \rightleftharpoons CH_3CH_2CH_2CH_2COOH(aq) + OH^-(aq)$

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

$CH_3CH_2NH_3^+(aq) \rightleftharpoons CH_3CH_2NH_2(aq) + H^+(aq)$

59 a The smaller the value of pK_a or pK_b the stronger the acid/base, so NH_3 is a stronger base than HCN is an acid. The pH of the solution will therefore be on the basic side of pH, that is pH > 7.

b CH_3NH_2 is a stronger base than HCOOH is an acid. The pH of the solution will therefore be on the basic side of pH, that is pH > 7.

60 a $HCOOH(aq) \rightleftharpoons H^+(aq) + HCOO^-(aq)$

$K_a = 10^{-pK_a} = 10^{-3.75} = 1.78 \times 10^{-4}$

Assuming that dissociation of the acid is negligible compared to its concentration

$$K_a = \frac{[HCOO^-(aq)][H^+(aq)]}{[HCOOH(aq)]} = 1.78 \times 10^{-4} = \frac{[H^+(aq)]^2}{0.100}$$

$[H^+(aq)] = \sqrt{[1.78 \times 10^{-4} \times 0.100]} = 4.22 \times 10^{-3}$ mol dm^{-3}

$pH = -\log_{10}[H^+(aq)] = -\log_{10}[4.22 \times 10^{-3}] = 2.38$

b A solution of HCOONa contains $HCOO^-$ ions. $HCOO^-$ is the conjugate base of HCOOH

$pK_a + pK_b = 14$ (assuming 25 °C), therefore the pK_b of $HCOO^-$ is 14 – 3.75 = 10.25.

$K_b = 10^{-pK_b} = 10^{-10.25} = 5.62 \times 10^{-11}$

$HCOO^-(aq) + H_2O(l) \rightleftharpoons HCOOH(aq) + OH^-(aq)$

Assuming that ionisation of the base is negligible compared to its concentration.

$$K_b = \frac{[HCOOH(aq)][OH^-(aq)]}{[HCOO^-(aq)]} = \frac{[OH^-(aq)]^2}{0.100} = 5.62 \times 10^{-11}$$

$[OH^-(aq)] = \sqrt{[0.100 \times 5.62 \times 10^{-11}]} = 2.37 \times 10^{-6}$ mol dm^{-3}

$pOH = -\log_{10}[OH^-(aq)] = -\log_{10}[2.37 \times 10^{-6}] = 5.625$

pOH + pH = 14 assuming 25 °C

pH = 14 – 6.625 = 8.38

61 a $pOH = \frac{1}{2}(pK_b - \log_{10} c)$

$pOH = \frac{1}{2}(4.75 - \log_{10} 0.200) = 2.72$

pH = 14 – pOH = 14 – 2.72 = 11.28

Chemistry for the IB Diploma – Owen © Cambridge University Press & Assessment 2023

b $NH_4Cl(aq)$ contains $NH_4^+(aq)$ ions. $NH_4^+(aq)$ is the conjugate acid of NH_3, therefore

$pK_a = 14 - pK_b = 14 - 4.75 = 9.25$ assuming 25 °C

The rest of the question is then just working out the pH of a weak acid and we can use the shortcut:

$pH = \frac{1}{2}(pK_a - \log_{10} c) = \frac{1}{2}(9.25 - \log_{10} 0.200) = 4.97$

62 a A solution of KCN contains CN^- ions. CN^- is the conjugate base of HCN

$pK_a + pK_b = 14$, therefore the pK_b of CN^- is $14 - 9.21 = 4.79$ (assuming 25 °C)

The rest of the question is then just working out the pH of a weak base and we can use the shortcut:

$pOH = \frac{1}{2}(pK_b - \log_{10} c)$

$pOH = \frac{1}{2}(4.79 - \log_{10} 0.100) = 2.895$

$pH = 14 - pOH = 14 - 2.895 = 11.11$

b $pK_a + pK_b = 14$, therefore the pK_b of $CH_3CH_2COO^-$ is $14 - 4.87 = 9.13$ (assuming 25 °C)

The rest of the question is then just working out the pH of a weak base and we can use the shortcut:

$pOH = \frac{1}{2}(pK_b - \log_{10} c)$

$pOH = \frac{1}{2}(9.13 - \log_{10} 0.200) = 4.91$

$pH = 14 - pOH = 14 - 4.91 = 9.09$

63 a Initial pH: strong acid, therefore ionises completely and $pH = -\log_{10} [0.100] = 1.00$

volume of alkali = 25.0 cm^3; The acid and alkali have the same concentrations, therefore the same volume will be required.

pH at equivalence point = 7; strong acid – strong base

final pH tends to 13.0; This is the pH of the 0.100 mol dm^{-3} NaOH(aq):

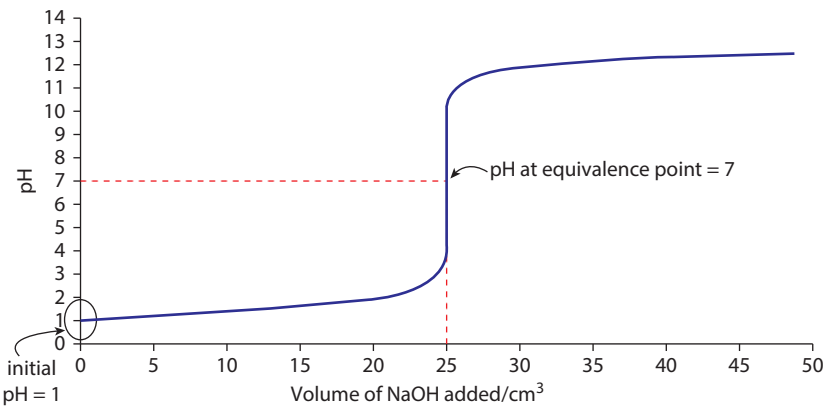
Strong base, therefore ionises completely and $[OH^-(aq)] = 0.100$ mol dm^{-3}

$K_w = [H^+(aq)][OH^-(aq)]$

$1.0 \times 10^{-14} = [H^+(aq)] \times [0.100]$

$[H^+(aq)] = 1.00 \times 10^{-13}$ mol dm^{-3}

$pH = -\log_{10} [H^+(aq)] = -\log_{10} [1.00 \times 10^{-13}] = 13.0$



Chemistry for the IB Diploma – Owen © Cambridge University Press & Assessment 2023

b initial pH = 1.00

volume of alkali:

amount of HCl

$= \frac{20.0}{1000} \times 0.100 = 2.00 \times 10^{-3}$ mol

$NH_3 + HCl \rightarrow NH_4Cl$

amount of $NH_3 = 2.00 \times 10^{-3}$ mol

volume of NH_3 in $cm^3 = \frac{2.00 \times 10^{-3}}{0.200} \times 1000 = 10.0\ cm^3$

pH at equivalence point < 7; strong acid –weak base, so the equivalence point pH is in the acidic region

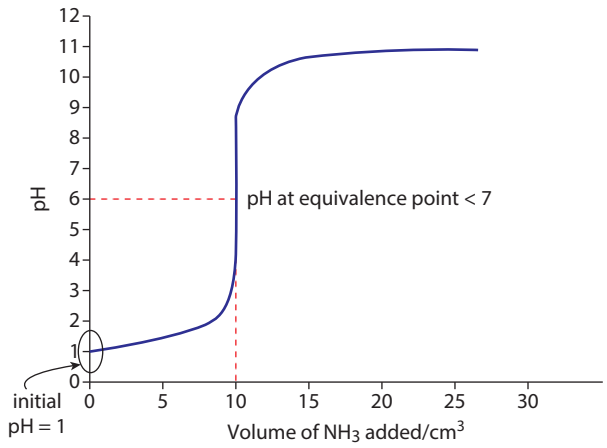
final pH tends to:

this will be the pH of 0.200 mol dm^{-3} NH_3

$pOH = \frac{1}{2}(pK_b - \log_{10} c)$

$pOH = \frac{1}{2}(4.75 - \log_{10} 0.200) = 2.72$

pH = 14 – pOH = 14 – 2.72 = 11.28



c initial pH: $\frac{1}{2}(4.76 - \log_{10} 0.200) = 2.73$

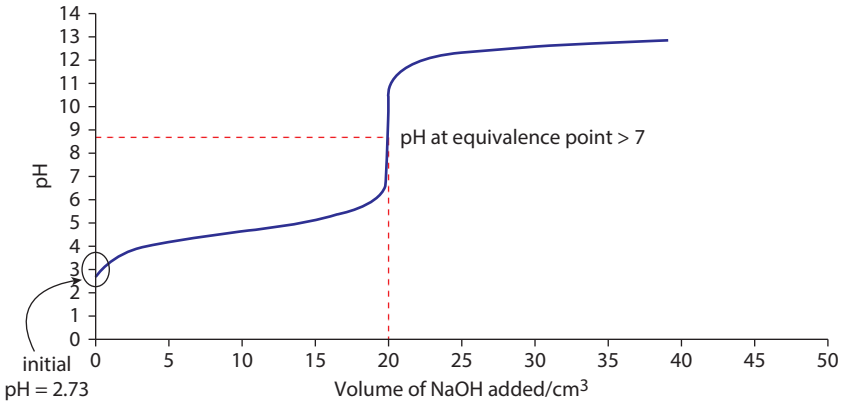
volume of alkali = 20.0 cm^3; The alkali has half the concentration of the acid, so twice the volume will be required.

pH at equivalence point > 7.0; strong base-weak acid, so the equivalence point pH is in the basic region

final pH tends to: pOH of 0.100 mol dm^{-3} NaOH = $-\log_{10} 0.100 = 1.00$

14 – pOH = pH = 13.00

Chemistry for the IB Diploma – Owen © Cambridge University Press & Assessment 2023



d initial pH: $\frac{1}{2}(4.76 - \log_{10} 0.100) = 2.88$

volume of alkali = 25.0 cm^3; The acid and alkali have the same concentrations, therefore the same volume will be required.

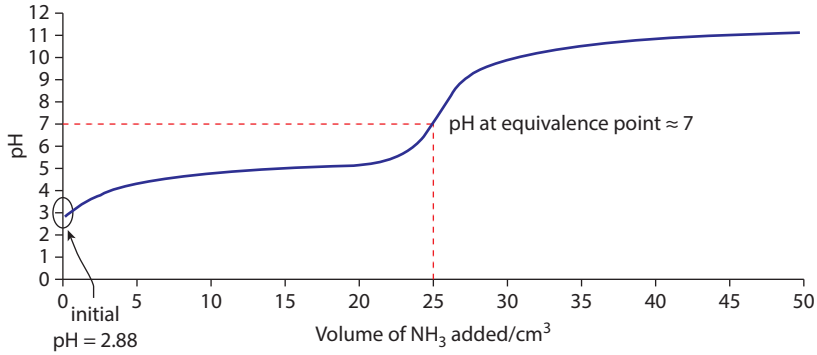
pH at equivalence point approximately 7 as the pK_a of the acid and pK_b of the base are essentially equal.

final pH tends to:

$pOH = \frac{1}{2}(pK_b - \log_{10} c)$

$pOH = \frac{1}{2}(4.75 - \log_{10} 0.100) = 2.875$

$pH = 14 - pOH = 14 - 2.875 = 11.13$



64 Half the number of moles of NaOH to reach the equivalence point has been added (the concentration of the NaOH is half that of the CH^3COOH) – so this is the half-equivalence point and pH is equal to the pK_a of the weak acid: 4.76

65 a $\frac{1}{2}(4.20 - \log_{10} 0.0800) = 2.65$

b amount of HA = $\frac{30.0}{1000} \times 0.0800$
$= 2.40 \times 10^{-3}$ mol

$NaOH + HA \rightarrow NaA + H_2O$

amount of NaOH = 2.40×10^{-3} mol

volume of NaOH in cm^3 =
$\frac{2.40 \times 10^{-3}}{0.100} \times 1000 = 24.0\ cm^3$

Chemistry for the IB Diploma – Owen © Cambridge University Press & Assessment 2023

c pH > 7; strong base–weak acid, so the equivalence point pH is in the basic region

d pOH of 0.100 mol dm^{-3} NaOH $= -\log_{10} 0.100 = 1.00$

$14 - \text{pOH} = \text{pH} = 13.00$

66 a From the graph, the equivalence point occurs when 20.0 cm^3 of HCl has been added (the very steep part of the curve)

amount of HCl $= \frac{20.0}{1000} \times 0.125$
$= 2.50 \times 10^{-3}$ mol

B + HCl → BHCl

amount of B $= 2.50 \times 10^{-3}$ mol dm^{-3}

Concentration of B $= \frac{2.50 \times 10^{-3}}{(25.00/1000)}$
$= 0.100$ mol dm^{-3}

b The half-equivalence point occurs when 10.0 cm^3 of HCl has been added. The pH at this point is 9.0. pK_b of the base is 14 – 9.0 = 5.0.

67 a red – below its pH range, therefore the acid colour

b blue – above its pH range, therefore the alkali colour

c orange – within pH range, so mixture of red and yellow

d colourless – below its pH range, therefore the acid colour

68 a phenolphthalein; Weak acid-strong base titration, therefore pH at the equivalence point will be greater than 7. pK_a of phenolphthalein is above 7.

b bromothymol blue; Strong acid-strong base titration, therefore pH at the equivalence point will be 7. pK_a of bromothymol blue is 7.

c bromocresol green; Weak base-strong acid titration, therefore pH at the equivalence point will be < 7. pK_a of bromocresol green is below 7.

69 a yes – contains a weak acid and its salt

b no – the amount of the weak acid is the same as that of the NaOH. The NaOH will react with all of the weak acid to produce the salt - there will be no weak acid left over, therefore the solution just contains a salt and is not a buffer.

c no – the amount of the weak acid is less than that of the NaOH. The NaOH will react with all of the weak acid to produce the salt - there will be no weak acid left over, therefore the solution is not a buffer.

d yes – the amount of the weak acid is greater than that of the NaOH. The NaOH will react with some of the weak acid to produce the salt, but there will still be some weak acid left over, therefore the solution contains a weak acid and its salt

e no – contains a *strong* acid and its salt

f yes – contains a weak base and its salt

g yes – the amount of the weak base is greater than that of the HCl. The HCl will react with some of the weak base to produce the salt, but there will still be some weak base left over, therefore the solution contains a weak base and its salt.

70 a $\text{pH} = \text{p}K_a + \log_{10}\left(\frac{[\text{conjugate base}]}{[\text{acid}]}\right)$

The concentration of the conjugate base is the same as that of the salt.

$\text{pH} = 4.87 + \log_{10}\left(\frac{0.800}{0.800}\right) = 4.87$

b $\text{pH} = 4.87 + \log_{10}\left(\frac{0.600}{0.500}\right) = 4.95$

c $\text{pH} = 4.87 + \log_{10}\left(\frac{0.700}{1.00}\right) = 4.72$

71 a $\text{pH} = \text{p}K_w - \text{p}K_b + \log_{10}\left(\frac{[\text{base}]}{[\text{conjugate acid}]}\right)$

The concentration of the conjugate acid is the same as that of the salt.

$\text{pH} = 14 - 3.34 + \log_{10}\left(\frac{0.500}{0.500}\right) = 10.66$

b $\text{pH} = 14 - 3.34 + \log_{10}\left(\frac{0.400}{0.600}\right) = 10.48$

c $\text{pH} = 14 - 3.34 + \log_{10}\left(\frac{0.750}{0.500}\right) = 10.84$

72 a pH = 5.00; for an acidic buffer system, when the concentration of the weak acid and its salt are equal, pH = pK_a of the weak acid.

b $\text{pH} = \text{p}K_a + \log_{10}\left(\frac{[\text{conjugate base}]}{[\text{acid}]}\right)$

Chemistry for the IB Diploma – Owen © Cambridge University Press & Assessment 2023

Total volume = 50.0 + 50.0 = 100.0 cm^3

concentration of HA = $\frac{50.0}{100.0} \times 1.00$
= 0.500 mol dm^{-3}

concentration of NaA = $\frac{50.0}{100.0} \times 0.900$
= 0.450 mol dm^{-3}

$$pH = 5.00 + \log_{10}\left(\frac{0.450}{0.500}\right) = 4.95$$

c Total volume = 25.0 + 40.0 = 65.0 cm^3

concentration of HA = $\frac{25.0}{65.0} \times 0.500$
= 0.192 mol dm^{-3}

concentration of NaA = $\frac{40.0}{65.0} \times 0.800$
= 0.492 mol dm^{-3}

$$pH = 4.60 + \log_{10}\left(\frac{0.492}{0.192}\right) = 5.01$$

d Total volume = 100.0 + 80.0 = 180.0 cm^3

concentration of HA = $\frac{100.0}{180.0} \times 0.645$
= 0.358 mol dm^{-3}

concentration of NaA = $\frac{80.0}{180.0} \times 0.560$
= 0.249 mol dm^{-3}

$$pH = 6.32 + \log_{10}\left(\frac{0.249}{0.358}\right) = 6.16$$

73 a $$pH = pK_w - pK_b + \log_{10}\left(\frac{[\text{base}]}{[\text{conjugate acid}]}\right)$$

Total volume = 40.0 + 60.0 = 100.0 cm^3

concentration of B = $\frac{40.0}{100.0} \times 1.00$
= 0.400 mol dm^{-3}

concentration of BHCl = $\frac{60.0}{100.0} \times 1.00$
= 0.600 mol dm^{-3}

$$pH = 14 - 4.00 + \log_{10}\left(\frac{0.400}{0.600}\right) = 9.82$$

b Total volume = 40.0 + 60.0 = 100.0 cm^3

concentration of B = $\frac{60.0}{100.0} \times 1.00$
= 0.600 mol dm^{-3}

concentration of BHCl = $\frac{40.0}{100.0} \times 1.00$
= 0.400 mol dm^{-3}

$$pH = 14 - 4.00 + \log_{10}\left(\frac{0.600}{0.400}\right) = 10.18$$

c Total volume = 30.0 + 50.0 = 80.0 cm^3

concentration of B = $\frac{30.0}{80.0} \times 0.728$
= 0.273 mol dm^{-3}

concentration of BHCl = $\frac{50.0}{80.0} \times 0.640$
= 0.400 mol dm^{-3}

$$pH = 14 - 3.80 + \log_{10}\left(\frac{0.273}{0.400}\right) = 10.03$$

d Total volume = 200.0 + 150.0 = 350.0 cm^3

concentration of B = $\frac{200.0}{350.0} \times 0.510$
= 0.291 mol dm^{-3}

concentration of BHCl = $\frac{150.0}{350.0} \times 0.420$
= 0.180 mol dm^{-3}

$$pH = 14 - 5.27 + \log_{10}\left(\frac{0.291}{0.180}\right) = 8.94$$

74 a The pH of the buffer is equal to the pK_a of the weak acid and so there must be equal concentrations of HA and NaA, so the $[A^-]/[HA] = 1$, i.e. ratio is 1:1

b Let $[A^-]/[HA] = X$

We can re-write the Henderson-Hasselbalch equation as:

$pH = pK_a + \log_{10}X$

$5.00 = 4.60 + \log_{10}X$

$\log_{10}X = 0.40$

$X = 10^{0.40} = 2.5 = [A^-]/[HA]$, i.e. ratio is 2.5:1

c Let $[A^-]/[HA] = X$

$pH = pK_a + \log_{10}X$

$4.80 = 5.20 + \log_{10}X$

$\log_{10}X = -0.40$

$X = 10^{-0.40} = 0.40 = [A^-]/[HA]$, i.e. ratio is 0.40:1 or 1:2.5

75 a Let $[B]/[BHCl] = X$

For a basic buffer we have:

$pH = pK_w - pK_b + \log_{10}X$

$9.80 = 14 - 4.20 + \log_{10}X$

$\log_{10}X = 0$

$X = 1 = [B]/[BHCl]$,

therefore an equal volume of BHCl must be added, 100.0 cm^3.

