# Answers

## AS Level

## Topic 1: Chemical formulae and moles

### *Answers to in-text questions*

#### *Questions 1.1*

1 1.5 mol
2 0.75 mol
3 0.667 mol

#### *Questions 1.2*

1 16.7 mol
2 $8.3 \times 10^{-3}$ mol

#### *Questions 1.3*

1 9
2 11
3 12
4 24
5 22

#### *Questions 1.4*

1 a) 151.9
b) 162.1
c) 60.0
d) 132.1
e) 388.8
2 a) 0.5 mol
b) 2.5 mol
c) 0.6 mol
d) 2.0 mol
e) 0.38 mol
3 a) 180.6 g
b) 44.46 g

#### *Questions 1.5*

1 $M_r$ = 277.9 moles of oxygen = 11
2 $M_r$ = 474.3 moles of oxygen = 20

#### *Questions 1.6*

1 $Cu_2S$
2 $C_3H_8$
3 $CaFe_2O_4$

#### *Questions 1.7*

1 a) $2H_2 + O_2 \rightarrow 2H_2O$
b) $I_2 + 3Cl_2 \rightarrow 2ICl_3$
c) $NaOH + Al(OH)_3 \rightarrow NaAlO_2 + 2H_2O$
d) $2H_2S + SO_2 \rightarrow 3S + 2H_2O$
e) $4NH_3 + 3O_2 \rightarrow 2N_2 + 6H_2O$
2 a) $MgCO_3 \rightarrow MgO + CO_2$
b) $Pb(s) + 2AgNO_3(aq) \rightarrow Pb(NO_3)_2(aq) + 2Ag(s)$
c) $Na_2O(s) + H_2O(l) \rightarrow 2NaOH(aq)$
d) $2FeCl_2 + Cl_2 \rightarrow 2FeCl_3$
e) $Fe_2(SO_4)_3 + 6NaOH \rightarrow 2Fe(OH)_3 + 3Na_2SO_4$

#### *Questions 1.8*

1 17.0 g
2 60.7 g
3 51.1%

#### *Questions 1.9*

1 1.2 $dm^3$
2 Volume of $SO_2$ = 50 $cm^3$; mass of sulfur = 0.20 g

#### *Questions 1.10*

1 a) 2.67 mol $dm^{-3}$
b) 0.025 mol $dm^{-3}$
c) 0.833 mol $dm^{-3}$
2 a) 0.75 mol
b) 0.044 mol
c) 0.010 mol

#### *Questions 1.11*

1 1.2 $dm^3$
2 12 $dm^3$
3 Volume of acid = 0.41 $dm^3$; volume of $H_2$ = 4.9 $dm^3$
4 0.64 g
5 1.27 mol $dm^{-3}$

### *Answers to end of topic questions*

1 a) Any two of $ZnCO_3$, $Zn(OH)_2$ and ZnO
b) i) To make sure no water of crystallisation remained
ii) Mass of zinc sulfate = mass of tube and salt after heating – mass of tube
= 76.34 – 74.25 = 2.09 g
Relative molecular mass of zinc sulfate ($ZnSO_4$) = 65.4 + 32.1 + (4 × 16.0) = 161.5
Amount in moles = 2.09 ÷ 161.5 = 0.01294
$= 1.29 \times 10^{-2}$
iii) Mass of water = mass of tube and hydrated salt – mass of tube and salt after heating
= 77.97 – 76.34 = 1.63 g
Molar mass of water ($H_2O$) = (2 × 1) + 16 = 18
Amount in moles = 1.63 ÷ 18 = 0.0905
$= 9.1 \times 10^{-2}$
iv) Value of $x = 9.1 \times 10^{-2} \div 1.29 \times 10^{-2} = 7.054$ which is 7 as a whole number

c) i) The number of moles required for 15 mg (0.015 g) of Zn = $0.015 \div 65.4 = 2.29 \times 10^{-4}$
Therefore $2.29 \times 10^{-4}$ moles of the crystal are required, which will have a mass of $2.29 \times 10^{-4} \times 219.4 = 0.0502655$, which is approximately 0.05 g or 50 mg

ii) Concentration = $2.29 \times 10^{-4} \div 0.005$ = $0.0458 = 4.85 \times 10^{-2}$ mol $dm^{-3}$

2 a) i) $Na_2CO_3 + 2HCl \rightarrow 2NaCl + H_2O + CO_2$

ii) Amount in moles of HCl is $35.8 \div 1000 \times 0.100 = 3.58 \times 10^{-3}$

iii) Amount in moles of $Na_2CO_3$ in 25.0 $cm^3$ = $35.8 \div 2 \times 10^{-3} = 1.79 \times 10^{-3}$ mol

iv) Amount in moles of $Na_2CO_3$ in 250 $cm^3$ = $1.79 \times 10^{-3} \times 10 = 1.79 \times 10^{-2}$ mol

v) Mass of $Na_2CO_3 = 1.79 \times 10^{-2} \times ((23 \times 2) + 12 + (16 \times 3)) = 1.90$ g

b) Mass of water is $5.13 - 1.9 = 3.23$ g
Amount in moles of water = $3.23 \div 18 = 1.79 \times 10^{-1}$
Amount in moles of $Na_2CO_3 = 1.79 \times 10^{-2}$ so $x = 10$

3 a) $6 \times 10^{-3}$ (mol)

b) $NaOH + HCl \rightarrow NaCl + H_2O$

c) $6 \times 10^{-3}$ (mol)

d) $4 \times 10^{-3}$ (mol)

e) $4 \times 10^{-3}$ (mol)

f) $1 \times 10^{-3}$ (mol)

g) 170

h) 28(.0), X = Si (silicon)

## Topic 2: The structure of the atom

### Answers to in-text questions

### Questions 2.1

12.0 $dm^3$

### Questions 2.2

1 11 protons, 11 electrons, 12 neutrons
2 53 protons, 53 electrons, 74 neutrons
3 15 protons, 18 electrons, 16 neutrons
4 23 protons, 18 electrons, 28 neutrons

### Questions 2.3

a) Three orbitals
b) Seven orbitals

### Questions 2.4

1 N: $1s^2 2s^2 2p_x^1 2p_y^1 2p_z^1$
2 Ca: $1s^2 2s^2 2p_x^2 2p_y^2 2p_z^2 3s^2 3p_x^2 3p_y^2 3p_z^2 4s^2$
3 $Al^{3+}$: $1s^2 2s^2 2p_x^2 2p^2 2p_z^2$

### Question 2.5

*Y* is in Group 2 (large gap between the second and third ionisation energies).

### Answers to end of topic questions

1 a) i) The atomic radii get smaller across the period. The proton numbers increase from Na to Cl so the nuclear charge increases. As the electrons are all in the same shell they get more firmly attracted to the nucleus across the period.

ii) Argon is always a single atom.

b) i)

| Radius of cation/nm | | | Radius of anion/nm | | |
|---|---|---|---|---|---|
| $Na^+$ | $Mg^{2+}$ | $Al^{3+}$ | $P^{3-}$ | $S^{2-}$ | $Cl^-$ |
| 0.095 | 0.065 | 0.050 | 0.212 | 0.184 | 0.181 |

ii) The radii of the cations are smaller than their atoms since they have lost their outer shells, so have one fewer electron shell than the atoms.

iii) The radii of the anions are greater than their atoms because they have more electrons. These electrons not only repel each other, but also partially shield one another from the attractive force of the positive nucleus.

2 a)

| particle | relative mass | relative charge | location | total number in an atom of $^{197}Au$ |
|---|---|---|---|---|
| electron | 0.0005 | –1 | **shell(s)** | 79 |
| neutron | **1.(001)** | **0** | nucleus | **118** |

b) Metallic bonding

c) i) Isotopes are atoms of the same element with the same proton or atomic number and different numbers of neutrons/different mass numbers.

ii) Isotopes of the same element have the same number of electrons/electronic structure and therefore identical chemical properties.

d) i) (100 – 56.36 – 25.14) = 18.5(0)%

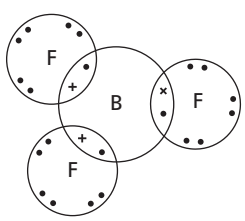
ii) $A_r = (63 \times 56.36/81.5) + (65 \times 25.14/81.5)$ = 63.62

## Topic 3: Chemical bonding in simple molecules

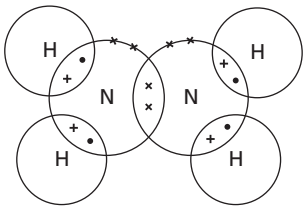
### Answers to in-text questions

### Questions 3.1

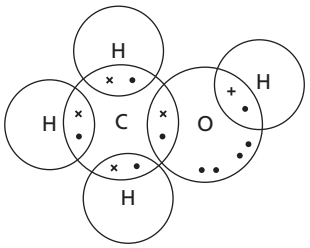
1



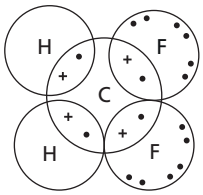
2




3

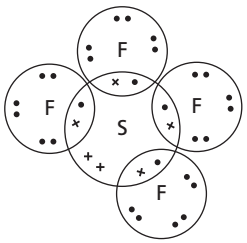



4




## Questions 3.2

1




2 a) 3
b) 4
c) 2

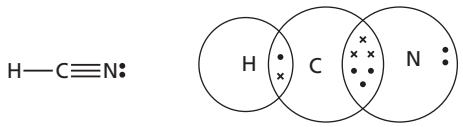
## Questions 3.3

1 SO, $SO_2$, $SO_3$

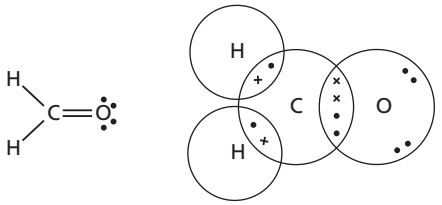
2 a) $CH_4$
b) $OF_2$
c) $BCl_3$
d) $NBr_3$
e) CO

## Questions 3.4

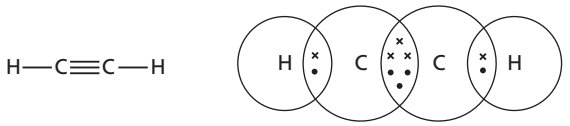
1




2

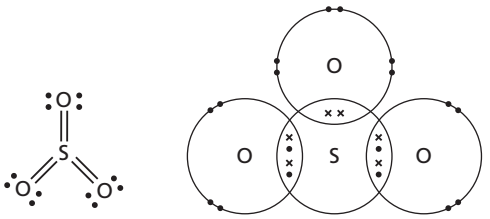



3

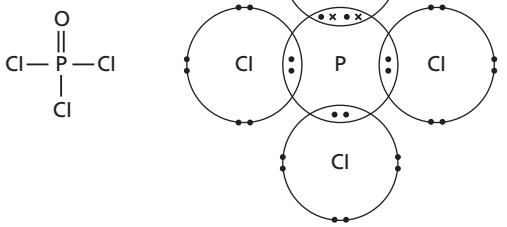



## Questions 3.5

1

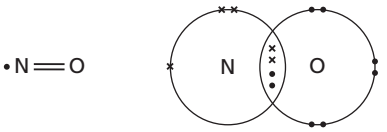



2

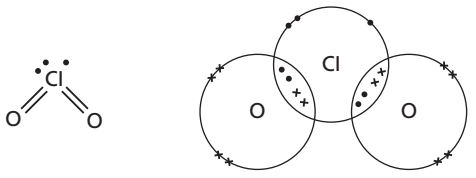



## Questions 3.6

1




2

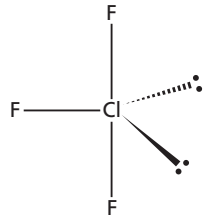



## Questions 3.7

1 $BeH_2$ is linear because the two shared pairs forming the Be—H bonds repel each other.

2 $ClF_3$ is planar – 'T-shaped' – because the three shared pairs and two lone pairs are in a trigonal bipyramid arrangement around the chlorine, with the lone pairs taking up equatorial positions, so

as to keep as far apart as possible (120°), leaving the three Cl—F bonds to take up the remaining equatorial position and the two axial positions.




3 $SF_6$ is octahedral because all six valence electrons on sulfur are used to form bond pairs with fluorine.

## Questions 3.8

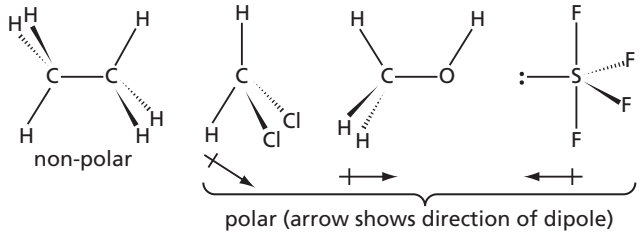
1 HCN will be linear: two bonding electron areas and no lone pairs around carbon.
2 $H_2CO$ will be triangular planar: three bonding electron areas and no lone pairs around carbon.
3 $C_2H_2$ will be linear: two bonding electron areas and no lone pairs around each carbon atom.

## Question 3.9

Electronegativity differences: Si—H = 0.3; P—C = 0.4 and S—Cl = 0.6.
S—Cl is the most polar.

## Questions 3.10

1 Compound **A** will have a larger dipole moment than compound **B**: the angle between the two C—Cl bonds is 60° in **A** but 120° in **B**, so the resulting component is larger.
2




## Questions 3.11

1 $ClO_3^-$; triangular pyramid (one lone pair)
2 $PO_3^{3-}$; triangular pyramid (one lone pair)
3 $PO_4^{3-}$; tetrahedral (no lone pairs)

## Questions 3.12

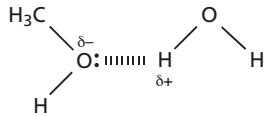
1 $CH_2$=CHCl: The carbon atoms are $sp^2$ hybridised; this contains σ bonds between the hydrogens and carbon, and a σ bond between carbon and chlorine; the carbons are joined by a σ bond and a π bond. Shape: planar
2 HN=NH: The nitrogens are $sp^2$ hybridised; this contains σ bonds between the hydrogens and nitrogen; the nitrogens are joined by a σ bond and a π bond, and the lone pair on each nitrogen is held in a $sp^2$ orbital. Shape: planar

## Questions 3.13

1 Boiling points: $ClCH_2CH_2Cl < BrCH_2CH_2Br < HOCH_2CH_2OH$. The first two have id–id forces between their molecules, which are stronger in the dibromide due to the greater number of electrons. The molecules of the diol are hydrogen bonded to each other, which is stronger than id–id.
2 The extra intermolecular force of hydrogen bonding in the alcohols makes up a large proportion of the intermolecular force in the lower molecular mass alcohols, but, as the chain length increases, so do the id–id forces. Eventually these become as strong as, or even stronger than, the hydrogen bonding, which will remain the same.

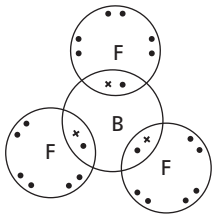
## Answers to end of topic questions

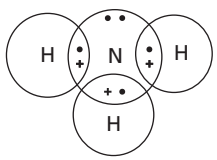
1 **a) i)** Two
**ii)** 103–105°
**b) i)** A
**ii)** C
**iii)** A
**iv)** B
**c) i)** Hydrogen bonds
**ii)**




**d)** Ethoxyethane does not form hydrogen bonds so if the hydrogen bonds in water are broken the energy required to do this cannot be regained.

2 **a)** The electronegativity of an atom is a measure of its ability to attract the electrons in a covalent bond to itself.
**b)** $^{\delta+}N–F^{\delta-}$ and $^{\delta-}N–Br^{\delta+}$
**c) i)** Octahedral
**ii)** In $BF_3$ the three bond pairs repel each other and need to get as far apart from each other as possible. A bond angle of 120° achieves this. In $NH_3$ the lone pair repels the bond pairs more than they do each other, so reducing the tetrahedral H—N—H bond angle from 109.5° to 107°.



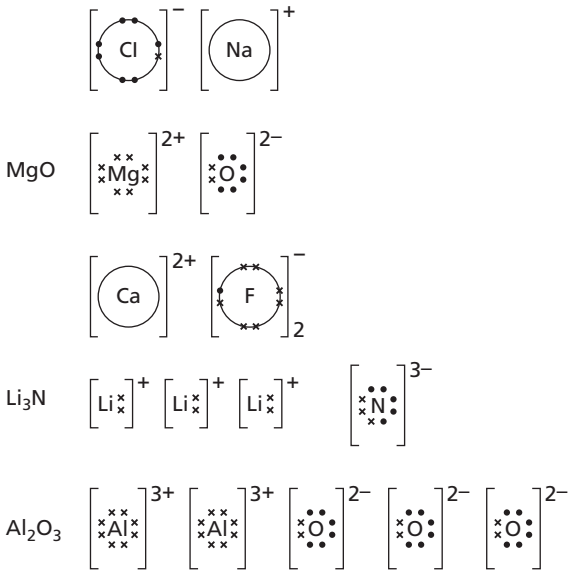




**iii)** As $BF_3$ is symmetrical the bond dipoles cancel each other.

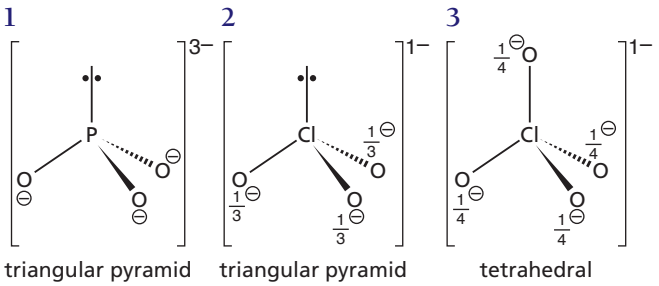
# Topic 4: Solids, liquids and gases

## *Answers to in-text questions*

### *Questions 4.1*




### *Questions 4.2*




### *Questions 4.3*

1 a) $FeF_2$
b) $Mg_2N_3$
c) $Cu_2O$
d) $Fe(OH)_3$
e) $Ca_3PO_4$
f) $(NH_4)_2SO_4$
g) $Cu(NO_3)_2$

2 a) Iron(II) sulfate
b) Barium sulfide
c) Magnesium hydrogen carbonate
d) Potassium nitrite

3 a) $Ag_2O$
b) Correct
c) $Pb(NO_3)_2$
d) $AlI_3$
e) Correct

### *Questions 4.4*

1 **C** is giant covalent: if ionic it would have conducted when molten; if simple covalent it would have a lower melting point.

2 **D** is giant ionic: conduction when molten is due to ions being able to move; not metallic because it does not conduct when solid.

3 **E** is simple covalent: low melting point due to weak intermolecular forces; no conduction as no ions present.

### *Questions 4.5*

a) $M_r = 2.88 \times 10^{11}$
b) $4.8 \times 10^{-13}$ g

### *Questions 4.6*

1 a) 76 K
b) 546 K

2 a) –75 °C
b) 227 °C

### *Questions 4.7*

1 0.12 mol
2 3.7 mol
3 0.028 mol

### *Questions 4.8*

1 $CO_2$ has larger molecules than does $N_2$, with 20 electrons per molecule rather than 14 in $N_2$, so there are greater id–id forces between the $CO_2$ molecules. As they are pushed together, they attract each other with sufficient force to cause the molecules to coalesce to a liquid. In $N_2$, on the other hand, the id–id forces are lower, and the translational energy each molecule possesses at 298 K, that causes them to bump apart on collision, is greater than the id–id force of attraction, no matter how close the molecules are compressed.

2 In decreasing order of ideality: $H_2 > CH_4 > Cl_2 > HCl > CH_3Br$
Explanation: $H_2$: weak id–id (only two electrons); no dipole.
$CH_4$: stronger id–id (10 electrons); no dipole.
$Cl_2$: stronger id–id (34 electrons); no dipole.
HCl: intermediate id–id (18 electrons); strong dipole.
$CH_3Br$: strong id–id (44 electrons); also has a dipole.

## Answers to end of topic questions

**1 a)**

| substance | type of bonding | type of lattice structure |
|---|---|---|
| copper | **metallic** | **giant metallic** |
| ice | **covalent and hydrogen bonding** | **simple molecular** |
| silicon(IV) oxide | **covalent** | **giant (macro) molecular** |
| iodine | **covalent and id–id** | **simple molecular** |
| sodium chloride | **ionic** | **giant ionic** |

**b) i)** Hydrogen bonding

**ii)** Diagram showing H-bond between O and H of different molecules with partial charges labelled and a lone pair of electrons on O of H-bond, in line with the H-bond.

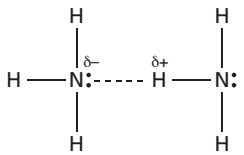
**c) i)** X = liquid; Z = solid; Y = liquid and solid

**ii)** The (kinetic) energy of the particles is reducing and their motion is slowing.

**iii)** As the liquid solidifies to form the copper lattice, more bonds are being formed. Bond formation is always exothermic. The heat given out by bond formation exactly cancels out the heat loss due to cooling. The equilibrium continues until all the copper has solidified.

**2 a)** The delocalised electrons in metallic lattices are able to move. A solid ionic lattice has no mobile ions but when it is molten the ions are able to move and can carry electric charge.

**b) i)**




**ii)** The water molecule has two lone pairs of electrons so can form two hydrogen bonds per molecule, whereas ammonia can only form one hydrogen bond per molecule. Hence it requires more energy (i.e. a higher temperature) to break the molecules apart.

**c)** $SiO_2$ is a giant covalent lattice so when it melts strong covalent bonds need to be broken. $SiCl_4$ is a simple molecular compound and the molecules are held together by weak van der Waals' (id–id) forces. These weak forces require only a small amount of (heat) energy to be broken, whereas the strong covalent bonds in $SiO_2$ need much more energy to break. Since the liquids contain uncharged molecules, they cannot conduct electricity.

# Topic 5: Energy changes in chemistry

## Answers to in-text questions

### Questions 5.1

**1 a)** Heat evolved = $(25 + 25) \times 4.18\ (24.1 - 17.5) = 1380\,J$

**b)** Amount = $25 \times \frac{1.0}{1000} = 0.025\,mol$

**c)** $\Delta H = \frac{1380}{0.025} = 55\,176 = 55\,kJ\,mol^{-1}$

**2** Heat evolved = $150 \times 4.18 \times 12.4 = 7775\,J$

Amount = $75 \times \frac{2}{1000} = 0.15\,mol$

$\Delta H = \frac{7775}{0.15} = 51832 = 52\,kJ\,mol^{-1}$

**3 a)** $Mg + 2HCl \rightarrow MgCl_2 + H_2$

**b)** HCl is in excess as all of the Mg dissolved.

Amount of Mg = $\frac{0.48}{24.3} = 0.0198\,mol$

Heat evolved = $200 \times 4.18 \times 1.2 = 1003\,J$

$\Delta H = \frac{1003}{0.0198} = 504\,000\,J = 50\,777\,J\,mol^{-1}$

### Questions 5.2

**1 a)** Experiment carried out at 1 bar (or 1 atm) pressure and at a specified temperature (often 298 K).

**b)** At different pressures and temperatures, the reactants and products have different internal energies and the enthalpy change of reaction will be different.

**2** Mass of hexanol burnt = 1.31 g

$M_r$ hexanol = 102

Amount of hexanol burnt = $\frac{1.31}{102}$ mol

**a)** Heat evolved = $250 \times 4.18 \times 12.4 = 12\,958\,J$

**b)** $\Delta H_c = 12\,958 \times \frac{102}{1.31} = 1\,008\,944 = 1009\,kJ\,mol^{-1}$

**3 a)** Incomplete combustion of the hexanol and heat loss to the atmosphere.

**b)** Hexanol is burnt in an excess of oxygen and the products of the combustion are transferred to the water by means of a copper tube.

### Questions 5.3

**1** $\Delta H_f(HBr) + E(H{-}Br) = \Delta H_a(H) + \Delta H_a(Br)$

$-36.2 + E(H{-}Br) = +218 + 119$

$E(H{-}Br) = +337 - (-36.2)$ Ans = $+373\,kJ\,mol^{-1}$

**2** $\Delta H_f(H_2O)(g) + 2E(H{-}O) = 2\Delta H_a(H) + \Delta H_a(O)$

$-285.9 + 44.1 + 2E(H{-}O) = 2 \times 218 + 249.2$

$2E(H{-}O) = 685.2 - (-241.8) = 927$

$E(H{-}O) = 927/2$ Ans = $+463\,kJ\,mol^{-1}$

**3** $\Delta H_f(PCl_3)(g) + 3E(P{-}Cl) = 3\Delta H_a(Cl) + \Delta H_a(P)$

$-272.4 + 30.7 + 3E(P{-}Cl) = 3 \times 121.3 + 333.9$

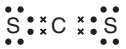
$3E(P{-}Cl) = +697.8 - (-241.7) = +939.5$

$E(P{-}Cl) = +939.5/3$ Ans = $+313\,kJ\,mol^{-1}$

## Answers to end of topic questions

**1 a)** $CH_3OCH_3(g) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l)$
This is the enthalpy change when one mole of DME is completely burnt in excess oxygen.

**b)** $2CH_3OH(l) \rightarrow CH_3OCH_3(g) + H_2O(l)$
$\Delta H^{\ominus}_{reaction} = \quad -184 + \quad (-286) - 2(-239)$
$= +8 \text{ kJ mol}^{-1}$

**2 a) i)** 

**ii)** Shape is linear, bond angle is 180°

**b) i)** $CS_2 + 3O_2 \rightarrow CO_2 + 2SO_2$

**ii)** The enthalpy change when one mole of the substance is completely burnt in excess oxygen at 1 atm pressure and at a specified temperature

**c)**

| | $CS_2 + 3O_2 \rightarrow$ | $CO_2 + 2SO_2$ |
|---|---|---|
| $\Delta H_f^{\ominus}$/kJ mol$^{-1}$ | x | −395 2(−298) |
| $\Delta H^{\ominus}_{reaction}$ | | −395 + 2(−298) − x = −1110 kJ mol$^{-1}$ |
| | x = | −395 + 2(−298) + 1110 = 119 kJ mol$^{-1}$ |

**d) i)** $CS_2 + 2NO \rightarrow CO_2 + 2S + N_2$
or $CS_2 + 2NO \rightarrow CO + 2S + N_2O$

**ii)** It goes from −2 to 0

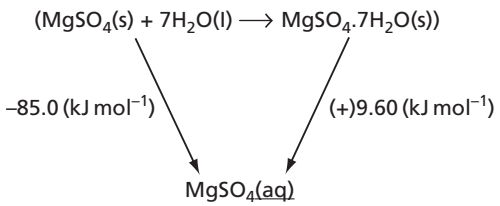
**3 a)** The *standard enthalpy change of reaction* is the energy change (measured at constant pressure) that occurs when the molar amounts of reactants, as shown in the equation, react to give products.

