OCR A LEVEL CHEMISTRY

A WEEKLY REVISION PLAN

| SEPTEMBER 9, 2023

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Week 1

Foundations in Chemistry

2.1. Atoms and Reactions

2.1.1 Atomic structure and isotopes

(a) isotopes as atoms of the same element with different numbers of neutrons and different masses					
(b) atomic structure in terms of the numbers of protons, neutrons and electrons for atoms and ions, given the atomic number, mass number and any ionic charge					
(c) explanation of the terms relative isotopic mass (mass compared with 1/12th mass of carbon-12) and relative atomic mass (weighted mean mass compared with 1/12th mass of carbon-12), based on the mass of a ^{12}C atom, the standard for atomic masses					
(d) use of mass spectrometry in: **(i)** the determination of relative isotopic masses and relative abundances of the isotope, **(ii)** calculation of the relative atomic mass of an element from the relative abundances of its isotopes					
(e) use of the terms relative molecular mass, Mr, and relative formula mass and their calculation from relative atomic masses.					

2.1.2 Compounds, formulae and equations

(a) the writing of formulae of ionic compounds from ionic charges, including: **(i)** prediction of ionic charge from the position of an element in the periodic table **(ii)** recall of the names and formulae for the following ions: NO^{3-}, CO_3^{2-}, SO_4^{2-}, OH^-, NH_4^+, Zn^{2+} and Ag^+					
(b) construction of balanced chemical equations (including ionic equations), including state symbols, for reactions studied and for unfamiliar reactions given appropriate information.					

2.1.3 Amounts of substance

(a) explanation and use of the terms: **(i)** *amount of substance* **(ii)** *mole* (symbol 'mol'), as the unit for amount of substance **(iii)** the *Avogadro constant*, N_A (the number of particles per mole, 6.02×10^{23} mol^{-1}) **(iv)** *molar mass* (mass per mole, units g mol^{-1}), **(v)** *molar gas volume* (gas volume per mole, units dm^3 mol^{-1})					
(b) use of the terms: **(i)** *empirical formula* (the simplest whole number ratio of atoms of each element present in a compound) **(ii)** *molecular formula* (the number and type of atoms of each element in a molecule)					
(c) calculations of empirical and molecular formulae, from composition by mass or percentage compositions by mass and relative molecular mass					
(d) the terms *anhydrous*, *hydrated* and *water of crystallisation* and calculation of the formula of a hydrated salt from given percentage composition, mass composition or based on experimental results					
(e) calculations, using amount of substance in mol, involving: **(i)** mass **(ii)** gas volume **(iii)** solution volume and concentration					
(f) the ideal gas equation: $pV = nRT$					
(g) use of stoichiometric relationships in calculations					
(h) calculations to determine: **(i)** the percentage yield of a reaction or related quantities **(ii)** the atom economy of a reaction					
(i) the techniques and procedures required during experiments requiring the measurement of mass, volumes of solutions and gas volumes					

(j) the benefits for sustainability of developing chemical processes with a high atom economy.					

2.1.4 Acids

(a) the formulae of the common acids (HCl, H_2SO_4, HNO_3 and CH_3COOH) and the common alkalis ($NaOH$, KOH and NH_3) and explanation that acids release H^+ ions in aqueous solution and alkalis release OH^- ions in aqueous solution					
(b) qualitative explanation of strong and weak acids in terms of relative dissociations					
(c) neutralisation as the reaction of: **(i)** H^+ and OH^- to form H_2O **(ii)** acids with bases, including carbonates, metal oxides and alkalis (water-soluble bases), to form salts, including full equations					
(d) the techniques and procedures used when preparing a standard solution of required concentration and carrying out acid–base titrations					
(e) structured and non-structured titration calculations, based on experimental results of familiar and non-familiar acids and bases.					
(f) describe the redox reactions of metals with dilute hydrochloric and dilute sulfuric acids					
(g) interpret and make predictions from redox equations in terms of oxidation numbers and electron loss/gain					

2.1.5 Redox

(a) rules for assigning and calculating oxidation number for atoms in elements, compounds and ions					
(b) writing formulae using oxidation numbers					
(c) use of a Roman numeral to indicate the magnitude of the oxidation number when an element may have compounds/ions with different oxidation numbers					
(d) oxidation and reduction in terms of: **(i)** electron transfer **(ii)** changes in oxidation number					
(e) redox reactions of metals with acids to form salts, including full equations **(see also 2.1.4 c)**					
(f) interpretation of redox equations in **(e)**, and unfamiliar redox reactions, to make predictions in terms of oxidation numbers and electron loss/ gain.					
(g) interpret and make predictions from redox equations in terms of oxidation numbers and electron loss/gain					

Module 2.2: Electrons, bonding and structure

2.1 Electron structure

(a) the number of electrons that can fill the first four shells					
(b) atomic orbitals, including: **(i)** as a region around the nucleus that can hold up to two electrons, with opposite spins **(ii)** the shapes of s- and p-orbitals **(iii)** the number of orbitals making up s-, p- and d-sub-shells, and the number of electrons that can fill s-, p- and d-sub-shells					
(c) filling of orbitals: **(i)** for the first three shells and the 4s and 4p orbitals in order of increasing energy **(ii)** for orbitals with the same energy, occupation singly before pairing					
(d) deduction of the electron configurations of: **(i)** atoms, given the atomic number, up to $Z = 36$ **(ii)** ions, given the atomic number and ionic charge, limited to s- and p-blocks up to $Z = 36$.					

2.2.2 Bonding and structure

(a) ionic bonding as electrostatic attraction between positive and negative ions, and the construction of '*dot-and-cross*' diagrams					
(b) explanation of the solid structures of giant ionic lattices, resulting from oppositely charged ions strongly attracted in all directions e.g. NaC*l*					
(c) explanation of the effect of structure and bonding on the physical properties of ionic compounds, including melting and boiling points, solubility and electrical conductivity in solid, liquid and aqueous states					
(d) covalent bond as the strong electrostatic attraction between a shared pair of electrons and the nuclei of the bonded atoms					
(e) construction of '*dot-and-cross*' diagrams of molecules and ions to describe: **(i)** single covalent bonding **(ii)** multiple covalent bonding **(iii)** dative covalent (coordinate) bonding					
(f) use of the term *average bond enthalpy* as a measurement of covalent bond strength					
(g) the shapes of, and bond angles in, molecules and ions with up to six electron pairs (including lone pairs) surrounding the central atom as predicted by electron pair repulsion, including the relative repulsive strengths of bonded pairs and lone pairs of electrons					
(h) electron pair repulsion to explain the following shapes of molecules and ions: linear, non-linear, trigonal planar, pyramidal, tetrahedral and octahedral					
(i) electronegativity as the ability of an atom to attract the bonding electrons in a covalent bond; interpretation of Pauling electronegativity values					
(j) explanation of: polar bond and permanent dipole within molecules containing covalently-bonded atoms with different electronegativities **(ii)** a polar molecule and overall dipole in terms of permanent dipole(s) and molecular shape					
(k) intermolecular forces based on permanent dipole–dipole interactions and induced dipole– dipole interactions					
(l) hydrogen bonding as intermolecular bonding between molecules containing N, O or F and the H atom of –NH, –OH or HF					
(m) explanation of anomalous properties of H_2O resulting from hydrogen bonding, e.g.: **(i)** the density of ice compared with water **(ii)** its relatively high melting and boiling points					
(n) explanation of the solid structures of simple molecular lattices, as covalently bonded molecules attracted by intermolecular forces, e.g. I_2, ice					
(o) explanation of the effect of structure and bonding on the physical properties of covalent compounds with simple molecular lattice structures including melting and boiling points, solubility and electrical conductivity					

Atomic Structure

Key Recall Question	Answer
1. Give the location, relative mass and relative charge of each subatomic particle	Nucleus: protons (charge +1, mass 1), neutrons (charge 0, mass 1) Orbitals/shell: electrons (charge -1, mass = near 0)
2. What does mass number (A) tell you?	Number of protons and neutrons
3. What does atomic number (Z) mean?	Number of protons
4. Define an ion	An atom that has gained or lost electrons to become charged
5. Define isotope	Atoms with the same number of protons and electrons but differing numbers of neutrons (and therefore atomic mass)
6. How do you calculate neutron number from atomic mass and number?	atomic mass – atomic number
7. How has the atomic model changed over time?	**Dalton** – atoms as solid spheres **Thomson** – discovered electron – 'plum pudding model' – positive sphere studded with electrons **Rutherford** – gold foil experiment – fired alpha particles at thin gold foil – most pass through but some are deflected back suggesting mass concentrated in certain spots – atom is mostly empty space with dense nucleus **Bohr** – electrons are in fixed orbits, each with a fixed energy
8. Define relative atomic mass, Ar	The relative mass of an atom of an element on a scale where an atom of carbon-12 is exactly 12

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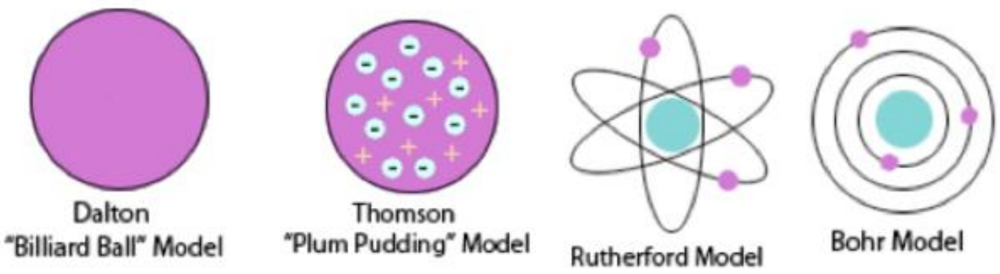

Electron Substructure

Key Recall Question	Answer
1. Electron shells are divided into….	Subshells
2. Subshells are divided into…	Orbitals
3. Each orbital can hold up to ____ electrons	2
4. The s subshell has ____ orbitals	1
5. The p subshell has ____ orbitals	3 (holding 6 electrons in total)
6. The d subshell has ____ orbitals	5 (holding 10 electrons in total)
7. The f subshell has ____ orbitals	7 (holding 14 electrons in total)
8. The p block elements are called that because…	The outer electrons are in p orbitals
9. Give the electron configuration for oxygen (Z=8)	$1s^2 2s^2 p^4$
10. Give the electron config for chlorine (z=17)	$1s^2 2s^2 p^6 3s^2 3p^5$
11. Which two elements have exception configs?	Chromium $1s^2 2s^2 p^6 3s^2 3p^6 3d^5 4s^1$ Cobalt $1s^2 2s^2 p^6 3s^2 3p^6 3d^{10} 4s^1$
12. What are the rules for the order of 3d and 4s filling and emptying?	4s fills before 3d because it has a lower energy due to repulsion in the atom. When ions form, 4s is lost before 3d.

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Ionisation Energy

Key Recall Question	Answer
1. What is the definition of ionisation energy?	The energy needed to remove one mole of electrons from one mole of gaseous atoms to form gaseous ions
2. What is the general equation for first ionisation energy	$X(g) \rightarrow X^{+} (g) + e^{-}$
3. What does it mean if ionisation energy is low?	It is easy to remove the outer electron
4. What does a high ionisation energy indicate?	A strong attraction between the electron and the nucleus making it hard to remove the electron
5. What three factors affect ionisation energy?	**Nuclear charge** – the more the protons, the greater the attraction between nuceus and electrons **Distance** from nucleus – the further from the nucleus, the weaker an electron is held **Shielding** – as the number of electrons between the outer electrons and the nucleus increases, the less the attraction between the outer electron and nucleus
6. What is second ionisation energy and its equation?	The energy required to remove the next electron $X^{+(}g) \rightarrow X^{2+} (g) + e^{-}$
7. What is the trend in ionisation energy down a group?	It decreases because distance and shielding increase so it is easier to remove the electron (has more impact than nuclear charge)
8. What is the general trend in ionisation energy across a period?	Increases across a period (in general) as nuclear charge increases (with no change to shielding or distance).
9. Why are there dips in the increase in ionisation energy?	There is a small drop from group 2 to 3 showing the shuft from s to p orbitals. There is a small drop between groups 5 and 6 due to electron repulsion as electrons start pairing up in p orbitals
10. How can graphs of ionisation energy show electron shell structure?	The big jumps show where a new shell is broken into. Work from right to left and count how many points there are before each jump – gives no of e-s in each shell

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Bonding 1

Key Recall Question	Answer
1. What forms when an atom gains or loses electrons	Ion – positive if electrons lost, negative if gained
2. How does group number in the periodic table relate to the charge of the ion formed?	They need to get a full shell (up to 8 electrons usually) and take the easiest route: Group 1: 1+ Group 5: 3- Group 2: 2+ Group 6: 2- Group 3: 3+ Group 7: 1-
3. What are the formulae for these ions? Carbonate, sulfate, nitrate, hydroxide, ammonium	CO_3^{2-}, SO_4^{2-}, NO_3^{-}, OH^{-}, NH_3^{4+}
4. How does a bond form between a metal and a non-metal element and what is the bond type?	The non-metal gains electrons to form a negative ion. The metal loses electrons to form a positive ion. The opposite charges attract with strong electrostatic forces. Ionic bond.
5. Describe and explain the properties of ionic substances	High melting point due to strong electrostatic forces between oppositely charged ions. Conduct when molten or dissolved when the ions are free to move but not when solid as the charges can't move.

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Bonding 2;

1. Name the bonding type between non-metals and describe the bond	Covalent; the atoms share electrons so each effectively has a full shell. Single bond – each shares one electron. Double bond – each shares two
2. What is a dative bond?	A covalent bond in which one atom shares two electrons. Has same strength as a normal covalent bond
3. Name three substances that have giant covalent structure and describe their properties	Diamond, graphite, silicon dioxide High melting point due to strong covalent bonds throughout the structure, don't conduct as no free electrons; except for graphite because each carbon forms 3 bonds and the 4th delocalises and can moves through the structure.
4. What are the properties of simple covalent substances	Low melting/boiling point due to weak intermolecular forces between molecules, don't conduct as no charged particles free to move across structure.
5. Describe metallic bonding and explain why metals have their properties	Positive metals ions in a sea of delocalised electrons. High melting point due to strong electrostatic forces between ions and electrons; mp decreases as ion radius gets larger due to distance, conduct as electrons free to move. Ductile/malleable as ions are the same size and can slide over each other.

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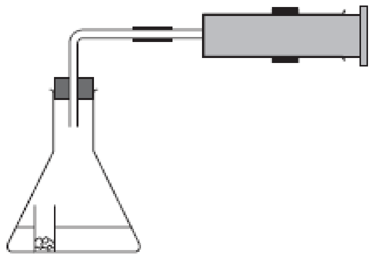
Questions

Q1.

A student wanted to measure the volume of a gas and use the results to find the volume occupied by one mole of the gas. The following method was used.

- A sample of calcium carbonate was weighed out in a small plastic container.
- 20 cm^3 of hydrochloric acid of concentration 2.00 mol dm^{-3} was added to a conical flask. A small pinch of calcium carbonate was added to the acid.
- The container was placed in the conical flask and a gas syringe was connected to the top of the conical flask.
- The flask was carefully shaken so that the small plastic container fell over, allowing the acid and calcium carbonate to mix.

The apparatus set up is shown.



The student repeated the experiment five times using different masses of calcium carbonate on each occasion, with the concentration and volume of the hydrochloric acid constant.

Experiment number	Mass / g	Volume of CO_2 / cm^3
1	0.10	23
2	0.20	44
3	0.30	67
4	0.40	96
5	0.50	115

(a) (i) Write the equation for the reaction between calcium carbonate and hydrochloric acid. Include state symbols.

(2)

(ii) Calculate the molar mass of calcium carbonate.

(1)

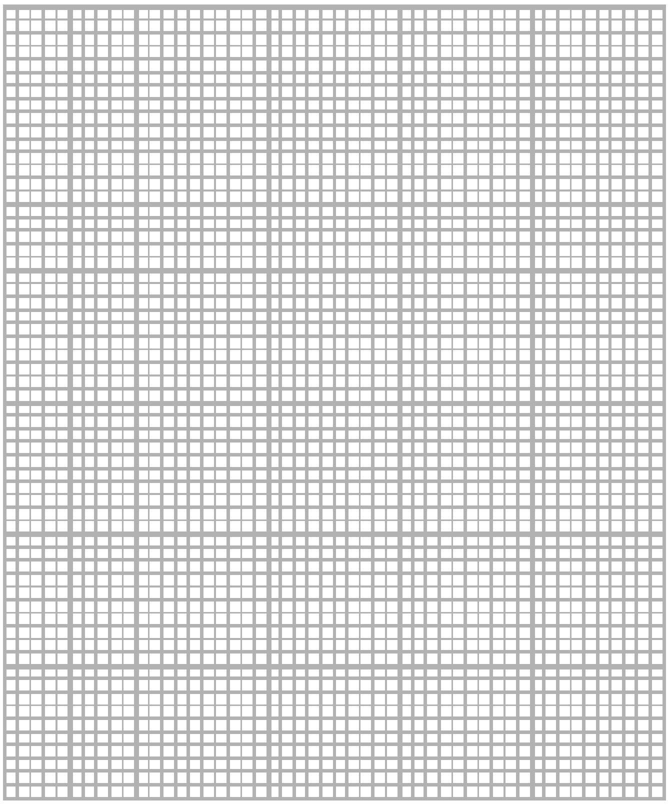
.... g mol^{-1}

(iii) Show that, in each experiment, the hydrochloric acid is in excess.

(2)

(b) (i) Plot a graph of volume of carbon dioxide produced against mass of calcium carbonate on the grid. Include a line of best fit.

(2)



(ii) State how your graph supports the idea that the volume of gas produced depends directly on the mass of calcium carbonate added.

(1)

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....

(c) Calculate the volume, under these conditions, of one mole of carbon dioxide gas from these data. Give your answer in dm^3 to **two** significant figures.

(2)

(d) Give a reason why the student added a small pinch of calcium carbonate to the acid before starting the reaction.

(1)

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(Total for question = 11 marks)

Q2.

Which of the following compounds has the highest boiling temperature?

☒ **A** CH_4

☒ **B** CH_3Cl

☒ **C** HCHO

☒ **D** CH_3OH

(Total for question = 1 mark)

Q3.

This question is about halogens and redox reactions.

The boiling temperatures of three halogens are shown in the table.

Halogen	Boiling temperature / °C
chlorine	–35
bromine	59
iodine	184

Explain why the boiling temperatures increase from chlorine to iodine.

(2)

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(Total for question = 2 marks)

Q4.

Which of these bond angles is the **largest**?

⊠ **A** Cl—B—Cl in BCl_3

⊠ **B** H—N—H in NH_3

⊠ **C** Cl—Be—Cl in $BeCl_2$

⊠ **D** H—O—H in H_2O

(Total for question = 1 mark)

Q5.

In propene, CH2⊠CH—CH_3,

⊠ **A** the C⊠C double bond is longer and stronger than the C—C single bond.

⊠ **B** the C⊠C double bond is shorter and stronger than the C—C single bond.

⊠ **C** the C⊠C double bond is shorter and weaker than the C—C single bond.

⊠ **D** the C⊠C double bond is longer and weaker than the C—C single bond.

(Total for question = 1 mark)

Q6.

Electrons in atoms occupy orbitals.

Successive ionisation energies can give information about the electronic structure of an element.

Which of the following sets of data showing the first four ionisation energies, in kJ mol^{-1}, of four elements is most likely to belong to boron?

(1)

⊠ **A** 1086, 2353, 4621, 6223.

☒ **B** 900, 1757, 14 849, 21 007.

☒ **C** 801, 2427, 3660, 25 026.

☒ **D** 578, 1817, 2745, 11 578.

(Total for question = 1 mark)

Q7.

This question is about magnesium.

The relative atomic mass of a sample of magnesium was found to be 24.3. The percentage composition for two of the three isotopes is given in the table. Use these data to calculate the percentage composition of the third isotope and hence its relative isotopic mass. Give your answer to an appropriate number of significant figures. You **must** show your working.

Relative isotopic mass	Percentage abundance
25.0	10.00
26.0	11.01

(4)

(Total for question = 4 marks)

Q8.

Nickel is an element in the d-block of the Periodic Table.

(a) Complete the electronic configuration of a nickel atom using the s, p, d notation.

(1)

$1s^2$..

(b) A sample of nickel is made up of three isotopes. The percentage abundances are shown in the table below.

Isotope	Percentage abundance
^{58}Ni	69.02
^{60}Ni	27.32
^{62}Ni	3.66

Calculate the relative atomic mass of nickel. Give your answer to **two** decimal places.

(2)

(c) Nickel reacts with carbon monoxide, CO, to give the compound nickel carbonyl, $Ni(CO)_4$.

$$Ni(s) + 4CO(g) \rightarrow Ni(CO)_4(g)$$

(i) Calculate the volume of carbon monoxide, in dm^3, measured at room temperature and pressure, that is required to react completely with 5.87 g of nickel.

[Relative atomic mass: Ni = 58.7
Molar volume of a gas = 24 dm^3 mol^{-1} at room temperature and pressure.]

(3)

(ii) Calculate the **number** of carbon monoxide molecules present in the volume of gas you have calculated in (c)(i).

[The Avogadro constant, $L = 6.02 \times 10^{23}$ mol^{-1}]

(1)

(d) Nickel(II) nitrate, $Ni(NO_3)_2$, can be made by several different methods.

Method 1
Nickel(II) oxide, NiO, was reacted with dilute nitric acid according to the equation

$$NiO(s) + 2HNO_3(aq) \rightarrow Ni(NO_3)_2(aq) + H_2O(l)$$

(i) Calculate the volume of 2.00 mol dm^{-3} dilute nitric acid, in cm^3, that was required to exactly neutralize 1.494 g of nickel(II) oxide.

Use the relative atomic masses: Ni = 58.7, O = 16.0

(3)

Method 2
A volume of 25.0 cm^3 of 2.00 mol dm^{-3} nitric acid, HNO_3, was transferred to a beaker. Solid nickel(II) carbonate, $NiCO_3$, was added until it was in excess.

(ii) Why was **excess** nickel(II) carbonate used?

(1)

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....

(iii) Why must the beaker be **much** larger than the volume of acid used?

(1)

....

....

....

(iv) Write a balanced equation for the reaction between nickel(II) carbonate and dilute nitric acid, including state symbols.

(2)

*(v) For **Method 2**, describe the practical steps that you would take to obtain pure dry crystals of hydrated nickel(II) nitrate, $Ni(NO_3)_2.6H_2O$, from a mixture of nickel(II) nitrate solution and unreacted solid nickel(II) carbonate.

(4)

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(Total for question = 18 marks)

Q9.

Which of the following species contains the same number of electrons as neutrons?

☒ **A** $^{11}_{5}B$

☒ **B** $^{23}_{11}Na^{+}$

☒ **C** $^{24}_{12}Mg^{2+}$

☒ **D** $^{19}_{9}F^{-}$

(Total for question = 1 mark)

Q10. A compound was found to contain 2.8 g of nitrogen and 8.0 g of oxygen.

What is the empirical formula of the compound?

Use the Periodic Table as a source of data.

☒ **A** NO

☒ **B** NO_2

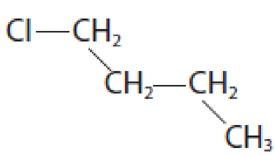
☒ **C** N_2O_3

☒ **D** N_2O_5

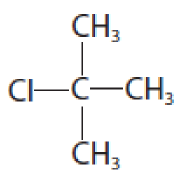
(Total for Question = 1 mark)

Q11.

Consider the following compounds, **E**, **F**, **G** and **H**.



E



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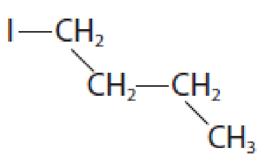
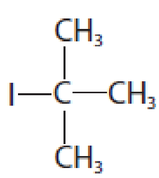


G



H

The boiling temperature of these compounds **increases** in the order

☒ **A** **H G F E**

☒ **B** **G H E F**

☒ **C** **E F G H**

☒ **D** **F E H G**

(Total for question = 1 mark)

Q12.

Sodium and sodium chloride can both be good conductors of electricity.

Under what conditions do these substances conduct electricity?

Compare the method of conductivity in each case.

(3)

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Q13.

In which series of compounds does covalent character **increase** when going from left to right?

☒ **A** KI, KBr, KCl

☒ **B** NaI, KI, RbI

☒ **C** NaCl, $MgCl_2$, $AlCl_3$

☒ **D** SO_2, P_4O_{10}, SiO_2

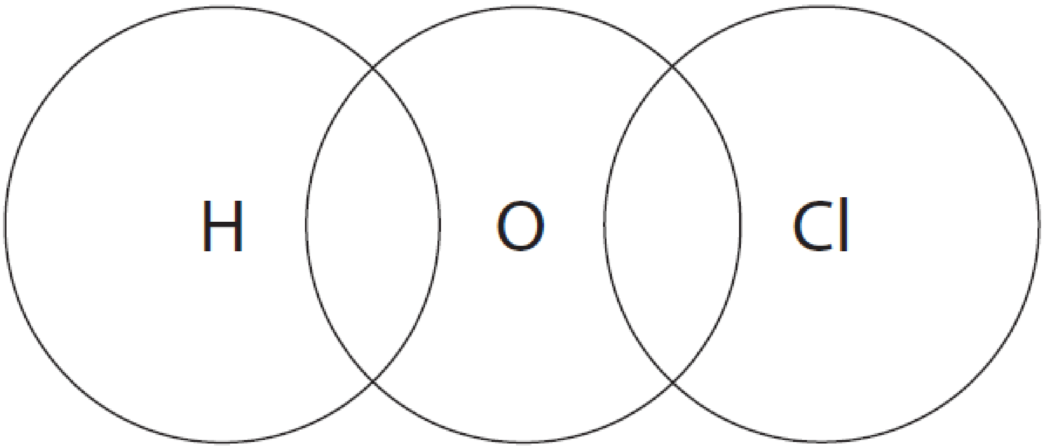
(Total for question = 1 mark)

Q14.

(i) Complete the dot and cross diagram for chloric(I) acid (HOCl). Use a dot (•) to represent the hydrogen electron, circles (o) to represent the oxygen electrons and crosses (×) to represent the chlorine electrons.

Show the outer electrons only, but include non-bonding electrons.

(2)



*(ii) Predict the bond angle in chloric(I) acid. Explain your answer fully.

(5)

Bond angle = ...

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Q15.

Which of the following contains a dative covalent bond?

☐ **A** N_2

☐ **B** NH_3

☐ **C** NH_2^-

☐ **D** NH_4^+

(Total for question = 1 mark)

Q16.

Sodium and chlorine react together to produce sodium chloride. The bonding in the product is different from that in both of the reactants. Evidence for the type of bonding present can be obtained in a number of different ways.

Sodium chloride is ionically bonded. What is meant by the term **ionic bond**?

(1)

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....

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Q17.

Which of the following diagrams represents the electrons in the ground state of a boron atom?

	$1s$	$2s$	$2p_x$	$2p_y$	$2p_z$
☒ **A**	↑↓	↑↓	↑		
☒ **B**	↑	↑↓	↑	↑	
☒ **C**	↑↓	↑	↑	↑	
☒ **D**	↑	↑	↑	↑	↑

(Total for question = 1 mark)

Q18. Which of the following statements about electronegativity is true?

☒ **A** Non-metals have lower electronegativity than metals.

☒ **B** Electronegativity decreases across a period in the Periodic Table.

☒ **C** Electronegativity decreases going down a group in the Periodic Table.

☒ **D** The bonds between atoms with equal electronegativity are always weak.

(Total for Question = 1 mark)

Q19.

This question is about magnesium.

(i) Complete the electronic structure of a magnesium atom.

(1)

$1s^2$

....

(ii) The bonding in magnesium results from

(1)

☒ **A** strong electrostatic attractions between oppositely charged ions

☒ **B** strong electrostatic attractions between the nuclei of magnesium atoms and a shared pair of electrons

☒ **C** strong electrostatic attractions between positively charged ions and a sea of delocalised electrons

☒ **D** weak dispersion forces between magnesium atoms

(Total for question = 2 marks)

Q20.

When an Al^{4+} ion is formed from an Al atom, the fourth electron is lost from the

☒ **A** 1s sub-shell.

☒ **B** 2s sub-shell.

☒ **C** 2p sub-shell.

☒ **D** 3s sub-shell.

(Total for question = 1 mark)

Q21.

This is a question about halogenoalkanes and related compounds.

Explain why ethene has a boiling temperature of −104 °C, whereas ethanol has a boiling temperature of 78 °C.

(3)

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(Total for question = 3 marks)

Q22.

Hydrogen has three isotopes, ^{1}H, known as protium, ^{2}H, deuterium, and ^{3}H, tritium.

(a) In terms of sub-atomic particles, give the similarities and differences between atoms of these three isotopes of hydrogen.

(3)

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(b) When a nitrogen atom collides with a high energy neutron, one atom of tritium and one atom of another element are formed. Complete the equation below.

(1)

$$^{14}_{7}N + ^{1}_{0}n \rightarrow ^{3}_{1}H + \text{.................}$$

(c) Tritium-deuterium gas, consisting of molecules each containing one deuterium atom and one tritium atom, is used in some nuclear warheads. Typically, each warhead has about 4.0 g of the gas added.

(i) Calculate the number of moles of tritium-deuterium in 4.0 g.

(2)

(ii) Calculate the volume, in cm^3, of 4.0 g of tritium-deuterium gas.

[Molar volume of a gas under these conditions = 24 000 cm^3 mol^{-1}]

(1)

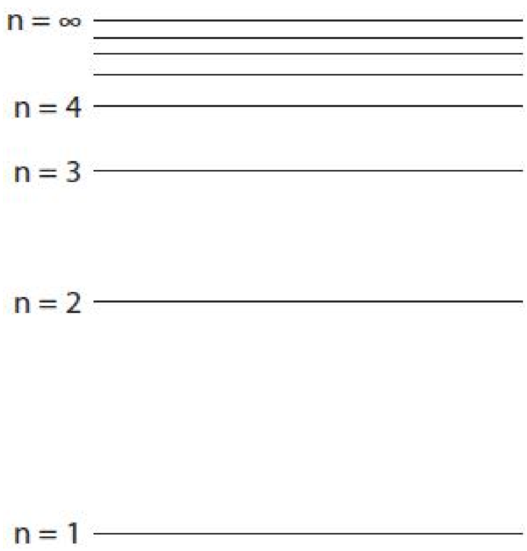
(d) Tritium is not usually included in calculations of the relative atomic mass of hydrogen, because it is radioactive and has a relatively short half-life.

Calculate the relative atomic mass of hydrogen with the following isotopic composition. Give your answer to four decimal places.

(2)

Isotope	Mass number	Relative abundance
^{1}H	1.0078	99.9850
^{2}H	2.0141	0.0150

(e) The electronic energy levels in hydrogen are shown below.



(i) Mark on the energy level diagram, with an arrow, the transition that represents the ionization energy of hydrogen.

(1)

(ii) In some versions of the Periodic Table, hydrogen is placed in the same group as sodium. Give the electronic configurations for both a hydrogen atom and a sodium atom, using the *s* and *p* notation.

Use these electronic configurations to suggest why this is a reasonable grouping.

(2)

H

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Na

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*(f) Which element in the Periodic Table has the highest first ionization energy? Justify your answer.

(3)

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Week 2

Periodicity

3.1 The periodic table

(a) the periodic table as the arrangement of elements: **(i)** by increasing atomic (proton) number **(ii)** in periods showing repeating trends in physical and chemical properties (periodicity) **(iii)** in groups having similar chemical properties					
(b) **(i)** the periodic trend in electron configurations across Periods 2 and 3 **(see also 2.2.1 d)** **(ii)** classification of elements into s-, p- and d-blocks					
(c) first ionisation energy (removal of 1 mol of electrons from 1 mol of gaseous atoms) and successive ionisation energy, and: **(i)** explanation of the trend in first ionisation energies across Periods 2 and 3, and down a group, in terms of attraction, nuclear charge and atomic radius **(ii)** prediction from successive ionisation energies of the number of electrons in each shell of an atom and the group of an element					
(d) explanation of: **(i)** metallic bonding as strong electrostatic attraction between cations (positive ions) and delocalised electrons **(ii)** a giant metallic lattice structure, e.g. all metals					
(e) explanation of the solid giant covalent lattices of carbon (diamond, graphite and graphene) and silicon as networks of atoms bonded by strong covalent bonds					
(f) explanation of physical properties of giant metallic and giant covalent lattices, including melting and boiling points, solubility and electrical conductivity in terms of structure and bonding					
(g) explanation of the variation in melting points across Periods 2 and 3 in terms of structure and bonding **(see also 2.2.2 o)**.					

3.1.2 Group 2

(a) the outer shell s^2 electron configuration and the loss of these electrons in redox reactions to form 2^+ ions					
(b) the relative reactivities of the Group 2 elements Mg → Ba shown by their redox reactions with: **(i)** oxygen **(ii)** water **(iii)** dilute acids					
(c) the trend in reactivity in terms of the first and second ionisation energies of Group 2 elements down the group **(see also 3.1.1 c)**					
(d) the action of water on Group 2 oxides and the approximate pH of any resulting solutions, including the trend of increasing alkalinity					
(e) uses of some Group 2 compounds as bases, including equations, for example (but not limited to): (i) $Ca(OH)_2$ in agriculture to neutralise acid soils (ii) $Mg(OH)_2$ and $CaCO_3$ as 'antacids' in treating indigestion.					

3.1.3 Group 7

(a) existence of halogens as diatomic molecules and explanation of the trend in the boiling points of Cl_2, Br_2 and I_2, in terms of induced dipole–dipole interactions (London forces) **(see also 2.2.2 k)**					
(b) the outer shell s^2p^5 electron configuration and the gaining of one electron in many redox reactions to form 1^- ions					
(c) the trend in reactivity of the halogens Cl_2, Br_2 and I_2, illustrated by reaction with other halide ions					
(d)) explanation of the trend in reactivity shown in **(c)**, from the decreasing ease of forming 1– ions, in terms of attraction, atomic radius and electron shielding					
(e) explanation of the term *disproportionation* as oxidation and reduction of the same element, illustrated by:					

(i) the reaction of chlorine with water as used in water purification **(ii)** the reaction of chlorine with cold, dilute aqueous sodium hydroxide, as used to form bleach **(iii)** reactions analogous to those specified in **(i)** and **(ii)**					
(f) the benefits of chlorine use in water treatment (killing bacteria) contrasted with associated risks (e.g. hazards of toxic chlorine gas and possible risks from formation of chlorinated hydrocarbons)					
(g) the precipitation reactions, including ionic equations, of the aqueous anions Cl^-, Br^- and I^- with aqueous silver ions, followed by aqueous ammonia, and their use as a test for different halide ions.					

Group 7

Key Recall Question	Answer
. What is the trend in boiling point down the group and why? (2)	increases, because larger molecules, more electrons so stronger van der Waals
2. What is the trend in electronegativity down the group and why? (2)	decreases because greater distance and shielding between outer electrons and nucleus
3. Which halogen is the best oxidising agent? Why? (2)	fluorine – most electronegative, so gains electrons (is reduced) most easily
4. What colour are halide ions in solution?	Colourless – colour appears when halogen is displaced
5. What are the colours of chlorine water, bromine water, iodine water?	Colourless, orange, brown (NB get darker down group)
6. What will the colour change be if potassium iodide solution is mixed with bromine water? (1)	bromine will displace iodine, solution will go brown from yellow/orange
7. What's the reaction between chlorine and hydroxide? (2)	chlorine + sodium hydroxide -> sodium chlorate + water + sodium chloride $Cl_2 + 2OH^- \rightarrow ClO^- + Cl^- + H_2O$
8. What's the reaction between chorine and water?	chlorine + water -> hydrogen chloride + hypochlorous acid $Cl_2 + H_2O \rightarrow HCl + HClO$
9. How does (8) change in sunlight?	$Cl_2(g) + H_2O(l) \rightarrow 2H^+(aq) + 2Cl^-(aq) + ½\ O_2(g)$ the chlorate ion breaks down giving free oxygen and more chloride.
10. Why is chlorine added to water? Name one risk (2)	to kill microbes, small risk of bladder cancer

Question	Date:	Date:	Date:	Date:	Date:	Date:	Date:	Date:	Date:	Date:	Date:	Date:	Date:
1													
2													
3													
4													
5													
6													
7													
8													

Intermolecular forces

Key Recall Question	Answer
1. If a substance has intermolecular forces, what kind of bonding must it have?	Simple covalent. Every other type is giant/lattice so no imf
2. What the three types of imf in order of strength?	Hydrogen bonding> dipole diploe > van der Waals
3. What is a polar bond?	When there is a big difference in electronegivity, the more electronegative atom pulls the electrons closer to itself, giving is a slightly (delta) negative charge. The other atom has a slight positive charge.
4. What is a polar molecule?	A molecule that overall has a positively charged end and a negatively charged end. A molecule may have polar bonds but if they are symmetrical e.g. CF_4 they will cancel out and the molecule will not be polar.
5. What is a permanent dipole?	When a molecule is polar and has a positive and negative side e.g. CHF_3
6. What is a dipole dipole bond?	Molecules with a permanent dipole are attracted to each other via their oppositely charged sides.
7. How does hydrogen bonding arise? (make sure you can draw it)	It arises when a very electronegative element (F,O,N only) is bonded to a hydrogen. The hydrogens form weak bonds with the lone pairs of electrons on the other atom
8. How do van der Waals forces arise?	Electrons in charge clouds are always moving. At any one time electrons may gather on one side of an atom, creating an area of slight negative charge, inducing a slight positive charge in the neighbouring atom. These temporary dipoles attract. They are continuously changing.
9. What affects the strength of VdW forces?	How many electrons there are; larger atom, more electrons so more chances for dipoles to occur
10. All intermolecular forces are…	electrostatic

Question	Date:	Date:	Date:	Date:	Date:	Date:	Date:	Date:	Date:	Date:	Date:	Date:	Date:
1													
2													
3													
4													
5													
6													
7													
8													
9													
10													

Shapes of Molecules

Key Recall Question	Answer
1. Why do molecules take 3D shapes? VSER – valence shell electron repulsion theory	The clouds of electrons repel each other. The molecule takes a shape that minimises the repulsion, lone pairs repel more than
2. How do we show 3D shapes on paper?	Solid line – bond on plane of paper Dashed line – bond points behind Wedge – shows bond coming forward
3. How do you work out the shape a molecule will havew?	1. Draw a dot-cross diagram 2. Count the areas of electron density (bonding pairs bp) around the central atom) 3. Count the lone pairs (non-bonding pairs nbp) around central atom 4. Use your extensive knowledge to work out shape.
4. What will the shape & bonding angle be if central atom surrounded by: a) 2 bp e.g. BeCl2 b) 3bp e.g. BF3 c) 4bp e.g. CH4 d) 4bp + 1 nbp e.g. NH_4^+ e) 2bp + 2nbp e.g. H_2O f) 5bp e.g. PCl_5 g) 4bp + 1 nbp e.g. SF4 h) 6bp e.g. SF6 i) 5bp + 1nbp e.g. ClF5 j) 4bp + 2 nbp e.g. XeF_4	a) Linear (180) b) Trigonal planar (120) c) Tetrahedral (109.5) d) Trigonal pyramidal (107) e) Bent (104.5) f) Trigonal bipyramidal (120/90) NB breaks octet rule g) See saw (102 & 86.5) h) Octahedral (90) i) Square pyramidal j) Square planar
5. Which repels more – bonding pair or lone pair (nbp)	Lone pair
6. By how much does a lone pair typically reduce the bond angle by	2.5
7. How do you handle an ion e.g. BF4-	You can still do a dot cross diagram and count the bp/nbp
8. How do you treat double bonds?	The same as single ones!

Question	Date:	Date:	Date:	Date:	Date:	Date:	Date:	Date:	Date:	Date:	Date:	Date:	Date:
1													
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5													
6													
7													
8													

Questions

Q1.

Magnesium bromide, $MgBr_2$, is an ionic compound.

(i) The first ionisation energy of sodium is 496 kJ mol^{-1}.

Explain why the first ionisation energy of magnesium is higher than that of sodium.

(3)

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(ii) Write the equation, including state symbols, to show the **third** ionisation energy of magnesium.

(1)

(Total for question = 4 marks)

Q2.

This question is about halogens and redox reactions.

Potassium halides react with concentrated sulfuric acid to form potassium hydrogensulfate and the different products shown in the table.

Potassium halide	Products
potassium chloride	hydrogen chloride
potassium bromide	hydrogen bromide, bromine and sulfur dioxide
potassium iodide	hydrogen iodide, iodine, hydrogen sulfide and sulfur

By referring to any changes in oxidation numbers when these halides react with concentrated sulfuric acid, explain which halide is the strongest reducing agent.

(3)

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(Total for question = 3 marks)

Q3.

Which of the following statements is correct?

☒ **A** Barium sulfate is less soluble in water than calcium sulfate.

☒ **B** Barium hydroxide is less soluble in water than calcium hydroxide.

☒ **C** Barium nitrate undergoes thermal decomposition more readily than calcium nitrate.

☒ **D** Barium shows more than one oxidation state in its compounds.

(Total for question = 1 mark)

Q4.

This is a question about Group 2 elements and their compounds.

*(a) Explain why the first ionization energy of calcium (590 kJ mol^{-1}) is greater than that of strontium (550 kJ mol^{-1}).

(2)

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(b) (i) Describe how you would carry out a flame test on a sample of a Group 2 metal salt.

(2)

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(ii) What result of the flame test would confirm the presence of a barium salt?

(1)

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*(iii) Explain, in terms of electronic transitions, how the result of the flame test arises.

(3)

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(c) Barium reacts with water to form a clear, colourless solution.

(i) Give the name or formula of the barium compound formed.

(1)

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(ii) State **another** observation that would be made when barium reacts with water.

(1)

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....

(d) Barium reacts with chlorine gas to form barium chloride as shown in the equation below.

$$Ba(s) + Cl_2(g) \rightarrow BaCl_2(s)$$

(i) Use the changes in oxidation numbers to show that this is a redox reaction.

(2)

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(ii) Write the ionic equation for the reaction between barium chloride solution and dilute sulfuric acid. Include state symbols in the equation.

(2)

(iii) The reaction in (d)(ii) is used to test for sulfate ions.

Why is dilute hydrochloric acid added with the barium chloride solution in this test?

(1)

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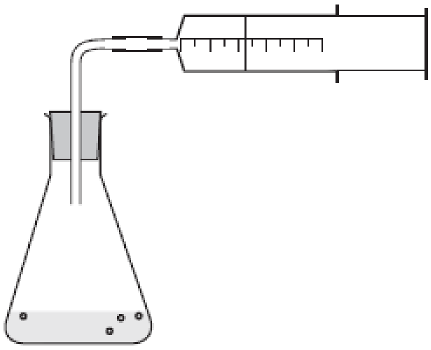
(e) Magnesium carbonate, $MgCO_3$, readily reacts with hydrochloric acid.

(i) Write the equation for this reaction. State symbols are not required.

(1)

*(ii) The rate of the reaction between powdered magnesium carbonate and dilute hydrochloric acid was monitored using the experimental apparatus shown below.



State two factors that would **decrease** the rate of this reaction, other than by changing the reaction temperature.

Explain how these two factors decrease the reaction rate.

(4)

Factor 1

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Explanation 1

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Factor 2

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Explanation 2

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(f) Suggest why pressure has little or no effect on the rate of the reaction of magnesium oxide and hydrochloric acid, the equation for which is given below.

$$MgO(s) + 2HCl(aq) \rightarrow MgCl_2(aq) + H_2O(l)$$

(1)

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....

(Total for question = 21 marks)

Q5.

Which of the following properties **decreases** on descending Group 2 of the Periodic Table?

☒ **A** Solubility of the sulfates.

☒ **B** Solubility of the hydroxides.

☒ **C** Reactivity of the elements.

☒ **D** Ionic character of the oxides.

(Total for question = 1 mark)

Q6.

This question concerns the Periodic Table.

(a) An atom of argon has mass number 40. Complete the table below showing the numbers of sub-atomic particles in this atom of argon. Use the Periodic Table as a source of data.

(1)

Sub-atomic particles present in one atom of ^{40}Ar	Number
protons	
electrons	
neutrons	

(b) An atom of potassium has mass number 39. Explain why argon is placed before potassium in the modern Periodic Table.

(1)

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(c) In the context of the Periodic Table, explain what is meant by the term **periodicity**.

(2)

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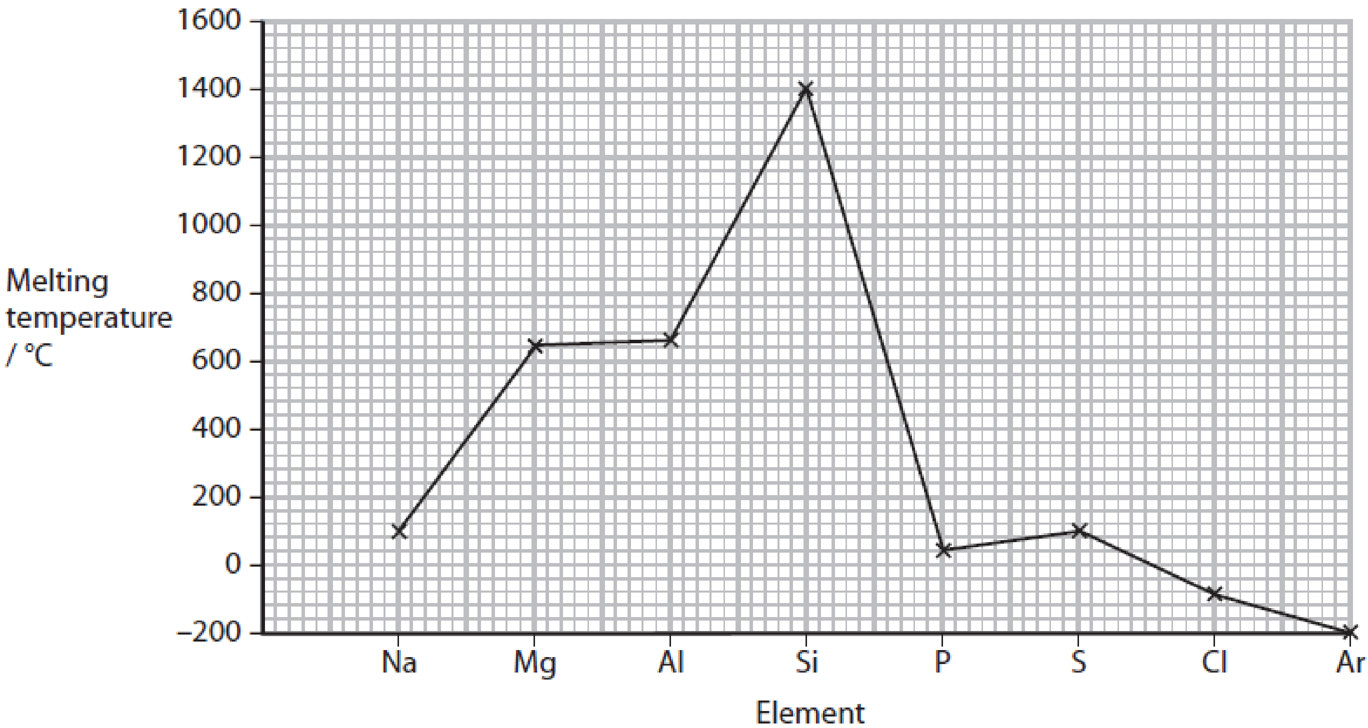
(d) The graph shows the variation in melting temperatures of the elements across Period 3 (Na to Ar) of the Periodic Table.



(i) Name **one** of the elements above that is composed of **simple molecules** at room temperature and pressure.

(1)

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(ii) Silicon has a giant atomic structure. Explain how this structure results in the high melting temperature shown on the graph.

(2)

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(iii) Explain why the melting temperature of magnesium is higher than that of sodium.

(3)

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(Total for question = 10 marks)

Q7. The first five ionization energies of an element, **X**, are shown in the table.

Ionization energy	1st	2nd	3rd	4th	5th
Value / $kJ\ mol^{-1}$	631	1235	2389	7089	8844

What is the mostly likely formula of the oxide that forms when **X** burns in oxygen?

☐ **A** X_2O

☐ **B** XO

☐ **C** X_2O_3

☐ **D** XO_2

(Total for Question = 1 mark)

Q8.

White phosphorus consists of

☒ **A** a giant structure of atoms.

☒ **B** a giant structure of ions.

☒ **C** small molecules.

☒ **D** single atoms.

(Total for question = 1 mark)

Q9. Going down Group 2 from calcium to barium

☒ **A** the first ionization energy of the element increases.

☒ **B** the strength of the metallic bonding increases.

☒ **C** the polarizing power of the 2+ ion decreases.

☒ **D** the stability of the nitrate to heat decreases.

(Total for Question = 1 mark)

Q10.

Consider the following Group 2 compounds.