Chemistry for the IB Diploma – Owen © Cambridge University Press & Assessment 2023

b Let [B]/[BHCl] = X

For a basic buffer we have:

$pH = pK_w - pK_b + \log_{10}X$

$9.50 = 14 - 4.80 + \log_{10}X$

$\log_{10}X = 0.30$

$X = 10^{0.30} = 2.0 = [B]/[BHCl]$,

therefore half the volume of BHCl must be added, 50.0 cm^3, to produce half as many moles.

c Let [B]/[BHCl] = X

For a basic buffer we have:

$pH = pK_w - pK_b + \log_{10}X$

$9.10 = 14 - 4.50 + \log_{10}X$

$\log_{10}X = -0.40$

$X = 10^{-0.40} = 0.40 = [B]/[BHCl]$,

The volume that must be added is $\frac{1}{0.40} \times 100.0 = 250\ cm^3$.

76 Amount of methanoic acid $= \frac{100.0}{1000} \times 0.500$
$= 0.0500$ mol

This is the same in each question

a The pH = pK_a therefore there must be equal concentrations of HCOOH and HCOONa.

Therefore 0.0500 mol HCOONa must be dissolved

mass of HCOONa = 0.0500 × 68.01
= 3.40 g

b Let [HCOONa]/[HCOOH] = X

For an acidic buffer: $pH = pK_a + \log_{10}X$

$4.00 = 3.75 + \log_{10}X$

$\log_{10}X = 0.25$

$X = 10^{0.25} = 1.78 = [HCOONa]/[HCOOH]$

amount of sodium methanoate
= 1.78 × amount of HCOOH to give the correct ratio of concentrations, i.e.
1.78 × 0.0500 = 0.0889 mol

mass of HCOONa = 0.0889 × 68.01
= 6.05 g

c $pH = pK_a + \log_{10}X$

$3.65 = 3.75 + \log_{10}X$

$\log_{10}X = -0.10$

$X = 10^{-0.10} = 0.794 = [HCOONa]/[HCOOH]$

amount of sodium methanoate
= 0.794 × 0.0500 = 0.0397 mol

mass of HCOONa = 0.0397 × 68.01
= 2.70 g

77 Amount of ammonia $= \frac{50.0}{1000} \times 0.200$
$= 0.0100$ mol

This is the same in each question

a pH = 14 – pK_b therefore there must be equal concentrations of NH_3 and NH_4Cl.

Therefore 0.0100 mol NH_4Cl must be dissolved

mass of NH_4Cl = 0.0100 × 53.50
= 0.535 g

b Let $[NH_3]/[NH_4Cl] = X$

For a basic buffer we have:

$pH = pK_w - pK_b + \log_{10}X$

$10.00 = 14 - 4.75 + \log_{10}X$

$\log_{10}X = 0.75$

$X = 10^{0.75} = 5.62 = [NH_3]/[NH_4Cl]$,

amount of NH_4Cl = amount of NH_3/5.62 to give the correct ratio of concentrations,

i.e. $\frac{0.0100}{5.62} = 1.78 \times 10^{-3}$ mol

mass of $NH_4Cl = 1.78 \times 10^{-3} \times 53.50$
= 0.0951 g

c $pH = pK_w - pK_b + \log_{10}X$

$9.00 = 14 - 4.75 + \log_{10}X$

$\log_{10}X = -0.25$

$X = 10^{-0.25} = 0.562 = [NH_3]/[NH_4Cl]$,

amount of NH_4Cl =
amount of NH_3/0.562

i.e. 0.0100/0.562 = 1.78×10^{-2} mol

mass of $NH_4Cl = 1.78 \times 10^{-2} \times 53.50$
= 0.951 g

Chemistry for the IB Diploma – Owen © Cambridge University Press & Assessment 2023

78 pH = 5.00 – diluting a buffer does not change its pH

79 With equal concentrations of acid and conjugate base, the pH of the buffer originally is equal to pK_a of the acid, i.e. 4.76.

a Amount ethanoic acid = amount sodium ethanoate = $\frac{100.0}{1000} \times 0.500 = 0.0500$ mol

Add acid: $CH_3COO^- + H^+ \rightarrow CH_3COOH$

amount of HCl = $\frac{10.0}{1000} \times 0.100$
$= 1.00 \times 10^{-3}$ mol

amount of CH_3COO^- decreases by 1.00×10^{-3}
$\Rightarrow 0.0500 - 1.00 \times 10^{-3} = 0.0490$ mol

amount of CH_3COOH increases by
$1.00 \times 10^{-3} \Rightarrow 0.0500 + 1.00 \times 10^{-3}$
$= 0.0510$ mol

Total volume = 100.0 + 10.0 = 110.0 cm^3

$[CH_3COO^-] = \frac{0.0490}{(110.0/1000)}$
$= 0.445$ mol dm^{-3}

$[CH_3COOH] = \frac{0.0510}{(110.0/1000)}$
$= 0.464$ mol dm^{-3}

Acidic buffer, therefore

$pH = pK_a + \log_{10}\{[CH_3COO^-]/[CH_3COOH]\}$
$= 4.76 + \log_{10}(0.445/0.464) = 4.74$

pH change = 4.76 − 4.74 = 0.02

The pH decreases by 0.02

b amount of HCl = $\frac{20.0}{1000} \times 0.200$
$= 4.00 \times 10^{-3}$ mol

Add acid: $CH_3COO^- + H^+ \rightarrow CH_3COOH$

amount of CH_3COO^- decreases by
$4.00 \times 10^{-3} \Rightarrow 0.0500 - 4.00 \times 10^{-3}$
$= 0.0460$ mol

amount of CH_3COOH increases by
$4.00 \times 10^{-3} \Rightarrow 0.0500 + 4.00 \times 10^{-3}$
$= 0.0540$ mol

Total volume = 100.0 + 20.0 = 120.0 cm^3

$[CH_3COO^-] = \frac{0.0460}{\left(\frac{120.0}{1000}\right)}$
$= 0.383$ mol dm^{-3}

$[CH_3COOH] = \frac{0.0540}{\left(\frac{120.0}{1000}\right)}$
$= 0.450$ mol dm^{-3}

$pH = pK_a + \log_{10}\{[CH_3COO^-]/[CH_3COOH]\}$
$= 4.76 + \log_{10}\left(\frac{0.383}{0.450}\right) = 4.69$

pH change = 4.76 – 4.69 = 0.07

The pH decreases by 0.07

c amount of NaOH = $\frac{10.0}{1000} \times 0.100$
$= 1.00 \times 10^{-3}$ mol

$CH_3COOH + OH^- \rightarrow CH_3COO^- + H_2O$

amount of CH_3COO^- increases by
$1.00 \times 10^{-3} \Rightarrow 0.0500 + 1.00 \times 10^{-3}$
$= 0.0510$ mol

amount of CH_3COOH decreases by
$1.00 \times 10^{-3} = 0.0500 - 1.00 \times 10^{-3}$
$= 0.0490$ mol

Total volume = 100.0 + 10.0 = 110.0 cm^3

$[CH_3COO^-] \Rightarrow \frac{0.0510}{\left(\frac{110.0}{1000}\right)} = 0.464$ mol dm^{-3}

$[CH_3COOH] = \frac{0.0490}{\left(\frac{110.0}{1000}\right)} = 0.445$ mol dm^{-3}

$pH = pK_a + \log_{10}\{[CH_3COO^-]/[CH_3COOH]\}$
$= 4.76 + \log_{10}\left(\frac{0.464}{0.445}\right) = 4.78$

pH change = 4.78 – 4.76 = 0.02

The pH increases by 0.02

d amount of NaOH = $\frac{5.0}{1000} \times 0.500$
$= 2.50 \times 10^{-3}$ mol

$CH_3COOH + OH^- \rightarrow CH_3COO^- + H_2O$

amount of CH_3COO^- increases by
$2.50 \times 10^{-3} \Rightarrow 0.0500 + 2.50 \times 10^{-3}$
$= 0.0525$ mol

amount of CH_3COOH decreases by
$2.50 \times 10^{-3} \Rightarrow 0.0500 - 2.50 \times 10^{-3}$
$= 0.0475$ mol

Total volume = 100.0 + 5.0 = 105.0 cm^3

$[CH_3COO^-] = \frac{0.0525}{\left(\frac{105.0}{1000}\right)} = 0.500$ mol dm^{-3}

Chemistry for the IB Diploma – Owen © Cambridge University Press & Assessment 2023

$$[CH_3COOH] = \frac{0.0475}{\left(\frac{105.0}{1000}\right)} = 0.452 \text{ mol dm}^{-3}$$

$pH = pK_a + \log_{10}\{[CH_3COO^-]/[CH_3COOH]\} = 4.76 + \log_{10}(0.500/0.452) = 4.80$

pH change = 4.80 – 4.76 = 0.04

The pH increases by 0.04

Exam-style question answers

1 D

2 C

3 B

4 C

5 A

6 A

7 B

8 B

9 C

10 A

11 C

12 D

13 D

14 A

15 B

16 C

17 B

18 a An acid is a proton/H^+ donor and a base is a proton/H^+ acceptor. **[1]**

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

or

$CH_3COOH(aq) \rightleftharpoons CH_3COO^-(aq) + H^+(aq)$;

The conjugate base is formed when ethanoic acid acts as an acid and loses a proton (H^+). The conjugate base is, therefore, CH_3COO^-; **[2]**

c A strong acid dissociates completely in solution, but a weak acid dissociates only partially. **[1]**

d HCl is a strong acid, so it dissociates completely:

$[H^+(aq)] = 1.00 \times 10^{-3} \text{ mol dm}^{-3}$

$pH = -\log_{10}[H^+(aq)] = -\log_{10}(1.00 \times 10^{-3}) = 3.00$ **[1]**

e This is correct if the strong and weak acid have the same concentration;

The pH depends on the concentration, so it is possible that a concentrated solution of a weak acid could have a lower pH than a very dilute solution of a strong acid; **[2]**

f i $Na_2CO_3(aq) + 2CH_3COOH(aq) \rightarrow 2CH_3COONa(aq) + CO_2(g) + H_2O(l)$;

sodium ethanoate and carbon dioxide and water; **[2]**

ii Ethanoic acid will react less vigorously/fizzes less rapidly/sodium carbonate takes longer to disappear/react;

Ethanoic acid is a weak acid but hydrochloric acid is a strong acid, therefore, ethanoic acid dissociates less and the concentration of H^+ ions is lower in the ethanoic acid; **[2]**

19 a $H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq)$ **[1]**

b $K_w = [H^+(aq)][OH^-(aq)]$ **[1]**

c NaOH is a strong base, so it ionises fully.

$[OH^-(aq)] = 0.10 \text{ mol dm}^{-3}$

$[H^+(aq)][OH^-(aq)] = 1.0 \times 10^{-14}$

$[H^+(aq)] = 1.0 \times 10^{-13} \text{ mol dm}^{-3}$;

$pH = -\log_{10}[H^+(aq)] = 13$; **[2]**

d Barium hydroxide will have a higher pH;

Barium hydroxide has the formula $Ba(OH)_2$ and is a strong base. A 0.10 mol dm^{-3} solution will ionise to produce $[OH^-(aq)] = 0.20 \text{ mol dm}^{-3}$/a higher concentration of $OH^-(aq)$; **[2]**

Chemistry for the IB Diploma – Owen © Cambridge University Press & Assessment 2023

20 a $KOH(aq) + HCl(aq) \rightarrow KCl(aq) + H_2O(l)$ **[1]**

b i $[OH^-(aq)] = 0.0100 \text{ mol dm}^{-3}$

$[H^+(aq)][OH^-(aq)] = 1.0 \times 10^{-14}$

$[H^+(aq)] = 1.0 \times 10^{-12} \text{ mol dm}^{-3}$

$pH = -\log_{10}[H^+(aq)] = 12 = \text{initial pH};$ **[1]**

ii amount in mol of KOH =

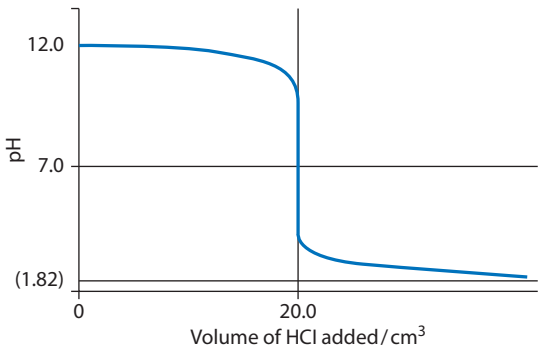
$\frac{30.0}{1000} \times 0.0100 = 3.00 \times 10^{-4} \text{ mol} =$

This is equal to the amount in mol of HCl required to reach the equivalence point

volume of HCl $= \frac{3.00 \times 10^{-4}}{0.0150} \times 1000$

$= 20.0 \text{ cm}^3$; **[1]**

iii This is a strong acid–strong base titration, therefore, the pH at the equivalence point is seven; **[1]**



[1]

c initial amount of KOH $= \frac{30.0}{1000} \times 0.0100 =$

3.00×10^{-4} mol = amount of OH^- ions, since KOH is a strong base

amount of HCl $= \frac{10.0}{1000} \times 0.0150 =$ 1.50×10^{-4} mol =

amount of H^+ ions, since HCl is a strong acid

excess of OH^- ions $= 3.00 \times 10^{-4} - 1.50 \times 10^{-4} = 1.50 \times 10^{-4}$ mol OH^-;

total volume = 40.0 cm^3

concentration of OH^-

$= \frac{1.50 \times 10^{-4}}{\left(\frac{40.0}{1000}\right)}$

$= 3.75 \times 10^{-3} \text{ mol dm}^{-3}$

$[H^+(aq)][OH^-(aq)] = 1.0 \times 10^{-14}$

$[H^+(aq)] = \frac{1.0 \times 10^{-14}}{3.75 \times 10^{-3}}$

$= 2.67 \times 10^{-12} \text{ mol dm}^{-3};$

$pH = -\log_{10}[H^+(aq)] = -\log_{10}[2.67 \times 10^{-12}]$
$= 11.6;$ **[3]**

21 a $pH = -\log_{10}[H^+(aq)]$ **[1]**

b $K_a = 10^{-pK_a}$

$K_a = 10^{-4.82} = 1.51 \times 10^{-5}$

The equation for the dissociation of butanoic acid is:

$CH_3CH_2CH_2COOH(aq) \rightleftharpoons CH_3CH_2CH_2COO^-(aq) + H^+(aq)$

The expression for K_a is:

$$K_a = \frac{[CH_3CH_2CH_2COO^-(aq)][H^+(aq)]}{[CH_3CH_2CH_2COOH(aq)]}$$

Because one molecule of $CH_3CH_2CH_2COOH$ dissociates to form one $CH_3CH_2CH_2COO^-$ ion and one H^+ ion, the concentrations of $CH_3CH_2CH_2COO^-$ and H^+ ions in the solution will be equal:
$[CH_3CH_2CH_2COO^-(aq)] = [H^+(aq)]$

We will make the assumption that the dissociation of the acid is negligible compared with the concentration of the acid, that is, we will assume that the concentration of the acid at equilibrium is the same as the initial concentration, 0.150 mol dm^{-3} in this case;

These terms are substituted into the K_a expression:

$1.51 \times 10^{-5} = \frac{[H^+(aq)]^2}{0.150};$

$[H^+(aq)]^2 = 1.51 \times 10^{-5} \times 0.150$
$= 2.27 \times 10^{-6}$

$[H^+(aq)] = \sqrt{(2.27 \times 10^{-6})} =$ $1.51 \times 10^{-3} \text{ mol dm}^{-3}$

$pH = -\log_{10}[H^+(aq)] = -\log_{10}(1.51 \times 10^{-3})$
$= 2.82;$ **[3]**

Chemistry for the IB Diploma – Owen © Cambridge University Press & Assessment 2023

c It will be higher than 7 because sodium butanoate is the salt of a strong base (NaOH) and a weak acid (butanoic acid);

When sodium butanoate dissolves in water, the two ions separate from each other – the solution contains $CH_3CH_2CH_2COO^-(aq)$ and $Na^+(aq)$ ions. The $CH_3CH_2CH_2COO^-$ ion is the conjugate base of the weak acid butanoic acid, and so, acting as a base, will react with water molecules to accept a proton and, therefore, increase the concentration of OH^- ions in the solution;

$CH_3CH_2CH_2COO^-(aq) + H_2O(l) \rightleftharpoons CH_3CH_2CH_2COOH(aq) + OH^-(aq)$; **[3]**

d i The equation for the reaction is

$CH_3CH_2CH_2COOH(aq) + NaOH(aq) \rightarrow CH_3CH_2CH_2COONa(aq) + H_2O(l)$

amount of butanoic acid $= \frac{25.00}{1000} \times 0.150 = 3.75 \times 10^{-3}$ mol;

From the chemical equation: 1 mol of butanoic acid reacts with 1 mol of sodium hydroxide. Therefore, 3.75×10^{-3} mol butanoic acid reacts with 3.75×10^{-3} mol sodium hydroxide. So, there are 3.75×10^{-3} mol present in 27.60 cm^3 of sodium hydroxide.