**b) i)** q = 2125 J

**ii)** 0.025(0) moles

**iii)** $\Delta H_{soln} = -85.(0)$

**iv)**




**v)** $\Delta H + 9.6 = -85.0$
$\Delta H_{hyd} = -85.0 - 9.6 = -94.6 \text{ (kJ mol}^{-1})$

# Topic 6: Ionic equations, acids and bases

## Answers to in-text questions

### Questions 6.1

**1** $CO_3^{2-}(aq) + Ca^{2+}(aq) \rightarrow CaCO_3(s)$. $2Na^+(aq)$ and $2Cl^-(aq)$

**2** $2OH^-(aq) + Mg^{2+}(aq) \rightarrow Mg(OH)_2(s)$. $2Li^+(aq)$ and $SO_4^{2-}(aq)$

### Questions 6.2

**1** $2H^+(aq) + 2OH^-(aq) \rightarrow 2H_2O(aq)$. $2Cl^-(aq)$ and $Ca^{2+}(aq)$

**2** $2H^+(aq) + 2OH^-(aq) \rightarrow 2H_2O(aq)$. $SO_4^{2-}(aq)$ and $2K^+(aq)$

### Question 6.3

$Zn(s) + 2H^+(aq) \rightarrow Zn^{2+}(aq) + H_2(g)$

### Questions 6.4

**1** $H_2SO_4(aq) + 2NaOH(aq) \rightarrow Na_2SO_4(aq) + 2H_2O(l)$
$2H^+(aq) + 2OH^-(aq) \rightarrow 2H_2O(aq)$

**2** $3HCl(aq) + Fe(OH)_3(s) \rightarrow FeCl_3(aq) + 3H_2O(l)$
$3H^+(aq) + Fe(OH)_3(s) \rightarrow Fe^{3+}(aq) + 3H_2O(l)$

**3** $2HNO_3(aq) + ZnO(s) \rightarrow Zn(NO_3)_2(aq) + H_2O(aq)$
$2H^+(aq) + ZnO(s) \rightarrow Zn^{2+}(aq) + H_2O(l)$

### Questions 6.5

$NH_4Cl + NaNH_2 \rightarrow NaCl + 2NH_3$
$NH_4^+ + NH_2^- \rightarrow 2NH_3$

### Questions 6.6

**1** 0.0441 mol dm$^{-3}$

**2** 0.120 mol dm$^{-3}$

### Questions 6.7

**1** The amount of sulfuric acid in 25.0 cm$^3$ is $\frac{1}{2} \times 24.85 \times \frac{0.102}{1000} = 1.267 \times 10^{-3}$ mol

$M_r$ $H_2SO_4 = 96$

The mass of sulfuric acid in 250 cm$^3$ is $98 \times 1.267 \times 10^{-3} = 1.242$

Purity of sulfuric acid is $1.242 \times \frac{100}{1.250}$ Ans = 99.4%

**2** The amount of ethanedioic acid in 25.0 cm$^3$ = $\frac{1}{2} \times 26.75 \times \frac{0.0532}{1000} = 7.116 \times 10^{-4}$ mol
$M_r$ $H_2C_2O_4 = 90$; $M_r$ $H_2O = 18$
The mass of anhydrous ethanedioic acid in 250 cm$^3$ is $90 \times 10 \times 7.116 \times 10^{-4}$ g = 0.640 g
The mass of water in 0.900 g of hydrated ethanedioic acid is 0.900 − 0.640 = 0.260 g
The amount of water weighed out is $\frac{0.260}{18}$ = 0.0144 mol
The amount of $H_2C_2O_4$ weighed out is 0.007116 mol
Therefore $x = \frac{0.0144}{0.007116} = 2.02 \sim 2$

### Question 6.8

$K_2CO_3 + HCl \rightarrow KHCO_3 + H_2O$

### Questions 6.9

**1** $H_2SO_4 + MgO \rightarrow MgSO_4 + H_2OzH_2SO_4 + 2NaOH \rightarrow Na_2SO_4 + H_2O$
$M_r$ MgO = 40
Amount of sulfuric acid at start = $25.0 \times \frac{1.00}{1000} = 2.50 \times 10^{-2}$ mol
Amount of sulfuric acid left over = $\frac{100}{25} \times \frac{1}{2} \times 27.80 \times \frac{0.100}{1000} = 5.56 \times 10^{-3}$ mol

Amount of sulfuric acid used = $2.50\times10^{-2} - 5.56\times10^{-3} = 1.944\times10^{-2}$ mol
This reacts with the same amount of MgO which has a mass of $1.944\times10^{-3}\times40 = 0.7776$ g
Therefore purity of MgO = $0.776\times\frac{100}{0.789} = 98.3$

**2** $M_r(LiOH) = 24$; $M_r(H_2O) = 18$
$[LiOH] = 0.05\times\frac{20.02}{25} = 0.0401$ mol dm$^{-3}$
$n(LiOH)$ in 250 cm$^3$ = $0.0401\times\frac{250}{1000} = 0.010025$ mol
$M_r = \frac{0.421}{0.010025} = 42.0$
$24 + 18x = 42$
$x = 1$
$LiOH.H_2O$

**3** $M_r\ (NH_4)_2SO_4 = 132$
Amount of NaOH at start = $\frac{25.0\times2.00}{1000} = 0.0500$ mol
Amount of NaOH left over = $10\times24.55\times\frac{0.0500}{1000} = 0.012275$ mol
Amount of NaOH used = 0.0500 − 0.012275 = 0.037725 mol
This reacted with $0.037725\times\frac{132}{2} = 2.49$ g of ammonium sulfate
Therefore percentage of ammonium sulfate
$= 2.49\times\frac{100}{10.0} = 24.9\%$

### Answers to end of topic questions

**1 a) i)** The hydrogen ions of the acid have been replaced by the metal ion $Ca^{2+}$
**ii)** $2HNO_3(aq) + Ca(OH)_2(aq) \rightarrow Ca(NO_3)_2(aq) + 2H_2O(l)$
**iii)** It accepts an $H^+$ ion (proton)
**b) i)** $0.0880\times25.00\div1000 = 2.20\times10^{-3}$ mol
**ii)** $2.20\times10^{-3}\div2 = 1.10\times10^{-3}$
**iii)** $(1.10\times10^{-3}\times1000)\div17.60 = 0.0625$ mol dm$^{-3}$
**c) i)** Water of crystallisation
**ii)** Molar mass $Na_2SO_4 = (2\times23) + 32.1 + (4\times16) = 142.1$
Molar mass $H_2O = (1\times2) + 16 = 18$
$x = (322.1 - 142.1)\div18 = 10$

**2 a)** $NH_3 + HZ \rightarrow NH_4^+ + Z^-$
$CH_3OH + HZ \rightarrow CH_3OH_2^+ + Z^-$
**b)** $NH_3 + B^- \rightarrow NH_2^- + BH$
$CH_3OH + B^- \rightarrow CH_3O^- + BH$

## Topic 7: Oxidation and reduction

### Answers to in-text questions

### Questions 7.1

**1 a)** $2H^+ + 2e^- \rightarrow H_2$
$Mg \rightarrow Mg^{2+} + 2e^-$
$2H^+(aq) + Mg(s) \rightarrow Mg^{2+}(aq) + H_2(g)$
**b)** $Br + 2e^- \rightarrow 2Br^-$
$Li \rightarrow Li^+ + e^-$
$Br_2(l) + 2Li(s) \rightarrow 2Li^+(aq) + 2Br^-(aq)$
**c)** $O_2 + 4e^- \rightarrow 2O^{2-}$
$Al \rightarrow Al^{3+} + 3e^-$
$3O_2(g) + 4Al(s) \rightarrow 2Al_2O_3(s)$
(The product could be written as $2Al^{3+}\ 3O^{2-}(s)$, but the charges on ions that make up a solid are not normally shown.)
**d)** $Zn \rightarrow Zn^{2+} + 2e^-$
$Ag^+ + e^- \rightarrow Ag$
$Zn(s) + 2Ag^+(aq) \rightarrow Zn^{2+}(aq) + 2Ag(s)$
(It is not necessary to put the '–' by each 'e' but it is helpful.)

**2**

| | Oxidised | Reduced |
|---|---|---|
| **a)** | Fe(s) | S(s) |
| **b)** | $Cl^-(aq)$ | $MnO_2(s)$ |
| **c)** | $Fe^{2+}(aq)$ | $Cl_2(aq)$ |
| **d)** | Cu(s) | CuO(s) or $Cu^{2+}(s)$ |

**3 a)** Neither
**b)** Reduced
**c)** Oxidised
**d)** Oxidised

### Questions 7.2

**1** +7
**2** +3
**3** +2
**4** –2
**5** –1

### Questions 7.3

**1 a)** +3
**b)** +3
**c)** +4
**d)** +3
**e)** +2
**f)** +4

**2 a)** $Cu_2O$
**b)** $VCl_2$
**c)** $Cr_2(SO_4)_3$

**3 a)** Phosphorus(V) oxide
**b)** Tin(IV) chloride
**c)** Potassium chlorate(VII)

### Questions 7.4

**1** $Cr(OH)_3 + 5OH^- \rightarrow CrO_4^{2-} + 3e^- + 4H_2O$
**2** $VO_2^+ + 3e^- + 4H^+ \rightarrow V^{2+} + 2H_2O$
**3** $H_2C_2O_4 \rightarrow 2CO_2 + 2e^- + 2H^+$
**4** $Cr_2O_7^{2-} + 6e^- + 14H^+ \rightarrow 2Cr^{3+} + 7H_2O$
**5** $2IO_3^- + 10e^- + 12H^+ \rightarrow I_2 + 6H_2O$
**6** $O_2 + 4e^- + 2H_2O \rightarrow 4OH^-$
**7** $H_2O_2 + 2e^- + 2H^+ \rightarrow 2H_2O$
**8** $H_2O_2 + 2OH^- \rightarrow O_2 + 2H_2O + 2e^-$

### Questions 7.5

1 a) $IO_3^-(aq) + 5I^-(aq) + 6H^+(aq) \rightarrow 3I_2(aq) + 3H_2O(l)$
b) $2MnO_4^-(aq) + 5NO_2^-(aq) + 6H^+(aq) \rightarrow 2Mn^{2+}(aq) + 5NO_3^-(aq) + 3H_2O(l)$
c) $VO^{2+}(aq) + Zn(s) + 2H^+(aq) \rightarrow V^{2+}(aq) + Zn^{2+}(aq) + H_2O(l)$
d) $4Fe(OH)_2(s) + O_2(g) + 2H_2O(l) \rightarrow 4Fe(OH)_3(s)$

2 a) $Cr_2O_7^{2-} + 3Mg(s) + 14H^+ \rightarrow 2Cr^{3+} + 3Mg^{2+}(aq) + 7H_2O$
b) $3NO_3^-(aq) + 8Al(s) + 18H_2O(aq) \rightarrow 3NH_3(aq) + 8Al^{3+}(aq) + 27OH^-(aq)$
c) $2Cr(OH)_3(s) + 3H_2O_2(aq) + 4OH^-(aq) \rightarrow 2CrO_4^{2-}(aq) + 8H_2O(l)$

### Questions 7.6

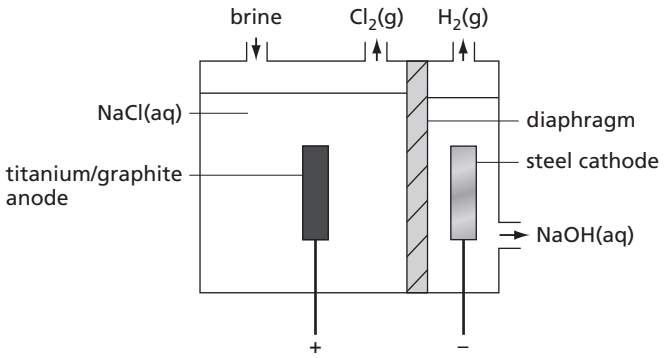
1 $3MnO_4^{2-} + 4H^+ \rightarrow MnO_2 + 2MnO_4^- + 2H_2O$

2 Oxidation number of carbon in $H_2CO = 0$
Oxidation number of carbon in $CH_3OH = -2$
Oxidation number of carbon in $HCO_2^- = +2$

### Answers to end of topic questions

1 a) $Ra^{2+}(aq) + 2e^- \rightarrow Ra(Hg)$
$2Br^-(aq) - 2e^- \rightarrow Br_2(l)$

2 a) i)




ii) Anode $2Cl^-(aq) \rightarrow Cl_2(g) + 2e^-$
Cathode $2H^+(aq) + 2e^- \rightarrow H_2(g)$
iii) Sodium hydroxide

## Topic 8: Rates of reaction

### Answers to in-text questions

### Question 8.1

Volume increase of $O_2$ evolved; absorption of colour of $KMnO_4$
Graphs: first like Figure 8.6, second the inverse with absorption decreasing with time

### Questions 8.2

1 First graph initially twice as steep, finishing at 160 $cm^3$. Second graph initially half as steep, finishing at 40 $cm^3$. Because the surface area of the calcium carbonate remains the same, the rate is determined by the concentration of the acid. Because the calcium carbonate is in excess, the final volume of carbon dioxide is determined by the amount of hydrochloric acid.

2 a) Suitable graph with time on *x*-axis and origin included.
b) i) Rate = $2.2 \times 10^{-3}\ s^{-1}$
Rate = $1.6 \times 10^{-3}\ s^{-1}$
ii) $0.15\ s^{-1}$
c) At $t = 120$ s the concentration of both reactants are lower than they were at $t = 60$ s, so the rate decreases.

3 a) Suitable graph with concentration on *x*-axis and origin included. Best straight line.
b) Because the concentration of the hydrochloric acid is constant, the rate is determined by concentration of sodium thiosulfate.
c) 0.25 mol $dm^{-3}$

### Questions 8.3

1 a) Similar to graph from Table 8.3 (page 172) but with initial gradient only half as large. The final volume will be the same but it may not be reached in 80 s.
b) Uses same reactants under same conditions, so the only change is the decrease in temperature of 10 K. This makes all the rates smaller by about a half.

2 a) Low activation energy with product level just below that of reactants.
b) Small activation energy with product level slightly above that of reactants.

### Questions 8.4

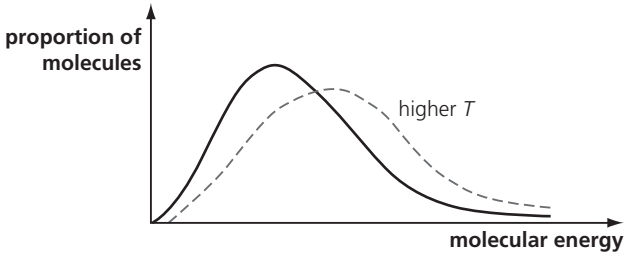
1 a) Graph, labelled *T*, as the red one in Figure 8.14.
b) New green graph, labelled *T*–100, with maximum to left of red graph and maximum higher.
$E_a$ as in Figure 8.14.

2 Heavier molecules move more slowly which makes them less likely to collide, but they are larger which increases the chance of collision. The two effects tend to cancel each other out.

### Answers to end of topic questions

1 a) i) *Bond energy* is the energy change when 1 mole of bonds are broken in the gas phase.
ii) $E(N–H) = 391\ kJ\ mol^{-1}$

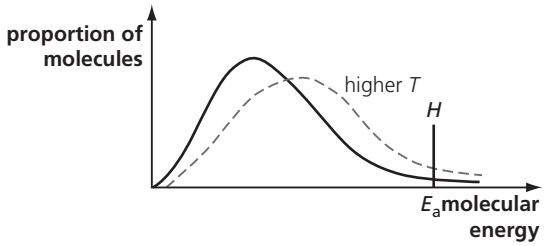
**b) i)**




**ii)** The rate of production increases due to the increase in the number of successful collisions per unit time.
At a higher temperature, there are more molecules where $E \geq E_a$.

**iii)** The yield of ammonia is reduced.
Increasing the temperature shifts the equilibrium to the left/towards the reactants ($N_2$ and $H_2$)/in the endothermic direction, so the yield of ammonia decreases. This has the effect of negating the increase in temperature.

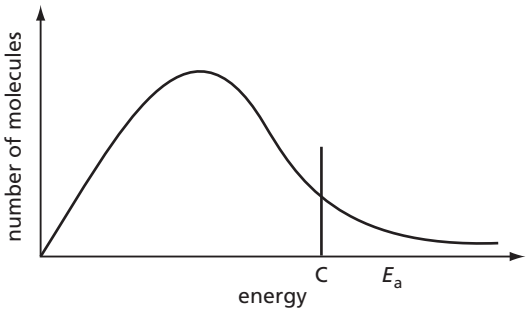
**2 a)** **i** and **ii**




**b)** The minimum energy that reactants must have, when their particles collide, to react successfully and form products

**c) i)** Iron, 250 atmospheres and 400 °C

**ii)**




**iii)** There are more molecules with energy greater than the activation energy.

**d)** In reaction 1 covalent bonds need to be broken so the activation energy is high.
In reaction 2 the reactants contain ions and the opposite charges attract each other so the activation energy is low.

**3 a)** CO is produced by the incomplete combustion of the hydrocarbons in petrol or diesel.
NO is produced by the reaction between $N_2$ and $O_2$ from the air.

**b)** CO is poisonous, as it binds with haemoglobin in red blood cells and hampers the transport of oxygen to the muscles and brain.
NO causes smog, and can also catalyse the oxidation of $SO_2$ to $SO_3$, causing acid rain.

# Topic 9: Equilibria

## *Answers to in-text questions*

### *Questions 9.1*

**1** Small because the reaction does not go to completion in either direction.

**2 a)** In dynamic equilibrium, the rate of the forward reaction equals the rate of the backward reaction.

**b)** There is no reason why a reaction, once it has started, should suddenly stop. The reaction rate will decrease but will not become zero while there are still reactants present (as there are at equilibrium).

**c)** Describe the experiment shown in Figure 9.1 or the one in Figure 9.2.

### *Questions 9.2*

**1 a)** Move to the right

**b)** Move to the left

**c)** Move to the left

### *Questions 9.3*

**1** Nil

**2** Move to the right

**3** Move to the left

**4** Move to the left

### *Questions 9.4*

**1** Move to the right

**2** Move to the left

### *Questions 9.5*

**1 a)** $\dfrac{[Cr_2O_7^{2-}]}{[CrO_4^{2-}]^2[H^+]^2}\ \text{mol}^{-3}\,\text{dm}^9$

**b)** $\dfrac{[I^-]^2[Fe^{3+}]^2}{[I_2][Fe^{2+}]^2}\ \text{mol}\,\text{dm}^{-3}$

### *Questions 9.6*

**1** At equilibrium $[H^+] = [IO_3^-] = 0.22$: $[HIO_3] = 0.50 - 0.22$

$$K_c = \frac{[H^+][IO_3^-]}{[HIO_3]} = \frac{0.22 \times 0.22}{0.28};$$

Ans = $0.17\ \text{mol}\,\text{dm}^{-3}$

**2** At equilibrium $[Ag^+] = 0.10/2 - 0.035$:

$$[NH_3] = \frac{0.20}{2} - 2 \times 0.035$$

$$K_c = \frac{[Ag(NH_3)_2]^+}{[Ag^+][NH_3]^2} = 0.035/(0.015 \times 0.03)^2;$$

Ans = $1.73 \times 10^5\ \text{mol}^{-2}\,\text{dm}^6$

### Question 9.7

At equilibrium let [HI] = $2x$ mol dm$^{-3}$.
Then [$H_2$] = [$I_2$] = 0.5 $-x$ mol dm$^{-3}$
$K_c = 4x^2/(0.5 - x)^2 = 54$
$\pm 2x = \sqrt{54}(0.5 - x)$
$\pm 2x = (3.67 - 7.34x)$
$9.34\,x = 3.67$ or $-5.34x = -3.67$
$x = 0.39$ or 0.68 (impossible > 0.5)
Ans = [HI] 0.78 mol dm$^{-3}$, [$H_2$] = [$I_2$] 0.22 mol dm$^{-3}$

### Question 9.8

$$\frac{K_p = (p_{NH_3})^2}{p_{N_2} \times (p_{H_2})^3}\ \text{atm}^{-2}$$

Position of equilibrium favoured by high pressure and low temperature (but rate is favoured by high pressure and high temperature).

### Answers to end of topic questions

**1 a)** $K_c$ = [NO(g)]$^2$ × [$Cl_2$(g)] ÷ [NOCl(g)]$^2$ mol dm$^{-3}$

**b)** At 230 °C:
$K_c = (1.46 \times 10^{-3})^2 \times (1.15 \times 10^{-2}) \div (2.33 \times 10^{-3})^2$
$= 4.52 \times 10^{-3}$
At 465 °C:
$K_c = (7.63 \times 10^{-3})^2 \times (2.14 \times 10^{-4}) \div (3.68 \times 10^{-4})^2$
$= 9.20 \times 10^{-2}$

**2 a)** $K_c$ = [$CH_3CO_2R$][$H_2O$] ÷ [$CH_3CO_2H$][ROH] (no units)

**b) i)** Amount in moles of NaOH = 22.5 × 2.00 ÷ 1000 = 0.045

**ii)** 0.005

**iii)** $CH_3CO_2H + NaOH \rightarrow CH_3CO_2Na + H_2O$

**iv)** 0.045 − 0.005 = 0.04

**c) i)**

| | $CH_3CO_2H$ | ROH | $CH_3CO_2R$ | $H_2O$ |
|---|---|---|---|---|
| Initial amount | 0.10 | 0.10 | 0 | 0 |
| Equilibrium amount/mol | 0.04 | 0.04 | 0.06 | 0.06 |

**ii)** $K_c = (0.06 \times 0.06) \div (0.04 \times 0.04) = 2.25$

**d)** The activation energy for the reaction of $OH^-$ with ester is high.

**e)** More ester would be formed so that equilibrium is restored and the value of $K_c$ maintained.

**3 a) i)** $N_2$ = 0.850 (mol); $H_2$ = 2.55 (mol)

**ii)** $n$TOTAL = 3.7 mol
mol fraction of $NH_3$ = 0.3 / 3.7
$p$NH$_3$ = $2 \times 10^7 \times (0.3 / 3.7) = 1.62 \times 10^6$

**b) i)** $K_p = \dfrac{p\text{NH}_3^2}{p\text{N}_2 \times p\text{H}_2^3}$

**ii)** $K_p = 1.(00) \times 10^{-16}$ Pa$^{-2}$

**iii)** The yield of ammonia increases and the value of $K_p$ stays the same.

**4 a) i)** Increasing the pressure means the molecules/particles/reacting species are closer together, so the frequency of collisions increases. There are fewer moles on the right so the equilibrium shifts right/towards the products.

**ii)** The reactant concentrations decrease as reaction progresses, so the rate decreases.

**iii)** The lines becomes horizontal when the forward and reverse rates are equal and equilibrium is established.

**iv)** Two moles of $SO_2$ react for every 1 mole of $O_2$, so the rate of decrease in [$SO_2$] will be twice that for [$O_2$].

**b) i)** $K_c = \dfrac{[SO_3]^2}{[SO_2]^2 \times [O_2]}$

**ii)** $SO_2$ = 0.02 (mol)
$O_2$ = 1.01 (mol)

**iii)** $K_c = \dfrac{(1.98/40)^2}{(0.02/40)^2\,(1.01/40)}$
$= 3.88 \times 10^5$ mol$^{-1}$ dm$^3$

## Topic 10: Periodicity

### Answers to in-text questions

### Question 10.1

Continuing the decreasing trend in r$^+$, radius of $Si^{4+}$ might be 0.04 ± 0.005 nm. Looking at the increasing trend in r$^-$ back from $Cl^-$ to $P^{3-}$, we see that there is a big jump from $S^{2-}$ to $P^{3-}$. If this were to continue, radius of $Si^{4-}$ might be 0.24 ± 0.01 nm.

### Questions 10.2

**a)** IE(Al)<IE(Mg) because the new electron in Al goes into a 3p orbital, which is further away from the nucleus than the 3s.

**b)** IE(S)<IE(P) because the new electron in S is in a doubly-occupied p orbital, and experiences inter-electron repulsion from the other electron sharing the same space.

### Questions 10.3

**1 a)** Giant covalent

**b)** Semiconductor

**2** Possible same reason why mp of S > P: namely, P is $P_4$ but S is $S_8$

### Questions 10.4

**1 a)** The chloride of **Y** is simple/discrete covalent. Its oxide is also simple covalent, as it has quite a low melting point.

**b)** The oxide of element **Z** is either giant ionic or giant covalent (high melting point). Its chloride is ionic (dissolves in water to give a **neutral** solution), so its oxide is likely to be giant ionic too.

### Questions 10.5

**Q** is a non-metal, since its molten chloride does not conduct. Q could be in Group 14 (like Si), as it has a covalency of 4, forms a simple molecular chloride (low melting point) but a giant molecular oxide (high melting point).
**R** is a metal: its molten chloride conducts, so is ionic. R is in Group 2 (like Ca), as it has an ionic valency of +2, and the pH 7 of the aqueous solution of its chloride shows that no hydrolysis occurs.

### Answers to end of topic questions

**1 a) i)** S
**ii)** K
**iii)** Na or Li
**iv)** Cl or Br or F
**v)** Mg or Ca or Li
**b) i)** $F_2O$
**ii)** $SO_2$ and $SO_3$ or $P_2O_3$ and $P_2O_5$
**c) i)** Any two of NaF, $MgF_2$, $AlF_3$
**ii)** Octahedral
**iii)** The Cl atom is too small so there is no space to pack seven F atoms round it.

**2 a)** Sodium burns with a yellow flame and forms a white solid.
$2Na + Cl_2 \rightarrow 2NaCl$
Phosphorus burns with a white flame and forms a colourless liquid or a white solid.
$P_4 + 6Cl_2 \rightarrow 4PCl_3$ or
$P_4 + 10Cl_2 \rightarrow 4PCl_5$
**b)** $MgCl_2$ pH 6 to 7; $SiCl_4$ pH 0 to 3
$MgCl_2$ dissolves without reaction and $SiCl_4$ reacts with water
$SiCl_4 + 2H_2O \rightarrow SiO_2 + 4HCl$ or
$SiCl_4 + 4H_2O \rightarrow Si(OH)_4 + 4HCl$ or
$SiCl_4 + 4H_2O \rightarrow SiO_2.2H_2O + 4HCl$

**3 a) i)** There is a general increase in the first ionisation energy across the third period due to the increasing nuclear attraction for electrons that results from increasing nuclear charge.
**ii)** Ne = cross shown on first vertical line from the y-axis, clearly higher than all others
Na = cross shown on second vertical line from the y-axis, lower than all others
**iii)** In Al the outer valence electron, which is lost in ionisation, is in 3p (higher energy) sub-shell and experiences greater shielding, whereas in Mg it is in 3s sub-shell.
S has a pair of electrons sharing the same 3p orbital, which repel each other, making the ionisation energy of S less than that of P.

**b)** **L** is $MgCl_2$, which has a high melting point because it has a giant ionic structure with strong ionic bonds. It dissolves to form $Mg^{2+}(aq)$ ions which undergo only a very small amount of hydrolysis. The white precipitate is $Mg(OH)_2$.
$MgCl_2 + 2NaOH \rightarrow Mg(OH)_2 + 2NaCl$
**M** is $SiCl_4$, which is a liquid (low melting point) because it exists as simple covalent molecules. It hydrolyses readily to give a solution of hydrochloric acid because of the presence of accessible d orbitals in silicon.
$SiCl_4 + 2H_2O \rightarrow SiO_2 + 4HCl$

## Topic 11 Group 2, nitrogen and sulfur

### Answers to in-text questions

### Question 11.1

**a)**

| metal | density | Ar | atomic radius | $Ar/r^3$ | $(Ar/r^3)$/ density |
|---|---|---|---|---|---|
| Mg | 1.74 | 24.3 | 0.16 | 5933 | 3410 |
| Ca | 1.54 | 40.1 | 0.174 | 7612 | 4943 |
| Sr | 2.6 | 87.6 | 0.191 | 12572 | 4835 |
| Ba | 3.51 | 137.3 | 0.198 | 17688 | 5039 |

**b)** Mg is the odd one out. Its density is larger than expected, due to its atoms being packed more tightly than those of the other metals.

### Questions 11.2

**1** Either $Ca(s) + \frac{1}{2} O_2(g) \rightarrow CaO(s)$ or
$2Ca(s) + O_2(g) \rightarrow 2CaO(s)$
**2** $Sr(s) + 2H_2O(l) \rightarrow Sr(OH)_2(aq) + H_2(g)$

### Questions 11.3

**a)** Either $CaCO_3(s) + 2H^+(aq) + CO_3^{2-}(aq) \rightarrow Ca(HCO_3)_2(aq)$
or $CaCO_3(s) + H_2CO_3(aq) \rightarrow Ca(HCO_3)_2(aq)$
**b)** $Ba(OH)_2(aq) + CO_2(g) \rightarrow BaCO_3(s) + H_2O(l)$

### Question 11.4

Either $O_2 + 4N_2 + 3\frac{1}{2} CH_4 + 5H_2O \rightarrow 3\frac{1}{2} CO_2 + 12H_2 + 4N_2$
or $2O_2 + 8N_2 + 7CH_4 + 10H_2O \rightarrow 7CO_2 + 24H_2 + 8N_2$

### Questions 11.5

**a)** $4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O$
**b)** $2NO + O_2 \rightarrow 2NO_2$
**c)** $4NO_2 + O_2 + 2H_2O \rightarrow 4HNO_3$

## Answers to end of topic questions

**1 a) i)** Atoms become larger as the number of electron shells increases down the group. As the outer electrons are further from the nucleus there is increased shielding.