Group 2 hydroxides	Group 2 sulfates
$Mg(OH)_2$	$MgSO_4$
$Ca(OH)_2$	$CaSO_4$
$Sr(OH)_2$	$SrSO_4$

The solubility

☒ **A** increases down the group for both hydroxides and sulfates.

☒ **B** increases down the group for hydroxides but increases up the group for sulfates.

☒ **C** increases up the group for hydroxides but increases down the group for sulfates.

☒ **D** increases up the group for both hydroxides and sulfates.

(Total for question = 1 mark)

Q11.

This question is about water.

Liquid water is a good solvent for many, but not all, ionic compounds. Which is **least** soluble in water?

(1)

☒ **A** barium hydroxide

☒ **B** calcium hydroxide

☒ **C** magnesium hydroxide

☒ **D** sodium hydroxide

(Total for question = 1 mark)

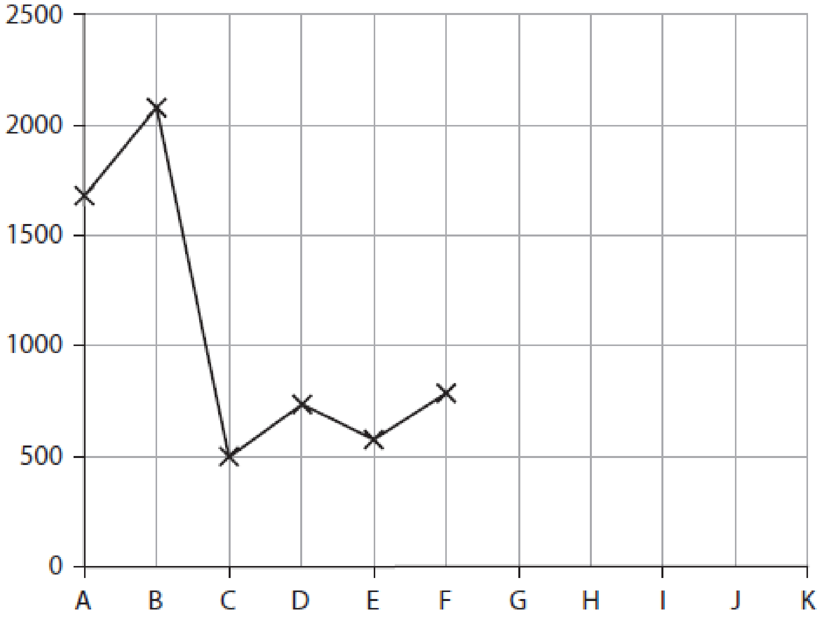
Q12.

Electrons in atoms occupy orbitals.

(i) The graph shows the first ionisation energies for a series of six consecutive elements **A**–**F**. The letters are not their chemical symbols.

Complete the graph of the first ionisation energies for the next five elements.

(3)



(ii) Explain why the value of the first ionisation energy for **D** is **greater** than for **C**.

(2)

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(iii) Explain why the value of the first ionisation energy of **E** is **less** than for **D**.

(2)

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(Total for question = 7 marks)

Q13. For Period 3 of the Periodic Table, from sodium to argon, what is the trend in the melting temperatures of the elements?

☒ **A** A steady decrease

☒ **B** A steady increase

☒ **C** A decrease to silicon then an increase

☒ **D** An increase to silicon then a decrease

(Total for Question = 1 mark)

Q14. This is a question about Group 2 compounds.

Limewater is a solution of calcium hydroxide, commonly used in the identification of carbon dioxide gas. Since calcium hydroxide is only sparingly soluble in water, technicians often make the solution by adding an excess of the solid calcium hydroxide to the required volume of deionised water, shaking the container and then leaving the mixture to settle. In this way, a saturated solution is produced but it can be of variable concentration.

Two students were each given a sample of limewater, from the same batch, in order to determine its concentration. Using 50.0 cm^3 portions of the limewater, they carried out titrations using 0.100 mol dm^{-3} hydrochloric acid. One of the students obtained the following results:

Titration	Trial	1	2
Final Volume /cm^3	14.50	28.60	42.70
Initial Volume /cm^3	0.00	14.50	28.60
Volume Added /cm^3	14.50	14.10	14.10

The student decided that the mean titre was 14.10 cm^3

The equation for the reaction is:

$$Ca(OH)_2(aq) + 2HCl(aq) \rightarrow CaCl_2(aq) + 2H_2O(l)$$

(a) (i) Calculate the number of moles of hydrochloric acid that reacted.

(1)

(ii) Calculate the number of moles of calcium hydroxide, $Ca(OH)_2$, that reacted with the acid.

(1)

(iii) the concentration of $Ca(OH)_2$, in mol dm^{-3}, in this sample of limewater.

(1)

(iv) Calculate the concentration of $Ca(OH)_2$, in g dm^{-3}, in this sample of limewater. Use the Periodic Table as a source of data.

(2)

(v) This student did not include the trial value when calculating the mean titre. Explain why.

(1)

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(vi) The second student obtained a different mean titre value for the experiment and thought that this difference may be due to the use of a faulty pipette.

Suggest a simple method, involving distilled water and a balance, by which the accuracy of the pipette in measuring out exactly 50.0 cm^3 could be checked.

(2)

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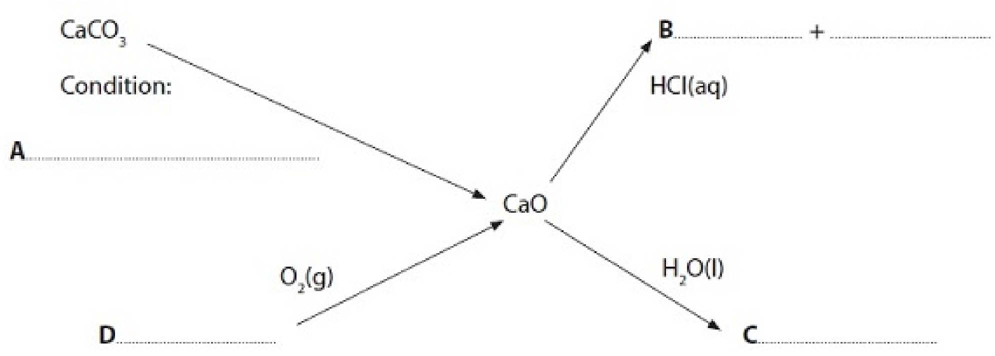
(b) Complete the missing details from the reaction flowchart shown below, giving the condition for **A** and using chemical formulae for answers **B**, **C** and **D**. State symbols are not required.

(4)



(c) In certain areas of the UK, calcium and magnesium carbonates tend to be deposited as an off-white solid on the inside surface of pipes and the surface of heating elements in kettles. These deposits can be removed by treatment with a weak acid. An equation for this is shown below.

$$CaCO_3(s) + 2HA(aq) \rightarrow CaA2(aq) + H_2O(l) + CO_2(g)$$

State **one** observation, other than the solid disappearing, that would be made when the above reaction is carried out.

(1)

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(d) The thermal stability of these carbonates depends on a combination of factors, including the size of their lattice energies.

Explain why the lattice energy of calcium carbonate is less exothermic than that of magnesium carbonate.

(2)

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(e) Calcium and magnesium ions can be distinguished by the use of a flame test. State the difference in the flame colour and explain how colours in a flame are produced in terms of electronic transitions.

(3)

Calcium

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Magnesium

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Colour produced by

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(Total for Question = 18 marks)

Week 3

Reaction mechanisms

4.1.1 Basic organic chemistry

(f) the different types of covalent bond fission: **(i)** homolytic fission (in terms of each bonding atom receiving one electron from the bonded pair, forming two radicals) i) **(ii)** heterolytic fission (in terms of one bonding atom receiving both electrons from the bonded pair)					
(g) the term *radical* (a species with an unpaired electron) and use of 'dots' to represent species that are radicals in mechanisms					
(h) a 'curly arrow' described as the movement of an electron pair, showing either heterolytic fission or formation of a covalent bond					
(i) reaction mechanisms, using diagrams, to show clearly the movement of an electron pair with 'curly arrows' and relevant dipoles.					

4.1.2 Alkanes

(f) the reaction of alkanes with chlorine and bromine by radical substitution using ultraviolet radiation, including a mechanism involving homolytic fission and radical reactions in terms of initiation, propagation and termination **(see also 4.1.1 f–g)**					
(g) the limitations of radical substitution in synthesis by the formation of a mixture of organic products, in terms of further substitution and reactions at different positions in a carbon chain.					

4.1.3 Alkenes

(f) addition reactions of alkenes with: **(i)** hydrogen in the presence of a suitable catalyst, e.g. Ni, to form alkanes **(ii)** halogens to form dihaloalkanes, including the use of bromine to detect the presence of a double C=C bond as a test for unsaturation in a carbon chain **(iii)** hydrogen halides to form haloalkanes **(iv)** steam in the presence of an acid catalyst, e.g. H_3PO_4, to form alcohols					
(g) definition and use of the term *electrophile* (an electron pair acceptor)					
(h) the mechanism of electrophilic addition in alkenes by heterolytic fission **(see also 4.1.1 h–i)**					
(i) use of Markownikoff's rule to predict formation of a major organic product in addition reactions of H–X to unsymmetrical alkenes, e.g. H–Br to propene, in terms of the relative stabilities of carbocation intermediates in the mechanism					

4.2.2 Halogenoalkanes

(a) hydrolysis of haloalkanes in a substitution reaction: **(i)** by aqueous alkali **(ii)** by water in the presence of $AgNO_3$ and ethanol to compare experimentally the rates of hydrolysis of different carbon– halogen bonds					
(b) definition and use of the term *nucleophile* (an electron pair donor)					
(c) the mechanism of nucleophilic substitution in the hydrolysis of primary haloalkanes with aqueous alkali **(see also 4.1.1 h–i)**					
(d) explanation of the trend in the rates of hydrolysis of primary haloalkanes in terms of the bond enthalpies of carbon–halogen bonds (C–F, C–C*l*, C–Br and C–I)					

6.1 Aromatic compounds, carbonyls and acids

6.1.1 Aromatic compounds

Electrophilic substitution (d) the electrophilic substitution of aromatic compounds with:					

(i) concentrated nitric acid in the presence of concentrated sulfuric acid (ii) a halogen in the presence of a halogen carrier (iii) a haloalkane or acyl chloride in the presence of a halogen carrier (Friedel–Crafts reaction) and its importance to synthesis by formation of a C–C bond to an aromatic ring (see also 6.2.4 d)					
(e) the mechanism of electrophilic substitution in arenes for nitration and halogenation					
(f) the explanation of the relative resistance to bromination of benzene, compared with alkenes, in terms of the delocalised electron density of the π-system in benzene compared with the localised electron density of the π-bond in alkenes					
(g) the interpretation of unfamiliar electrophilic substitution reactions of aromatic compounds, including prediction of mechanisms					
(i) the electrophilic substitution reactions of phenol: (i) with bromine to form 2,4,6-tribromophenol (ii) with dilute nitric acid to form 2-nitrophenol					
(j) the relative ease of electrophilic substitution of phenol compared with benzene, in terms of electron pair donation to the π-system from an oxygen p-orbital in phenol					
(k) the 2- and 4-directing effect of electrondonating groups (OH, NH_2) and the 3-directing effect of electron-withdrawing groups (NO_2) in electrophilic substitution of aromatic compounds					
(l) the prediction of substitution products of aromatic compounds by directing effects and the importance to organic synthesis (see also 6.2.5 Organic Synthesis).					

6.1.2 Carbonyl compounds

Reactions of carbonyl compounds (a) oxidation of aldehydes using $Cr_2O_7{}^{2-}/H^+$ (i.e. $K_2Cr_2O_7/H_2SO_4$) to form carboxylic acids					
(b) nucleophilic addition reactions of carbonyl compounds with: (i) $NaBH_4$ to form alcohols (ii) HCN [i.e. $NaCN_{(aq)}/H+_{(aq)}$], to form hydroxynitriles (see also 6.2.4 b)					
(c) the mechanism for nucleophilic addition reactions of aldehydes and ketones with $NaBH_4$ and HCN					

6.1.3 Carboxylic acids and esters

Properties of carboxylic acids (a) explanation of the water solubility of carboxylic acids in terms of hydrogen bonding					
(b) reactions in aqueous conditions of carboxylic acids with metals and bases (including carbonates, metal oxides and alkalis)					
Esters (c) esterification of: (i) carboxylic acids with alcohols in the presence of an acid catalyst (e.g. concentrated H_2SO_4) (ii) acid anhydrides with alcohols					
(d) hydrolysis of esters: (i) in hot aqueous acid to form carboxylic acids and alcohols (ii) in hot aqueous alkali to form carboxylate salts and alcohols					
Acyl chlorides (e) the formation of acyl chlorides from carboxylic acids using $SOCl_2$					
(f) use of acyl chlorides in synthesis in formation of esters, carboxylic acids and primary and secondary amides.					

6.2 Nitrogen compounds, polymers and synthesis

6.2.1 Amines

(b) the preparation of: (i) aliphatic amines by substitution of haloalkanes with excess ethanolic ammonia and amines (ii) aromatic amines by reduction of nitroarenes using tin and concentrated hydrochloric acid.					

6.2.2 Amino acids, amides and chirality

Reactions of amino acids (a) the general formula for an α-amino acid as $RCH(NH_2)COOH$ and the following reactions of amino acids: (i) reaction of the carboxylic acid group with alkalis and in the formation of esters (see also 6.1.3 c) (ii) reaction of the amine group with acids					

6.2.3 Polyesters and polyamides

Condensation polymers (a) condensation polymerisation to form: (i) polyesters (ii) polyamides					
(b) the acid and base hydrolysis of: (i) the ester groups in polyesters (ii) the amide groups in polyamides					

6.2.4 Carbon–carbon bond formation

Extending carbon chain length (a) the use of C–C bond formation in synthesis to increase the length of a carbon chain (see also 6.1.1 d, 6.1.2 b)					
(b) formation of C-CN by reaction of: (i) haloalkanes with CN^- and ethanol, including nucleophilic substitution mechanism (ii) carbonyl compounds with HCN, including nucleophilic addition mechanism (see also 6.1.2 b–c)					
(c) reaction of nitriles from (b): (i) by reduction (e.g. with H_2/Ni) to form amines (ii) by acid hydrolysis to form carboxylic acids					
(d) formation of a substituted aromatic C–C by alkylation (using a haloalkane) and acylation (using an acyl chloride) in the presence of a halogen carrier (Friedel–Crafts reaction) (see also 6.1.1 d).					

Revise aliphatic reaction mechanisms

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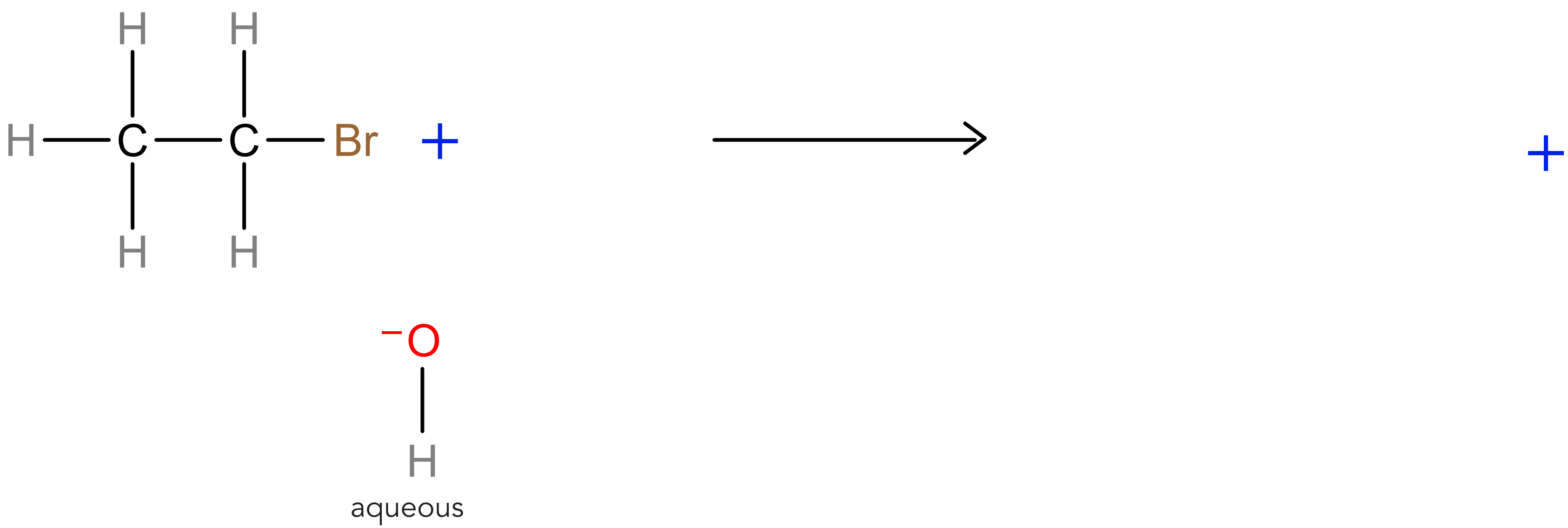
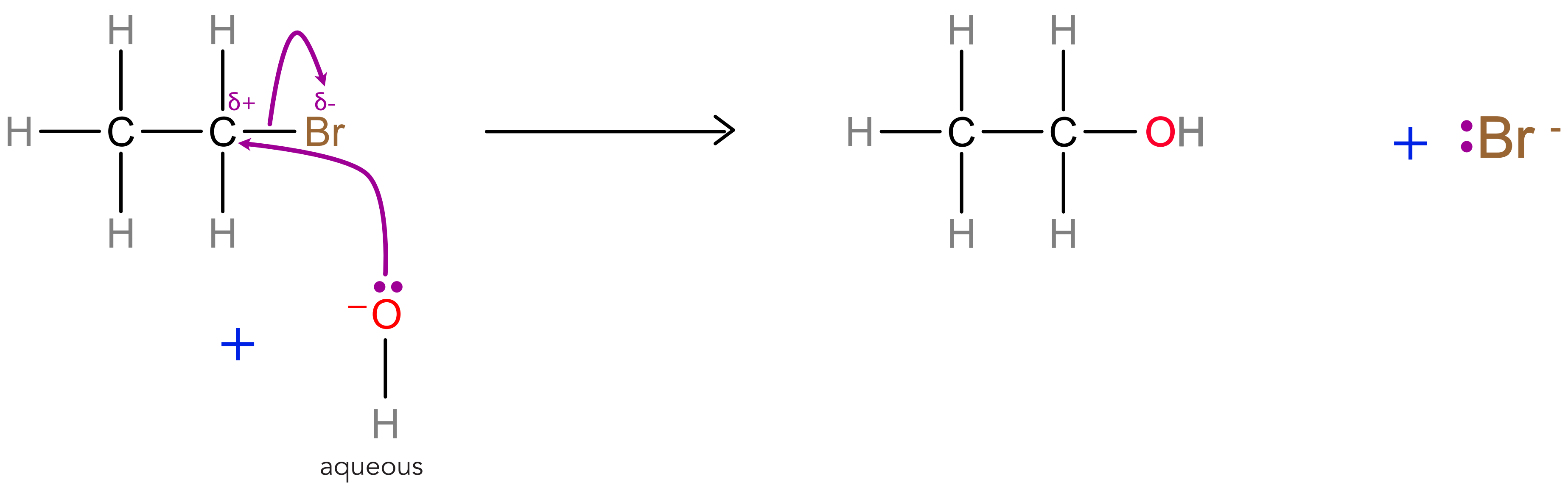
Mechanism revision 1: nucleophilic substitution by a negative ion.

Add any curly arrows, partial charges, and lone pairs of electrons to complete the following mechanism.



Mechanism revision 1: nucleophilic substitution by a negative ion.

Add any curly arrows, partial charges, and lone pairs of electrons to complete the following mechanism.



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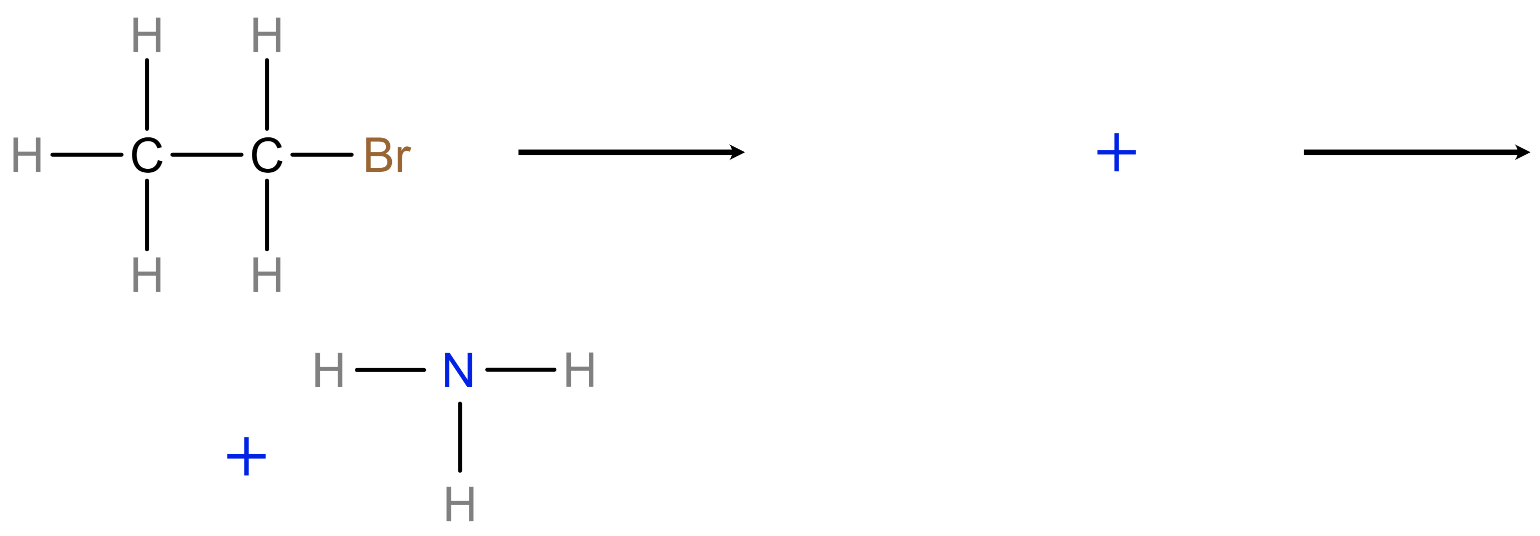
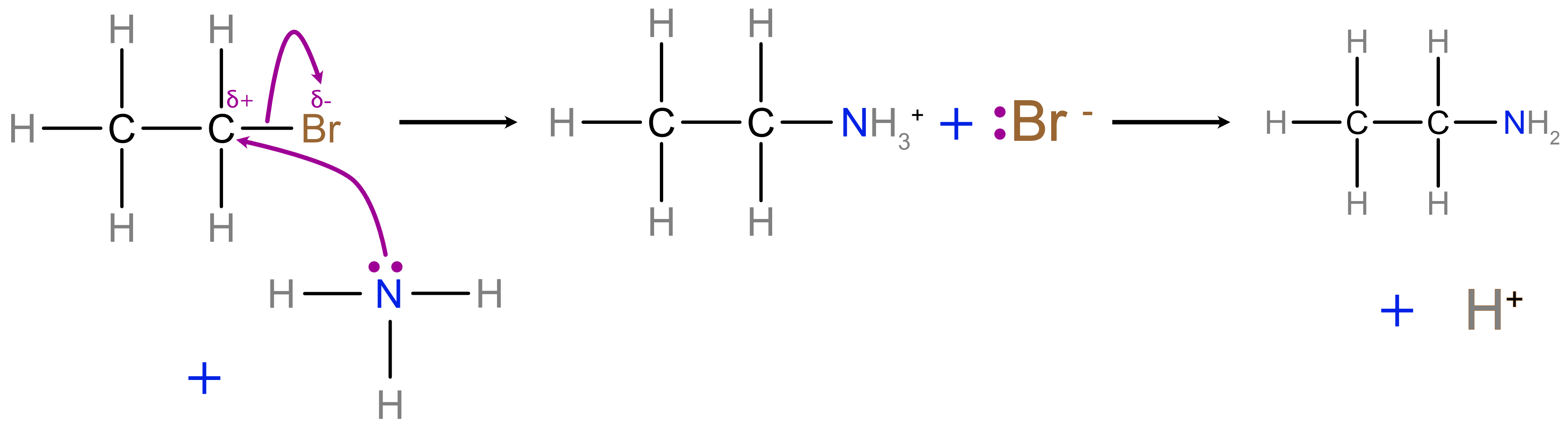
Mechanism revision 1(b): nucleophilic substitution by a neutral molecule.

Add any curly arrows, partial charges, and lone pairs of electrons to complete the following mechanism.



Mechanism revision 1(b): nucleophilic substitution by a neutral molecule.

Add any curly arrows, partial charges, and lone pairs of electrons to complete the following mechanism.



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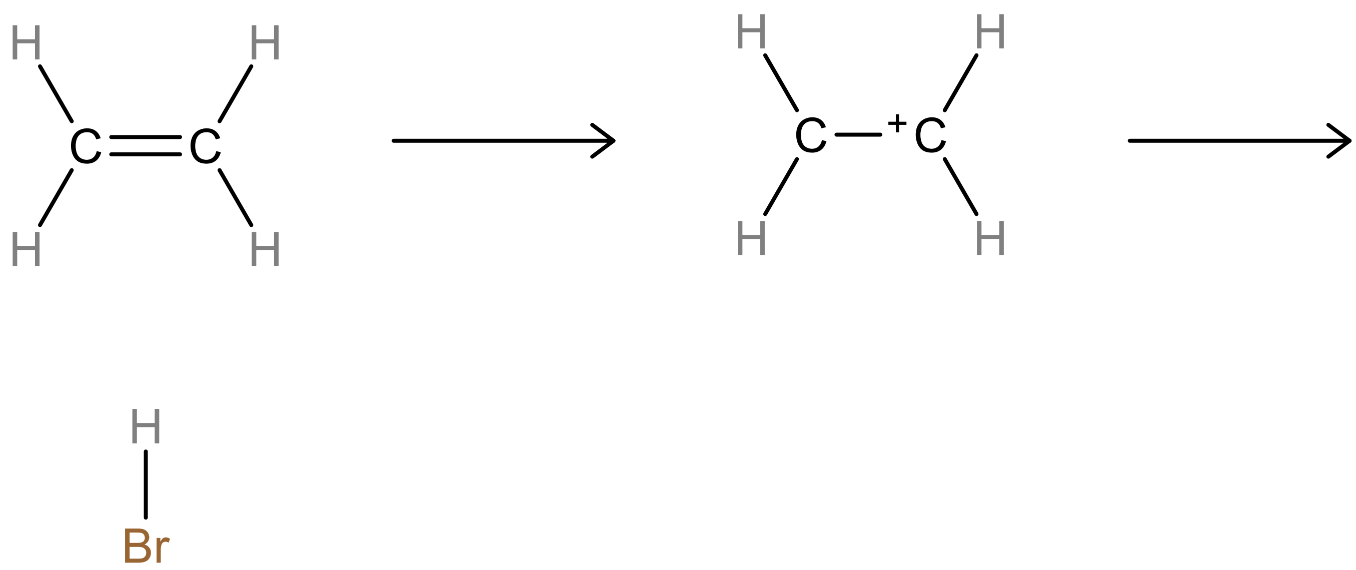
Mechanism revision 2: electrophilic addition

Add any curly arrows, partial charges, and lone pairs of electrons to complete the following mechanism.



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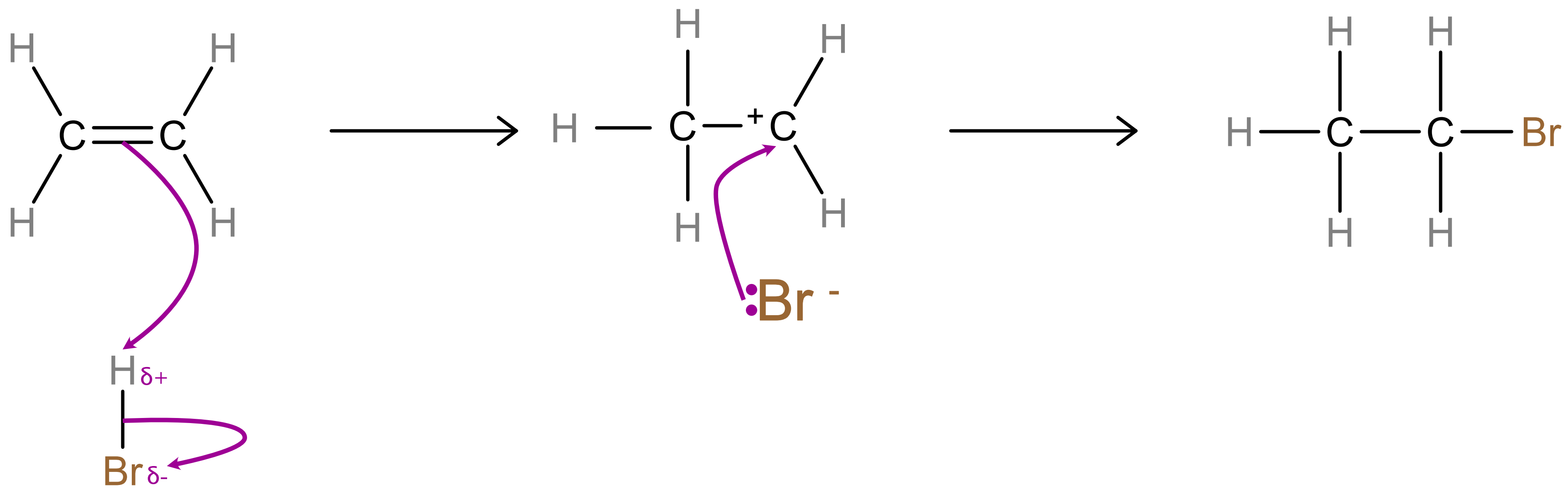
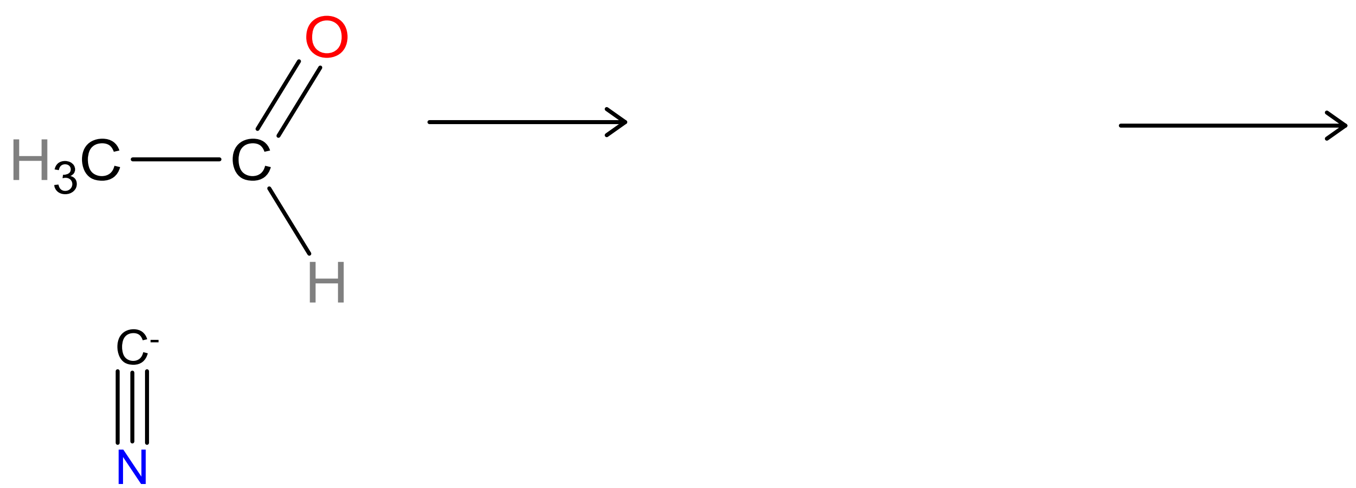
Mechanism revision 2: electrophilic addition

Add any curly arrows, partial charges, and lone pairs of electrons to complete the following mechanism.



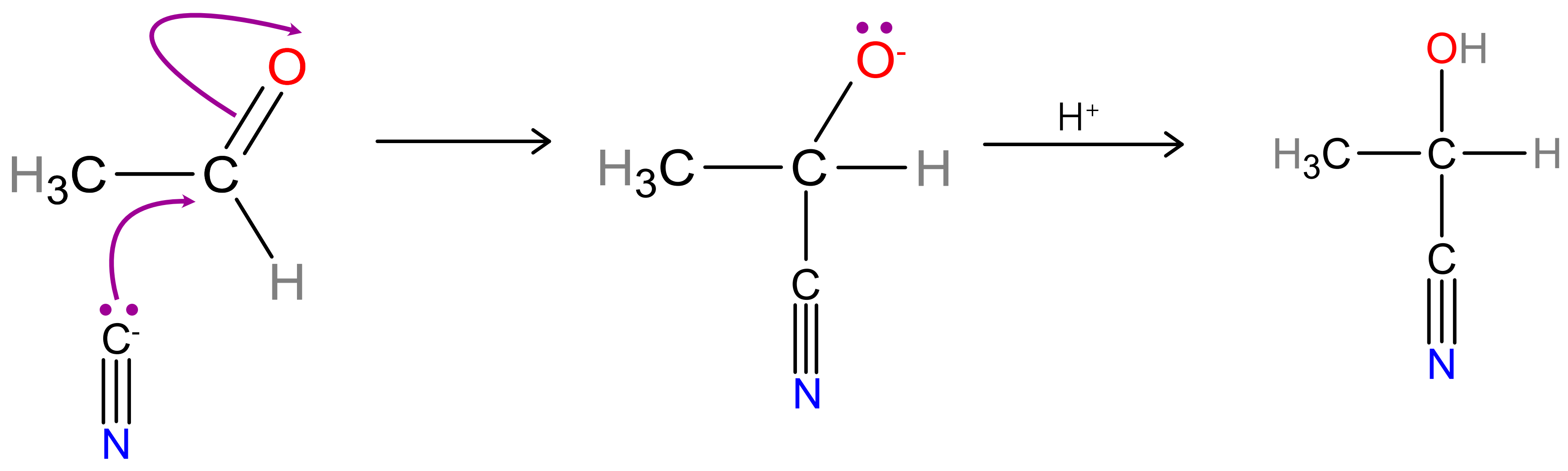
Mechanism revision 3: nucleophilic addition.

Add any curly arrows, partial charges, and lone pairs of electrons to complete the following mechanism.



Mechanism revision 3: nucleophilic addition.

Add any curly arrows, partial charges, and lone pairs of electrons to complete the following mechanism.



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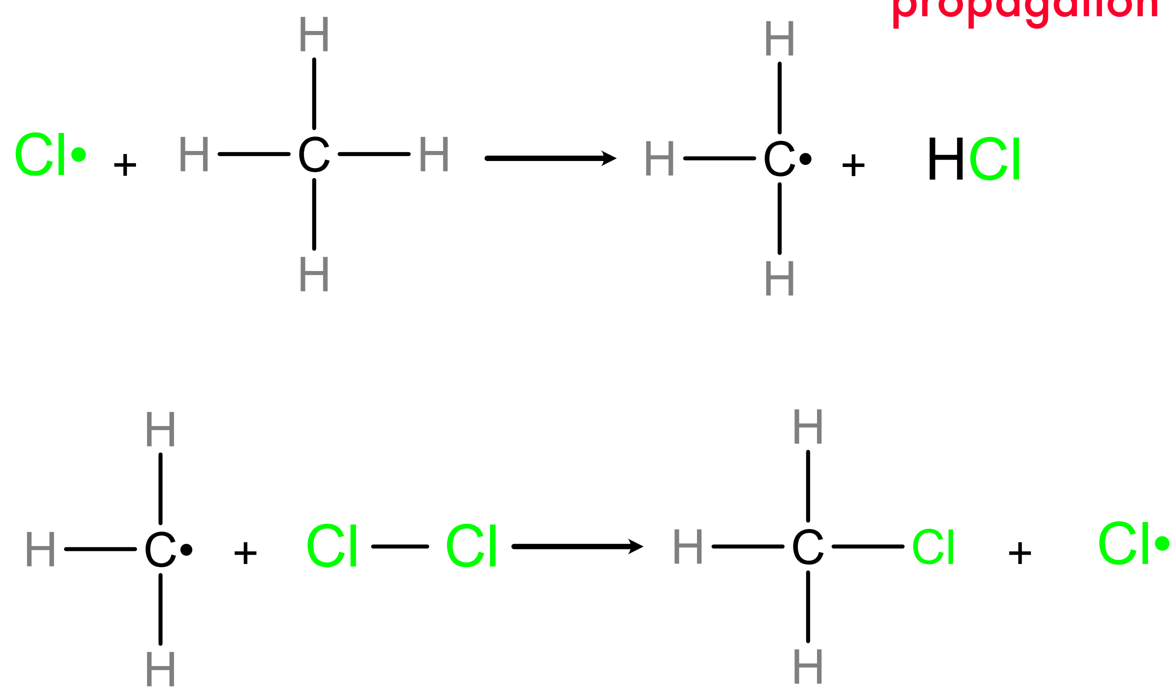
Mechanism revision 4: radical substitution.

initiation

$$Cl{-}Cl \xrightarrow{h\nu} 2Cl\bullet$$

propagation



termination

$$2Cl\bullet \longrightarrow Cl_2$$

$$CH_3\bullet + Cl\bullet \longrightarrow CH_3Cl$$

$$CH_3\bullet + CH_3\bullet \longrightarrow CH_3CH_3$$

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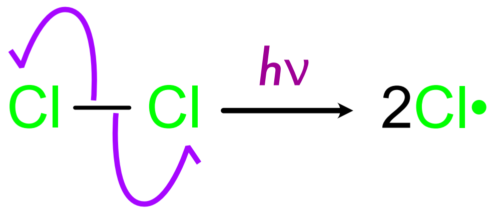
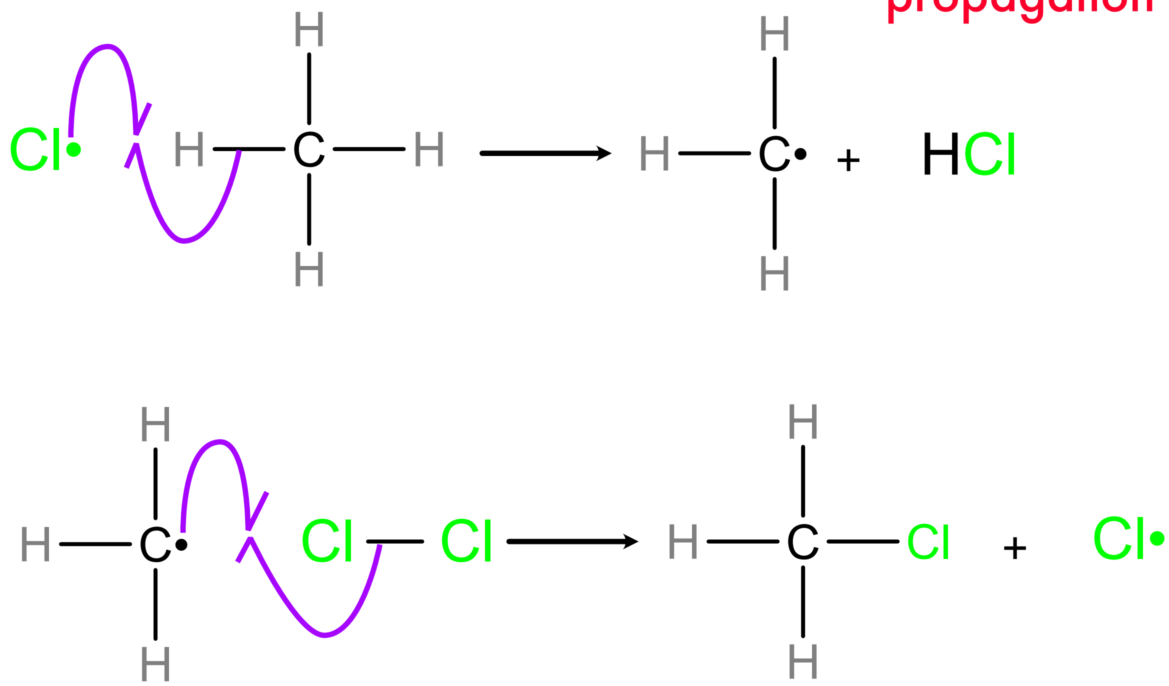
Mechanism revision 4: radical substitution.

initiation



propagation



termination

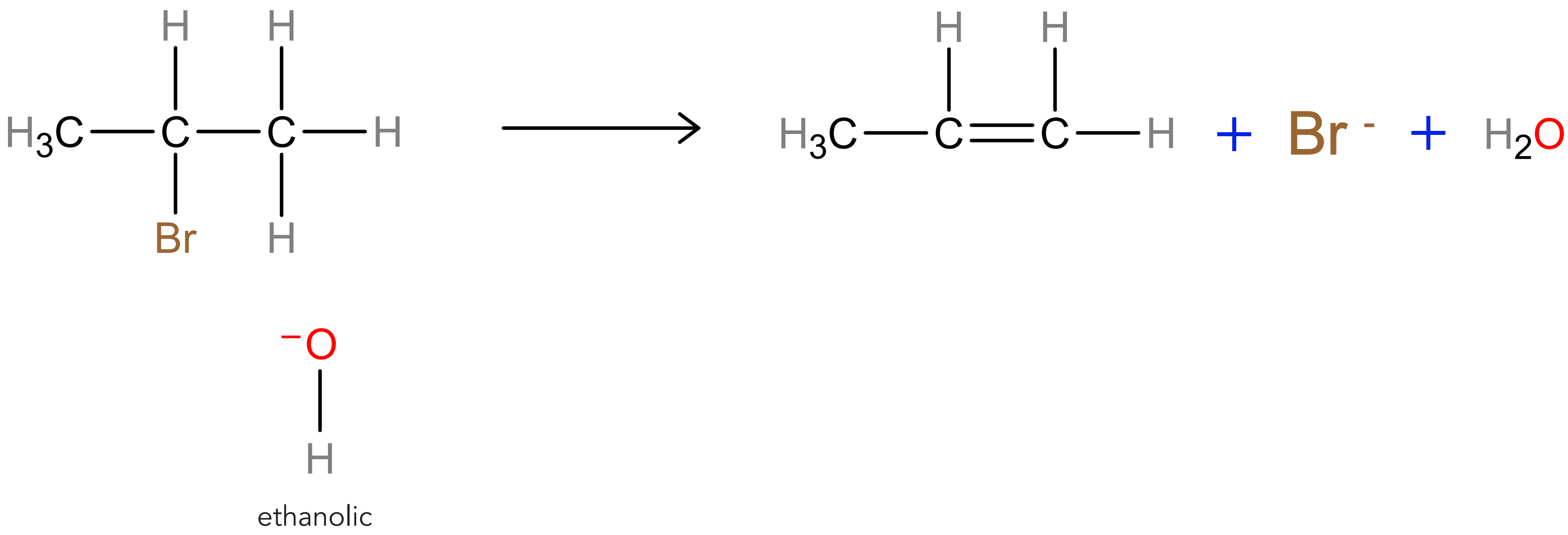
$2Cl\cdot \longrightarrow Cl_2$

$CH_3\cdot + Cl\cdot \longrightarrow CH_3Cl$

$CH_3\cdot + CH_3\cdot \longrightarrow CH_3CH_3$

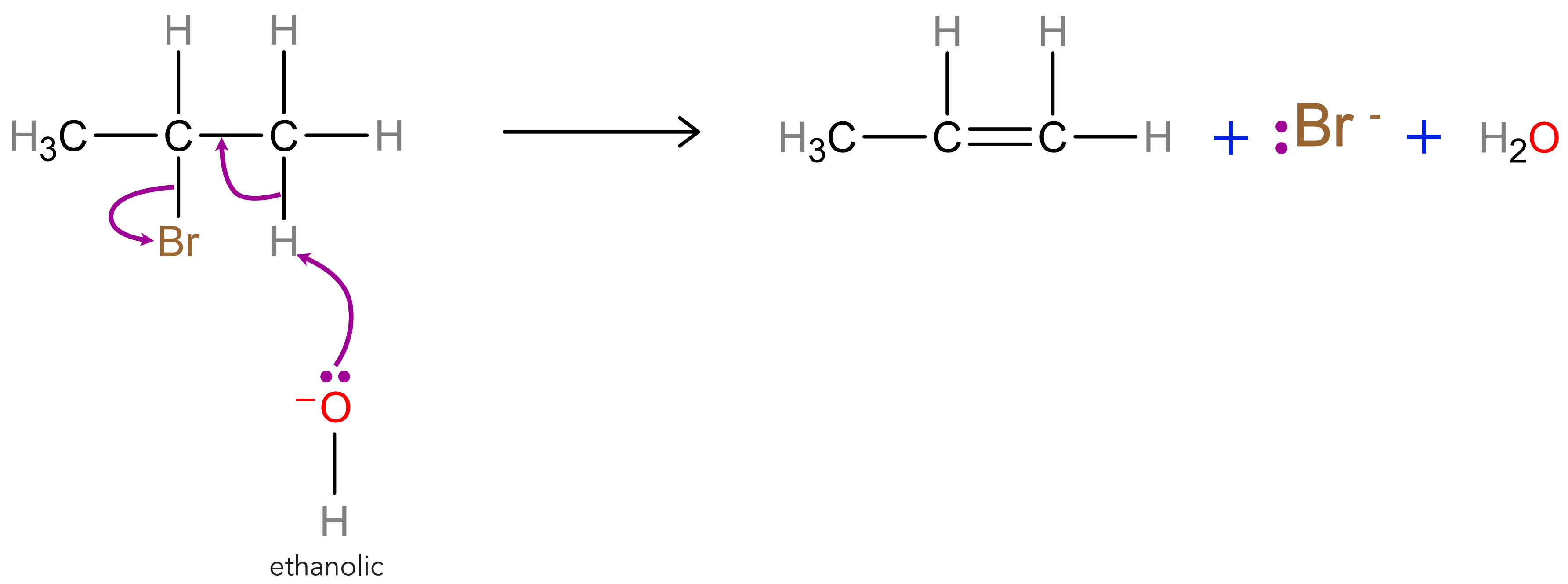
Mechanism revision 5: elimination

Add any curly arrows, partial charges, and lone pairs of electrons to complete the following mechanism.



Mechanism revision 5: elimination

Add any curly arrows, partial charges, and lone pairs of electrons to complete the following mechanism.



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Questions

Q1. Crude oil is a complex mixture of hydrocarbons. Initial separation is achieved by fractional distillation of the crude oil. The separate fractions are further refined to produce hydrocarbons such as decane, $C_{10}H_{22}$.

(a) Give the general formula of alkanes.

(1)

(b) Carbon monoxide, CO, is formed during the incomplete combustion of decane.

(i) Write an equation for the incomplete combustion of decane, forming carbon monoxide and water only.

(1)

(ii) Explain why incomplete combustion can occur.

(1)

....

....

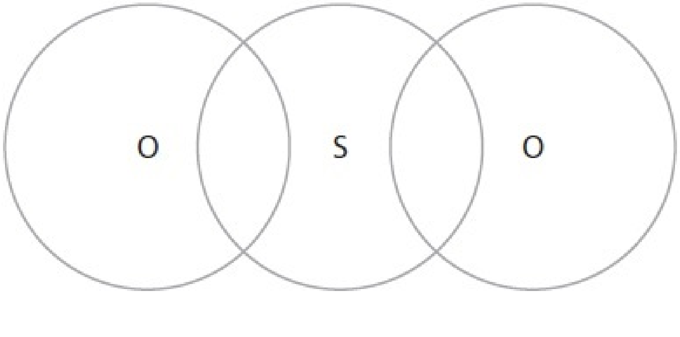
(c) 'Low-sulfur fuel' is now supplied to petrol stations. The removal of sulfur from diesel and petrol reduces the emission of toxic oxides of sulfur from vehicle exhausts. One such oxide is sulfur dioxide, SO_2.

The bonding in sulfur dioxide may be represented as shown below.

$$O = S \rightarrow O$$

Complete the dot and cross diagram below for the SO_2 molecule, showing only outer shell electrons. Use dots to represent the oxygen electrons and crosses to represent the sulfur electrons.

(3)



(d) Another alkane produced from crude oil is heptane, C_7H_{16}. The reforming of heptane produces methylcyclohexane and only one other product. A methylcyclohexane molecule is made from a ring of six carbon atoms bonded to a methyl group.

(i) Use the information given above to give the **skeletal** formula of methylcyclohexane.

(1)

(ii) Write a balanced equation, using **molecular** formulae, for the reforming of heptane into methylcyclohexane and one other product. State symbols are not required.