The concentration of sodium hydroxide is $\frac{3.75 \times 10^{-3}}{(27.60/1000)} = 0.136$ mol dm^{-3}; **[2]**

ii NaOH is a strong base and, therefore, completely ionises in solution:

$[OH^-(aq)] = 0.136$ mol dm^{-3}

$pOH = -\log_{10}[OH^-(aq)]$

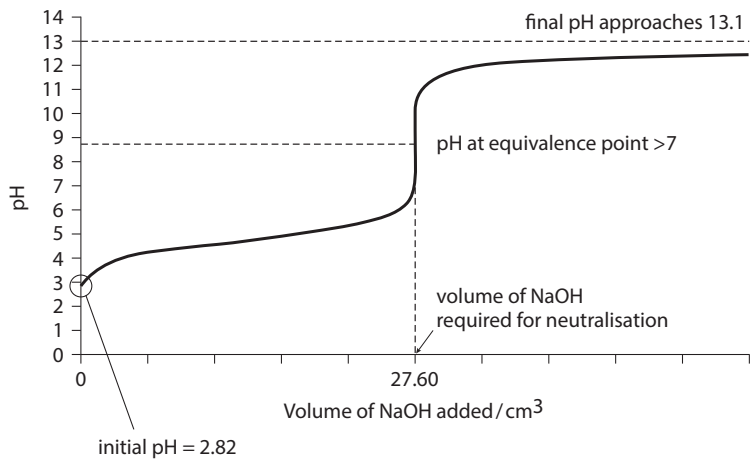
$pOH = -\log_{10}0.136 = 0.866$;

Assuming that the temperature is 25 °C:

$14 = pH + pOH$

$pH = 14 - 0.866 = 13.1$; **[2]**

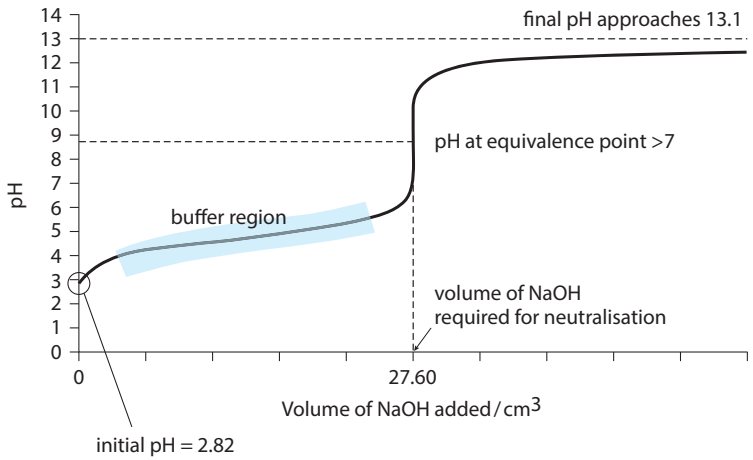
iii **[1]**



Chemistry for the IB Diploma – Owen © Cambridge University Press & Assessment 2023

The values quoted are from the previous parts of the question. The pH at the equivalence point is higher than 7 because sodium butanoate is formed in the titration. The final pH will approach the pH of the sodium hydroxide solution used. [1] for general form of curve, correct axes, and pH at equivalence point clearly >7

iv **[1]**



v This is the half-equivalence point; therefore, pH = pK_a of butanoic acid, i.e. 4.82. **[1]**

vi The most suitable indicator is phenolphthalein;

The pH range of the indicator (8.0–10.0) comes entirely within the very steep part of the titration curve. **[2]**

e **i** A buffer solution is a solution that resists changes in pH when *small* amounts of acid or alkali are added. **[1]**

ii When sodium hydroxide is added:

$CH_3CH_2CH_2COOH(aq) + OH^-(aq) \rightarrow CH_3CH_2CH_2COO^-(aq) + H_2O(l)$;

When hydrochloric acid is added:

$CH_3CH_2CH_2COO^-(aq) + H^+(aq) \rightarrow CH_3CH_2CH_2COOH(aq)$;

The equilibrium in the buffer solution is

$CH_3CH_2CH_2COOH(aq) \rightleftharpoons CH_3CH_2CH_2COO^-(aq) + H^+(aq)$

because the initial concentrations of butanoic acid and the butanoate ion in solution are large compared to the changes in concentration that occur when acid/alkali are added the position of equilibrium shifts very little and the $[H^+(aq)]$ and, hence, the pH, remains essentially constant; **[3]**

iii $pH = pK_a + \log_{10}\frac{[\text{conjugate base}]}{[\text{acid}]}$

$pH = 4.82 + \log_{10}\left(\frac{0.200}{0.100}\right)$;

pH = 5.12; **[2]**

22 **a** The lower the pK_a value, the stronger the acid:

propanoic acid < ethanoic acid < methanoic acid **[1]**

b $K_a = 10^{-pK_a} = 10^{-4.76} = 1.74 \times 10^{-5}$ **[1]**

c This is correct because ethanoic acid is a stronger acid than propanoic acid and, therefore, will dissociate more in aqueous solution;

Chemistry for the IB Diploma – Owen © Cambridge University Press & Assessment 2023

The concentrations of the acids are equal, so the concentration of H^+ ions will just depend on the strength of the acid; **[2]**

d $K_a = 10^{-pK_a} = 10^{-3.75} = 1.78 \times 10^{-4}$

The equation for the dissociation of methanoic acid is

$HCOOH(aq) \rightleftharpoons HCOO^-(aq) + H^+(aq)$

and its dissociation constant expression is

$$K_a = \frac{[HCOO^-(aq)][H^+(aq)]}{[HCOOH(aq)]}$$

We will make the assumption that the dissociation of the acid is negligible compared with the concentration of the acid, so the concentration of the acid at equilibrium is the same as its initial concentration, 0.200 mol dm^{-3} in this case.

$$1.78 \times 10^{-4} = \frac{[H^+(aq)]^2}{0.200};$$

$[H^+(aq)]^2 = 1.78 \times 10^{-4} \times 0.200$
$= 3.56 \times 10^{-5}$

$$[H^+(aq)] = \sqrt{(3.56 \times 10^{-5})}$$
$$= 5.96 \times 10^{-3} \text{ mol dm}^{-3}$$

$pH = -\log_{10}[H^+(aq)] = -\log_{10}(5.96 \times 10^{-3})$
$= 2.22;$

Assuming that the temperature is 25 °C, pOH = 14 − 2.22 = 11.78; **[3]**

e **i** $CH_3CH_2COO^-(aq) + H_2O(l) \rightleftharpoons CH_3CH_2COOH(aq) + OH^-(aq)$ **[1]**

ii $K_a \times K_b = K_w$ for a conjugate acid–base pair.

Assuming that the temperature is 25 °C and, therefore, that $K_w = 1.0 \times 10^{-14}$.

K_a for propanoic acid is $10^{-4.87} = 1.35 \times 10^{-5}$

so $1.35 \times 10^{-5} \times K_b = 1.00 \times 10^{-14}$

$K_b = 7.41 \times 10^{-10}$ **[1]**

iii $CH_3CH_2COO^-(aq) + H_2O(l) \rightleftharpoons CH_3CH_2COOH(aq) + OH^-(aq)$

$$K_b = \frac{[CH_3CH_2COOH(aq)][OH^-(aq)]}{[CH_3CH_2COO^-(aq)]}$$

approximation: the ionisation of $CH_3CH_2COO^-$ is negligible compared with its concentration

$$7.41 \times 10^{-10} = \frac{[OH^-(aq)]^2}{0.200};$$

$[OH^-] = 1.22 \times 10^{-5}$ mol dm^{-3};

$pOH = -\log_{10}[OH^-(aq)]$

$pOH = -\log_{10}(1.22 \times 10^{-5}) = 4.91$

$pOH + pH = pK_w$

At 25 °C, pOH + pH = 14, therefore:

pH = 14 − 4.91 = 9.09; **[3]**

f $$pH = pK_a + \log_{10}\frac{[CH_3COO^-(aq)]}{[CH_3COOH(aq)]}$$

$$4.20 = 4.76 + \log_{10}\frac{[CH_3COO^-(aq)]}{[CH_3COOH(aq)]}$$

$$\frac{[CH_3COO^-(aq)]}{[CH_3COOH(aq)]} = 10^{(4.20-4.76)} = 0.275;$$

The amount of ethanoic acid in the solution is $\frac{100.0}{1000} \times 0.100 = 0.0100$ mol

The amount of sodium ethanoate that must be added is $0.275 \times 0.0100 = 2.75 \times 10^{-3}$ mol;

mass of sodium ethanoate = $2.75 \times 10^{-3} \times 82.04 = 0.226$ g; **[3]**

23 **a** $K_w = [H^+(aq)][OH^-(aq)]$

Because one H_2O molecule dissociates to form one H^+ ion and one OH^- ion, in pure water the concentration of H^+ ions is equal to the concentration of OH^- ions. We can, therefore, write $K_w = [H^+(aq)]^2$ for pure water.

So, at 323.15:

$5.48 \times 10^{-14} = [H^+(aq)]^2;$

$$[H^+(aq)] = \sqrt{(5.48 \times 10^{-14})}$$
$$= 2.34 \times 10^{-7} \text{ mol dm}^{-3}$$

$pH = -\log_{10}[H^+(aq)] = -\log_{10}(2.34 \times 10^{-7})$
$= 6.63;$ **[2]**

Chemistry for the IB Diploma – Owen © Cambridge University Press & Assessment 2023

b The pOH for a neutral solution at 323.15 K will be the same as the pH, i.e. 6.63;

This solution has a pOH of 7.0. A higher pOH indicates a lower concentration of OH^- ions than in a neutral solution, therefore, the solution is acidic; **[2]**

24 a It only ionises partially in aqueous solution. **[1]**

b $NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$;

the reversible arrow is essential

Conjugate acid–base pairs differ by one proton (H^+).

NH_3/NH_4^+ and H_2O/OH^- are the two pairs; **[2]**

c $K_b = 10^{-pK_b} = 10^{-4.75} = 1.78 \times 10^{-5}$

$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$

$$K_b = \frac{[NH_4^+(aq)][OH^-(aq)]}{[NH_3(aq)]}$$

$$K_b = \frac{[OH^-(aq)]^2}{[NH_3(aq)]}$$

Assumption: the concentration of NH_3 at equilibrium is equal to the initial concentration, i.e. that the ionisation of the base is negligible compared with its concentration/temperature is 25 °C *(this is required in the last part of the calculation – we assume that pK_w is 14)*;

$$1.78 \times 10^{-5} = \frac{[OH^-(aq)]^2}{0.125};$$

$[OH^-(aq)]^2 = 1.78 \times 10^{-5} \times 0.125 = 2.22 \times 10^{-6}$

$[OH^-(aq)] = 1.49 \times 10^{-3}$ mol dm^{-3}

$pOH = -\log_{10}[OH^-(aq)]$
$= -\log_{10}(1.49 \times 10^{-3}) = 2.83$

pH = 14 − 2.83 = 11.17; **[3]**

d $NH_3 + HCl \rightarrow NH_4Cl$ **[1]**

e It will be acidic because ammonium chloride is the salt of a strong acid (HCl) and a weak base (NH_3);

The NH_4^+ ion is the conjugate acid of the weak base ammonia, and so, acting as an acid, will dissociate and, therefore, increase the concentration of H^+/H_3O^+ ions in the solution, according to the equation:

$NH_4^+(aq) + H_2O(l) \rightleftharpoons NH_3(aq) + H_3O^+(aq)$
or $NH_4^+(aq) \rightleftharpoons NH_3(aq) + H^+(aq)$; **[2]**

f total volume of solution is 200.0 + 300.0 = 500.0 cm^3

$[NH_3(aq)]$ in the buffer:

$$\frac{200.0}{500.0} \times 0.125 = 0.0500 \text{ mol dm}^{-3}$$

$[NH_4^+(aq)]$ in the buffer:

$$\frac{300.0}{500.0} \times 0.100 = 0.0600 \text{ mol dm}^{-3};$$

$$pH = pK_w - pK_b + \log_{10}\frac{[\text{base}]}{[\text{conjugate acid}]}$$

$$= 14 - 4.75 + \log_{10}\left(\frac{0.0500}{0.0600}\right);$$

pH = 9.17; **[3]**

g The pH of the buffer solution is not affected by diluting it because the ratio of $[NH_3] : [NH_4^+]$ stays the same;

Diluting the buffer reduces its capacity to resist changes in pH – if the concentrations of the individual components are lower then any slight changes in concentration will have a larger relative effect on them and, hence, on the position of equilibrium and the pH; **[2]**

h amount in mol of $NH_3 = \frac{200.0}{1000} \times 0.125$

$= 0.0250$ mol

amount in mol of $NH_4Cl = \frac{300.0}{1000} \times 0.100$

$= 0.0300$ mol

amount in mol of $HCl = \frac{1.00}{1000} \times 1.00$

$= 1.00 \times 10^{-3}$ mol;

$NH_3(aq) + H^+(aq) \rightarrow NH_4^+(aq)$

Chemistry for the IB Diploma – Owen © Cambridge University Press & Assessment 2023

after HCl added:

amount in mol of NH_3 = 0.0250 − 1.00×10^{-3} = 0.0240 mol

amount in mol of NH_4Cl = 0.0300 + 1.00×10^{-3} = 0.0310 mol;

ignoring the volume of HCl, the total volume is 500.0 cm^3

$[NH_3(aq)]$ in the buffer:

$$\frac{0.0240}{\left(\frac{500.0}{1000}\right)} = 0.0480 \text{ mol dm}^{-3}$$

$[NH_4^+(aq)]$ in the buffer:

$$\frac{0.0310}{\left(\frac{500.0}{1000}\right)} = 0.0620 \text{ mol dm}^{-3};$$

$$\text{pH} = \text{p}K_\text{w} - \text{p}K_\text{b} + \log_{10}\frac{[\text{base}]}{[\text{conjugate acid}]} =$$

$$14 - 4.75 + \log_{10}\left(\frac{0.0480}{0.0620}\right);$$

pH = 9.14

change in pH = 9.17 – 9.14 = 0.03, so the pH goes down by 0.03 units; **[4]**

Chemistry for the IB Diploma – Owen © Cambridge University Press & Assessment 2023

Chapter 20

Test your understanding

1

N_2	CO_2	Cl_2O	PO_4^{3-}	HCl	$HClO_3$	ClO_4^-	C_2H_3Cl	$C_6H_{12}O_6$
N 0	C +4 O −2	Cl +1 O −2	P +5 O −2	H +1 Cl −1	H +1 Cl +5 O −2	Cl +7 O −2	C −1 H +1 Cl −1	C 0 H +1 O −2
Ca	Na_2CrO_4	$K_2Cr_2O_7$	Na_2O_2	Na_2SO_4	LiH	$LiAlH_4$	$(NH_4)_2SO_4$	NH_4NO_3
Ca 0	Na +1 Cr +6 O −2	K +1 Cr +6 O −2	Na +1 O −1	Na +1 S +6 O −2	Li +1 H −1	Li +1 Al +3 H −1	N −3 H +1 S +6 O −2	N −3 (NH_4^+) H +1 N +5 (NO_3^-) O −2

2

SO_2	SO_3	$Cr_2O_7^{2-}$	$FeCl_2$	$CuSO_4$	$KMnO_4$	$NaClO_4$	Cu_2O	$Fe_2(SO_4)_3$
sulfur(IV) oxide	sulfur(VI) oxide	dichromate (VI)	iron(II) chloride	copper(II) sulfate(VI)	potassium manganate (VII)	sodium chlorate (VII)	copper(I) oxide	iron(III) sulfate(VI)

3 **a** Not redox – no change in oxidation states

b Redox: the sulfide ion in zinc sulfide is oxidised – change in oxidation state: –2 in ZnS to +4 in SO_2

O_2 is reduced – change in oxidation state: 0 in O_2 to –2 in ZnO/SO_2

c Redox: the Na is oxidised – change in oxidation state: 0 in Na to +1 in NaOH

H in water is reduced – change in oxidation state: +1 in H_2O to 0 in H_2

d Not redox – no change in oxidation states

e Not redox – no change in oxidation states

f Redox: the Fe in $FeSO_4$ is oxidised – change in oxidation state: +2 in $FeSO_4$ to +3 in $Fe_2(SO_4)_3$