**ii)** The top (dotted) line represents atomic radii and the bottom (crosses) line is ionic radii. We know this because atoms, having more shells, are bigger than ions, which experience greater nuclear attraction.

**b) i)** Nitrate ($NO_3^-$)

**ii)** Ba (barium) OR Sr (strontium)
$Ba^{2+} + SO_4^{2-} \rightarrow BaSO_4$ or
$Sr^{2+} + SO_4^{2-} \rightarrow SrSO_4$

**iii)** $Ba(NO_3)_2$ or $Sr(NO_3)_2$
$2Ba(NO_3)_2 \rightarrow 2BaO + 4NO_2 + O_2$ or
$2Sr(NO_3)_2 \rightarrow 2SrO + 4NO_2 + O_2$

**c) i)** $H^+ + OH^- \rightarrow H_2O$ or
$Ca(OH)_2 + 2H^+ \rightarrow Ca^{2+} + 2H_2O$
$2H^+ + CO_3^{2-} \rightarrow CO_2 + H_2O$ or
$CaCO_3 + 2H^+ \rightarrow Ca^{2+} + CO_2 + H_2O$ or
$H^+ + CO_3^{2-} \rightarrow HCO_3^-$ or
$CaCO_3 + H^+ \rightarrow Ca^{2+} + HCO_3^-$

**ii)** Calcium carbonate is insoluble and less reactive, so won't get washed away and lasts longer.

**d)** $Mg(OH)_2$ and MgO

**2 a) i)** Strong heating to overcome the high activation energy

**ii)** Bright white flame, white smoke and white solid

**iii)** $Mg(s) + 2H_2O(l) \rightarrow Mg(OH)_2(s) + H_2(g)$

**b) i)** $2Mg(NO_3)_2 \rightarrow 2MgO + 4NO_2 + O_2$

**ii)** $CaCO_3 \rightarrow CaO + CO_2$
$CaO + H_2O \rightarrow Ca(OH)_2$

**c) i)** They are both bases that are used to reduce acidity (increase pH) of soil.

**ii)** $CaCO_3 + 2H^+ \rightarrow Ca^{2+} + CO_2 + H_2O$ or
$CaCO_3 + 2H^+ \rightarrow Ca^{2+} + H_2CO_3$

**3 a)** $NH_3 + HNO_3 \rightarrow NH_4NO_3$

**b) i)** Produce a line from the origin, below the left-hand end of original with peak to right of and lower than original. This line crosses the original once, above the right-hand end of original and above energy axis.

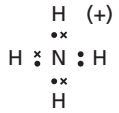
**ii)** At higher T the curves show more molecules with $E > E_a$, so there will be a greater frequency of successful collisions per unit time.

**iii)** Add a label to the left of the original on the horizontal axis, so in the presence of catalyst there are more molecules with $E > E_a$.

**iv)** The production of ammonia in the forward reaction is exothermic, so at higher T the position of equilibrium would move to the left, reducing yield.

**c)** $4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O$
N changes from –3 to +2 (so oxidation)
O changes from 0 to –2 (so reduction)

**d) i)**




**ii)** Tetrahedral
Angle = 109°–109.5°

# Topic 12: Group 17

## Answers to in-text questions

### Question 12.1

**a)** Red–brown colour changes to deep brown in water or to purple in non-polar solvents.

**b)** No colour change

**c)** Almost colourless solution turns dark brown in water or to purple in non-polar solvents.

### Question 12.2

$H_2 + Br_2 \rightarrow 2HBr$; $\Delta H = 436 + 193 - (2 \times 366) = -103\,kJ\,mol^{-1}$
Fits trend because value is between that of chlorine and iodine.

### Questions 12.3

**1** $NaClO_3 \rightarrow NaClO_4 + NaCl$
Cl(+5) Cl(+7) Cl(–1)
To balance $4 \times 5 = 3 \times 7 - 1$
$4NaClO_3 \rightarrow 3NaClO_4 + NaCl$

**2** $I^-(aq) + IO_3^-(aq) + H^+ \rightarrow I_2(aq) + H_2O(l)$
Balance for ON
I(–1) I(+5) I(0)
$5 \times -1 + 5 = 0$
$5I^-(aq) + IO_3^-(aq) + H^+ \rightarrow I_2(aq) + H_2O(l)$
Balance for charge, I and H
$5I^-(aq) + IO_3^-(aq) + 6H^+ \rightarrow 3I_2(aq) + 3H_2O(l)$

### Question 12.4

$MgBr_2(aq) + Ag_2SO_4(aq) \rightarrow MgSO_4(aq) + 2AgBr(s)$
$Br^-(aq) + Ag^+(aq) \rightarrow AgBr(s)$ (no need to be doubled up)

### Question 12.5

Ammonia forms a stable complex with silver ions and thus reduces the concentration of free silver ions in the solution. The silver ion concentration is now so low that some solid silver chloride dissolves. The resulting increase in the silver ion concentration is again reduced by the ammonia. This process is repeated. If the final silver ion concentration is less than that of the original solution, all the silver chloride will dissolve.

### Question 12.6

$HI(g) + H_2SO_4(l) \rightarrow I_2(s) + H_2O(l) + S(s)$

Balance for ON
I(−1) S(+6) I(0) S(0)
6 × −1 + 6 = 0
Balancing for I and S
$6HI(g) + H_2SO_4(l) \rightarrow 3I_2(s) + 4H_2O(l) + S$
$HI(g) + H_2SO_4(l) \rightarrow I_2(s) + H_2O(l) + H_2S(g)$
Balancing for ON
I(−1) S(+6) I(0) S(−2)
8 × −1 + 6 = −2
Balancing for I and S
$8HI(g) + H_2SO_4(l) \rightarrow 4I_2(s) + 4H_2O(l) + H_2S(g)$

### *Answers to end of topic questions*

**1 a) i)** Volatility decreases

**ii)** Going down the group, there are more electrons in molecules, increasing the strength of id–id forces.

**b)** $Cl_2 + 2NaI \rightarrow 2NaCl + I_2$

**c) i)**

| | **NaI(aq) + $AgNO_3$(aq)** | **NaCl(aq) + $AgNO_3$(aq)** |
|---|---|---|
| colour of precipitate | **yellow** | **white** |
| name of precipitate | **silver iodide** | **silver chloride** |
| effect of addition of an excess of aqueous ammonia to the precipitate | **No visible change** | **dissolves (soluble)** |

**ii)** $Ag^+(aq) + I^-(aq) \rightarrow AgI(s)$

**d)** Sulfuric acid reacts as an acid with NaCl but as an oxidising agent with NaI/I. Sulfuric acid can oxidise $I^-$ but not $Cl^-$ (sulfuric acid is a stronger oxidising agent than iodine but is not as strong an oxidising agent as chlorine).

**e) i)** An *oxidising agent* gains electrons.

**ii)** $Cl_2 + H_2O \rightarrow HCl + HClO$

**iii)** $3Cl_2 + 6NaOH \rightarrow 5NaCl + NaClO_3 + 3H_2O$
The oxidation number of chlorine changes from 0 to −1 and from 0 to +5, so chlorine has been reduced as well as oxidised.

**2 a) i)** The thermal stability of the hydrides decreases as you go down the Group.

**ii)** This is because the atoms become larger and the bonding pair is further from the nucleus so the H–X bond strength decreases. Smaller orbital overlap occurs.

**b)** $K_c = [HI]^2 \div [H_2][I_2]$ There are no units

**c) i)** There will be no change as there are the same number of gaseous molecules on both sides of the equation.

**ii)** The equilibrium position moves to the right-hand side since $K_c$ increases with decreasing temperature.

**d)**

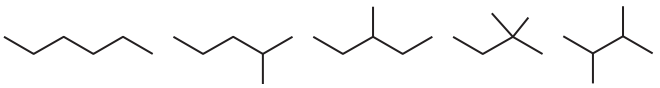
| | $H_2(g)$ + | $I_2(g)$ | $2HI(g)$ |
|---|---|---|---|
| Initial moles | 0.02 | 0.02 | 0 |
| Equilibrium moles | (0.02 − y) | (0.02 − y) | 2y |
| Equil conc./ mol $dm^{-3}$ | (0.02 − y) ÷ 1 | (0.02 − y) ÷ 1 | 2y ÷ 1 |

$K_c = [HI]^2 \div [H_2][I_2] = (2y)^2 \div (0.02 - y)^2 = 59$
$2y \div 0.02 - y = \sqrt{59} = 7.7$
$2y = (7.7 \times 0.02) - 7.7y$
$9.7y = 0.154$
$y = 0.0159 = 0.016$
so moles of $H_2 = 0.02 - 0.016 = 0.04$
moles of $I_2 = 0.02 - 0.016 = 0.04$
moles of $HI = 2 \times 0.016 = 0.032$

## Topic 13: Introduction to organic chemistry

### *Answers to in-text questions*

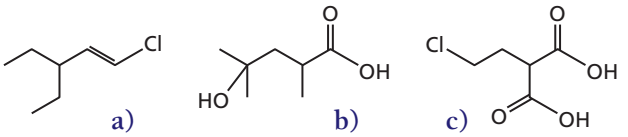
### *Question 13.1*



### *Questions 13.2*

**1** $CH_3CH_2CHClCH_3$; $C_4H_9Cl$; $C_4H_9Cl$
$CH_3CH(OH)CH_2Br$; $C_3H_7BrO$; $C_3H_7BrO$
$HOCH_2CH_2CO_2H$; $C_3H_6O_3$; $CH_2O$

**2**




**a)** **b)** **c)**

### *Questions 13.3*

**1** $C_7H_{14}O$
**2** $C_6H_4Cl_2$
**3** $C_5H_8O_2$

### *Questions 13.4*

**1 a)** 2,2-dimethylpentan-3-ol

**b)** But-2-ene

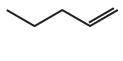
**c)** 1-methylcyclohexene

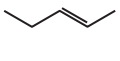
**2 a)** $(CH_3)_2CBrCHBrCH_2CH_3$

**b)** $(CH_3)_4C$

## Questions 13.5

**1**


pent-1-ene


*trans*-pent-2-ene


*cis*-pent-2-ene


2-methylbut-1-ene

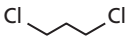

2-methylbut-2-ene


3-methylbut-1-ene

**2**


1,1-dichloropropane


1,2-dichloropropane (contains a chiral centre)


1,3-dichloropropane

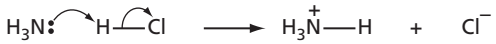

2,2-dichloropropane

**3** **a)** Geometrical
**b)** Optical
**c)** Geometrical and optical

## Question 13.6

**I** Oxidation
**II** Reduction
**III** Condensation

## Question 13.7



## Questions 13.8

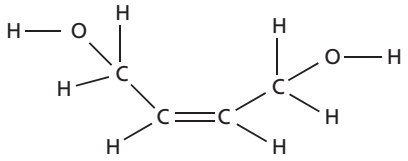
**1** $C_5H_{10}O$; $C_nH_{2n}O$
**2** $C_6H_{11}N$; $C_{n+1}H_{2n-1}N$
**3** $C_{10}H_{14}$; $C_{n-6}H_{2n-6}$

## Questions 13.9

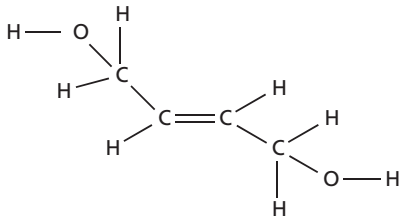
**1** 69%
**2** 61%
**3** *n*(ethanedioic acid) = 8/90 = 0.0889
*n*(ethanol) = 7/46 = 0.152
1 mol of the diacid would react with 2 mol of ethanol, so 0.0889 mol needs 0.177 mol.
Since we only have 0.152 mol, the diacid is in excess, and we calculate the yield based on ethanol.
*n*(diester) = 10/146 = 0.0685 mol
0.152 mol of ethanol should give 0.152/2 = 0.076 mol diester
so % yield = 0.0685 × 100/0.076 = **90.1%**

## Answers to end of topic questions

**1** **a)** **i** and **ii**

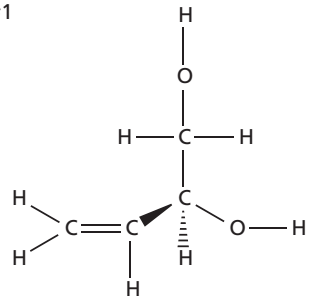


**pair 1** geometrical **or** *cis*/*trans* isomerism

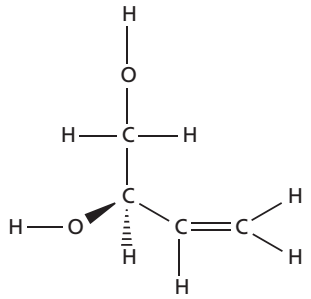


**pair 2** optical isomerism

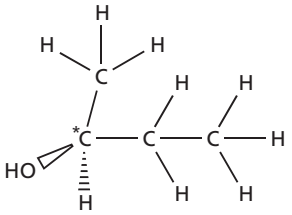
#1



#2



**2** **a)** **i)** mass of C = 12 × 1.32 ÷ 44 = 0.36 g
n(C) = 0.36 ÷ 12 = 0.03
**ii)** mass of H = (2 × 0.54) ÷ 18 = 0.06 g
n(H) = 0.06 ÷ 1 = 0.06
**iii)** It is an alkene because the ratio of C : H is 1 : 2 so the empirical formula is $CH_2$
**b)** **i)** C : H : O = 64.86 ÷ 12 : 13.50 ÷ 1 : 21.64 ÷ 16
= 5.41 : 13.5 : 1.35
= 4 : 10 : 1
$C_4H_{10}O$
**ii)**

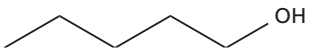


iii)

| | | |
|---|---|---|
| $CH_3CH_2CH_2CH_2OH$ | $CH_3CCH_2OH$ (H above C, $CH_3$ below C) | $CH_3CCH_3$ (OH above C, $CH_3$ below C) |

3 a) i) $C_2H_5O$

ii)




b) i) Functional group or structural isomerism

ii) P shows *cis*/*trans* or geometrical isomerism
T shows optical isomerism

c) i) Dehydration or elimination

ii) Concentrated $H_2SO_4$ or $P_4O_{10}$ or $Al_2O_3$ or $H_3PO_4$

iii) $CH_2{=}CHCH{=}CH_2$ or $CH_2{=}C{=}CHCH_3$

4 a) *Structural isomers* have the same molecular formula (and so same number of atoms of each element) but different structural formulae (and so a different arrangement of bonds).

b) $sp^2$ hybridisation occurs when there is overlap between the 2s and two 2p orbitals; $sp^3$ overlap is between the 2s and all three 2p orbitals.

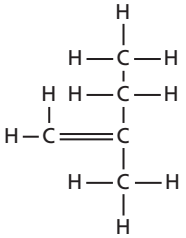
c) $sp^2 = 120$; $sp^3 = 109$

5 a) i) *Structural isomers* have the same molecular formula (and so same number of atoms of each element) but different structural formulae (and so a different arrangement of bonds).

ii) *Stereoisomers* have the same molecular and structural formula but a different arrangement of atoms in space.

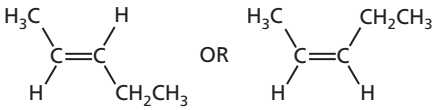
b) i) Pent-1-ene has no chiral carbon (no carbon with four different groups or atoms attached), so it has a superimposable mirror image.

ii)



2-methylbut-1-ene

iii)




*trans*–pent–2–ene or *cis*–pent–2–ene

# Topic 14: Alkanes

## *Answers to in-text questions*

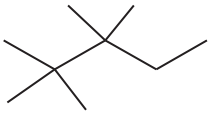
### *Questions 14.1*

1 a) 3-ethylpentane (NOT triethylmethane!)

b) 2,3,3,4-tetramethylpentane

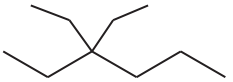
2 a) $(CH_3)_3CC(CH_3)_2CH_2CH_3$

$C_9H_{20}$



b) $(CH_3CH_2)_3CCH_2CH_2CH_3$

$C_{10}H_{22}$



### *Question 14.2*

For coal, $CO_2$ produced per kJ $= \frac{1}{394} = 2.54\times10^{-3}\,mol\,kJ^{-1}$; percentage reduction $= \frac{100(2.54\times10^{-3} - 1.12\times10^{-3})}{(2.54\times10^{-3})} = 56\%$

### *Question 14.3*

The alkane is $C_5H_{12}$.
Volume of $CO_2$ formed = 120 − 70 = 50 $cm^3$
Volume of $O_2$ used = 150 − 70 = 80 $cm^3$
1 volume of **X** reacts with 8 volumes $O_2$ to give 5 volumes of $CO_2$
1 mole of **X** reacts with 8 moles $O_2$ to give 5 moles $CO_2$
$C_5H_{12} + 8O_2 \rightarrow 5CO_2 + 6H_2O$

### *Question 14.4*

Reaction 3 with bromine: $\Delta H = +47\,kJ\,mol^{-1}$
Reaction 4 with bromine: $\Delta H = +137\,kJ\,mol^{-1}$
Both are now endothermic, but reaction (3) is still more favourable than reaction 4.

### *Question 14.5*


This will be the major product, as the tertiary hydrogen atom is the most readily replaced.

(* indicates a chiral carbon atom)

## *Answers to end of topic questions*

1 a) i) They are compounds that only contain hydrogen and carbon.

ii) Separating compounds by making use of their different boiling points

b) i) Heating with steam at 800°C under pressure or passing vapour over $Al_2O_3$ catalyst at 500°C.

ii) $C_{11}H_{24} \rightarrow C_5H_{12} + C_6H_{12}$

**c)** **i)** Isomer B $CH_3CH_2CH_2CH_2CH_3$

Isomer C $CH_3CH_2CHCH_3$ with $CH_3$ branch

Isomer D $CH_3CCH_3$ with $CH_3$ and $CH_3$ branches

**ii)** Isomer B, because straight chain molecules can pack together closely and have the greatest van der Waals' (id–id) forces

**d)** The enthalpy change when one mole of the substance is completely burnt in excess oxygen and 1 atm pressure and at 298 K.

**e)** **i)** Heat released = $mC\Delta T = 200 \times 4.18 \times 27.5$ = 22 990 J = 23.0 kJ

**ii)** Since 23.0 kJ is produced from 0.47 g then 2059 kJ will be produced from $0.47 \times 2059 \div 23.0$ g = 42.08 g so $M_r = 42.08$

**f)** $C_3H_6$ ($M_r = 42$)

**2** **a)** **i)** Bond breaking = Cl—Cl = 242
C—H = 410
Total = 652 kJ
Bond forming = C—Cl = 340
H—Cl = 431
Total = 771 kJ
Enthalpy change = 652 − 771 = −119 kJ mol$^{-1}$

**ii)** UV light or high temperature or sunlight

**iii)** Initiation: $Cl_2 \rightarrow 2Cl\bullet$
Propagation: $C_2H_6 + Cl\bullet \rightarrow \bullet C_2H_5 + HCl$
$\bullet C_2H_5 + Cl_2 \rightarrow C_2H_5Cl + Cl\bullet$
Termination: $\bullet C_2H_5 + \bullet C_2H_5 \rightarrow C_4H_{10}$

**b)** **i)** Ethene

**ii)** KOH or NaOH, ethanolic and heat or reflux

**iii)** $H_2$ and Pt or Ni (catalyst)

**3** **a)** **i)** It has to vaporise.

**ii)** From fraction **A** to fraction **F** the trends are increasing molecular size, more carbon atoms per molecule and increasing length of carbon chain.

**iii)** From fractions from **A** to **F** trends in properties are increasing boiling point (decreasing volatility), increasing viscosity, increasing density, decreasing flammability.

**b)** **i)** $C_{12}H_{26} \rightarrow 2C_2H_4 + C_8H_{18}$

**ii)** Ethene is used to make the polymer polythene. Ethene has a double (unsaturated) bond for polymerisation.
Octane is used as the fuel petrol. It has high flammability, releasing a great deal of energy when combusted.

**c)** **i)** Oxides of nitrogen are produced by the reaction of atmospheric oxygen and nitrogen due to the high temperature of the internal combustion engine. This provides the energy required for this endothermic reaction.

**ii)** $2NO + 2CO \rightarrow N_2 + 2CO_2$

**iii)** $NO + 1/2O_2 \rightarrow NO_2$
$NO_2 + SO_2 \rightarrow SO_3 + NO$
$SO_3 + H_2O \rightarrow H_2SO_4$

**iv)** *Any two from*: acid rain

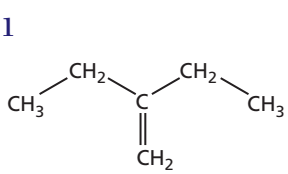
- lowers the pH of rivers and lakes, killing fish
- leaches aluminium, which is toxic, from the soil into rivers and lakes
- leaches away soil nutrients
- causes damage to buildings, statues, trees, plants and crops
- causes ocean acidification and damage to coral

## Topic 15: Alkenes

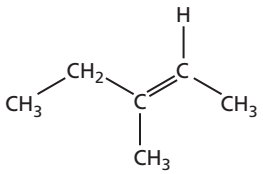
### *Answers to in-text questions*

### *Questions 15.1*

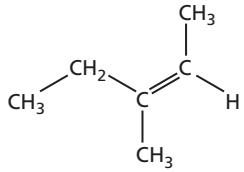
**1**



2-ethylbut-1-ene

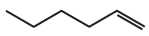


*cis*-3-methylpent-2-ene

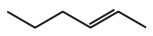


*trans*-3-methylpent-2-ene

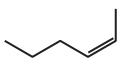
**2**



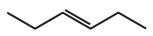
hex-1-ene



*trans*-hex-2-ene

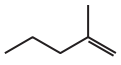


*cis*-hex-2-ene

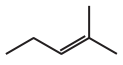


*trans*-hex-3-ene

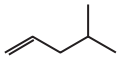
*cis*-hex-3-ene



2-methylpent-1-ene

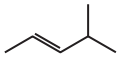


2-methylpent-2-ene



4-methylpent-1-ene

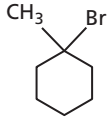
3,3-dimethylbut-1-ene



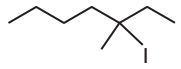
*trans*-4-methylpent-2-ene

*cis*-4-methylpent-2-ene

### Question 15.2

1 

1-bromo,1-methylcyclohexane

2 

3-iodo,3-methylheptane

### Question 15.3

Both will give the same alcohol: 2-methylbutan-1-ol, $CH_3CH_2C(OH)(CH_3)_2$

### Question 15.4

$(CH_3)_2C{=}O$, $CH_3COCH_2CH_2CO_2H$,
$HO_2C{-}CO_2H$ ($\rightarrow CO_2$ eventually)

### Questions 15.5

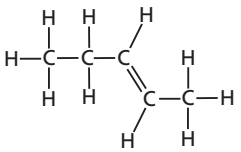
**a** $CH_2{=}C(CN)CO_2CH_3$
**b** $CH_2{=}CHCl$ and $CH_2{=}CHCO_2CH_3$
**c** $CH_2{=}CHOCOCH_3$ and $CH_2{=}CHOH$

### Answers to end of topic questions

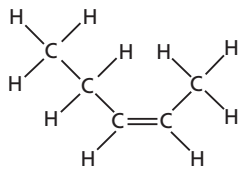
**1 a)** **P**: $CH_3CH_2CH_2CH{=}CH_2$
**Q**: $CH_3CH_2CH{=}CHCH_3$
**R**: $CH_3CH_2C(CH_3){=}CH_2$
**S**: $CH_3CH{=}C(CH_3)_2$
**T**: $CH_3CH_2COCH_3$

**b) i)** *Stereoisomers* are different molecules with the same molecular and structural formula but different arrangements of atoms in space.

**ii)**



*trans*-pent-2-ene



*cis*-pent-2-ene

**c)** Butan-2-ol

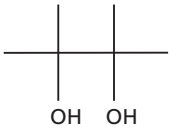
**2 a) i)** 4-methylhex-2-ene 1

**ii)** *Stereoisomers* are different molecules with the same molecular and structural formula but different arrangements of atoms in space.

**iii)** There are four stereoisomers. It is an alkene with a double bond and there are different groups on each double-bonded carbon. There is one chiral centre atom with four different groups attached.

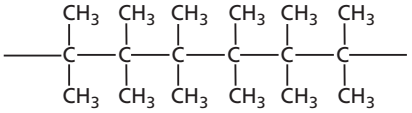
**b) i)** 2,3-dimethylbut-2-ene

**ii)**



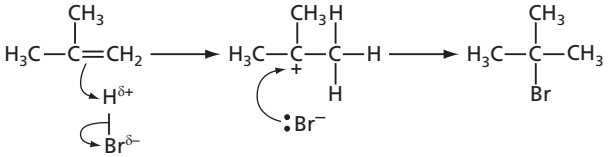
**iii)** Propanone

**iv)**



**c) i)** (2-)methylprop(-1-)ene

**ii)**



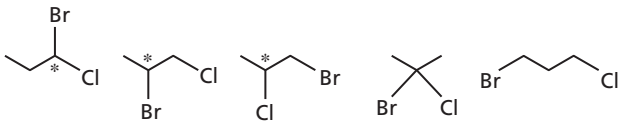
**iii)** The tertiary carbocation intermediate is more stable than the primary carbocation due to the electron-donating inductive effects of the alkyl groups.

## Topic 16: Halogenoalkanes

### Answers to in-text questions

### Question 16.1

There are five positional isomers, of which three can form optical isomers.
Structures:



* shows a chiral carbon atom

these isomers are not chiral

### Questions 16.2

1 $CH_3CHClCHCl_2$
2 $(CH_3)_3CCl$

### Questions 16.3

1 $(CH_3)_2C{=}CH_2$
2 $CH_3CH_2CH(OH)CH_2CH_3$

### Answers to end of topic questions

**1 a)** Reaction 1
Reagent NaOH/KOH Solvent $H_2O$
Reaction 2
Reagent $NH_3$ Solvent $C_2H_5OH$
Reaction 3
Reagent NaOH/KOH Solvent $C_2H_5OH$

**b)** With 1-iodobutane the rate would be faster because the C—I bond is weaker than the C—Br bond so it is more easily broken.
C—I is 240 kJ $mol^{-1}$ and C—Br is 280 kJ $mol^{-1}$

**c)** CFCs are non-toxic and chemically inert. They have low boiling points and are non-flammable.

**d)** **i)** When the two electrons in a covalent bond are shared between the atoms when the bond breaks.

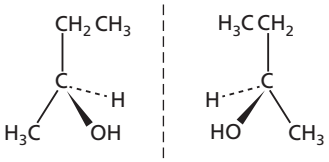
**ii)** $CCl_2F_2 \rightarrow CClF_2 + Cl$

**e)** They are flammable.

**2** **a)** **i)** The mechanism is nucleophilic substitution.

**ii)** There is a carbon (chiral centre) with four different groups attached, meaning the molecule has no line of symmetry.

**iii)**



**iv)** The mechanism is elimination.

**v)**

*cis*-but-2-ene *trans*-but-2-ene

**vi)** But-1-ene does not show geometrical isomerism as it has two hydrogens on one of the double-bonded carbons, rather than having two different groups on both double-bonded carbons.