(1)

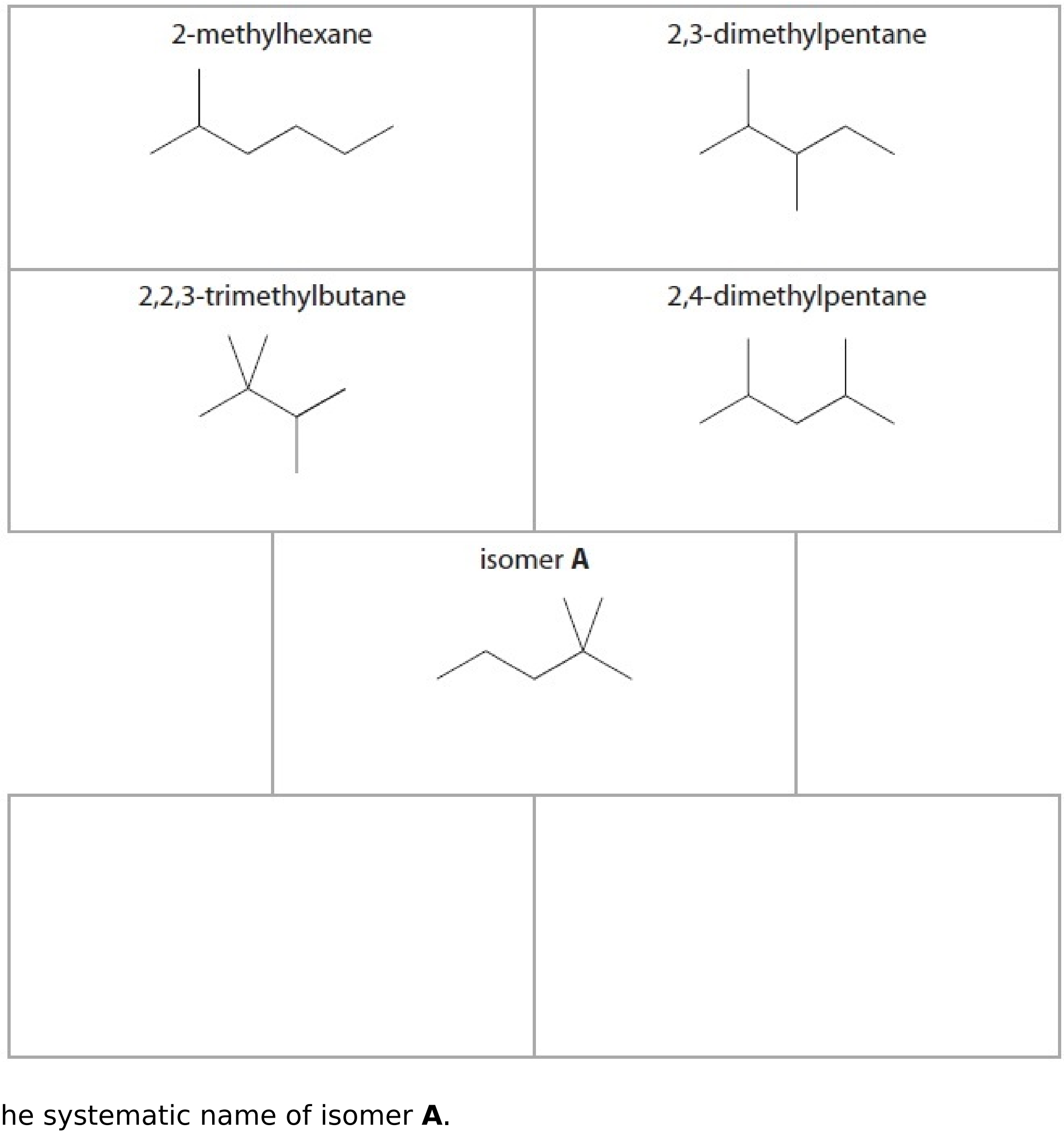
(iii) Suggest a reason why oil companies reform alkanes such as heptane.

(1)

....

....

(e) Five branched-chain isomers of heptane are shown in the boxes below.



(i) Give the systematic name of isomer **A**.

(1)

....

(ii) In the empty boxes above, draw skeletal formulae for two other **branched-chain** isomers of C_7H_{16}, with no side-chain having more than one carbon atom.

(2)

(f) Butane, C_4H_{10}, reacts with chlorine, Cl_2, at room temperature and pressure.

$$C_4H_{10} + Cl_2 \rightarrow C_4H_9Cl + HCl$$

(i) What other condition is essential for this reaction?

(1)

....

(ii) Write an equation for the initiation step of the mechanism for the above reaction. Curly arrows are not required.

(1)

(iii) State the type of bond fission involved in the initiation step.

(1)

....

(iv) Write equations for the two propagation steps of this mechanism. Curly arrows are not required.

(2)

First propagation step:

Second propagation step:

(v) Write **one** equation for a reaction that would terminate this mechanism.

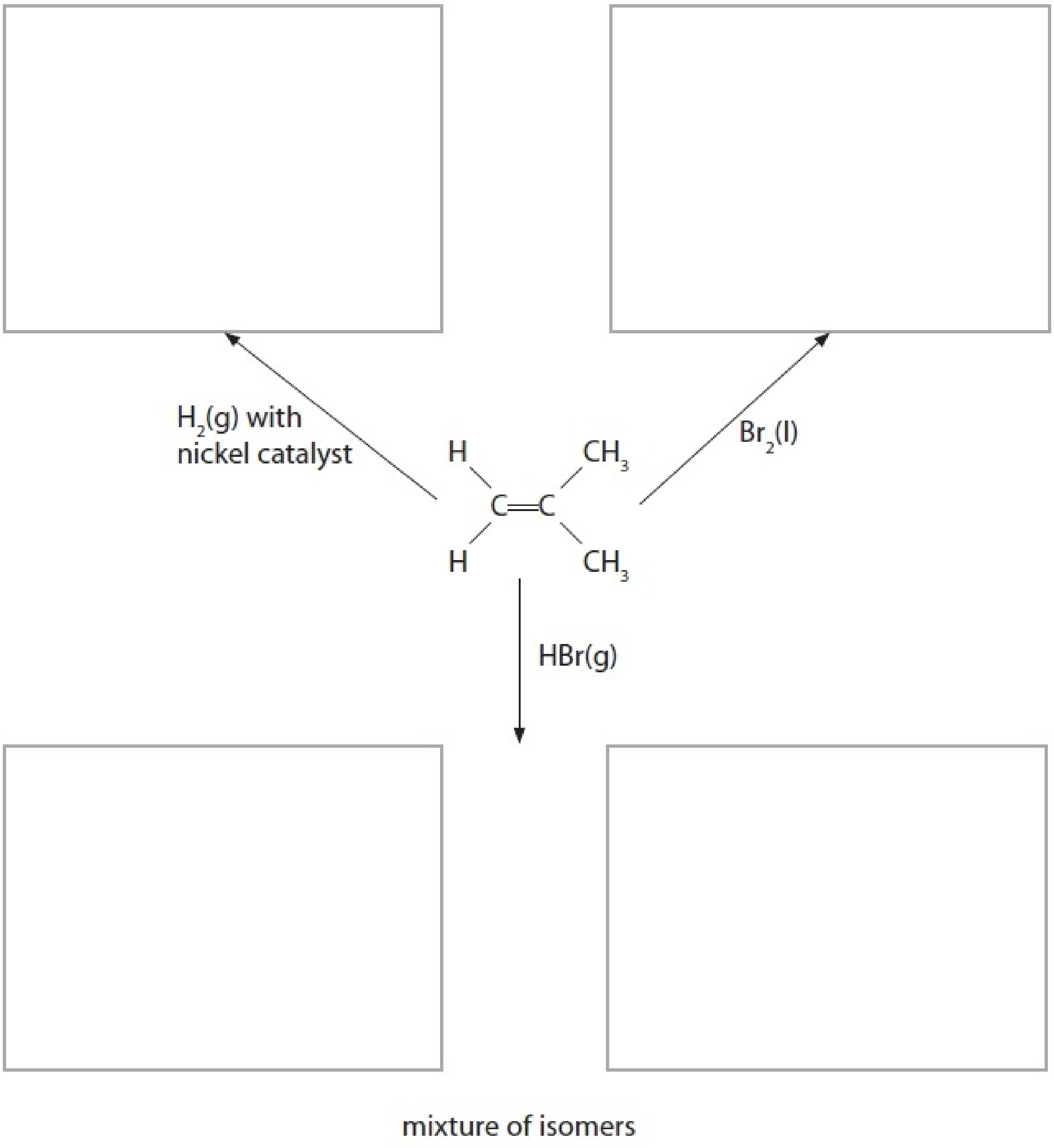
(1)

(Total for Question = 18 marks)

Q2. Alkenes are unsaturated hydrocarbons. They are used in the industrial production of many organic compounds.

(a) Add structural formulae to the flowchart below to show the organic product formed in each addition reaction of 2-methylpropene.

(4)



(b) Suggest a mechanism for the reaction of 2-methylpropene with bromine, Br_2(l). Include curly arrows.

(3)

(c) Ethene, C_2H_4, was prepared from ethanol, C_2H_5OH, by the following reaction

$$C_2H_5OH \rightarrow C_2H_4 + H_2O$$

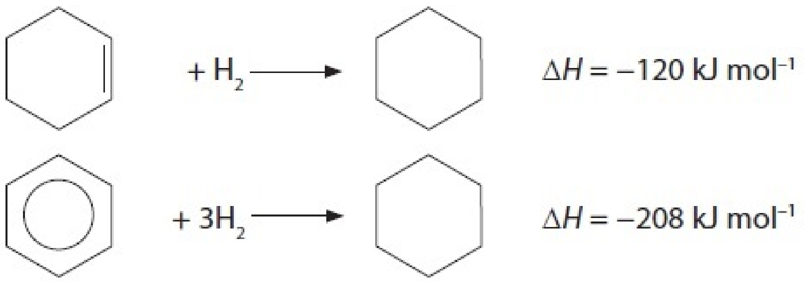
A chemist reacted 9.2 g of ethanol, C_2H_5OH, and obtained 4.2 g of ethene.

Calculate the percentage yield of ethene in the reaction.

(2)

(Total for Question = 9 marks)

Q3. (a) Equations for the catalytic hydrogenation of cyclohexene and of benzene are shown below.



(i) What is the type of reaction in both of these hydrogenations?

(1)

....

*(ii) The enthalpy of hydrogenation of benzene might be expected to be −360 kJ mol^{-1}. Explain why this is **not** the actual value.

(2)

....

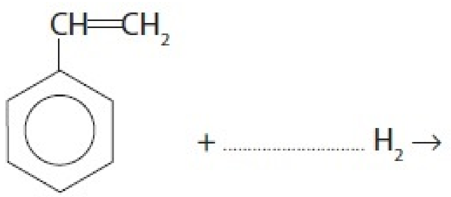
....

....

....

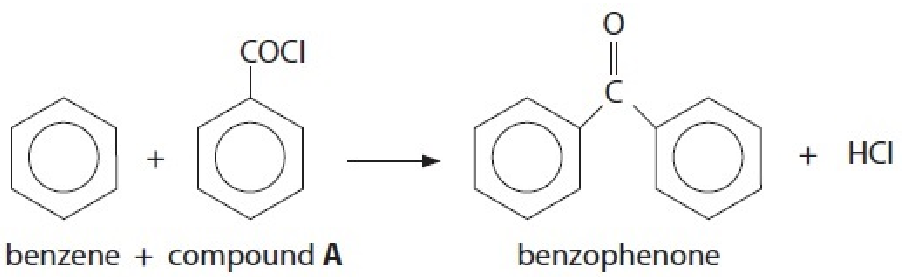
(iii) Complete the following equation for the total hydrogenation of phenylethene. Suggest a value for the enthalpy change of this reaction.

(3)



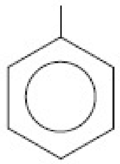
ΔH = ... kJ mol^{-1}

(b) The compound benzophenone is used as a sunscreen. It can be prepared from benzene, in the presence of aluminium chloride by the following reaction.



(i) Complete the diagram below by showing the **displayed** formula of the –COCl group in compound **A**.

(1)



(ii) Classify the type and mechanism of the reaction between benzene and compound **A**.

(1)

....

(iii) Give the names of the two chemists associated with the type of reaction described in (b)(ii).

(1)

.... and ....

(iv) Give the mechanism for the reaction between benzene and compound **A** in the presence of an aluminium chloride catalyst.

Start by showing the equation for the generation of the species which then attacks the benzene ring.

(4)

Equation to show generation of species attacking the benzene ring:

Rest of the mechanism:

(v) Suggest the essential property of a substance that will be used as a sunscreen.

(1)

....

....

(c) (i) The identity of a sample of benzophenone can be confirmed by recording its infrared and proton nmr spectra.

Identify **two** different bonds that would produce an absorption in the infrared spectrum of benzophenone. Use the Data Booklet to suggest the wavenumber of each of these absorptions.

(4)

....

....

....

....

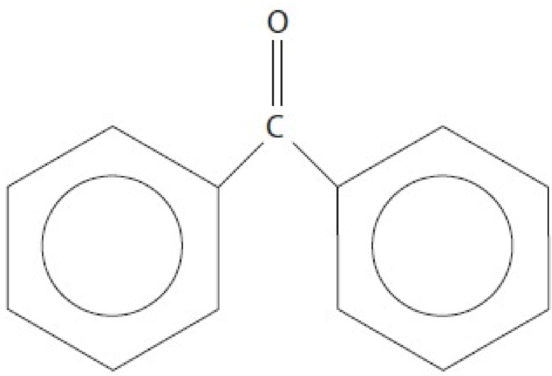
....

....

(ii) In benzophenone there are three different hydrogen environments, X, Y and Z, that produce signals in the ratio 2:2:1 respectively in the proton nmr spectrum.

Identify, **on the structure drawn below**, the positions of all the hydrogen atoms in each environment, labelling the different environments **X**, **Y** and **Z**.

(2)

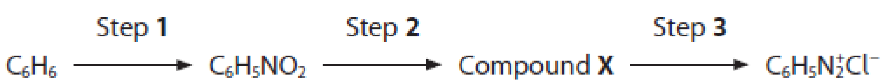


benzophenone

(Total for Question = 20 marks)

Q4.

Benzenediazonium chloride, $C_6H_5N_2^+Cl^-$, can be prepared from benzene in a series of steps.



(i) Identify the substances that are used to convert benzene into $C_6H_5NO_2$ in Step **1**.

(1)

....

(ii) Give the mechanism of the reaction taking place in Step **1**, including one or more equations for the formation of the electrophile.

(4)

(iii) Identify compound **X** and state the reagents needed to prepare it in Step **2**.

(2)

Compound **X**

....

Reagents

....

(iv) State the reagents and condition needed to convert compound **X** into benzenediazonium chloride in Step **3**.

(2)

Reagents

....

Condition

....

(Total for question = 9 marks)

Q5. A solution of 2,4-dinitrophenylhydrazine (Brady's reagent) is used as a test for organic functional groups.

(a) The positive result of the test is the formation of

(1)

☒ **A** a yellow solution.

☒ **B** an orange precipitate.

☒ **C** a red solution.

☒

D a green precipitate.

(b) Which of the following gives a positive result with a solution of 2,4-dinitrophenylhydrazine?

(1)

☒ **A** Only aldehydes

☒ **B** Only ketones

☒ **C** Only aldehydes and ketones

☒ **D** Any compound containing the C═O group

(c) The initial attack by 2,4-dinitrophenylhydrazine, when it reacts, is by

(1)

☒ **A** a free radical.

☒ **B** an electrophile.

☒ **C** a nucleophile.

☒ **D** a negative ion.

(d) The product of a positive test, a 2,4-dinitrophenylhydrazone, contains which of the following bonds?

(1)

☒ **A** N═N

☒ **B** C═N

☒ **C** C═C

☒ **D** C═O

(Total for Question = 4 marks)

Q6.

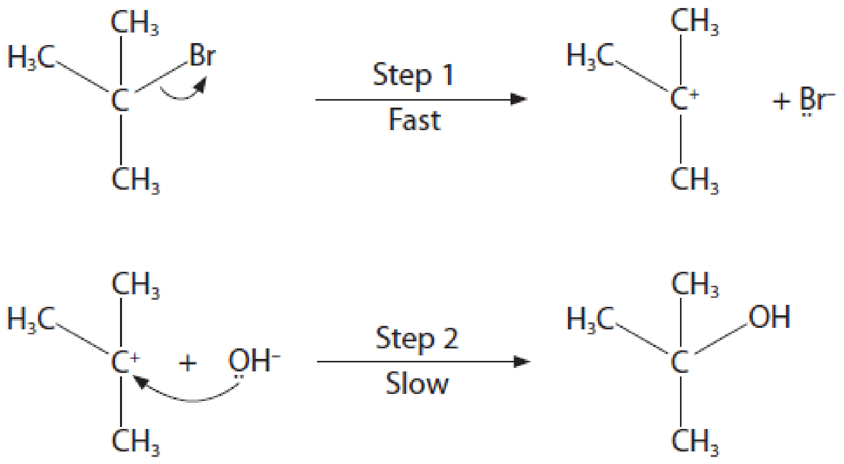
A student carried out a similar investigation into the kinetics of the reaction between 2-bromomethylpropane and hydroxide ions. A summary of the student's findings is shown below.

Kinetics Investigation - Summary of Key Findings

Reaction is first order with respect to 2-bromomethylpropane

Suggested Mechanism

S_N2 - as two steps in process



Use your knowledge of the mechanism of nucleophilic substitution reactions to suggest one feature of the summary, including the student's mechanism, that you agree with and two features you think are incorrect.

(3)

One feature you agree with.

....

....

Two features you think are incorrect.

....

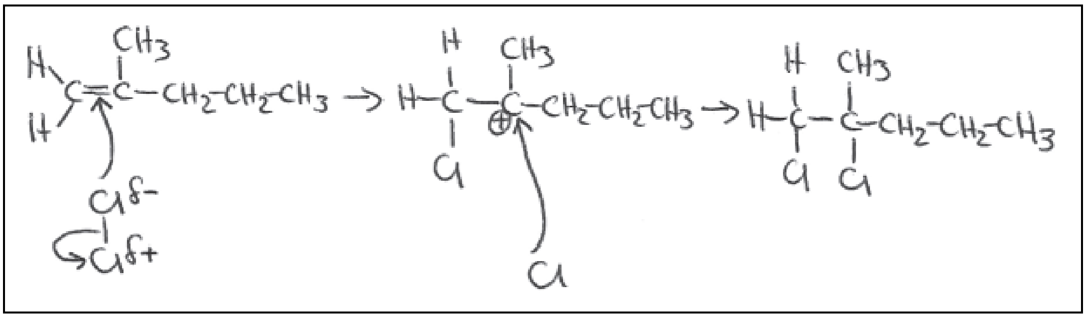
....

....

....

Q7.

* An example of an alkene with six carbon atoms is 2-methylpent-1-ene. It reacts with chlorine by means of an electrophilic addition reaction. The diagram below shows a student's attempt at drawing the mechanism for this reaction.



(i) Identify the three errors in this student's drawing of the mechanism.

(3)

Error 1

....

....

Error 2

....

....

Error 3

....

....

(ii) The structure of the carbocation intermediate is correctly drawn. Explain why the positive charge is on the carbon atom shown.

(1)

....

....

....

Q8.

(a) Which of the following represents a step in the mechanism during the reaction between ethene and hydrogen bromide?

(1)

☒ **A** $C_2H_4 + Br^+ \rightarrow C_2H_4Br^+$

☒ **B** $C_2H_4 + HBr \rightarrow C_2H_5^+ + Br^-$

☒ **C** $C_2H_4 + HBr \rightarrow C_2H_5\bullet + Br\bullet$

☒ **D** $C_2H_4 + HBr \rightarrow C_2H_4Br^- + H^+$

(b) The mechanism of the reaction between ethene and hydrogen bromide is

(1)

☒ **A** electrophilic addition.

☒ **B** electrophilic substitution.

☒ **C** nucleophilic addition.

☒ **D** nucleophilic substitution.

(Total for question = 2 marks)

Q9. An electrophile is **defined** as a species that

☒ **A** is an electron pair acceptor.

☒ **B** is an electron pair donor.

☒ **C** has a negative charge.

☒ **D** has a positive charge.

(Total for Question = 1 mark)

Q10. This question is about the reaction of methane with bromine in sunlight.

(1)

$$CH_4 + Br_2 \rightarrow CH_3Br + HBr$$

(a) This reaction is best described as

☒ **A** electrophilic addition.

☒ **B** electrophilic substitution.

☒ **C** free radical addition.

☒ **D** free radical substitution.

(b) One of the steps in the mechanism of this reaction is

(1)

$\bullet CH_3 + Br\bullet \rightarrow CH_3Br$

This step is

☒ **A** initiation.

☒ **B** propagation.

☒ **C** termination.

☒ **D** reduction.

(c) This reaction produces a mixture of products.

Which of the following is most likely to form, as well as bromomethane?

(1)

☒ **A** ethane

☒ **B** propane

☒ **C** butane

☒ **D** pentane

(d) When human skin is overexposed to sunlight, it is likely to lead to skin cancer.

What is the radiation in sunlight that leads to skin cancer?

(1)

☒ **A** microwaves

☒ **B** infrared

☒ **C** visible light

☒ **D** ultraviolet

(Total for Question = 4 marks)

Q11.

Chlorofluorocarbons, CFCs, damage the ozone layer. The mechanism of the process involves

☒ **A** homolytic fission.

☒ **B** heterolytic fission.

☒ **C** electrophilic addition.

☒ **D** nucleophilic substitution.

(Total for question = 1 mark)

Q12.

This question is about carbonyl compounds.

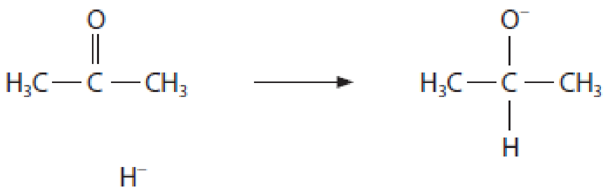
Sodium tetrahydridoborate, $NaBH_4$, acts as a source of H^- ions and is a reducing agent.

Complete the mechanism for the reduction of propanone to propan-2-ol.

(i) In **Step 1**, add the relevant dipole, a lone pair of electrons and curly arrows.

(2)

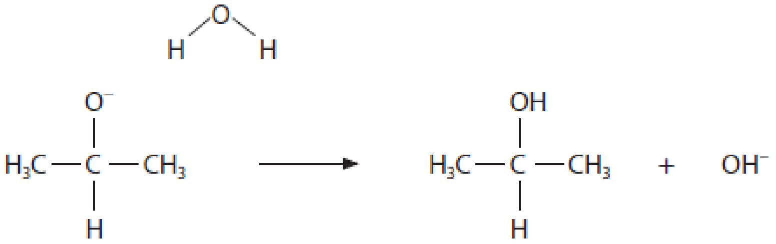
Step 1



(ii) In **Step 2**, add a relevant lone pair of electrons and curly arrows.

(1)

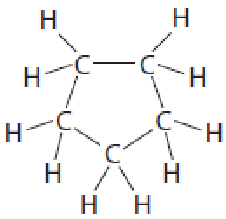
Step 2



(Total for question = 3 marks)

Q13.

Cycloalkanes are hydrocarbons which contain a ring of carbon atoms. Cycloalkanes have essentially the same chemical reactions as alkanes such as butane and pentane. Cyclopentane, which has a five-carbon ring, is a foam-blowing agent used to propel insulation into the doors and cases of refrigerators. The use of cyclopentane, rather than CFCs, reduces greenhouse gas emissions from this process by 99%.



cyclopentane

Cyclopentane and methane react with chlorine by the same mechanism.

(i) State the essential condition for the reaction between cyclopentane and chlorine.

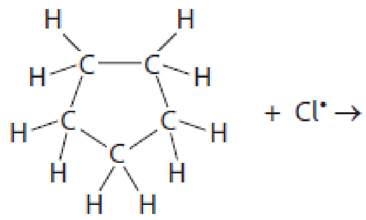
(1)

....

(ii) Give the **propagation** stage for the reaction between cyclopentane and chlorine by completing the first equation of this stage and then writing the second equation.

Curly half-arrows are **not** required.

(2)

Equation 1 

Equation 2

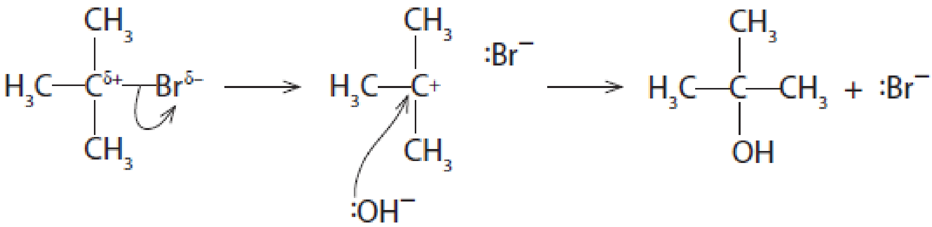
(iii) The termination stage of the reaction between cyclopentane and chlorine produces only one hydrocarbon. Draw the displayed formula of this hydrocarbon.

(1)

(Total for question = 4 marks)

Q14.

A reaction mechanism is shown below.



The hydroxide ion is acting as

☒ **A** an electrophile.

☒ **B** a catalyst.

☒ **C** a free radical.

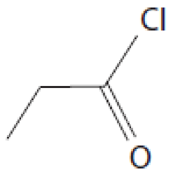
☒ **D** a nucleophile.

(Total for question = 1 mark)

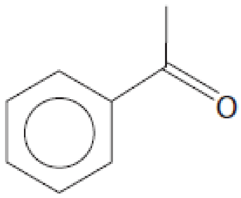
Q15.

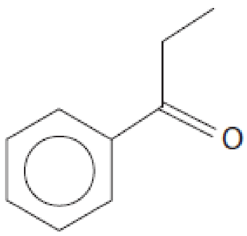
Benzene reacts with propanoyl chloride in the presence of a suitable catalyst.

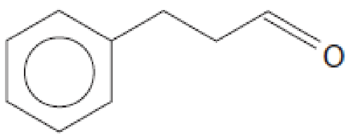
The skeletal formula of propanoyl chloride is

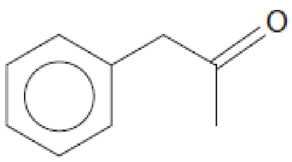


What is the organic product of this reaction?

☒ **A** 

☒ **B** 

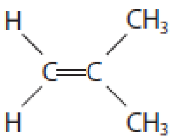
☒ **C** 

☒ **D** 

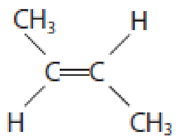
(Total for question = 1 mark)

Q16.

Compounds **A** and **B** are isomeric alkenes.

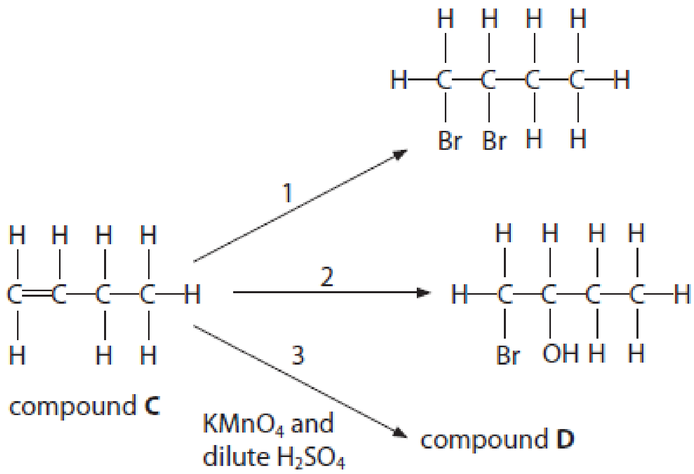


A



B

Compound **C** is an isomer of compounds **A** and **B**. Some reactions of compound **C** are shown below.



Compound **C** also reacts with hydrogen chloride.

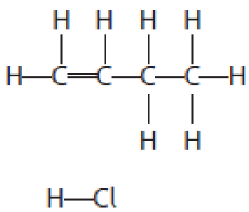
(i) Classify the type and mechanism of this reaction.

(2)

....

(ii) Complete the diagram below by adding any dipoles and curly arrows relevant to the **first** step of the mechanism of this reaction.

(2)



(iii) Draw the intermediate for the reaction which produces the major product.

Hence show the final step of the mechanism and the product.

Include relevant curly arrows, lone pairs and charges.

(4)

(Total for question = 8 marks)

Week 4

Enthalpy and energy

3.2.1 Enthalpy change

(a) explanation that some chemical reactions are accompanied by enthalpy changes that are exothermic (Δ*H*, negative) or endothermic (Δ*H*, positive)					
(b) construction of enthalpy profile diagrams to show the difference in the enthalpy of reactants compared with products					
(c) qualitative explanation of the term *activation energy*, including use of enthalpy profile diagrams					
(d) explanation and use of the terms: **(i)** *standard conditions* and *standard states* (physical states under standard conditions) **(ii)** *enthalpy change of reaction* (enthalpy change associated with a stated equation, $\Delta_r H$) **(iii)** *enthalpy change of formation* (formation of 1 mol of a compound from its elements, $\Delta_f H$) **(iv)** *enthalpy change of combustion* (complete combustion of 1 mol of a substance, $\Delta_c H$) **(v)** *enthalpy change of neutralisation* (formation of 1 mol of water from neutralisation, $\Delta_{neut} H$)					
(e) determination of enthalpy changes directly from appropriate experimental results, including use of the relationship: $q = mc\Delta T$					
(f) **(i)** explanation of the term *average bond enthalpy* (breaking of 1 mol of bonds in gaseous molecules) **(ii)** explanation of exothermic and endothermic reactions in terms of enthalpy changes associated with the breaking and making of chemical bonds **(iii)** use of average bond enthalpies to calculate enthalpy changes and related quantities **(see also 2.2.2 f)**					
(g) Hess' law for construction of enthalpy cycles and calculations to determine indirectly: **(i)** an enthalpy change of reaction from enthalpy changes of combustion **(ii)** an enthalpy change of reaction from enthalpy changes of formation **(iii)** enthalpy changes from unfamiliar enthalpy cycles					
(h) the techniques and procedures used to determine enthalpy changes directly and indirectly.					

5.2 Energy
5.2.1 Lattice enthalpy

(a) explanation of the term *lattice enthalpy* (formation of 1 mol of ionic lattice from gaseous ions, $\Delta_{LE}H$) and use as a measure of the strength of ionic bonding in a giant ionic lattice					
Born–Haber and related enthalpy cycles					
(b) use of the lattice enthalpy of a simple ionic solid (e.g. NaCl, $MgCl_2$) and relevant energy terms for: (i) the construction of Born–Haber cycles (ii) related calculations					
(c) explanation and use of the terms: (i) *enthalpy change of solution* (dissolving of 1 mol of solute, $\Delta_{sol}H$) (ii) *enthalpy change of hydration* (dissolving of 1 mol of gaseous ions in water, $\Delta_{hyd}H$)					
(d) use of the enthalpy change of solution of a simple ionic solid (e.g. NaCl, $MgCl_2$) and relevant energy terms (*enthalpy change of hydration* and *lattice enthalpy*) for: (i) the construction of enthalpy cycles (ii) related calculations					
(e) qualitative explanation of the effect of ionic charge and ionic radius on the exothermic value of a lattice enthalpy and enthalpy change of hydration.					

5.2.2 Enthalpy and entropy

Entropy (a) explanation that entropy is a measure of the dispersal of energy in a system which is greater, the more disordered a system					
(b) explanation of the difference in magnitude of the entropy of a system: (i) of solids, liquids and gases (ii) for a reaction in which there is a change in the number of gaseous molecules					
(c) calculation of the entropy change of a system, ΔS, and related quantities for a reaction given the entropies of the reactants and products					

Free energy (d) explanation that the feasibility of a process depends upon the entropy change and temperature in the system, $T\Delta S$, and the enthalpy change of the system, ΔH					
(e) explanation, and related calculations, of the free energy change, ΔG, as: $\Delta G = \Delta H - T\Delta S$ (the Gibbs' equation) and that a process is feasible when ΔG has a negative value					
(f) the limitations of predictions made by ΔG about feasibility, in terms of kinetics.					

Thermodynamics 1

Give definitions and exo/endo for:	Answer
1. Enthalpy change of formation	Enthalpy change when 1 mole of a compound is formed from its elements in their standard states under standard conditions (usually exo – bonds forming)
2. Enthalpy change of atomisation	Enthalpy change when one mole of gaseous atoms is produced from an element in its standard state (endo – needs energy)
3. Enthalpy of combustion	Enthalpy change when one mole of a substance is formed from its constituent elements with all substances in standard conditions (exo – energy released)
4. Enthalpy of neutralisation	Enthalpy change when one mole of water is formed in a reaction between an acid and alkali under standard conditions (exo)
5. Ionisation enthalpy - first	Enthalpy change when each atom in one mole of gaseous atoms loses one electron to form one mole of gaseous 1+ ions (endo – needs energy)
6. Electron affinity - first	Enthalpy change when each atom in one mole of gaseous atoms gains one electron to form one mole of gaseous 1- ions (exo, energy released. BUT! 2^{nd} Eaff will be endo)
7. Hydration enthalpy	Enthalpy change when one mole of gaseous ions becomes hydrated (dissolved in water) – (exo – bonds form)
8. Enthalpy of solution	Enthalpy change when one mole of an ionic solid dissolves in an amount of water large enough that the dissolved ions are well separated and don't interact (varies endo/exo)
9. Bond dissociation enthalpy	Enthalpy change when one mole of covalent bonds is broken in the gaseous state (exo – bond breaking)
10. Lattice enthalpy of formation	Enthalpy change when one mole of a solid ionic compound is formed from its constituent ions in the gas phase (exo)
11. Lattice enthalpy of dissociation	Enthalpy change when one mole of a solid ionic compound is broken up into its constituent ions in the gas phase (endo)
12. Enthalpy change of vaporisation	Enthalpy change when one mole of a liquid is turned into a gas (endo)

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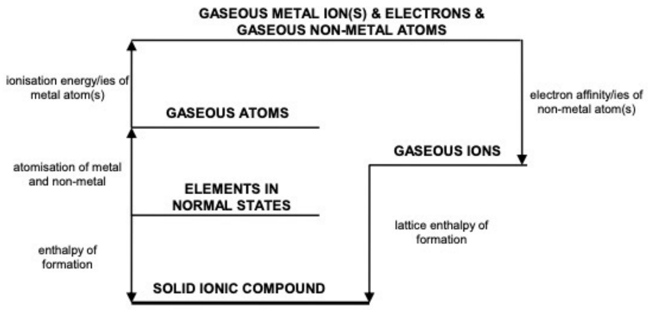
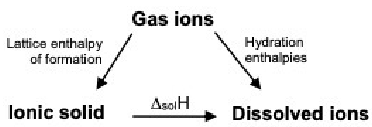
Thermodynamics 2

Key Recall Question	Answer
1. What assumptions are made when lattice enthalpy is calculated using theory only?	Spherical ions, purely ionic bonding (perfect charge separation), no covalent character, ions are point charges (charge concentrated at centre of ion)
2. What does it mean if the theoretical and experimental (from Born Haber cycle) values for lattice enthalpy differ?	The lattice must have some covalent character (the theory value tends to under estimate lattice enthalpy)
3. What factors affect the size of lattice enthalpy?	The size of the ions/ionic radii and the charges on the ions – higher charge density (small ion – high charge) means higher enthalpy
4. When are you most likely to see covalent character in a lattice?	With a large negative ion and a small highly charged positive ion e.g. aluminium oxide/when the electronegativity difference between the ions is too small to allow for a complete electron transfer
5. What sequence would you expect in a Born Haber cycle?	
6. How would you work out lattice enthalpy from hydration enthalpy and enthalpy of solution?	 reverse sign if lattice enthalpy of dissociation. Direction of arrows follows from defs.
7. What is indicated by a high lattice enthalpy?	A strong ionic bond
8. If you were comparing three lattices with different enthalpies of formation, how would you decide which is most likely to form?	The one with the largest value (more energy released on formation – most stable)
9. How does covalent character affect the properties of a lattice?	It makes it less soluble/insoluble, may have lower conductivity
10. Why is enthalpy of 2^{nd} electron affinity usually negative?	You are adding a negative electron to a negative ion (one electron has already been added)

Question	Date:	Date:	Date:	Date:	Date:	Date:	Date:	Date:	Date:	Date:	Date:	Date:	Date:
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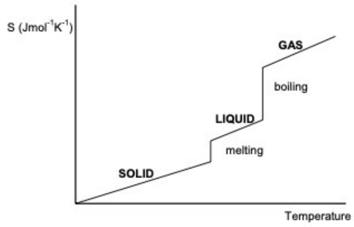
Thermodynamics 3

Key Recall Question	Answer
1. Define entropy	The disorder of a system ('simplification') the number of ways energy can be distributed among the particles of a system (more accurate)
2. Give the units of entropy	$J\ K^{-1}\ mol^{-1}$
3. How does entropy change with state of matter?	Solids < liquids < gases entropy increases as there are more ways for liquids and gases to be arranged.
4. How does entropy tend to change?	It tends to increase (2nd law of thermodynamics)
5. How does entropy change with temperature?	It increases with temperature; it is 0 at 0K
6. Sketch the graph for entropy and temperature	 state change – sharp increase
7. How do you work out the entropy change of a reaction?	S(products) – S(reactants) - positive if entropy increases
8. Is a reaction more likely if it has a positive or negative entropy change	Positive – as disorder increases
9. What is the equation for Gibbs Free Energy	$\Delta G = \Delta H - T\Delta S$
10. What value must delta G be for a reaction to be feasible (able to take place) ?	0 or negative. i.e. most likely with a negative enthalpy change and positive entropy change.
11. What is the value for delta G at a state change?	0 - the equation in 9 can therefore be used to work out melting point/boiling point
12. Why would a reaction with positive enthalpy and negative entropy not be feasible?	Delta G would always be positive.

Question	Date:	Date:	Date:	Date:	Date:	Date:	Date:	Date:	Date:	Date:	Date:	Date:	Date:
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Questions

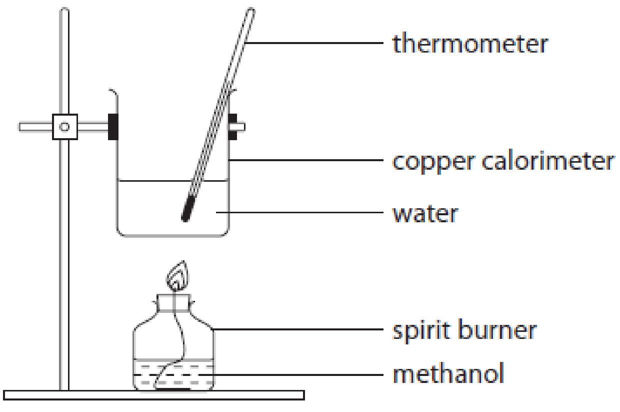
Q1.

This question is about the enthalpy change of combustion of methanol.

A teacher asked two students to carry out a practical task to determine the enthalpy change of combustion of methanol.
Both students were provided with the same apparatus and chemicals.
The following procedure was provided for the students.

Procedure

- Measure out 150 cm^3 of distilled water, using a 250 cm^3 measuring cylinder.
- Transfer the water to a copper calorimeter and note the initial temperature of the water (to the nearest 0.5°C) in **Table 1**.
- Weigh the spirit burner containing methanol and record its mass in **Table 1**.
- Place the spirit burner under the copper calorimeter, as shown in the diagram.
- Ignite the spirit burner and burn the methanol, whilst stirring the water with the thermometer.
- After heating the water for three minutes, extinguish the flame and immediately record the **highest** temperature reached by the water.
- As soon as possible, reweigh the spirit burner containing the methanol and record its mass in **Table 1**.



The results of Student 1 are recorded in **Table 1**.

Mass of spirit burner plus methanol before burning / g	213.47
Mass of spirit burner plus methanol after burning / g	211.87
Mass of methanol burned / g	
Highest temperature of the water / °C	64.5
Initial temperature of the water / °C	22.0
Temperature change of the water / °C	

Table 1

(a) Complete **Table 1**, giving the values to an appropriate number of decimal places.

(2)

(b) Write the equation that represents the reaction that occurs when the standard enthalpy change of combustion of methanol, $CH_3OH(l)$, is measured. Include state symbols.

(2)

(c) Use Student 1's result to calculate the enthalpy change of combustion of methanol in kJ mol^{-1}.
Give your answer to an appropriate number of significant figures.

Specific heat capacity of water = 4.18 J g^{-1} $°C^{-1}$
Density of water = 1.00 g cm^{-3}

(4)

(d) Student 1 compared the experimental value for the enthalpy change of combustion of methanol obtained in part (c) with the standard value given on the internet.
The student's value was **less exothermic** than the standard value.

Student 1 decided to evaluate the uncertainty in the measurements made in this experiment.

(i) Student 1 used a 250 cm^3 measuring cylinder to measure the volume of 150 cm^3 distilled water. The uncertainty in this volume measurement is ±1 cm^3.

Calculate the percentage uncertainty in the volume of distilled water that Student 1 measured in the experiment.

(1)

(ii) Compare and contrast the use of a 250 cm^3 measuring cylinder to measure out the 150 cm^3 distilled water with the use of a 25 cm^3 measuring cylinder (uncertainty ±0.2 cm^3 for each volume measurement) six times to measure the same volume.

(3)

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(iii) Student 1 calculated the uncertainties in the remaining measurements. However, Student 1 realised that the measurement uncertainties did **not** explain the difference between the experimental value for the enthalpy change of combustion of methanol calculated in part (c) and the value obtained from the internet.

Other than human error, give **three** reasons for the difference in the values.

(3)

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(e) Student 1 decided to repeat the experiment.

Student 1 used the copper calorimeter and water from the first experiment and recorded the initial temperature as 60.0°C.
Student 1 burned **exactly** the same mass of methanol as in the first experiment.

Explain, with a reason, how the value for the enthalpy change of combustion of methanol from this experiment would differ, if at all, from the value obtained in the first experiment.

(2)

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(f) Student 2 followed the **original** instructions provided, but extinguished the flame after **four** minutes rather than after three minutes.

Explain how the value calculated by Student 2 for the enthalpy change of combustion of methanol compared with that obtained in Student 1's first experiment.

(2)

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(g) Another student, Student 3, used the results from Student 1's first experiment to find the enthalpy change of combustion of methanol. Student 3 incorrectly used a value of 46.0 g mol^{-1} for the molar mass of methanol.

State and justify how this mistake would affect the calculated value for the enthalpy change of combustion of methanol.

(2)

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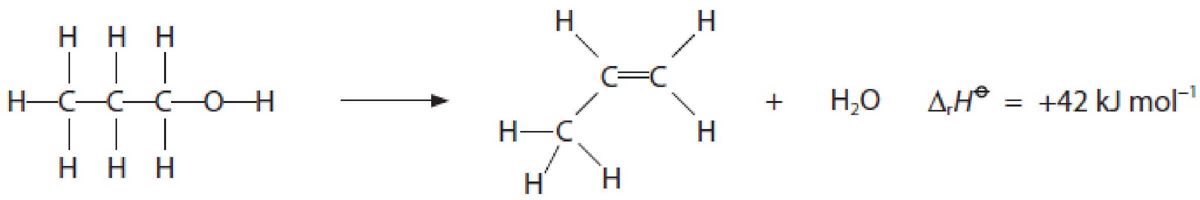
(Total for question = 21 marks)

Q2.

This question is about enthalpy changes and entropy changes.

Propan-1-ol is dehydrated to form propene.



The relevant mean bond enthalpies are given in the table.

Bond	Mean bond enthalpy / kJ mol^{-1}
C—C	347
C═C	612
C—H	413
O—H	464

Calculate the C—O mean bond enthalpy, using the mean bond enthalpies given in the table and the enthalpy change of reaction.

(3)

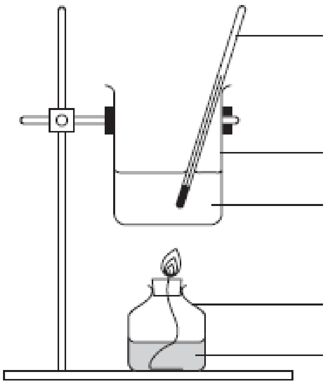
(Total for question = 3 marks)

Q3.

In an experiment, 1.000 g of a hydrocarbon, **A**, was burned completely in oxygen to produce 3.143 g of carbon dioxide and 1.284 g of water.

In a different experiment, the molar mass of the hydrocarbon, **A**, was found to be 84.0 g mol^{-1}.

A spirit burner was filled with the liquid hydrocarbon, **A**. The burner was weighed, lit and then used to raise the temperature of a quantity of water in a beaker, as shown in the diagram. The burner was then reweighed.



Results

Mass of spirit burner + hydrocarbon **A** before use	112.990 g
Mass of spirit burner + hydrocarbon **A** after use	112.732 g
Volume of water in the beaker	250 cm^3
Temperature of water before heating	21.3 °C
Temperature of water after heating	29.5 °C

Other data

Density of water	1.00 g cm^{-3}
Specific heat capacity of water	4.18 J g^{-1} $°C^{-1}$
Molar mass of hydrocarbon **A**	84.0 g mol^{-1}

(i) Use these results to calculate the enthalpy change of combustion of hydrocarbon **A** in kJ mol^{-1}.

Give your answer to an appropriate number of significant figures and include a sign.

(3)

(ii) The beaker used in this experiment was made of copper rather than glass. Give a reason for this.

(1)

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(Total for question = 4 marks)

Q4.

In acid-base neutralisation reactions, there is a temperature change.

The enthalpy change when hydrochloric acid reacts with aqueous ammonia is –53.4 kJ mol^{-1}.

$$HCl(aq) + NH_3(aq) \rightarrow NH_4Cl(aq)$$

Calculate the temperature change you would expect when
25.0 cm^3 of 1.00 mol dm^{-3} hydrochloric acid is mixed with
25.0 cm^3 of 1.00 mol dm^{-3} aqueous ammonia.

Give your answer to an appropriate number of significant figures.

[Assume: the density of the solution is 1.00 g cm^{-3}
the specific heat capacity of the solution is 4.18 J g^{-1} °C^{-1}]

(3)

(Total for question = 3 marks)

Q5.

In acid-base neutralisation reactions, there is a temperature change.

* The table shows the enthalpy changes of reaction when 1 mol of different acids are neutralised by sodium hydroxide solution, at 298 K.

Acid	Enthalpy change of reaction for 1 mol of acid / kJ mol^{-1}
hydrochloric acid, HCl	–58
nitric acid, HNO_3	–58
sulfuric acid, H_2SO_4	–115
ethanoic acid, CH_3COOH	–56

Comment on the relative enthalpy changes of reaction, using the data from the table and including any relevant equations.

(6)

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(Total for question = 6 marks)

Q6.

This question is about enthalpy changes and entropy changes.

Which is the equation for the standard enthalpy change of formation, $\Delta_f H^{\ominus}$, of aluminium oxide?

(1)

☒ **A** $4Al(s) + 3O_2(g) \rightarrow 2Al_2O_3(s)$

☒ **B** $4Al(s) + 6O(g) \rightarrow 2Al_2O_3(s)$

☒ **C** $2Al(s) + 1\frac{1}{2}O_2(g) \rightarrow Al_2O_3(s)$

☒ **D** $2Al(s) + 3O(g) \rightarrow Al_2O_3(s)$

(Total for question = 1 mark)

Q7.

This question is about enthalpy changes and entropy changes.

Calcium carbonate decomposes on heating.

$$CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$$

$\Delta_r H = +178 \text{ kJ mol}^{-1}$

$\Delta S_{system} = +165 \text{ J mol}^{-1} \text{ K}^{-1}$

Show, by calculating the value for the free energy change, ΔG, that this decomposition is not feasible at 298 K, and then calculate the minimum temperature to which calcium carbonate must be heated to make it decompose.

(3)

(Total for question = 3 marks)

Q8.

Adipic acid, $HOOC(CH_2)_4COOH$, is a dicarboxylic acid used in the production of polymers. It can be made by the reaction of buta-1,3-diene with carbon monoxide and water.

$$CH_2CHCHCH_2(g) + 2CO(g) + 2H_2O(l) \rightarrow HOOC(CH_2)_4COOH(s)$$

(a) (i) Use the Data Booklet to complete the table below.

(2)

	$CH_2CHCHCH_2(g)$	$CO(g)$	$H_2O(l)$	$HOOC(CH_2)_4COOH(s)$
$\Delta H_f^{\ominus}$ / kJ mol^{-1}	+109.9			−994.3
$S^{\ominus}$ / J mol^{-1} K^{-1}	278.7			250.0

(ii) Use data from the table to calculate the standard enthalpy change, in kJ mol^{-1}, when adipic acid is formed from buta-1,3-diene, carbon monoxide and water.

(2)

(iii) Use data from the table to calculate the standard entropy change of the system, in J mol^{-1} K^{-1}, when adipic acid is formed from buta-1,3-diene, carbon monoxide and water.

(2)

(iv) Use your answers to (ii) and (iii) to calculate $\Delta S_{surroundings}$ and ΔS_{total} for the reaction at 298 K.