O in H_2O_2 is reduced – change in oxidation state: –1 in H_2O_2 to –2 in H_2O

g Redox: the O in KNO_3 is oxidised – change in oxidation state: –2 in KNO_3 to 0 in O_2

the N in KNO_3 is reduced – change in oxidation state: +5 in KNO_3 to +3 in KNO_2

h Redox: the I^- is oxidised – change in oxidation state: –1 to 0 in I_2

the Cl in HOCl is reduced – change in oxidation state: +1 in HOCl to –1 in Cl^-

4 **a** $CuSO_4/Cu^{2+}$ is the oxidising agent (gets reduced/takes electrons from the Zn) and Zn is the reducing agent (gets oxidised/gives electrons to the Cu^{2+})

b Cl_2 is the oxidising agent (gets reduced to Cl^-) and Br^- is the reducing agent (gets oxidised to Br_2)

c I_2O_5 is the oxidising agent (change in oxidation state of I from +5 to 0) and CO is the reducing agent (change in oxidation state of C from +2 to +4)

d HNO_3 is the oxidising agent (change in oxidation state of N from +5 to +4) and S is the reducing agent (change in oxidation state of S from 0 to +6)

e I_2 is the oxidising agent (change in oxidation state from 0 to –1) and $Na_2S_2O_3/S_2O_3^{2-}$ is the reducing agent (change in oxidation state of S from +2 to +2.5)

f $KMnO_4/MnO_4^-$ is the oxidising agent and $Na_2C_2O_4/C_2O_4^{2-}$ is the reducing agent

g $K_2Cr_2O_7/Cr_2O_7^{2-}$ is the oxidising agent and $FeSO_4/Fe^{2+}$ is the reducing agent

Chemistry for the IB Diploma – Owen © Cambridge University Press & Assessment 2023

5 State whether each of the following half-equations involves oxidation or reduction:

a reduction – electrons added/e^- on the left-hand side

b reduction – electron added/e^- on the left-hand side

c oxidation – electron removed/e^- on the right-hand side

d oxidation – electrons removed/e^- on the right-hand side

e reduction – electrons added/e^- on the left-hand side

6 a $Fe^{3+} + 3e^- \rightarrow Fe$

b $Pb^{2+} \rightarrow Pb^{4+} + 2e^-$

c $I_2 + 2e^- \rightarrow 2I^-$

d $2S_2O_3^{2-} \rightarrow S_4O_6^{2-} + 2e^-$

e $C_2O_4^{2-} \rightarrow 2CO_2 + 2e^-$

7 a $I_2 + 2H_2O \rightarrow 2OI^- + 4H^+ + 2e^-$

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

c $2IO_3^- + 12H^+ + 10e^- \rightarrow I_2 + 6H_2O$

d $N_2 + 6H_2O \rightarrow 2NO_3^- + 12H^+ + 10e^-$

e $SO_4^{2-} + 4H^+ + 2e^- \rightarrow H_2SO_3 + H_2O$

8 a $VO^{2+} + 2H^+ + e^- \rightarrow V^{3+} + H_2O$

b $Xe + 3H_2O \rightarrow XeO_3 + 6H^+ + 6e^-$

c $NO_3^- + 4H^+ + 3e^- \rightarrow NO + 2H_2O$

d $2NO_3^- + 10H^+ + 8e^- \rightarrow N_2O + 5H_2O$

e $VO_2^+ + 2H^+ + e^- \rightarrow VO^{2+} + H_2O$

9 a $Cr_2O_7^{2-} + 14H^+ + 6Eu^{2+} \rightarrow 6Eu^{3+} + 2Cr^{3+} + 7H_2O$

$Cr_2O_7^{2-}$ is the oxidising agent (reduced – Cr oxidation state decreases from +6 to +3)

Eu^{2+} is the reducing agent (oxidised – oxidation state increases from +2 to +3)

b $2MnO_4^- + 6H^+ + 10HCN \rightarrow 2Mn^{2+} + 8H_2O + 5(CN)_2$

MnO_4^- is the oxidising agent (reduced – Mn oxidation state decrease from +7 to +2)

HCN is the reducing agent (oxidised – oxidation state of C increases from +2 to +3)

c $2IO_3^-(aq) + 12H^+(aq) + 10I^-(aq) \rightarrow 6I_2(aq) + 6H_2O(l)$

IO_3^- is the oxidising agent (reduced – I oxidation state decrease from +5 to 0)

I^- is the reducing agent (oxidised – oxidation state increases from –1 to 0)

d $2Cr_2O_7^{2-}(aq) + 16H^+(aq) + 3CH_3CH_2OH \rightarrow 3CH_3COOH^- + 4Cr^{3+}(aq) + 11H_2O(l)$

$Cr_2O_7^{2-}$ is the oxidising agent (reduced – Cr oxidation state decreases from +6 to +3)

CH_3CH_2OH is the reducing agent (oxidised – average oxidation state of C increases from –2 to 0)

10 a $Au(OH)_3 + 3H^+ + 3e^- \rightarrow Au + 3H_2O \times 2$

$Br^- + H_2O \rightarrow HBrO + H^+ + 2e^- \times 3$

$2Au(OH)_3 + 3H^+ + 3Br^- \rightarrow 2Au + 3H_2O + 3HBrO$

b $2IO_3^- + 12H^+ + 10e^- \rightarrow I_2 + 6H_2O \times 3$

$NO + 2H_2O \rightarrow NO_3^- + 4H^+ + 3e^- \times 10$

$6IO_3^- + 10NO + 2H_2O \rightarrow 3I_2 + 10NO_3^- + 4H^+$

c $ReO_4^- + 8H^+ + 7e^- \rightarrow Re + 4H_2O \times 3$

$P + 3H_2O \rightarrow H_3PO_3 + 3H^+ + 3e^- \times 7$

$3ReO_4^- + 3H^+ + 7P + 9H_2O \rightarrow 3Re + 7H_3PO_3$

11 a $Cl_2 + 2Br^- \rightarrow 2Cl^- + Br_2$

b $Zn + 2Ag^+ \rightarrow Zn^{2+} + 2Ag$

c $2Fe^{3+} + 2I^- \rightarrow 2Fe^{2+} + I_2$

12 a $Fe^{2+} \rightarrow Fe^{3+} + e^- \times 6$

$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$

$6Fe^{2+} + Cr_2O_7^{2-} + 14H^+ \rightarrow 6Fe^{3+} + 2Cr^{3+} + 7H_2O$

oxidising agent: $Cr_2O_7^{2-}$

reducing agent: Fe^{2+}

b $2Br^- \rightarrow Br_2 + 2e^- \times 3$

$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$

$6Br^- + Cr_2O_7^{2-} + 14H^+ \rightarrow 3Br_2 + 2Cr^{3+} + 7H_2O$

oxidising agent: $Cr_2O_7^{2-}$

reducing agent: Br^-

Chemistry for the IB Diploma – Owen © Cambridge University Press & Assessment 2023

c $Zn \rightarrow Zn^{2+} + 2e^-$

$VO^{2+} + 2H^+ + e^- \rightarrow V^{3+} + H_2O \times 2$

$Zn + 2VO^{2+} + 4H^+ \rightarrow Zn^{2+} + 2V^{3+} + 2H_2O$

oxidising agent: VO^{2+}

reducing agent: Zn

d $2BrO_3^- + 12H^+ + 10e^- \rightarrow Br_2 + 6H_2O$

$2I^- \rightarrow I_2 + 2e^- \times 5$

$2BrO_3^- + 10I^- + 12H^+ \rightarrow Br_2 + 5I_2 + 6H_2O$

oxidising agent: BrO_3^-

reducing agent: I^-

e $NpO_2^{2+} + e^- \rightarrow NpO_2^+$

$2H_2O + U^{4+} \rightarrow UO_2^+ + 4H^+ + e^-$

$2H_2O + NpO_2^{2+} + U^{4+} \rightarrow$
$NpO_2^+ + UO_2^+ + 4H^+$

oxidising agent: NpO_2^{2+}

reducing agent: U^{4+}

13 a The order or reactivity is Mg > Zn > Cu, so Mg will displace Zn and Cu and Zn will displace Cu.

	$ZnSO_4(aq)$	$MgCl_2(aq)$	$CuSO_4(aq)$
zinc	no reaction	no reaction	reaction
magnesium	reaction	no reaction	reaction
copper	no reaction	no reaction	no reaction

$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$

oxidising agent: Cu^{2+}

reducing agent: Zn

$Mg(s) + Zn^{2+}(aq) \rightarrow Mg^{2+}(aq) + Zn(s)$

oxidising agent: Zn^{2+}

reducing agent: Mg

$Mg(s) + Cu^{2+}(aq) \rightarrow Mg^{2+}(aq) + Cu(s)$

oxidising agent: Cu^{2+}

reducing agent: Mg

b $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$ oxidation
$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$ reduction

$Mg(s) \rightarrow Mg^{2+}(aq) + 2e^-$ oxidation
$Zn^{2+}(aq) + 2e^- \rightarrow Zn(s)$ reduction

$Mg(s) \rightarrow Mg^{2+}(aq) + 2e^-$ oxidation
$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$ reduction

14 a A reaction would be predicted to occur because iodine should be more reactive/a better oxidising agent than astatine.

$I_2(aq) + 2KAt(aq) \rightarrow 2KI(aq) + At_2(aq)$ OR

$I_2(aq) + 2At^-(aq) \rightarrow 2I^-(aq) + At_2(aq)$

oxidizing agent: I_2

reducing agent: KAt/At^-

b No reaction would be predicted to occur because astatine should not be a strong enough oxidising agent to oxidise iodide ions.

15 a Z reduces Q^{2+} to Q therefore Z is more reactive than Q

X reduces Z^{2+} to Z therefore X is more reactive than Z

Therefore the order of reactivity is:

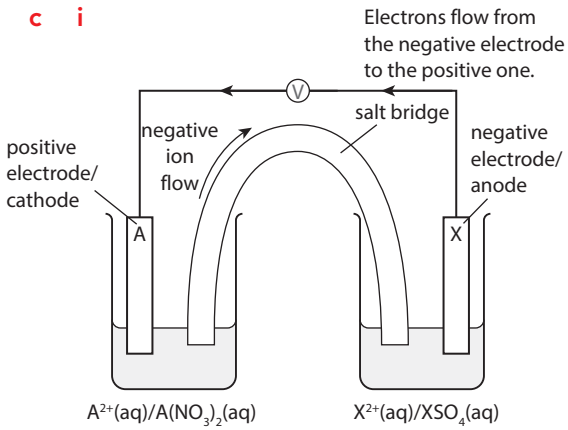
X > Z > Q

b i stronger, since A reduces Q^{2+} to Q

ii X > Z > A > Q; A must come between Z and Q since A reduces Q^{2+} but Z reduces A^{2+}.

iii Q^{2+}; since Q^{2+} oxidises all the metals to M^{2+}

c i



X is more reactive than *A*, so *X* must be the negative electrode: *X* is oxidised to produce X^{2+} and electrons. The production of electrons makes this the negative electrode.

ii $X(s) \rightarrow X^{2+}(aq) + 2e^-$; negative electrode/anode

$A^{2+}(aq) + 2e^- \rightarrow A(s)$; positive electrode/cathode

iii lower because Z and A are closer in reactivity than X and A

Chemistry for the IB Diploma – Owen © Cambridge University Press & Assessment 2023

16 a Reaction I is oxidation, so it occurs at the anode.

Reaction II is reduction, so it occurs at the cathode.

b The electrons are already balanced, so just add the two half-equations together to give:

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

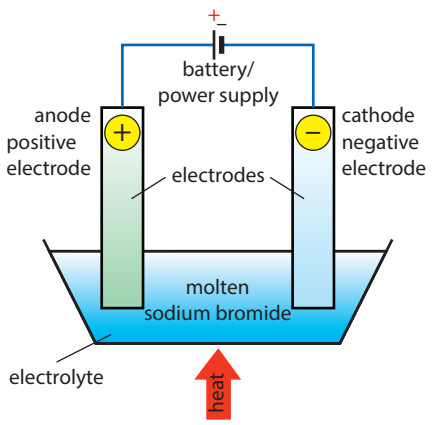
c The reactions are reversed during charging. Electrons are added at the negative electrode – reduction occurs, so the reaction is:

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

d The reactions are reversed during charging. Oxidation occurs at the anode, so the reaction is:

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

17



18

	ANODE	CATHODE
a	bromine	potassium
	$2Br^- \rightarrow Br_2 + 2e^-$	$K^+ + e^- \rightarrow K$
b	chlorine	copper
	$2Cl^- \rightarrow Cl_2 + 2e^-$	$Cu^{2+} + 2e^- \rightarrow Cu$
c	oxygen	nickel
	$2O^{2-} \rightarrow O_2 + 4e^-$	$Ni^{2+} + 2e^- \rightarrow Ni$
d	chlorine	calcium
	$2Cl^- \rightarrow Cl_2 + 2e^-$	$Ca^{2+} + 2e^- \rightarrow Ca$
e	chlorine	sodium
	$2Cl^- \rightarrow Cl_2 + 2e^-$	$Na^+ + e^- \rightarrow Na$
f	oxygen	iron
	$2O^{2-} \rightarrow O_2 + 4e^-$	$Fe^{3+} + 3e^- \rightarrow Fe$
g	bromine	magnesium
	$2Br^- \rightarrow Br_2 + 2e^-$	$Mg^{2+} + 2e^- \rightarrow Mg$

19 $CH_3CH_2CH_2CH_2OH + 6O_2 \rightarrow 4CO_2 + 5H_2O$

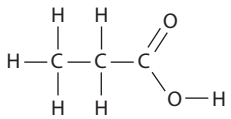
20 a propan-1-ol, primary; 1 C joined to the C with the OH

b pentan-2-ol, secondary; 2 C joined to the C with the OH

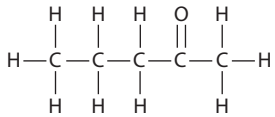
c 2-methylbutan-2-ol, tertiary; 3 C joined to the C with the OH

d 3.3-dimethylbutan-1-ol, primary; 1 C joined to the C with the OH

21 a

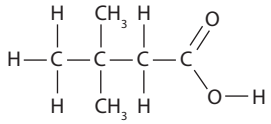


b

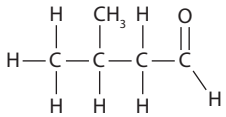


c Not oxidised

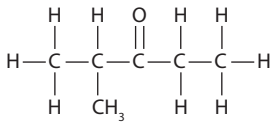
d



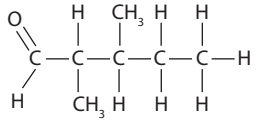
22 a Apparatus set up for distillation means that the major product from oxidation of a primary alcohol will be an aldehyde, rather than a carboxylic acid.



b



c Apparatus set up for distillation means that the major product from oxidation of a primary alcohol will be an aldehyde, rather than a carboxylic acid.



Chemistry for the IB Diploma – Owen © Cambridge University Press & Assessment 2023

23 **a** $CH_3OH \rightarrow HCHO + 2H^+ + 2e^-$

b $CH_3OH + H_2O \rightarrow HCOOH + 4H^+ + 4e^-$

c $CH_3CH(OH)CH_2CH_3 \rightarrow CH_3COCH_2CH_3 + 2H^+ + 2e^-$

d $CH_3CH_2CH_2CH_2CH_2OH \rightarrow CH_3CH_2CH_2CH_2CHO + 2H^+ + 2e^-$

24 **a** $CH_3CH_2OH \rightarrow CH_3CHO + 2H^+ + 2e^- \ (\times 5)$

$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O \ (\times 2)$

$5CH_3CH_2OH + 2MnO_4^- + 6H^+ \rightarrow 5CH_3CHO + 2Mn^{2+} + 8H_2O$

b $CH_3CHO + H_2O \rightarrow CH_3COOH + 2H^+ + 2e^- \ (\times 3)$

$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$

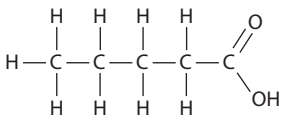
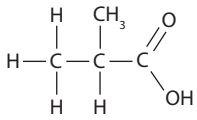
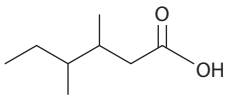
$3CH_3CHO + Cr_2O_7^{2-} + 8H^+ \rightarrow 3CH_3COOH + 2Cr^{3+} + 4H_2O$

c $(CH_3)_2CHOH \rightarrow (CH_3)_2CO + 2H^+ + 2e^- \ (\times 3)$

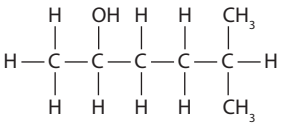
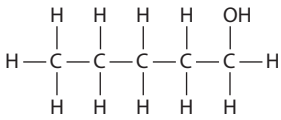
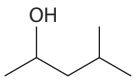
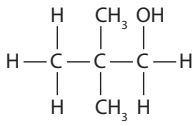
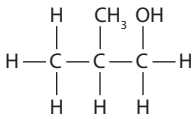
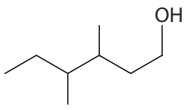
$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$

$3(CH_3)_2CHOH + Cr_2O_7^{2-} + 8H^+ \rightarrow 3(CH_3)_2CO + 2Cr^{3+} + 7H_2O$

25

no reaction ketones cannot be oxidised further using an oxidising agent		no reaction ketones cannot be oxidised further using an oxidising agent
a	**b**	**c**
no reaction carboxylic acids cannot be oxidised further using an oxidising agent		
d	**e**	**f**