**b)** **i)** Ammonia ($NH_3$)

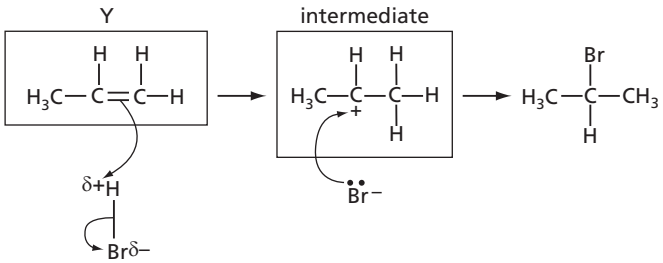
**ii)** Propanoyl chloride ($C_2H_5COCl$)

**iii)** $CH_3CH(NHCOC_2H_5)CH_3$

**iv)** Reduction with $LiAlH_4$

**v)** Aluminium oxide

**vi)**




**vii)** Electrophilic addition

**viii)** The secondary carbocation is more stable than the primary carbocation due to the inductive effect of the alkyl groups.

# Topic 17: Alcohols

## *Answers to in-text questions*

### *Questions 17.1*

**1** **a)** **A** and **B** show chain isomerism.

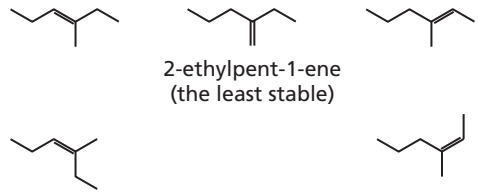
**b)** **B** and **E** show positional isomerism.

**c)** **A** and **C** show positional isomerism.

**d)** **C** and **D** show optical isomerism.

**2** **A** is butan-1-ol, **B** is 2-methylpropan-1-ol, **C** and **D** are butan-2-ol, **E** is 2-methylpropan-2-ol

### *Questions 17.2*



2-ethylpent-1-ene (the least stable)

*cis*- and *trans*-3-methylhex-3-ene *cis*- and *trans*-3-methylhex-2-er

### *Questions 17.3*

**1** None of **P**, **Q** or **R** can be a tertiary alcohol; only **P** is a primary alcohol – the other two are secondary alcohols. **Q** must have its —OH group on the second carbon of its chain.

Possibilities:

**P** could be $CH_3(CH_2)_4OH$ *or* $(CH_3)_2CHCH_2CH_2OH$ *or* $CH_3CH_2C(CH_3)CH_2OH$ *or* $(CH_3)_3CCH_2OH$

**Q** could be $CH_3CH_2CH_2CH(OH)CH_3$ *or* $(CH_3)_2CHCH(OH)CH_3$

**R** is $CH_3CH_2CH(OH)CH_2CH_3$

**2** **a)** Reading from the left-hand side of the molecule, the alcohol groups are classified as follows: secondary; tertiary; primary.

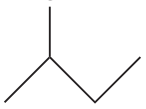
**b)** **i)** $CH_3COCH_2CH(OH)(CH_3)CH_2CO_2H$

**ii)** $HO_2CCH_2CH(OH)(CH_3)CH_2CH_2OH$ (or its carboxylate anion)

### *Answers to end of topic questions*

**1** **a)** **i)** $C_2H_5O$

**ii)** OH



**iii)** **A** shows *cis*/*trans* or geometrical isomerism
**D** shows optical isomerism

**b)** **i)** Elimination

**ii)** $Al_2O_3$ or $H_3PO_4$ or $H_2SO_4$

**iii)** $CH_2{=}CHCH{=}CH_2$

**c)** **i)** $CH_3CH_2CH(OH)CH_3$

**ii)** Either by warming with dilute $H_2SO_4$(aq) or by dissolving in concentrated $H_2SO_4$ and adding water

**iii)** $K_2Cr_2O_7$ or $KMnO_4$ with dilute $H_2SO_4$

**d)** Functional group isomerism or structural isomerism

**2** **a)** Conc. $H_2SO_4$ or conc. $H_3PO_4$ and heat or pass vapour over hot $Al_2O_3$

**b)** **i)** $C_3H_7OH + 2[O] \rightarrow C_2H_5CO_2H + H_2O$

**ii)** Sodium or potassium dichromate, $H^+$/acidified and heated under reflux

c) **U** = $CH_3CH(OH)CH_3$
**V** = $CH_3CHBrCH_3$

d) Reagent = sodium or potassium hydroxide and ethanol (alcohol) and heated under reflux

# Topic 18: Aldehydes and ketones

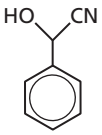
## Answers to in-text questions

### Questions 18.1

1 Cyclohexanone
2 2,2-dimethylpropanal
3 Heptan-4-one

### Questions 18.2

1 **I** is $NaBH_4$ *or* $LiAlH_4$ *or* $H_2$ + Ni; **II** is $Al_2O_3$ at 350 °C *or* conc. $H_2SO_4$ at 180 °C; **III** is HCN + trace of NaCN; **IV** is $H_2$ + Ni *or* $LiAlH_4$
**A** is $(CH_3)_2CHOH$; **B** is




2 a) $NaBH_4$
b) $H_2$ + Ni

### Question 18.3

**G** is $CH_3CH_2CH_2CHO$
**H** is $CH_3CH{=}CHCH_2OH$ or $CH_2{=}CHCH_2CH_2OH$

### Questions 18.4

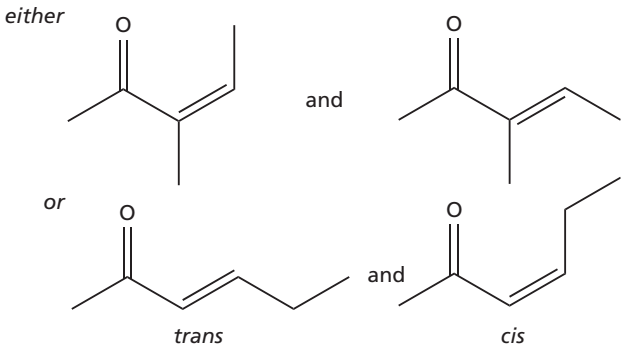
1 Fehling's solution *or* Tollens' reagent *or* alkaline aqueous iodine
2 Bromine water *or* Fehling's solution *or* Tollens' reagent *or* 2,4-DNPH

### Questions 18.5

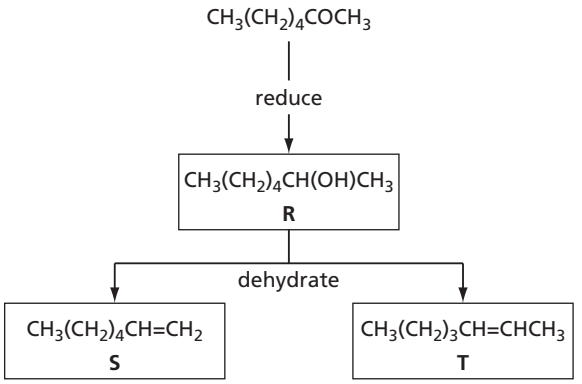
There is only one ketone with the formula $C_4H_8O$, namely butan-2-one, $CH_3CH_2COCH_3$, which will give the tri-iodomethane reaction, so this is **E**. Compound **F** is an aldehyde: either $CH_3CH_2CH_2CHO$ or $(CH_3)_2CHCHO$. Both of these would reduce Fehling's solution, whereas the ketone **E** will not.

## Answers to end of topic questions

1 a) $CH_3COCH_2CH(OH)(CH_3)_2$
b) Alkene would decolour bromine or potassium permanganate
Ketone would form an orange precipitate when a solution of 2,4-DNPH is added
c) i) Dehydration or elimination
ii) $Al_2O_3$ or $H_2SO_4$(conc.)
d) $NaBH_4$ in methanol-water or $LiAlH_4$ in dry ether
e)




2 a) i)




ii) Reduction $NaBH_4$ or $LiAlH_4$
Dehydration conc. $H_2SO_4$ or conc. $H_3PO_4$

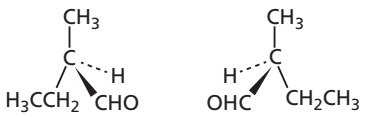
b)

| Tollens' reagent | No reaction |
|---|---|
| HCN | $CH_3(CH_2)_4C(OH)CH_3$ <br> \| <br> CN |
| $K_2Cr_2O_7/H^+$ | No reaction |

c) With $Na_2CO_3$ or $NaHCO_3$ there would be effervescence
With $C_2H_5OH$/conc. $H_2SO_4$ there would be the sweet smell of an ester
With $K_2Cr_2O_7/H^+$ the orange solution would turn green

3 a) i) **A** = $CH_3CH_2CH_2CH_2CHO$
**B** = $CH_3CH_2CH(CH_3)CHO$
**C** = $(CH_3)_2CHCH_2CHO$
**D** = $(CH_3)_3CCHO$

ii)



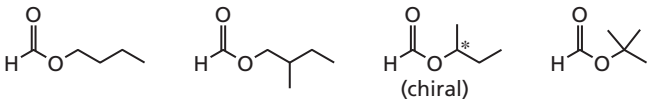
b) i) Fehling's/Benedict's = (brick)-red precipitate
or Tollens' = grey-black precipitate
or dichromate = orange to green with the aldehyde
or manganate = purple to colourless
ii) 2,4-DNP(H) (Brady's reagent) gives an orange-yellow precipitate

# Topic 19: Carboxylic acids, and organic synthesis

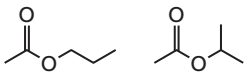
## Questions 19.1

There are nine esters with the formula $C_5H_{10}O_2$, of which one is chiral.

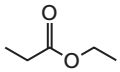
Four are methanoates, $HCO_2C_4H_9$



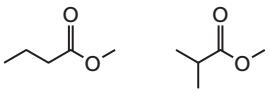

Two are ethanoates, $CH_3CO_2C_3H_7$



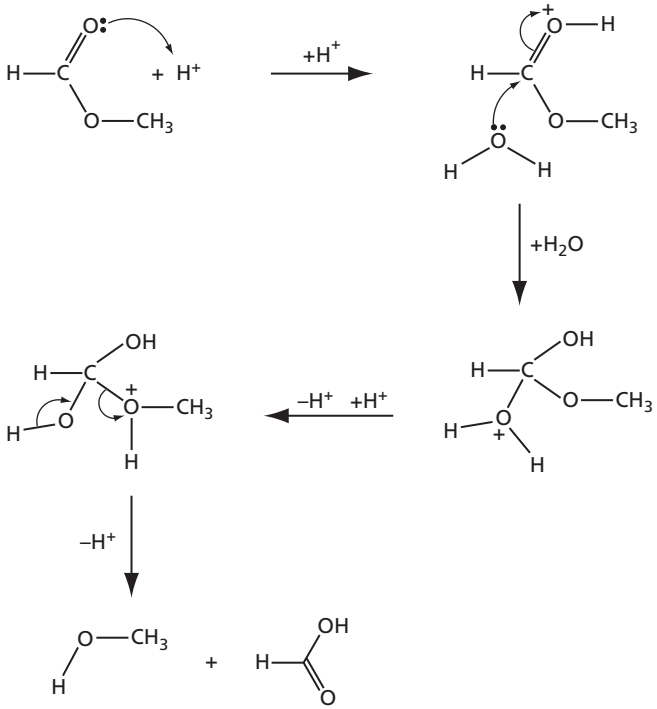
One is a propanoate



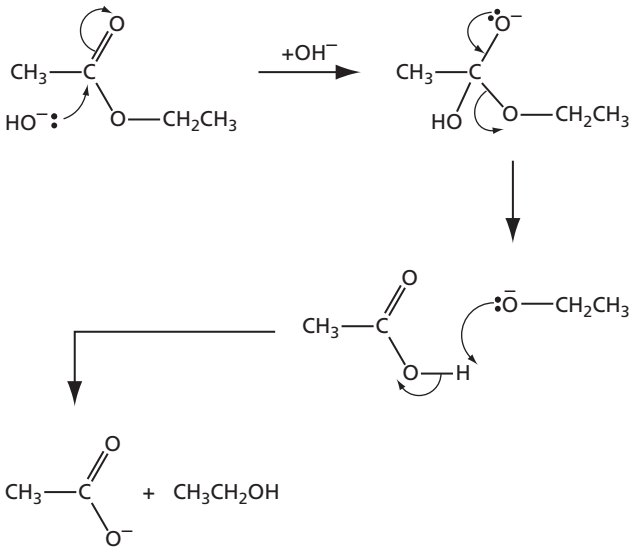
Two are methyl esters, $C_3H_7CO_2CH_3$



## Question 19.2




## Question 19.3




## Questions 19.4

1 $CH_3CH_2Br \rightarrow CH_3CH_2OH \rightarrow CH_3CHO \rightarrow CH_3CH(OH)CN$
Reagents and conditions:
i) NaOH(aq) + heat
ii) $Na_2Cr_2O_7$ + dil. $H_2SO_4$ + distil
iii) HCN + NaCN

2 $CH_3CN \rightarrow CH_3CO_2H$
$CH_3CO_2H + CH_3OH \rightarrow CH_3CO_2CH_3$
Reagents and conditions:
i) Heat with NaOH(aq), then add $H^+$(aq)
ii) Heat with a trace of conc. $H_2SO_4$

3 $CH_3CH_2OH \rightarrow CH_3CH_2Br \rightarrow CH_3CH_2CN \rightarrow CH_3CH_2CO_2H \rightarrow CH_3CH_2CH_2OH$
Reagents and conditions:
i) Heat with HBr
ii) Heat with NaCN in ethanol
iii) Heat with NaOH(aq), then add $H^+$(aq)
iv) $LiAlH_4$ in dry ether

4 $CH_3CH{=}CH_2 \rightarrow (CH_3)_2CHOH$
$CH_3CH{=}CH_2 \rightarrow (CH_3)_2CHBr \rightarrow (CH_3)_2CHCN \rightarrow (CH_3)_2CHCO_2H$
$(CH_3)_2CHCO_2H + (CH_3)_2CHOH \rightarrow (CH_3)_2CHCO_2CH(CH_3)_2$
Reagents and conditions:
i) Add conc. $H_2SO_4$, then dilute with water
ii) HBr
iii) Heat with NaCN in ethanol
iv) Heat with NaOH(aq), then add $H^+$(aq)
v) Heat with a trace of conc. $H_2SO_4$

### Questions 19.5

1 Step 1: reduction, $LiAlH_4$
Step 2: nucleophilic substitution, HBr
Step 3: nucleophilic substitution, NaCN

2 Step 1: oxidation, $Na_2Cr_2O_7$ + dil. $H_2SO_4$
Step 2: nucleophilic addition, HCN + NaCN
Step 3: hydrolysis, NaOH(aq), then add $H^+$(aq)

### Question 19.6

to form **W**: $NaBH_4$
to form **X**: $H_2$ + Ni
to form **Y**: $LiAlH_4$
to form **Z**: $LiAlH_4$, then $H_2$ + Ni (or vice versa)

### Answers to end of topic questions

1 a) i) Structural isomers differ as to which atoms in the molecules are bonded to which but they have the same molecular formula.

ii) There is a —C═C— bond present that cannot rotate or there is an asymmetric carbon atom

b) $NaO_2CCH(OH)CH(OH)CO_2Na$

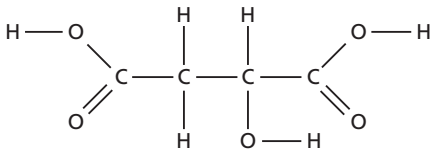
c) It does not as there is no chiral carbon atom

d) i) C : H : O = 35.8 ÷ 12 : 4.5 ÷ 1 : 59.7 ÷ 16
= 2.98 : 4.5 : 3.37
= 1 : 1.5 : 1.25 or 4 : 6 : 5
Empirical formula is $C_4H_6O_5$

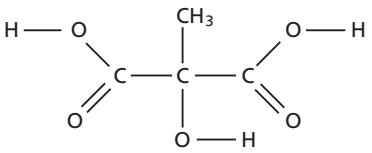
ii) $C_4H_6O_5$ = 12 × 4 + 1 × 6 + 16 × 5 = 134
Molecular formula is $C_4H_6O_5$

e) i) $n(OH^-)$ = 29.4 × 1.00 ÷ 1000 = 0.0294
1.97 g W = 0.0294 mol NaOH
134 g W = 0.0294 × 134 ÷ 1.97 = 1.999 ≈ 2
Number of —$CO_2H$ groups present in 1 molecule of W is 2

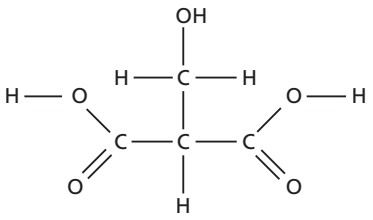
ii)



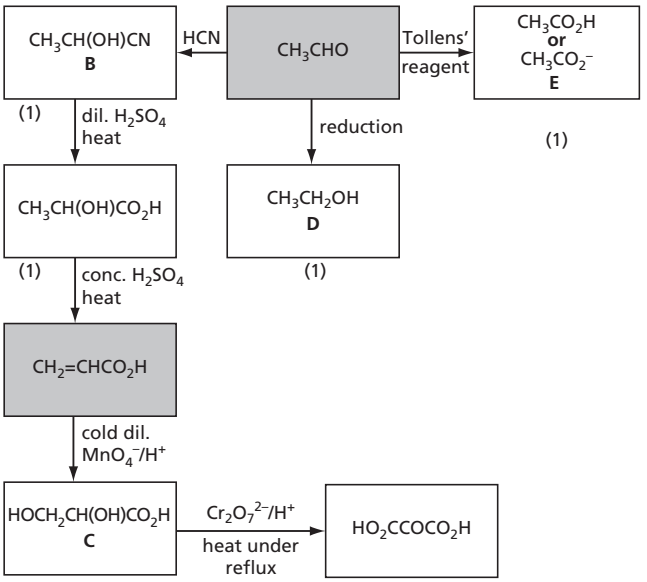
or



or



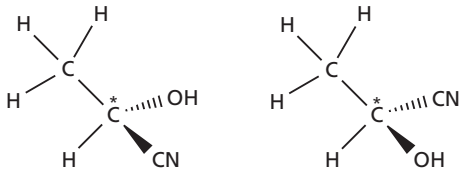
2 a)




b) i) $HOCH_2CH(OH)CO_2CH_2CH_3$

ii) $CH_3CO_2CH_2CH(OCOCH_3)CO_2H$

c)




## Topic 20: Mass spectrometry and infrared spectroscopy

### Answers to in-text questions

### Questions 20.1

IR spectrum of **V**: contains a 'peak' at 1750 $cm^{-1}$ showing a C═O group.
If **V** gives a silver mirror, it must be an aldehyde.
Therefore **V** is $CH_3CH_2CHO$.
IR spectrum of **W**: contains a broad 'peak' at 3300 $cm^{-1}$ showing alcohol –OH group.
**W** is obtained from **V**, so **W** is $CH_3CH_2CH_2OH$.
Reagent **X** is a reducing agent: $NaBH_4$, $LiAlH_4$ or $H_2$ + Ni.

### Questions 20.2

1 52.06
2 B = 10.8, Ne = 20.2, Mg = 24.3
3 38.5% $^{191}Ir$, 61.5% $^{193}Ir$

### Question 20.3

Ethanoic acid, $CH_3CO_2H$

### Questions 20.4

$100 \times 2.9/(1.1 \times 43.9) = 6.005$, in other words **6** carbon atoms.
$6 \times 12 = 72$, leaving $132 - 72 = 60$
$3 \times$ oxygen $= 48$, leaving $60 - 12 = 12$ hydrogens, giving **$C_6H_{12}O_3$**

### Questions 20.5

*m/e* = 26 → $C_2H_2$
*m/e* = 27 → $C_2H_3$
*m/e* = 28 → $C_2H_4$ (or possibly CO)
from: $CH_3CH_2CHO \rightarrow CH_3CH_2^+ \rightarrow CH_2CH_2^+ \rightarrow CH_2CH^+ \rightarrow CHCH^+$
(28) (27) (26)

### Questions 20.6

*m/e* = 27–29 could be $C_2H_3$, $C_2H_4$ and $C_2H_5$
*m/e* = 45 could be $CO_2H$ (M – $C_2H_5$)
*m/e* = 57 could be $C_2H_5CO$ (M – OH)
*m/e* = 73 could be $C_3H_5O_2$ (M – H)
*m/e* = 74 could be $C_3H_6O_2$ ($M^+$)
Propanoic acid fits the information given

$CH_3CH_2CO_2H \rightarrow CH_3CH_2CO^+$ (57) + OH

$CH_3CH_2CO_2H \rightarrow CH_3CH_2^+$ (29) + $CO_2H$ *or* $CH_3CH_2$ + $CO_2H^+$ (45)

### Answers to end of chapter questions

1 a) 3-hydroxybutan(-2-)one
b) $H_2/Cr_2O_7^{2-}$ and heated under reflux
c) i) Absorption at 1670–1740 C═O
Absorption at 2850–3000 C—H
Absorption at 3200–3650 O—H
ii) No absorption at 3200–3650; O—H disappears as there is no O—H bond in diacetyl.

2 a) i) $n = 100 \times (M+1)/(1.1 \times M) = 100 \times 3.4/(1.1 \times 33.9) = 9.1$, so 9 carbon atoms
ii) $C_9H_{10}O_2$
iii) (150 – 119 = 31), hence fragment is $CH_3O$
b) **V** is C=O and **W** is C—O

3 a) 101 = $P^{35}Cl^{35}Cl$
103 = $P^{35}Cl^{37}Cl$
105 = $P^{37}Cl^{37}Cl$
b) 9 : 6 : 1

4 a) M:M+1 = $100/(1.1 \times n)$
$20.4/0.9 = 100/(1.1 \times n)$
$x = 4$
b) $C_4H_{10}O$

## Topic 21: Practical work

### Answers to in-text questions

### Questions 21.1

1 **D** is $FeBr_2$; **E** is $Fe(OH)_2$; **F** is HBr; **G** is $Br_2$
Equations:
$Fe^{2+} + 2OH^- \rightarrow Fe(OH)_2$ (green ppt) **(E)**
$2Fe(OH)_2 + H_2O + \frac{1}{2} O_2 \rightarrow 2Fe(OH)_3$ (ppt turns brown)
$Br^- + 2H^+ \rightarrow 2HBr$ (acidic gas) **(D)**
$2HBr + H_2SO_4 \rightarrow Br_2 + SO_2 + 2H_2O$ (red-brown gas) **(G)**
$HBr + NH_3 \rightarrow NH_4Br$ (steamy white fumes) **(F)**
$Ag^+ + Cl^- \rightarrow AgCl$ (ppt formed)
$AgCl + 2NH_3 \rightarrow Ag(NH_3)_2^+$ (AgCl dissolves and ppt of $Fe(OH)_2$ formed, see first equation)

2 **H** is ZnO; **I** is $ZnCl_2$(aq)
Equations:
$ZnO + 2H^+ \rightarrow Zn^{2+} + H_2O$ (insoluble in water but dissolves in HCl)**(H)**
$Zn^{2+} + 2OH^- \rightarrow Zn(OH)_2$ (white ppt with NaOH or $NH_4OH$)**(H)**
$Zn(OH)_2 + 2OH^- \rightarrow Zn(OH)_4^{2-}$ (soluble in excess NaOH)
$Zn(OH)_2 + 4NH_3 \rightarrow Zn(NH_3)_4^{2+} + 2OH^-$ (soluble in excess $NH_3$)

### Questions 21.2

1 **L** is R–Br
Equations: R can be any alkyl group (not $CH_3$), e.g. $C_4H_9$
$RBr + OH^- \rightarrow ROH + Br^-$ (partially dissolves in NaOH)
$Br^- + Ag^+ \rightarrow AgBr$ (pale yellow ppt)**(M)**
$AgBr + 2NH_3 \rightarrow Ag(NH_3)_2^+ + Br^-$ (soluble in conc. $NH_3$)
$RBr + NH_3 \rightarrow RNH_3^+ + Br^-$ (or $RBr + 2NH_3 \rightarrow RNH_2 + NH_4Br$)

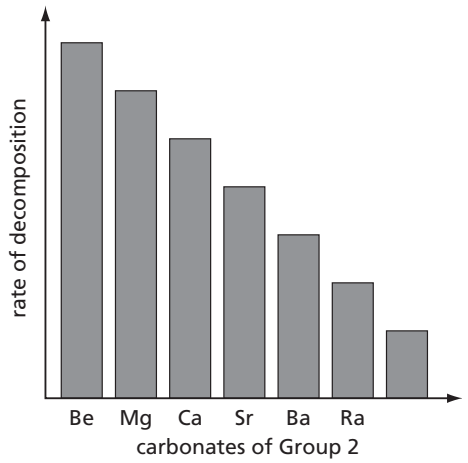
2 **O** is R–$CO_2H$
Equations: R is a small alkyl group, e.g $CH_3$
$RCO_2H + PCl_5 \rightarrow RCOCl + POCl_3 + HCl$ (fumes with $PCl_5$)
$2RCO_2H + CO_3^{2-} \rightarrow 2RCO_2^- + CO_2 + H_2O$
(or $RCO_2H + CO_3^{2-} \rightarrow RCO_2^- + HCO_3^- + CO_2$)

### Answers to end of topic questions

*This answer is provided as an indication of what might be given. The question asks for the student's own plans.*

1 a) i) The rate of decomposition slows down as you go down the Group as the carbonates become more stable. This is because the increasing size of the cation makes it more difficult to polarise the carbonate anion and highly polarised $CO_3^{2-}$ groups liberate carbon dioxide more readily

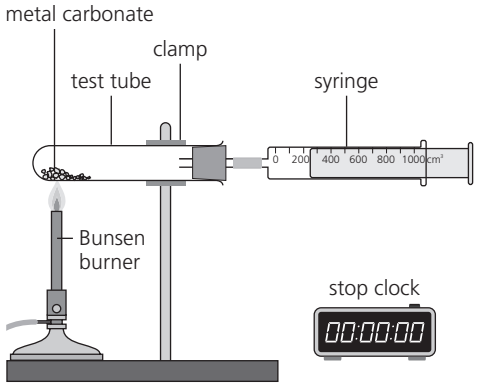
ii)




b) i) The independent variable is the carbonate being heated

ii) The dependent variable is the time taken for decomposition

c) **i** and **ii**




d) **i–iii**

1 Set up the equipment as shown above.

2 Measure 0.01 mol of each carbonate in turn.

| Group 2 element | $A_r$ | $M_r$ of $CO_3^{2-}$ | Relative molecular mass |
|---|---|---|---|
| Mg | 24.3 | 60 | 84.3 |
| Ca | 40.1 | 60 | 100.1 |
| Sr | 87.6 | 60 | 147.6 |
| Ba | 137.3 | 60 | 197.3 |

3 Place carbonate in a clean test tube and fix in a clamp above the Bunsen burner.

4 Establish that the same Bunsen setting is used each time and that the test tube is always at the same height above the Bunsen.

5 Start the stop clock when the lit Bunsen is under the test tube.

6 Stop the clock when 20 $cm^3$ of gas has been collected in the syringe.

7 Repeat for each carbonate.

e) Heatproof gloves need to be used when removing the hot test tube at the end of each experiment. Safety glasses should be worn.

f)

| Carbonate | First time to collect 20 $cm^3$/s | Second time to collect 20 $cm^3$/s | Average/s |
|---|---|---|---|
| $MgCO_3$ | | | |
| $CaCO_3$ | | | |
| $SrCO_3$ | | | |
| $BaCO_3$ | | | |

g) Screens could be set up round the equipment to reduce the loss of heat to the surrounding air. A longer tube could be inserted between the test tube and the gas syringe, to allow the $CO_2$ to cool to room temperature before its volume is read.