(3)

(v) It was suggested that **decreasing** the temperature of the reaction to less than 298 K would produce a greater yield of adipic acid.

Explain, in terms of the effect on ΔS_{system}, $\Delta S_{surroundings}$ and hence ΔS_{total}, whether this would be the case.

(3)

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(b) Infrared spectroscopy can be used to follow the progress of reactions. During the reaction to produce adipic acid, suggest **one** peak which diminishes and **one** peak which appears.

Use information from the Data Booklet to identify two such possible peaks, giving their wave numbers and the bonds involved.

(2)

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(c) Adipic acid is used as an additive in some fruit jellies. Suggest what effect the adipic acid will have on the flavour of the jelly.

(1)

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....

(Total for question = 15 marks)

Q9.

This question is about the gas ethane, C_2H_6, and its reactions.

(a) Write the equation, including state symbols, which represents the reaction taking place when the standard enthalpy change of combustion of ethane is measured.

(2)

(b) Ethane can react with chlorine to form chloroethane and hydrogen chloride.

$$C_2H_6(g) + Cl_2(g) \rightarrow C_2H_5Cl(g) + HCl(g)$$

Bond	Bond enthalpy/kJ mol^{-1}
C—H	413
C—C	347
C—Cl	346
H—Cl	432
Cl—Cl	243

Rewrite this equation using displayed formulae.

Use the equation you have written, together with the bond enthalpy data, to calculate the enthalpy change for the reaction.

(4)

(c) This reaction takes place in a number of steps, some of which are shown below.

Step 1 $Cl_2 \rightarrow 2Cl\bullet$

Step 2 $CH_3CH_3 + Cl\bullet \rightarrow HCl + CH_3CH_2\bullet$

(i) State the type of reaction occurring in step 1 and the conditions needed for this step.

(2)

Type

....

Conditions

....

(ii) Complete the equation below for the third step of the reaction, and show the movement of electrons using the appropriate arrows.

(3)

$CH_3CH_2\bullet + Cl—Cl \rightarrow$

(iii) Write equations for **two** termination steps in this reaction.

(2)

(d) Ethane can be cracked in industry. Write an equation for the cracking of ethane.

(1)

(e) Suggest **two** reasons why cracking of larger alkane molecules is important in industry.

(2)

Reason 1:

....

....

Reason 2:

....

....

(Total for question = 16 marks)

Q10.

This question is about enthalpy changes and entropy changes.

What is the expression for ΔS_{total}?

(1)

☒ **A** $\Delta S_{surroundings} + \frac{\Delta H}{T}$

☒ **B** $\Delta S_{surroundings} - \frac{\Delta H}{T}$

☒ **C** $\Delta S_{system} + \frac{\Delta H}{T}$

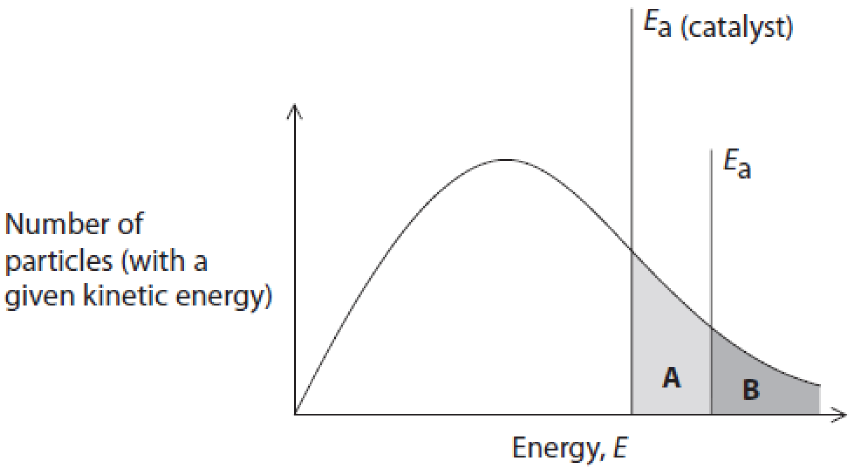
☒ **D** $\Delta S_{system} - \frac{\Delta H}{T}$

(Total for question = 1 mark)

Q11.

This is a question about catalytic converters in car exhaust systems.

Which area in the Maxwell-Boltzmann distribution diagram represents the **increase** in the number of particles with sufficient energy to react in the presence of a catalyst?



(1)

☒ **A** area A

☒ **B** area B

☒ **C** area A − area B

☒ **D** area A + area B

(Total for question = 1 mark)

Q12.

This question is about enthalpy changes and entropy changes.

Which reaction has a negative value for ΔS_{system}?

(1)

☒ **A** $2Cu(s) + O_2(g) \rightarrow 2CuO(s)$

☒ **B** $2H_2O_2(l) \rightarrow 2H_2O(l) + O_2(g)$

☒ **C** $MgCO_3(s) + H_2SO_4(aq) \rightarrow MgSO_4(aq) + H_2O(l) + CO_2(g)$

☒ **D** $Zn(s) + 2HCl(aq) \rightarrow ZnCl_2(aq) + H_2(g)$

(Total for question = 1 mark)

Q13.

One of the stages in the production of sulfuric acid from sulfide ores involves the oxidation of sulfur dioxide to sulfur trioxide. The equation for the reaction is

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g) \quad \Delta rH = –197 \text{ kJ mol}^{-1}$$

The conditions used in one industrial process are: 420°C and a pressure of 1.7 atm together with a vanadium(V) oxide catalyst.

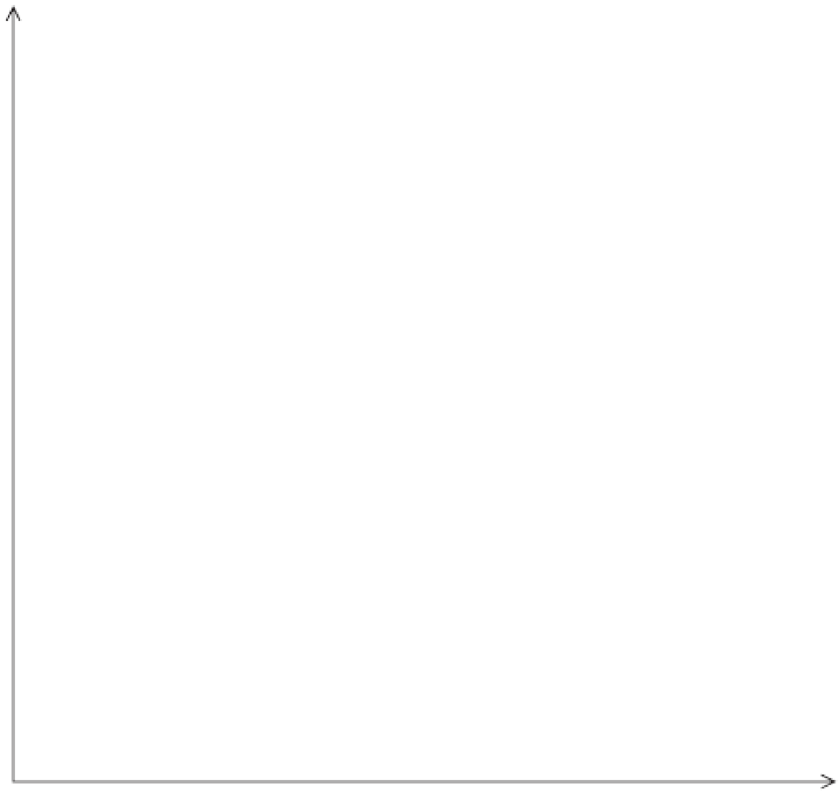
It is proposed to change the conditions to 600°C and 10 atm pressure, while still using the same catalyst.

(i) On the axes provided, sketch the reaction profiles for the uncatalysed and catalysed reaction.

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g) \quad \Delta rH = –197 \text{ kJ mol–}^{1}$$

Label the uncatalysed reaction, **A**, and the reaction catalysed by vanadium(V) oxide, **B**.

(3)



(ii) On your reaction profile, identify and label both the enthalpy change and the activation energy for the catalysed reaction.

(2)

(Total for question = 5 marks)

Week 5

Analysis

4.2.4 Analytical Techniques

(a) infrared (IR) radiation causes covalent bonds to vibrate more and absorb energy					
(b) absorption of infrared radiation by atmospheric gases containing C=O, O–H and C–H bonds (e.g. H_2O, CO_2 and CH_4), the suspected link to global warming and resulting changes to energy usage					
(c) use of an infrared spectrum of an organic compound to identify: n alcohol from an absorption peak of the O–H bond an aldehyde or ketone from an absorption peak of the C=O bond **(iii)** a carboxylic acid from an absorption peak of the C=O bond and a broad absorption peak of the O–H bond					
(d) interpretations and predictions of an infrared spectrum of familiar or unfamiliar substances using supplied data					
(e) use of infrared spectroscopy to monitor gases causing air pollution (e.g. CO and NO from car emissions) and in modern breathalysers to measure ethanol in the breath					
(f) use of a mass spectrum of an organic compound to identify the molecular ion peak and hence to determine molecular mass					
(g) analysis of fragmentation peaks in a mass spectrum to identify parts of structures.					
(h) deduction of the structures of organic compounds from different analytical data including: **(i)** elemental analysis **(see also 2.1.3 c)** **(ii)** mass spectra **(iii)** IR spectra.					

6.3 Analysis
6.3.1 Chromatography and qualitative analysis

Types of chromatography (a) interpretation of one-way TLC chromatograms in terms of Rf values					
(b) interpretation of gas chromatograms in terms of: (i) retention times (ii) the amounts and proportions of the components in a mixture.					
Tests for organic functional groups (c) qualitative analysis of organic functional groups on a test-tube scale; processes and techniques needed to identify the following functional groups in an unknown compound: (i) alkenes by reaction with bromine (ii) haloalkanes by reaction with aqueous silver nitrate in ethanol (i) phenols by weak acidity but no reaction with $CO_3{}^{2-}$ (ii) carbonyl compounds by reaction with 2,4- DNP (iii) aldehydes by reaction with Tollens' reagent (iv) primary and secondary alcohols and aldehydes by reaction with acidified dichromate (v) carboxylic acids by reaction with $CO_3{}^{2-}$					

6.3.2 Spectroscopy

NMR Spectroscopy (a) analysis of a carbon-13 NMR spectrum of an organic molecule to make predictions about: (i) the number of carbon environments in the molecule (ii) the different types of carbon environment present, from chemical					

shift values (iii) possible structures for the molecule					
(b) analysis of a high resolution proton NMR spectrum of an organic molecule to make predictions about: (i) the number of proton environments in the molecule (ii) the different types of proton environment present, from chemical shift values (iii) the relative numbers of each type of proton present from relative peak areas, using integration traces or ratio numbers, when required (iv) the number of non-equivalent protons adjacent to a given proton from the spin– spin splitting pattern, using the n + 1 rule (v) possible structures for the molecule					
(c) prediction of a carbon-13 or proton NMR spectrum for a given molecule					
(d) (i) the use of tetramethylsilane, TMS, as the standard for chemical shift measurements (ii) the need for deuterated solvents, e.g. $CDCl_3$, when running an NMR spectrum (iii) the identification of O–H and N–H protons by proton exchange using D_2O					
Combined techniques (e) deduction of the structures of organic compounds from different analytical data including: (i) elemental analysis (ii) mass spectra (iii) IR spectra (iv) NMR spectra.					

Questions

Q1.

Brand **X** is unlike many conventional toilet cleaners in that it does not contain bleach, but instead contains hydrochloric acid. The label states that the toilet cleaner contains 9 g of HCl per 100 cm^3 of the toilet cleaner.

An industrial technician was given the task of checking the validity of this statement. Using 25.0 cm^3 portions of the toilet cleaner, the technician carried out a titration using 2.50 mol dm^{-3} sodium hydroxide solution and obtained the following results.

Titration	Trial	1	2
Final Volume /cm^3	25.00	49.60	24.50
Initial Volume /cm^3	0.00	25.00	0.00
Volume Added /cm^3			

(a) (i) Complete the table and calculate the mean titre by selecting the appropriate results.

(1)

(ii) Write the equation for the titration reaction. State symbols are not required.

(1)

(iii) Calculate the number of moles of sodium hydroxide that reacted.

(1)

(iv) Hence state the number of moles of hydrochloric acid that reacted with the sodium hydroxide.

(1)

(v) Calculate the mass of HCl present in 100 cm^3 of the toilet cleaner. Give your answer to 3 significant figures.

(2)

(vi) Using the technician's results, comment on the validity of the manufacturer's statement that the toilet cleaner contained 9 g of HCl per 100 cm^3. Justify your answer.

(1)

....

....

....

(vii) Explain why titrations involving the use of a 2.50 mol dm^{-3} sodium hydroxide solution would **not** be advisable in a school or college laboratory.

(1)

....

....

....

(b) Conventional toilet cleaners contain a bleaching agent. Chloric(I) acid, HOCl, is one such substance.

Draw the dot and cross diagram for chloric(I) acid. Show outer electrons only.

(1)

(c) The instructions for the use of Brand **X** state that the toilet cleaner should not be used with bleaching agents.

Complete the equation for the reaction between the hydrochloric acid in the toilet cleaner and the chloric(I) acid in the bleaching agent. Give a reason why this reaction is to be avoided in accordance with the instructions for the use of the toilet cleaner.

(2)

Equation HCl + HOCl →

Reason

....

....

....

(d) Another bleaching agent is sodium chlorate(I), NaClO, which can be purchased as a solution. It can also be obtained by bubbling chlorine gas into sodium hydroxide solution.

(i) Give the oxidation numbers of the chlorine-containing species in the equation below and classify the reaction as a result of your answer.

$$2NaOH(aq) + Cl_2(g) \longrightarrow NaCl(aq) + NaClO(aq) + H_2O(l)$$

	2NaOH(aq)	$Cl_2(g)$	NaCl(aq)	NaClO(aq)	$H_2O(l)$
Oxidation Number		....	....	....	

(2)

Type of reaction

....

(ii) State how the reaction conditions would need to be changed in order to produce sodium chlorate(V) instead of sodium chlorate(I).

(1)

....

....

(iii) Give the equation for the reaction between chlorine and sodium hydroxide solution that forms sodium chlorate(V) as one of the products. State symbols are not required.

(2)

(Total for question = 16 marks)

Q2. This question is about the reactions of butanoic acid, $CH_3CH_2CH_2COOH$. It has a foul smell and behaves like a typical carboxylic acid.

(a) (i) The addition of sodium carbonate solution is often used as a chemical test to distinguish carboxylic acids, like butanoic acid, from other compounds, such as aldehydes.

Explain why old stocks of aldehydes often react with sodium carbonate solution.

(1)

....

....

(ii) How would the result of this test distinguish between a carboxylic acid and an old stock of an aldehyde?

(1)

....

....

(iii) Write the balanced chemical equation, including state symbols, for the reaction of sodium carbonate solution with butanoic acid.

(2)

*(iv) Infrared spectroscopy is a good physical method to distinguish carboxylic acids from other organic compounds. Give the wavenumbers of **two** characteristic absorptions for a carboxylic acid. Indicate the bond responsible for each absorption. Suggest why one of the absorptions is broad.

(3)

....

....

....

....

....

....

(v) High resolution nuclear magnetic resonance spectroscopy is a suitable physical method to use alongside infrared spectroscopy to identify butanoic acid. State the total number of peaks and suggest the splitting pattern for each peak that you would expect for butanoic acid, $CH_3CH_2CH_2COOH$.

(3)

....

....

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....

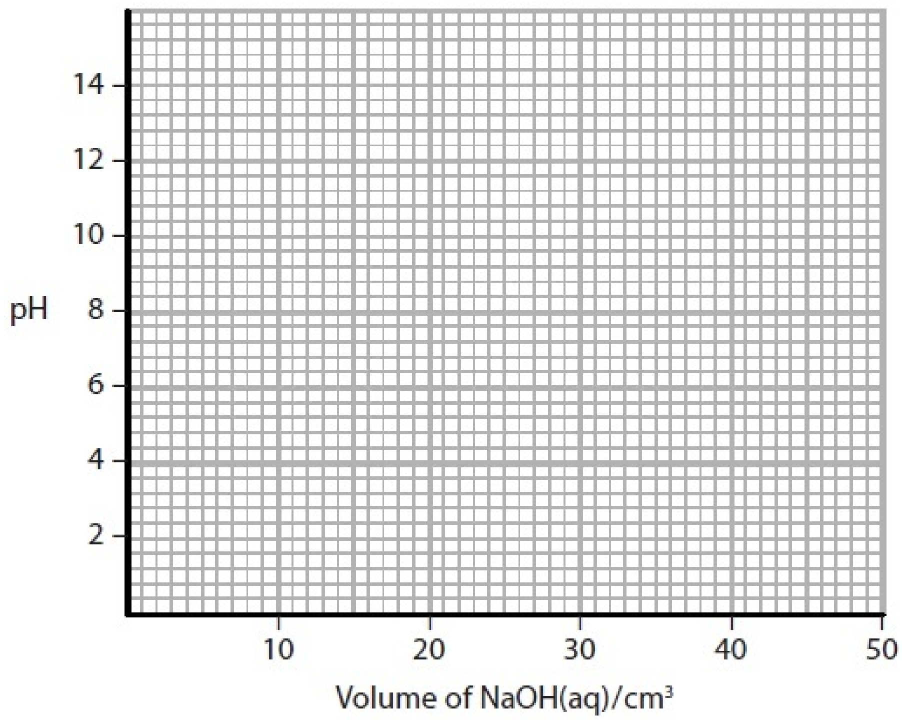
....

....

....

(b) Sketch the titration curve obtained when 50 cm^3 of 0.10 mol dm^{-3} sodium hydroxide solution is added to 25 cm^3 of 0.10 mol dm^{-3} butanoic acid.

(4)



(c) (i) What would you see when phosphorus pentachloride, PCl_5, reacts with butanoic acid?

(1)

....

....

(ii) Give the structural formula and name of the organic product of this reaction.

(2)

Structural formula

Name

....

(d) (i) Give the name or formula of the organic product of the reaction between butanoic acid and lithium tetrahydridoaluminate (lithium aluminium hydride).

(1)

....

(ii) Water cannot be used as the solvent in this reaction because it reacts with lithium tetrahydridoaluminate. Suggest a suitable solvent.

(1)

....

(iii) State the type of reaction that takes place between butanoic acid and lithium tetrahydridoaluminate. Justify your classification.

(2)

Type

....

Justification

....

....

....

(e) (i) Butanoic acid can be reacted with methanol to make methyl butanoate. State **two** conditions that help to speed up this reaction.

(2)

....

....

(ii) Draw the **displayed** formula of methyl butanoate.

(1)

(iii) Identify another chemical, by name or formula, which could be added to methanol to make methyl butanoate.

(1)

....

*(iv) Give **two** advantages and **one** disadvantage of using the reaction occurring in (e)(iii), compared to the reaction in (e)(i), when making methyl butanoate.

(3)

Advantages

....

....

....

....

Disadvantage

....

....

(Total for Question = 28 marks)

Q3.

The infrared spectrum of an organic compound with molecular formula $C_8H_8O_2$ has a strong peak in the range 1700–1680 cm^{-1} and a broad peak above 3300 cm^{-1}.

The compound could be

☒ **A** $H_3CC_6H_4COOH$

☒ **B** $C_6H_5CH_2COOH$

☒ **C** $C_6H_5COOCH_3$

☒ **D** $HOC_6H_4COCH_3$

(Total for question = 1 mark)

Q4. A 50 cm^3 sample of a gaseous hydrocarbon required exactly 250 cm^3 of oxygen for complete combustion. A volume of 150 cm^3 of carbon dioxide was produced.

[All volume measurements were made at the same temperature and pressure.]

Which of the following is the correct formula of the hydrocarbon?

☐ **A** C_3H_4

☐ **B** C_3H_8

☐ **C** C_5H_{10}

☐ **D** C_5H_{12}

(Total for Question = 1 mark)

Q5. The percentage by mass of tin in a piece of rock containing tin(IV) oxide, SnO_2, was determined as described in the procedure below.

Step 1 A sample of rock, with mass 10.25 g, was crushed and dissolved in sulfuric acid.

Step 2 The solution was treated with a reducing agent to convert the Sn^{4+} to Sn^{2+} ions.

Step 3 50 cm^3 of aqueous iodine solution with concentration 0.250 mol dm^{-3} was added to the solution of Sn^{2+} ions. The following reaction occurred:

$$Sn^{2+}(aq) + I_2(aq) \rightarrow Sn^{4+}(aq) + 2I^-(aq)$$

Step 4 The **excess** iodine was titrated with sodium thiosulfate solution with concentration 0.100 mol dm^{-3}. The volume of sodium thiosulfate solution required was 11.60 cm^3.

(a) Thiosulfate ions react with iodine as shown below.

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

(i) Calculate the number of moles of sodium thiosulfate which were used in **Step 4**.

(1)

(ii) Calculate the number of moles of iodine which reacted with this amount of sodium thiosulfate.

(1)

(iii) Calculate the number of moles of iodine added to the solution of Sn^{2+} ions in **Step 3**.

(1)

(iv) Use your results from (ii) and (iii) to calculate the number of moles of iodine which reacted with the Sn^{2+} ions from the rock.

(1)

(v) Hence calculate the percentage by mass of tin in the rock.

(2)

(b) (i) What change could be made in **Step 4** to improve the reliability of the result?

(1)

....

....

....

(ii) The error each time the burette was read was ± 0.05 cm^3. Calculate the percentage error in the titre value of 11.60 cm^3.

(1)

(iii) How could the percentage error in the titre value be reduced without using a different burette?

(1)

....

....

(c) The titration can be carried out with or without an indicator. What colour **change** would be seen at the end-point if an indicator was **not** used? The tin ions are colourless.

(1)

....

(Total for Question = 10 marks)

Q6. Which atoms are not detected by X-rays but are detected by nuclear magnetic resonance imaging which also shows their environments?

☒ **A** Carbon

☒ **B** Hydrogen

☒ **C** Nitrogen

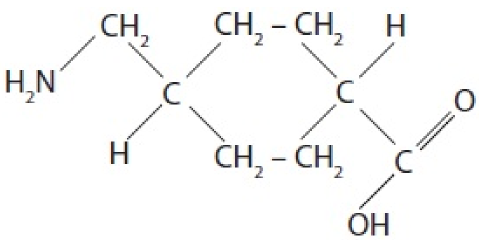
☒ **D** Oxygen

(Total for Question = 1 mark)

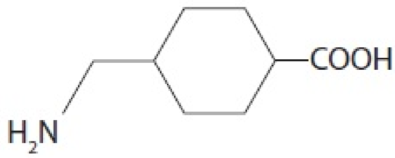
Q7.

Tranexamic acid

Tranexamic acid is an amino acid. It is a white crystalline solid which melts at 300 ºC. It is used to reduce bleeding during surgery and dental procedures and is especially useful where patients suffer from deficiencies in blood-clotting factors. The structure of tranexamic acid can be drawn as shown below.



or



As the name suggests, tranexamic acid is the *trans* form of a compound that forms geometric (or *cis*-*trans* or *E*-*Z*) isomers.

(a)

(i) Explain why some molecules which contain a C═C double bond show geometric isomerism.

(2)

....

....

....

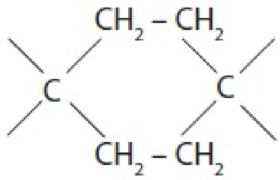
....

(ii) Suggest how tranexamic acid can form geometric isomers although it does not have a C═C double bond.

(1)

(iii) Complete the diagram to show the structure of the cis isomer.

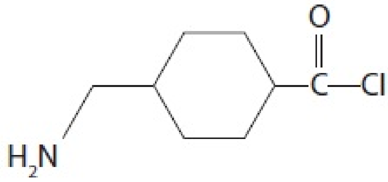
(1)



(iv) Explain why tranexamic acid melts at 300 ºC while the alkane, undecane ($C_{11}H_{24}$) which has almost the same number of electrons, melts at −26 ºC. A detailed description of the forces involved is **not** required.

(3)

(b) The diagram below shows a compound, **K**, which is a derivative of tranexamic acid.



(i) Identify by name or formula a compound that might react with tranexamic acid to form **K**.

(1)

....

(ii) Under suitable conditions, molecules of **K** react together forming a polymer, **L**. Draw the structure of **L**, showing two repeat units.

(2)

(iii) Name the type of polymerization that results in the formation of **L**.

(1)

....

(iv) State the type of naturally occurring substance which contains the same type of linkage as in the polymer **L**.

(1)

....

(c) If the sequence of reactions, that produces polymer *L* from tranexamic acid, is carried out starting with the *cis* isomer of tranexamic acid, an organic compound, **M**, is formed.

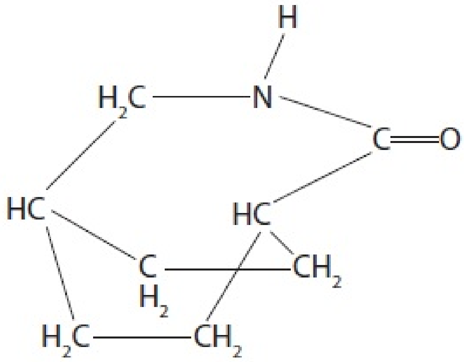
The low resolution nuclear magnetic resonance (nmr) spectrum of **M** has six peaks with relative heights 4:4:2:1:1:1.

The infrared (IR) spectrum of **M** has peaks in the region 1700−1630 cm^{-1} and 3500−3140 cm^{-1}.

(i) The structure of **M** is shown below.

The nmr spectrum shows that the molecule, **M**, has six different hydrogen environments. Use the letters **a** to **f** to label the H atoms of **M** showing the six hydrogen environments. All thirteen hydrogen atoms should be labelled.

(4)



(ii) Explain how the IR data are consistent with the structure of **M**.

(2)

....
....

....
....

....
....

(iii) Suggest why **M** is formed from the *cis* isomer but not from the *trans* isomer.

(2)

....
....

....
....

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....

(Total for question = 20 marks)

Week 6

pH and buffers

2.1.4 Acids

(a) the formulae of the common acids (HC*l*, H_2SO_4, HNO_3 and CH_3COOH) and the common alkalis (NaOH, KOH and NH_3) and explanation that acids release H^+ ions in aqueous solution and alkalis release OH^- ions in aqueous solution					
(b) qualitative explanation of strong and weak acids in terms of relative dissociations					
(c) neutralisation as the reaction of: **(i)** H^+ and OH^- to form H_2O **(ii)** acids with bases, including carbonates, metal oxides and alkalis (water-soluble bases), to form salts, including full equations					
(d) the techniques and procedures used when preparing a standard solution of required concentration and carrying out acid–base titrations					
(e) structured and non-structured titration calculations, based on experimental results of familiar and non-familiar acids and bases.					
(f) describe the redox reactions of metals with dilute hydrochloric and dilute sulfuric acids					
(g) interpret and make predictions from redox equations in terms of oxidation numbers and electron loss/gain					

5.1.3 Acids, bases and buffers

Brønsted–Lowry acids and bases (a) (i) a Brønsted–Lowry acid as a species that donates a proton and a Brønsted–Lowry base as a species that accepts a proton (ii) use of the term conjugate acid–base pairs (iii) monobasic, dibasic and tribasic acids					
(b) the role of H+ in the reactions of acids with metals and bases (including carbonates, metal oxides and alkalis), using ionic equations					
(c) (i) the acid dissociation constant, Ka, for the extent of acid dissociation (ii) the relationship between Ka and pKa					
pH and [H+(aq)]					
(d) use of the expression for pH as: pH = –log[H+] $[H+] = 10^{-pH}$					
(e) use of the expression for the ionic product of water, Kw					
(f) calculations of pH, or related quantities, for: (i) strong monobasic acids (ii) strong bases, using Kw					
(g) calculations of pH, Ka or related quantities, for a weak monobasic acid using approximations					
(h) limitations of using approximations to Ka related calculations for 'stronger' weak acids					
Buffers: action, uses and calculations					
(i) a buffer solution as a system that minimises pH changes on addition of small amounts of an acid or a base					
(j) formation of a buffer solution from: (i) a weak acid and a salt of the weak acid, e.g. CH_3COOH/CH_3COONa (ii) excess of a weak acid and a strong alkali, e.g. excess CH_3COOH/NaOH					
(k) explanation of the role of the conjugate acid–base pair in an acid buffer solution, e.g. $CH_3COOH/CH_3COO–$, in the control of pH					
(l) calculation of the pH of a buffer solution, from the Ka value of a weak acid and the equilibrium concentrations of the conjugate acid–base pair; calculations of related quantities					
(m) explanation of the control of blood pH by the carbonic acid–hydrogencarbonate buffer system					
Neutralisation					
(n) pH titration curves for combinations of strong and weak acids with strong and weak bases, including: (i) sketch and interpretation of their shapes (ii) explanation of the choice of suitable indicators, given the pH range of the indicator (iii) explanation of indicator colour changes in terms of equilibrium shift between the HA and A– forms of the indicator					
(o) the techniques and procedures used when measuring pH with a pH meter.					

Acids and Bases 1

Key Recall Question	Answer
1. Define a Bronsted-Lowry acid and base	Acid = proton donor (loses H+) Base = proton acceptor (gains H+)
2. Give the formula for pH	pH = log[H+]
3. Give the formula for [H+] from pH	$[H+] = 10^{-pH}$
4. For every unit change in pH (e.g. 2 to 1) how much does [H+] change?	By a factor of 10. This the meaning of the $\log_{10}$ business
5. What is the difference between a strong and weak acid (or base)	Strong – all of the molecules dissociate into ions Weak – some of the molecules dissociate
6. Give the equation for HCl splitting into H+ and its conjugate base	$HCl \rightarrow H^+ + Cl^-$
7. Give the equation for ethanoic acid splitting into H+ and its conjugate base	$CH_3COOH \rightleftharpoons H^+ + CH_3COO^-$
8. Give the general equation for an acid splitting into H+ and its conjugate base	$HA \rightarrow H^+ + A^-$
9. For a strong acid, how do you work out pH?	Work out the concentration of H+ from the concentration of the acid (all dissociates) then use pH = log[H+]
10. For a weak acid, how do you work out pH?	Use the acidity equilibrium constant: $Ka = \frac{[H^+][A^-]}{[HA]}$

Question	Date:	Date:	Date:	Date:	Date:	Date:	Date:	Date:	Date:	Date:	Date:	Date:	Date:
1													
2													
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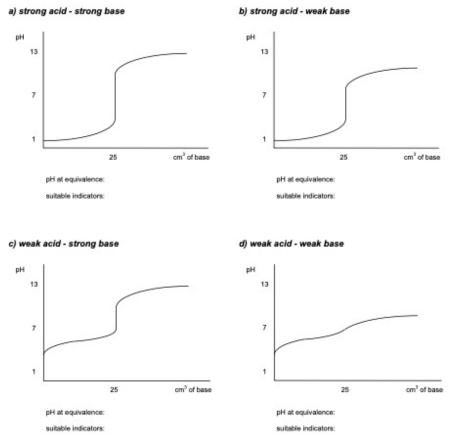
8													
9													
10													

Acids and Bases 2

Key Recall Question	Answer
1. Give the expression for the ionic product of water	$Kw = [H^+][OH^-]$ (remember water cancels out because water is in great excess)
2. The ionisation of water is endothermic: $H_2O \rightleftharpoons H^+ + OH^-$ How does pH change with temp	As temperature increases, the eqm shifts to the right to oppose the change so more H+ and pH decreases
3. The pH of water at a temperature other than 298K is not 7! Why it is still neutral?	$[H^+] = [OH^-]$
4. How do you work out the pH of a strong base using Kw?	Work out $[OH^-]$ from [base], rearrange Kw: $\frac{Kw}{[OH^-]} = [H^+]$
5. How do you work out the pH of a solution once its been diluted?	Concentration x $\frac{\text{old vol}}{\text{new vol}}$ (scale the conc)
6. How do you convert between Ka and pKa (which is used to get nicer numbers and a good scale)	pKa = -logKa $Ka = 10^{-pKa}$
7. What is a buffer?	A solution that resists changes in pH when small amounts of H+ and OH- are added
8. How do you make a buffer solution? Give both routes for both acidic and alkali buffers	Acidic buffer – mix weak acid with its salt. Excess weak acid + strong base Alkali buffer – mix weak base with its salt. Excess weak base + strong acid
9. Why are buffers useful?	To maintain pH of medicines, in printing, to maintain blood pH
10. What is an indicator?	A weak acid that changes colour as pH changes (because the conjugate base is a different colour to the acid)

Question	Date:	Date:	Date:	Date:	Date:	Date:	Date:	Date:	Date:	Date:	Date:	Date:	Date:
1													
2													
3													
4													
5													
6													
7													
8													
9													
10													

Acids and Bases 3

Key Recall Question	Answer
1. Titration curves can be produced by adding acid from a burette to alkali in a flask in small amounts (or vice versa) and using a pH logger. Sketch the shape for strong acid/strong base, strong acid/weak base, weak acid/strong base, weak acid/weak base.	
2. What is the name for the point where the mol acid = mol alkali and how do you identify on the graph	Equivalence point. Half way up the steep part of graph
3. How do you choose a suitable indicator?	Colour change must happen within steep part
4. For the weak acid/weak base what is the name for the small change around equivalance point	Point of inflexion
5. What is mean by 'end point' in a titration?	The point where indicator changes colour – usually at equivalence point with suitable indicator. s
6. How do you handle calculations involving weak acids (HA) and strong base? Remember this is a buffer solution when weak acid is in excess.	Work out mol [OH-] and [HA]. HA and OH- react 1:1, work out which is in excess. If XS HA; how much HA left A- formed, use Ka. $HA + OH^- \rightarrow A^- + H_2O$ (neutralisation) If XS OH-, use Kw to work out H+.
7. How do you find the pH of a pure weak acid?	[H+] = [A-] so $Ka = [H^+]^2/[HA]$
8. How do you handle calculations involving a solid salt added to an acid to make a buffer?	Use mass and Mr to work out moles of salt and therefore [A-]. Use Ka to work out [H+] from [HA].
9. When does pH = pKa?	Half neutralisation – when half the HA has reacted with OH-, [HA] = [A-] so Ka = [H+]
10. What's the golden rule for calculations?	Find something and do it. Work out moles of [H+], moles of [OH-], whats in excess, use Ka if a weak acid, use Kw if you need to wotk out H+ from OH-.

Question	Date:	Date:	Date:	Date:	Date:	Date:	Date:	Date:	Date:	Date:	Date:	Date:	Date:
1													
2													
3													
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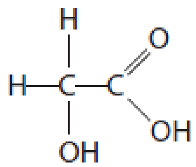
10													

Questions

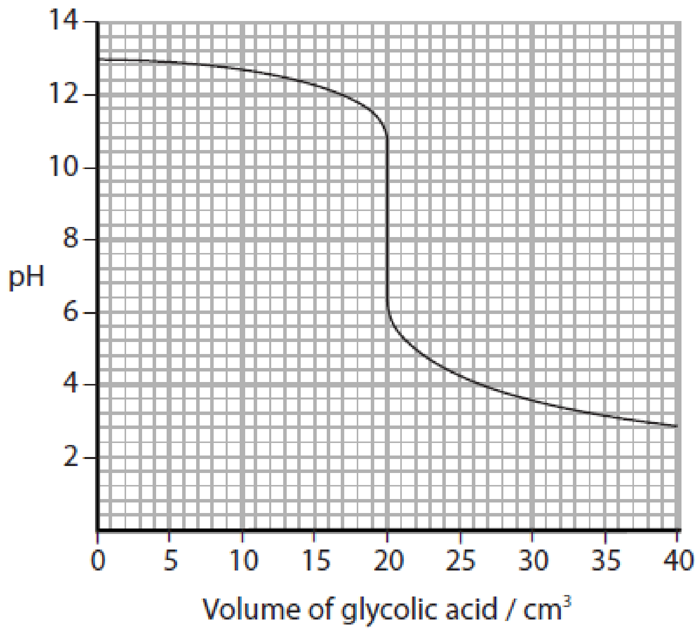
Q1.

2-Hydroxyethanoic acid, also known as glycolic acid, $CH_2OHCOOH$, is an alpha hydroxy acid used in some skincare products.
It has a K_a value of 1.5×10^{-4} mol dm^{-3}.

The structure of glycolic acid is



The titration curve for adding glycolic acid to 25.0 cm^3 of 0.100 mol dm^{-3} sodium hydroxide is shown.



(i) Use the information given in your Data Booklet to select a suitable indicator for this titration, including the colour change you would expect to see.

Justify your selection.

(3)

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(ii) What is the concentration of this glycolic acid in mol dm^{-3}?

(1)

☒ **A** 0.080

☒ **B** 0.100

☒ **C** 0.125

☒ **D** 0.250

(iii) The pH of the solution containing just sodium glycolate and water is

(1)

☒ **A** 2.8

☒ **B** 6.0

☒ **C** 8.3

☒ **D** 11.0

(Total for question = 5 marks)

Q2.

This question is about buffer solutions.

A buffer solution was formed by mixing 20.0 cm^3 of sodium hydroxide solution of concentration 0.100 mol dm^{-3} with 25.0 cm^3 of ethanoic acid of concentration 0.150 mol dm^{-3}.

$$CH_3COOH + NaOH \rightarrow CH_3COONa + H_2O$$

Calculate the pH of this buffer solution.

[K_a for ethanoic acid = 1.74×10^{-5} mol dm^{-3}]

(5)

(Total for question = 5 marks)

Q3.

Which of the following mixtures would form the best buffer solution with pH 9 for use in a school laboratory?

☒ **A** Ethanoic acid and sodium ethanoate

☒ **B** Sodium chloride and sodium hydroxide

☒ **C** Hydrocyanic acid and sodium cyanide

☒ **D** Ammonium chloride and ammonia

(Total for question = 1 mark)

Q4.

Which of the following mixtures would form the best buffer solution with pH 5 for use in a school laboratory?

☒ **A** Ethanoic acid and sodium ethanoate

☒ **B** Hydrochloric acid and sodium chloride

☒ **C** Sodium hydroxide and sodium methanoate

☒ **D** Ammonium chloride and ammonia

(Total for question = 1 mark)

Q5.

Calculate the pH of a solution of HCl, of concentration 0.25 mol dm^{-3}.

☒ **A** −0.60

☒ **B** 0.25

☒ **C** 0.60

☒ **D** 1.39

(Total for question = 1 mark)

Q6. This question is about the reactions of butanoic acid, $CH_3CH_2CH_2COOH$. It has a foul smell and behaves like a typical carboxylic acid.

(a) (i) The addition of sodium carbonate solution is often used as a chemical test to distinguish carboxylic acids, like butanoic acid, from other compounds, such as aldehydes.

Explain why old stocks of aldehydes often react with sodium carbonate solution.

(1)

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....

(ii) How would the result of this test distinguish between a carboxylic acid and an old stock of an aldehyde?

(1)

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....

(iii) Write the balanced chemical equation, including state symbols, for the reaction of sodium carbonate solution with butanoic acid.

(2)

*(iv) Infrared spectroscopy is a good physical method to distinguish carboxylic acids from other organic compounds. Give the wavenumbers of **two** characteristic absorptions for a carboxylic acid. Indicate the bond responsible for each absorption. Suggest why one of the absorptions is broad.

(3)

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(v) High resolution nuclear magnetic resonance spectroscopy is a suitable physical method to use alongside infrared spectroscopy to identify butanoic acid. State the total number of peaks and suggest the splitting pattern for each peak that you would expect for butanoic acid, $CH_3CH_2CH_2COOH$.

(3)

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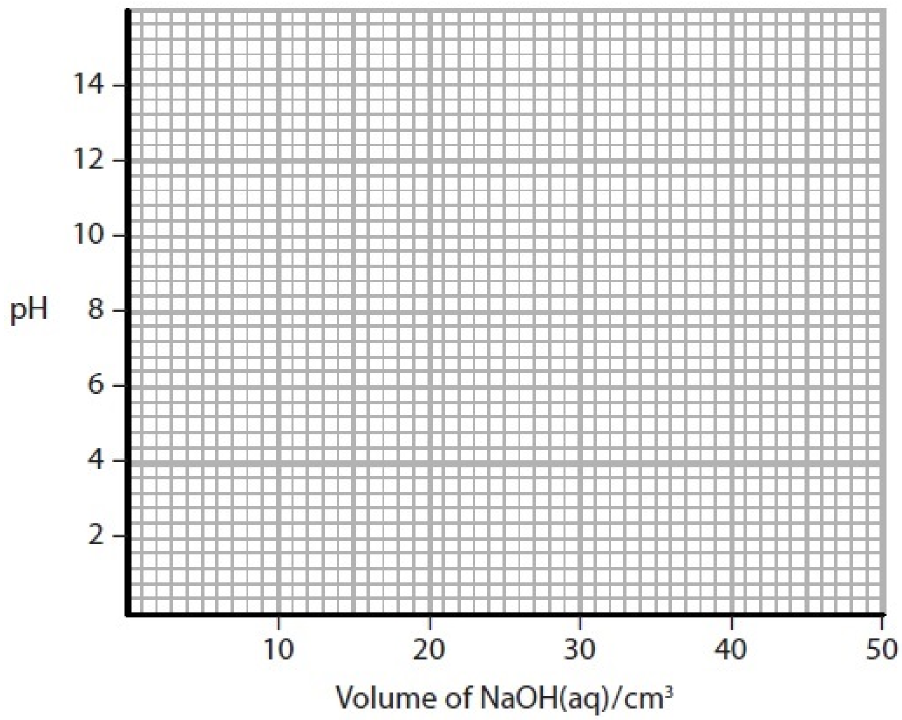
(b) Sketch the titration curve obtained when 50 cm^3 of 0.10 mol dm^{-3} sodium hydroxide solution is added to 25 cm^3 of 0.10 mol dm^{-3} butanoic acid.

(4)



(c) (i) What would you see when phosphorus pentachloride, PCl_5, reacts with butanoic acid?

(1)

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(ii) Give the structural formula and name of the organic product of this reaction.

(2)

Structural formula

Name

....

(d) (i) Give the name or formula of the organic product of the reaction between butanoic acid and lithium tetrahydridoaluminate (lithium aluminium hydride).

(1)

....

(ii) Water cannot be used as the solvent in this reaction because it reacts with lithium tetrahydridoaluminate. Suggest a suitable solvent.

(1)

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(iii) State the type of reaction that takes place between butanoic acid and lithium tetrahydridoaluminate. Justify your classification.

(2)

Type

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Justification

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(e) (i) Butanoic acid can be reacted with methanol to make methyl butanoate. State **two** conditions that help to speed up this reaction.

(2)

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(ii) Draw the **displayed** formula of methyl butanoate.

(1)

(iii) Identify another chemical, by name or formula, which could be added to methanol to make methyl butanoate.

(1)

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*(iv) Give **two** advantages and **one** disadvantage of using the reaction occurring in (e)(iii), compared to the reaction in (e)(i), when making methyl butanoate.

(3)

Advantages

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Disadvantage

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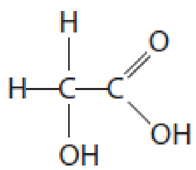
(Total for Question = 28 marks)

Q7.

2-Hydroxyethanoic acid, also known as glycolic acid, $CH_2OHCOOH$, is an alpha hydroxy acid used in some skincare products.
It has a K_a value of 1.5×10^{-4} mol dm^{-3}.

The structure of glycolic acid is



Glycolic acid has an acid dissociation constant of 1.5×10^{-4} mol dm^{-3} compared with a value of 1.7×10^{-5} mol dm^{-3} for ethanoic acid.

(i) Give a possible explanation as to why the value of K_a for glycolic acid is approximately ten times larger than that of ethanoic acid.

(2)

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(ii) Complete the equation to show the conjugate acid-base pairs that would be produced when pure samples of glycolic acid and ethanoic acid are mixed.

(1)

$CH_2OHCOOH + CH_3COOH \rightarrow$ .... + ...

(Total for question = 3 marks)

Q8.

The student made the following statement:

'The pH of pure water is always 7.0'

Is the student correct? Use the following information to justify your answer.

- $H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq)$
- $K_w = 1.0 \times 10^{-14}$ mol^2 dm^{-6} at 298 K
- ΔH is positive for the forward reaction in the equilibrium.

(3)

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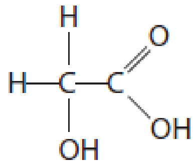
Q9.

2-Hydroxyethanoic acid, also known as glycolic acid, $CH_2OHCOOH$, is an alpha hydroxy acid used in some skincare products.
It has a K_a value of 1.5×10^{-4} mol dm^{-3}.

The structure of glycolic acid is



(a) A solution of glycolic acid of concentration 0.1 mol dm^{-3} has a pH of 2.4

What is the approximate pH of the resulting solution after it has been diluted by a factor of 100?

(1)

☒ **A** 1.4

☒ **B** 2.4

☒ **C** 3.4

☒ **D** 4.4

(b) Another solution of glycolic acid has a pH of 2.0

Calculate the concentration of this solution.

(3)

(Total for question = 4 marks)

Q10.

Which one of the following indicators is most suitable for titrating ethanoic acid with 0.1 mol dm^{-3} sodium hydroxide?

(Refer to page 19 of your data booklet.)

☒ **A** Thymol blue (acid)

☒ **B** Bromothymol blue

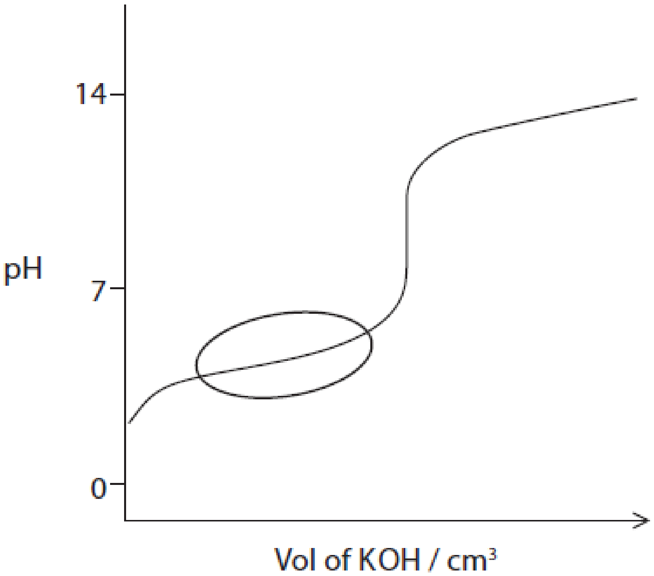
☒ **C** Thymol blue (base)

☒ **D** Alizarin yellow R

(Total for question = 1 mark)

Q11.

A student carried out a titration by adding 0.032 mol dm^{-3} potassium hydroxide solution to 25.0 cm^3 of 0.024 mol dm^{-3} propanoic acid. A sketch graph of pH against volume of potassium hydroxide solution added is shown below.



*(i) Describe and explain the behaviour of the solution formed in the region circled on the sketch graph.

(3)

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*(ii) Explain why the pH at the equivalence point of this titration is greater than 7.

(3)

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(iii) By considering the amount of excess alkali remaining, calculate the pH of the solution formed when 40 cm^3 of 0.032 mol dm^{-3} potassium hydroxide solution has been added to 25.0 cm^3 of 0.024 mol dm^{-3} propanoic acid.

$$K_w = 1.0 \times 10^{-14}\ mol^2\ dm^{-6}\ \text{at 298 K}$$

(5)

Q12.

Suggest the most likely pH for each of the following solutions.

(a) 5.0 mol dm^{-3} hydrochloric acid.

(1)

☐ **A** +5

☐ **B** +0.7

☐ **C** −0.7

☐ **D** −5

(b) 0.20 mol dm^{-3} strontium hydroxide, $Sr(OH)_2$

$K_w = 1.0 \times 10^{-14}\ mol^2\ dm^{-6}$

(1)

☐ **A** 13.3

☐ **B** 13.6

☒ **C** 14.0

☒ **D** 14.3

(c) A mixture of 20 cm^3 of 1.0 mol dm^{-3} nitric acid and 10 cm^3 of 1.0 mol dm^{-3} sodium hydroxide.

(1)

☒ **A** 0

☒ **B** 0.30

☒ **C** 0.48

☒ **D** 7

(Total for question = 4 marks)

Q13. Methyl orange and phenolphthalein are both acid-base indicators. In the titration of a strong acid against a weak alkali

☒ **A** methyl orange is a suitable indicator but phenolphthalein is not.

☒ **B** phenolphthalein is a suitable indicator but methyl orange is not.

☒ **C** both phenolphthalein and methyl orange are suitable indicators.

☒ **D** neither phenolphthalein nor methyl orange is a suitable indicator.

(Total for Question = 1 mark)

Q14. An aqueous solution of ethanoic acid is gradually diluted. Which of the following statements is **incorrect**?

☒ **A** The pH decreases.

☒ **B** The value of K_a is unchanged.

☒ **C** The concentration of ethanoic acid molecules decreases.

☒ **D** The proportion of ethanoic acid molecules which dissociates increases.