26

		
a	**b**	**c**
		
d	**e**	**f**

27 **a** propan-1-ol

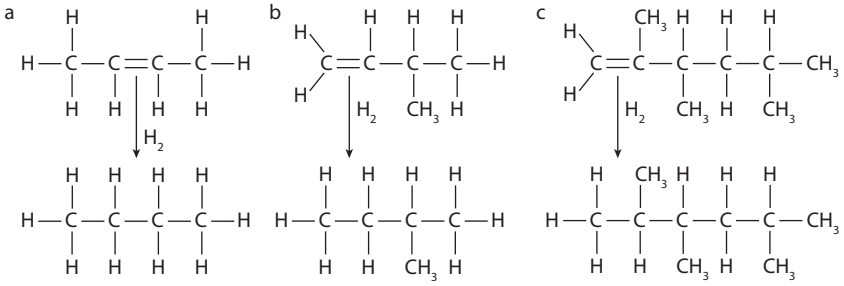
b 2-methylpentan-1-ol

c pentan-3-ol

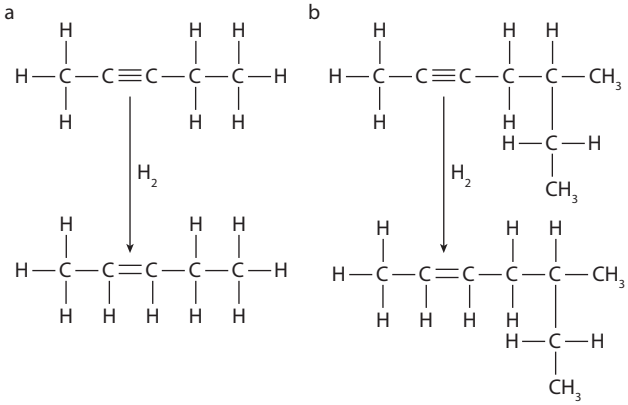
d 3-methylbutan-1-ol

Chemistry for the IB Diploma – Owen © Cambridge University Press & Assessment 2023

28 H_2 adds across the C═C converting it to C—C.



29 Addition of 1 mol H_2 converts the triple bond to a double bond.



30 a C_8H_{16}; $C_8H_{12} + 2H_2 \rightarrow C_8H_{16}$

b C_7H_{16}; $C_7H_{12} + 2H_2 \rightarrow C_7H_{16}$

c $C_{11}H_{22}$; $C_{11}H_{16} + 3H_2 \rightarrow C_{11}H_{22}$

31 a The maximum number of H atoms for 10 C atoms is given by $10 \times 2 + 2 = 22$

Every 2H fewer than this indicates a double bond equivalent. So the maximum number of C═C is given by:

$$\frac{22-18}{2} = 2$$

b The maximum number of H atoms for 15 C atoms is $15 \times 2 + 2 = 32$

The maximum number of C═C is given by:

$$\frac{32-22}{2} = 5$$

c The maximum number of H atoms for 37 C atoms is $37 \times 2 + 2 = 76$

The maximum number of C═C is given by:

$$\frac{76-60}{2} = 8$$

32 a decreases by 2;

The difference in the number of H atoms is 18 – 14 = 4.

We need 2H to decrease the degree of unsaturation by 1 since 2H are needed to convert C═C to C—C. Therefore divide the difference in the number of H atoms by 2.

Chemistry for the IB Diploma – Owen © Cambridge University Press & Assessment 2023

b decreases by 4;

$38 - 30 = 8$

$\frac{8}{2} = 4$

c decreases by 5;

$60 - 50 = 10$

$\frac{10}{2} = 5$

33 a $Fe^{2+}(aq) + 2e^- \rightleftharpoons Fe(s)$ –0.45 V

$Ni^{2+}(aq) + 2e^- \rightleftharpoons Ni(s)$ –0.26V

Reverse the more negative one (the one higher up in the table) then add values:

$-0.26 + 0.45 = 0.19$ V

The one that had the more negative $E^{\ominus}$ value in the table (higher up the table) is the negative electrode/anode, therefore the Fe electrode is negative and the Ni electrode is positive. The reaction at the Fe electrode is: $Fe(s) \rightarrow Fe^{2+}(aq) + 2e^-$ This is oxidation, so this is the anode. The reaction at the nickel electrode is $Ni^{2+}(aq) + 2e^- \rightarrow Ni(s)$ – reduction, therefore this is the cathode.

Oxidation occurs at the negative electrode. Electrons are produced at the negative electrode: $Fe(s) \rightarrow Fe^{2+}(aq) + 2e^-$ and they flow around the external circuit to the positive (nickel) electrode. Therefore the direction of electron flow in the external circuit is from the iron half-cell to the nickel half-cell.

Negative charge always flows in the same continuous way around the circuit, so if electrons are flowing from iron to nickel in the external circuit, the negative ions must flow through the salt bridge from the nickel half-cell to the iron half-cell.

Overall equation: $Ni^{2+}(aq) + Fe(s) \rightarrow Ni(s) + Fe^{2+}(aq)$

Always write the overall equation with a single direction arrow.

b $I_2(s) + 2e^- \rightleftharpoons 2I^-(aq)$ +0.54 V

$Cl_2(g) + 2e^- \rightleftharpoons 2Cl^-(aq)$ +1.36 V

Reverse the more negative one (the one higher up in the table: I_2/I^-) then add values:

$1.36 - 0.54 = +0.82$ V

the I_2/I^- half cell has the more negative $E^{\ominus}$ value and therefore the (platinum) electrode in this half-cell is the negative electrode – electrons are produced here:

$2I^-(aq) \rightarrow I_2(s) + 2e^-$

Oxidation occurs, therefore this is the anode.

The platinum electrode in the Cl_2/Cl^- half-cell is the positive electrode. The reaction is:

$Cl_2(g) + 2e^- \rightarrow 2Cl^-(aq)$

This is reduction, therefore the cathode.

Direction of electron flow in the external circuit is from the iodine half-cell (negative electrode) to the chlorine half-cell (positive electrode).

Negative ions flow through the salt bridge from the chlorine half-cell to the iodine half-cell

$Cl_2(g) + 2I^-(aq) \rightarrow 2Cl^-(aq) + I_2(s)$

c $Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s)$ –0.76 V

$Ag^+(aq) + e^- \rightleftharpoons Ag(s)$ +0.80V

Reverse the more negative one (the one higher up in the table: Zn^{2+}/Zn) then add values:

$0.76 + 0.80 = +1.56$ V

Zn electrode negative/anode and Ag electrode positive/cathode.

Direction of electron flow in the external circuit from the zinc half-cell to the silver half-cell.

Negative ions flow through salt bridge from the silver half-cell to the zinc half-cell

$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$

$Ag^+(aq) + e^- \rightarrow Ag(s) \times 2$

The Ag^+/Ag half-equation must be multiplied by 2 to balance the electrons.

$Zn(s) + 2Ag^+(aq) \rightarrow Zn^{2+}(aq) + 2Ag(s)$

Chemistry for the IB Diploma – Owen © Cambridge University Press & Assessment 2023

d 1.36 − 0.77 = +0.59 V

The (platinum electrode) in the Fe^{3+}/Fe^{2+} half-cell is the negative electrode (this reaction was higher up the table). Oxidation occurs here, so it is the anode:

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

Electrons are produced here and they flow around the external circuit from here. Therefore direction of electron flow in the external circuit is from the iron half-cell to the chromium half-cell

Negative ions flow through the salt bridge from the chromium half-cell to the iron half-cell.

$6Fe^{2+}(aq) + Cr_2O_7^{2-}(aq) + 14H^+(aq) \rightarrow$

$6Fe^{3+}(aq) + 2Cr^{3+}(aq) + 7H_2O(l)$

e 1.51 − 1.36 = +0.15 V

The (platinum) electrode in the chlorine/chloride half-cell is the negative/anode and the (platinum) electrode in the manganese/manganate(VII) half-cell is the positive electrode/cathode.

Direction of electron flow in the external circuit is from the chlorine half-cell to the manganese half-cell.

Negative ions flow through the salt bridge from the manganese half-cell to the chlorine half-cell.

$MnO_4^-(aq) + 16H^+(aq) + 10Cl^-(aq) \rightarrow$
$2Mn^{2+}(aq) + 8H_2O(l) + 5Cl_2(g)$

f 0.80 − 0.34 = +0.46 V

Cu electrode negative/anode and Ag electrode positive/cathode

Direction of electron flow through external circuit from copper half-cell to silver half-cell.

Negative ions flow through salt bridge from silver half-cell to copper half-cell.

$2Ag^+(aq) + Cu(s) \rightarrow Ag(s) + Cu^{2+}(aq)$

34 a cell potential is negative (−2.37 − 0.34 = −2.71 V) and, therefore, not spontaneous

b cell potential is positive (0.8 − 0.77 = 0.03 V), therefore, spontaneous; Ag^+ is the oxidising agent and Fe^{2+} is the reducing agent

c cell potential is positive (1.36 − 1.07 = 0.29 V), therefore, spontaneous; $Cr_2O_7^{2-}$ is the oxidising agent and Br^- is the reducing agent

d cell potential negative (1.36 − 2.87 = −1.51 V), therefore, not spontaneous

e cell potential negative (0.77 − 1.51 = −0.74 V), therefore, not spontaneous

35 a i Po^{2+} most positive $E^{\ominus}$ value, therefore most favourable reduction reaction – has a greater tendency to gain electrons/take them from another species to oxidise it.

ii Np; most negative $E^{\ominus}$ value, therefore the reverse reaction (oxidation) is most favourable for Np – Np has a greater tendency to donate electrons. Note: it is Np and not Np^{3+} that is the oxidising agent.

b i true; Eu^{2+} is a stronger reducing agent than In (more negative $E^{\ominus}$ value) therefore it can reduce the oxidised form (In^{3+}) to In. The cell potential is positive for $3Eu^{2+}(aq) + In^{3+}(aq) \rightarrow 3Eu^{3+}(aq) + In(s)$ $E^{\ominus}_{cell} = +0.09V$

ii true; Sm^{3+} is a stronger oxidising agent (more positive $E^{\ominus}$) than Np^{3+}.

$3Sm^{3+}(aq) + Np(s) \rightarrow 3Sm^{2+}(aq) + Np^{3+}(aq)$

$E^{\ominus}_{cell} = (-1.15 + 1.86) = 0.71\,V$

$E^{\ominus}_{cell}$ positive, therefore spontaneous.

iii false; Po is a weaker reducing agent (less negative $E^{\ominus}$) than Sm^{2+}, therefore cannot reduce Sm^{3+}. $2Sm^{3+}(aq) + Po(s) \rightarrow 2Sm^{2+}(aq) + Po^{2+}(aq)$

$E^{\ominus}_{cell} = (-1.15 - 0.65) = -1.80$ V. $E^{\ominus}_{cell}$ negative, therefore not spontaneous.

Chemistry for the IB Diploma – Owen © Cambridge University Press & Assessment 2023

iv true; To decide which is the better reducing agent, we must look at the oxidation reactions, because reducing agents are oxidised in reactions:
$Np^{3+} \rightarrow Np^{4+} + e^-$ $E_{ox} = -0.15V$
is more favourable (more positive potential for oxidation) than
$Po \rightarrow Po^{2+} + 2e^-$ $E_{ox} = -0.65V$

v false; U^{3+}/U has a less negative $E^{\ominus}$ value, than Np^{3+}/Np, therefore U has a lower tendency to donate electrons (reverse reaction has a less positive potential) than Np.
$U(s) \rightarrow U^{3+}(aq) + 3e^-$ $E_{ox} = +1.79$ V
is less favourable (less positive potential for oxidation) than
$Np(s) \rightarrow Np^{3+}(aq) + 3e^-$ $E_{ox} = +1.86V$

vi true; For the reduction of Po^{2+} to Po we have to look at Np^{4+}/Np^{3+} (because if we are looking at Np^{3+} acting as a reducing agent, we have to look at a reaction in which it gets oxidised) the $E^{\ominus}$ value is more negative than that for Po^{2+}/Po, therefore Np^{3+} is a stronger reducing agent than Po and will reduce Po^{2+} to Po.

$2Np^{3+}(aq) + Po^{2+}(aq) \rightarrow 2Np^{4+}(aq) + Po(s)$

$E^{\ominus}_{cell} = (-0.15 + 0.65) = +0.50$ V.
$E^{\ominus}_{cell}$ positive, therefore spontaneous.

For the oxidation of Eu^{2+} to Eu^{3+}, Np^{3+} has to act as an oxidising agent and we must look at a reaction in which it gets reduced: Np^{3+}/Np. Np^{3+} is a weaker oxidising agent (less positive $E^{\ominus}$) than Eu^{3+}, therefore cannot oxidise Eu^{2+}: $Np^{3+}(aq) + 3Eu^{2+}(aq) \rightarrow Np(s) + 3Eu^{3+}(aq)$
$E^{\ominus}_{cell} = (-1.86 + 0.43) = -1.43$ V.
$E^{\ominus}_{cell}$ negative, therefore not spontaneous.

vii true; Sm^{2+} is a stronger reducing agent (more negative $E^{\ominus}$) than U^{3+} (looking at the U^{4+}/U^{3+} reaction) but a weaker reducing agent (less negative $E^{\ominus}$) than U (looking at the U^{3+}/U reaction).
$Sm^{2+}(aq) + U^{4+}(aq) \rightarrow Sm^{3+}(aq) + U^{3+}(aq)$ $E^{\ominus}_{cell} = (+1.15 - 0.61) = +0.54$ V. $E^{\ominus}_{cell}$ positive, therefore spontaneous.

$3Sm^{2+}(aq) + U^{3+}(aq) \rightarrow 3Sm^{3+}(aq) + U(s)$

$E^{\ominus}_{cell} = (+1.15 - 1.79) = -0.64$ V.
$E^{\ominus}_{cell}$ negative, therefore not spontaneous.

Sm^{2+} will therefore reduce U^{4+} to U^{3+}, but the reduction will stop there.

c i not spontaneous; Cell potential is negative (–0.09 V)

ii spontaneous; Cell potential is positive (+1.08 V)

iii not spontaneous (both oxidation reactions)

36 a $E^{\ominus}_{cell} = 0.76 - 0.26 = 0.50$ V

$\Delta G^{\ominus} = -nFE^{\ominus}_{cell}$

Half equations are:

$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$ and
$Ni^{2+}(aq) + 2e^- \rightarrow Ni(s)$

Therefore $2e^-$ transferred and $n = 2$.

$\Delta G^{\ominus} = -2 \times 96500 \times 0.50 = -96\,500$ J mol^{-1}

Divide by 1000 to convert to kJ

$\Delta G^{\ominus} = -96.5$ kJ mol^{-1}

$\Delta G^{\ominus}$ negative, therefore the reaction is spontaneous

b $E^{\ominus}_{cell} = -0.13 - 0.34 = -0.47$ V

$$\Delta G^{\ominus} = \frac{-(2 \times 96500 \times -0.47)}{1000} = +91 \text{ kJ mol}^{-1}$$

$\Delta G^{\ominus}$ is positive, therefore the reaction is not spontaneous

c $E^{\ominus}_{cell} = 1.36 - 0.54 = 0.82$ V

The half-equations are:

$6I^- \rightarrow 3I_2 + 6e^-$

$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$

6 electrons are transferred, therefore $n = 6$.

$$\Delta G^{\ominus} = \frac{-(6 \times 96500 \times 0.82)}{1000} = -470 \text{ kJ mol}^{-1}$$

$\Delta G^{\ominus}$ negative, therefore the reaction is spontaneous

d $E^{\ominus}_{cell} = 1.07 - 0.54 = 0.53$ V

$$\Delta G^{\ominus} = \frac{-(2 \times 96500 \times 0.53)}{1000} = -100 \text{ kJ mol}^{-1}$$

$\Delta G^{\ominus}$ negative, therefore the reaction is spontaneous

e $E^{\ominus}_{cell} = 1.07 - 0.77 = 0.30$ V

$$\Delta G^{\ominus} = \frac{-(1 \times 96500 \times 0.30)}{1000} = -29 \text{ kJ mol}^{-1}$$

$\Delta G^{\ominus}$ negative, therefore the reaction is spontaneous

Chemistry for the IB Diploma – Owen © Cambridge University Press & Assessment 2023

f $E^{\ominus}_{cell} = 1.07 - 0.77 = 0.30$ V

$$\Delta G^{\ominus} = \frac{-(2 \times 96500 \times 0.30)}{1000} = -58 \text{ kJ mol}^{-1}$$

This is the same reaction as in part **e**. Writing the equation in a different way does not affect the cell potential but it does affect the value of $\Delta G^{\ominus}$ – this is double the value in part **e** because twice as many electrons have been transferred.