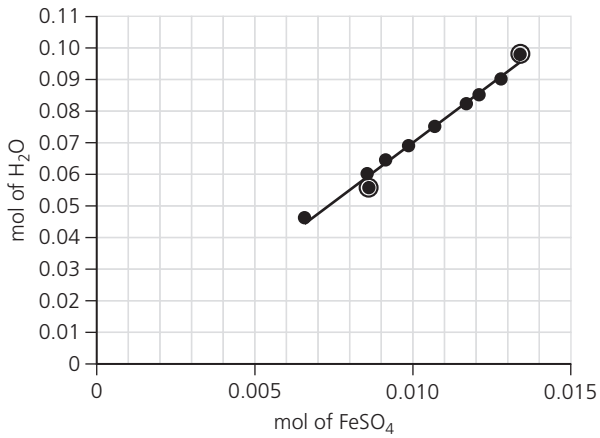
2 a) $M_r$ $FeSO_4 = 55.8 + 32.1 + (4 \times 16) = 151.9$

$M_r$ $H_2O = (2 \times 1) + 16 = 18$

b)

| A | B | C | D | E | F | G |
|---|---|---|---|---|---|---|
| Mass of crucible/g | Mass of crucible + $FeSO_4 \cdot xH_2O$/g | Mass of crucible + $FeSO_4$/g | $FeSO_4$ (C – A) /g | $H_2O$ (B – C) /g | $FeSO_4$ /151.9 mol | $H_2O$/18 mol |
| 15.20 | 17.03 | 16.20 | 1.00 | 0.83 | 0.00658 | 0.0461 |
| 15.10 | 17.41 | 16.41 | 1.31 | 1.00 | 0.00862 | 0.0556 |
| 14.95 | 17.33 | 16.25 | 1.30 | 1.08 | 0.00856 | 0.0600 |
| 15.15 | 17.70 | 16.54 | 1.39 | 1.16 | 0.00915 | 0.0644 |
| 15.05 | 17.79 | 16.55 | 1.50 | 1.24 | 0.00987 | 0.0689 |
| 14.90 | 17.88 | 16.53 | 1.63 | 1.35 | 0.0107 | 0.0750 |
| 14.92 | 18.18 | 16.70 | 1.78 | 1.48 | 0.0117 | 0.0822 |
| 15.30 | 18.67 | 17.14 | 1.84 | 1.53 | 0.0121 | 0.0850 |
| 15.07 | 18.64 | 17.02 | 1.95 | 1.62 | 0.0128 | 0.0900 |
| 15.01 | 18.80 | 17.04 | 2.03 | 1.76 | 0.0134 | 0.0978 |

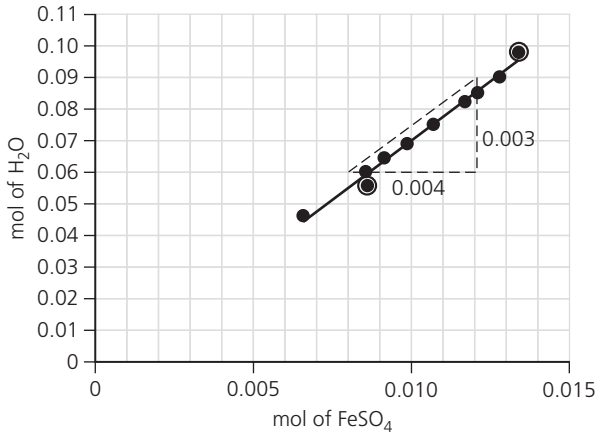
c) and d)




d) Point 2: The anhydrous $FeSO_4$ has absorbed some water.

Point 10: The anhydrous $FeSO_4$ has decomposed.

**e)**




Gradient = 0.03 ÷ 0.004 = 7.5

**f)** Enough readings were taken so that most of the results are on the line, which indicates that the results are reliable.

**g)** **i)** $FeSO_4.7H_2O$

**ii)** The ratio of moles of $H_2O$ : $FeSO_4$ is given by the gradient of the slope.

# Topic 22: Further energy changes

## *Answers to in-text questions*

### *Questions 22.1*

**1** Similar to Figure 22.1 but with 2 × Na and two EA for O

$(2 \times +107) + (\frac{1}{2} \times +496) + (2 \times +494) - 141 + 790 + LE = -414$

LE = −414 − 2099; Ans = −2513 kJ mol$^{-1}$

**2** Similar to Figure 22.2 but with O instead of 2Cl

$+147 + (\frac{1}{2} \times +496) + 736 + 1450 - 141 + 790 + LE = -602$

LE = −602 − 3230; Ans = −3832 kJ mol$^{-1}$

### *Questions 22.2*

**1** **a)** Similar to Figure 22.2 but with Ba instead of Mg and S instead of 2Cl

**b)** +180 +249.2 +502 +966 −141.4 +790.8 +LE = −595.8

LE = −595.8 − 2546.6; Ans = −3142 kJ mol$^{-1}$

**2** **a)** Larger $K^+$ ion makes attraction smaller

**b)** $Mg^{2+}$ ion is slightly smaller than $Na^+$ ion, but big factor are the two charges on the $Mg^{2+}$ and $S^{2-}$ ions. This increases the magnitude of LE by a factor of four.

**c)** Ions similar size but double charge on $Ca^{2+}$ ion and there are twice as many $Cl^-$ ions. This increases the magnitude of LE by a factor of four but larger $Cl^-$ to $Cl^-$ repulsion makes it slightly less than this.

### *Questions 22.3*

**1** Similar to Figure 22.2 but with Al instead of Mg and 3F not 2Cl

**2** $+324.3 + 577 + 1820 + 2740 + 3 \times 79.0 - 3 \times 328 + LE = -1504.1$

LE = −1504.1 − 4714.3; Ans = −6218 kJ mol$^{-1}$

**3** Similar to Figure 22.5 but with Al instead of Mg and 3F instead of 2Cl

**4** $\Delta H_{hyd} = -4750 - 3 \times 473 = -6169$ kJ mol$^{-1}$

$\Delta H_{sol} = -6169 - (-6218)$; Ans = +49 kJ mol$^{-1}$

### *Question 22.4*

+19.6 J mol$^{-1}$ K$^{-1}$

### *Questions 22.5*

**1** +109 J mol$^{-1}$ K$^{-1}$

**2** +7.9 J mol$^{-1}$ K$^{-1}$

### *Questions 22.6*

**1** +160 J mol$^{-1}$ K$^{-1}$

**2** −128.7 J mol$^{-1}$ K$^{-1}$

**3** −198.8 J mol$^{-1}$ K$^{-1}$

### *Questions 22.7*

**1** −2108.6 kJ mol$^{-1}$ (assuming $H_2O(l)$ not $H_2O(g)$)

**2** −115.2 kJ mol$^{-1}$

### *Questions 22.8*

**1** 405 K

**2** **a)** +116 J mol$^{-1}$ K$^{-1}$

**b)** = −68.6 kJ mol$^{-1}$

**c)** Very large increase

**3** **a)** +9 kJ mol$^{-1}$

**b)** −84 kJ mol$^{-1}$

**c)** $\Delta H^\ominus$ and $\Delta S^\ominus$ will not remain the same as there will be phase changes when the heptane and methylbenzene boil.

### *Questions 22.9*

**1** H—H bond and weak π bond in ethene broken, but two strong C—H bonds formed: $\Delta H^\ominus$ negative.

$\Delta n = -1$: $\Delta S^\ominus$ negative

**2** Intermolecular hydrogen bonds broken: $\Delta H^\ominus$ positive; (l) to (g) transition: $\Delta S^\ominus$ positive

**3** Weak O—O bond broken and strong O═O bond formed: $\Delta H^\ominus$ negative. Gas released: $\Delta S^\ominus$ positive

**4** $NH_4^+$ and $NO_3^-$ ions do not hydrate strongly as they are singly charged; $\Delta H^\ominus$ positive; ordering of water molecules greater than disorder created by breaking up lattice; $\Delta S^\ominus$ negative

## Question 22.10

$\Delta G = \Delta H - T\Delta S$

$\Delta G$ becomes zero for $MgCO_3$ when +100, $300 = T \times +174$.

$T = 576\,K$ or $303\,^oC$

$BaCO_3$ when +269, $300 = T \times +172$. $T = 1566\,K$ or $1293\,^oC$

## Answers to end of topic questions

**1 a)** $Ca^{2+}(g) + 2Cl^-(g) \rightarrow CaCl_2(s)$

**b) i)** $CaF_2$ has a larger lattice energy than $CaCl_2$ because $F^-$ is smaller than $Cl^-$

**ii)** CaS has a larger lattice energy than $CaCl_2$ because $S^{2-}$ is more highly charged than $Cl^-$

**c)** LE + –[178 + 590 + 1150] – [244 – 2 × 349] –796 = –2260 kJ mol$^{-1}$

**d) i)** Ca : C : H : O

28.2 ÷ 40.1 : 25.2 ÷ 12 : 1.4 ÷ 1 : 45.1 ÷ 16

0.703 : 2.10 : 1.4 : 2.82

1 : 3 : 2 : 4

Empirical formula is $CaC_3H_2O_4$

**ii)** Malonic acid is $CH_2(CO_2H)_2$

**2 a) i)** The enthalpy change of hydration is the enthalpy change when one mole of gaseous ions dissolves in an infinite volume of water at 1 atm pressure and 298 K

**ii)** $Mg^{2+}(g) + aq \rightarrow Mg^{2+}(aq)$

**iii)** $Mg^{2+}$ is smaller and more highly charged than $Ca^{2+}$ and so attracts water molecules more strongly.

**iv)** $O^{2-}$ reacts with water rather than just dissolving in it $O^{2-} + H_2O \rightarrow 2OH^-$

**b)** Apparatus – insulated calorimeter, water, thermometer

Measure – the volume/mass of water, the temperature of the water, the mass of $MgCl_2$, the highest temperature

**c) i)** $\Delta H^\ominus_{sol} = 641 - 801 = -160$ kJ mol$^{-1}$

**ii)** $\Delta H^\ominus_{hyd} = (1890 - 2526 - 160) \div 2 = -398$ kJ mol$^{-1}$

**d)** $MgSO_4$ is more soluble than $BaSO_4$ because of the smaller charge density of $Ba^{2+}$, which leads to smaller LE and HE. However, HE decreases more than LE from Mg to Ba.

**3 a)** The sulphates become less soluble as you go down Group 2. Both the lattice energies and hydration energies decrease but HE decreases more than LE. The general trend is for $\Delta H^\ominus_{sol}$ to become more positive going down the Group.

**b) i)** Mg: $\Delta H = 2993 - 1890 - (2 \times 550) = +3$ kJ mol$^{-1}$

Sr: $\Delta H = 2467 - 1414 - (2 \times 550) = -47$ kJ mol$^{-1}$

**ii)** $Sr(OH)_2$ is likely to be more soluble since $\Delta H$ is more negative, assuming other factors such as temperature $\Delta S$ remain the same.

**iii)** $Sr(OH)_2$ is likely to be more soluble in cold water since $\Delta H$ is negative.

**c) i)** $K_{sp} = [Ca^{2+}][OH^-]^2$ mol$^3$ dm$^{-9}$

**ii)** $n(H^+) = n(OH^-) = 0.05 \times 21 \div 1000 = 1.05 \times 10^{-3}$ mol in 25cm$^3$

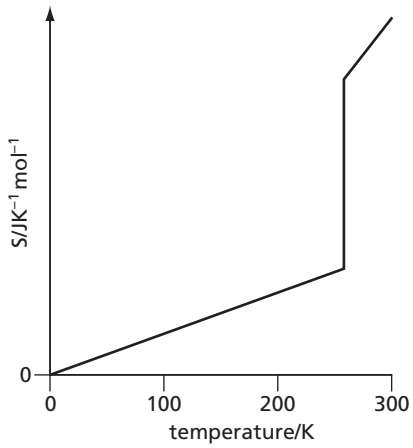
$[OH^-] = 1.05 \times 10^{-3} \times 1000 \div 25 = 4.2 \times 10^{-2}$ mol dm$^{-3}$

$[Ca^{2+}] = 2.1 \times 10^{-2}$ mol dm$^{-3}$

$K_{sp} = 2.1 \times 10^{-2} \times (4.2 \times 10^{-2})^2 = 3.7 \times 10^{-5}$

**iii)** $Ca(OH)_2$ would be less soluble in NaOH compared to water, since the equilibrium position will be shifted to the $Ca(OH)_2(s)$ side because of the high concentration of $OH^-$ ions.

**4 a)**




**b)**

| | $\Delta S$ is negative | $\Delta S$ is positve |
|---|---|---|
| solid dissolving in water | | ✓ |
| water boiling to steam | | ✓ |

**c)** $\Delta H^\ominus = (2 \times C{=}O) + (3 \times H{-}H) - (3 \times C{-}H) - (C{-}O) - (3 \times O{-}H)$

$\Delta H^\ominus = (2 \times 805) + (3 \times 436) - (3 \times 410) - (1 \times 360) - (3 \times 460)$

$\Delta H^\ominus = 1610 + 1308 - 1230 - 360 - 1380 = -52$(kJ mol$^{-1}$)

**d) i)** $\Delta S^\ominus = 127 + 70 - (214 + 3 \times 131) = -410$ (J K$^{-1}$ mol$^{-1}$)

**ii)** $\Delta G^\ominus = \Delta H^\ominus - T\Delta S$

$\Delta G^\ominus = -131 - (298 \times -0.41) = -8.8(2)$ (kJ mol$^{-1}$)

**iii)** As the temperature increases the feasibility decreases.

**e) i)** $2CH_3OH + 3O_2 \rightleftharpoons 2CO_2 + 4H_2O$

**ii)** $E^\ominus_{cell} = 1.23 - 0.02 = 1.21$ V

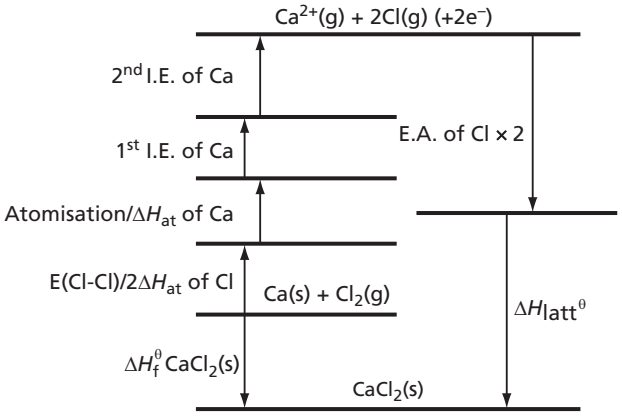
**5 a) i)** $2Ca(NO_3)_2(s) \rightarrow 2CaO(s) + 4NO_2(g) + O_2(g)$

**ii)** A brown gas is given off while the white solid stays the same.

**b)** Solubility of sulfates decreases down Group 2. $\Delta H_{latt}$ and $\Delta H_{hyd}$ both decrease, although $\Delta H_{latt}$ decreases by a smaller extent. $\Delta H_{sol}$ becomes less negative.

6 a) i) $Ca^{2+}(g) + 2Cl^-(g) \rightarrow CaCl_2(s)$

ii)




iii) $\Delta H_{latt} = -796 - 242 - 178 - 590 - 1150 + (2 \times 349) = -2258\,kJ\,mol^{-1}$

b) At a higher temperature the molecules of a gas have more (translational) energy. There are more ways of arranging this increased number of energy quanta, and so the gas is more disordered.

c) i)

| reaction | sign of $\Delta S^\ominus$ |
|---|---|
| $CO(g) + O_2(g) \rightarrow CO_2(g)$ | negative |
| $Mg(s) + ½\ O_2(g) \rightarrow MgO(s)$ | **negative** |
| $CuSO_4(s) + 5H_2O(l) \rightarrow CuSO_4.5H_5O(s)$ | **negative** |
| $NaHCO_3(s) + H^+(aq) \rightarrow Na^+(aq) + CO_2(g) + H_2O(l)$ | **positive** |

ii) There is a reduction in the overall number of gaseous molecules.

d) $\Delta S_f^\ominus = 386 - (192 + (3 \times 131)) = -199\,(J\,K^{-1}\,mol^{-1})$

e) i) $\Delta G^\ominus = \Delta H^\ominus - T\Delta S^\ominus$
$= 117 - ((298 \times 175)/1000)$
$= (+)64.85\ (kJ\,mol^{-1})$

ii) $\Delta G^\ominus$ is positive and so the reaction is not spontaneous (at 298 K).

# Topic 23: Quantitative kinetics

## Answers to in-text questions

### Questions 23.1

1 Using experiments 2, 4, 5 $[ClO^-]$ constant, $[I^-]$ varies in ratio 1.0 : 0.73 : 1.4
Rate varies in ratio 6.2 : 4.6 : 8.6 or 1.0 : 0.74 : 1.4
Therefore 1st order with respect to $[I^-]$
Using experiments 1, 2, 3 $[I^-]$ constant, $[ClO^-]$ varies in ratio 0.73 : 1.0 : 1.4
Rate varies in ratio 4.5 : 6.2 : 8.7 or 0.73 : 1.0 : 1.4
Therefore 1st order with respect to $[ClO^-]$

2 Rate = $k[I^-(aq)]^1[ClO^-(aq)]^1$

3 Using experiment 1, $4.5 \times 10^{-4} = k[0.0010][0.0072]$;
Answer $k = 62\,mol^{-1}\,dm^3\,s^{-1}$

### Questions 23.2

1 Rate = $k[A][B]$

2 Rate = $k[A][B][D]$

3 Rate = $k[A][B][D]$

### Questions 23.3

1 a) $H_2O_2 + I^- \rightarrow HOI + OH^-$ slow rate-determining step: $HOI + 2I^- \rightarrow OH^- + I_3^-$ fast

b) $ClO^- + H^+ \rightarrow HClO$ slow: $HClO + I^- \rightarrow IO^- + Cl^- + H^+$ slow
These answers are suggestions as other solutions are possible.

c) There are various possibilities. One could be:
$H^+(aq) + BrO_3^-(aq) \rightarrow HBrO_3(aq)$
$HBrO_3(aq) + Br^-(aq) \rightarrow BrO^-(aq) + HBrO_2(aq)$ slow rate-determining
$HBrO_2(aq) + Br^-(aq) \rightarrow BrO^-(aq) + HbrO(aq)$ rapid
$HBrO + Br^-(aq) \rightarrow Br_2(aq) + OH^-(aq)$ rapid
Any postulated mechanism must have only one $H^+$, one $BrO_3^-$ and one $Br^-$ before (or at) the rds.

2 a) Acid and base catalysis going on at same time.

b) Rate of forward reaction = $k_1[H_2][I_2]$;
rate of back reaction = $k_{-1}[HI]^2$.
Both reactions taking place.

### Question 23.4

Uncatalysed reaction is slow as it involves two negatively charged ions. Addition of $Fe^{2+}$ makes it possible for the reaction to go in two steps, both involving oppositely charged ions. The following values show that $S_2O_8^{2-}$ will oxidise $Fe^{2+}$ and that $Fe^{3+}$ will oxidise $I^-$.

$I_2 + 2e^- \rightleftharpoons 2I^-$ $\quad E^\ominus = +0.54\,V$
$Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$ $\quad E^\ominus = +0.77\,V$
$S_2O_8^{2-} + 2e^- \rightleftharpoons 2SO_4^{2-}$ $\quad E^\ominus = +2.01\,V$

The following values show that $VO_3^-$, $ClO^-$ and $NO_3^-$ could oxidise $I^-$. However they are all ineffective catalysts as they are negatively charged and repelled by $I^-$ ions.

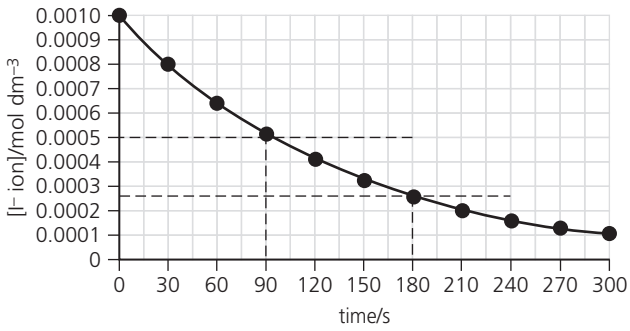
$VO_3^- + 4H^+ + e^- \rightleftharpoons VO^{2+} + 2H_2O$ $\quad E^\ominus = +1.00\,V$
$ClO^- + H_2O + 2e^- \rightleftharpoons Cl^- + 2OH^-$ $\quad E^\ominus = +0.89\,V$
$NO_3^- + 3H^+ + 2e^- \rightleftharpoons NO_2^- + H_2O$ $\quad E^\ominus = +0.94\,V$

## Answers to end of topic questions

1 a) The solution will become brown/purple.

b)

| Case | Numerical value | | |
|---|---|---|---|
| | a | b | c |
| Step 1 is the slowest overall | 1 | 1 | 0 |
| Step 2 is the slowest overall | 1 | 1 | 1 |
| Step 3 is the slowest overall | 1 | 2 | 2 |




**c)** Rate = $6.5 - 7.5 \times 10^{-6}$ mol dm$^{-3}$ s$^{-1}$

**d)** Half life is approximately 90 s. The second half life is also 90 s.

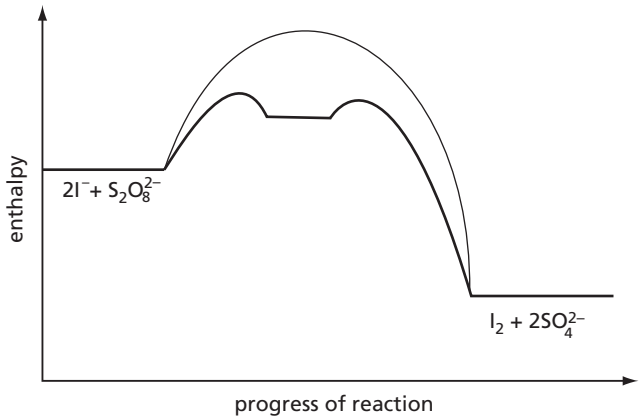
**e)** As $[H_2O_2]$ increases from 0.05 to 0.07, the relative rate increases from 1.0 to 1.4. $0.07 \div 0.05 = 1.4$ and $1.4 \div 1.0 = 1.4$ so the rate order with respect to $[H_2O_2]$ is 1.
As $[H_2O_2]$ increases from 0.05 to 0.09 the rate increases from 1.0 to 1.8. $0.09 \div 0.05 = 1.8$ and $1.8 \div 1.0 = 1.8$ so the rate is independent of $[H^+]$.

**f)** The first step

**2 a) i)** Homogeneous

**ii)** In reaction 1 the ions, $I^-$ and $SO_4^{2-}$, are both negatively charged so repel each other. In reactions 2 and 3 the ions, $I^-$ and $Fe^{3+}$, and $Fe^{2+}$ and $S_2O_8^{2-}$ have opposite charges so attract each other.

**iii)**




**b) i)** It leads to acid rain, which can kill plants, causes corrosion of buildings and makes lakes more acidic.

**ii)** Volcanoes and the burning of fossil fuels

**iii)** $SO_2 + NO_2 \rightarrow SO_3 + NO$
$2NO + O_2 \rightarrow 2NO_2$

**3 a) i)** The order with respect to $[CH_3CHO] = 1$
The order with respect to $[CH_3OH] = 1$
The order with respect to $[H^+] = 1$

**ii)** Rate = $k[CH_3CHO][CH_3OH][H^+]$

**iii)** Units = mol$^{-2}$ dm$^6$ s$^{-1}$

**iv)** If the concentration of $CH_3OH$ goes up from 0.10 to 0.2 mol dm$^{-3}$ and the concentration of $H^+$ goes up from 0.05 to 0.02, the relative rate will be $2 \times 4 = 8$

**b)** **i** and **ii**

| | $[CH_3CHO]$/ mol dm$^3$ | $[CH_3OH]$/ mol dm$^3$ | $[H^+]$/ mol dm$^3$ | [acetal A]/ mol dm | $[H_2O]$/ mol dm$^3$ |
|---|---|---|---|---|---|
| At start | 0.20 | 0.10 | 0.05 | 0.00 | 0.00 |
| At equilibrium | (0.20 – x) | (0.10 – 2x) | 0.05 | x | x |
| At equilibrium | 0.175 | 0.05 | 0.05 | 0.025 | 0.025 |

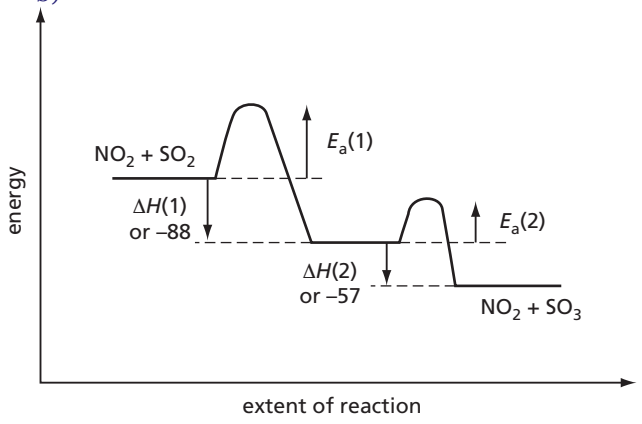
**iii)** $K_c = [\text{acetal A}][H_2O] \div [CH_3CHO][CH_3OH]^2$ mol$^{-1}$ dm$^3$

**iv)** $K_c = 0.25^2 \div (0.175 \times 0.05)^2$
$= 816$ mol$^{-1}$ dm$^3$

**4 a) i)** Homogeneous catalysts are uniformly mixed with, and in the same phase as, the reactants but with heterogeneous catalysts the catalyst and reactants are in different physical states.

**ii)** $Fe^{2+}$ or $Fe^{3+}$ is a homogeneous catalyst in the oxidation of iodide ions by peroxodisulfate(VI) ions:
$S_2O_8^{2-} + 2I^- \rightarrow 2SO_4^{2-} + I_2$
This reaction involves two negatively charged ions, which would repel, but the addition of the positively charges $Fe^{3+}$ ions leads to:
$Fe^{3+} + I^- \rightarrow Fe^{2+} + \frac{1}{2}I_2$
Fe is a heterogeneous catalyst in the Haber process:
$N_2 + 3H_2 \rightarrow 2NH_3$
The reaction of the gases takes place on the surface of the solid catalyst. The reactants are adsorbed; the reaction takens place; and the products are desorbed.

**b)**




**5 a)** A change in colour could be measured by colorimetry.

**b)** Experiments 1 and 2: rate × 1.75 and $[H_2]$ × 1.75 (when [ICl] no change)
or by calculation, order = (0.007/0.004)/(1.75/1.00) = 1
or Experiments 1 and 3: rate × 2.5 and $[H_2]$ × 2.5 (when [ICl] no change)
or Experiments 2 and 3: rate × 10/7(1.43) and $[H_2]$ × 10/7(1.43) (when [ICl] no change)

**c)** Experiments 4 and 5: rate × 1.4 and [ICl] × 1.4 (when $[H_2]$ no change)
**d)** Rate = $k[ICl][H_2]$
**e)** 62 500 **or** $6.25 \times 10^4$
**f)** $ICl + H_2 \rightarrow HCl + HI$
$HI + ICl \rightarrow HCl + I_2$
**g)** **i)** Plot a graph of concentration of $[H_2]$ against time, show a constant half-life (1st order) and draw tangent. Determine gradient (on conc. vs time graph) **or** draw two tangents to determine two gradients.
conc. 1 (at time 1)/conc. 2 (at time 2) = gradient 1/gradient 2
Plot a graph of rate (straight-line through the origin of graph) against concentration of $[H_2]$.
**ii)** [ICl] doesn't change or only changes slightly.
**h)** A catalyst provides an alternative reaction route with lower activation energy ($E_a$), so that there are more molecules with $E \geq E_a$.