(Total for Question = 1 mark)

Q15. The dissociation constant of water, K_w, increases with increasing temperature. When the temperature increases, water

☒ **A** remains neutral.

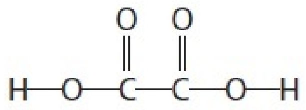
☒ **B** dissociates less.

☒ **C** becomes acidic.

☒ **D** becomes alkaline.

(Total for Question = 1 mark)

Q16. Ethanedioic acid, $H_2C_2O_4$, is a dicarboxylic acid which occurs in many plants, for example in rhubarb leaves, and is used as a rust remover and strong descaler. The structure of ethanedioic acid is shown below.



Ethanedioic acid is a much stronger acid than carboxylic acids such as ethanoic acid, having a pK_a of 1.38. The hydrogenethanedioate ion, $HC_2O_4^-$, is a weaker acid than ethanedioic acid, having a pK_a of 4.28, although slightly stronger than ethanoic acid.

(a) (i) Write an equation for the reaction of the hydrogenethanedioate ion with water to form an acidic solution. Include state symbols in your equation.

(2)

(ii) Write the expression for the acid dissociation constant, K_a, of the weak acid, $HC_2O_4^-$.

(1)

(iii) A solution containing hydrogenethanedioate ions behaves as a typical weak acid. Use your answer to (a)(ii) and the pK_a of the hydrogenethanedioate ion to calculate the pH of a 0.050 mol dm^{-3} solution of sodium hydrogenethanedioate, $NaHC_2O_4$.

(3)

(b) (i) State **two** approximations used in the calculation of pH in (a)(iii).

(2)

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2 ....

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*(ii) Explain why the calculation of the pH of a solution of sodium hydrogenethanedioate gives a more accurate value than a similar calculation for ethanedioic acid.

(2)

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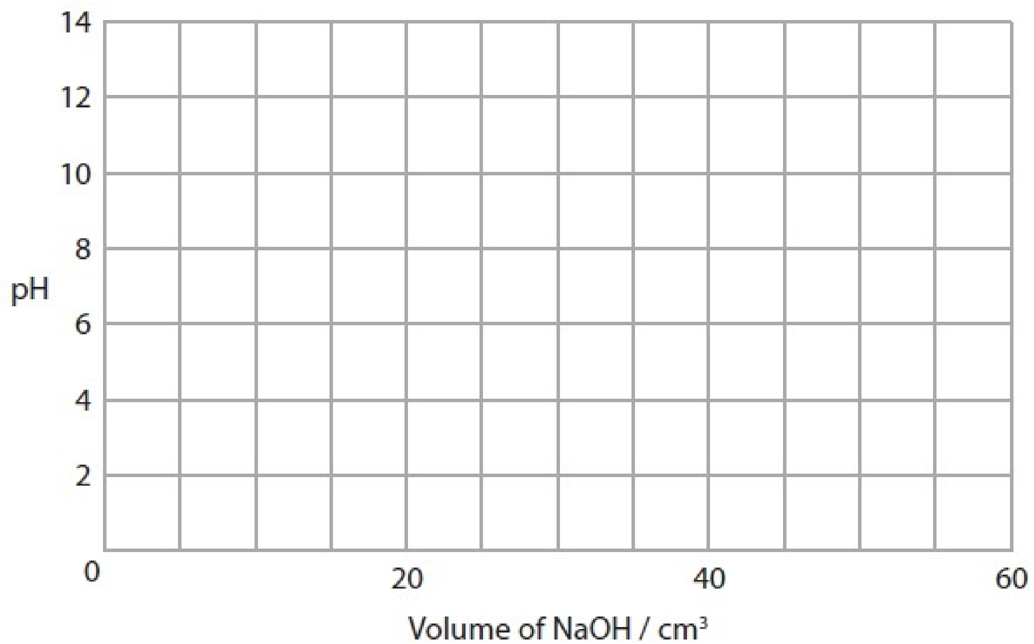
(c) 25 cm^3 of a 0.050 mol dm^{-3} solution of sodium hydrogenethanedioate was titrated with a sodium hydroxide solution of the same concentration.

(i) On the axis below, sketch the curve for this titration.

(3)



*(ii) When 25 cm^3 of a 0.050 mol dm^{-3} solution of **ethanedioic acid** is titrated with sodium hydroxide solution of the same concentration using phenolphthalein as the indicator, the end point is 50 cm^3.

When methyl yellow indicator is used, the colour changes at around 25 cm^3.

Using the information given at the start of the question and quoting data from page 19 of your data booklet, suggest why these volumes are different.

(2)

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(Total for Question = 15 marks)

Q17. The reaction between concentrated sulfuric acid and pure ethanoic acid is

$$CH_3COOH + H_2SO_4 \rightleftharpoons CH_3COOH_2^+ + HSO_4^-$$

The Brønsted-Lowry acids in this equilibrium are

☒ **A** CH_3COOH and H_2SO_4

☒ **B** CH_3COOH_2 + and HSO_4^-

☒ **C** H_2SO_4 and $CH_3COOH_2^+$

☒ **D** CH_3COOH and HSO_4^-

(Total for Question = 1 mark)

Q18. Which of the following statements is true about **all** substances that form acidic solutions in water?

☒ **A** They are corrosive.

☒ **B** They are liquids.

☒ **C** They contain hydrogen atoms.

☒ **D** They form H^+(aq) ions.

(Total for Question = 1 mark)

Q19.

In liquid ammonia the following equilibrium is present.

$$NH_2^- + NH_4^+ \rightleftharpoons 2NH_3$$

Identify the Brønsted-Lowry base(s).

☒ **A** NH_2^- only

☒ **B** NH_4^+ only

☒ **C** NH_2^- and NH_3

☒ **D** NH_4^+ and NH_3

(Total for question = 1 mark)

Week 7

Reaction mechanisms

4.1.1 Basic organic chemistry

(f) the different types of covalent bond fission: **(i)** homolytic fission (in terms of each bonding atom receiving one electron from the bonded pair, forming two radicals) i) **(ii)** heterolytic fission (in terms of one bonding atom receiving both electrons from the bonded pair)					
(g) the term *radical* (a species with an unpaired electron) and use of 'dots' to represent species that are radicals in mechanisms					
(h) a 'curly arrow' described as the movement of an electron pair, showing either heterolytic fission or formation of a covalent bond					
(i) reaction mechanisms, using diagrams, to show clearly the movement of an electron pair with 'curly arrows' and relevant dipoles.					

4.1.2 Alkanes

(f) the reaction of alkanes with chlorine and bromine by radical substitution using ultraviolet radiation, including a mechanism involving homolytic fission and radical reactions in terms of initiation, propagation and termination **(see also 4.1.1 f–g)**					
(g) the limitations of radical substitution in synthesis by the formation of a mixture of organic products, in terms of further substitution and reactions at different positions in a carbon chain.					

4.1.3 Alkenes

(f) addition reactions of alkenes with: **(i)** hydrogen in the presence of a suitable catalyst, e.g. Ni, to form alkanes **(ii)** halogens to form dihaloalkanes, including the use of bromine to detect the presence of a double C=C bond as a test for unsaturation in a carbon chain **(iii)** hydrogen halides to form haloalkanes **(iv)** steam in the presence of an acid catalyst, e.g. H_3PO_4, to form alcohols					
(g) definition and use of the term *electrophile* (an electron pair acceptor)					
(h) the mechanism of electrophilic addition in alkenes by heterolytic fission **(see also 4.1.1 h–i)**					
(i) use of Markownikoff's rule to predict formation of a major organic product in addition reactions of H–X to unsymmetrical alkenes, e.g. H–Br to propene, in terms of the relative stabilities of carbocation intermediates in the mechanism					

4.2.2 Halogenoalkanes

(a) hydrolysis of haloalkanes in a substitution reaction: **(i)** by aqueous alkali **(ii)** by water in the presence of $AgNO_3$ and ethanol to compare experimentally the rates of hydrolysis of different carbon– halogen bonds					
(b) definition and use of the term *nucleophile* (an electron pair donor)					
(c) the mechanism of nucleophilic substitution in the hydrolysis of primary haloalkanes with aqueous alkali **(see also 4.1.1 h–i)**					
(d) explanation of the trend in the rates of hydrolysis of primary haloalkanes in terms of the bond enthalpies of carbon–halogen bonds (C–F, C–C*l*, C–Br and C–I)					

6.1 Aromatic compounds, carbonyls and acids

6.1.1 Aromatic compounds

Electrophilic substitution (d) the electrophilic substitution of aromatic compounds with:					

(i) concentrated nitric acid in the presence of concentrated sulfuric acid (ii) a halogen in the presence of a halogen carrier (iii) a haloalkane or acyl chloride in the presence of a halogen carrier (Friedel–Crafts reaction) and its importance to synthesis by formation of a C–C bond to an aromatic ring (see also 6.2.4 d)					
(e) the mechanism of electrophilic substitution in arenes for nitration and halogenation					
(f) the explanation of the relative resistance to bromination of benzene, compared with alkenes, in terms of the delocalised electron density of the π-system in benzene compared with the localised electron density of the π-bond in alkenes					
(g) the interpretation of unfamiliar electrophilic substitution reactions of aromatic compounds, including prediction of mechanisms					
(i) the electrophilic substitution reactions of phenol: (i) with bromine to form 2,4,6-tribromophenol (ii) with dilute nitric acid to form 2-nitrophenol					
(j) the relative ease of electrophilic substitution of phenol compared with benzene, in terms of electron pair donation to the π-system from an oxygen p-orbital in phenol					
(k) the 2- and 4-directing effect of electrondonating groups (OH, NH_2) and the 3-directing effect of electron-withdrawing groups (NO_2) in electrophilic substitution of aromatic compounds					
(l) the prediction of substitution products of aromatic compounds by directing effects and the importance to organic synthesis (see also 6.2.5 Organic Synthesis).					

6.1.2 Carbonyl compounds

Reactions of carbonyl compounds (a) oxidation of aldehydes using $Cr_2O_7{}^{2-}/H^+$ (i.e. $K_2Cr_2O_7/H_2SO_4$) to form carboxylic acids					
(b) nucleophilic addition reactions of carbonyl compounds with: (i) $NaBH_4$ to form alcohols (ii) HCN [i.e. $NaCN_{(aq)}/H+_{(aq)}$], to form hydroxynitriles (see also 6.2.4 b)					
(c) the mechanism for nucleophilic addition reactions of aldehydes and ketones with $NaBH_4$ and HCN					

6.1.3 Carboxylic acids and esters

Properties of carboxylic acids (a) explanation of the water solubility of carboxylic acids in terms of hydrogen bonding					
(b) reactions in aqueous conditions of carboxylic acids with metals and bases (including carbonates, metal oxides and alkalis)					
Esters (c) esterification of: (i) carboxylic acids with alcohols in the presence of an acid catalyst (e.g. concentrated H_2SO_4) (ii) acid anhydrides with alcohols					
(d) hydrolysis of esters: (i) in hot aqueous acid to form carboxylic acids and alcohols (ii) in hot aqueous alkali to form carboxylate salts and alcohols					
Acyl chlorides (e) the formation of acyl chlorides from carboxylic acids using $SOCl_2$					
(f) use of acyl chlorides in synthesis in formation of esters, carboxylic acids and primary and secondary amides.					

6.2 Nitrogen compounds, polymers and synthesis

6.2.1 Amines

(b) the preparation of: (i) aliphatic amines by substitution of haloalkanes with excess ethanolic ammonia and amines (ii) aromatic amines by reduction of nitroarenes using tin and concentrated hydrochloric acid.					

6.2.2 Amino acids, amides and chirality

Reactions of amino acids (a) the general formula for an α-amino acid as $RCH(NH_2)COOH$ and the following reactions of amino acids: (i) reaction of the carboxylic acid group with alkalis and in the formation of esters (see also 6.1.3 c) (ii) reaction of the amine group with acids					

6.2.3 Polyesters and polyamides

Condensation polymers (a) condensation polymerisation to form: (i) polyesters (ii) polyamides					
(b) the acid and base hydrolysis of: (i) the ester groups in polyesters (ii) the amide groups in polyamides					

6.2.4 Carbon–carbon bond formation

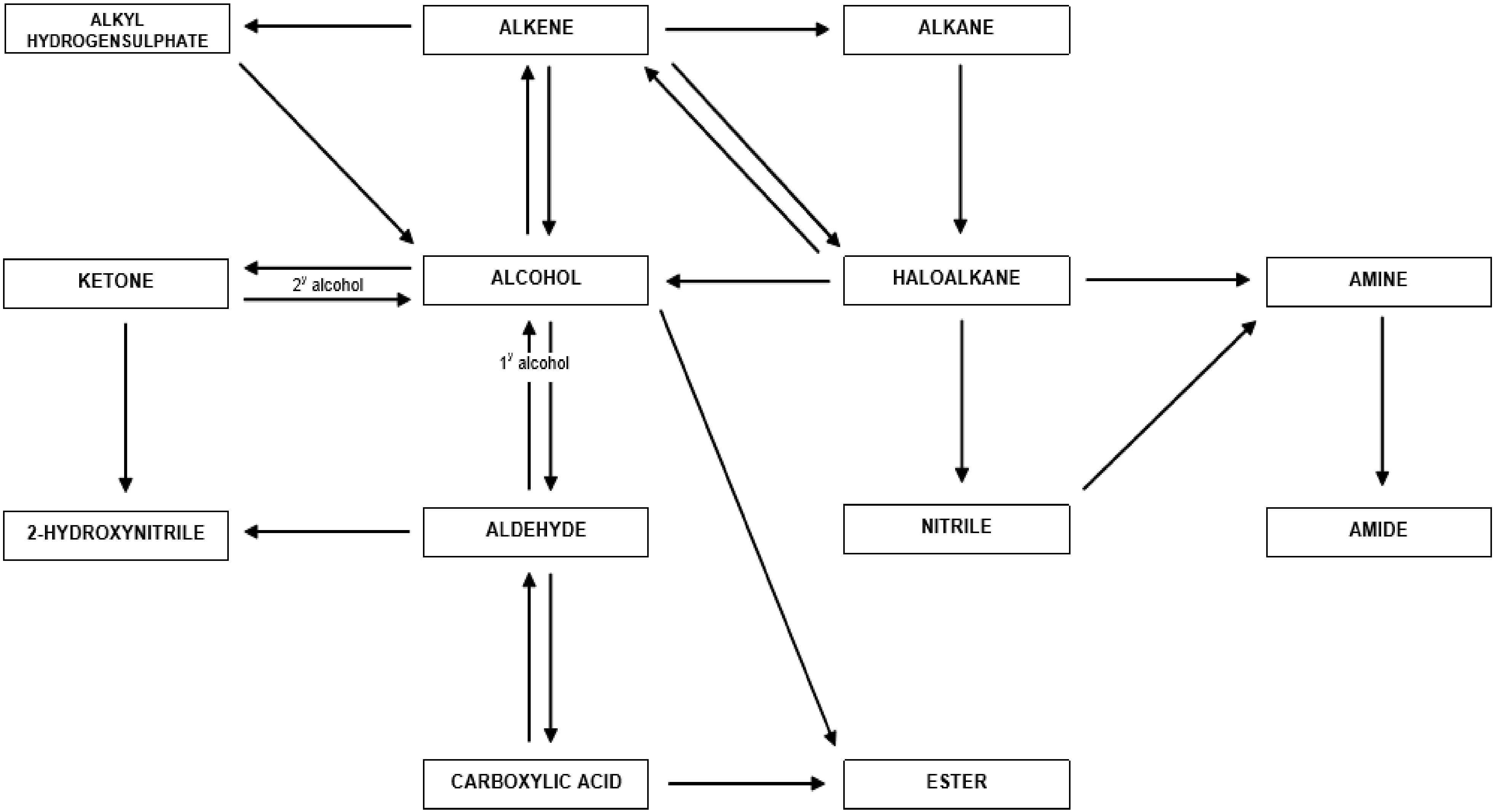
Extending carbon chain length (a) the use of C–C bond formation in synthesis to increase the length of a carbon chain (see also 6.1.1 d, 6.1.2 b)					
(b) formation of C-CN by reaction of: (i) haloalkanes with CN^- and ethanol, including nucleophilic substitution mechanism (ii) carbonyl compounds with HCN, including nucleophilic addition mechanism (see also 6.1.2 b–c)					
(c) reaction of nitriles from (b): (i) by reduction (e.g. with H_2/Ni) to form amines (ii) by acid hydrolysis to form carboxylic acids					
(d) formation of a substituted aromatic C–C by alkylation (using a haloalkane) and acylation (using an acyl chloride) in the presence of a halogen carrier (Friedel–Crafts reaction) (see also 6.1.1 d).					

ORGANIC SYNTHESIS 1

ALKYL HYDROGENSULPHATE	ALKENE	ALKANE	
KETONE	ALCOHOL	HALOALKANE	AMINE
2-HYDROXYNITRILE	ALDEHYDE	NITRILE	AMIDE
	CARBOXYLIC ACID	ESTER	

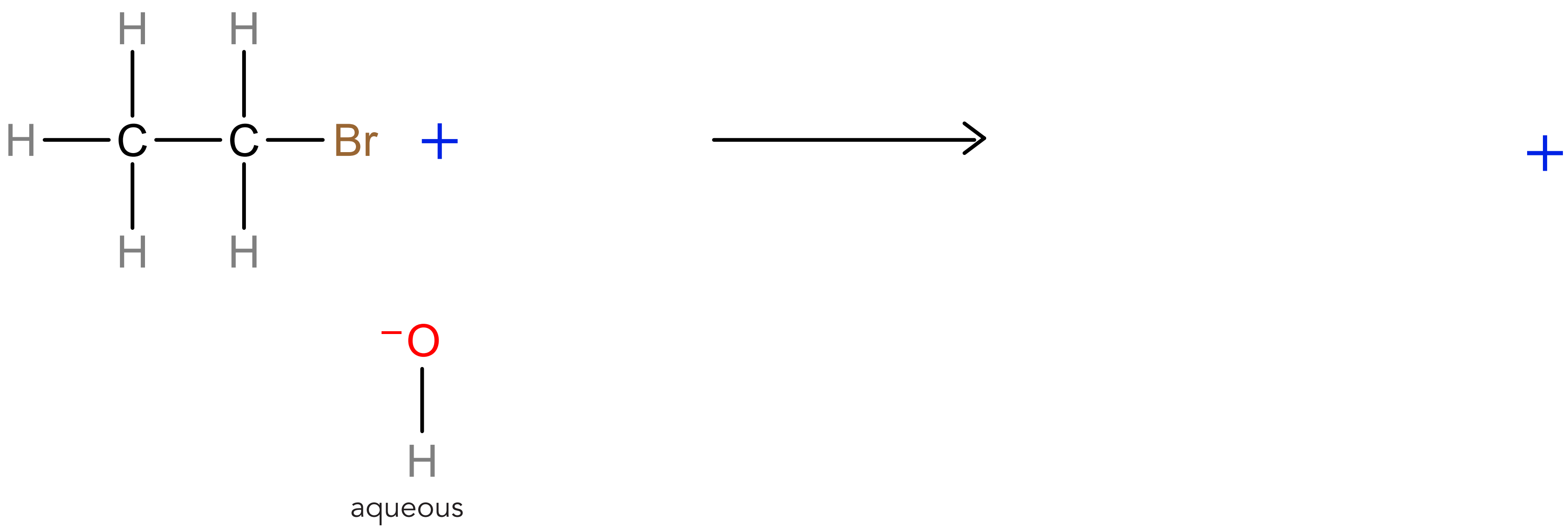
Add arrows and reagents so show how you could synthesis one to another.

ORGANIC SYNTHESIS 1



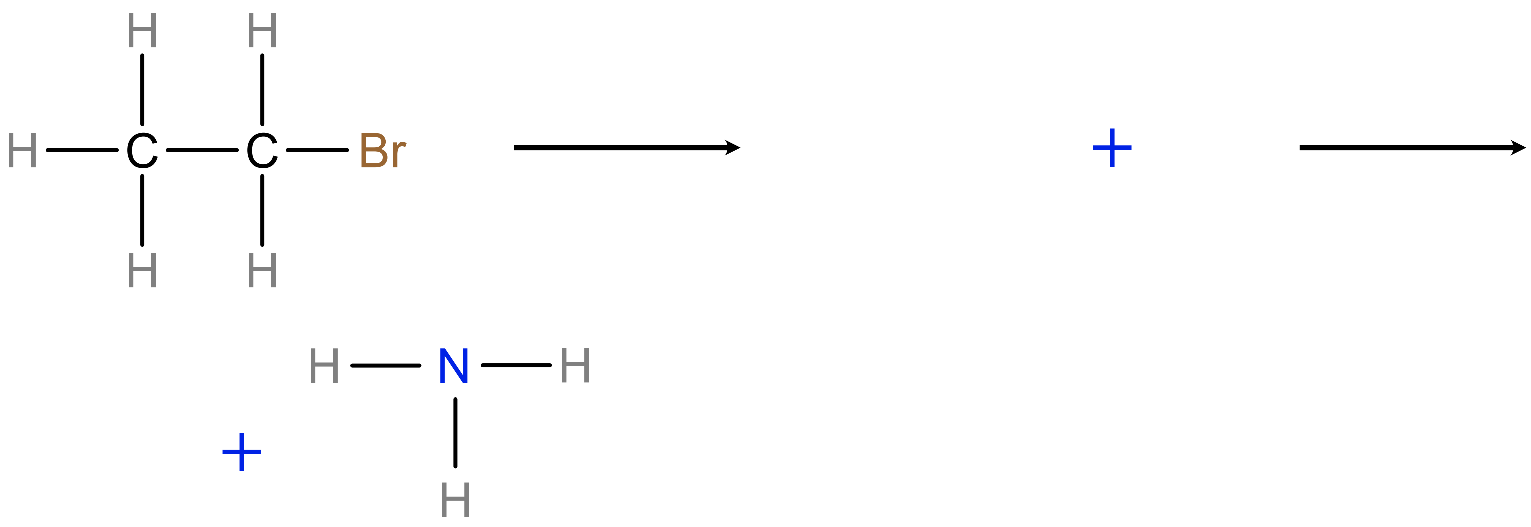
Mechanism revision 1: nucleophilic substitution by a negative ion.

Add any curly arrows, partial charges, and lone pairs of electrons to complete the following mechanism.



Mechanism revision 1(b): nucleophilic substitution by a neutral molecule.

Add any curly arrows, partial charges, and lone pairs of electrons to complete the following mechanism.



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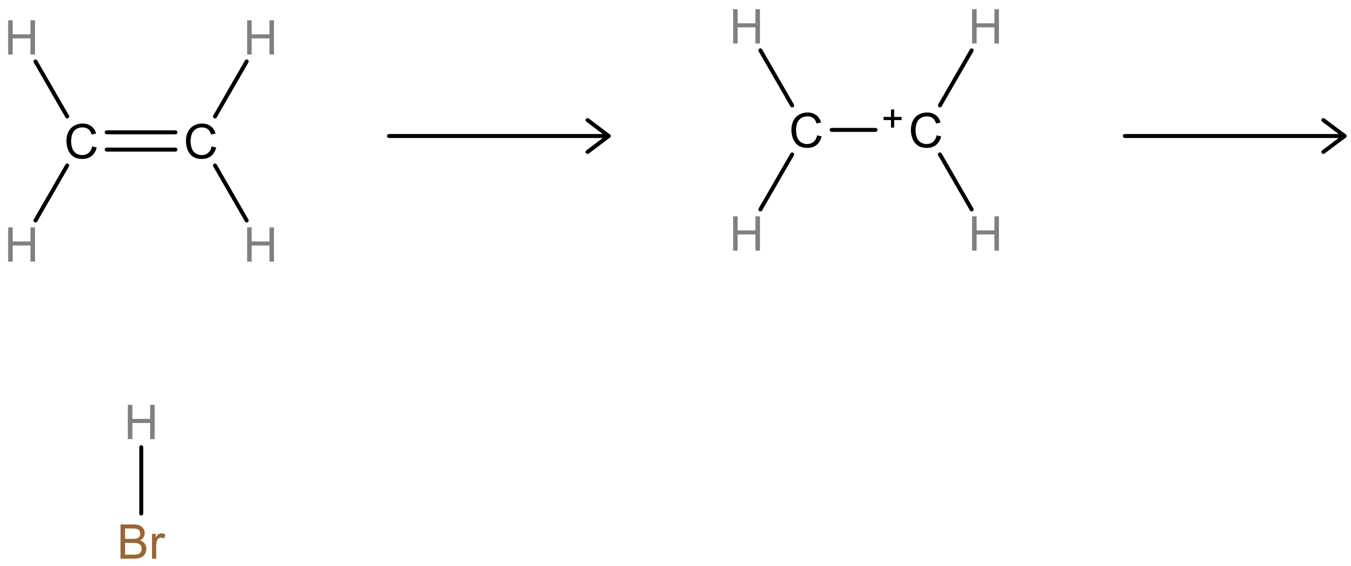
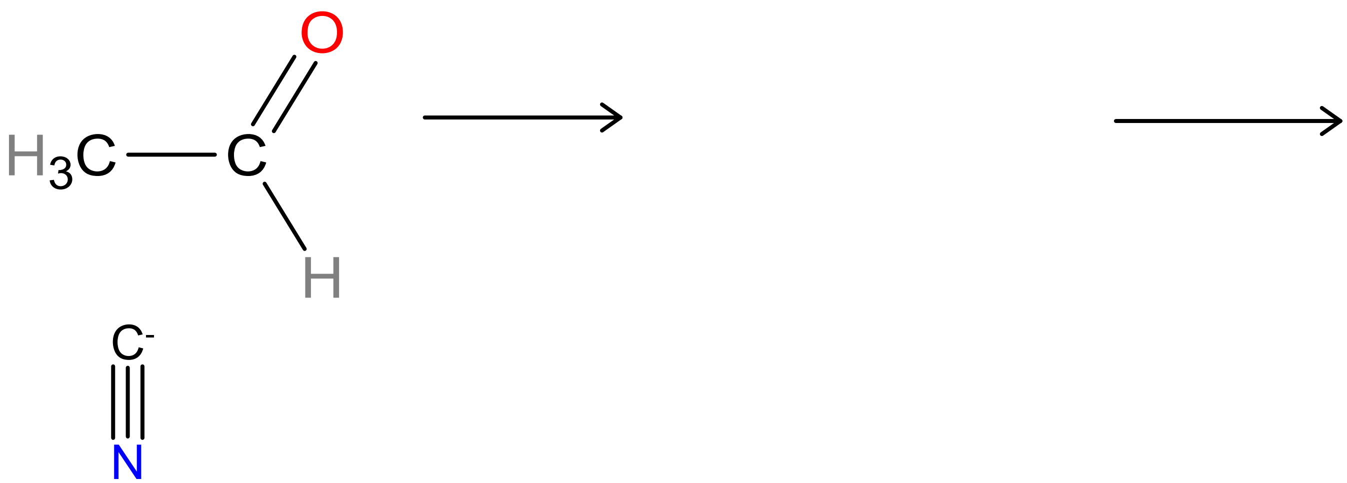
Mechanism revision 2: electrophilic addition

Add any curly arrows, partial charges, and lone pairs of electrons to complete the following mechanism.



Mechanism revision 3: nucleophilic addition.

Add any curly arrows, partial charges, and lone pairs of electrons to complete the following mechanism.



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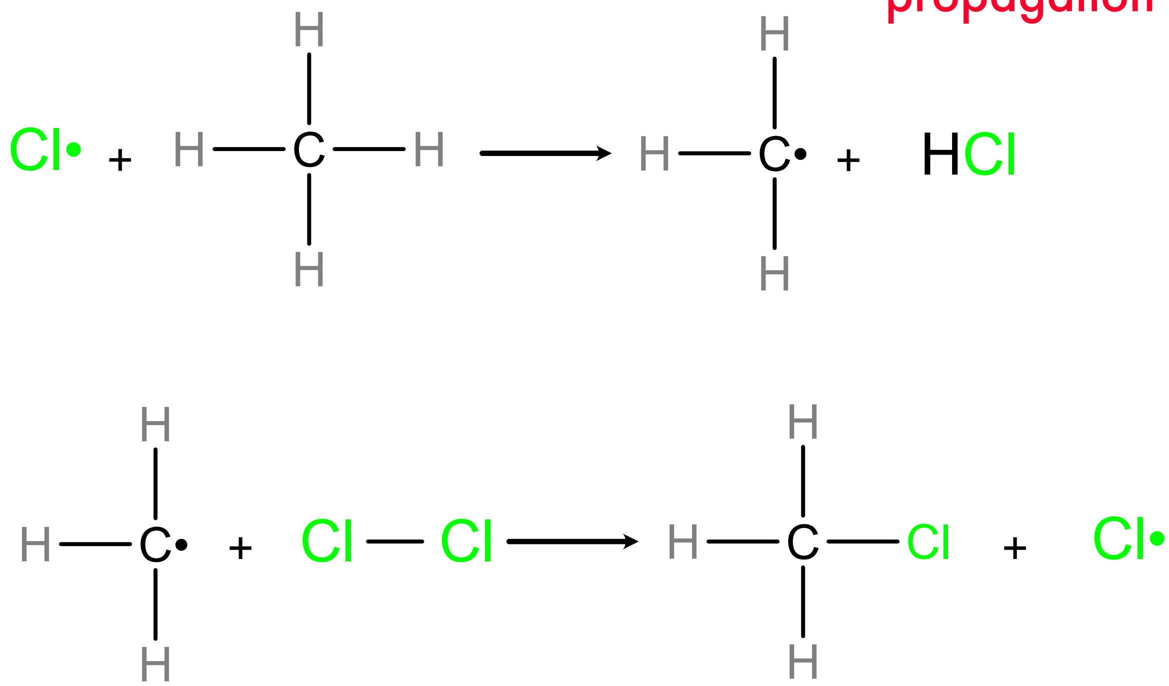
Mechanism revision 4: radical substitution.

initiation

$$Cl - Cl \xrightarrow{h\nu} 2Cl\bullet$$

propagation



termination

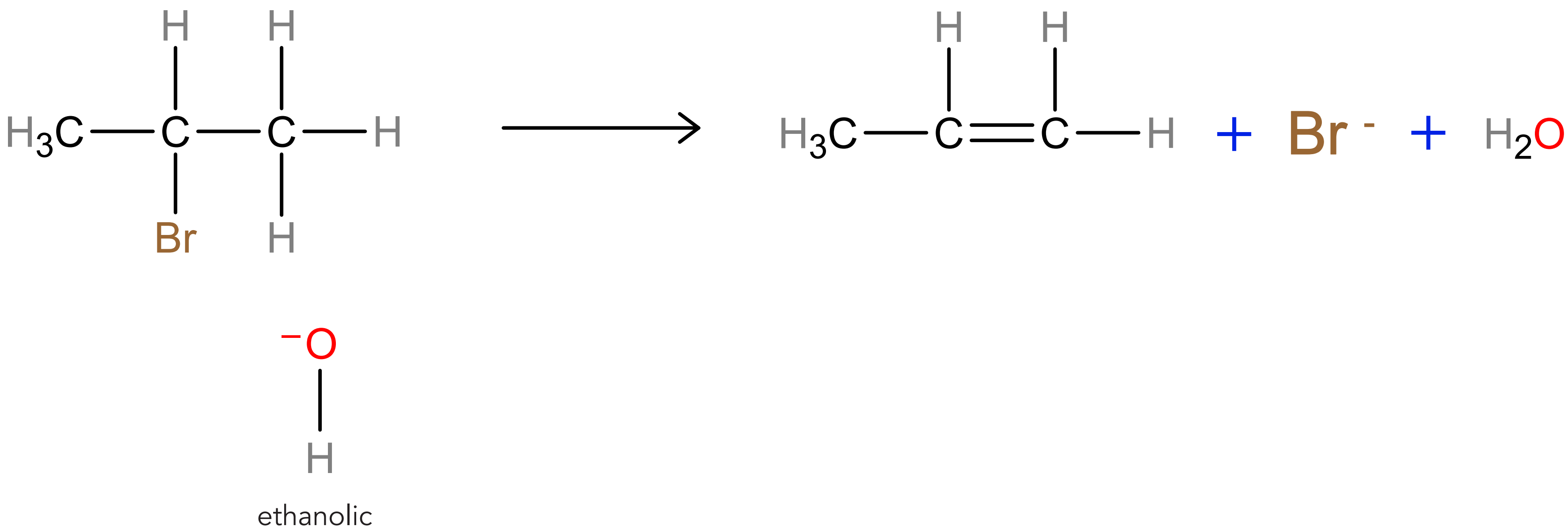
$$2Cl\bullet \longrightarrow Cl_2$$

$$CH_3\bullet + Cl\bullet \longrightarrow CH_3Cl$$

$$CH_3\bullet + CH_3\bullet \longrightarrow CH_3CH_3$$

Mechanism revision 5: elimination

Add any curly arrows, partial charges, and lone pairs of electrons to complete the following mechanism.



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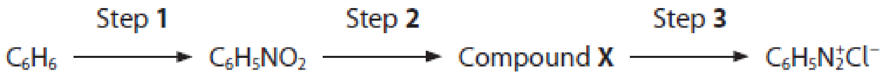
Questions

Q1.

Benzenediazonium chloride, $C_6H_5N_2^+Cl^-$, can be prepared from benzene in a series of steps.



(i) Identify the substances that are used to convert benzene into $C_6H_5NO_2$ in Step **1**.

(1)

....

(ii) Give the mechanism of the reaction taking place in Step **1**, including one or more equations for the formation of the electrophile.

(4)

(iii) Identify compound **X** and state the reagents needed to prepare it in Step **2**.

(2)

Compound **X**

....

Reagents

....

(iv) State the reagents and condition needed to convert compound **X** into benzenediazonium chloride in Step **3**.

(2)

Reagents

....

Condition

....

(Total for question = 9 marks)

Q2.

This question is about carbonyl compounds.

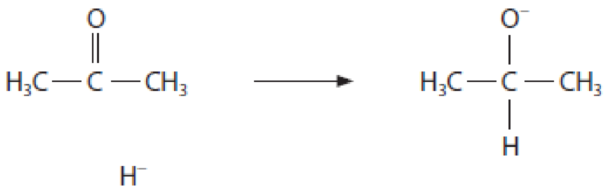
Sodium tetrahydridoborate, $NaBH_4$, acts as a source of H^- ions and is a reducing agent.

Complete the mechanism for the reduction of propanone to propan-2-ol.

(i) In **Step 1**, add the relevant dipole, a lone pair of electrons and curly arrows.

(2)

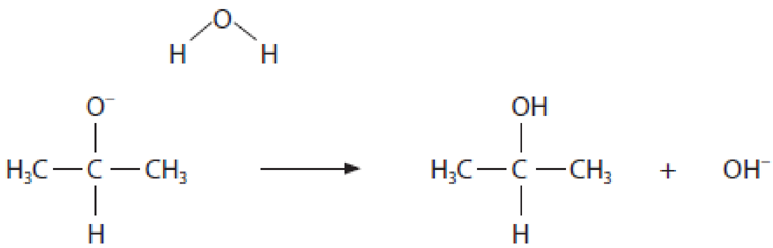
Step 1



(ii) In **Step 2**, add a relevant lone pair of electrons and curly arrows.

(1)

Step 2



(Total for question = 3 marks)

Q3.

Benzene reacts with ethanoyl chloride in the presence of aluminium chloride. The equation for the reaction of ethanoyl chloride with aluminium chloride is

☐ **A** $CH_3COCl + AlCl_3 \rightarrow [CH_3CO]^- + AlCl_4^+$

☐ **B** $CH_3COCl + AlCl_3 \rightarrow [CH_3CO]^+ + AlCl_4^-$

☐ **C** $CH_3COOCl + AlCl_3 \rightarrow [CH_3COO]^- + AlCl_4^+$

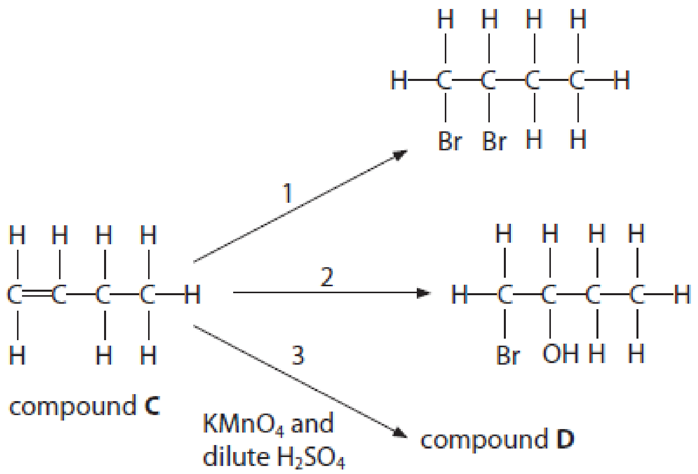
☒ **D** CH_3COOCl + $AlCl_3$ → $[CH_3COO]^+$ + $AlCl_4^-$

(Total for question = 1 mark)

Q4.

Compounds **A** and **B** are isomeric alkenes.

Compound **C** is an isomer of compounds **A** and **B**. Some reactions of compound **C** are shown below.



Compound **C** also reacts with hydrogen chloride.

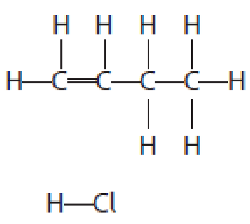
(i) Classify the type and mechanism of this reaction.

(2)

....

(ii) Complete the diagram below by adding any dipoles and curly arrows relevant to the **first** step of the mechanism of this reaction.

(2)



(iii) Draw the intermediate for the reaction which produces the major product.

Hence show the final step of the mechanism and the product.

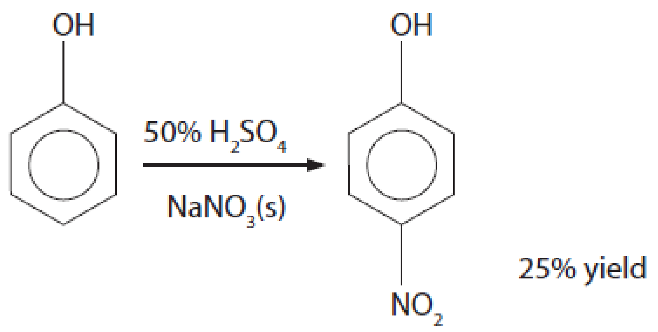
Include relevant curly arrows, lone pairs and charges.

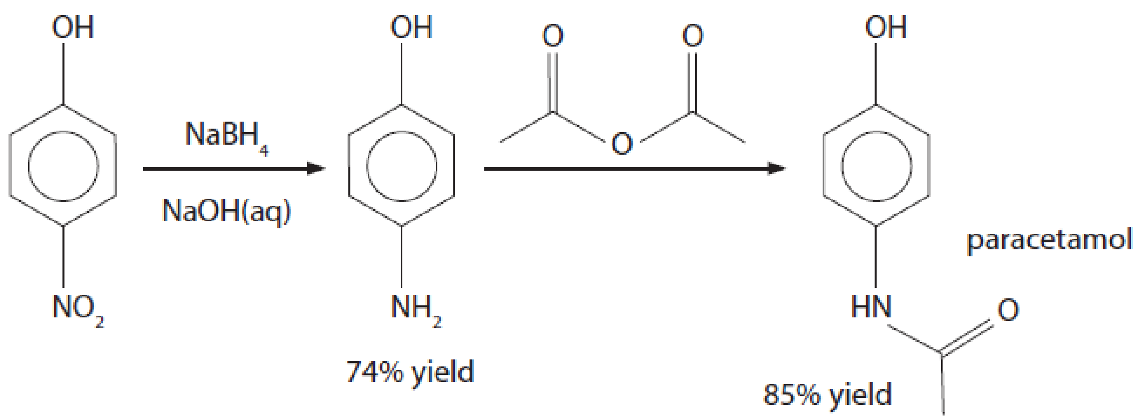
(4)

(Total for question = 8 marks)

Q5.

Paracetamol is a mild painkiller which also reduces the temperature of patients with fever, actions known as analgesic and antipyretic respectively. The reaction scheme below summarises a laboratory synthesis of paracetamol starting from phenol. The yields shown are for the particular product of each step in the synthesis.





(a) The nitration of benzene is an electrophilic substitution reaction that requires concentrated nitric and sulfuric acids.

(i) Write an equation for the formation of the electrophile by the reaction between concentrated nitric and concentrated sulfuric acids.

(2)

(ii) Give the mechanism for the formation of nitrobenzene from benzene.

(3)

(iii) Explain why phenol is nitrated in much milder conditions than benzene.

(2)

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(iv) Suggest why the yield for the nitration of phenol is so low.

(1)

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....

(v) Suggest an alternative to $NaBH_4$ that could be used in aqueous solution.

(1)

....

(vi) Calculate the overall yield of the synthesis.

(1)

(b) The paracetamol, prepared by the synthesis shown at the start of the question, may be purified by recrystallization. In this process, the paracetamol is dissolved in a minimum volume of hot water, the hot mixture filtered, the filtrate cooled and the resulting crystals filtered and dried. The table below summarises the solubility of paracetamol in water at various temperatures.

Temperature / °C	5	10	20	95
Solubility / g / 100 g	0.82	0.94	1.3	5.2

(i) Explain the purpose of each of the filtrations in the recrystallization of paracetamol.

(2)

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(ii) From the temperatures given in the table, choose the pair of temperatures that will give the highest yield of paracetamol from the recrystallization. Explain your choice.

(2)

....

....

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....

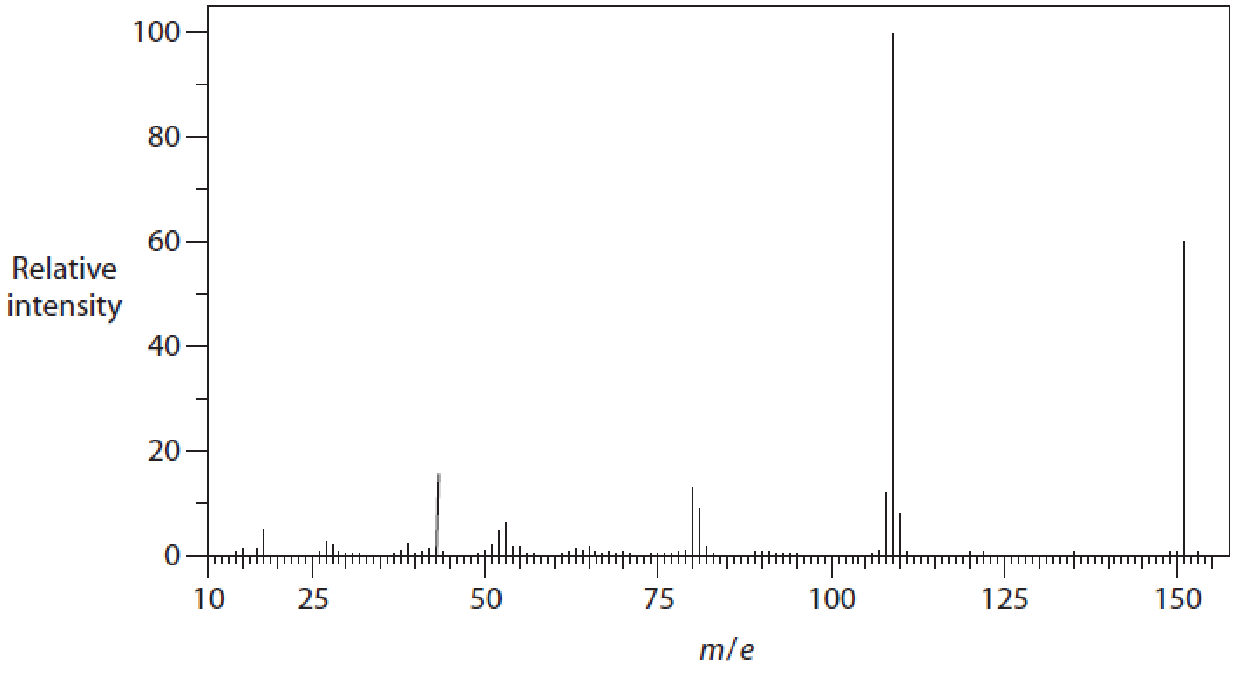
....

(iii) Name the technique that could be used in a **school** laboratory to check the purity of the recrystallized paracetamol.

(1)

....

(c) The mass spectrum of paracetamol is shown below.



(i) Label the molecular ion peak, with an **M**, on the mass spectrum.

(1)

(ii) Suggest the formula of an ion that could cause the peak at *m*/*e* = 43.

(1)

(d) Paracetamol is highly toxic: overdosing causes irreversible liver damage. Despite this, paracetamol is readily available from pharmacies and even supermarkets.
Suggest **one** control measure that sellers might employ to reduce the risk to paracetamol users.

(1)

....

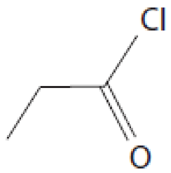
....

(Total for question = 18 marks)

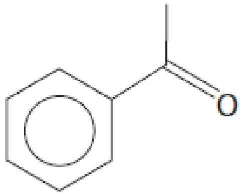
Q6.

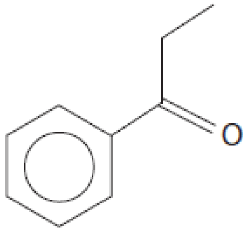
Benzene reacts with propanoyl chloride in the presence of a suitable catalyst.

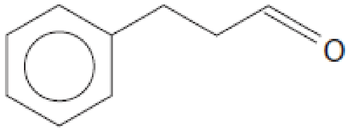
The skeletal formula of propanoyl chloride is

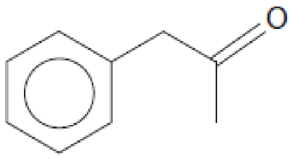


What is the organic product of this reaction?

☒ **A** 

☒ **B** 

☒ **C** 

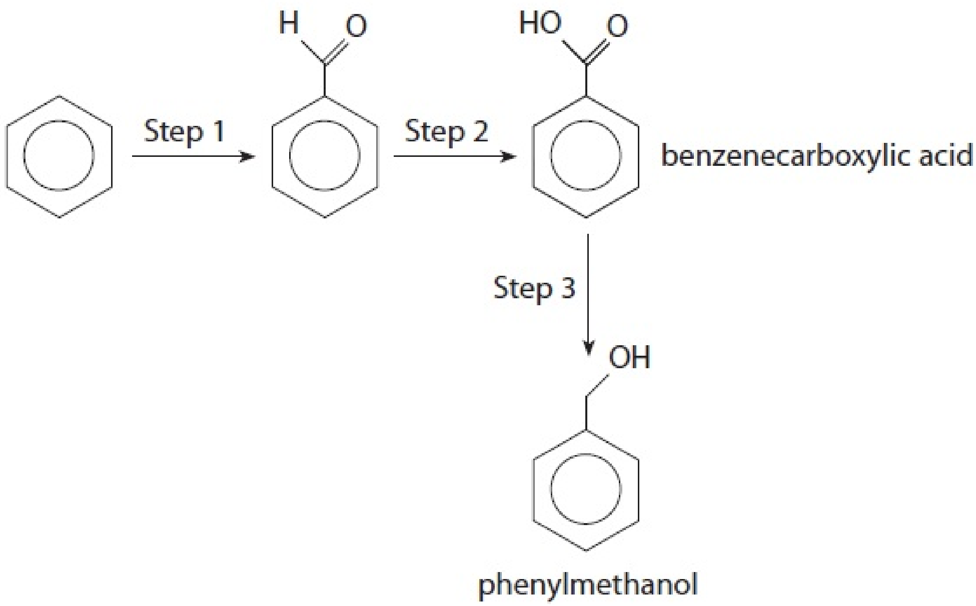
☒ **D** 

(Total for question = 1 mark)

Q7.

Benzenecarboxylic acid (benzoic acid) and phenylmethanol (benzyl alcohol) are compounds which occur naturally and have a wide range of uses. For example, benzenecarboxylic acid is used as a food preservative and phenylmethanol is used as a solvent.

A laboratory sequence for the preparation of these two compounds is shown below.



(a) In the first step of the synthesis, benzene reacts with hydrogen chloride and carbon monoxide in the presence of aluminium chloride in an electrophilic substitution called the Gattermann-Koch reaction. The hydrogen chloride and carbon monoxide together behave as if they form the unstable species methanoyl chloride (HCOCl).

(i) Explain why benzene undergoes substitution rather than addition reactions. A detailed description of the bonding in benzene is **not** required.

(2)

....

....

....

....

(ii) Give the mechanism for step 1, including the formation of the electrophile.

(4)

(iii) Identify the reagents and essential conditions used in the remaining steps of the sequence. You may assume that the correct reaction temperatures are being used.

(4)

Step 2

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Step 3

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*(b) Phenol reacts faster than phenylmethanol in electrophilic substitution reactions. Suggest why this is so.

(4)

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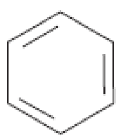
(Total for question = 14 marks)

Q8.

Benzene is sometimes represented as Structure **X**, shown below, called a Kekulé structure after the chemist who suggested it.