$\Delta G^{\ominus}$ negative, therefore the reaction is spontaneous

g $E^{\ominus}_{cell} = 1.51 - 0.77 = 0.74$ V

$$\Delta G^{\ominus} = \frac{-(5 \times 96500 \times 0.74)}{1000} = -360 \text{ kJ mol}^{-1}$$

$\Delta G^{\ominus}$ negative, therefore the reaction is spontaneous

h $E^{\ominus}_{cell} = 1.51 - 1.36 = 0.15$ V

$$\Delta G^{\ominus} = \frac{-(10 \times 96500 \times 0.15)}{1000} = -140 \text{ kJ mol}^{-1}$$

$\Delta G^{\ominus}$ negative, therefore the reaction is spontaneous

37 i

	ANODE	CATHODE
a	iodine	hydrogen
b	oxygen	hydrogen
c	chlorine	hydrogen
d	oxygen	hydrogen
e	oxygen	silver
f	oxygen	hydrogen
g	oxygen	copper
h	oxygen	hydrogen

ii a anode: $2I^-(aq) \rightarrow I_2(aq)/(s) + 2e^-$

cathode:
$2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$

b anode:
$2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$

cathode:
$2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$

c anode: $2Cl^-(aq) \rightarrow Cl_2(aq)/(g) + 2e^-$

cathode:
$2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$

d anode:
$2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$

cathode:
$2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$

e anode:
$2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$

cathode: $Ag^+(aq) + e^- \rightarrow Ag(s)$

f anode:
$2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$

cathode:
$2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$

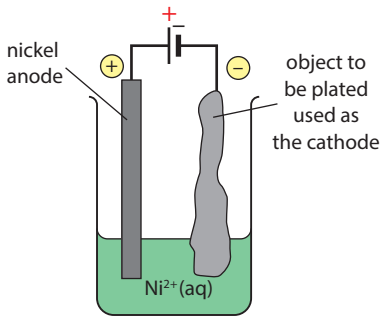
g anode:
$2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$

cathode: $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$

h anode:
$2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$

cathode:
$2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$

38 a



b any soluble nickel salt, e.g. nickel(II) nitrate

c anode: $Ni(s) \rightarrow Ni^{2+}(aq) + 2e^-$

cathode: $Ni^{2+}(aq) + 2e^- \rightarrow Ni(s)$

Exam-style questions

1 A

2 C

3 C

4 D

5 C

6 D

7 B

8 D

Chemistry for the IB Diploma – Owen © Cambridge University Press & Assessment 2023

9 A

10 C

11 B

12 C

13 B

14 A

15 A

16 D

17 a Oxidation is the loss of electrons. **[1]**

b i +7

O has an oxidation state of −2

4 × −2 = −8 so the oxidation state of Mn must be +7 to cancel out all but one of the negative charges and leave an overall charge of −1. **[1]**

ii Fe^{2+} because it has been oxidised/it reduces MnO_4^-. **[1]**

iii Separate into its two half-equations:

$MnO_4^-(aq) + H^+(aq) \rightarrow Mn^{2+}(aq) + H_2O(l)$

$Fe^{2+}(aq) \rightarrow Fe^{3+}(aq)$

Each is balanced separately by following the procedure given in Section 20.2, or they can be looked up in the IB Chemistry data booklet!

$MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O(l)$

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

The number of electrons is balanced by multiplying the bottom equation by 5 and then the equations can be recombined:

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

for coefficient of Fe^{2+} five times that of MnO_4^- **[1]**

for everything else correct **[1]**

iv amount in mol of $KMnO_4$

$$= \frac{21.50}{1000} \times 5.00 \times 10^{-3}$$

$$= 1.08 \times 10^{-4}\,\text{mol}$$ **[1]**

v The amount of Fe^{2+} is 5 times the amount of MnO_4^- from the balanced equation for the reaction, so the amount of Fe^{2+} = 5 × 1.08 × 10^{-4} = 5.38 × 10^{-4} mol **[1]**

vi amount of Fe^{2+} in 250.0 cm^3 solution = 10 × 5.38 × 10^{-4} = 5.38 × 10^{-3} mol;

This is the amount of iron in five iron tablets.

The mass of iron in 5 iron tablets is 5.38 × 10^{-3} × 55.85 = 3.00 × 10^{-1} g

So, the mass of iron in 1 iron tablet is

$$\frac{3.00 \times 10^{-1}}{5} = 6.00 \times 10^{-2}\,\text{g};$$ **[2]**

vii 1 mg is 1 × 10^{-3} g so 6.00 × 10^{-2} g is 60.0 mg of iron per tablet, so the manufacturer's claim seems to be wrong; however, some solution would be lost in the filtering process/ *description of another systematic error*, and so, it could be correct; **[2]**

18 a i $Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$ **[1]**

ii Copper is less reactive than lead, as it is unable to displace lead from solution. **[1]**

iii magnesium (most reactive) > zinc > lead > copper (least reactive)

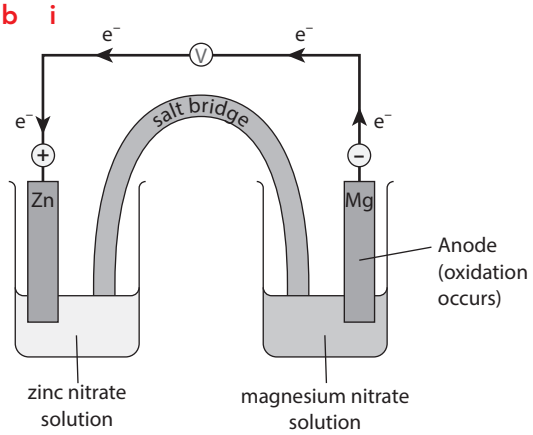
Zinc can displace copper and lead from solution but cannot displace magnesium, so zinc must be more reactive than lead and copper but less reactive than magnesium. **[1]**

iv Magnesium is the strongest reducing agent as it will reduce Zn^{2+} to Zn, Pb^{2+} to Pb and Cu^{2+} to Cu;

Zinc is able to reduce only lead and copper ions, lead can reduce only copper ions and copper cannot reduce the ions of any of these metals; **[2]**

Chemistry for the IB Diploma – Owen © Cambridge University Press & Assessment 2023

b i



for diagram **[1]**

for anode correctly labelled **[1]**

for correct direction of electron flow **[1]**

ii $Zn^{2+}(aq) + 2e^- \rightarrow Zn(s)$;

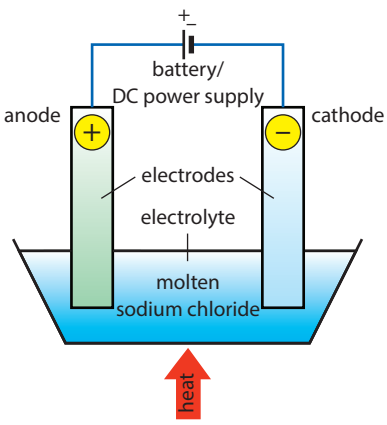
The zinc ion gains electrons, so this is reduction; **[2]**

19 a i Sodium is the reducing agent – it loses electrons/donates electrons to the water. **[1]**

ii $2H_2O(l) + 2e^- \rightarrow 2OH^-(aq) + H_2(g)$ **[1]**

b i In the solid, the ions are held tightly in the lattice but when molten the ions are free to move. **[1]**

ii



for diagram **[1]**

for at least three labels **[1]**

iii anode: $2Cl^- \rightarrow Cl_2 + 2e^-$;

cathode: $Na^+ + e^- \rightarrow Na$; **[2]**

[1] max if electrodes not stated

c MnO_2 is the oxidising agent – it takes electrons from Cl^- ions/gains electrons. **[1]**

d $Cl_2(aq) + 2Br^-(aq) \rightarrow 2Cl^-(aq) + Br_2(l)/(aq)$ **[1]**

e i The oxidation state of chlorine changes from 0 in Cl_2 to +1 in NaOCl and −1 in NaCl. **[1]**

ii The oxidation state of Cl is +1, therefore, the name is sodium chlorate(I). **[1]**

f Amount in mol of thiosulfate is

$$\frac{22.40}{1000} \times 0.0200 = 4.48 \times 10^{-4}\,\text{mol}$$

Amount of iodine is

$$\frac{4.48 \times 10^{-4}}{2} = 2.24 \times 10^{-4}\,\text{mol};$$

This is the same as the amount of ClO^- in 15.00 cm^3 of diluted bleach.

Amount of ClO^- in 250.0 cm^3 of diluted bleach is

$$\frac{250.0}{15.00} \times 2.24 \times 10^{-4} = 3.73 \times 10^{-3}\,\text{mol};$$

This amount of ClO^- was present in 10.00 cm^3 of the original bleach, so the concentration of OCl^- is

$$\frac{3.73 \times 10^{-3}}{\left(\frac{10.00}{1000}\right)} = 0.373\ \text{mol dm}^{-3};$$

which is the same as the concentration of NaOCl. **[3]**

20 a Magnesium and zinc both react with hydrochloric or sulfuric acid to form the metal salt and a metal salt is also formed here;

Magnesium and zinc do not form NO/H_2O/magnesium and zinc from hydrogen;

All the reactions are redox reactions/the metal is oxidized in each reaction;

any 2 points **[2]**

b Separate into half-equations:

$Ag(s) \rightarrow Ag^+(aq)$

$HNO_3(aq) \rightarrow NO_3^-(aq) + H_2O(l) + NO(g)$

Chemistry for the IB Diploma – Owen © Cambridge University Press & Assessment 2023

Balance the half-equations:

$Ag(s) \rightarrow Ag^+(aq) + e^-$

$2HNO_3(aq) + 2H^+(aq) + 3e^- \rightarrow NO_3^-(aq) + 2H_2O(l) + NO(g)$

Combine the two half-equations, balancing the electrons:

$2HNO_3(aq) + 2H^+(aq) + 3Ag(s) \rightarrow NO_3^-(aq) + 2H_2O(l) + NO(g) + 3Ag^+(aq)$

The original equation contained HNO_3 rather than H^+ and $AgNO_3$ rather than Ag^+. If we realise that the H^+ must come from the HNO_3, then that also gives us an extra 2 NO_3^- on the other side, which then allows us to write 3 $AgNO_3$ on the other side:

$4HNO_3(aq) + 3Ag(s) \rightarrow 3AgNO_3(aq) + 2H_2O(l) + NO(g)$

correct ratio between HNO_3 and Ag **[1]**

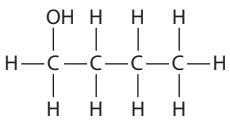
equation completely balanced **[1]**

accept ionic equation

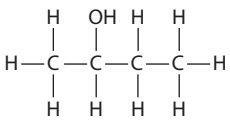
The oxidising agent is HNO_3/nitric acid because it gets reduced to NO; **[3]**

c The oxidation state of nitrogen is +2, therefore, the name is nitrogen(II) oxide. **[1]**

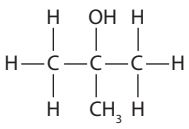
21 a



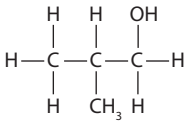
butan-1-ol



butan-2-ol



2-methylpropan-2-ol



2-methylpropan-1-ol

all four correct structures and names **[2]**

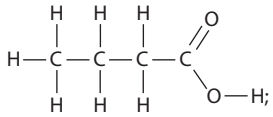
two/three correct **[1]**

four correct names only **[1]**

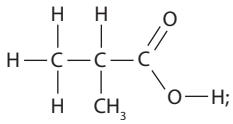
four correct structures only **[1]**

b i Only primary alcohols can be oxidised to a carboxylic acid. **[2]**

butan-1-ol becomes:



2-methylpropan-1-ol becomes:



ii The apparatus must be set up for distillation rather than reflux;

The aldehyde boils off as soon as it is formed and before it can be oxidised further – aldehydes have lower boiling points than the equivalent alcohols because there is no hydrogen bonding between molecules; **[2]**

c i $CH_3CH(OH)CH_2CH_3 \rightarrow CH_3COCH_2CH_3 + 2H^+ + 2e^-$

for correct structural formulas **[1]**

for balanced half-equation **[1]**

ii $Cr_2O_7^{2-}(aq) + 8H^+(aq) + 3CH_3CH(OH)CH_2CH_3 \rightarrow 3CH_3COCH_2CH_3 + 2Cr^{3+}(aq) + 7H_2O(l)$

for coefficient of alcohol 3× that of dichromate(VI) **[1]**

for correct equation **[1]**

d $CH_3OH(aq) + H_2O(l) \rightarrow CO_2(g) + 6H^+(aq) + 6e^-$

for all species on correct sides **[1]**

for correctly balanced equation **[1]**

e Advantages: fuel cell cars can be re-fuelled more quickly/higher energy-to-mass ratio so the vehicles can travel further for the same mass of fuel cell + fuel compared to a battery;

Disadvantages: lithium-ion batteries are more efficient than fuel cells/hydrogen is an explosive gas, so storage can be difficult, and there is a risk of explosions/battery-powered vehicles are cheaper to run than fuel cell vehicles; **[2]**

Chemistry for the IB Diploma – Owen © Cambridge University Press & Assessment 2023

f i Reaction 1 because electrons (negatively charged) are produced in this reaction. **[1]**

ii The reverse of reaction 1 – electrons must be added from the negative pole of the power supply to reverse the reaction:

$M + H_2O + e^- \rightarrow MH + OH^-$;

Electrons are gained, therefore, this is reduction; **[2]**

22 a

	$CaC_2(s)$	$2H_2O(l)$	$C_2H_2(g)$	$Ca(OH)_2(aq)$
oxidation states	+2 −1	+1 −2	−1 +1	+2 −2 +1

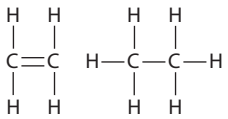
[1] for working out oxidation states;

No change in oxidation states; therefore, not a redox reaction; **[2]**

b i $C_2H_2 + H_2 \rightarrow C_2H_4$

$C_2H_2 + 2H_2 \rightarrow C_2H_6$ **[1]**

ii **[1]**



iii The reaction is reduction because it involves the addition of hydrogen.

The oxidation state of C decreases from −1 to −2 when C_2H_4 is formed and to −3 when C_2H_6 is formed. **[1]**

iv Equal volumes of the two organic products are formed, therefore we can assume that 50 cm^3 of ethyne reacts to form ethene and 50 cm^3 reacts to form ethane (this is probably easier than thinking about it as 100 cm^3 ethyne reacting to form ethene and then half the ethene reacting further) 50 cm^3 C_2H_2 reacts with 50 cm^3 of hydrogen to form 50 cm^3 ethene:

C_2H_2	+ H_2	→ C_2H_4
50 cm^3	50 cm^3	50 cm^3

Therefore, the total volume goes down by 50 cm^3

50 cm^3 C_2H_2 reacts with 100 cm^3 of hydrogen to form 50 cm^3 ethane:

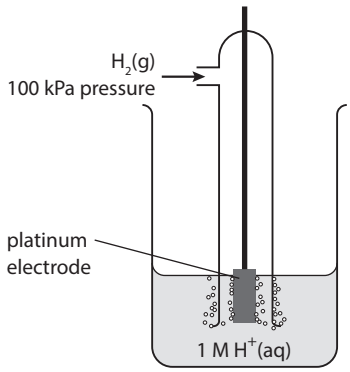
C_2H_2	+ $2H_2$	→ C_2H_6
50 cm^3	100 cm^3	50cm^3

Therefore, the total volume goes down by 100 cm^3;

Initial total volume is 500 + 100 = 600 cm^3

This decreases by 150 cm^3 when the ethyne reacts; therefore, the total volume of gas left at the end of the experiment is 600 − 150 = 450 cm^3; **[2]**

23 a



for H_2 100 kPa **[1]**

for platinum electrode **[1]**

for 1 mol dm^{-3} $H^+(aq)$ **[1]**

b i X is the salt bridge; the salt bridge completes the circuit / it allows ions to flow into or out of the half-cells to balance out the charges in the half-cells; **[2]**

ii

$Fe^{3+}(aq) + e^- \rightleftharpoons Fe^{2+}(aq)$	+0.77
$Mn^{2+}(aq) + 2e^- \rightleftharpoons Mn(s)$	−1.18

reverse the more negative value:

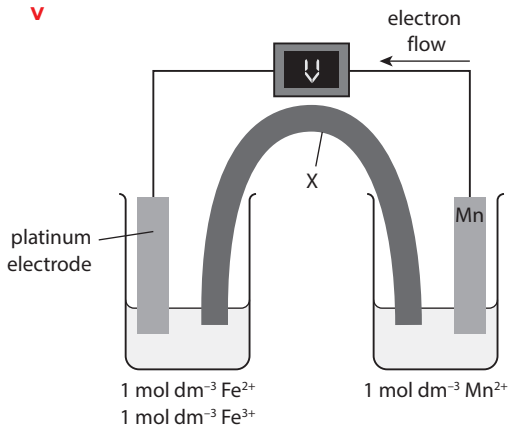
$E^{\ominus}_{cell} = 1.18 + 0.77 = 1.95$ V **[1]**

iii $2Fe^{3+}(aq) + Mn(s) \rightarrow 2Fe^{2+}(aq) + Mn^{2+}(aq)$ **[1]**

iv The Mn electrode is the anode because this is where oxidation occurs – Mn is oxidised. **[1]**

Chemistry for the IB Diploma – Owen © Cambridge University Press & Assessment 2023

v



[1]

vi Faraday's constant = 96 500 C mol^{-1}

Two electrons are transferred, therefore, $n = 2$;

$\Delta G^{\ominus} = -nFE^{\ominus}$

$\Delta G^{\ominus} = -2 \times 96500 \times 1.95$

$\Delta G^{\ominus} = -376\,000$ J mol^{-1} or -376 kJ mol^{-1} **[2]**

24 a Pb^{2+} is the stronger oxidising agent because it has the more positive (less negative) standard electrode potential; therefore a greater tendency to remove electrons/gain electrons/reduction is more favourable; **[2]**

b Will be spontaneous because: $Cr_2O_7^{2-}$ is a stronger oxidising agent/has more positive standard electrode potential than I_2 (therefore, it will oxidize I^- to I_2)/the overall cell potential is positive/+ 0.82 V. **[1]**

c

$I_2(s) + 2e^- \rightleftharpoons 2I^-(aq)$	+0.54
$Fe^{3+}(aq) + e^- \rightleftharpoons Fe^{2+}(aq)$	+0.77

The first half-equation is reversed because I^- is added to Fe^{3+}

The iodide ion reduces iron(III) to iron(II) because the cell potential is positive/+0.23V;

$2I^-(aq) + 2Fe^{3+}(aq) \rightarrow I_2(s) + 2Fe^{2+}(aq)$ or

$2KI(aq) + 2FeCl_3(aq) \rightarrow I_2(s) + 2FeCl_2(aq) + 2KCl(aq)$; **[1]**

d Faraday's constant = 96 500 C mol^{-1}

−0.15	$Cu^+(aq) \rightleftharpoons Cu^{2+}(aq) + e^-$
+0.52	$Cu^+(aq) + e^- \rightleftharpoons Cu(s)$

$E^{\ominus}_{cell} = -0.15 + 0.52 = 0.37$ V;

One electron is transferred; therefore, $n = 1$

$\Delta G^{\ominus} = -nFE^{\ominus}$

$\Delta G^{\ominus} = -1 \times 96\,500 \times 0.37 =$
$-36\,000$ J mol^{-1} or -36 kJ mol^{-1};

Since $\Delta G^{\ominus}$ is negative, the reaction is spontaneous; **[2]**

e

$Mn^{2+}(aq) + 2e^- \rightleftharpoons Mn(s)$	−1.18
$HCOOH(aq) + 2H^+(aq) + 2e^- \rightleftharpoons HCHO(aq) + H_2O(l)$	+0.06

Based on the standard electrode potentials, the reaction

$HCOOH(aq) + 2H^+(aq) + Mn(s) \rightleftharpoons HCHO(aq) + H_2O(l) + Mn^{2+}(aq)$

has $E^{\ominus}_{cell} = 1.18 + 0.06 = 1.24$. Since the value is positive, the reaction is spontaneous;

However, this does not tell us whether this reaction will actually occur when manganese is added to methanoic acid, as other reactions could occur instead, such as methanoic acid reacting with manganese to form a salt and hydrogen gas;

Accept: the activation energy could be very high so that the reaction occurs very slowly **[2]**

25 a The product is hydrogen gas from the reduction of water to hydrogen:

$2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$;

It is more difficult to reduce sodium ions to sodium (more negative standard electrode potential) than it is to reduce water to hydrogen/the standard electrode potential for $Na^+(aq) + e^- \rightarrow Na(s)$ is more negative than that for the reduction of water; **[2]**

b i Anode/positive electrode is silver;

Cathode/negative electrode is the piece of nickel;

Chemistry for the IB Diploma – Owen © Cambridge University Press & Assessment 2023

Electrolyte is a solution of silver ions/ $Ag^+(aq)$/named soluble silver salt e.g., silver nitrate.