# Topic 24: Quantitative equilibria

## Answers to in-text questions

### Questions 24.1

**1** **a)** $Br^-$
**b)** $NO_3^-$
**c)** $HSO_4^-$
**d)** $SO_4^{2-}$
**e)** $S^{2-}$

**2** **a)** HF
**b)** $H_2S$
**c)** $HCO_3^-$
**d)** $H_2SO_4$
**e)** $H_3O^+$
**f)** $NH_4^+$

### Questions 24.2

**1** Acid, $SO_4^{2-}$
**2** Base, $H_2NO_3^+$
**3** Acid, $OH^-$

### Questions 24.3

**1** $7.6 \times 10^{-4}$ mol dm$^{-3}$
**2** $2.5 \times 10^{-5}$ mol dm$^{-3}$

### Questions 24.4

**1** 2.7
**2** −4.2

### Questions 24.5

**1** 0.3
**2** 14.4
**3** 2.3

### Questions 24.6

**1** 5.3
**2** 4.5
**3** **a)** 5.6
**b)** 0.05

### Questions 24.7

**a)** $HCO_3^- + H^+ \rightarrow H_2CO_3$
**b)** $H_2CO_3 + OH^- \rightarrow HCO_3^- + H_2O$

### Questions 24.8

**1** $4.0 \times 10^{-12}$ mol$^3$ dm$^{-9}$
**2** $2.0 \times 10^{-3}$ mol dm$^{-3}$

### Questions 24.9

$5.6 \times 10^{-5}$ mol dm$^{-3}$

### Question 24.10

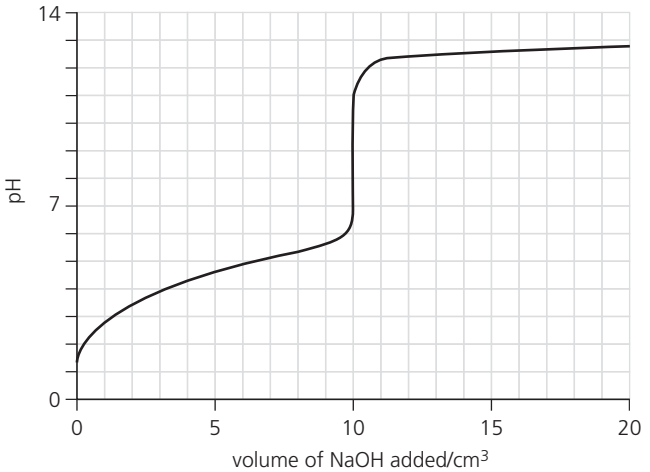
There are five intermolecular forces to be considered: iodine/iodine, hexane/hexane, water/water, iodine/hexane and iodine/water. All are weak except for the water/water which is strong (hydrogen bonding). As a result, iodine/water attractions are much less than the water/water attractions making $\Delta H_{sol}$ positive and the solubility low.

### Question 24.11

**a)** 12
**b)** 75 cm$^3$

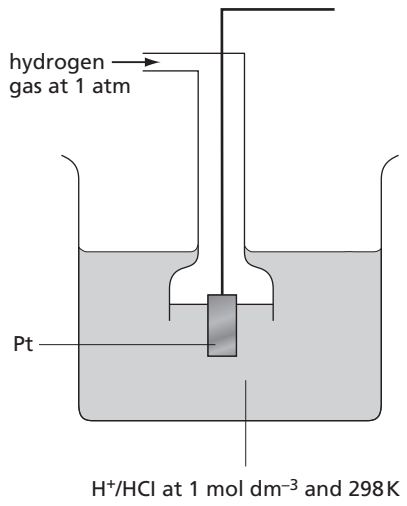
## Answers to end of topic questions

**1** **a)** **i)** As the number of chlorine atoms increases the value of the acid dissociation constant increases, which means that the acid becomes stronger. This is because the electronegativity of the chlorine atoms polarises and weakens the O–H bond, and stabilises the $RCO_2^-$ anion.
**ii)** $[H^+] = \sqrt{(K_a \times c)} = \sqrt{(0.0013 \times 0.10)} = 0.0114$ mol dm$^{-3}$
$pH = -\log_{10} 0.0114 = 1.94$
**iii)**




**b)** **i)** $CH_3CO_2H + OH^- \rightarrow CH_3CO_2^- + H_2O$
$CH_3CO_2^- + H^+ \rightarrow CH_3CO_2H$
**ii)** $pK_a = -\log_{10} (1.7 \times 10^{-5}) = 4.77$
$pH = pK_a + \log_{10} (0.2 \div 0.1) = 5.07$

2 a) i)




ii) $E^{\ominus} = 1.33 - (-0.41) = 1.74$ V
$Cr_2O_7^{2-} + 14H^+ + 6Cr^{2+} \rightarrow 8Cr^{3+} + 7H_2O$

iii) The colour of the solution would change from orange to green.

b) $pK_a = -\log_{10}(K_a) = -\log_{10}(1.79 \times 10^{-5}) = 4.747$
$\log_{10}([B] \div [A]) = pH - pK_a = 5.50 - 4.747 = 0.753$
$[B] \div [A] = 10^{0.753} = 5.66$
$B + A = 100$ so $(100 - A) \div A = 5.66$
$100 = 5.66A + A$
$A = 100 \div 6.66 = 15$
Volume of acid = 15 $cm^3$, volume of salt = 85 $cm^3$

c) i) $CH_3CO_2Na + HCl \rightarrow CH_3CO_2H + NaCl$

ii) $CH_3CO_2H + NaOH \rightarrow CH_3CO_2Na + H_2O$

d) The following organic reactions are all catalysed by an acid:
the hydrolysis of esters $RCO_2R'(+H_2O) \rightarrow RCO_2H + R'OH$
the hydrolysis of amides $RCONH_2$ $(+H_3O^+) \rightarrow RCO_2H + NH_4^+$
the hydrolysis of nitriles RCN $(+ H_3O^+ + H_2O) \rightarrow RCO_2H + NH_4^+$
the nitration of benzene $C_6H_6 + HNO_3 \rightarrow C_6H_5NO_2$ $(+ H_2O)$
the dehydration of alcohols $CH_3CH(OH)CH_3 \rightarrow CH_3CH{=}CH_2 + H_2O$
the halogenation of ketones $CH_3COCH_3 + X_2 \rightarrow CH_3COCH_2X$ $(+ HX)$

3 a) i) $K_w = [H^+][OH^-]$

ii)

| effect of increasing temperature of water | decrease | stay the same | increase |
|---|---|---|---|
| pH | ✓ | | |
| ratio $[H^+]:[OH^-]$ | | ✓ | |

b) $[H^+] = 10^{-13.25} = 5.62 \times 10^{-14}$
$[OH^-] = K_w/[H^+] = \frac{1.0 \times 10^{-14}}{5.62 \times 10^{-14}}$
$[OH^-] = 0.18$ (0.178) (mol $dm^{-3}$)

c) $HCO_3^- + H^+ \rightarrow H_2CO_3$
or $HCO_3^- + H^+ \rightarrow CO_2 + H_2O$
$H_2CO_3 + OH^- \rightarrow HCO_3^- + H_2O$

d) i) $CH_3COOH + H_2O \rightarrow CH_3COO^- + H_3O^+$
acid + base → base + acid

ii) Moles NaOH = $0.15 \times \frac{20}{1000} = 0.0030$
and initial moles $CH_3COOH = 0.25 \times \frac{30}{1000}$ or 0.0075
Equilibrium moles $CH_3COOH = 0.0045$
and equilibrium moles $CH_3COONa = 0.0030$
$[CH_3COOH] = \frac{0.0045}{0.05} = 0.090$
and $[CH_3COONa] = \frac{0.003}{0.05} = 0.060$
$[H^+] = \frac{K_a[CH_3COOH]}{[CH_3COONa]} = 2.625 \times 10^{-5}$
$pH = -\log[H^+] = 4.6$

4 a) The *partition coefficient* is the ratio of the concentrations of a solute in two immiscible solvents at equilibrium.

b) $[NH_3]aq = 0.1 \times 12.5/10 = 0.125$ mol $dm^{-3}$
$[NH_3]CHCl_3 = 0.1 \times 13/25 = 0.052$ mol $dm^{-3}$
ratio = $K_{partition} = 0.052/0.125 = 0.416$

c) $K_{partition}$ will be larger for butylamine than for ammonia since butylamine contains a non-polar (C4) group. This would increase id–id bonding with chloroform molecules, thus increasing its solubility in $CHCl_3$. It would also cause more disruption of the hydrogen bonding between water molecules, thus deceasing its solubility in $H_2O$.

## Topic 25: Electrochemistry

### *Answers to in-text questions*

### *Questions 25.1*

1 $Cu(s)|Cu^{2+}(aq)\,Cr^{3+}(aq), Cr^{2+}(aq)|Pt(s)$
2 $Pt|2Cl^-(aq), Cl_2(aq)\,Al^{3+}(aq)|Al(s)$
3 $Pt(s)|2Br^-(aq), Br_2(aq)\,MnO_4^-(aq), Mn^{2+}(aq), 8H^+(aq)|Pt(s)$
4 $Pt, H_2(g)|2H^+(aq), H_2O(l)|\frac{1}{2}O_2(g), Pt$
(no bridge required; $H_2O(l)$ unnecessary but useful as it shows reduced form of $\frac{1}{2}O_2(g)$)

### *Questions 25.2*

Experimental set-up based on Figure 25.2 and Figure 25.4 (for oxygen electrode).

1 $Zn(s)|Zn^{2+}(aq)\,Mg^{2+}(aq)|Mg(s)$ −1.62 V
2 $Pt(s)|2Br^-(aq), Br_2(aq)\,Cl_2(aq), 2Cl^-(aq)|Pt(s)$ +0.33 V
3 $Cu(s)|Cu^{2+}(aq), 2H_2O(l), 4H^+(aq)|O_2(g), Pt(s)$ +0.89 V

## Questions 25.3

1 $E = -2.20\,V$. Left-hand electrode is positive. Electrons move from right to left around external circuit.

2 $E = -1.23\,V$. Left-hand electrode is positive. Electrons move from right to left around external circuit.

## Questions 25.4

1 $2Al + 3Cl_2 \rightarrow 2Al^{3+}(aq) + 6Cl^-(aq)$ $E_{cell} = +3.02\,V$
$\Delta G = -1748.6\,kJ\,mol^{-1}$

2 $MnO_4^- + 8H^+ + 5Fe^{2+} \rightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$
$E_{cell} = +0.74\,V$
$\Delta G = -357.1\,kJ\,mol^{-1}$

## Questions 25.5

1 **a)** +0.80 V; yes
**b)** +0.15 V; yes
**c)** +1.21 V; yes
**d)** +0.03 V; doubtful (actually equilibrium)

2 **a)** Anions repelled by $S_2O_8^{2-}$ and $Cl^-$ ions; therefore $ClO^-$ ineffective.

**b)**

| | |
|---|---|
| $Fe^{3+} + I^- \rightleftharpoons \frac{1}{2}I_2 + Fe^{2+}$ | $E^\ominus = +0.23\,V$ |
| $Ce^{4+} + I^- \rightleftharpoons \frac{1}{2}I_2 + Ce^{3+}$ | $E^\ominus = +1.16\,V$ |
| $Co^{3+} + I^- \rightleftharpoons \frac{1}{2}I_2 + Co^{2+}$ | $E^\ominus = +1.27\,V$ |
| $S_2O_8^{2-} + 2Fe^{2+} \rightleftharpoons 2SO_4^{2-} + 2Fe^{3+}$ | $E^\ominus = +1.24\,V$ |
| $S_2O_8^{2-} + 2Ce^{3+} \rightleftharpoons 2SO_4^{2-} + 2Ce^{4+}$ | $E^\ominus = +0.31\,V$ |
| $S_2O_8^{2-} + 2Co^{2+} \rightleftharpoons 2SO_4^{2-} + 2Co^{3+}$ | $E^\ominus = +0.20\,V$ |

## Questions 25.6

1 $E = -0.52\,V$

2 $E = +0.50\,V$

## Questions 25.6

1 −0.69 V

2 +0.17 V

## Questions 25.7

1 336 g

2 **a)** $60 \times 10 \times 1.0/(96\,500 \times 4) = 0.0016$ mol
**b)** $37\,cm^3$
**c)** Some oxygen may dissolve in the water.

3 **a)** At cathode, $H^+$ ions preferentially discharged compared to $Na^+$ ions; at anode $OH^-$ ions discharged.
**b)** At cathode, $Cu^{2+}$ ions are preferentially discharged to $H^+$ ions (lower in series); at anode $OH^-$ ions preferentially discharged to $SO_4^{2-}$ ions (higher in series).
**c)** At anode $Cu^{2+}/Cu$ is above $O_2/OH^-$ (higher in series).

## Questions 25.8

1 **a)** Anode: $Br_2$, cathode: Ca. No other ions present.
**b)** Anode: $Br_2$, cathode: $H_2$. $E^\ominus$ for $O_2$ more positive than $E^\ominus$ for $Br_2$; $E^\ominus$ for $Ca^{2+}$ more negative than $E^\ominus$ for $H^+$.
**c)** Anode: $Br_2$, cathode: $H_2$. $E^\ominus$ for $Cl_2$ more positive than $E^\ominus$ for $Br_2$. $E^\ominus$ for both $Na^+$ and $K^+$ more negative than $E^\ominus$ for $H^+$.

2 $E^\ominus$ for $Cl_2$ more positive than $E^\ominus$ for $O_2$, but $E^\ominus$ for $I_2$ less positive than $E^\ominus$ for $O_2$.

3 **a)** $O_2(g)$.
**b)** $O_2(g)$. The $E^\ominus$ for $F_2$ is too positive to be influenced by concentration effects.

## Answers to end of topic questions

1 **a)** **i)** $Cu(s) - 2e^- \rightarrow Cu^{2+}(aq)$
**ii)** $E^\ominus$ $Ag^+/Ag = +0.80$ V
$E^\ominus$ $Cu^{2+}/Cu = +0.34$ V.
The $E^\ominus$ for silver is more positive so it is less easily oxidised so it remains as a metal.
**iii)** $E^\ominus$ $Ni^{2+}/Ni = -0.25$ V so it is easily oxidised and goes into solution as $Ni^{2+}(aq)$
**iv)** $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$
**v)** $E^\ominus = -0.76$ V so it is not readily reduced
**vi)** Copper ions give rise to the blue colour in the solution and as the $Cu^{2+}(aq)$ is replaced by the other metal ions the colour fades

**b)** **i)** Relative atomic mass of copper = 63.5 so amount of copper = 225 ÷ 63.5 = 3.54 mol
1 mole copper requires 2 moles of electrons so number of electrons required = 2 × 3.54 = 7.08 mol
10 hours = 10 × 60 × 60 seconds so number of coulombs = 20 × 3600 = $7.2 \times 10^5$ C
Faraday constant = $9.65 \times 10^4$ so number of moles of electrons passing through the cell = $7.2 \times 10^5 \div 9.65 \times 10^4 = 7.64$ mol
**ii)** Percentage wasted = (7.46 − 7.08) ÷ 7.46 × 100 = 5.09%

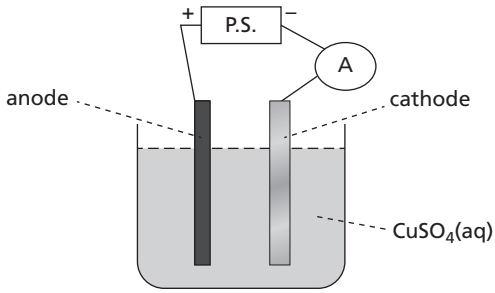
**c)** $E^\ominus$ $Ni^{2+}/Ni = -0.25$ V and $Fe^{2+}/Fe = -0.44$ V
Since the $E^\ominus$ for iron is more negative it will dissolve but stay in solution.

2 **a)** **i)** **X** is an ammeter.
**ii)** **Y** is $AgNO_3$ or AgF or $AgClO_4$.

**b)** $n(Ag) = 0.500/107.9 = 4.6(34) \times 10^{-3}$
$n(C) = 0.200 \times 40 \times 60 = 480$ C
$n(e-) = 480/1.60 \times 10^{-19} = 3(.00) \times 10^{21}$
$n(e-)/n(Ag) = 3.00 \times 10^{21}/4.634 \times 10^{-3}$
$= 6.474 \times 10^{23}$ $(6.5 \times 10^{23})$

3 **a)** $F = Le$

b) i)




ii) $n(Cu) = (52.542 - 52.243) \div 63.5$
$= 4.71 \times 10^{-3}$ mol
$n(e^-)$ needed $= 2 \times 4.71 \times 10^{-3}$
$= 9.42 \times 10^{-3}$ mol
Number of coulombs $= 0.5 \times 30 \times 60 = 900$ C
Number of electrons $900 \div 1.6 \times 10^{-19}$
$= 5.625 \times 10^{21}$
Number of electrons/$n(e^-) = L = 5.625 \times 10^{21}$
$\div 9.42 \times 10^{-3} = 5.97 \times 10^{23}$ mol$^{-1}$

c)

| Compound | Product at anode | Product at cathode |
|---|---|---|
| AgF | $O_2$ | Ag |
| $FeSO_4$ | $O_2$ | $H_2$ |
| $MgBr_2$ | $Br_2$ | $H_2$ |

4 a) $E^\ominus$ for $X_2/X^-$ decreases down the group, so the halogens are less reactive (as oxidants) down the group.

b) i) $Cl_2 + H_2O \rightarrow HCl + HClO$

ii) $Cl_2/Cl^- = +1.36$ V **and** $ClO^-/(Cl^- + OH^-)$
$= +0.89$ V
so $E^\ominus_{cell} = 1.36 - 0.89 = (+)0.47$ V

iii)

| | |
|---|---|
| $E_{cell}$ becomes less positive than $E^\ominus_{cell}$ | |
| $E_{cell}$ stays the same as $E^\ominus_{cell}$ | |
| $E_{cell}$ becomes more positive than $E^\ominus_{cell}$ | ✓ |

Using Le Chatelier's argument, with an increase in the reactant concentration ($OH^-$) the equilibrium shifts right.

c) i) $Br^- + 3ClO^- \rightarrow BrO_3^- + 3Cl^-$

ii) $E^\ominus_{cell} = 0.89 - 0.58 = +0.31$ V

iii) $4HBrO_3 \rightarrow 2Br_2 + 5O_2 + 2H_2O$

5 a)

| electrolyte | substance liberated at the anode | substance liberated at the cathode |
|---|---|---|
| NaOH(aq) | **oxygen/$O_2$** | **hydrogen/$H_2$** |
| dilute $CuCl_2$(aq) | **oxygen/$O_2$** | **copper/Cu** |
| concentrated $MgCl_2$(aq) | **chlorine/$Cl_2$** | **hydrogen/$H_2$** |

b) i) $2Br^- \rightarrow Br_2 + 2e^-$ or $2Br^- - 2e^- \rightarrow Br_2$
$Zn^{2+} + 2e^- \rightarrow Zn$
$Zn^{2+}$ is reduced and $Br^-$ is oxidised.

ii) Molten metal (at cathode) or brown gas (at anode) or the amount of electrolyte decreases.

c) amount of charged passed $= 1.2 \times 50 \times 60 = 3600$ C
moles of electrons $= 3600/96\,500 = 3.73 \times 10^{-2}$
Each mole of $H_2$ required 2 moles of electrons, so
moles of $H_2 = 3.73 \times 10^{-2}/2 = 1.86(5) \times 10^{-2}$
volume of $H_2 = 1.86(5) \times 10^{-2} \times 24\,000 = 448$ cm$^3$

## Topic 26: The 3d block

### *Answers to in-text questions*

### *Questions 26.1*

1 a) [Ar] $3d^{10}4s^1$
b) [Ar] $3d^7$
c) [Ar] $3d^1$

2 a) With copper, second electron is removed from complete $3d^{10}$ subshell; with zinc it is being removed from half-filled 4s subshell.

b) $Mn^{2+}$ has stable $3d^5$configuration. The third I.E. of Mn is at a maximum (drops when going to Fe).

c) The first I.E.s increase very little because they involve removal of a 4s electron which is screened from the increasing $Z$ by the addition of 3d electrons. The third I.E.s increase a lot because they involve the removal of a 3d electron which is not screened from the increasing $Z$.

### *Questions 26.2*

1 $Cr_2O_7^{2-} + 14H^+ + 6e^- \rightleftharpoons 2Cr^{3+} + 7H_2O$ $\quad E^\ominus = +1.33$ V
$MnO_4^- + 8H^+ + 5e^- \rightleftharpoons Mn^{2+} + 4H_2O$ $\quad E^\ominus = +1.52$ V

2 $Cr_2O_7^{2-} + 14H^+ + 6Fe^{2+} \rightleftharpoons 2Cr^{3+} + 6Fe^{3+} + 7H_2O$
$E^\ominus = +0.56$ V
$MnO_4^- + 8H^+ + 5Fe^{2+} \rightleftharpoons Mn^{2+} + 5Fe^{3+} + 4H_2O$
$E^\ominus = +0.75$ V

### *Questions 26.3*

1 $8.1 \times 10^7$

2 +0.36 V

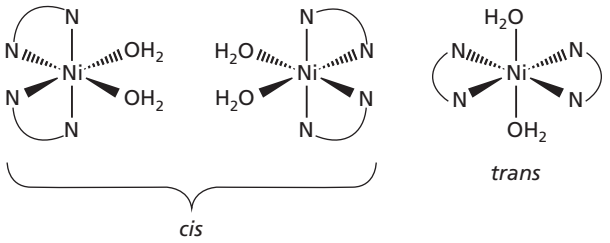
### *Questions 26.4*

a) Hexaamminechromium(III) ion
b) Tetrachlorocuprate(II) ion
c) Tetrahydroxozincate ion
d) Dichlorotetraaquachromium(III) ion

## Questions 26.5

**a)** Three isomers: one is *trans*; two are the optical isomers of the *cis*.

**b)**




**c)** *Trans*: no dipole moment. *Cis*: each stereoisomer has (the same) dipole moment.

## Questions 26.6

**1** $5Fe^{2+}$ react with $1MnO_4^-$; $A_r$ Fe = 55.8

**a)** Amount of $Fe^{2+}$ in 25.0 $cm^3 = 5 \times 18.7 \times \frac{0.0105}{1000} = 9.8175 \times 10^{-4}$ mol
conc. of $Fe^{2+} = 0.003927$ mol $dm^{-3}$
Ans = 0.0039 mol $dm^{-3}$

**b)** Mass in 250 $cm^3$ flask = $0.003927 \times 10 \times 55.8 = 2.19$ g
Ans = 2.19 g

**c)** Percentage purity = $2.19 \times \frac{100}{2.47}$
Ans = 88.6%

**2** **a)** Amount of $NaNO_2 = 25.0 \times \frac{0.0370}{1000} = 9.25 \times 10^{-4}$ mol

Amount of $KMnO_4 = 23.9 \times \frac{0.0155}{1000} = 3.7045 \times 10^{-4}$ mol

1 mol of $KMnO_4$ react with $\frac{9.25}{3.7045} = 2.50$ mol $NaNO_2$
Ans = 2.5

**b)** $2MnO_4^-(aq) + 5NO_2^-(aq) + 6H^+(aq) = 2Mn^{2+}(aq) + 5NO_3^-(aq) + 3H_2O(aq)$

**3** $5K_2C_2O_4$ react with $2MnO_4^-$

**a)** Amount of $MnO_4^- = 28.5 \times \frac{0.01000}{1000}$ mol
Ans = $2.85 \times 10^{-4}$ mol

**b)** Amount of ethanedioate = $2.5 \times 10 \times 2.85 \times 10^{-4}$ mol
Ans = $7.125 \times 10^{-3}$ mol

**c)** $\frac{1.31}{7.125 \times 10^{-3}} = 183.86$
Ans = 184

**d)** $166 + 18x = 184$; $x = \frac{18}{18}$
Ans = 1

## Questions 26.7

**1** **a)** Amount of $S_2O_8^{2-} = 25.0 \times \frac{0.0210}{1000}$;
Ans = $5.25 \times 10^{-4}$ mol
Amount of $I^- = 21.0 \times \frac{0.0500}{1000}$;
Ans = $1.05 \times 10^{-3}$ mol

**b)** 1.05/0.525; Ans = 2

**c)** $2KI(aq) + K_2S_2O_8(aq) = I_2(aq) + 2K_2SO_4(aq)$

**2** **a)** $27.8 \times \frac{0.0425}{25.0}$; Ans = 0.047 mol $dm^{-3}$

**b)** $0.25 \times 63.5 \times 0.04726$; Ans = 0.075 g

**c)** 75%

## Answers to end of topic questions

**1** **a)** A d–block element that forms one or more stable ions with incomplete d orbitals

**b)** **i)** $(1s^2 2s^2 2p^6) 3s^2 3p^6 3d^3 4s^2$

**ii)** $(1s^2 2s^2 2p^6) 3s^2 3p^6 3d^9$

**c)** +2, +3, +4, +5

**d)** A solid blue precipitate of $Cu(OH)_2$ is produced. The precipitate redissolves in excess $NH_3$. $[Cu(NH_3)_4]^{2+}$ ions are formed by ligand exchange. The solution becomes dark blue or purple.

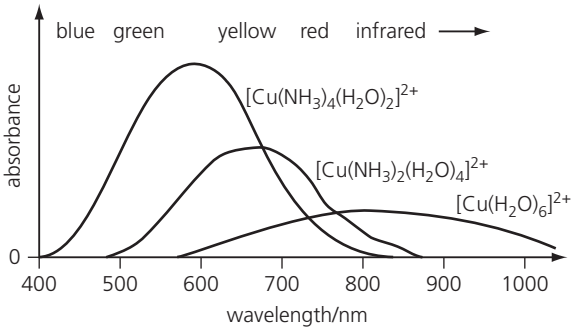
**e)** $2VO_3^- + 8H^+ + Cu \rightarrow 2VO^{2+} + 4H_2O + Cu^{2+}$

**2** **a)** d block elements can absorb in the visible region because they have two energy levels that are close together. The light is absorbed when electrons move from a lower to the higher level. The colour we see is white light minus the colour being absorbed.

**b)** **i)** $[Cu(H_2O)_6]^{2+}$ – pale blue
$[Cu(NH_3)_4(H_2O)_2]^{2+}$ – purple

**ii)** Because the maximum absorbance is within the visible region so more visible light is absorbed and it has a large absorbance peak.

**iii)**




**c)** **i)** $K_c = [CuCl_4^{2-}]/[Cu^{2+}][Cl^-]^4$ $mol^{-4}$ $dm^{12}$

**ii)** $[CuCl_4^{2-}]/[Cu^{2+}] = K_c[Cl^-]^4$
$= 42 \times 10^5 \times (0.2)^4$
$= 672$

**3** **a)** Fe atom = $(1s^2\ 2s^2\ 2p^6)\ 3s^2\ 3p^6\ 3d^6\ 4s^2$
$Fe^{3+}$ ion = $(1s^2\ 2s^2\ 2p^6)\ 3s^2\ 3p^6\ 3d^5$

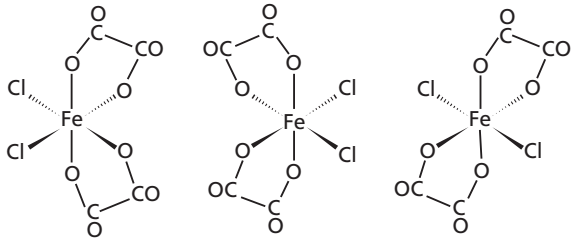
**b)** $[H^+]^2 = 8.9 \times 10^{-4} \times 0.25 = 2.225 \times 10^{-4}$
$[H^+] = 0.0149$
$pH = -\log(0.0149) = 1.83$

**c)** **i)** The *stability constant* $K_{stab}$ is the equilibrium constant for the formation of a complex ion in a solvent from its constituents

**ii)** $[Fe(H_2O)_5F]^{2+}$ and $[Hg(H_2O)_5Cl]^+$

**d)** $K_{stab} = \frac{[[Fe(ed)_2\ Cl_2]^{3-}]}{[[Fe(H_2O)_4\ Cl_2]^+][ed]^2}$
$mol^{-2}\ dm^6$

e) i)



*cis* *cis* *trans*

ii) Either *cis* isomer **and** the *trans* isomer
iii) Both *cis* isomers
iv) The *trans* isomer

4 a)

| | number of unpaired electrons | |
|---|---|---|
| | 3d | 4s |
| Cr | 5 | 1 |
| Mn | 5 | 0 |
| Fe | 4 | 0 |

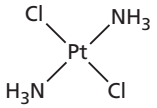
b) $2KMnO_4 \rightarrow K_2MnO_4 + O_2 + MnO_2$

c) d orbitals are split into upper and lower orbitals. Visible light is absorbed by electrons as they become excited and move into higher orbitals – the complementary colour is observed.

d) i) **A** $[Cu(H_2O)_4(OH)_2]$ or $Cu(OH)_2$
**B** $[Cu(NH_3)_4(H_2O)_2]^{2+}$
**C** $Cu(CH_3CO_2)_2$
ii) $Na_2CO_3$ or $CO_3^{2-}$
iii) $CuCO_3 + 2CH_3CO_2H \rightarrow Cu(CH_3CO_2)_2 + CO_2 + H_2O$
iv) *Any two from:*
» fizzing, bubbles or effervescence
» solid disappears
» a green-blue solution forms.

e) The sum of the charges of the four ligands equals the oxidation number (charge) of Pt. (Pt has charge +2, $NH_3$ is neutral (no charge) and there are $2 \times Cl^{-1}$).