Structure **X**

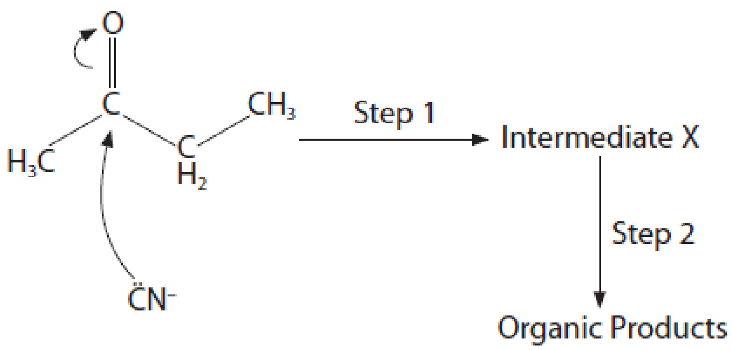
Benzene reacts with bromine in the presence of a catalyst of iron(III) bromide.

Write a mechanism for the reaction of benzene with bromine to form bromobenzene. Include an equation to show the involvement of the catalyst.

(4)

Q9.

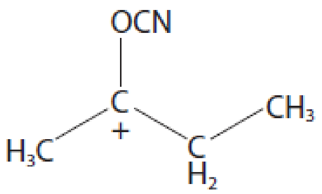
The diagram below shows part of the mechanism for the nucleophilic addition of hydrogen cyanide to butanone.



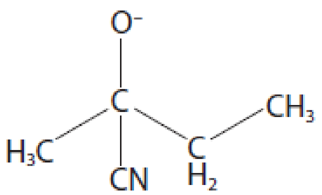
(a) The formula of the intermediate X is

(1)

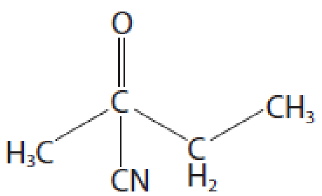
☒ **A**



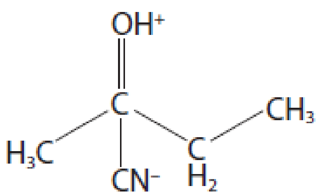
☒ **B**



☒ **C**



☒ **D**



(b) Consider the dissociation of the weak acid, HCN.

$$HCN(aq) \rightleftharpoons H^+(aq) + CN^-(aq)$$

Which of the following reagents would shift the position of the equilibrium towards formation of the nucleophile, CN^-?

(1)

☒ **A** KOH

☒ **B** KCN

☒ **C** H_2SO_4

☒ **D** CH_3COOH

(c) Which statement about the mixture of organic products formed is **not** correct?

(1)

☒ **A** The mixture contains products with chiral molecules.

☒ **B** The mixture rotates the plane of plane-polarized light.

☒ **C** The mixture contains products with the nitrile functional group.

☒ **D** The mixture contains products each of which has four carbon atoms in a straight chain.

(Total for question = 3 marks)

Q10.

(a) An example of a cycloalkane is cyclobutane. This compound, like other cycloalkanes, can also react with chlorine.

The overall reaction of cyclobutane with chlorine is as follows:

$$C_4H_8 + Cl_2 \rightarrow C_4H_7Cl + HCl$$

(i) This reaction can occur at room temperature and pressure.
What further condition is needed for this reaction to take place?

(1)

....

(ii) Using the appropriate arrows, complete the equation for the initiation step of the reaction mechanism for the reaction of chlorine with cyclobutane.

(2)

$$Cl - Cl \quad \rightarrow$$

(iii) Using molecular formulae, write equations for the **two** propagation steps of this mechanism.

(2)

First propagation step:

Second propagation step:

(iv) Name the type of bond fission which occurs in these propagation steps.

(1)

....

(v) There are also termination steps in this mechanism. Explain how these differ from the other steps in the mechanism and why these result in the reaction ending.

(2)

....

....

....

....

(b) If the reaction with cyclobutane is carried out with an excess of chlorine, how are the products of the reaction affected?

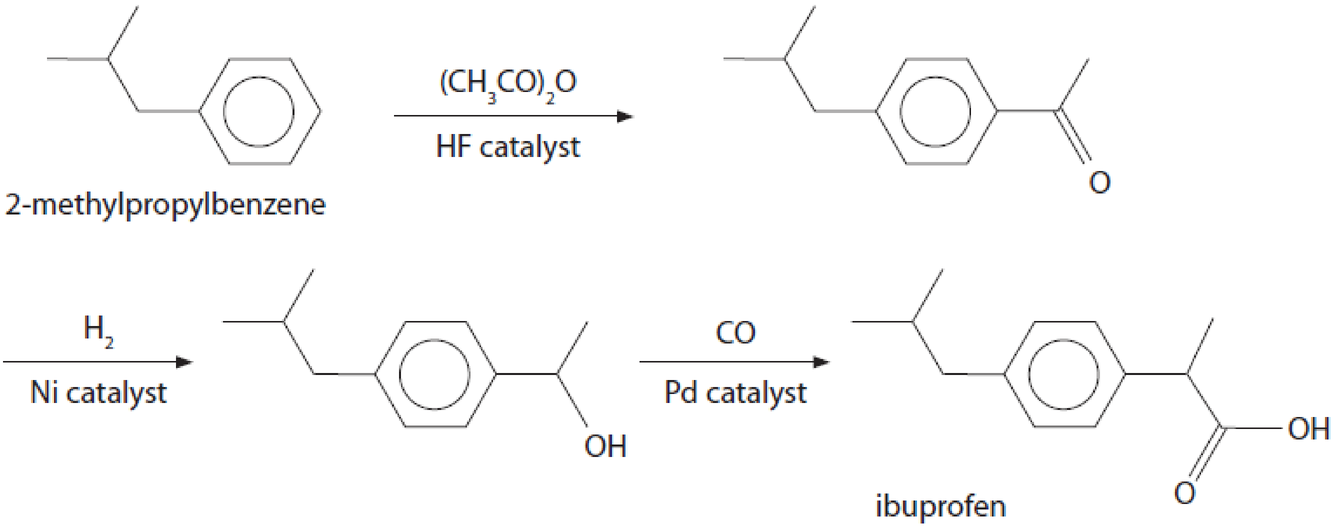
(1)

....

....

Q11.

Ibuprofen is a nonsteroidal anti-inflammatory drug (NSAID) widely used as an analgesic (pain reliever). It was discovered in the 1960s by the Boots Group which developed a six step synthesis from 2-methylpropylbenzene. The synthesis shown below was introduced in the 1990s by the BHC Company and received a Presidential Green Chemistry Challenge award in 1997. The citation noted that the synthesis has just three steps, all of which are catalytic, and an effective atom economy of 99%. Both syntheses are carried out in solution.



(a) (i) Suggest why a three step synthesis is likely to be 'greener' than a six step process.

(1)

....

....

(ii) Why does the use of catalysts make processes 'greener' (as well as faster)?

(1)

....

....

(b) The first step of the synthesis is an electrophilic substitution which is usually carried out in a school laboratory using ethanoyl chloride and an aluminium chloride catalyst.

(i) Write an equation showing the formation of the electrophile in the **school** experiment.

(1)

(ii) Give the mechanism for the electrophilic substitution of 2-methylpropylbenzene by ethanoyl chloride, using the electrophile you have given in (b)(i).

(3)

(iii) Suggest **one** environmental benefit of using $(CH_3CO)_2O$, rather than ethanoyl chloride, in the manufacture of ibuprofen.

(1)

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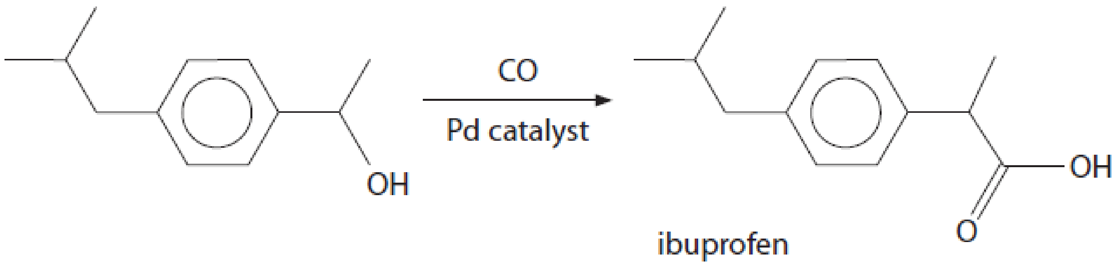
....

....

(c) The final stage of the modern synthesis for ibuprofen is shown below.



(i) Suggest a benefit of using a **solid** catalyst in this reaction.

(1)

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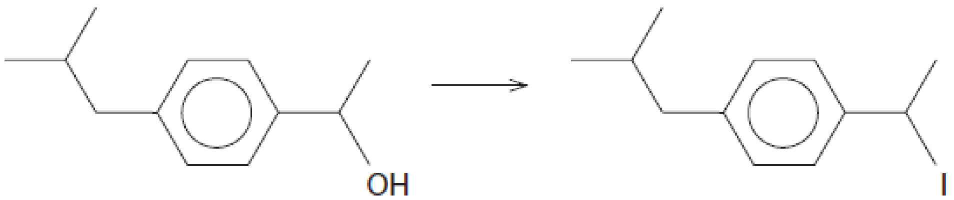
....

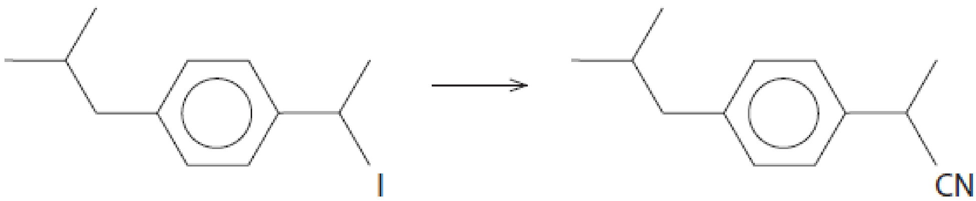
(ii) The preparation in part (c) can be carried out in a laboratory in three reactions.

(3)

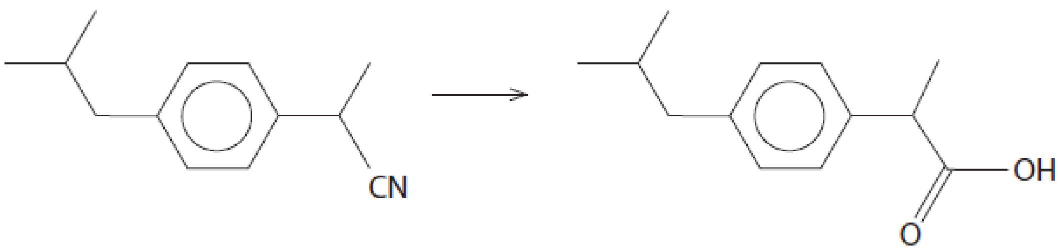
Reaction 1



Reaction 2



Reaction 3



Give:

The reagents for **Reaction 1**

....

....

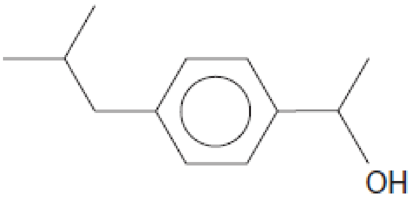
The reagents and conditions for **Reaction 3**

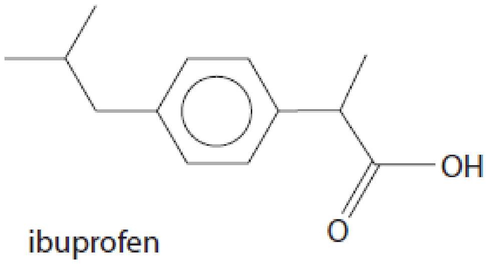
....

....

(iii) Using your Data Booklet, explain how infrared spectroscopy can be used to distinguish between the two structures shown below.

(2)





ibuprofen

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(d) Ibuprofen is a chiral molecule and only one of its enantiomers is biologically active. However, although the synthesis produces a racemic mixture, an isomerase enzyme in the body converts the inactive enantiomer into the active enantiomer.

(i) Explain the term 'chiral molecule'.

(1)

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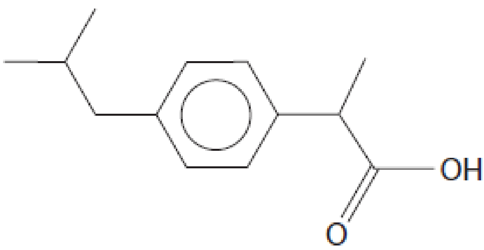
....

....

(ii) Mark with an asterisk (*) the chiral centre on the structure of ibuprofen below.

(1)



(iii) Explain the term 'racemic mixture'.

(1)

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(iv) Suggest **two** benefits that arise from the isomerization of the inactive enantiomer of ibuprofen.

(2)

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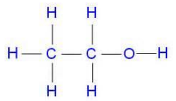
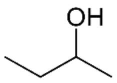
(Total for question = 18 marks)

Week 8

Organic compounds

4.1.1 Basic organic chemistry

(a) application of IUPAC rules of nomenclature for systematically naming organic compounds					
(b) interpretation and use of the terms: **(i)** *general formula* (the simplest algebraic formula of a member of a homologous series) e.g. for an alkane: C_nH_{2n+2} **(ii)** *structural formula* (the minimal detail that shows the arrangement of atoms in a molecule) e.g. for butane: $CH_3CH_2CH_2CH_3$ or $CH_3(CH_2)_2CH_3$ **(iii)** *displayed formula* (the relative positioning of atoms and the bonds between them) e.g. for ethanol:  **(iv)** *skeletal formula* (the simplified organic formula, shown by removing hydrogen atoms from alkyl chains, leaving just a carbon skeleton and associated functional groups) e.g. for butan-2-ol: 					
(c) interpretation and use of the terms: **(i)** *homologous series* (a series of organic compounds having the same functional group but with each successive member differing by CH_2) **(ii)** *functional group* (a group of atoms responsible for the characteristic reactions of a compound) **(iii)** *alkyl group* (of formula C_nH_{2n+1}) **(iv)** *aliphatic* (a compound containing carbon and hydrogen joined together in straight chains, branched chains or non-aromatic rings) **(v)** *alicyclic* (an aliphatic compound arranged in non-aromatic rings with or without side chains) *aromatic* (a compound containing a benzene ring) **(vii)** *saturated* (single carbon–carbon bonds only) and *unsaturated* (the presence of multiple carbon–carbon bonds, including C=C, CC /and aromatic rings)					
(d) use of the general formula of a homologous series to predict the formula of any member of the series					
(e) explanation of the term *structural isomers* (compounds with the same molecular formula but different structural formulae) and determination of possible structural formulae of an organic molecule, given its molecular formula					
(f) the different types of covalent bond fission: **(i)** homolytic fission (in terms of each bonding atom receiving one electron from the bonded pair, forming two radicals) i) **(ii)** heterolytic fission (in terms of one bonding atom receiving both electrons from the bonded pair)					
(g) the term *radical* (a species with an unpaired electron) and use of 'dots' to represent species that are radicals in mechanisms					
(h) a 'curly arrow' described as the movement of an electron pair, showing either heterolytic fission or formation of a covalent bond					
(i) reaction mechanisms, using diagrams, to show clearly the movement of an electron pair with 'curly arrows' and relevant dipoles.					

4.1.2 Alkanes

(a) alkanes as saturated hydrocarbons containing single C–C and C–H bonds as σ-bonds (overlap of orbitals directly between the bonding atoms); free rotation of the σ-bond					
(b) explanation of the tetrahedral shape and bond angle around each carbon atom in alkanes in terms of electron pair repulsion **(see also 2.2.2 g–h)**					
(c) explanation of the variations in boiling points of alkanes with different carbon-chain length and branching, in terms of induced dipole–dipole interactions (London forces) **(see also 2.2.2 k)**					
(d) the low reactivity of alkanes with many reagents in terms of the high bond enthalpy and very low polarity of the σ-bonds present **(see also 2.2.2 j)**					

(e) complete combustion of alkanes, as used in fuels, and the incomplete combustion of alkane fuels in a limited supply of oxygen with the resulting potential dangers from CO					
(f) the reaction of alkanes with chlorine and bromine by radical substitution using ultraviolet radiation, including a mechanism involving homolytic fission and radical reactions in terms of initiation, propagation and termination **(see also 4.1.1 f–g)**					
(g) the limitations of radical substitution in synthesis by the formation of a mixture of organic products, in terms of further substitution and reactions at different positions in a carbon chain.					

4.1.3 Alkenes

(a) alkenes as unsaturated hydrocarbons containing a C=C bond comprising a π-bond (sideways overlap of adjacent p-orbitals above and below the bonding C atoms) and a σ-bond (overlap of orbitals directly between the bonding atoms) **(see also 4.1.2 a)**; restricted rotation of the π-bond					
(b) explanation of the trigonal planar shape and bond angle around each carbon in the C=C of alkenes in terms of electron pair repulsion **(see also 2.2.2 g–h, 4.1.2 b)**					
(c) **(i)** explanation of the terms: • *stereoisomers* (compounds with the same structural formula but with a different arrangement in space) • *E*/*Z isomerism* (an example of stereoisomerism, in terms of restricted rotation about a double bond and the requirement for two different groups to be attached to each carbon atom of the C=C group) • *cis–trans isomerism* (a special case of *E*/*Z* isomerism in which two of the substituent groups attached to each carbon atom of the C=C group are the same) **(ii)** use of Cahn–Ingold–Prelog (CIP) priority rules to identify the *E* and *Z* stereoisomers					
(d) determination of possible *E*/*Z* or *cis–trans* stereoisomers of an organic molecule, given its structural formula					
(e) the reactivity of alkenes in terms of the relatively low bond enthalpy of the π-bond					
(f) addition reactions of alkenes with: **(i)** hydrogen in the presence of a suitable catalyst, e.g. Ni, to form alkanes **(ii)** halogens to form dihaloalkanes, including the use of bromine to detect the presence of a double C=C bond as a test for unsaturation in a carbon chain **(iii)** hydrogen halides to form haloalkanes **(iv)** steam in the presence of an acid catalyst, e.g. H_3PO_4, to form alcohols					
(g) definition and use of the term *electrophile* (an electron pair acceptor)					
(h) the mechanism of electrophilic addition in alkenes by heterolytic fission **(see also 4.1.1 h–i)**					
(i) use of Markownikoff's rule to predict formation of a major organic product in addition reactions of H–X to unsymmetrical alkenes, e.g. H–Br to propene, in terms of the relative stabilities of carbocation intermediates in the mechanism					
(j) addition polymerisation of alkenes and substituted alkenes, including: **(i)** the repeat unit of an addition polymer deduced from a given monomer **(ii)** identification of the monomer that would produce a given section of an addition polymer					
(k) the benefits for sustainability of processing waste polymers by: **(i)** combustion for energy production **(ii)** use as an organic feedstock for the production of plastics and other organic chemicals **(iii)** removal of toxic waste products, e.g. removal of HC*l* formed during disposal by combustion of halogenated plastics (e.g. PVC)					

4.2.1 Alcohols

(a) **(i)** the polarity of alcohols and an explanation, in terms of hydrogen bonding, of the water solubility and the relatively low volatility of alcohols compared with alkanes **(see also 2.2.2 l and 4.1.2 c)** **(ii)** classification of alcohols into primary, secondary and tertiary alcohols						
(b) combustion of alcohols						

(c) oxidation of alcohols by an oxidising agent, e.g. $Cr_2O_7^{2-}$/H+ (i.e. $K_2Cr_2O_7$/H_2SO_4), including: **(i)** the oxidation of primary alcohols to form aldehydes and carboxylic acids; the control of the oxidation product using different reaction conditions **(ii)** the oxidation of secondary alcohols to form ketones **(iii)** the resistance to oxidation of tertiary alcohols						
(d) elimination of H_2O from alcohols in the presence of an acid catalyst (e.g. H_3PO_4 or H_2SO_4) and heat to form alkenes						
(e) substitution with halide ions in the presence of acid (e.g. NaBr/H_2SO_4) to form haloalkanes.						

4.2.2 Halogenoalkanes

(a) hydrolysis of haloalkanes in a substitution reaction: **(i)** by aqueous alkali **(ii)** by water in the presence of $AgNO_3$ and ethanol to compare experimentally the rates of hydrolysis of different carbon– halogen bonds					
(b) definition and use of the term *nucleophile* (an electron pair donor)					
(c) the mechanism of nucleophilic substitution in the hydrolysis of primary haloalkanes with aqueous alkali **(see also 4.1.1 h–i)**					
(d) explanation of the trend in the rates of hydrolysis of primary haloalkanes in terms of the bond enthalpies of carbon–halogen bonds (C–F, C–C*l*, C–Br and C–I)					

6.1 Aromatic compounds, carbonyls and acids

6.1.1 Aromatic compounds

Benzene and aromatic compounds (a) the comparison of the Kekulé model of benzene with the subsequent delocalised models for benzene in terms of p-orbital overlap forming a delocalised π-system					
(b) the experimental evidence for a delocalised, rather than Kekulé, model for benzene in terms of bond lengths, enthalpy change of hydrogenation and resistance to reaction (see also 6.1.1 f)					
(c) use of IUPAC rules of nomenclature for systematically naming substituted aromatic compounds					
Electrophilic substitution (d) the electrophilic substitution of aromatic compounds with: (i) concentrated nitric acid in the presence of concentrated sulfuric acid (ii) a halogen in the presence of a halogen carrier (iii) a haloalkane or acyl chloride in the presence of a halogen carrier (Friedel–Crafts reaction) and its importance to synthesis by formation of a C–C bond to an aromatic ring (see also 6.2.4 d)					
(e) the mechanism of electrophilic substitution in arenes for nitration and halogenation					
(f) the explanation of the relative resistance to bromination of benzene, compared with alkenes, in terms of the delocalised electron density of the π-system in benzene compared with the localised electron density of the π-bond in alkenes					
(g) the interpretation of unfamiliar electrophilic substitution reactions of aromatic compounds, including prediction of mechanisms					
Phenols (h) the weak acidity of phenols shown by the neutralisation reaction with NaOH but absence of reaction with carbonates					
(i) the electrophilic substitution reactions of phenol: (i) with bromine to form 2,4,6-tribromophenol (ii) with dilute nitric acid to form 2-nitrophenol					
(j) the relative ease of electrophilic substitution of phenol compared with benzene, in terms of electron pair donation to the π-system from an oxygen p-orbital in phenol					
(k) the 2- and 4-directing effect of electrondonating groups (OH, NH_2) and the 3-directing effect of electron-withdrawing groups (NO_2) in electrophilic substitution of aromatic compounds					

(l) the prediction of substitution products of aromatic compounds by directing effects and the importance to organic synthesis (see also 6.2.5 Organic Synthesis).					

6.1.2 Carbonyl compounds

Reactions of carbonyl compounds (a) oxidation of aldehydes using $Cr_2O_7^{2-}/H^+$ (i.e. $K_2Cr_2O_7/H_2SO_4$) to form carboxylic acids					
(b) nucleophilic addition reactions of carbonyl compounds with: (i) $NaBH_4$ to form alcohols (ii) HCN [i.e. $NaCN_{(aq)}/H^+{}_{(aq)}$], to form hydroxynitriles (see also 6.2.4 b)					
(c) the mechanism for nucleophilic addition reactions of aldehydes and ketones with $NaBH_4$ and HCN					
Characteristic tests for carbonyl compounds (d) use of 2,4-dinitrophenylhydrazine to: (i) detect the presence of a carbonyl group in an organic compound (ii) identify a carbonyl compound from the melting point of the derivative					
(e) use of Tollens' reagent (ammoniacal silver nitrate) to: (i) detect the presence of an aldehyde group (ii) distinguish between aldehydes and ketones, explained in terms of the oxidation of aldehydes to carboxylic acids with reduction of silver ions to silver.					

6.1.3 Carboxylic acids and esters

Properties of carboxylic acids (a) explanation of the water solubility of carboxylic acids in terms of hydrogen bonding					
(b) reactions in aqueous conditions of carboxylic acids with metals and bases (including carbonates, metal oxides and alkalis)					
Esters (c) esterification of: (i) carboxylic acids with alcohols in the presence of an acid catalyst (e.g. concentrated H_2SO_4) (ii) acid anhydrides with alcohols					
(d) hydrolysis of esters: (i) in hot aqueous acid to form carboxylic acids and alcohols (ii) in hot aqueous alkali to form carboxylate salts and alcohols					
Acyl chlorides (e) the formation of acyl chlorides from carboxylic acids using $SOCl_2$					
(f) use of acyl chlorides in synthesis in formation of esters, carboxylic acids and primary and secondary amides.					

6.2 Nitrogen compounds, polymers and synthesis

6.2.1 Amines

Basicity and preparation of amines (a) the basicity of amines in terms of proton acceptance by the nitrogen lone pair and the reactions of amines with dilute acids, e.g. HCl(aq), to form salts					
(b) the preparation of: (i) aliphatic amines by substitution of haloalkanes with excess ethanolic ammonia and amines (ii) aromatic amines by reduction of nitroarenes using tin and concentrated hydrochloric acid.					

6.2.2 Amino acids, amides and chirality

Reactions of amino acids (a) the general formula for an α-amino acid as $RCH(NH_2)COOH$ and the following reactions of amino acids: (i) reaction of the carboxylic acid group with alkalis and in the formation of esters (see also 6.1.3 c) (ii) reaction of the amine group with acids					
Amides (b) structures of primary and secondary amides (see also 6.1.3 f, 6.2.3 a–b)					
Chirality (c) optical isomerism (an example of stereoisomerism, in terms of non-superimposable mirror images about a chiral centre)					
(d) identification of chiral centres in a molecule of any organic compound.					

6.2.3 Polyesters and polyamides

Condensation polymers (a) condensation polymerisation to form: (i) polyesters (ii) polyamides					
(b) the acid and base hydrolysis of: (i) the ester groups in polyesters (ii) the amide groups in polyamides					
(c) prediction from addition and condensation polymerisation of: (i) the repeat unit from a given monomer(s) (ii) the monomer(s) required for a given section of a polymer molecule (iii) the type of polymerisation.					

6.2.4 Carbon–carbon bond formation

Extending carbon chain length (a) the use of C–C bond formation in synthesis to increase the length of a carbon chain (see also 6.1.1 d, 6.1.2 b)					
(b) formation of C-CN by reaction of: (i) haloalkanes with CN^- and ethanol, including nucleophilic substitution mechanism (ii) carbonyl compounds with HCN, including nucleophilic addition mechanism (see also 6.1.2 b–c)					
(c) reaction of nitriles from (b): (i) by reduction (e.g. with H_2/Ni) to form amines (ii) by acid hydrolysis to form carboxylic acids					
(d) formation of a substituted aromatic C–C by alkylation (using a haloalkane) and acylation (using an acyl chloride) in the presence of a halogen carrier (Friedel–Crafts reaction) (see also 6.1.1 d).					

Bonding Revision

What is an ion?

What ions will be formed by:

Mg? Cl?

Draw dot and cross diagrams for both ions.

What is the trend in ionic radii as you go down a group? Explain this trend.

What evidence is there for covalent bonding?

What is an ionic bond?

What is an ionic crystal. Draw a diagram to represent sodium chloride.

What is a covalent bond/ dative covalent bond? How are they different?

Draw dot and cross diagrams to represent these molecules:

H_2

NH_3

C_2H_4

NH_4

Draw examples of molecules with the following shapes and give the bond angles. Linear; non-linear; trigonal planar; pyramidal; tetrahedral and octahedral.

What is polarisation of ions?

What is covalent character?

What increases the polarisation of an anion?

Draw and label a diagram to show how metallic bonding occurs.

Why are metals good conductors?

Why do metals have high melting points?

Organic chemistry

no. of carbons	Stem for name
1	
2	
3	
4	
5	
6	
7	
8	
9	
10	

Draw the skeletal formula for butan-2-ol

Explain the term structural isomer and give an example.

Define the following terms

Homologous series –

Functional group –

Alkyl group –

Aliphatic –

Aromatic -

Homologous series	Prefix or suffix	example
Alkanes		
Alkenes		
Alcohols		
Carboxylic acid		
Haloalkane		

Draw the structure of cyclohexane and benzene.

Explain the terms

Homolytic fission

Hetrolytic fission

Alkanes

What is the general formula of alkanes.

What does saturated mean?

What is a hydrocarbon?

Write the combustion reaction for octane C_8H_{18}.

What is the difference between complete and incomplete combustion?

Draw and explain the shape around each carbon atom in alkanes.

Explain the variation in boiling points of alkanes with different carbon-chain lengths and branching.

What conditions are needed for the free radiacal substitution of methane by chlorine?

Draw the mechanism for an initiation step.

Draw the mechanisms for2 propagation steps.

Draw the mechanisms for 2 different termination steps

Explain why alkanes have a low reactivity?

What is meant by the term free radical?

What is the difference between homolytic and heterolytic bond fission? Show mechanisms to illustrate the difference?

Alkenes

What is the genergal formula of an alkane?

What is meant by unsaturated?

How do you test chemically for unsaturation?

Write an equation for this reaction

Draw a diagram of a double bond. Label the sigma and pi bonds.

Write an equation for the reaction of:

Ethene + hydrogen →

What conditions are needed?

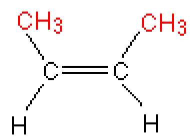
Ethene + Br_2 →

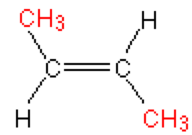
Ethene + HBr →

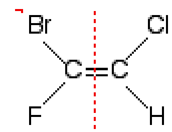
Ethene + $KMnO_4$ →

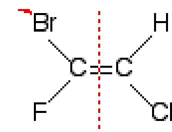
What causes stereoisomers?

What are the names of these 2 isomers? Using the cis/trans notation and the E/Z notation









Draw the mechanism for

Bromine + ethene

hydrogen bromide + propene

What is an electrophile?

What is polymerization?

Draw the repeating units for polyethene and polypropene.

Alcohols

Explain the benefits for sustainability of processing waste polymers.

Explain the properties of alcohols including solubility and volatility?

What is a nucleophile?

Write and equation for the combustion of methanol?

Alcohols can be oxidised using an oxidising agent.

Name an appropriate oxidising agent?

Illustrate how we would represent an oxidising agent in an equation?

What would be produced if we oxidise a primary alcohol?

What is produced if we oxidise a secondary alcohol?

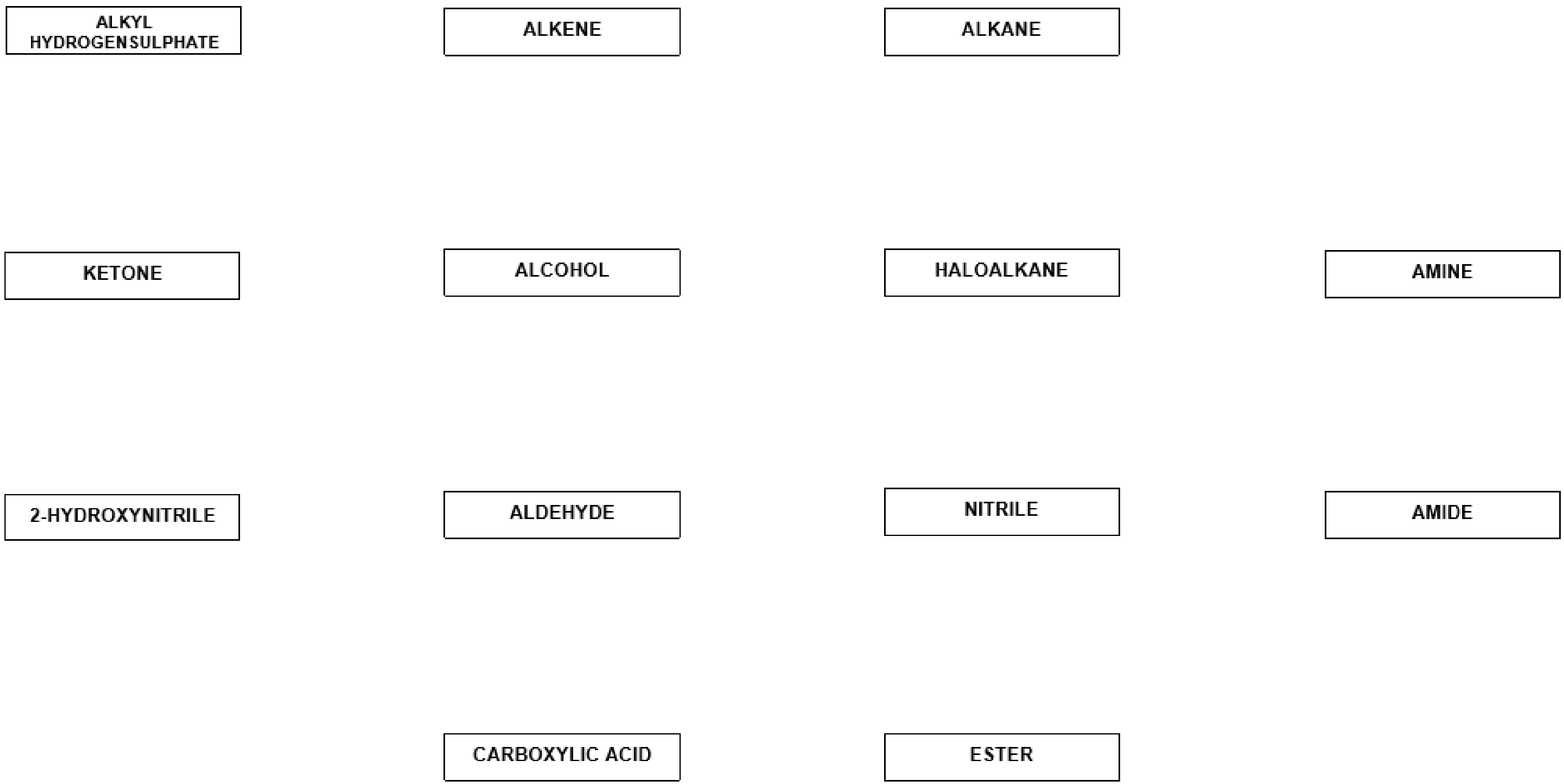
Tertiary alcohol?

Draw a mechanism of nucleophilic substitution in the hydrolysis of primary haloalkanes with aqueous alkali?

Explain the trend in the rate of hydrolysis of primary halo-alkanes in terms of the bond enthalpies of carbon-halogen bonds?

Explain the environmental concerns of the production of halogen radicals?

ORGANIC SYNTHESIS 1



Add arrows and reagents so show how you could synthesis one to another.

Aromatic compounds

Draw and compare the Kekule model of benzene with the delocalised models?

What evidence is there for a delocalised model for benzene?

Draw 2,4-dinitromethylbenzene.

Draw the mechanism for electrophilic substitution for the nitration of benzene. Include ALL equations and reactant conditions.

Explain why benzene is resistant to bromination and compare with alkenes.

Draw the electrophilic substitution of phenol with bromine to form 2,4,6-tribromophenol. Include all equations and reactant conditions.

Draw phenol.

What properties does phenol have?

Explain the 2- and 4-directing effect of electron donating groups and the 3-directing effect of electron-withdrawing groups.

Carbonyl compounds

What are aldehydes oxidised to?

What reagents are used in oxidation?

Write an equation to represent propanal being oxidised.

What are the products of nucleophilic addition reactions of carbonyl compounds with:

$NaBH_4$ –

HCN [$NaCN/H^+$]

Draw the mechanism for the nucleophilic addition reaction Propanal with $NaBH_4$.

What results would we see if we use 2,4-dinitrophenylhydrazine to AND explain how you could also use melting points to identify them?

- Detect an aldehyde?
- Detect a ketone?
- Detect a carboxylic acid or ester?

Draw the mechanism for the nucleophilic addition reaction of propanone with HCN.

What results would you achieve if your added Tollens' reagent to the following?

- Aldehydes?
- Ketones?

Explain in terms of oxidation and reduction what happens to the silver ions during the Tollens' reagent tests?

Carboxylic acids and ester

Draw the following:

- Ethanoic acid

- Ethyl ethanoate.

Explain what happens to the solubility of carboxylic acids as the get bigger? Include hydrogen bonding.

Explain how carboxylic acids react with metals and bases? Include an example of a reaction.

Esterification: What reactants come together to form Ethyl ethanoate?

Draw out the reaction of propanol and ethanoic acid? Highlight the ester link.

Hydrolysis of esters: What is produced if propyl ethanoate is hydrolysed with hot aqueous acid?

What is produced if ethyl ethanoate is hydrolysed with hot aqueous alkali?

How are acyl chlorides form from a carboxylic acid usng $SOCl_2$?

Using an acyl chloride write the equation for esterification of phenol?

Amines and Amino acids

What is an amine?

Draw N-methyl propylamine?

Why are amines classed as bases?

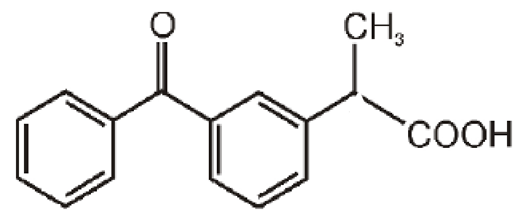
Describe the reaction of amines with acids, include what is formed?

Describe the preparation of aliphatic amines by substitution of haloalkane with excess ethanolic ammonia and amines.

Define optical isomers?

Define a chiral centre,

label the chiral centre on the compound shown?



Write the general formula an α-amino acid?

Describe the reaction of amino acids with alkalis to form esters?

Draw the structure of primary and secondary amides?

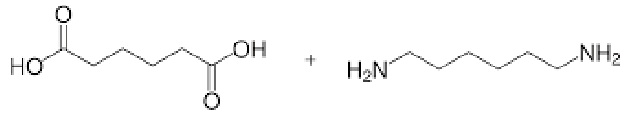
Polyester and Polyamides

Draw the repeating link in polyester?

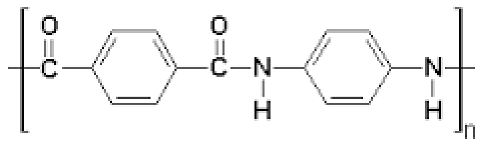
Draw the repeating link in polyamides?

Describe what happens when polyester is hydrolysed?

Draw the product from these 2 monomers?



Draw the two monomers that are used to create the following polymer?

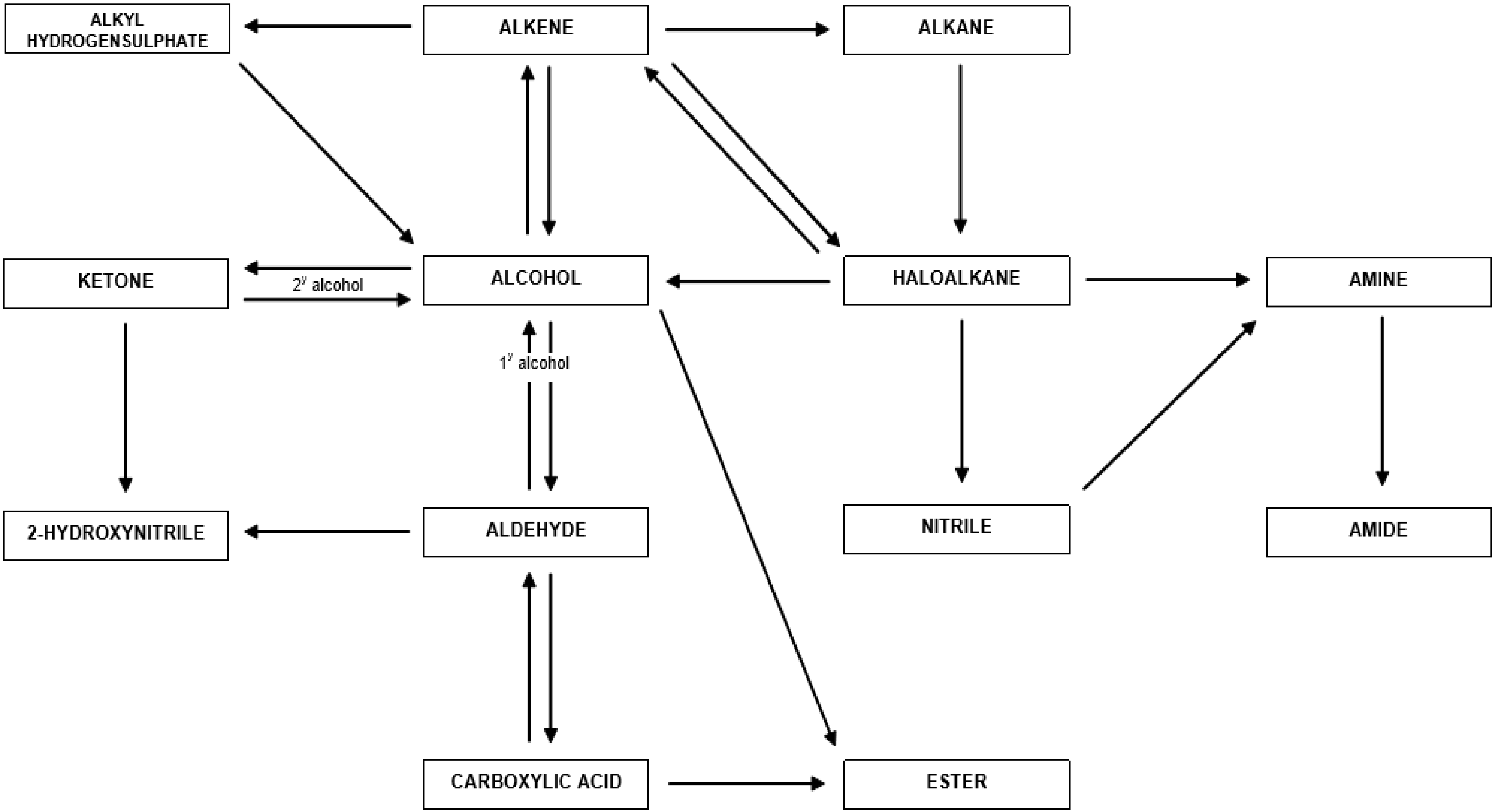


Kevlar™

Draw a general mechanism for nucleophilic attack of a cyanide ion on a haloalkane?

Draw the general mechanism for nucleophilic addition of a cyanide ion on an organic carbonyl group?

ORGANIC SYNTHESIS 1



Questions

Q1. Crude oil is a complex mixture of hydrocarbons. Initial separation is achieved by fractional distillation of the crude oil. The separate fractions are further refined to produce hydrocarbons such as decane, $C_{10}H_{22}$.

(a) Give the general formula of alkanes.

(1)

(b) Carbon monoxide, CO, is formed during the incomplete combustion of decane.

(i) Write an equation for the incomplete combustion of decane, forming carbon monoxide and water only.

(1)

(ii) Explain why incomplete combustion can occur.

(1)

....

....

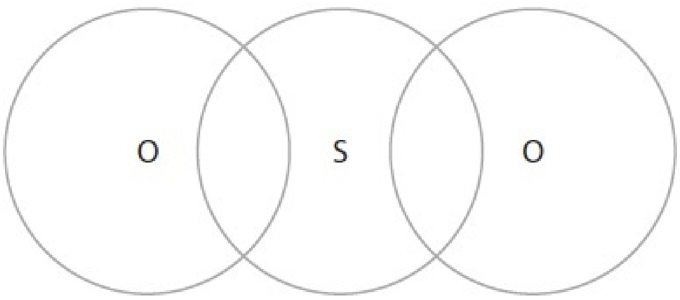
(c) 'Low-sulfur fuel' is now supplied to petrol stations. The removal of sulfur from diesel and petrol reduces the emission of toxic oxides of sulfur from vehicle exhausts. One such oxide is sulfur dioxide, SO_2.

The bonding in sulfur dioxide may be represented as shown below.

$$O = S \rightarrow O$$

Complete the dot and cross diagram below for the SO_2 molecule, showing only outer shell electrons. Use dots to represent the oxygen electrons and crosses to represent the sulfur electrons.

(3)



(d) Another alkane produced from crude oil is heptane, C_7H_{16}. The reforming of heptane produces methylcyclohexane and only one other product. A methylcyclohexane molecule is made from a ring of six carbon atoms bonded to a methyl group.

(i) Use the information given above to give the **skeletal** formula of methylcyclohexane.

(1)

(ii) Write a balanced equation, using **molecular** formulae, for the reforming of heptane into methylcyclohexane and one other product. State symbols are not required.

(1)

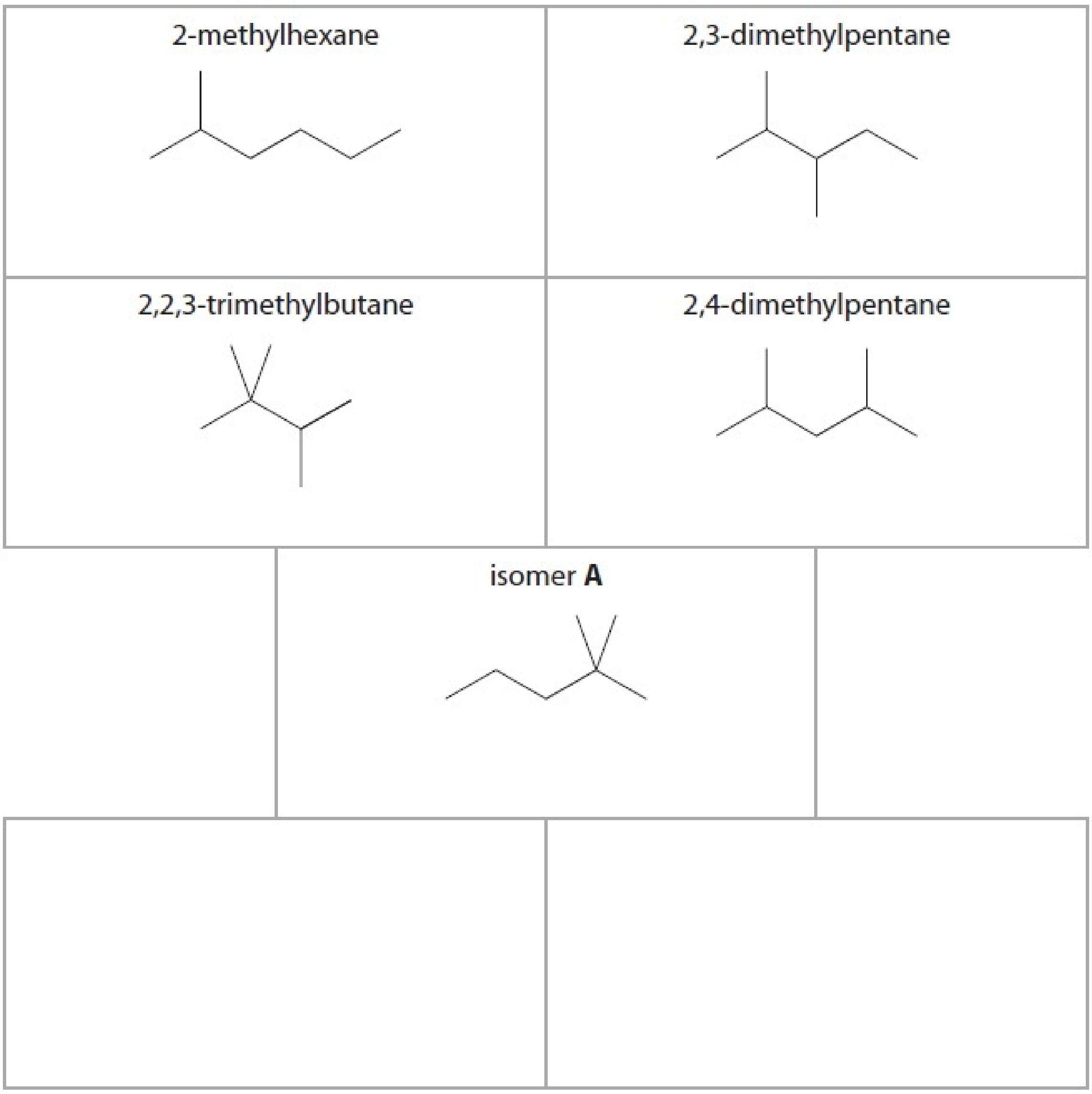
(iii) Suggest a reason why oil companies reform alkanes such as heptane.

(1)

....

....

(e) Five branched-chain isomers of heptane are shown in the boxes below.



(i) Give the systematic name of isomer **A**.

(1)

....

(ii) In the empty boxes above, draw skeletal formulae for two other **branched-chain** isomers of C_7H_{16}, with no side-chain having more than one carbon atom.

(2)

(f) Butane, C_4H_{10}, reacts with chlorine, Cl_2, at room temperature and pressure.

$$C_4H_{10} + Cl_2 \rightarrow C_4H_9Cl + HCl$$

(i) What other condition is essential for this reaction?

(1)

....

(ii) Write an equation for the initiation step of the mechanism for the above reaction. Curly arrows are not required.

(1)

(iii) State the type of bond fission involved in the initiation step.

(1)

....

(iv) Write equations for the two propagation steps of this mechanism. Curly arrows are not required.