All three points **[2]**

Any 2 points **[1]**

ii $Ag(s) \rightarrow Ag^+(aq) + e^-$ **[1]**

c i Oxygen gas is formed at the anode;

$2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$; **[2]**

ii The electrolyte will become less blue as the copper(II) ions, which are responsible for the blue colour, are removed at the cathode; The electrolyte will become more acidic / the pH decreases as $H^+(aq)$ ions are produced at the anode/the electrolyte will become sulfuric acid because copper ions are removed from the solution and replaced by $H^+(aq)$ ions; **[2]**

iii The blue colour of the solution remains constant because there is no change in the concentration of copper(II) ions/a $Cu^{2+}(aq)$ ion is produced at the anode for each one discharged at the cathode;

The pH of the solution remains constant because there is no change in the concentration of $H^+(aq)$ ions; **[2]**

Chemistry for the IB Diploma – Owen © Cambridge University Press & Assessment 2023

Chapter 21

Test your understanding

1 **b** Br; 35 electrons – an odd number

c OH; 8 + 1 = 9 electrons – an odd number

e C_2H_5; 2 × 6 + 5 = 17 electrons – an odd number

g ClO_2; 17 + 2 × 8 = 33 electrons – an odd number

h NO_2; 7 + 2 × 8 = 23 electrons – an odd number

j O_2^-; 2 × 8 + 1 = 17 electrons – an odd number

l CH_4^+; 6 + 4 × 1 – 1 = 9 electrons – an odd number

n O_2^+; 2 × 8 – 1 = 15 electrons – an odd number

o O_3^-; 3 × 8 + 1 = 25 electrons – an odd number

NH_3, OH^-, CO, SO_2, CH_3^+, NH_4^+

all have an even number of electrons and are therefore not radicals.

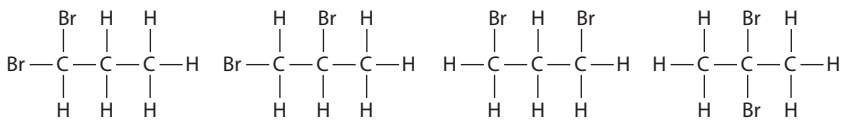
2 $C_2H_6 + Cl_2 \rightarrow C_2H_5Cl + HCl$

3 **a** 3; 1-chlorohexane, 2-chlorohexane, 3-chlorohexane are the possible products. 4-chlorohexane is the same as 3-chlorohexane.

b 2; Cl can either go on one of the methyl (CH_3) groups or on the central C

c 1

4



5 initiation: $Cl_2 \xrightarrow{UV} 2Cl\bullet$

propagation: $Cl\bullet + C_2H_6 \rightarrow \bullet CH_2CH_3 + HCl$

propagation:
$\bullet CH_2CH_3 + Cl_2 \rightarrow CH_3CH_2Cl + Cl\bullet$

termination: $Cl\bullet + Cl\bullet \rightarrow Cl_2$

termination: $Cl\bullet + \bullet CH_2CH_3 \rightarrow CH_3CH_2Cl$

termination: $\bullet CH_2CH_3 + \bullet CH_2CH_3 \rightarrow C_4H_{10}$

6 $Cl\bullet + CHCl_2CH_3 \rightarrow \bullet CCl_2CH_3 + HCl$

$\bullet CCl_2CH_3 + Cl_2 \rightarrow CCl_3CH_3 + Cl\bullet$

Exam-style questions

1 C

2 C

3 A

Chemistry for the IB Diploma – Owen © Cambridge University Press & Assessment 2023

4 B

5 D

6 **a** $CH_4 + Cl_2 \rightarrow CH_3Cl + HCl$ **[1]**

b **i** radical substitution **[1]**

ii initiation: $Cl_2 \rightarrow 2Cl\bullet$

propagation: $Cl\bullet + CH_4 \rightarrow HCl + \bullet CH_3$

propagation:
$\bullet CH_3 + Cl_2 \rightarrow CH_3Cl + Cl\bullet$

termination: $Cl\bullet + Cl\bullet \rightarrow Cl_2$

termination: $Cl\bullet + \bullet CH_3 \rightarrow CH_3Cl$

termination: $\bullet CH_3 + \bullet CH_3 \rightarrow C_2H_6$ **[3]**

[1] for the initiation step;

[1] for both propagation steps;

[1] for any termination step;

[2] max if steps not labeled.

iii *Homolytic fission* occurs in the initiation step. In the presence of ultraviolet light, the Cl—Cl bond breaks so that one electron goes to each Cl atom:

$Cl_2 \rightarrow 2Cl\bullet$;

A *radical* is an atom/group of atoms /molecular entity with an unpaired electron. In this case, Cl• is a radical. A $CH_3\bullet$ radical is also formed in this reaction;

A *termination step* occurs when two free radicals react together – this ends a chain reaction. There are three possible termination steps in this mechanism:

termination: $Cl\bullet + Cl\bullet \rightarrow Cl_2$

termination: $Cl\bullet + \bullet CH_3 \rightarrow CH_3Cl$

termination: $\bullet CH_3 + \bullet CH_3 \rightarrow C_2H_6$

[1] for any one termination step and an explanation

7 **a** $C\ \frac{51.9}{12.01} = 4.32$ mol

$H\ \frac{9.8}{1.01} = 9.70$ mol

$Cl\ \frac{38.3}{35.45} = 1.08$ mol;

Divide by smallest to find ratio:

$C\ \frac{4.32}{1.08} = 4$

$H\ \frac{9.70}{1.08} = 8.98$

$Cl\ \frac{1.08}{1.08} = 1$

empirical formula is C_4H_9Cl; **[2]**

b $P = 100$ kPa

$V = 0.178\ dm^3$ (a consistent set of units with pressure in kPa)

$R = 8.31\ J\ K^{-1}\ mol^{-1}$

$T = 200.00 + 273.15 = 473.15$ K

$$n = \frac{PV}{RT} = \frac{100 \times 0.178}{8.31 \times 473.15} = 4.53 \times 10^{-3}\ \text{mol};$$

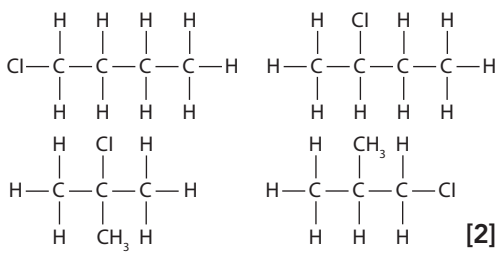
molar mass:

$$M = \frac{0.420}{4.53 \times 10^{-3}} = 92.72\ \text{g mol}^{-1}$$

If all figures are carried through on the calculator 92.8 is obtained.

Empirical formula mass is 92.58, therefore, the molecular formula is C_4H_9Cl; **[2]**

c



[2]

All 4 correct = [2]

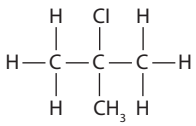
2/3 correct = [1]

0/1 correct = [0]

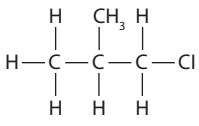
d $C_4H_{10} + Cl_2 \xrightarrow{UV} C_4H_9Cl + HCl$ **[1]**

Chemistry for the IB Diploma – Owen © Cambridge University Press & Assessment 2023

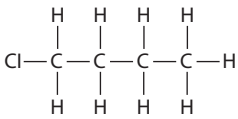
e 2-chloro-2-methylpropane and 1-chloro-2-methylpropane can be distinguished from the other two compounds because they have different numbers of signals in the NMR spectrum;



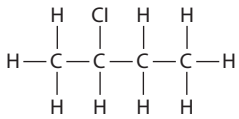
1 signal in the NMR spectrum due to only 1 chemical environment for H



3 signals in the NMR spectrum due to 3 different chemical environments for H

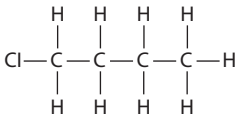


4 signals in the NMR spectrum due to 4 different chemical environments for H

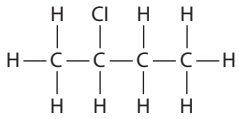


4 signals in the NMR spectrum due to 4 different chemical environments for H

1-chloropropane and 2-chloropropane can be distinguished from each other because they have different ratios of areas under the signals/the integration trace is different;



ratio of areas under signals: 2:2:2:3



ratio of areas under signals: 3:1:2:3

any 3 points that allow all 4 compounds to be distinguished from each other – all 4 compounds must be mentioned. **[3]**

8 initiation: $Cl_2 \rightarrow 2Cl\bullet$

propagation:
$Cl\bullet + C_6H_5CH_3 \rightarrow HCl + C_6H_5CH_2\bullet$

propagation:
$C_6H_5CH_2\bullet + Cl_2 \rightarrow C_6H_5CH_2Cl + Cl\bullet$

termination: $Cl\bullet + Cl\bullet \rightarrow Cl_2$

termination: $Cl\bullet + C_6H_5CH_2\bullet \rightarrow C_6H_5CH_2Cl$

termination:
$C_6H_5CH_2\bullet + C_6H_5CH_2\bullet \rightarrow C_6H_5CH_2CH_2C_6H_5$ **[3]**

[1] for the initiation step;

[1] for both propagation steps;

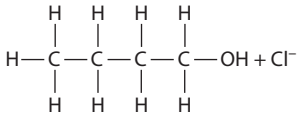
[1] for any termination step;

Chemistry for the IB Diploma – Owen © Cambridge University Press & Assessment 2023

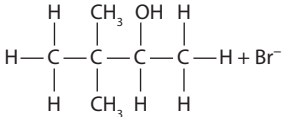
Chapter 22

Test your understanding

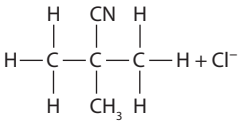
1 a



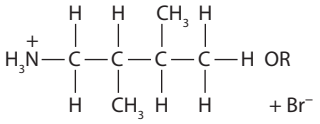
b



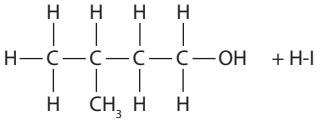
c



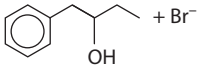
d



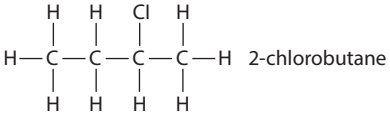
e



f

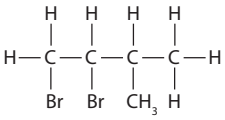


2 a



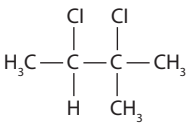
2-chlorobutane

b



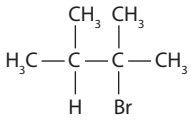
1,2-dibromo-3-methylbutane

c



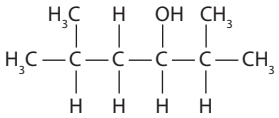
2,3-dichloro-2-methylbutane

d



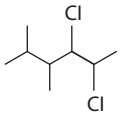
2-bromo-2,3-dimethylbutane

e



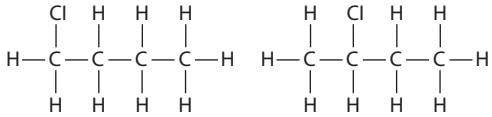
2,5-dimethylhexan-3-ol

f

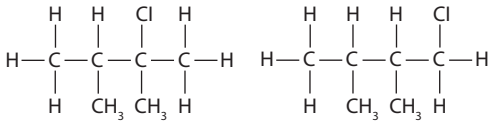


2,3-dichloro-4,5-dimethylhexane

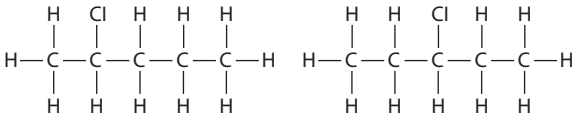
3 a The H—Cl can add either way around across the C═C.



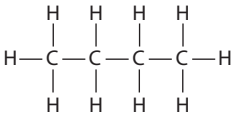
b



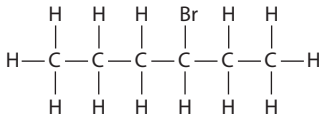
c



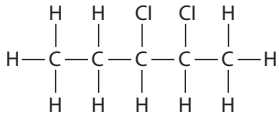
4 a



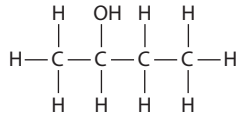
b



c

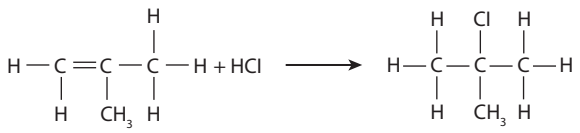


d

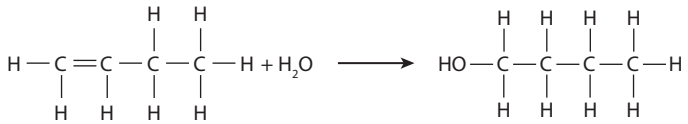


Chemistry for the IB Diploma – Owen © Cambridge University Press & Assessment 2023

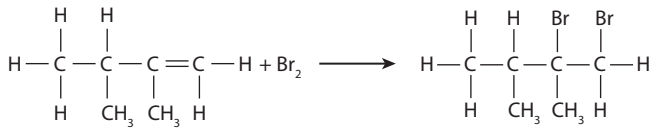
5 **a**



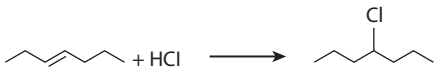
b



c



d



6 Brønsted–Lowry definition: An acid is a proton (H^+) donor and a base is a proton (H^+) acceptor.

Lewis definition: An acid is an electron-pair acceptor and a base is an electron-pair donor.

7 coordination bond

8 H_2O = base; BF_3 = acid; HCO_3^- = base;

H^+ = acid; NH_3 = base; CO = base; Fe^{2+} = acid; CN^- = base

The bases all possess at least one lone pair and the acids all have space in the outer shell to accept a pair of electrons. i.e. they do not have full outer shells,

9 Lewis acid because it accepts a pair of electrons from Cl^-.

$AlCl_3$ only has 6 electrons in its outer shell and so has space to accept a pair from the Cl^-.

10

	Lewis acid	Lewis base
a	H^+; accepts a pair of electrons from an O of the COO^- group	CH_3COO^-
b	H^+; accepts a pair of electrons from the OH^-	OH^-
c	$(CH_3)_3C^+$; accepts a pair of electrons from the Br^-	Br^-
d	$Cu^{2+}/[Cu(H_2O)_6]^{2+}$; accepts a pair of electrons from the NH_3	NH_3

11 **a** (3+) + 6 × 0 = 3+; Water is a neutral ligand

b (2+) + (4 × 1−) = 2−; Cl has a 1- charge, i.e. Cl^-

c 0 + 4 × 0 = 0; CO is a neutral ligand

d (3+) + (6 × 1−) = 3−; CN has a 1 – charge, i.e. CN^-

e (3+) + (1−) + 5 × 0 = 2+; Water is a neutral ligand but OH has a 1 – charge, i.e. OH^-.

12 **a** Lewis definition only – no H^+ is transferred

b both Lewis and Brønsted–Lowry definitions – NH_3 is a Brønsted-Lowry base because it accepts a proton (H^+). It bonds to the H^+ by donation of a pair of electrons to form a coordination bond, therefore also a Lewis base.

c Lewis definition only – no H^+ is transferred

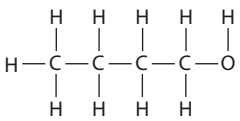
Chemistry for the IB Diploma – Owen © Cambridge University Press & Assessment 2023

d both Lewis and Brønsted–Lowry definitions – H^+ is donated by $[Fe(H_2O)_6]^{2+}$, so it is a Brønsted-Lowry acid. The proton is accepted by the H_2O, the Brønsted-Lowry base. The H_2O bonds to the proton by donating a pair of electrons, so the H_2O is the Lewis base. In the Lewis classification, H^+ is the Lewis acid.