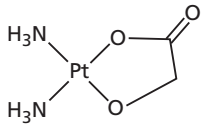
f) i)



square planar and 180°

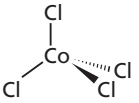
ii) *Cis*-platin can bind to DNA, preventing replication of the DNA and disrupting cell division.

g)



5 a) $3s^2\ 3p^6\ 3d^7\ 4s^2$ or $3s^2\ 3p^6\ 4s^2\ 3d^7$
$3s^2\ 3p^6\ 3d^7$

b) i) A *complex ion* is formed by a central metal atom or ion surrounded by and bonded to one or more ligand(s).
ii) The charge is 2–.

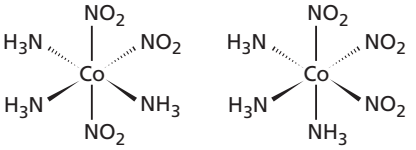


iii) d orbitals are split into upper and lower orbitals. Visible light is absorbed by electrons as they become excited and move into higher orbitals – the complementary colour is observed.
iv) Blue light is not absorbed; red and yellow, orange and green is absorbed.

c) From blue to pink. The reaction is ligand exchange or ligand substitution.

d) i) $F_2$ or $S_2O_8^{2-}$
ii) $E^{\ominus}_{cell} = +1.05$ or $+0.19$
iii) $2Co^{2+} + F_2 \rightarrow 2Co^{3+} + 2F^-$
or $2Co^{2+} + S_2O_8^{2-} \rightarrow 2Co^{3+} + 2SO_4^{2-}$

e)



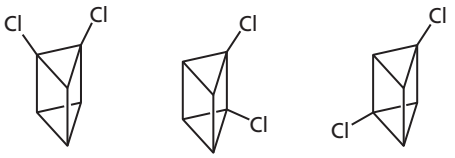
*cis/trans* or geometrical isomerism

## Topic 27: Arenes and phenols

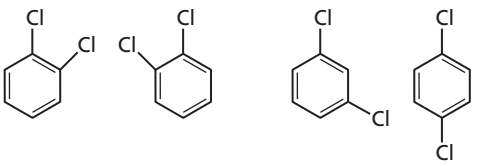
### *Answers to in-text questions*

### *Questions 27.1*

1



2



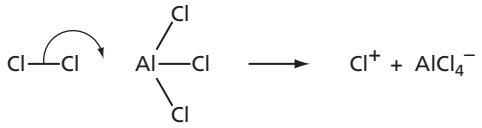
### *Question 27.2*

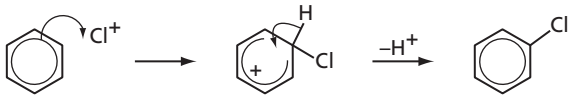
The N is joined to one oxygen by a single σ bond; the N is joined to another oxygen by a dative σ bond using a lone pair on N; the N is joined to the third oxygen by a σ bond and a π bond. A lone pair in the p orbital on each of the singly-bonded oxygens overlaps with the π bond to give a four-centre delocalised π orbital similar to that in the $CO_3^{2-}$ ion.

## Question 27.3

There are six isomers: 2,3,4-; 2,3,5-; 2,3,6-; 2,4,5-; 2,4,6-, 3,4,5-trichloromethylbenzene

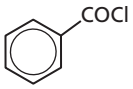
## Question 27.4



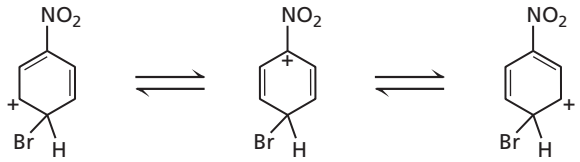




## Questions 27.5

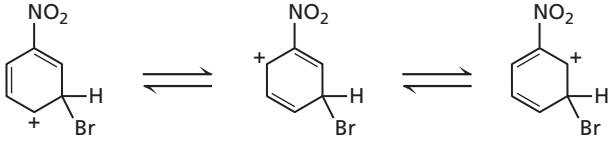
1 $(CH_3)_3C–Cl$

2 


## Question 27.6




4-bromo intermediate not favoured: + charge is adjacent to electron-withdrawing $NO_2$ group

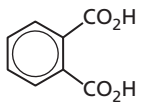


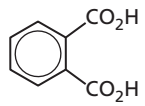

3-bromo intermediate favoured: + charge is not adjacent to electron-withdrawing $NO_2$ group

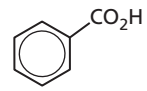
## Question 27.7

**A** is phenylmethyl bromide, $C_6H_5CH_2Br$. Side chain substitution occurs with $Br_2$ + UV light.
**B** is bromophenylmethane, Br-$C_6H_4$-$CH_3$.
Ring substitution occurs with $Br_2$ + $AlCl_3$. The Br will substitute in the 2- and 4- positions relative to the $CH_3$ group (a mixture will be formed). (**A** and **B** can be reversed.)

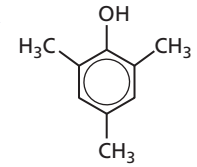
## Questions 27.8

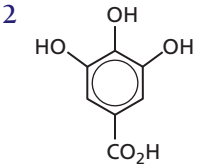
1 


2 

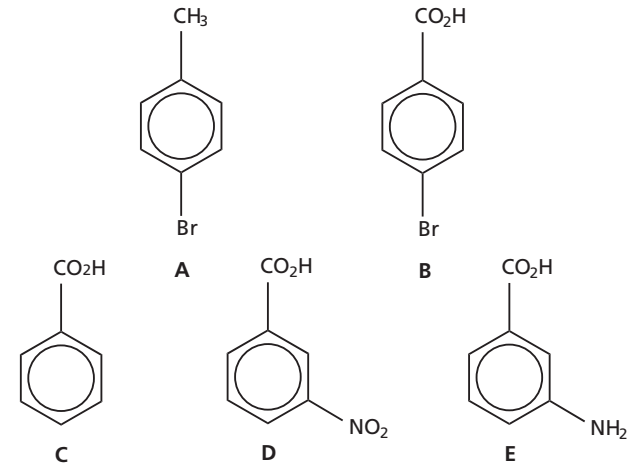

3 


## Questions 27.9

1 


2 


## Answers to end of topic questions

1 


2 a) The polar –OH group readily forms hydrogen bonds with water. For cyclohexane and benzene, which have no –OH group, there are only van der Waals' (id–id) forces which are much weaker.

b) The negative charge of the anion, $ArO^-$, can be delocalised over the benzene ring and hence is more stable.

c)

| Reagent | Product with cyclohexanol | Product with phenol |
|---|---|---|
| Na(s) | RONa | ArONa |
| NaOH(aq) | No reaction | ArONa |
| $Br_2$(aq) | No reaction | Tribromophenol |
| $I_2$(aq) + $OH^-$(aq) | No reaction | No reaction |
| An excess of acidified $Cr_2O_7^{2-}$(aq) | Cyclohexanone | No reaction |

d) With $Br_2$(aq) there would be no reaction with cyclohexanol while with phenol the orange bromine solution is decolourised and a white precipitate appears.
With an excess of acidified $Cr_2O_7^{2-}$(aq) the solution would turn from orange to green with cyclohexanol but there would be no reaction with phenol.

3 a) *Any two from:* potassium (K) or potassium hydroxide (KOH) or potassium oxide ($K_2O$)
Products are: (in reaction with K) hydrogen, (in reaction with KOH) water, (in reaction with $K_2O$) water.

**b)** **i)** Circle the N═N bond

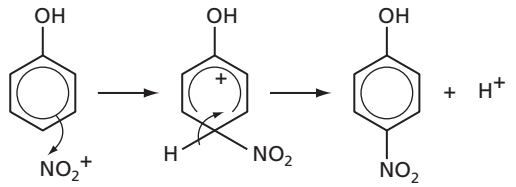
**ii)** Phenylamine and $HNO_2$ at a temperature of 10 °C or below, forming a diazonium ion ($[C_6H_5N_2^+]$, or diazonium salt)
Add 2-naphthol in aqueous NaOH.

**c)** **i)** Dilute nitric acid ($HNO_3$(aq)) at room temp.
For nitration of benzene, *any two from*:

- concentrated acid needed
- sulfuric acid ($H_2SO_4$) needed
- higher temperature needed.

**ii)** Phenol is more reactive than benzene because the p orbital on oxygen overlaps with the ring p orbitals, allowing the lone pair of electrons it contains to delocalise over the ring, making the ring more susceptible to electrophilic attack.

**iii)**




**iv)** 4-nitrophenol

## Topic 28: Carboxylic acids: derivatives and further reactions

### Answers to in-text questions

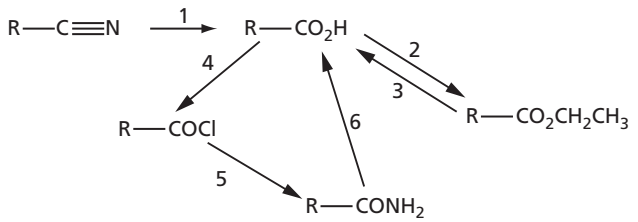
### Questions 28.1

**1** **a)** One $CH_3$ group raised the p$K_a$ by about 0.1 unit, so three will raise it by about 0.3 units from 4.76 of ethanoic acid. Predict p$K_a$ = 5.0–5.2 (actual = 5.03)

**b)** The electron-withdrawing effect of the Cl atom will be reduced by the extra —$CH_2$— group in the chain, so p$K_a$ will be less than 4.76 but greater than 2.87. Predict p$K_a$ = 3.5–4.0 (actual = 3.98)

**2** As the chlorine atom is further away from the –$CO_2H$ group, its effect is reduced. The p$K_a$ of 3-chlorobutanoic acid should be between the other two – about 3.5–4.0 (actual = 4.05)

### Questions 28.2




**1** Heat with $H_3O^+$ *or* $OH^-$(aq), then $H^+$(aq)

**2** Heat with $C_2H_5OH$ + conc. $H_2SO_4$

**3** As 1

**4** $SOCl_2$ *or* $PCl_5$

**5** $NH_3$(aq)

**6** As 1

### Question 28.3

Compared to chloroalkanes, chloroarenes are unreactive because:

**a)** the C—Cl bond is strong, due to the delocalisation of the lone pair on Cl

**b)** the $S_N2$ route is unavailable due to the ring hindering the attack of the nucleophile onto the back side of the C—Cl bond.

Compared to chloroalkanes, acyl chlorides are more reactive because:

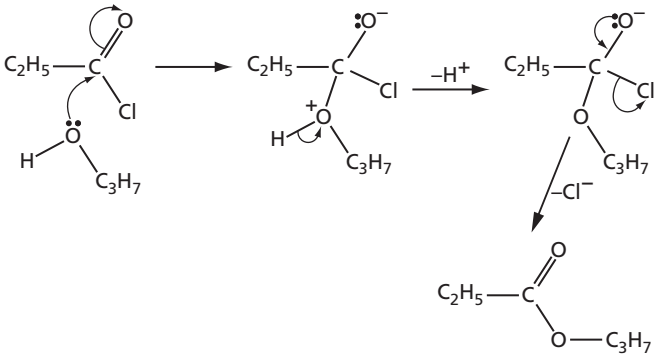
**a)** the δ– oxygen of the carbonyl group makes the carbon more δ+ than in chloroalkanes

**b)** the addition–elimination mechanism can operate, wherein bond formation can occur before bond breaking, thus powering the activation energy (see later in this chapter).

The same relative rates should be observed with any nucleophile.

### Question 28.4

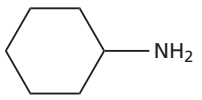
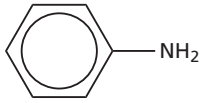
Product will be the ester $CH_3CH_2CO_2CH_2CH_2CH_3$.
Mechanism:



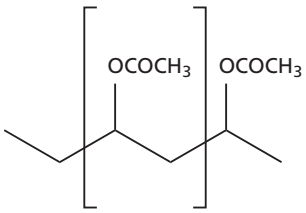

### Answers to end of topic questions

**1** **a)** Most acidic: $CHCl_2CO_2H$
Next: $CH_2ClCO_2H$
Least acidic: $CH_3CO_2H$
This is because the Cl draws electrons away from the —$CO_2^-$ group and helps the anion to form

b)

| First compound | Second compound | Test | Observation with first compound | Observation with second compound |
|---|---|---|---|---|
|  |  | $Br_2$ (aq) | None | Decolourises solution and white precipitate |
| | | $NaNO_2$ + HCl or $HNO_2$ then phenol and NaOH | $N_2$(g) evolved but no colour change | Yellow–orange–red precipitate |
| $CH_3CH_2COCl$ | $CH_3COCH_2Cl$ | $AgNO_3$(aq) | White precipitate forms quickly | white precipitate forms very slowly |
| | | Add $H_2O$/ROH | White fumes or steam | None |
| | | (2,4–)DNPH | None | Orange precipitate |
| | | $I_2/OH^-$ | None | Yellow precipitate and an antiseptic smell |
| $CH_3CH_2CHO$ | $CH_3COCH_3$ | $I_2$/OH– | None | Yellow precipitate and an antiseptic smell |
| | | Warm with Fehling's or Benedict's solution | Red precipitate | None |
| | | Warm with Tollens' reagent | Silver or black precipitate | None |
| | | Warm with $Cr_2O_7^{2-}$ + $H^+$ | Turns green | None |
| | | Warm with $MnO_4^-$ + $H^+$ | Decolourises the solution | None |

2 a) i)

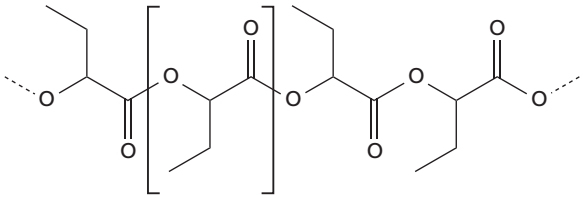



ii) $CH_2$═CHOH

iii) $CH_3CH$═O

iv) An orange or red precipitate forms if you add (2,4–)DNPH or DNP or Brady's reagent. Alternatively, a red precipitate is formed with Fehling's solution or a silver mirror with Tollens' reagent.

b) i)




ii) Ester

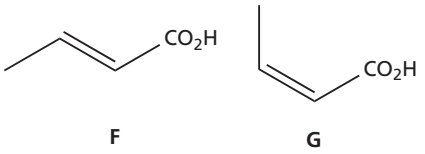
iii) $CH_3CH_2CH(OH)CO_2H$

iv) Condensation polymerisation

v) They are isomers with the formula $C_4H_6O_2$ and they are both esters.

c) i) Optical isomerism

ii)




F G

*Cis/trans* or geometrical isomerism

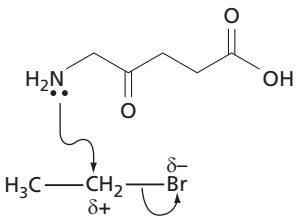
3 a) $CH_3CH_2COCl > CH_3CH_2CH_2Cl > C_6H_5Cl$

*Any two from*:

- C—Cl bond strength is weakest in $CH_3CH_2COCl$.
- In $C_6H_5Cl$, the C—Cl bond is part of a delocalised system or the p-orbital on Cl overlaps with π system or electrons from Cl overlap with π system.
- In $CH_3CH_2COCl$ the carbon in C—Cl bond is more electron deficient since it is also attached to an oxygen atom.
- For $CH_3CH_2COCl$ an addition-elimination mechanism is available during hydrolysis, which has a lower $E_a$ and hence is quicker.

b) Ketone, amine and carboxylic acid

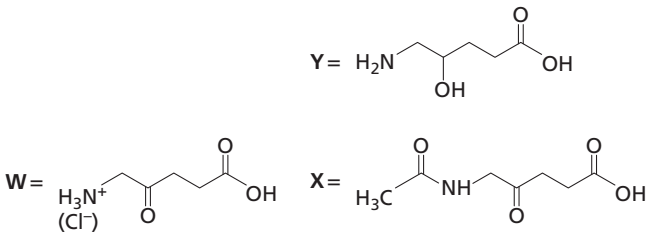
c) i)



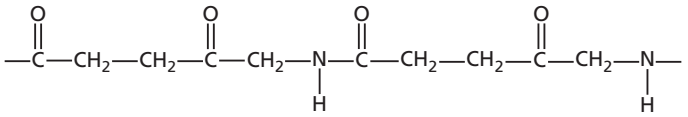
ii) Nucleophilic substitution

iii) HBr (hydrogen bromide)

d)



e



4 a) There are three acceptable alternatives: RCOCl, $RCOOCH_2CH_3$ and $RCO_2^-NH_4^+$

| D is | RCOCl | $RCOOCH_2CH_3$ | $RCO_2^-NH_4^+$ |
|---|---|---|---|
| step 1 | $SOCl_2$ (or $PCl_3$ or $PCl_5$) | ethanol (e.g.) + conc. $H_2SO_4$ | $NH_3$ |
| step 2 | $NH_3$ | | heat |
| step 3 | $LiAlH_4$ (aq) (Not $NaBH_4$; Sn + HCl etc.) | | |

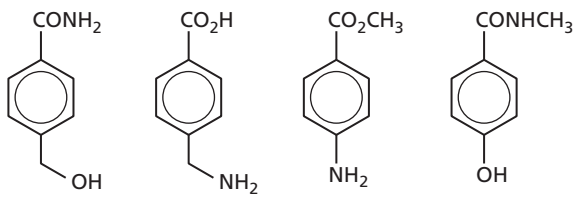
b) i) Amine

ii) Phenol and carboxylic acid

iii)

| compound | first functional group | second functional group |
|---|---|---|
| E | amide | alcohol |
| F | amine | carboxylic acid |
| G | amine | ester |
| H | amide | phenol |

iv) For each structure of **E**, **F**, **G** and **H**: the molecular formula should be $C_8H_9NO_2$.



**E** **F** **G** **H**

# Topic 29: Amines, amides and amino acids

## *Answers to in-text questions*

### *Questions 29.1*

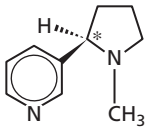
1 a) Alcohol, alkene, arene (ether)

b) Ester (×2), arene

2 a) $C_{20}H_{24}N_2O_2$

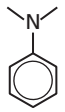
b) $C_8H_{10}N_4O_2$

3

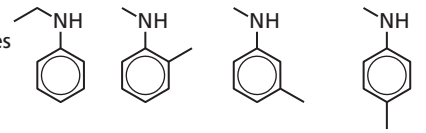


### *Question 29.2*

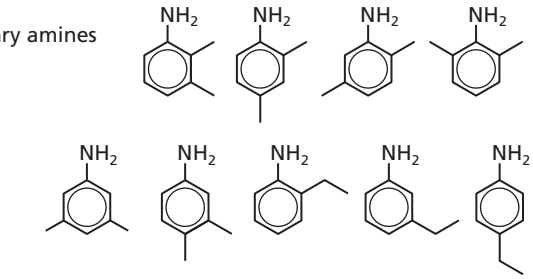
One tertiary amine



Four secondary amines

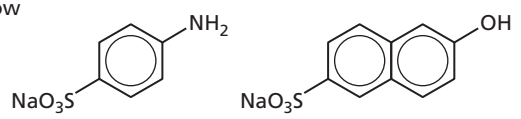


Nine primary amines



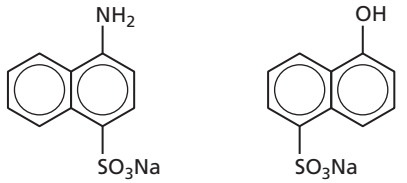
### *Questions 29.3*

1 Sunset yellow



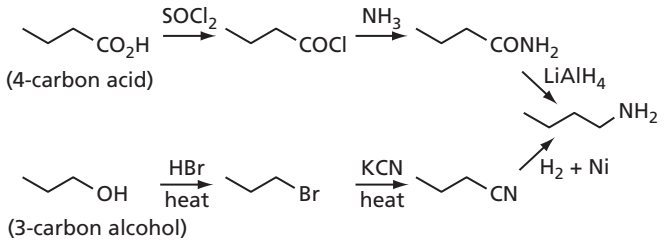
(or diazonium salt)

2 Carmoisine



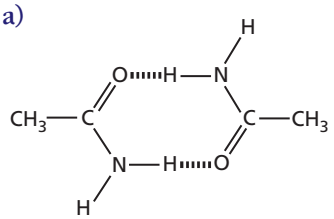
(or diazonium salt)

## Question 29.4

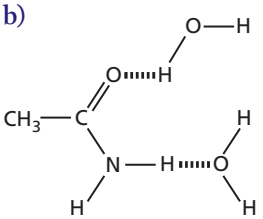



## Question 29.5

a)



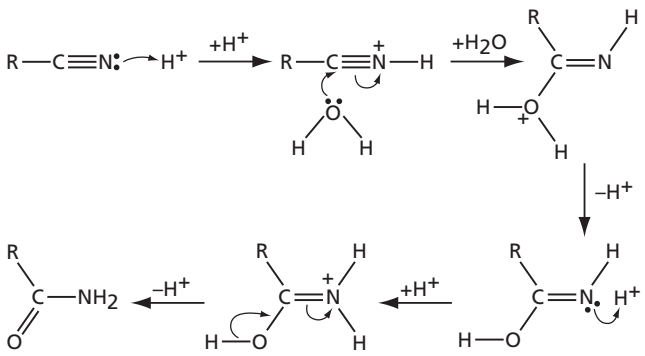
b)



## Questions 29.6

1 $CH_3CN + 2H_2O + HCl \rightarrow CH_3CO_2H + NH_4Cl$

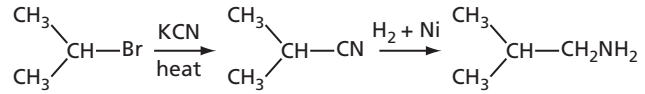
2



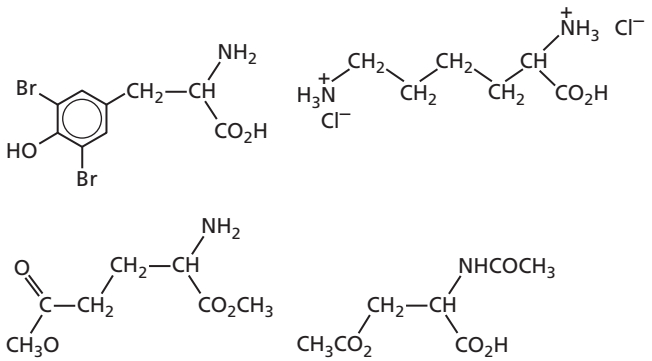

## Questions 29.7

1


2




## Questions 29.8



## Answers to end of topic questions

1 a) i) (I) $SOCl_2$ or $PCl_5$ or HCl and $ZnCl_2$ or $PCl_3$ and heat or $Cl_2$ and P and heat (II) $NH_3$ heat under pressure in ethanol

ii) Nucleophilic substitution

iii) A strong C—Cl bond is formed because the lone pair on Cl are delocalised over the benzene ring

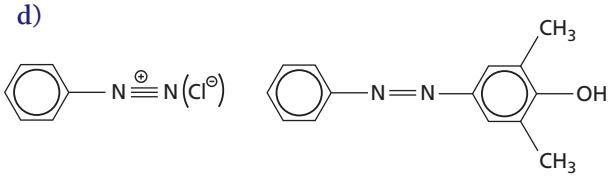
b) i) III Concentrated $HNO_3 + H_2SO_4$ at a temperature below 60°C
IV Sn + concentrated HCl

ii) III is electrophillic substitution
IV is reduction or redox

c) If bromine water is added it will be decolourised by phenylamine but not by hexylamine

If universal indicator is used it will turn blue with hexylamine but remain green with phenylamine

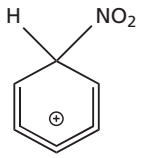
d)



2 a) i) Concentrated $HNO_3 + H_2SO_4$ at temperatures between 30°C and 60°C

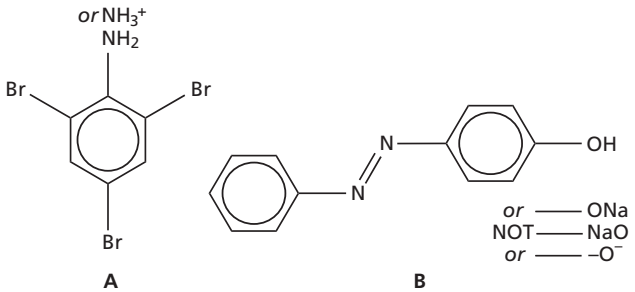
ii) Dilute $HNO_3$ at room temperature

b)



c) Sn/tin + HCl

d) i)

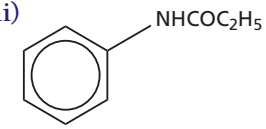


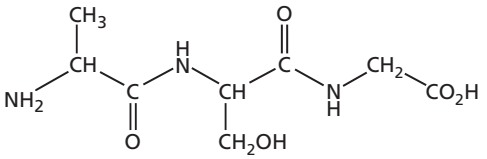

ii) $HNO_2$, on $NaNO_2 + HCl/H_2SO_4$ at a temperature below or equal to 10°C

e i) Amide

ii) Relative molecular mass = 108 + 11 + 14 + 16 = 149
Percentage of nitrogen = 14 ÷ 149 × 100 = 9.4%

iii)



3 a) i) 

ii) $M_r = 233$

b) i) $NH_2CH(CH_2OH)CO_2$

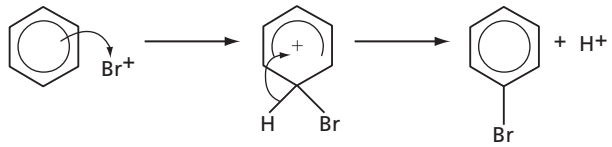
ii) **F** = DC power supply
**G** = anode (positive electrode)
**I** = cathode (negative electrode)
**H** = filter paper (or gel) soaked in buffer solution

iii) **P** is $NH_2CH_2CO_2^-$ or $NH_2CH_2CO_2H$ or glycine
S is [ala–ser–gly](⁻)
Glycine is the smallest molecule, so travels fastest; the tripeptide is the largest, so travels slowest.

c) i) Heat with $H^+/H_2O$

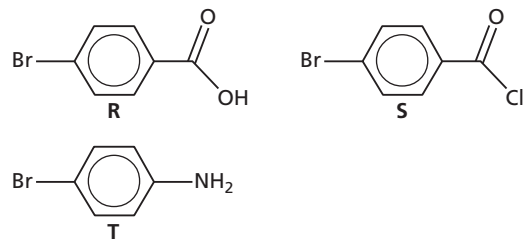
ii) Hydrolysis

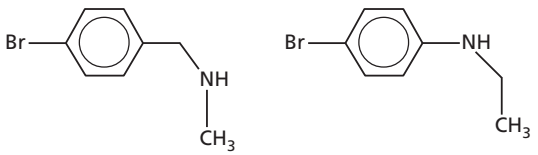
4 a) i) Electrophilic substitution

ii) 

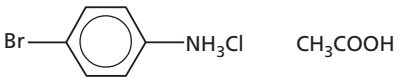
b) **V** and **W** are both amides.

c) i) Step 1 = $AlBr_3$ and $CH_3Br$ or another suitable halogen instead of Br.
Step 2 = $KMnO_4$
Step 3 = conc. $H_2SO_4$ and conc. $HNO_3$
Step 4 = Sn and (conc.) HCl (heat)

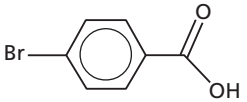
ii) 

d) i) 

ii) Reduction

e) i) 

(or ionic)

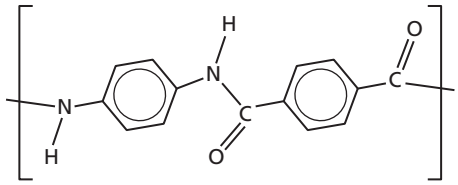
ii) 

iii) Precipitate X is less polar, resulting in less hydrogen bonding to water. Significant id–id interactions between molecules of X, due to large Br atom.