(2)

First propagation step:

Second propagation step:

(v) Write **one** equation for a reaction that would terminate this mechanism.

(1)

(Total for Question = 18 marks)

Q2.

This question is about halogenoalkanes.

The tables show some relevant data.

Bond	Bond enthalpy / kJ mol⁻¹
C—F	467
C—Cl	346
C—Br	290
C—I	228

Atom	Electronegativity
C	2.5
F	4.0
Cl	3.0
Br	2.8
I	2.5

(a) In an experiment, 1 cm^3 of ethanol and 5 cm^3 of 0.1 mol dm^{-3} silver nitrate were placed in each of three test tubes X, Y and Z. The test tubes and their contents were placed in a water bath at 50°C for five minutes.

Two drops of 1-chlorobutane were then added to test tube X and the tube was shaken to mix the contents. The time taken for a precipitate to appear was measured.

The experiment was repeated using two drops of 1-bromobutane in test tube Y and two drops of 1-iodobutane in test tube Z.

(i) The time taken for a precipitate to appear increases in the order

(1)

☒ **A** X, Y, Z

☒ **B** Z, Y, X

☒ **C** Y, X, Z

☒ **D** Z, X, Y

(ii) Give a reason for the addition of ethanol to each test tube.

(1)

....

....

(iii) Give a reason why the test tubes were left in the water bath for five minutes before adding the halogenoalkanes.

(1)

....

....

....

(iv) The precipitates form as a result of reactions between aqueous silver ions and aqueous halide ions.

Explain why halide ions are present in the mixture containing a halogenoalkane which has only covalent bonds.

(2)

....

....

....

....

....

....

(v) Write the ionic equation, including state symbols, for the reaction involving the silver nitrate in test tube X.

(1)

(b) 1-bromo-2-methylpropane was mixed with a large excess of potassium hydroxide solution.

The 1-bromo-2-methylpropane is hydrolysed during the reaction and its concentration decreases as the reaction proceeds. Samples of the reaction mixture were analysed at time intervals to determine the remaining concentration of 1-bromo-2-methylpropane.

Time/s	[1-bromo-2-methylpropane]/mol dm^{-3}
0	0.1000
50	0.0500
100	0.0250
200	0.0063
300	0.0016

(i) Draw a graph of [1-bromo-2-methylpropane] against time.

(3)

(ii) Use your graph to calculate a value for the rate of reaction at 100 s. Include units in your answer.

(3)

(c) (i) Which term best describes the role of the OH^- ion in the reaction in (b)?

(1)

☒ **A** catalyst

☒ **B** electrophile

☒ **C** free radical

☒ **D** nucleophile

(ii) Draw a diagram to show the mechanism for the hydrolysis of 1-bromo-2-methylpropane by the hydroxide ion. Include any appropriate lone pairs and dipoles.

(4)

(iii) The hydrolysis reaction described in part (b) may also be classified as

(1)

☒ **A** addition

☒ **B** elimination

☒ **C** redox

☒ **D** substitution

(Total for question = 18 marks)

Q3.

This question is about the gas ethane, C_2H_6, and its reactions.

(a) Write the equation, including state symbols, which represents the reaction taking place when the standard enthalpy change of combustion of ethane is measured.

(2)

(b) Ethane can react with chlorine to form chloroethane and hydrogen chloride.

$$C_2H_6(g) + Cl_2(g) \rightarrow C_2H_5Cl(g) + HCl(g)$$

Bond	Bond enthalpy/kJ mol^{-1}
C—H	413
C—C	347
C—Cl	346
H—Cl	432
Cl—Cl	243

Rewrite this equation using displayed formulae.

Use the equation you have written, together with the bond enthalpy data, to calculate the enthalpy change for the reaction.

(4)

(c) This reaction takes place in a number of steps, some of which are shown below.

Step 1 $Cl_2 \rightarrow 2Cl\bullet$

Step 2 $CH_3CH_3 + Cl\bullet \rightarrow HCl + CH_3CH_2\bullet$

(i) State the type of reaction occurring in step 1 and the conditions needed for this step.

(2)

Type

....

Conditions

....

(ii) Complete the equation below for the third step of the reaction, and show the movement of electrons using the appropriate arrows.

(3)

$CH_3CH_2\cdot + Cl{-}Cl \rightarrow$

(iii) Write equations for **two** termination steps in this reaction.

(2)

(d) Ethane can be cracked in industry. Write an equation for the cracking of ethane.

(1)

(e) Suggest **two** reasons why cracking of larger alkane molecules is important in industry.

(2)

Reason 1:

....

....

Reason 2:

....

....

(Total for question = 16 marks)

Q4. A solution of 2,4-dinitrophenylhydrazine (Brady's reagent) is used as a test for organic functional groups.

(a) The positive result of the test is the formation of

(1)

- **A** a yellow solution.
- **B** an orange precipitate.
- **C** a red solution.
-

D a green precipitate.

(b) Which of the following gives a positive result with a solution of 2,4-dinitrophenylhydrazine?

(1)

- **A** Only aldehydes
- **B** Only ketones
- **C** Only aldehydes and ketones
- **D** Any compound containing the C=O group

(c) The initial attack by 2,4-dinitrophenylhydrazine, when it reacts, is by

(1)

- **A** a free radical.
- **B** an electrophile.
- **C** a nucleophile.
- **D** a negative ion.

(d) The product of a positive test, a 2,4-dinitrophenylhydrazone, contains which of the following bonds?

(1)

- **A** N=N
- **B** C=N
- **C** C=C
- **D** C=O

(Total for Question = 4 marks)

Q5.

This question is about the chemistry of propane-1,3-diol and propanedioic acid.

In an experiment, 15.2 g of propane-1,3-diol was oxidised to propanedioic acid, which is a solid **dibasic** acid. This acid may be represented as H_2X.

250 cm^3 of a solution was prepared from all of the acid in a volumetric flask.

10.0 cm^3 portions of this solution were then titrated with 0.400 mol dm^{-3} sodium hydroxide solution. The mean titre was 18.45 cm^3.

$$H_2X + 2NaOH \rightarrow Na_2X + 2H_2O$$

[Relative formula masses: propane-1,3-diol = 76.0; propanedioic acid = 104.0]

(i) Calculate the moles of propanedioic acid in 10.0 cm^3 of the acid solution.

(2)

(ii) Calculate the mass of propanedioic acid in the 250 cm^3 solution.

(2)

(iii) Calculate the percentage yield for the oxidation of propane-1,3-diol to propanedioic acid.

(2)

(iv) Give **one** reason why the yield calculated in (iii) is less than 100%.

(1)

....

....

....

(Total for question = 7 marks)

Week 9

Synthesis

4.2.3 Organic synthesis

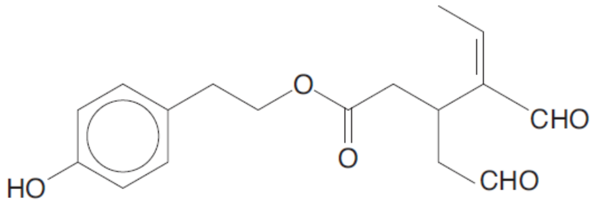
(a) the techniques and procedures for: **(i)** use of Quickfit apparatus including for distillation and heating under reflux **(ii)** preparation and purification of an organic liquid including: • use of a separating funnel to remove an organic layer from an aqueous layer • drying with an anhydrous salt (e.g. $MgSO_4$, $CaCl_2$) • redistillation					
(b) for an organic molecule containing several functional groups: **(i)** identification of individual functional groups **(ii)** prediction of properties and reactions					
(c) two-stage synthetic routes for preparing organic compounds.					

6.2.5 Organic synthesis

Practical skills (a) the techniques and procedures used for the preparation and purification of organic solids involving use of a range of techniques including: (i) organic preparation • use of Quickfit apparatus • distillation and heating under reflux (ii) purification of an organic solid • filtration under reduced pressure • recrystallization • measurement of melting points					
Synthetic routes (b) for an organic molecule containing several functional groups: (i) identification of individual functional groups (ii) prediction of properties and reactions					
(c) multi-stage synthetic routes for preparing organic compounds.					

Module 6.2: Synthesis Tasks

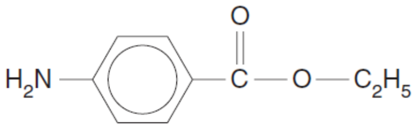
1. Olecanthal has shown pharmacological activity as an anti-inflammatory drug. A formula for olecanthal is shown below.



oleocanthal

Chemists have attempted to synthesise olecanthal in the laboratory. The product form this synthesis had a lower pharmacological activity than olecanthal extracted from olive oil. Suggest why. [2]

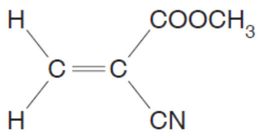
2. Benzocaine is a local anaesthetic with the structure shown below.



benzocaine

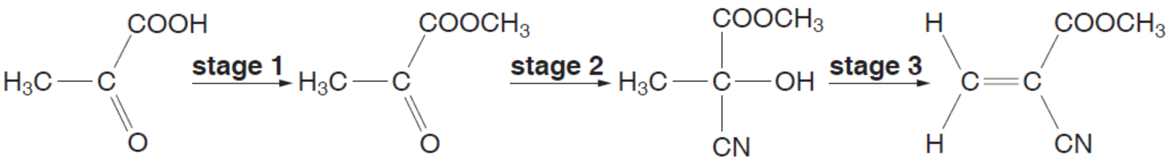
a. Benzocaine can be synthesised from **4-nitrobenzoic acid** in **two** stages.
   Write an equation for the reaction in each stage, and state any essential reagents and conditions. [6]
b. A sample of benzocaine was warmed in dilute hydrochloric acid for an hour.
   Draw the structures of the **two** organic products formed in these acidic conditions. [2]

3. Compound **E** is used by forensic scientists to investigate fingerprints.



compound **E**

a. Compound **E** forms a polymer when its vapour comes into contact with the fingerprint.
   Draw a short section of this polymer showing **two** repeat units. [1]
b. Compound **E** reacts with hot aqueous hydrochloric acid to form an unsaturated organic compound.
   Suggest the structure of this compound. [2]
c. Compound **E** can be manufactured from 2-oxopropanoic acid in three stages shown below.

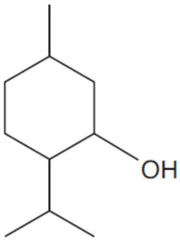


2-oxopropanoic acid

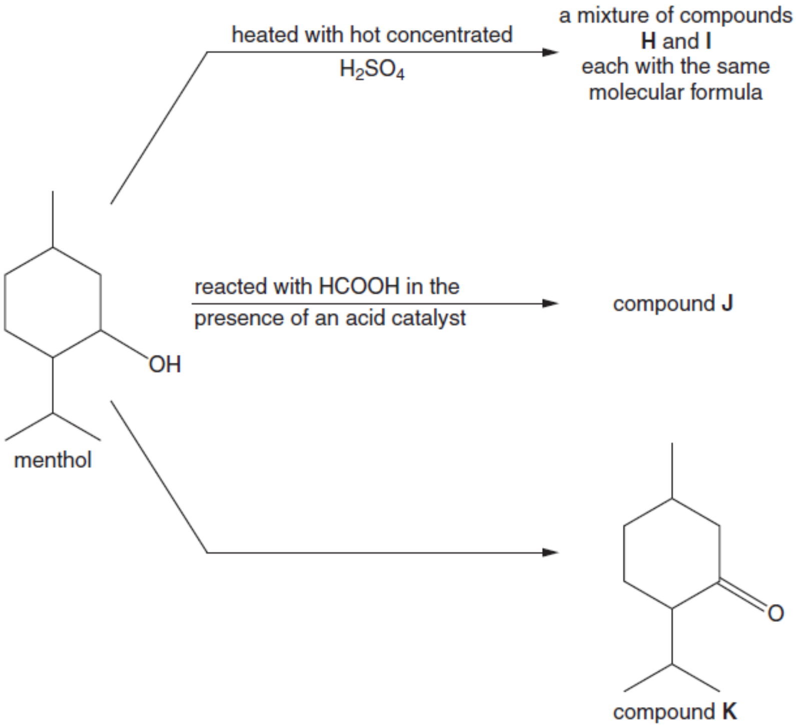
   i. Identify the reagents and conditions required for **stage 1**. [2]
   ii. Deduce the other product formed in **stage 3**. [1]
d. A typical yield of compound **E** from 2-oxopropanoic acid is 30%.
   Calculate the mass of compound **E** you would expect to produce from 10 kg of 2-oxopropanoic acid.
   Give you answer to **two** significant figures and show your working. [4]

Module 6.2: Synthesis Tasks

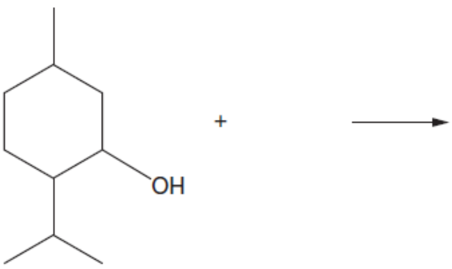
4. Menthol is a naturally occurring cyclic alcohol found in peppermint oil. It has been used in throat sprays and cough drops for many years.
   The skeletal formula of menthol is shown below.



   a. i. What is the molecular formula of menthol? [1]
      ii. Classify menthol as a primary, secondary or tertiary alcohol. [1]
   b. The reaction scheme below shows some of the reagents and conditions needed to convert menthol into four **organic** compounds **H**, **I, J** and **K**.



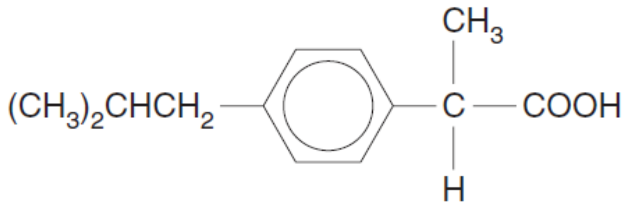
      i. Draw compounds **H** and **I**. [2]
      ii. State the functional group in compound **J**.
   c. Menthol can be oxidised to form compound **K**.
      i. State the reagents and conditions. [2]
      ii. State what you would see during the oxidation. [1]
      iii. Write a balanced equation for the oxidation.
      Use **[O]** to represent the oxidising agent. [1]



      iv. Explain how you could use infra-red spectroscopy to confirm that no menthol remains. [1]

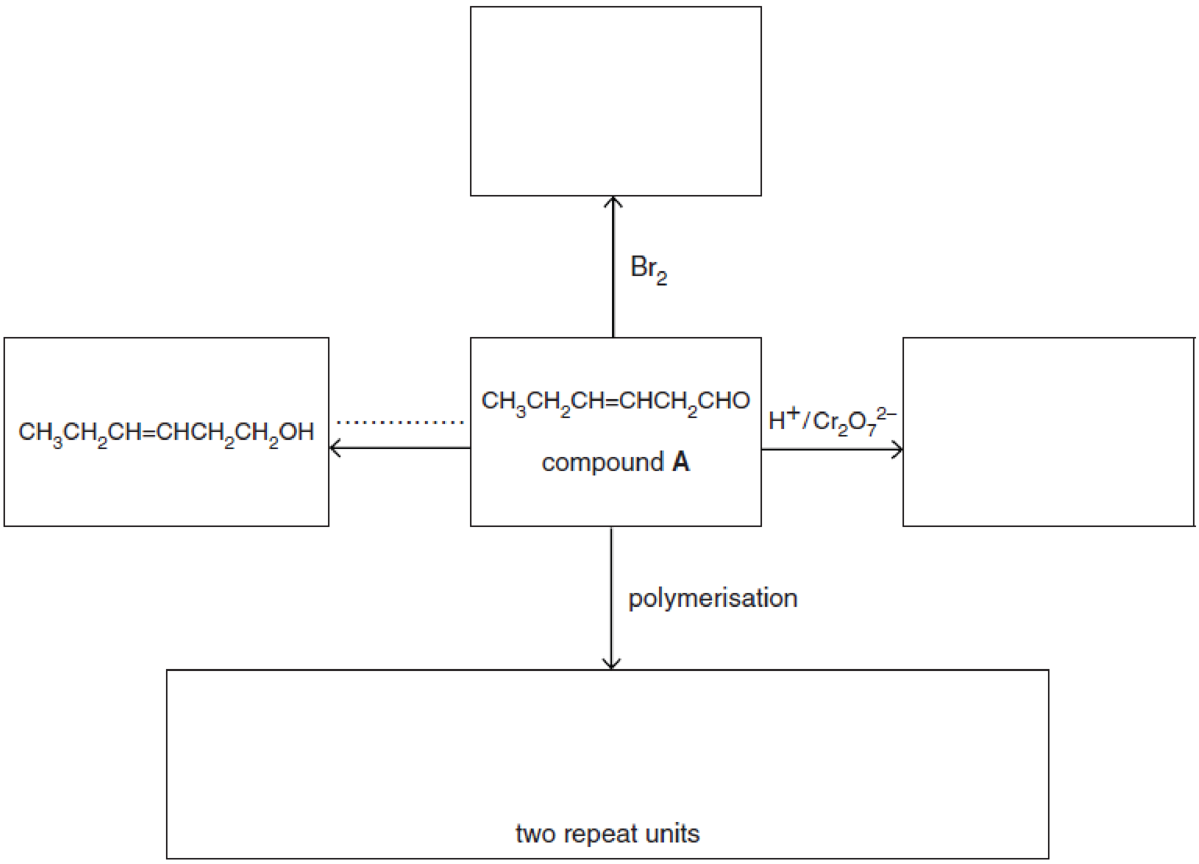
Module 6.2: Synthesis Tasks

5. Ibuprofen is a highly successful anti-inflammatory drug. The structure of ibuprofen is shown below.



   a. Ibuprofen is sometimes sold as the sodium salt of the compound shown above.
      i. State a reagent that would convert the structure above into the sodium salt. [1]
      ii. Draw the structure of the sodium salt of ibuprofen. [1]
   b. Ibuprofen is a chiral drug that is usually produced as a mixture of stereoisomers.
      Using ibuprofen as an example, explain what is meant by the term chiral;
      Discuss the possible disadvantages of producing a chiral drug as a mixture of stereoisomers. [6]

6. Compound **A**, $CH_3CH_2CH{=}CHCH_2CHO$, is produced in small amounts by most plants and insects.
   a. Name compound **A**. [2]
   b. The flowchart shows some reactions of compound **A**.
      Complete the flowchart below. [5]



   c. There are two stereoisomers of $CH_3CH_2CH{=}CHCH_2CHO$.
      Draw and label these stereoisomers. [2]

Questions

Q1.

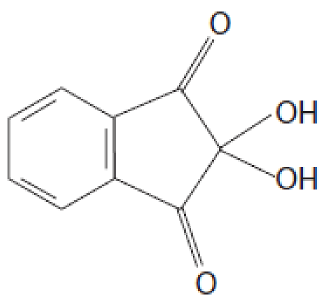
Read the passage below carefully and answer the question which follows.

The general formula of most naturally occurring amino acids can be written $RCH(NH_2)COOH$, though in some amino acids, such as proline, the nitrogen atom is part of a five-membered ring. Amino acids are water soluble, though the extent of their solubility varies. All but one of the naturally occurring amino acids show optical activity.

The formula of the R group for some naturally occurring amino acids is shown below.

Amino acid	Formula of R group
serine	$-CH_2OH$
lysine	$-(CH_2)_4NH_2$
phenylalanine	$-CH_2C_6H_5$
leucine	$-CH_2CH(CH_3)_2$
iso-leucine	$-CH(CH_3)CH_2CH_3$
alanine	$-CH_3$

Mixtures of amino acids can be separated by electrophoresis. This method depends on amino acids moving different distances through paper or gel when an electric field is applied. They can also be separated by chromatography. Ninhydrin, shown below, is the chemical which is used to locate the position of the amino acids on chromatograms.



Ninhydrin detects ammonia and primary and secondary amines. When it reacts with primary amines, a deep blue or purple colour is produced in a complex series of reactions. With proline, a yellow compound forms.

Ninhydrin is widely used to detect fingerprints. Sweat secretions from ridges on the finger contain dipeptides and proteins. These are left on porous surfaces such as paper, and react with ninhydrin.

When ninhydrin reacts with amino acids, carbon dioxide is released from the carboxylic acid group. Archaeologists have used this reaction to release the carbon from proteins in ancient bones, and, by comparing the proportions of carbon and nitrogen in the remains, they have obtained evidence for the diets of these animals.

(a) (i) At a pH of 5.68, serine exists as a zwitterion. Draw the formula of serine at this pH.

(1)

*(ii) At pH 5.68, serine and lysine can be separated by electrophoresis. By considering the structures of the amino acids at this pH, suggest why this separation occurs.

(2)

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*(b) Serine is very soluble in water, whilst phenylalanine is much less soluble. Explain the difference, disregarding any effect of zwitterion formation.

(2)

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....

(c) The naturally occurring amino acid which does not show optical activity is not shown in the table. Give the formula of the R group for this acid.

(1)

(d) The optical activity of equimolar solutions of naturally occurring samples of leucine and iso-leucine can be measured in an experiment using plane-polarized light.

(i) What measurement is made to show the optical activity of amino acids?

(1)

....

(ii) By considering the structures of iso-leucine and leucine, explain why iso-leucine has more stereoisomers than leucine.

Amino acid	Formula of R group
leucine	$-CH_2CH(CH_3)_2$
iso-leucine	$-CH(CH_3)CH_2CH_3$

(1)

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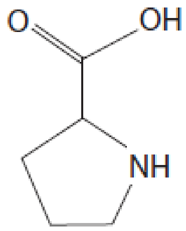
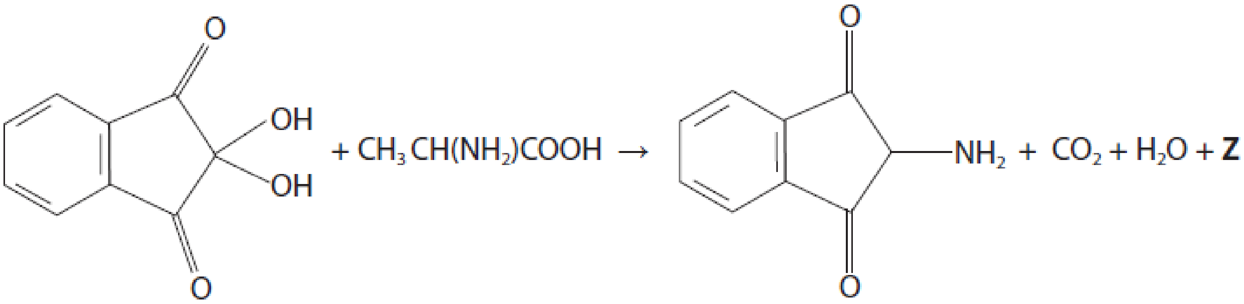
(e) The amino acid proline, shown below, does not contain a primary amine group, but it can still form peptide bonds.



Draw the structure of the dipeptide formed when the carboxylic acid group of alanine reacts with proline. Circle the peptide group on your drawing.

(2)

(f) The first steps of the reaction of ninhydrin with alanine can be summarised in the equation shown below.

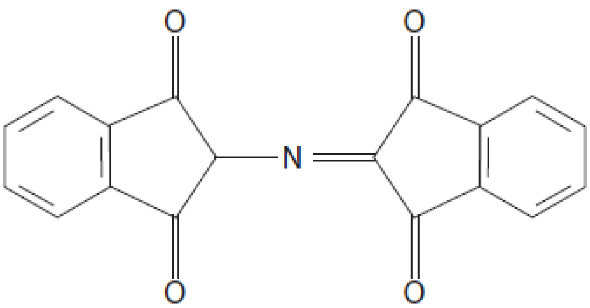


Y

(i) By balancing the equation, suggest the structural formula of the product **Z**.

(1)

(ii) In the final stage, **Y** reacts with another molecule of ninhydrin to form a dye, **Q**, shown below.



What is the molecular formula of **Q**?

(1)

(iii) On combustion, 1.000 g of **Q** produces 2.614 g carbon dioxide, 0.2673 g water and 0.04620 g nitrogen.

Use these data to calculate the percentage composition by mass of **Q**, and hence its empirical formula. Show whether your answer is consistent with the molecular formula of **Q**.

(4)

(iv) Evidence for the structure of **Q** is obtained from data in its mass spectrum, and the number of peaks in its low resolution nmr spectrum.

Suggest **one** piece of evidence from **each** type of spectroscopy which would support the structure shown in (ii). Give data where appropriate.

(2)

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Q2.

The **distinguishing** characteristic of combinatorial chemistry is that it involves the

☒ **A** simultaneous synthesis of many products.

☒ **B** interaction of starting materials to form a unique product.

☒ **C** use of catalysts.

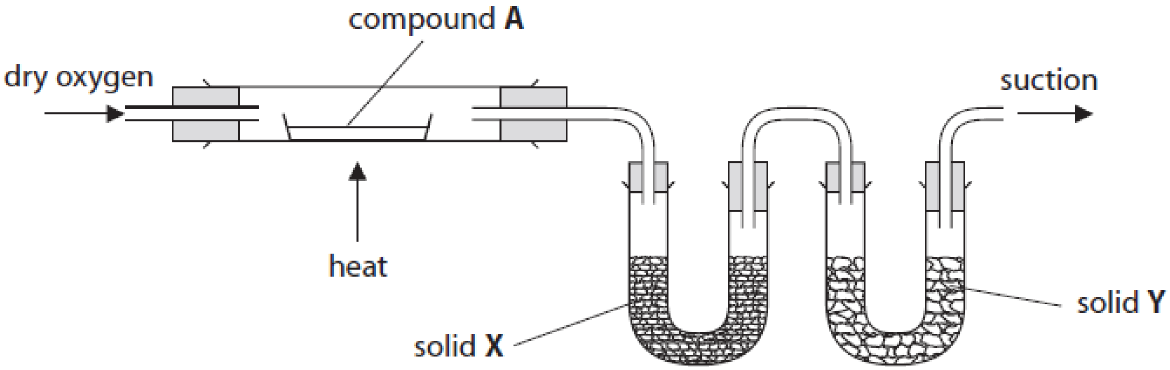
☒ **D** use of polymer supports.

(Total for question = 1 mark)

Q3.

A compound **A**, known to contain only the elements carbon, hydrogen and oxygen, was subjected to detailed analysis.

(a) A sample of **A** was burned completely in the apparatus shown below. Solid **X** absorbed the water formed in the combustion and solid **Y** absorbed the carbon dioxide.



(i) Explain why the oxygen must be dry.

(1)

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(ii) Suggest a suitable substance to use as solid **X**.

(1)

....

....

(iii) Suggest a suitable substance to use as solid **Y**.

(1)

....

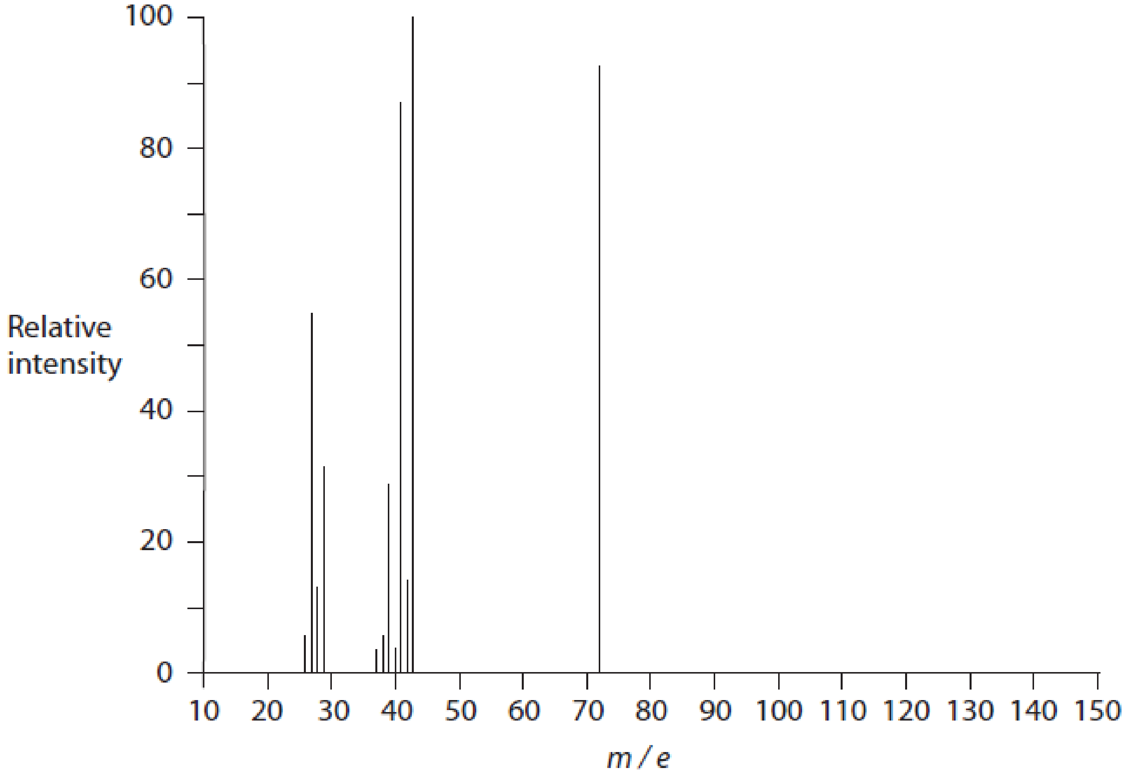
....

(iv) 3.60 g of compound **A** was burned completely. The mass of solid **X** increased by 3.60 g and the mass of solid **Y** increased by 8.80 g.

Use these data to calculate the empirical formula of compound **A**.
You **must** show your working.

(5)

(b) The mass spectrum of **A** is shown below.



(i) Identify the molecular ion peak and hence deduce the molecular formula of **A**.

(2)

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....

(ii) Given that **A** does **not** have a ring structure, suggest the **structural** formulae of three of the species that might cause the peak at *m*/*e* = 43 in the mass spectrum of **A**.

(3)

*(c) The low resolution nmr spectrum of **A** has three peaks in the ratio 6:1:1. Draw the structure of **A** and show how your structure is consistent with the nmr data.

(3)

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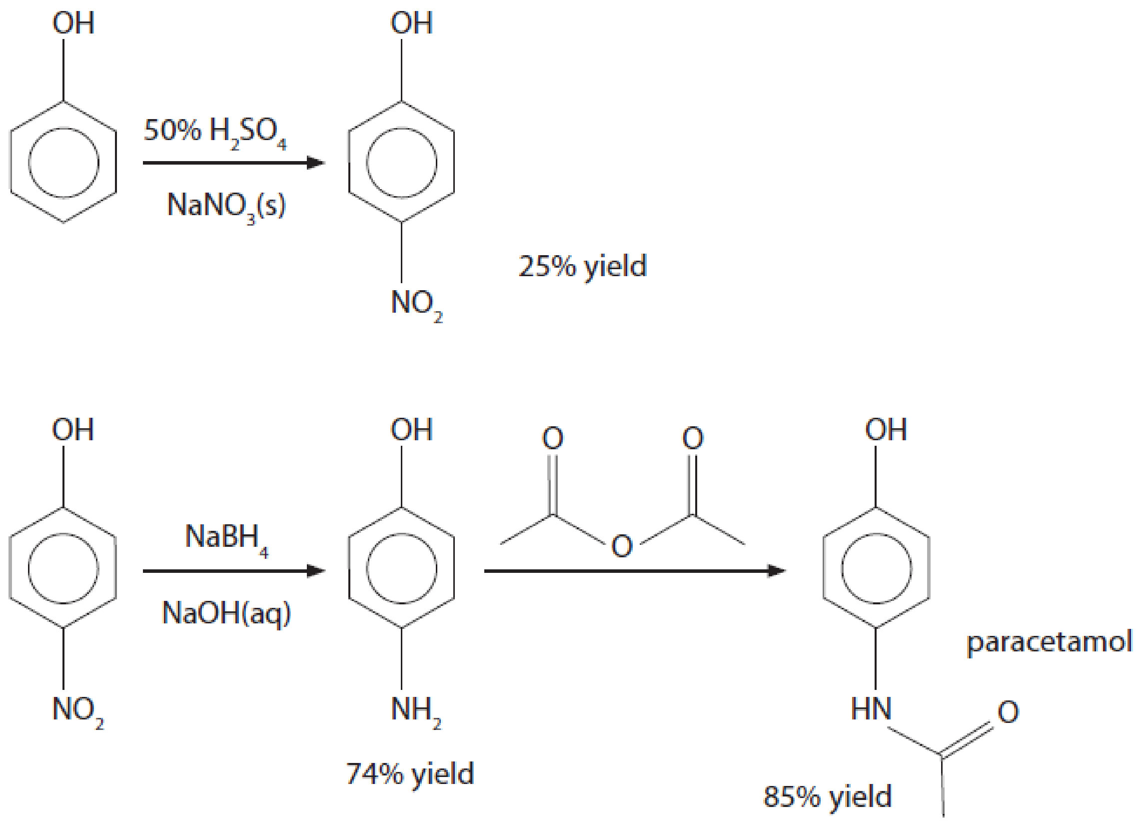
(Total for question = 16 marks)

Q4.

Paracetamol is a mild painkiller which also reduces the temperature of patients with fever, actions known as analgesic and antipyretic respectively. The reaction scheme below summarises a laboratory synthesis of paracetamol starting from phenol. The yields shown are for the particular product of each step in the synthesis.



(a) The nitration of benzene is an electrophilic substitution reaction that requires concentrated nitric and sulfuric acids.

(i) Write an equation for the formation of the electrophile by the reaction between concentrated nitric and concentrated sulfuric acids.

(2)

(ii) Give the mechanism for the formation of nitrobenzene from benzene.

(3)

(iii) Explain why phenol is nitrated in much milder conditions than benzene.

(2)

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(iv) Suggest why the yield for the nitration of phenol is so low.

(1)

....

....

(v) Suggest an alternative to $NaBH_4$ that could be used in aqueous solution.

(1)

....

(vi) Calculate the overall yield of the synthesis.

(1)

(b) The paracetamol, prepared by the synthesis shown at the start of the question, may be purified by recrystallization. In this process, the paracetamol is dissolved in a minimum volume of hot water, the hot mixture filtered, the filtrate cooled and the resulting crystals filtered and dried. The table below summarises the solubility of paracetamol in water at various temperatures.

Temperature / °C	5	10	20	95
Solubility / g / 100 g	0.82	0.94	1.3	5.2

(i) Explain the purpose of each of the filtrations in the recrystallization of paracetamol.

(2)

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(ii) From the temperatures given in the table, choose the pair of temperatures that will give the highest yield of paracetamol from the recrystallization. Explain your choice.

(2)

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....

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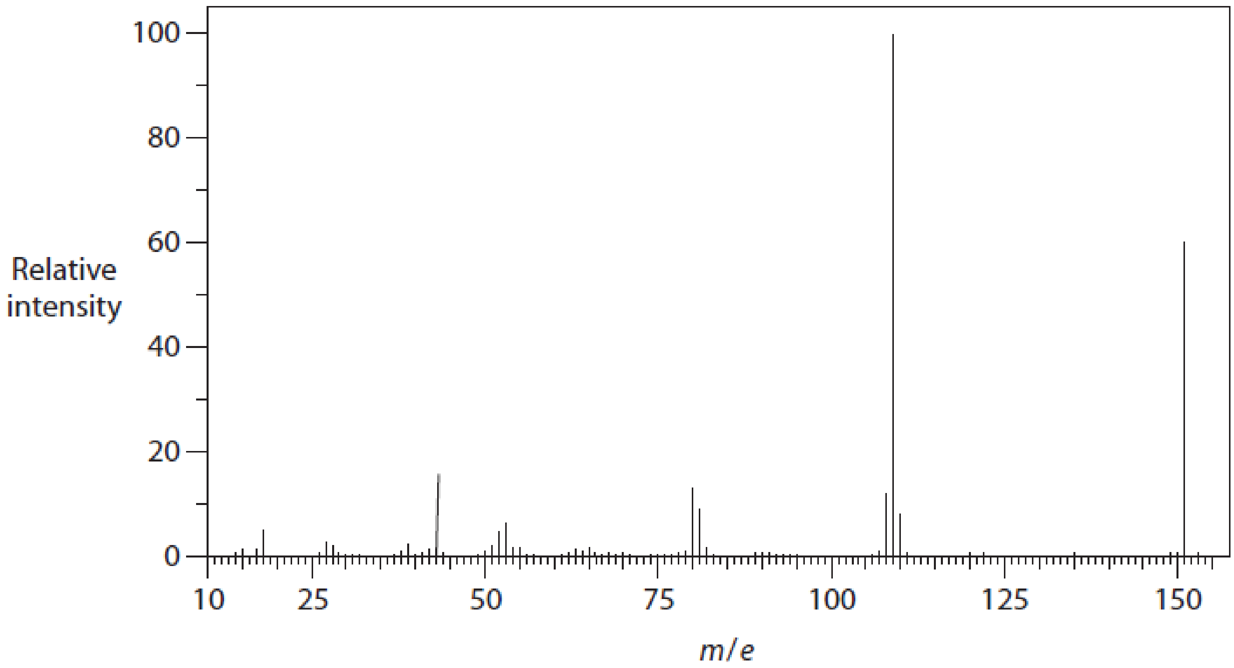
....

(iii) Name the technique that could be used in a **school** laboratory to check the purity of the recrystallized paracetamol.

(1)

....

(c) The mass spectrum of paracetamol is shown below.



(i) Label the molecular ion peak, with an **M**, on the mass spectrum.

(1)

(ii) Suggest the formula of an ion that could cause the peak at *m/e* = 43.

(1)

(d) Paracetamol is highly toxic: overdosing causes irreversible liver damage. Despite this, paracetamol is readily available from pharmacies and even supermarkets.
Suggest **one** control measure that sellers might employ to reduce the risk to paracetamol users.

(1)

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....

(Total for question = 18 marks)

Q5.

When a solid is purified by recrystallization, the procedure involves the removal of impurities by filtration of the hot mixture followed by filtration of the cold mixture.
Which impurities are removed by these two filtrations?

		Hot filtration	Cold filtration
☒	**A**	insoluble impurities	insoluble impurities
☒	**B**	insoluble impurities	soluble impurities
☒	**C**	soluble impurities	insoluble impurities
☒	**D**	soluble impurities	soluble impurities

(Total for question = 1 mark)

Q6. A scientist investigated the typical behaviour of primary amines.

(a) Amines such as butylamine, $CH_3CH_2CH_2CH_2NH_2$, and phenylamine, $C_6H_5NH_2$, both behave as bases.

(i) Which feature of an amine molecule allows it to act as a base?

(1)

....

....

(ii) The scientist reacted butylamine with two different acids.

Give the **formulae** of the salts that are formed when butylamine reacts with

(2)

sulfuric acid,
H_2SO_4
....

ethanoic acid,
CH_3COOH
....

(b) Phenylamine, $C_6H_5NH_2$, is formed by the reduction of nitrobenzene, $C_6H_5NO_2$.

Give the reagents that are used for this reduction.

(2)

....

....

(c) Phenylamine was reacted with a mixture of sodium nitrite, $NaNO_2$, and hydrochloric acid at a temperature between 0 °C and 5 °C. A diazonium ion was formed. In a second step, the scientist reacted the diazonium ion with phenol, under suitable conditions. A precipitate of 4-hydroxyazobenzene (4-hydroxyphenylazobenzene) was formed.

(i) Draw the structure of the diazonium ion, clearly displaying the functional group present in the ion.

(1)

(ii) Draw the structural formula of 4-hydroxyazobenzene.

(1)

(iii) State a condition, other than a suitable temperature, required for the reaction of the diazonium ion with phenol and give a use for 4-hydroxyazobenzene.

(2)

Condition required:

....

Use for 4-hydroxyazobenzene:

....

(d) The scientist repeated the first step in experiment (c), but the temperature was allowed to rise above 10°C. Under these conditions, the diazonium ion reacted with water to produce phenol. An unreactive gas, of molar mass 28.0 g mol^{-1}, was also formed along with one other product.

Use this information to write the equation for the reaction of the diazonium ion with water.

(2)

(e) The impure sample of 4-hydroxyazobenzene formed in part (c) may be purified by recrystallization. During this process

- the solid is dissolved in the minimum volume of hot solvent
- the mixture is then filtered whilst still hot
- the filtrate is cooled in an ice bath to produce crystals of 4-hydroxyazobenzene
- the crystals are removed by filtration and dried.

(i) Why is the "minimum volume of hot solvent" used?

(1)

....

....

....

(ii) The impure 4-hydroxyazobenzene may contain both insoluble and soluble impurities. Describe how

(2)

I. insoluble impurities are removed during recrystallization

....

....

....

II. soluble impurities are removed during recrystallization

....

....

....

(iii) How would you check the purity of 4-hydroxyazobenzene after recrystallization, other than by using spectroscopy?

(1)

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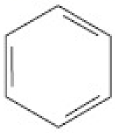
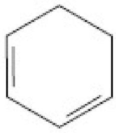
(Total for Question = 15 marks)

Q7. Bromine reacts with benzene on heating in the presence of a catalyst and with cyclohexa-1,3-diene in the cold. The types of reaction involved are

	bromine with benzene 	bromine with cyclohexa-1,3-diene 
☒ **A**	addition	addition
☒ **B**	addition	substitution
☒ **C**	substitution	addition
☒ **D**	substitution	substitution

(Total for Question = 1 mark)

Week 10

Rates and equilibria

3.2.2 Reaction rates

(a) the effect of concentration, including the pressure of gases, on the rate of a reaction, in terms of frequency of collisions					
(b) calculation of reaction rate from the gradients of graphs measuring how a physical quantity changes with time					
(c) explanation of the role of a catalyst: **(i)** in increasing reaction rate without being used up by the overall reaction **(ii)** in allowing a reaction to proceed via a different route with lower activation energy, as shown by enthalpy profile diagrams					
(d) **(i)** explanation of the terms *homogeneous* and *heterogeneous* catalysts **(ii)** explanation that catalysts have great economic importance and benefits for increased sustainability by lowering temperatures and reducing energy demand from combustion of fossil fuels with resulting reduction in CO_2 emissions					
(e) the techniques and procedures used to investigate reaction rates including the measurement of mass, gas volumes and time					
(f) qualitative explanation of the Boltzmann distribution and its relationship with activation energy **(see also 3.2.1 c)**					
(g) explanation, using Boltzmann distributions, of the qualitative effect on the proportion of molecules exceeding the activation energy and hence the reaction rate, for: **(i)** temperature changes **(ii)** catalytic behaviour **(see also 3.2.2 c)**.					

3.2.3 Chemical equilibrium

(a) explanation that a dynamic equilibrium exists in a closed system when the rate of the forward reaction is equal to the rate of the reverse reaction and the concentrations of reactants and products do not change					
(b) le Chatelier's principle and its application for homogeneous equilibria to deduce qualitatively the effect of a change in temperature, pressure or concentration on the position of equilibrium					
(c) explanation that a catalyst increases the rate of both forward and reverse reactions in an equilibrium by the same amount resulting in an unchanged position of equilibrium					
(d) the techniques and procedures used to investigate changes to the position of equilibrium for changes in concentration and temperature					
(e) explanation of the importance to the chemical industry of a compromise between chemical equilibrium and reaction rate in deciding the operational conditions					
(f) expressions for the equilibrium constant, K_c , for homogeneous reactions and calculations of the equilibrium constant, K_c , from provided equilibrium concentrations					
(g) estimation of the position of equilibrium from the magnitude of K_c.					

5.1 Rates, equilibrium and pH

5.1.1 How fast?

Orders, rate equations and rate constants (a) explanation and use of the terms: *rate of reaction, order, overall order, rate constant, half-life, rate-determining step*					
(b) deduction of: (i) orders from experimental data (ii) a rate equation from orders of the form: rate = $k[A]^m[B]^n$, where m and n are 0, 1 or 2					
(c) calculation of the rate constant, k, and related quantities, from a rate equation including determination of units					
Rate graphs and orders					
(d) from a concentration–time graph: (i) deduction of the order (0 or 1) with respect to a reactant from the shape of the graph (ii) calculation of reaction rates from the measurement of gradients					

(e) from a concentration–time graph of a first order reaction, measurement of constant half-life, $t_{1/2}$					
(f) for a first order reaction, determination of the rate constant, *k*, from the constant half-life, $t_{1/2}$, using the relationship: $k = \ln 2/t_{1/2}$					
(g) from a rate–concentration graph: (i) deduction of the order (0, 1 or 2) with respect to a reactant from the shape of the graph (ii) determination of rate constant for a first order reaction from the gradient					
(h) the techniques and procedures used to investigate reaction rates by the initial rates method and by continuous monitoring, including use of colorimetry					
Rate-determining step					
(i) for a multi-step reaction, prediction of, (i) a rate equation that is consistent with the rate-determining step (ii) possible steps in a reaction mechanism from the rate equation and the balanced equation for the overall reaction					
Effect of temperature on rate constants					
(j) a qualitative explanation of the effect of temperature change on the rate of a reaction and hence the rate constant					
(k) the Arrhenius equation: (i) the exponential relationship between the rate constant, *k* and temperature, *T* given by the Arrhenius equation, $k = Ae^{-E_a/RT}$ ii) determination of E_a and *A* graphically using: $\ln k = -E_a/RT + \ln A$ derived from the Arrhenius equation.					

5.1.2 How far?

Equilibrium (a) use of the terms *mole fraction* and *partial pressure*					
(b) calculation of quantities present at equilibrium, given appropriate data					
(c) the techniques and procedures used to determine quantities present at equilibrium					
(d) expressions for Kc and Kp for homogeneous and heterogeneous equilibria					
(e) calculations of Kc and Kp, or related quantities, including determination of units					
(f) (i) the qualitative effect on equilibrium constants of changing temperature for exothermic and endothermic reactions (ii) the constancy of equilibrium constants with changes in concentration, pressure or in the presence of a catalyst					
(g) explanation of how an equilibrium constant controls the position of equilibrium on changing concentration, pressure and temperature					
(h) application of the above principles in 5.1.2 How far? for Kc , Kp to other equilibrium constants, where appropriate					

Equilibrium

Key Recall Question	Answer
1. Name 3 features of dynamic equilibria	closed system, rate of forwards reaction = rate of reverse reaction, reversible reaction, constant temp
2. State Le chatelier's principle	if a reaction at eqm is subject to change in conc/pressure/temp the position of the eqm will move to counteract the change.
3. Describe how a dynamic equilibrium with an exothermic forwards reaction will react to an increase in temperature	shift to left/shift towards reactants because endothermic reaction will reverse the temp increase
4. Describe how a dynamic eqm will react if more reactant is added	shift to right/towards products to use up the reactant and restore balance
5. Describe how a catalyst affects a dynamic equilibrium	speeds up both reactions, position of equilibrium/yield does not change
6. Describe how an increase in pressure will affect this reaction: $3H_{2(g)} + N_{2(g)}$ -> $2NH_{3(g)}$ deltaH = -92kJ/mol	shift to right/products because there are fewer moles of gas (2) in products than reactants (4)
7.Why is the reaction for making ammonia done at 'compromise' conditions for pressure and temperature	High pressure increases yield but is expensive and less safe, low temperature increases yield but is too slow, so medium temp and pressure used.
8. Derive the expression for Kc with units for: 2A + B → C + 3D	$Kc = [C][D]^3 / [A]^2[B]$ units = mol dm^{-3} (units cancel out depending on numbers)

Question	Date:	Date:	Date:	Date:	Date:	Date:	Date:	Date:	Date:	Date:	Date:	Date:	Date:
1													
2													
3													
4													
5													
6													
7													
8													

Questions

Q1.

The first stage in the manufacture of nitric acid is the oxidation of ammonia:

$$4NH_3(g) + 5O_2(g) \rightleftharpoons 4NO(g) + 6H_2O(g) \quad \Delta H = -906 \text{ kJ mol}^{-1}$$

(a) In modern industrial plants this reaction is carried out at a pressure of around 3 atm. Which of the following statements is **incorrect**? The raised pressure

(1)

- ☐ **A** helps push the reactants through the reactor.
- ☐ **B** shifts the position of equilibrium to the right.
- ☐ **C** increases the cost of the reactor.
- ☐ **D** increases the energy cost of this part of the process.

(b) A platinum-rhodium alloy catalyst is used in this reaction. Which of the following statements is **incorrect**? The catalyst

(1)

- ☐ **A** lowers the activation energy of the reaction.
- ☐ **B** has no effect on the equilibrium constant for the reaction.
- ☐ **C** alters the enthalpy change of the reaction.
- ☐ **D** reduces the energy cost of this part of the process.

(c) The operating temperature of this reaction is about 900°C. The use of a high temperature

(1)

- ☐ **A** increases the rate of the reaction and the equilibrium yield.
- ☐ **B** increases the rate of the reaction and decreases the equilibrium yield.
- ☐ **C** decreases the rate of the reaction and the equilibrium yield.
- ☐ **D** decreases the rate of the reaction and increases the equilibrium yield.

(Total for Question = 3 marks)

Q2.