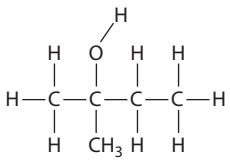
13 a

i	S_N2; primary halogenoalkane
ii	S_N1; tertiary halogenoalkane
iii	S_N2; primary halogenoalkane
iv	S_N1 and S_N2; secondary halogenoalkane
v	S_N1 and S_N2; secondary halogenoalkane
vi	S_N1; tertiary halogenoalkane

b i

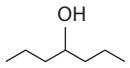


ii



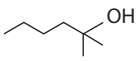
iii $(CH_3)_3CCH_2OH$

iv



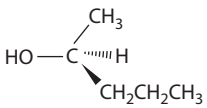
v $(CH_3)_2CHCH(OH)CH_3$

vi



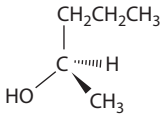
14 $(CH_3)_3CI$; The C—I bond is the longest and, therefore weakest. The RDS involves breaking the C—Halogen bond and this will happen most readily with I. I^- is a better leaving group.

15 a

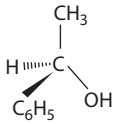


Inversion occurs at the central C – like an umbrella turning inside out. Draw the product as a mirror image of the molecule you started with (then just replace the halogen atom with an OH group).

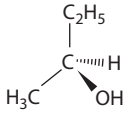
b



c



d



16 In each case, double the % of the less common isomer to get the percentage of molecules that reacted via an S_N1 mechanism. If we call the enantiomers formed P (p%) and Q (q%), where p > q. The q% of Q can only be formed by the S_N1 mechanism, but an S_N1 mechanism produces a racemic mixture, so, at the same time q% of P was also produced by the S_N1 mechanism – total % by S_N1 is 2q%.

a 100% S_N2; because S_N2 is stereospecific. (0% of the other isomer, therefore $2 \times 0 = 0\%$ via S_N1)

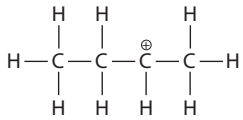
b 100% S_N1; because S_N1 produces a racemic mixture – both enantiomers equally likely to be formed. ($2 \times 50\% = 100\%$)

c 50% S_N1 and 50% S_N2; ($2 \times 25\% = 50\%$ by S_N1 mechanism)

d 40% S_N1 and 60% S_N2; ($2 \times 20\% = 40\%$ by S_N1 mechanism)

e 80% S_N1 and 20% S_N2; ($2 \times 40\% = 80\%$ by S_N1 mechanism)

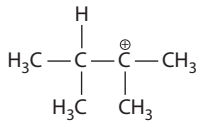
17 a



secondary

– 2 other C atoms attached to the C with the positive charge.

b

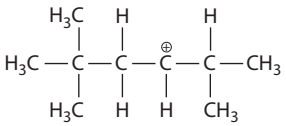


tertiary

– 3 other C atoms attached to the C with the positive charge.

Chemistry for the IB Diploma – Owen © Cambridge University Press & Assessment 2023

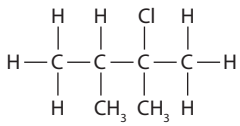
c



secondary

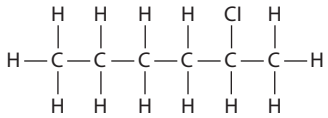
–2 other C atoms attached to the C with the positive charge.

18 a



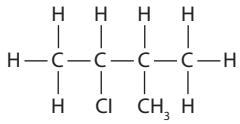
2 H on the C at the right-hand side of the C═C, but none on the left-hand side, therefore the H becomes bonded to the right-hand C.

b



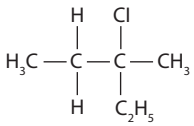
2 H on the C at the right-hand side of C═C, but only 1 on the left-hand side, therefore the H becomes bonded to the right-hand C.

c



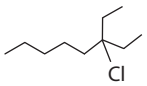
2 H on the C at the left-hand side of C═C, but only 1 on the right-hand side, therefore the H becomes bonded to the left-hand C.

d



1 H on the C at the left-hand side of C═C, but 0 on the right-hand side, therefore the H becomes bonded to the left-hand C.

e



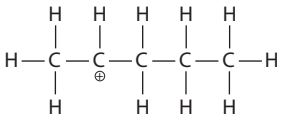
1 H on the C at the left-hand side of C═C, but 0 on the right-hand side, therefore the H becomes bonded to the left-hand C.

19 a butan-2-ol; Using Markovnikov's rule – there were 2H on carbon 1 and 1 on carbon 2, therefore the H bonds to C1 and the OH to C2.

b 3-methylbutan-2-ol – there were 2H on carbon 1 and 1 on carbon 2, therefore the H bonds to C1 and the OH to C2.

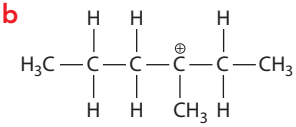
c 2,4-dimethylpentan-2-ol – there were 0H on carbon 2 and 1H on carbon 3, therefore the H bonds to C3 and the OH to C2.

20 a



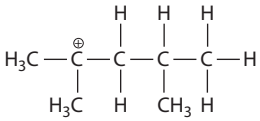
secondary

b



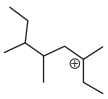
tertiary

c



tertiary

d

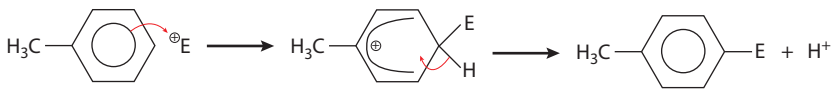


tertiary

21 I and III because they have the same number (1 in I and 0 in III) of H atoms each side of the C═C

Chemistry for the IB Diploma – Owen © Cambridge University Press & Assessment 2023

22



E^+ is a Lewis acid because it accepts a pair of electrons;

$C_6H_5CH_3$ is a Lewis base because it donates a pair of electrons;

23 $CH_3C_6H_5 + HNO_3 \rightarrow CH_3C_6H_4NO_2 + H_2O$

Exam-style questions

1 B

2 D

3 D

4 A

5 B

6 C

7 A

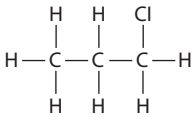
8 B

9 B

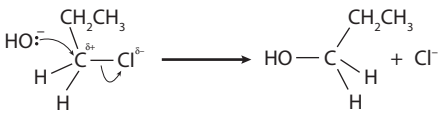
10 D

11 a **[1]**

b A nucleophile is a molecule or negatively charged ion that has a lone pair of electrons – it is attracted to a more positively charged region in a molecule and donates a lone pair of electrons to an electrophile to form a covalent bond. **[1]**

c  **[1]**

d hydroxyl (group) **[1]**

e  **[3]**

for each correct curly arrow **[1]**

for all other aspects of the equation correct **[1]**

f The leaving group is Cl^- and the electrophile is 1-chloropropane. **[1]**

g Heterolytic fission; the C—Cl bond breaks such that both electrons from the C—Cl bond go back to the chlorine atom; **[2]**

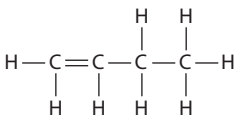
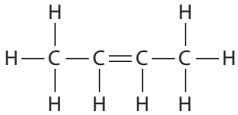
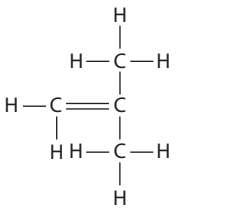
h i **[1]**

ii The reaction of the hydroxide ion will be faster because it has a negative charge and will, therefore, be more strongly attracted to the δ+ C atom in 1-chloropropane, than water, which is a neutral molecule **[1]**

12 a An addition reaction is one in which a molecule is added to another molecule, but a substitution reaction involves one atom or group being replaced by another atom or group;

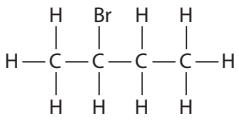
Just one product/no other molecules/ions are formed in an addition reaction, but the organic product and another product are formed in a substitution reaction; **[2]**

b

	but-1-ene
	but-2-ene
	2-methylpropene

[1] for each row correct **[3]**

c but-2-ene **[1]**

d  **[1]**

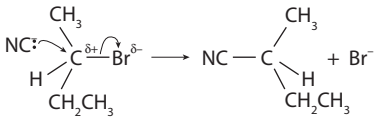
Chemistry for the IB Diploma – Owen © Cambridge University Press & Assessment 2023

e Electrophiles are attracted to regions of higher electron density and the C═C double bond in an alkene contains four electrons, so is a region of high electron density;

A coordination bond is formed – a pair of electrons is donated from the nucleophile (the alkene) to the electrophile **[2]**

f i It is a nucleophile – it has a negative charge and a lone pair of electrons, and so, will be attracted to more positively charged regions in a molecule and be able to donate a pair of electrons to form a covalent bond. **[1]**

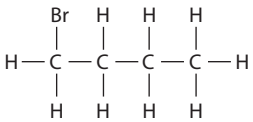
ii **[3]**



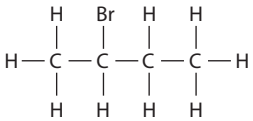
for each correct curly arrow **[1]**

for all other aspects of the equation correct **[1]**

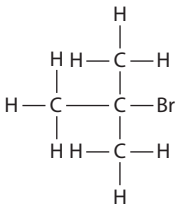
13 a **[4]**



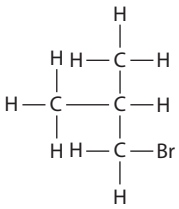
primary



secondary



tertiary



primary

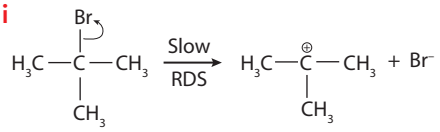
[1] for each structure with classification **[1]**

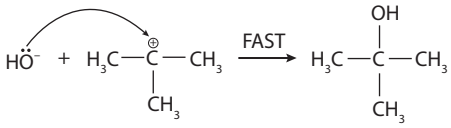
all four structures but no classification = [3]

three structures but no classification = [2]

two structures but no classification = [1]

b i **[3]**





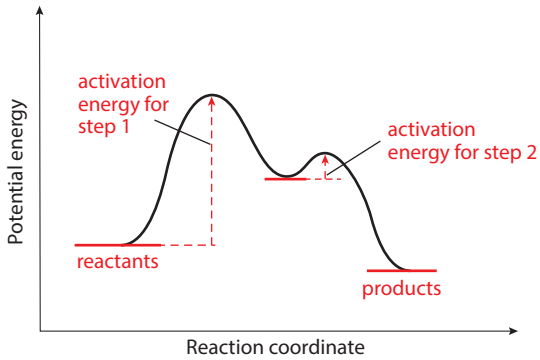
for correct carbocation **[1]**

for each step correct **[1]**

ii Lewis base – it donates a pair of electrons to the carbocation, and a Lewis base is an electron–pair donor. **[1]**

iii The first step has a molecularity of one – only one species/molecule reacts, and the second step has a molecularity of two – two species/ions react. **[1]**

iv **[2]**



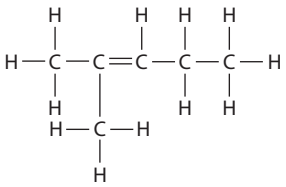
for two peaks **[1]**

for activation energy for second step lower **[1]**

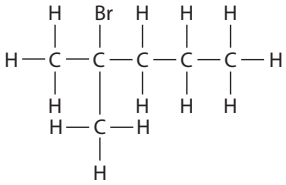
Chemistry for the IB Diploma – Owen © Cambridge University Press & Assessment 2023

v This will have no effect on the rate of the reaction as the hydroxide ion/sodium hydroxide is not in the rate equation; hydroxide only gets involved in the mechanism in a fast step after the rate-determining step; **[2]**

14 a **[1]**

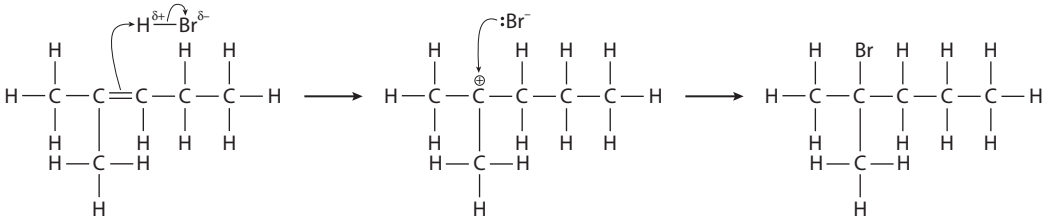


b **[1]**



c electrophilic addition **[1]**

d **[3]**



for step 1 **[1]**

for correct carbocation **[1]**

for curly arrow from Br^- to carbocation **[1]**

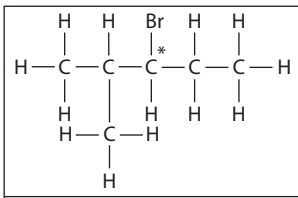
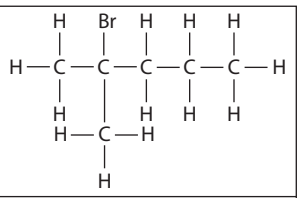
e In the mechanism for the formation of X, a tertiary carbocation is formed, but, in the formation of Z, a secondary carbocation is formed. The tertiary carbocation is more stable than the secondary carbocation;

The tertiary carbocation is more stable because there are more electron-releasing alkyl groups next to the positively charged carbon; **[2]**

f Br^- is a Lewis base because it donates a pair of electrons, and the carbocation is a Lewis acid because it accepts a pair of electrons; **[1]**

g This statement is correct *AND*

the structures of **Z** and **X** are

	
Z	**X**

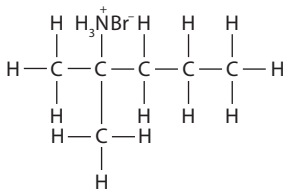
Z is chiral because it contains an asymmetric C atom/chirality centre/chiral centre – a C atom with four different groups attached (marked with *) but X does not contain a C atom with four different groups attached; **[2]**

[1] for structure of Z and stating that the statement is correct, [1] for explanation in terms of chirality centre.

Chemistry for the IB Diploma – Owen © Cambridge University Press & Assessment 2023

h i X is a tertiary halogenoalkane, therefore, the mechanism will be S_N1. **[1]**

ii



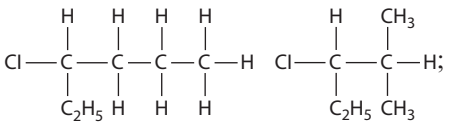
[1]

iii $CH_3CH_2CH_2C(CH_3)_2NH_3^+Br^- + NaOH \rightarrow CH_3CH_2CH_2C(CH_3)_2NH_2 + H_2O + NaBr$;

Sodium hydroxide is a base – it removes/accepts a proton from the $CH_3CH_2CH_2C(CH_3)_2NH_3^+$ion; **[2]**

15 a This is correct because the C_3H_7 group could be joined to the C by the end C or the middle one;

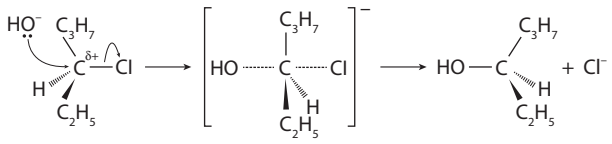
The two possible structural isomers are



[2]

b i The reaction is bimolecular/the molecularity is two, therefore, there are two species involved in the only step in the reaction. **[1]**

ii



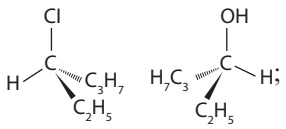
[3]

for curly arrow from lone pair of OH^- to C and from C—Cl bond to Cl **[1]**

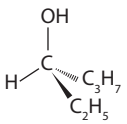
for structure of transition state **[1]**

for products **[1]**

iii There is inversion of configuration/the products are mirror images (ignoring the difference between Cl and OH); **[2]**



c Instead of just one enantiomer being formed, both enantiomers of the product will be formed in equal amounts / the same amount of

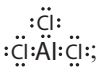


will also be formed / a racemic mixture will be formed;

There is a planar intermediate carbocation formed in the S_N1 mechanism and OH^- can attack this from either side (with equal probability) to form (equal amounts of the) two enantiomers of the product; **[2]**

16 a 2-chloro-2-methylpropane **[1]**

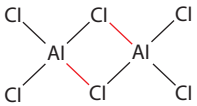
b



Chemistry for the IB Diploma – Owen © Cambridge University Press & Assessment 2023

Al only has six electrons in its outer shell/main energy level and atoms usually have eight electrons in the outer shell/main energy level; **[2]**

c

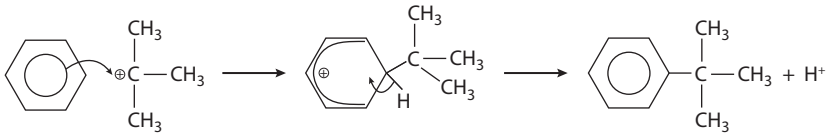


The bonds shown in red are coordination bonds. **[1]**

d There is no proton/H^+ transfer, so it is not a Brønsted–Lowry acid–base reaction, but it is a Lewis acid–base reaction because an electron pair is donated from the Cl of $(CH_3)_3CCl$ to $AlCl_3$;

$AlCl_3$ is the Lewis acid because it accepts a pair of electrons; **[2]**

e **[3]**



[1] for curly arrow from benzene π ring to C+ of $(CH_3)_3C^+$;

[1] for structure of intermediate;

[1] curly arrow from C—H bond to ring AND products;

f Benzene acts as a Lewis base because it donates a pair of electrons and Lewis bases are electron-pair donors. **[1]**

g The π system of delocalised electrons imparts extra stability to benzene (resonance energy);

Substitution reactions preserve the π system of delocalised electrons and the extra stability, but addition reactions would involve the loss of the delocalised system since single C—C bonds would be formed; **[2]**

Chemistry for the IB Diploma – Owen © Cambridge University Press & Assessment 2023