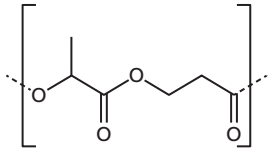
# Topic 30: Condensation polymers

## *Answers to in-text questions*

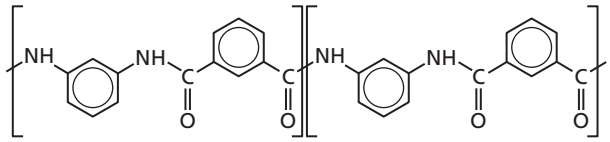
### *Questions 30.1*

1 a) 

b) Kevlar is a II polymer.

2 

### *Questions 30.2*

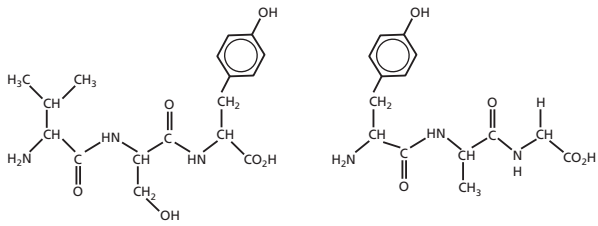
a) 

b) Nomex is likely to be more flexible, because chain is not as 'linear' as in Kevlar, so interchain hydrogen bonding will be less.

### *Question 30.3*

Monomers are $HO—CH_2CH_2CO_2H$ and $HOCH_2CO_2H$.

### *Questions 30.4*

1 

2 Ser-Asp-Gly-Val

### *Questions 30.5*

1 $HOCH_2CH_2OH$ and $COCl_2$

2 $CH_2{=}CH(OCOCH_3)$, $CH_2{=}CHCN$, $CH{=}C(CN){—}CH{=}CH_2$

## *Answers to end of topic questions*

1 a) i) $CH_2{=}CH{—}CO_2H$ or $CH_2{=}CH{—}CO_2R$ or $CH_2{=}CH{—}COCl$

ii) Addition polymerisation

iii) $C(CH_2OH)_4$

iv) Water

b) The water molecules form hydrogen bonds with the polymer and these bonds are not strong so are easily broken.

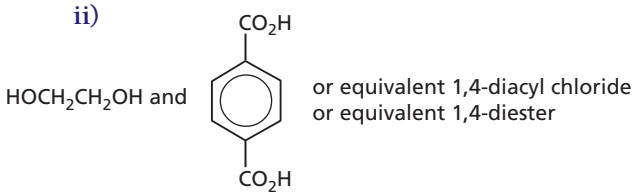
c) i) The $C(CH_2OH)_4$ molecule that forms the cross-link has two spare –OH groups that can form hydrogen bonds with water.

ii) The hydrogel becomes stronger and has a higher melting point because the chains of the polymer are more tightly held together and are more rigid.

2 a) i) Polyester: terylene, polylactic acid (PLA)
Polyamide: nylon, Kevlar, Nomex

ii) Water (or hydrogen chloride)

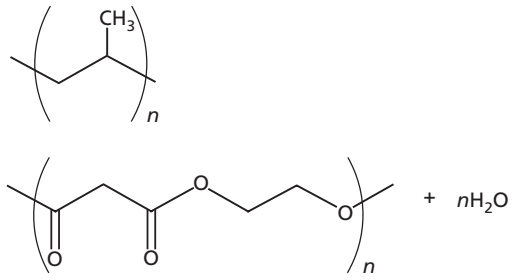
b) i) **A** biodegradable
**B** biodegradable
**C** non-biodegradable
**D** biodegradable

ii) 


c) i) **V** has the highest pH in aqueous solution because it has two amine ($NH_2$) groups that can be protonated (it has an amine ($NH_2$) group on its side chain/R-group.)

ii) Four: TT, TU, UT, UU

iii) Hydrogen bonds form between the O and N atoms in the polypeptide and water, or there are ion–dipole attractions between $NH_3^+$ and $CO^{2-}$ and water.

3 a) i) 


ii) For addition polymerisation, $\Delta S^{\ominus}$ will be negative as many gas molecules are combining to form one (large) molecule. For condensation polymerisation $\Delta S^{\ominus}$ is likely to be positive. As each pair of monomer molecules join to form a chain, two molecules of water form.

b) i) $RCO_2H + H_2NR' \rightarrow RCONHR' + H_2O$

ii) Bonds broken: C—O, N—H
Bonds formed: C—N, O—H

iii) Bonds formed: 305 + 460 or 765
Bonds broken: 360 + 390 or 750 (both)
$\Delta H = 750 - 765 = -15$ (kJ)

c) (If $\Delta G = 0$, then) $\Delta H = T\Delta S$
$\Delta S = \Delta H/T = -6000/298 = -20.1$ ($J\,mol^{-1}\,K^{-1}$)

d) i) Heat with (conc.) $KMnO_4$

ii) Sn and HCl, heat + conc. (then add NaOH)

e)

| intermolecular force | group(s) involved |
|---|---|
| hydrogen bonding | N—H and C=O (of amide) |
| induced dipole | benzene rings |

# Topic 31: Chromatography and NMR spectroscopy

## *Answers to in-text questions*

### *Questions 31.1*

**a)** For one other proton, we have just two possibilities: ↑ or ↓, so we see a 1 : 1 doublet.

**b)** For four other protons we have the following:

↑↑↑↑ ↑↑↑↓ ↑↑↓↓ ↑↓↓↓ ↓↓↓↓
↑↑↓↑ ↑↓↑↓ ↓↑↓↓
↑↓↑↑ ↓↑↑↓ ↓↓↑↓
↓↑↑↑ ↑↓↓↑ ↓↓↓↑
↓↑↓↑
↓↓↑↑

Therefore, we see five lines, in the ratio 1 : 4 : 6 : 4 : 1.

### *Questions 31.2*

**1** The NMR spectrum of **W** shows:
- a 3—H singlet at δ 2.1 ($CH_3$ group next to electron-withdrawing group such as C=O)
- a 2—H triplet at δ 2.6 ($CH_2$ group next to $CH_2$)
- a 1—H singlet at δ 3.4 (—OH group)
- a 2—H triplet at δ 3.8 ($CH_2$ group next to $CH_2$, and possibly next to electronegative oxygen atom).

Compound **W** could be 1-hydroxybutan-3-one, $CH_3COCH_2CH_2OH$.

The NMR spectrum of **X** shows:
- a 3—H triplet at δ 1.1 ($CH_3$ group adjacent to a $CH_2$ group)
- a 2—H quartet at δ 2.3 ($CH_2$ group adjacent to a $CH_3$ group, next to C=O – δ is not high enough to be adjacent to oxygen)
- a 3—H singlet at δ 3.7 ($CH_3$ group with no adjacent CH groups, next to an electronegative oxygen atom)

Compound **X** could be methyl propanoate, $CH_3CH_2CO_2CH_3$.

**2** The 3-proton triplet at δ 1.3 suggests a $CH_3$ group adjacent to a $CH_2$ group. The two-proton quartet at δ 2.5 suggests a $CH_2$ group next to a $CH_3$ group. The one-proton broad singlet at δ 10.7 suggests the –OH group of a carboxylic acid. Therefore **Y** is propanoic acid, $CH_3CH_2CO_2H$.

**3** The NMR spectrum of **Z** shows:
- a 6—H doublet at δ 0.9 (two equivalent $CH_3$ groups adjacent to a single H)
- a 1—H multiplet at δ 1.7 (a single CH split by many protons)
- a 1—H singlet at δ 2.1 (the –OH proton, disappears with $D_2O$)
- a 2—H doublet at δ 3.4 (a $CH_2$ group split by a single H).

Compound **Z** could be 2-methylpropan-1-ol, $(CH_3)_2CHCH_2OH$.

## Question 31.3

Propyl methanoate is $HCO_2CH_2CH_2CH_3$, so has four different C-atom environments. Prop-2-yl methanoate is $HCO_2CH(CH_3)_2$, so has only three C-atom environments. Therefore spectrum (a) is that of prop-2-yl methanoate and spectrum (b) is that of propyl methanoate.

Analysis of δ values: Both spectra have the $sp^2$ $^{13}C$ (of the C═O group) at δ 162 and an $sp^3$ $^{13}C$ of the O—$CHR_2$ or O—$CH_2R$ at δ 68. The remaining peak in spectrum (a), at δ 22, is due to the two $CH_3$ groups, whereas spectrum (b) has two peaks in the $sp^3$ $^{13}C$ region (δ 22 and δ 10) for its —$CH_2$—$CH_3$ group.

## Answers to end of topic questions

**1 a) i)** They have a magnetic moment with a spin of $\frac{1}{2}$

**ii)** Number of carbon atoms = (100 ÷ 1.1) × (2 ÷ 25) = 7.3. *x* must be a whole number so *x* = 7

The peaks show there are eight protons or hydrogen atoms.

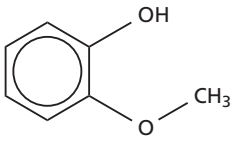
The high carbon-to-hydrogen ratio indicates an aromatic ring.

The peak at about δ 6.8 indicates four aromatic protons.

The peak at about δ 4.7 indicates a phenolic –OH proton.

The peak at about δ 3.8 indicates a methyl group on an oxygen atom.

The formula could be $C_7H_8O_2$




(any orientation)

**2 a) i)** n = (100 ÷ 1.1) × (3.35 ÷ 43.3) = 7.03 so the number of carbon atoms is seven.

**ii)** The ratio of M : M + 2 peaks is 3 : 1 so the halogen is chlorine.

**iii)** The number of protons is 4 + 2 + 1 = 7 so the number of hydrogen atoms is seven.

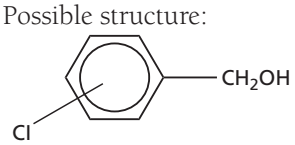
**iv)** The peak at about δ 7.3 indicates a benzene ring.

The peak at about δ 4.7 indicates a —$CH_2$— group.

The peak at about δ 2.3 indicates an —OH group.

Mass of seven hydrogen, seven oxygen and chlorine = 126.6 so there can only be a single atom of oxygen.

Possible structure:




(allow the 2-, 3- or 4-isomer)

**b) i)** The mass spectrum of propene might have a peak at *m/e* = 15, corresponding to a $CH_3$ group, whereas the mass spectrum of cyclopropane will not.

**ii)** There is only one type of proton in cyclopropane, whereas in propene there are three types of proton. Therefore the $^1H$ NMR spectrum of cyclopropane will show one singlet line, whereas that of propene will show several, with splitting.

**3 a)** $n(MnO_4^-) = 0.02 \times 15.2/1000 = 3.04 \times 10^{-4}$ mol

$n(C_2O_4H_2) = 3.04 \times 10^{-4} \times 5/2 = 7.6 \times 10^{-4}$ (in 25 $cm^3$) = $3.04 \times 10^{-3}$ mol in 100 $cm^3$

$M_r = 24 + 64 + 2 = 90$

mass of $C_2O_4H_2 = 3.04 \times 10^{-3} \times 90$

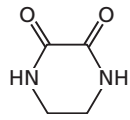
= 0.2736 (0.274) g

percentage = 0.2736 × 100/40 = 0.68%

**b) i)** $SOCl_2$ or $PCl_5$ or $PCl_3$

**ii)** **J** is $CH_3OCO$—$COOCH_3$

**K** is




**c) i)** $CH_3$ at δ 15

$CH_2O$ at δ 65

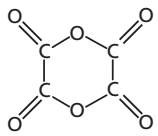
**ii)** There is only one peak, so only one type of environment of a C atom.

**d) i)** **M** is $HO_2C$—$CO_2H$

**N** is $CH_3OCO$—$CO_2H$

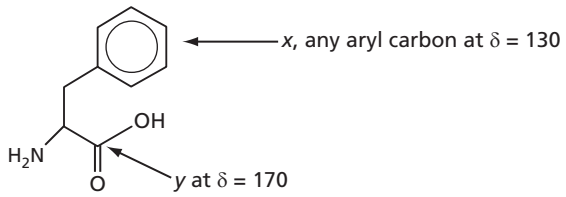
**O** is $CH_3OCO$—$COOCH_3$

**ii)** **L** is




**4 a)** Seven

**b)**



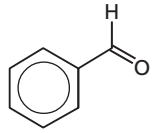

**5 a) i)** *n* = (100/1.1)(8/100) = 7.3 (so 7 C atoms)

**ii)** $C_7H_7^+$

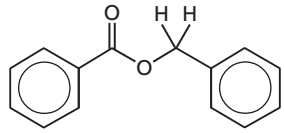
**iii)** **F** = $C_7H_6O$

**G** = $C_{14}H_{12}O_2$

**iv)**

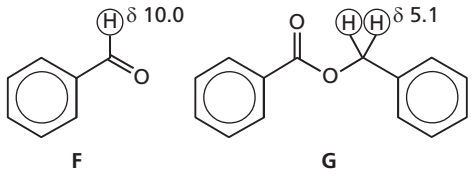



F




G

v)




vi) Hydrolysis

b) Benzoic acid > methylphenol > phenylmethanol
The methylphenoxide anion has delocalisation of the oxygen lone pair over the ring.
Benzoic acid has an (extra) electronegative oxygen or electron withdrawing C═O. In addition, the oxygen lone pair and negative charge are spread equally between the two oxygen atoms of the $—CO_2^-$ group.

c) Step 1: treat benzoic acid with $SOCl_2$ or $PCl_5$ to make the acyl chloride ($C_6H_5COCl$).
Step 2: dissolve the methylphenol in NaOH(aq) and shake with the benzoyl chloride.

# Topic 32: Chirality, organic synthesis and analysis

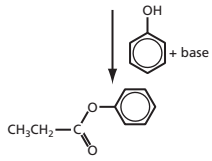
## *Answers to in-text questions*

### *Questions 32.1*

1 $CH_3CH_2Br \xrightarrow[\text{heat}]{\text{NaOH(aq)}} CH_3CH_2OH \xrightarrow[\text{heat and distil}]{Na_2Cr_2O_7 + H^+} CH_3CHO \xrightarrow[\text{NaCN}]{\text{HCN +}} CH_3CH(OH)CN$

2 $CH_3CN \xrightarrow[H_2SO_4(aq)]{\text{heat with}} CH_3CO_2H \xrightarrow[\text{and trace of conc. } H_2SO_4]{\text{heat with } CH_3OH} CH_3CO_2CH_3$

3 $CH_3CH_2CH_2OH \xrightarrow[\text{heat}]{Na_2Cr_2O_7 + H^+} CH_3CH_2CO_2H \xrightarrow{SOCl_2} CH_3CH_2COCl$




### *Questions 32.2*

1 Conc. $HNO_3$ + $H_2SO_4$, T = 55°C, electrophilic substitution
Sn + conc. HCl + heat, reduction

2 $HNO_2$ or $NaNO_2$ + HCl at 5°C, then heat in water

3 Cl-$CH_2$-$CH_2$-CHO, Dissolve the naphthol in NaOH(aq) and add the chloroaldehyde, nucleophilic substitution

4 Reaction 4: NaBH4, reduction
Reaction 5: heat over $Al_2O_3$, dehydration *or* elimination

5 Reaction 6: dilute $KMnO_4$ at room temperature
Reaction 8: $(CH_3)_2NH$

6 It is an $S_N2$ reaction. The primary carbon atom on the end is less sterically hindered than the secondary carbon atom in the chain, so the nucleophile can attack more easily.

### *Questions 32.3*

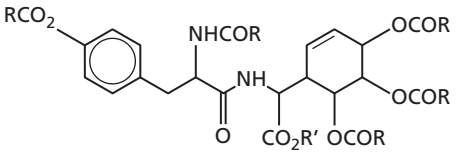
a) All contain a secondary amine group, which is two carbons away from an aromatic ring.
All contain a secondary alcohol group, which is on the carbon adjacent to the ring.

b) All contain a quaternary nitrogen atom, with three methyl groups. All contain an oxygen atom two carbons away from the quaternary nitrogen.

### *Questions 32.4*

a) *Four from:* phenol, alcohol, amine, amide, carboxylic acid.

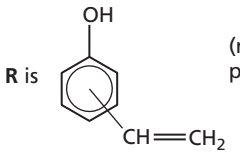
b) The phenol and all the alcohol –OH groups could be esterified with an acyl chloride derived from a longer-chain carboxylic acid (to make it less water soluble). The amine group could be reacted with the same acyl chloride to form an amide (amides are less polar than amines). The carboxylic acid could be esterified with an alcohol.
The resulting structure:




where R = long-chain alkyl group and
R′ = a different long-chain alkyl group
reagents: (1) R′OH + conc. $H_2SO_4$ + heat
(2) RCOCl (an excess)

### *Questions 32.5*

1 Na metal: **R** contains an OH group (alcohol, phenol or acid).
No reaction with $PCl_5$: not alcohol or acid.
White ppt with $Br_2$(aq): phenol.
Decolourises $KMnO_4$(aq): alkene.




(not possible to identify position of substitution)

2 Two oxygen atoms: could be an ester, an acid or a diol, dicarbonyl etc.
No reaction with hot $H_2SO_4$(aq): not an ester.
No reaction with hot acidified $Na_2Cr_2O_7$(aq): not a secondary or primary alcohol, or an aldehyde.
Na metal: contains OH group (tertiary alcohol or acid).
Reaction with $I_2 + OH^-$(aq): contains $—CH(OH)CH_3$ or $—COCH_3$
2,4-DNPH: contains C═O group
No reaction with Fehling's: not an aldehyde
If **S** contains a ketone group, it cannot be an acid (not enough oxygens). The second oxygen must therefore be in a tertiary alcohol group (reacts with Na).
**S** is either $(CH_3)_2C(OH)CH_2COCH_3$ or $CH_3CH_2C(CH_3)(OH)COCH_3$.

## Questions 32.6

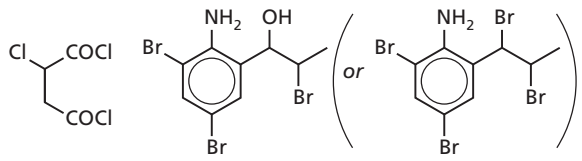
1 Either of the following tests would distinguish these two compounds.
   a) Add $Br_2$ (aq): the methlyphenol would decolourise the reagent and give a white ppt; the phenylmethanol would have no reaction.
   b) Warm with acidified $Na_2Cr_2O_7$: the methyphenol would have no reaction; the phenylmethanol would change the colour of the reagent from orange to green (as it is oxidised to the aldehyde or the carboxylic acid)

2 The first compound is a ketone: 2,4-DNPH would give an orange ppt. The second compound is an acid: it would fizz with $Na_2CO_3$(aq) or turn universal indicator red. (Note that Na metal would **not** distinguish – both would give off $H_2$(g)).

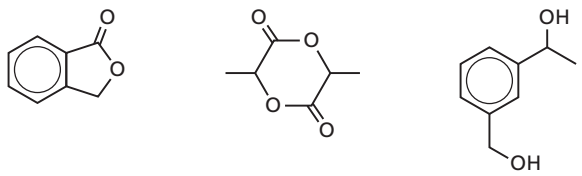
3 Both compound are esters, which have similar reactions to most reagents. So they will need to be hydrolysed first (by heating with aqueous acid and distilling). The second compound would give methanoic acid, which would reduce blue Fehling's solution, giving a dull red ppt; the ethanoic acid from the first would not. Furthermore, the ethanol formed by the hydrolysis of the second compound would give the tri-iodomethane test (yellow ppt with alkaline aqueous iodine), whereas the methanol from the first compound would not.

4 The first compound is an acyl chloride – it would fume in moist air, and give an *immediate* ppt of AgCl(s) with $AgNO_3$(aq), and an acidic solution (turing universal indicator red). The second compound is an aldehyde: it would give an orange ppt with 2,4-DNPH; reduce Fehling's solution to a dull red ppt; and give a silver mirror with Tollens' reagent.

## Questions 32.7




A B

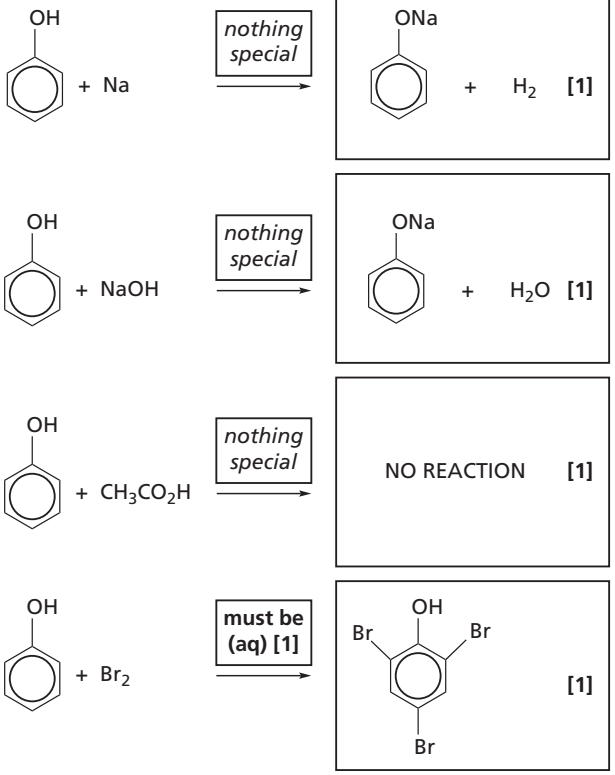



C D E

## Answers to end of topic questions

1 a) The acidity of ethanol is less than that of water because the $C_2H_5$ group is election-donating, so will destabilise the $RO^-$ anion, compared with $OH^-$. Phenol is more acidic than water because the negative charge on the $ArO^-$ anion is delocalised over the aryl ring, making it more stable.

b)




c)

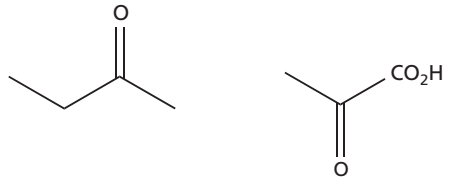

Step 1: Dilute $HNO_3$

Step 2: $Sn/SnCl_2/Fe + HCl$

Step 3: $CH_3COCl$ or $(CH_3CO)_2O$

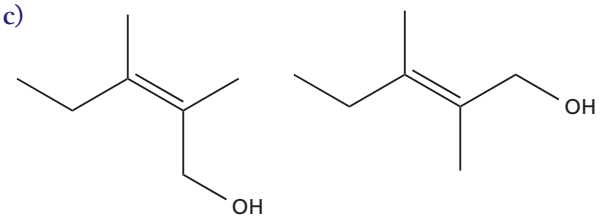
2 a) i) C═C double bonds
   ii) —OH groups
   iii) $CH_3CO$— or $CH_3CH(OH)$— groups
   iv) >C═O carbonyl groups

b)



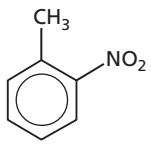

D E

c)




*cis* *trans*

3 a) i)




ii) $HNO_3 + 2H_2SO_4 \rightarrow H_3O^+ + NO_2^+ + 2HSO_4^-$

iii) *Any three from:*

- Electrons in bonds are partially delocalised in **T** or the delocalised π-bond extends over only five carbons.
- There are four π electrons in the delocalised system of **T** or methylbenzene has two more delocalised π electrons.
- There is a carbon that is $sp^3$ hybridised in **T** or all the carbons are $sp^2$ hybridised in methylbenzene.
- One carbon has a bond angle of 109.5°, giving a tetrahedral shape in **T** or C—C bond strengths and lengths are not all the same or not all the bond angles are 120° in **T**.

b) i) 4-aminobenzoic acid

ii) Step 1: Sn + HCl, concentrated and heated under reflux
Step 2: $CH_3COCl$
Step 3: $KMnO_4$/manganate(VII)/$MnO_4^-$ (acidified/alkaline) and heat
Step 4: aqueous HCl and heat
Step 5: ethanol, $H_2SO_4$, concentrated and heated under reflux

c) Benzocaine is less basic than ethylamine and the lone pair on the N is less available to accept a proton, since the lone pair on the N is delocalised over the ring.
Ethylamine is more basic (than benzocaine) and the lone pair on the N is more available to accept a proton, since the ethyl (alkyl) group is electron-donating.

d) i) Seven peaks

ii) $CDCl_3$ produces no signal in the spectrum; $CHCl_3$ would produce a signal that would be detected. This signal might obscure important signals from the hydrogen atoms in the sample.

iii)

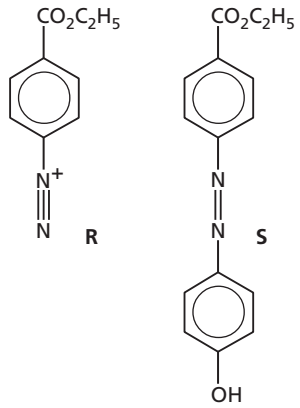
| δ/ppm | group responsible for the peak | number of 1 H atoms responsible for the peak | splitting pattern |
|---|---|---|---|
| 1.2 | **$CH_{(3)}$** | **3** | **triplet** |
| 3.5 | **$CH_{(2)}O$** | **2** | **quartet** |
| 5.5 | **$NH_2$** | **2** | **singlet (broad)** |
| 7.1–7.4 | **H attached to benzene ring** | **4** | multiplet |

iv) The adjacent carbon **atom** has two protons attached to it or there is an adjacent $CH_2(O)$ group.

v) The $NH_2$ peak at 5.5 will disappear **and** the $NH_2$ protons exchange with deuterium.

e) i) $NaNO_2$ + HCl or $HNO_2$

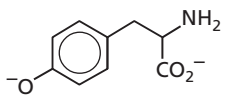
ii)

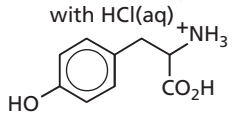


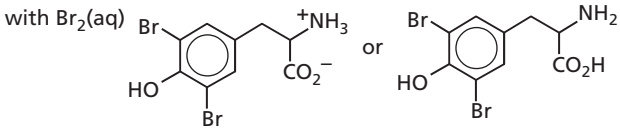

4 a) i) Step 1: electrophilic substitution
Step 2: nucleophilic addition

ii) Hydrolysis

iii Step 1: $ClCH_2CHO$, $AlCl_3$
Step 2: HCN + NaCN
Step 3: heat in $H_3O^+$/heat $H^+$(aq)
Step 5: $NH_3$ under pressure (+ heat) or heat $NH_3$ in a sealed tube with NaOH(aq)




b) i) **P** is tyr.
Tyr is 2– and it is a small molecule with a low $M_r$.

ii) The dipeptide phe-tyr is 2– and is about double the mass ($M_r$) of (*phe*) or the mass : charge ratios are about the same for both.

5 a) i) Seven peaks

ii) C═O 1670–1740
OH 3200–3600 or C—O 1000–1260
C—O 1000–1260

b) i) Step 1: heat with $AlCl_3$ + $(CH_3)_2CHCl$ or $CH_3CH{=}CH_2$
Step 2: heat with $AlCl_3$ + $CH_3COCl$
Step 3: NaOH + $I_2$ (or $Cl_2$) (then $H^+$)
Step 4: $LiAlH_4$ (in dry ether)

ii) Step 2: electrophilic (aromatic) substitution
Step 4: reduction