Bromate(V) ions, BrO_3^-, oxidize bromide ions, Br^-, in the presence of dilute acid, H^+, as shown in the equation below.

$$BrO_3^-(aq) + 5Br^-(aq) + 6H^+(aq) \rightarrow 3Br_2(aq) + 3H_2O(l)$$

Three experiments were carried out using different initial concentrations of the three reactants.
The initial rate of reaction was calculated for each experiment.
The results are shown in the table below.

Experiment number	$[BrO_3^-(aq)]$ / mol dm^{-3}	$[Br^-(aq)]$ / mol dm^{-3}	$[H^+(aq)]$ / mol dm^{-3}	Initial rate of reaction / mol dm^{-3} s^{-1}
1	0.050	0.25	0.30	1.68×10^{-5}
2	0.050	0.25	0.60	6.72×10^{-5}
3	0.15	0.50	0.30	1.01×10^{-4}

*(a) (i) This reaction is first order with respect to $BrO_3^-(aq)$. State, with reasons, including appropriate experiment numbers, the order of reaction with respect to

(5)

$H^+(aq)$

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$Br^-(aq)$

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(ii) Write the rate equation for the reaction.

(1)

(iii) Use the data from experiment 1 and your answer to (a)(ii) to calculate the value of the rate constant. Include units in your answer.

(3)

(b) What evidence suggests that this reaction proceeds by more than one step?

(1)

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(c) The initial rate of reaction was obtained from measurements of the concentration of bromine at regular time intervals. How is the **initial** rate of formation of bromine calculated from a concentration-time graph?

(2)

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(Total for question = 12 marks)

Q3.
The ionic equation for the reaction of ammonium peroxodisulfate (persulfate), $(NH_4)_2S_2O_8$, with potassium iodide, KI, is

$$S^2O^{82-}(aq) + 2I^-(aq) \rightarrow 2SO_4^{2-}(aq) + I_2(aq)$$

(a) In a series of experiments to determine the rate equation for this reaction, 10 cm^3 of 0.0050 mol dm^{-3} sodium thiosulfate was mixed with 20 cm^3 of $(NH_4)_2S_2O_8$ solution and 5 drops of starch solution. 20 cm^3 of KI solution was added with mixing and the time taken for the solution to darken was noted. The initial concentrations of the $(NH_4)_2S_2O_8$ and KI solutions and the times for the mixture to darken are shown below.

Experiment Number	Initial concentration / mol dm^{-3}		Time for solution to darken / s
	$S_2O_8^{2-}$	I^-	
1	0.10	0.20	35
2	0.05	0.20	69
3	0.10	0.10	70

(i) Explain the purpose of the sodium thiosulfate solution.

(2)

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(ii) Use the data in the table to deduce the rate equation for the reaction between $S_2O_8^{2-}$ and I^- ions. Explain, by referring to the data, how you arrived at your answer.

(3)

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(b) A further experiment was carried out to confirm the order of the reaction with respect to iodide ions. $(NH_4)_2S_2O_8$ was mixed with KI to form a solution in which the initial concentration of $(NH_4)_2S_2O_8$ was 2.0 mol dm^{-3} and that of KI was 0.025 mol dm^{-3}. The concentration of iodine was measured at various times until the reaction was complete.

(i) Outline a method, **not** involving sampling the mixture, which would be suitable for measuring the iodine concentrations in this experiment. Experimental details are not required but you should state how you would use your measurements to obtain iodine concentrations.

(3)

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(ii) Explain why the initial concentration of $(NH_4)_2S_2O_8$ is much higher than that of KI.

(1)

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(iii) State how the initial rate of reaction may be obtained from the results of this type of experiment.

(2)

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(iv) In such an experiment a student calculated the initial rate of reaction to be 8.75×10^{-5} mol dm^{-3} s^{-1}. Use this value, the initial concentrations in (b) and the rate equation that you obtained in (a)(ii), to calculate the rate constant for this reaction. Include units in your answer.

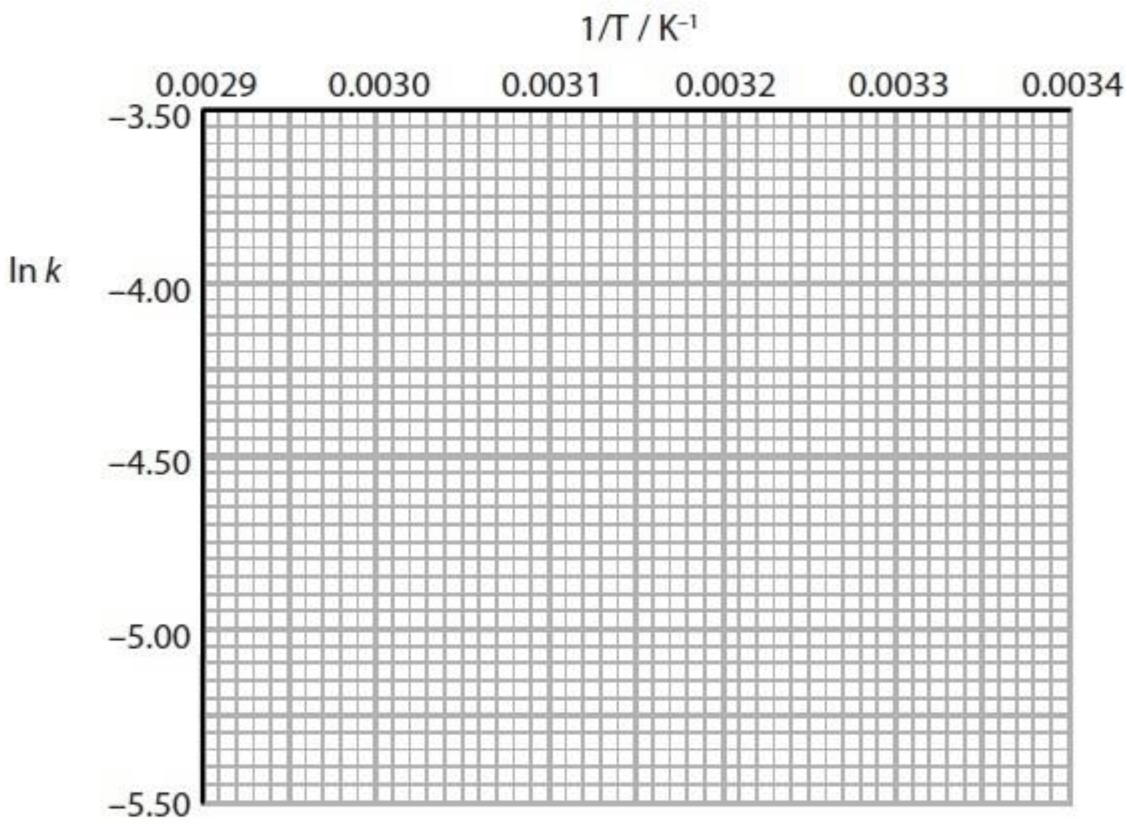
(2)

(c) Using the method outlined in (b), the rate constant for this reaction was determined at various temperatures. The data from these experiments are shown in the table below. Note that none of the temperatures corresponds to that used in (b) and that the rate constant is given in appropriate units.

Temperature T / K	Rate constant *k*	ln *k*	1/T / K^{-1}
300	0.00513	–5.27	0.00333
310	0.00833	–4.79	0.00323
320	0.0128	–4.36	0.00313
330	0.0201	–3.91	0.00303
340	0.0301	–3.50	0.00294

(i) Use the data in the table to plot a graph of ln *k* (on the y axis) against 1/T (on the x axis) and draw a best fit line through the points.

(2)



(ii) Determine the gradient of the best fit line in (c)(i) and use this value to calculate the activation energy,

E_a, of the reaction, stating the units.

(4)

The rate constant of a reaction, *k*, is related to the temperature, T, by the expression

$$\ln k = -\frac{E_a}{R} \times \frac{1}{T} + \text{constant} \qquad R = 8.31\ J\ K^{-1}\ mol^{-1}$$

(Total for Question = 19 marks)

Q4.
The reaction between concentrated sulfuric acid and pure ethanoic acid is

$$CH_3COOH + H_2SO_4 \rightleftharpoons CH_3COOH_2^+ + HSO_4^-$$

The Brønsted-Lowry acids in this equilibrium are

☐ **A** CH_3COOH and H_2SO_4

☐ **B** CH_3COOH_2 + and HSO_4^-

☐ **C** H_2SO_4 and $CH_3COOH_2^+$

☐ **D** CH_3COOH and HSO_4^-

(Total for Question = 1 mark)

Q5.

(a) Sea water is a source of chemicals. The most abundant chemical dissolved in sea water is sodium chloride. Compounds of magnesium and bromine are also present. Magnesium occurs at 1300 parts per million (ppm) and bromine at 60 ppm by mass.

The solution left after crystallizing sodium chloride from sea water is even richer in bromine, and contains around 2.2 g dm^{-3} of bromine.

Bromine is extracted from this solution by passing in chlorine gas. The mixture is acidified to prevent hydrolysis of bromine by the reaction

$$Br_2(aq) + H_2O(l) \rightleftharpoons 2H^+(aq) + Br^-(aq) + BrO^-(aq)$$

The bromine can be separated by heating the solution to collect bromine vapour which is then condensed, or by blowing air through the solution.

(i) Show by calculation that a solution containing 2.2 g dm^{-3} of bromine is richer in bromine than one containing 60 ppm.

[Assume that the mass of 1 dm^3 of the bromine solution is 1000 g]

(1)

(ii) Write an ionic equation, including state symbols, for the reaction in which chlorine gas reacts with bromide ions in solution to produce bromine.

(2)

(iii) What would be observed when the reaction in (ii) occurs?

(1)

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(iv) Explain why the addition of an acid, such as hydrochloric acid, prevents hydrolysis of bromine.

(2)

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(v) Assuming the hydrolysis of bromine is endothermic, explain how an increase in temperature would affect the equilibrium position for the hydrolysis of bromine.

(2)

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(vi) Use your knowledge of activation energy to explain why an increase in temperature increases the rate of hydrolysis of bromine.

(1)

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(vii) Use the equation for the hydrolysis of bromine to show that it is a disproportionation reaction.

$$Br_2(aq) + H_2O(l) \rightleftharpoons 2H^+(aq) + Br^-(aq) + BrO^-(aq)$$

(2)

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(b) At the surface of the sea, there is a dynamic equilibrium between carbon dioxide gas in air and dissolved carbon dioxide in the surface sea water.

$$CO_2(g) \; CO_2(aq)$$

(i) State **two** features of a system which has reached dynamic equilibrium.

(2)

1. ....

....

....

2. ....

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*(ii) Carbon dioxide dissolves more easily in seawater than in pure water because seawater contains carbonate ions, $CO_3^{2-}(aq)$, and the following reaction occurs.

$$CO_2(aq) + H_2O(l) + CO_3^{2-}(aq) \rightleftharpoons 2HCO_3^{-}(aq)$$

Explain how an increase in concentration of carbonate ions in sea water affects the amount of carbon dioxide gas in the atmosphere.

(2)

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(iii) Carbon dioxide and water vapour both contain polar bonds.

What effect does infrared radiation have on the bonds in these molecules?

(1)

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*(iv) Outline the mechanism by which molecules such as carbon dioxide and water cause global warming.

(2)

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*(v) Without water vapour in the atmosphere, the earth would be many degrees colder than it is at present. Why are many climate change scientists more concerned about warming due to carbon dioxide in the atmosphere, than warming due to the presence of water vapour? Refer to the difference between anthropogenic climate change and natural climate change in your answer.

(4)

(Total for Question = 22 marks)

Q6.

The decomposition of hydrogen iodide to form iodine and hydrogen is an equilibrium reaction.

$$2HI(g) \rightleftharpoons I_2(g) + H_2(g)$$

The equilibrium was investigated by taking sealed tubes containing the same mass of hydrogen iodide and heating them at 700 K for some time. At this temperature, the equilibrium takes about two days to be established.

The tubes were rapidly cooled to room temperature, which maintained the equilibrium concentrations, because at this temperature the reaction is extremely slow.

Each tube was opened under an aqueous solution of potassium iodide, which dissolved the hydrogen iodide and the iodine. The amount of iodine was found by titration and the composition of the equilibrium mixture calculated. From the number of moles of each substance at equilibrium, and the volume of the tubes, the equilibrium concentrations were calculated.

(a) (i) How would the appearance of the contents of a tube change as it was cooled to room temperature?

(2)

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....

(ii) How could you show that equilibrium had been established?

(2)

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(b) The equilibrium concentrations of one experiment are shown in the table below.

[HI] /mol dm^{-3}	[H_2] /mol dm^{-3}	[I_2] /mol dm^{-3}
0.00353	0.00048	0.00048

*(i) The volume of the tube in this experiment was 30 cm^3. Calculate the initial mass of hydrogen iodide. Show your working.

(5)

(ii) Write an expression for the equilibrium constant, K_c, at 700 K.

(1)

(iii) Calculate the value for this equilibrium constant.

(1)

(iv) Does this equilibrium constant have units? Explain your answer.

(1)

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(c) The equation for the reaction at 700 K can also be written

$$HI(g) \rightleftharpoons \frac{1}{2}H_2(g) + \frac{1}{2}I_2(g)$$

(i) Write the equilibrium constant, K_c', for this reaction.

(1)

(ii) Using the same equilibrium concentrations as below, calculate the equilibrium constant, K_c'. Deduce the relationship between this value and the value calculated in part (b)(iii).

(2)

[HI] /mol dm^{-3}	[H_2] /mol dm^{-3}	[I_2] /mol dm^{-3}
0.00353	0.00048	0.00048

(d) Consider the following equilibrium reaction.

$$2HI(g) \rightleftharpoons I_2(s) + H_2(g)$$

For this reaction $K_p = \frac{P_{H_2}}{P_{HI}^2}$

Use the expression for K_p to explain the effect of an increase in total pressure on the position of the equilibrium.

(3)

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(Total for question = 18 marks)

Q7.

This question is about an experiment to determine the equilibrium constant, K_c, for the reaction between ethanoic acid and ethanol to form ethyl ethanoate and water.

Two sealed test tubes were prepared.

The first test tube contained 0.0400 mol ethanoic acid, 0.0400 mol of ethanol and 0.20 cm^3 of concentrated hydrochloric acid.

The second test tube contained 0.0400 mol ethyl ethanoate, 0.0400 mol of water and 0.20 cm^3 of concentrated hydrochloric acid.

After standing at 25°C for two weeks, to ensure equilibrium is reached, the contents of each test tube were separately titrated with 0.200 mol dm^{-3} sodium hydroxide solution.

0.20 cm^3 of concentrated hydrochloric acid was also titrated with the same sodium hydroxide solution.

(a) (i) Using data from the Data Booklet, calculate the volume, in cm^3, of 0.0400 mol of ethanoic acid.

(2)

(ii) What would be the best piece of apparatus to measure out the volumes of the liquids for the sealed test tubes?

(1)

....

(iii) Suggest a reason why the test tubes were sealed.

(1)

....

....

(iv) Suggest a suitable indicator for the titration of the equilibrium mixture in either test tube, with the expected colour change. Justify your suggestion.

(3)

Indicator

....

Colour change from .... to ....

Justification

....

....

(b) In this experiment, the following titres were obtained.

Titration	Volume of 0.200 mol dm^{-3} sodium hydroxide solution/cm^3
Contents of first test tube	77.10
Contents of second test tube	77.05
0.20 cm^3 concentrated hydrochloric acid	11.70

(i) Write the equation for the reaction between ethanoic acid and ethanol to form ethyl ethanoate and water, using structural formulae. State symbols are not required.

(1)

(ii) Calculate the number of moles of ethanoic acid present at equilibrium in the first test tube.

(2)

(iii) Deduce the number of moles of ethanol present at equilibrium in the first test tube.

(1)

(iv) Calculate the number of moles of ethyl ethanoate formed at equilibrium in the first test tube.

(1)

(v) Write an expression for the equilibrium constant, K_c, for the reaction.
Assuming the number of moles of water and ethyl ethanoate present at equilibrium are the same, calculate the equilibrium constant, K_c.

(2)

(vi) Explain why the equilibrium constant for this reaction has no units.

(1)

....

....

(vii) Why, in fact, is the number of moles of water present in the equilibrium mixture greater than the number of moles of ethyl ethanoate?

(1)

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....

(c) (i) What is the type of reaction that took place in each test tube?

(2)

First test tube

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Second test tube

....

*(ii) Comment on the value of the titre for the equilibrium mixture in the second test tube compared to the first test tube.
What characteristic feature of equilibrium reactions is demonstrated by the values of these titres?

(2)

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(iii) State the role of the concentrated hydrochloric acid in the equilibrium reaction.

(1)

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....

(Total for question = 21 marks)

Q8.

Carbon monoxide and chlorine react together and reach equilibrium:

$$CO(g) + Cl_2(g) \rightleftharpoons COCl_2(g)$$

If the pressure of the system is then **increased** at constant temperature, which of the following statements is correct?

☐ **A** The equilibrium moves to the left and K_p decreases.

☐ **B** The equilibrium moves to the right and K_p increases.

☐ **C** The equilibrium moves to the right, then back to the left and K_p remains the same.

☐ **D** The equilibrium moves to the right and K_p remains the same.

(Total for question = 1 mark)

Q9.

An important step in the production of sulfuric acid is the oxidation of sulfur dioxide.

$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$ $\Delta H = -196$ kJ mol^{-1}

Which of the conditions below is best suited to produce a high yield of sulfur trioxide, SO_3?

☐ **A** 1 atm pressure and 800 °C.

☐ **B** 2 atm pressure and 800 °C.

☐ **C** 1 atm pressure and 400 °C.

☐ **D** 2 atm pressure and 400 °C.

(Total for Question = 1 mark)

Q10.
This question is about the equilibrium reaction below.

$$Fe^{2+}(aq) + Ag^{+}(aq) \rightleftharpoons Fe^{3+}(aq) + Ag(s)$$

The equilibrium is reached slowly.

*(a) Describe the changes you would see if aqueous solutions of iron(II) sulfate and silver nitrate were mixed and allowed to stand for a few hours.

(2)

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(b) The concentration of silver ions in the equilibrium mixture can be found by titration with potassium thiocyanate. Silver thiocyanate precipitates.

$$Ag^{+}(aq) + CNS^{-}(aq) \rightleftharpoons AgCNS(s)$$

When all the silver ions have reacted, a deep red complex ion of iron(III) thiocyanate forms.

In an experiment, 25.0 cm^3 of 0.100 mol dm^{-3} silver nitrate solution was added to 25.0 cm^3 of 0.100 mol dm^{-3} of iron(II) sulfate solution, mixed thoroughly, and allowed to stand overnight in an air-tight container.

10.0 cm^3 samples of the reaction mixture were then titrated with 0.0200 mol dm^{-3} potassium thiocyanate solution. The average titre was 5.60 cm^3.

(i) The initial concentrations of silver ions and iron(II) ions **in the reaction mixture** are the same.

Calculate this initial concentration in mol dm^{-3}.

(1)

(ii) Calculate the number of moles of silver ions in the 10.0 cm^3 sample at equilibrium and hence calculate the equilibrium concentration of silver ions in the mixture.

(2)

(iii) Deduce the equilibrium concentration of iron(II) ions.

(1)

(iv) Hence calculate the equilibrium concentration of iron(III) ions.

(1)

(v) Write the expression for the equilibrium constant, K_c, for the reaction

$$Fe^{2+}(aq) + Ag^{+}(aq) \rightleftharpoons Fe^{3+}(aq) + Ag(s)$$

Calculate its value and give your answer, with appropriate units, to **three** significant figures.

(4)

(c) (i) The relationship between the total entropy change for a reaction and the equilibrium constant is

$$\Delta S^{\ominus}_{total} = R \ln K$$

Calculate the total entropy change for this reaction, giving a sign and appropriate units.

[R = 8.31 J mol^{-1} K^{-1}]

(2)

(ii) $Fe^{2+}(aq) + Ag^{+}(aq) \rightleftharpoons Fe^{3+}(aq) + Ag(s)$

for this reaction is −208.3 J mol^{-1} K^{-1}

Use ideas about entropy to explain why this value is negative.

(2)

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(iii) Calculate the entropy change of the surroundings, $\Delta S^{\ominus}_{surroundings}$.

(1)

(iv) Use your answer to (c)(iii) to calculate the standard enthalpy change, $\Delta H^{\ominus}$, for this reaction at 298 K.

Hence state and explain the effect of increasing temperature on the value of $\Delta S^{\ominus}_{system}$

(3)

Week 11

Redox and transition metals

2.1.5 Redox

(a) rules for assigning and calculating oxidation number for atoms in elements, compounds and ions					
(b) writing formulae using oxidation numbers					
(c) use of a Roman numeral to indicate the magnitude of the oxidation number when an element may have compounds/ions with different oxidation numbers					
(d) oxidation and reduction in terms of: **(i)** electron transfer **(ii)** changes in oxidation number					
(e) redox reactions of metals with acids to form salts, including full equations **(see also 2.1.4 c)**					
(f) interpretation of redox equations in **(e)**, and unfamiliar redox reactions, to make predictions in terms of oxidation numbers and electron loss/ gain.					
(g) interpret and make predictions from redox equations in terms of oxidation numbers and electron loss/gain					

5.2.3 Redox and electrode potentials

Redox (a) explanation and use of the terms *oxidising agent* and *reducing agent*					
(b) construction of redox equations using half equations and oxidation numbers					
(c) interpretation and prediction of reactions involving electron transfer					
Redox titrations (d) the techniques and procedures used when carrying out redox titrations including those involving Fe^{2+}/MnO_4^- and $I_2/S_2O_3^{2-}$					
(e) structured and non-structured titration calculations, based on experimental results of redox titrations involving: (i) Fe^{2+}/MnO_4^- and $I_2/S_2O_3^{2-}$ (ii) non-familiar redox systems					
Electrode potentials (f) use of the term standard electrode (redox) potential, $E^⦵$ including its measurement using a hydrogen electrode					
(g) the techniques and procedures used for the measurement of cell potentials of: (i) metals or non-metals in contact with their ions in aqueous solution (ii) ions of the same element in different oxidation states in contact with a Pt electrode					
(h) calculation of a standard cell potential by combining two standard electrode potentials					
(i) prediction of the feasibility of a reaction using standard cell potentials and the limitations of such predictions in terms of kinetics and concentration					
Storage and fuel cells (j) application of principles of electrode potentials to modern storage cells					
(k) explanation that a fuel cell uses the energy from the reaction of a fuel with oxygen to create a voltage and the changes that take place at each electrode.					

5.3 Transition elements
5.3.1 Transition elements

Properties (a) the electron configuration of atoms and ions of the d-block elements of Period 4 (Sc–Zn), given the atomic number and charge					
(b) the elements Ti–Cu as transition elements i.e. d-block elements that have an ion with an incomplete d-sub-shell					
(c) illustration, using at least two transition elements, of: (i) the existence of more than one oxidation state for each element in its compounds (see also 5.3.1 k) (ii) the formation of coloured ions (see also 5.3.1 h, j–k) (iii) the catalytic behaviour of the elements and their compounds and their importance in the manufacture of chemicals by industry					
Ligands and complex ions					

(d) explanation and use of the term ligand in terms of coordinate (dative covalent) bonding to a metal ion or metal, including bidentate ligands					
(e) use of the terms complex ion and coordination number and examples of complexes with: (i) six-fold coordination with an octahedral shape (ii) four-fold coordination with either a planar or tetrahedral shape					
(f) types of stereoisomerism shown by complexes, including those associated with bidentate and multidentate ligands: (i) cis–trans isomerism e.g. $Pt(NH_3)_2Cl_2$ (see also 4.1.3 c–d) (ii) optical isomerism e.g. $[Ni(NH_2CH_2CH_2NH_2)_3]^{2+}$					
(g) use of cis-platin as an anti-cancer drug and its action by binding to DNA preventing cell division					
Ligand substitution (h) ligand substitution reactions and the accompanying colour changes in the formation of: (i) $[Cu(NH_3)_4(H_2O)_2]^{2+}$ and $[CuCl_4]^{2-}$ from $[Cu(H_2O)_6]^{2+}$ (ii) $[Cr(NH_3)_6]^{3+}$ from $[Cr(H_2O)_6]^{3+}$					
(i) explanation of the biochemical importance of iron in haemoglobin, including ligand substitution involving O_2 and CO					
Precipitation reactions (j) reactions, including ionic equations, and the accompanying colour changes of aqueous Cu^{2+}, Fe^{2+}, Fe^{3+}, Mn^{2+} and Cr^{3+} with aqueous sodium hydroxide and aqueous ammonia, including: (i) precipitation reactions (ii) complex formation with excess aqueous sodium hydroxide and aqueous ammonia					
Redox reactions (k) redox reactions and accompanying colour changes for: (i) interconversions between Fe^{2+} and Fe^{3+} (ii) interconversions between Cr^{3+} and $Cr_2O_7{}^{2-}$ (iii) reduction of Cu^{2+} to Cu^+ and disproportionation of Cu^+ to Cu^{2+} and Cu					
(l) interpretation and prediction of unfamiliar reactions including ligand substitution, precipitation, redox.					

Electrochemistry 1

Key Recall Question	Answer
1. What are the three types of half cell?	Metal, gas, redox (the one with two solutions)
2. What metal is often used in gas and redox half cells and why?	Platinum, inert (unreactive), conducts elect
3. What does the electrode potential of a half cell tell you?	Whether the equilibrium lies to the left (negative) or to the right (positive) relative to the standard hydrogen electrode
4. What is the standard hydrogen electrode (SHE)?	Gas electrode, 1M solution of H+ ions, Pt electrode, standard conditions.
5. What is the electrode potential of the SHE and why?	0. Set by convention and all others compared to it.
6. What is the electrochemical series?	List of standard electrode potentials
7. What does $E^{\ominus}$ mean? i.e. what are standard conditions?	Standard electrode potential, $E^{\ominus}$, refers to conditions of 298 K, 100 kPa and 1.00 mol dm^{-3} solution of ions.
8. How do you work out E_{cell} (the electron-motive force, emf) if two half cells joined to make a cell?	$E_{cell} = E_{right} - E_{left}$ = most positive – most negative (aka biggest gap)
9. Which way round should an electrochemical cell be set up?	Most negative half cell on left (OR standard hydrogen electrode)
10. How are electrochemical cells represented?	ROOR! | = phase difference || = salt bridge Pt = electrode e.g. Pt|Fe2+,Fe3+||Cu2+|Cu
11. How do you work out the overall reaction for an electrochemical cell?	The one with the more negative $E^{\ominus}$ will go 'backwards' (to produce electrons), the one with the more positive $E^{\ominus}$ will go forwards
12. How can concentration affect E_{cell}?	The half cell equilibrium will shift to oppose the change – if it moves left, the cell is relatively more negative and vice versa. This will change the size of E_{cell}.

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Electrochemistry 2 – Commercial Cells

Key Recall Question	Answer
1. What are the types of commercial cell?	Non-rechargeable, rechargeable,fuel cells
2. What does 'battery' mean?	Several cells joined together
3. How do non-rechargeable cells work? Give an example and a pro and con.	The chemicals are used up over time and emf drops (battery goes flat), can't be recharged. Zinc-carbon, alkaline. + cheap - waste
4. How do rechargeable cells work? Give an example and a pro and con.	The overall reaction is reversible, a electric current can be applied to reverse the reaction and regenerate the chemicals e.g. lithium ion, lead-acid, nickel-cadmium +less waste, long term cost benefit, lower eco impact -some waste issues
5. How do fuel cells work? Give an example	They have a continuous supply of chemicals so never run out if kept supplied e.g. hydrogen oxygen fuel cell
6. How does pH affect the hydrogen-oxygen fuel cell?	The overall equation and emf are the same, half equations differ
7. What are the advantages of hydrogen-oxygen fuel cell?	Very efficient, only give off water as waste product, no need to recharge
8. What are the disadvantages of hydrogen-oxygen fuel cell?	Need constant supply of fuels, hydrogen flammable/explosive, hydrogen usually from fossil fuels, expensive

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Transition Metals 1 – basics, shapes, isomers

Key Recall Question	Answer
1. What are the rules for working out electron substructures?	Lowest energy orbital fills first. Two electrons per orbital. 4s fills AND empties before 3d.
2. What are the two exception elements?	Cr $[Ar]4s^1 3d^5$ and Cu: $[Ar]4s^1 3d^{10}$
3. Define a transition metal	Element that has an incomplete d subshell in its atom or one of its common ions
4. What 4 properties make transition metals unusual (and result from incomplete 3d)?	1. variable oxidation state, 2. Catalytic action 3. Coloured compounds, 4. Formation of complexes
5. What is a complex (ion)?	Metal ion with coordinate (dative) bonded ligands
6. What is a ligand?	Particle with a lone pair that can make a dative covalent bond to a metal ion
7. What is a Lewis base?	Lone pair donor (e.g . ligand bonding to a transition metal)
8. What is a Lewis acid	Lone pair acceptor e.g. transition metal attached to ligand)
9. What is coordination number?	The number of dative/coordinate bonds from ligand to metal ion
10. What are the shapes of complex ions with i) two ligands ii) 4 ligands (2 types, be specific) iii) 6 ligands	i) linear, bond angle 180 ii) square planar (cisplatin, Ni+ complexes) 90 or tetrahedral 109.5 (the rest) iii) octahedral (usu with small ligands)
11. What is meant by monodentate ligands? Give 3 examples	Can form one dative bond e.g. H2O, NH3, Cl-
12. What is meant by bidentate ligands? Give2 examples	Can form two dative bonds e.g. $H_2NCH_2CH_2NH_2$ and $C_2O_4^{2-}$
13. What is meant by multidentate ligands? Give 1 examples	Can form multiple dative bonds $EDTA^{4-}$
14. What is cis-trans isomerism?	Special case of E-Z isomerism seen in octahedral/square planar complexes where there are two ligands of the same type that differ from the others. Cis = same side, trans = opposite. Cisplatin is a cancer drug but not transplatin
15. When does optical isomerism happen with complexes?	Octahedral complex with 3 bidentate ligands

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Transition Metals 2 – Ligand Substitution

Key Recall Question	Answer
1. Define ligand substitution	When a ligand is replaced by another
2. How does substitution with similar sized ligands affect coordination number? Give example of similar sized ligands	Does not change, e.g. H2O and NH3 are similar sizes so same number can fit around ion
3. How does substitution with different sized ligands affect coordination number? Give example of different sized ligands	It may change – will go down if larger ligand joins and vice versa. Cl- is bigger than water/NH3 so coordination number may drop from 6 to 4 as only 4 can fit on most ions.
4. What is the enthalpy change for most substitutions?	Negligible if the coordination number doesn't change
5. How do substitutions affect entropy?	If a bi/multidentate ligand replaces a monodentate ligand entropy will go up as the number of aqueous particles increases. (recall free energy equation).
6. Why is a monodentate ligand unlikely to replace a bidentate ligand?	Entropy will decrease so free energy means less feasible
7. What is the chelate effect?	The tendancy for ligands to be substituted for those that can form more coordinate bonds due to favourable entropy
8. What is a chelating agent?	A bi/multidentate ligand as they are good at bonding to ions and hard to remove due to entropy change being -ve.
9. Give an example of a chelating agent	$EDTA^{4-}$ as it forms 6 bonds
10. Why are chelating agents useful?	They can render a metal ion harmless as can't bond to anything else
11. What is haem and haemoglobin?	Haem= iron(II) complex with a multidentate ligand Haemoglobin – globular protein with 4 haem centres each with a porphyrn ligand taking up 4 out of 6 coordination sites
12. How does haemoglobin carry oxygen?	One of the unused sites can take an oxygen ligand (the other is bonded to the rest of the structure)
13. Why are CO and CN- poisonous?	They are better ligands than oxygen so will bond to the haemoglobin more easily.
14. Must all ligands be substituted at once?	No, it can be incomplete. (eg the formation of $[Cu(NH_3)_4(H_2O)_2]^{2+}$)

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Transition Metals 3 – Formation of Coloured Ions

Key Recall Question	Answer
1.How can transition metals be identified?	By their colour
2. Why are transition metal compounds coloured? (3 items)	1. the 5 d orbitals do not have the same energy 2. The gap in energy corresponds to the energy of UV/visible light. 3. Electrons absorb light and become excited.
3. How is the energy difference between ground state and excited state worked out?	$\Delta E = h\nu = hc/\lambda$ (where ΔE= *change in energy, h= plancks constant,* Λ = wavelength, c = speed of light
4. What is the colour that is seen?	The colour that is NOT absorbed e.g. hydrated copper sulfate is blue because the other colours in white light are absorbed to promote d electrons and blue is reflected.
5. Which Transition metal ions are not coloured?	Zn^{2+} ([Ar] $3d^{10}$), Cu^{+} ([Ar] $3d^{10}$), Sc^{3+} ([Ar]) because they have full or empty d sub-shells
6. Which factors affect the colour?	Changes in oxidation state, co-ordination number and ligand alter ΔE and this leads to a change in colour.
7. How can the frequencies absorbed by a complex by measured?	With a uv/visible light spectrometer – pass UV/sisible ight through complex, the frequencies of light that pass through are detected. More concentration – more light absorption so can measure concentration.
8. What other method can be used to identify concentration? (4 steps)	Colorimetry. 1. The greater the conc, the greater the absorption. 2. A ligand can be added to intensify colour. 3. Coloured light is passed through the sample (a complementary colour to the compound is chosen e.g. blue compounds absorb red light). 4. A calibration curve is produced using known concentrations, conc of unknown solutions can be worked out from this .

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Transition Metals 4 – Variable Oxidation States

Key Recall Question	Answer
1. What is meant by 'variable' oxidation states?	Transition metal ions can have a range of oxidation states
2. How is this used to test for aldehydes?	1. Tollen's reagent $[Ag(NH_3)_2]^+$ is reduced to Ag in silver mirror. Aldehyde-> carboxylic acid but not ketones. 2. Fehling's solution Cu2+ reduced to brick red Cu2O in presence of aldehydes but not ketones.
3. How is this used for identifying aldehydes, primary and secondary alcohols?	Acidified $K_2Cr_2O_7$. Colour change from orange ($Cr_2O_7^{2-}$) to green (Cr^{3+}). Alcohol/aldehyde is oxidised.
4. What affects the redox potential of a transition metal	pH and ligands
5. How does pH affect ease of oxidation?	In general, it is easier to oxidise a transition metal in alkaline conditions/reduce a transition metal in acidic conditions (seen from electrode potentials)
6. Vanadium (V) can be reduced to…(which oxidation states and what reagents?	V(+4) to V(+3) to V(+2) in acidic conditions (hydrochloric acid or sulfuric acid) using zinc as the reducing agent.
7. What are the corresponding colours of these oxidation states?	(**Y**ou **B**etter **G**et **V**anadium) 5 = yellow, 4 = blue, 3 = green, 2 = violet
8. Why is a cotton wool plug used for the oxidation of vanadium?	To keep oxygen out, which would prevent V2+ being formed
9. Under what conditions will V2+ not form?	alkaline
10. Which substances can be titrated with acidified KMnO4 to work out concentration? (redox titration)	Fe^{2+}, $C_2O_4^{2-}$ and H_2O_2

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Transition Metals 5 – Catalysts and redox titations

Key Recall Question	Answer
1. For redox titrations with KMnO4, why can HCl not be used to acidify the solution?	the MnO_4^- would also oxidise Cl^- to Cl_2 so affect the volume of $KMnO_4$ required in the titration
2. For redox titrations with KMnO4, why can conc H2SO4 or HNO3 not be used to acidify?	They are oxidising agents and will affect the volume required
3. For redox titrations with KMnO4, why can ethanoic acid not be used to acidify the solution?	It's a weak acid, not enough H+
4. Which way round is the titration usually carried out?	Burette – purple KMnO4 Flask – sample + excess weak sulfuric acid
5. Why is an indicator not needed for redox titration with KMnO4?	It is self indicating. The KMnO4 is oxidised to Mn2+ (colourless), at the end point the sample has all reacted and the purple ions remain. End point = first hint of pink.
6. If Fe is not already in the 2+ oxidation state what is done?	Fe metal – react with sulfuric to make Fe2+ Fe3+ - reduce with zinc (remove zinc prior to titration)
7. Why must the reactants be warmed prior to redox titration with ethanedioate ion ($C_2O_4^{2-}$)	Reaction is slow as both ions are negative and repel.
8. Why does the redox titration with ethanedioate speed up as it progresses? (need to explain with aid of equations)	Initially, KMnO4 is slow to decolourise but Mn2+ is produced which catalyses the reaction (auto catalysis) • $4Mn^{2+} + MnO_4^- + 8H^+ \rightarrow 5Mn^{3+} + 4H_2O$ $2Mn^{3+} + C_2O_4^{2-} \rightarrow 2CO_2 + 2Mn^{2+}$
9. Why is Mn2+ a good catalyst?	It can easily cycle between 2+ and 3+
10. What is the word for reactions that produce their own catalyst?	Auto catalysis

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Transition Metals 6 – Catalysts

Key Recall Question	Answer
1. What is a catalyst?	Increases rate of a chemical reaction without being used up
2. How do catalysts work?	Provide an alternative route for the reaction with a lower activation energy.
3. What effect do catalysts have on delta G, H and S?	None
4. What effect do catalysts have on position of equilibrium?	None – they catalyse forwards and backwards reactions equally
5. What is a heterogeneous catalyst?	One that is in a different phase to the reactants e.g. solid catalyst for aqueous reactants e.g. Haber process, Contact
6. How does a heterogeneous catalyst work?	1+ reactant(s) **ad**sorbed onto surface at active site(s)
7. What makes an effective catalyst?	Reactants can move between active sites. Adsorption mustn't be too strong (molecules can't move around active sites and less likely to react e.g.W) or too weak (little effect e.g. Ag)
8. How does adsorption onto surface catalyse the reaction?	1. can increase local concentration of reactants 2. can weaken the bonds by straining them, so easier to break 3. may position the molecules in orientation that favours reaction
9. Why are Nickel and platinum good catalysts?	Adsorption is not too weak/strong
10. How can impact of a catalyst be increased?	Increase the surface area (catalysts often expensive)
11. What is catalyst poisoning?	Other substances adsorb and block the active site. This can be hard to undo – can be expensive. E.g. sulfur contamination of hydrogen in Haber process poisons Fe catalyst
12 Which catalyst is used in the Contact process (making sulfuric acid) – sorry you have to explain this with equations.	V_2O_5 catalyses the slow conversion of SO2 to SO3 1. $V_2O_5 + SO_2 \rightarrow V_2O_4 + SO_3$ 2. $V_2O_4 + 1/2 O_2 \rightarrow V_2O_5$ *Overall:* $SO_2 + 1/2\ O_2 \rightarrow SO_3$
13 How do reactions with homogenous catalysts work?	All are in same phase (usually solution); intermediate species is formed which further reacts and regenerates the catalyst.
14 How does a homogenous transition metal catalyst work?	The variable oxidation states
15 How do iron ions catalyse the reaction between iodone and peroxodisulfate	$2\ I^- + S_2O_8^{2-} \xrightarrow{Fe^{2+}/Fe^{3+}} I_2 + 2\ SO_4^{2-}$ main reaction is slow – 2 -ve ions. $2\ Fe^{2+} + S_2O_8^{2-} \rightarrow 2\ Fe^{3+} + 2\ SO_4^{2-}$ (sulfate reduced) 2Fe +2I → 2Fe +I_2 (Fe2+ regenerated) Fe3+ can be used instead and the reactions occur other way around)

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Questions

Q1.

A **heterogeneous** catalyst is often preferred to a **homogenous** catalyst for an industrial process because

☒ **A** it is easily separated from the products.

☒ **B** it has empty d-orbitals.

☒ **C** it has more than one oxidation state.

☒ **D** it cannot be poisoned.

(Total for question = 1 mark)

Q2.

(a) The following method was used to estimate the concentration of ethanol in an aqueous solution, **Q**, prepared by the fermentation of sucrose.

25 cm^3 of **Q** was measured using a pipette and transferred to a 250 cm^3 volumetric flask; the flask was made up to the mark with distilled water and mixed thoroughly, forming a diluted solution, **R**.

25 cm^3 samples of **R** were mixed with an equal volume of a 0.200 mol dm^{-3} potassium dichromate(VI) solution and excess dilute sulfuric acid.

The mixture was allowed to stand for several hours and then the amount of unreacted potassium dichromate(VI) was determined by titration against a 0.255 mol dm^{-3} iron(II) ammonium sulfate solution. The mean titre was 23.85 cm^3.

(i) Use the ionic half-equations below to write the full ionic equation for the reaction between potassium dichromate(VI) and iron(II) ammonium sulfate.

State symbols are not required.

(1)

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

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$$

(ii) Calculate the number of moles of potassium dichromate(VI) that remained **unreacted** after standing for several hours with solution **R**.

(2)

(iii) Calculate the number of moles of potassium dichromate(VI) that reacted with the ethanol while standing for several hours with solution **R**.

(2)

(iv) Write an ionic half-equation for the oxidation of ethanol to ethanoic acid.

Use your equation, and the half-equation for the reduction of dichromate(VI) ions, to show that 3 mol of ethanol are oxidized by 2 mol of potassium dichromate(VI).

(2)

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(v) Calculate the concentration of ethanol (in mol dm^{-3}) in solution **Q**.

(3)

*(b) The indicator used in this titration was barium diphenylamine sulfonate, which turns from deep purple to colourless at the end-point.

Identify the ion responsible for turning the indicator from deep purple to colourless at the end-point.

By considering the type of reaction involved when this ion reacts with barium diphenylamine sulfonate, suggest how barium diphenylamine sulfonate acts as an indicator in this titration. Note that complex formation does **not** occur. The detailed reactions of this particular indicator are **not** required.

(3)

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*(c) This method of determining ethanol concentration does not give very reliable results, although the titration is very accurate.

Suggest **one** reason why this might be the case, explaining how the measured concentration would differ from the actual concentration of the ethanol.

(3)

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(Total for question = 16 marks)

Q3.

The compound 1,2-diaminoethane, $H_2NCH_2CH_2NH_2$, is a bidentate ligand; in formulae, it is usually abbreviated to 'en'.

When 1,2-diaminoethane is added to $[Co(NH_3)_6]^{2+}$ in aqueous solution, $[Co(en)_3]^{2+}$ is formed. What is the **best** explanation for this?

☒ **A** There are much stronger bonds between the ligands and the cobalt(II) ion in $[Co(en)_3]^{2+}$ than in $[Co(NH_3)_6]^{2+}$.

☒ **B** When $[Co(en)_3]^{2+}$ is formed from $[Co(NH_3)_6]^{2+}$ the reaction is exothermic.

☒ **C** When $[Co(en)_3]^{2+}$ is formed from $[Co(NH_3)_6]^{2+}$ the total entropy change is positive.

☒ **D** When $[Co(en)_3]^{2+}$ is formed from $[Co(NH_3)_6]^{2+}$ the reaction has a low activation energy.

(Total for question = 1 mark)

Q4. The ligands that form complex ions are either neutral, like NH_3, or negatively charged, like CN^-. Nickel(II) ions, Ni^{2+}, form complexes with both these ligands. The bonding between Ni^{2+} and the ligands in these complexes is

		NH_3	CN^-
☒	**A**	dative covalent	dative covalent
☒	**B**	ionic	dative covalent
☒	**C**	dative covalent	ionic
☒	**D**	ionic	ionic

(Total for Question = 1 mark)

Q5. Which of the following physical methods of chemical analysis is used in modern breathalysers?

☒ **A** Infrared spectroscopy

☒ **B** Mass spectrometry

☒ **C** Nuclear magnetic resonance

☒ **D** Ultraviolet spectroscopy

(Total for Question = 1 mark)

Q6. In the manufacture of sulfuric acid, sulfur dioxide is converted to sulfur trioxide using a catalyst of vanadium(V) oxide:

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

The electronic configuration of vanadium is [Ar] $3d^3$ $4s^2$, so the mechanism for this reaction is most likely to involve a sequence in which vanadium(V) is converted to

☒ **A** vanadium(VI) by oxygen then back to vanadium(V) by sulfur dioxide.

☒ **B** vanadium(VI) by sulfur dioxide then back to vanadium(V) by oxygen.

☒ **C** vanadium(IV) by oxygen then back to vanadium(V) by sulfur dioxide.

☒ **D** vanadium(IV) by sulfur dioxide then back to vanadium(V) by oxygen.

(Total for Question = 1 mark)

Q7. (a) Sea water is a source of chemicals. The most abundant chemical dissolved in sea water is sodium chloride. Compounds of magnesium and bromine are also present. Magnesium occurs at 1300 parts per million (ppm) and bromine at 60 ppm by mass.

The solution left after crystallizing sodium chloride from sea water is even richer in bromine, and contains around 2.2 g dm^{-3} of bromine.

Bromine is extracted from this solution by passing in chlorine gas. The mixture is acidified to prevent hydrolysis of bromine by the reaction

$$Br_2(aq) + H_2O(l) \rightleftharpoons 2H^+(aq) + Br^-(aq) + BrO^-(aq)$$

The bromine can be separated by heating the solution to collect bromine vapour which is then condensed, or by blowing air through the solution.

(i) Show by calculation that a solution containing 2.2 g dm^{-3} of bromine is richer in bromine than one containing 60 ppm.

[Assume that the mass of 1 dm^3 of the bromine solution is 1000 g]

(1)

(ii) Write an ionic equation, including state symbols, for the reaction in which chlorine gas reacts with bromide ions in solution to produce bromine.

(2)

(iii) What would be observed when the reaction in (ii) occurs?

(1)

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(iv) Explain why the addition of an acid, such as hydrochloric acid, prevents hydrolysis of bromine.

(2)

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(v) Assuming the hydrolysis of bromine is endothermic, explain how an increase in temperature would affect the equilibrium position for the hydrolysis of bromine.

(2)

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(vi) Use your knowledge of activation energy to explain why an increase in temperature increases the rate of hydrolysis of bromine.

(1)

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(vii) Use the equation for the hydrolysis of bromine to show that it is a disproportionation reaction.

$$Br_2(aq) + H_2O(l) \rightleftharpoons 2H^+(aq) + Br^-(aq) + BrO^-(aq)$$

(2)

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(b) At the surface of the sea, there is a dynamic equilibrium between carbon dioxide gas in air and dissolved carbon dioxide in the surface sea water.

$$CO_2(g)\ CO_2(aq)$$

(i) State **two** features of a system which has reached dynamic equilibrium.

(2)

1. ....

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2. ....

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*(ii) Carbon dioxide dissolves more easily in seawater than in pure water because seawater

contains carbonate ions, $CO_3^{2-}(aq)$, and the following reaction occurs.

$$CO_2(aq) + H_2O(l) + CO_3^{2-}(aq) \rightleftharpoons 2HCO_3^{-}(aq)$$

Explain how an increase in concentration of carbonate ions in sea water affects the amount of carbon dioxide gas in the atmosphere.

(2)

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(iii) Carbon dioxide and water vapour both contain polar bonds.

What effect does infrared radiation have on the bonds in these molecules?

(1)

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*(iv) Outline the mechanism by which molecules such as carbon dioxide and water cause global warming.

(2)

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*(v) Without water vapour in the atmosphere, the earth would be many degrees colder than it is at present. Why are many climate change scientists more concerned about warming due to carbon dioxide in the atmosphere, than warming due to the presence of water vapour? Refer to the difference between anthropogenic climate change and natural climate change in your answer.

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(Total for Question = 22 marks)

Q8.

Platinum forms a complex with the formula $Pt(NH_3)_2Cl_2$ and chromium forms a complex ion with the formula $CrCl_4^-$.

(a) Considering the shapes of these complexes,

(1)

☒ **A** both complexes are square planar.

☒ **B** both complexes are tetrahedral.

☒ **C** $Pt(NH_3)_2Cl_2$ is tetrahedral and $CrCl_4^-$ is square planar.

☒ **D** $Pt(NH_3)_2Cl_2$ is square planar and $CrCl_4^-$ is tetrahedral.

(b) Considering the structures of these complexes,

(1)

☒ **A** both complexes form stereoisomers.

☒ **B** neither complex forms a stereoisomer.

☒ **C** $Pt(NH_3)_2Cl_2$ forms a stereoisomer but $CrCl_4^-$ does not.

☒ **D** $CrCl_4^-$ forms a stereoisomer but $Pt(NH_3)_2Cl_2$ does not.

(c) Considering the bonding between the central atom and the ligands in these complexes

(1)

☒ **A** the bonding in both complexes is dative covalent.

☒ **B** the bonding in both complexes is ionic.

☒ **C** the bonding in $Pt(NH_3)_2Cl_2$ is dative covalent and in $CrCl_4^-$ is ionic.

☒ **D** the bonding in $Pt(NH_3)_2Cl_2$ is ionic and in $CrCl_4^-$ is dative covalent.

(Total for question = 3 marks)

Q9.

Chromium has the electronic configuration $[Ar]3d^54s^1$. Which of the following compounds is **unlikely** to exist?

☒ **A** K_3CrO_4

☒ **B** CrO_2Cl_2

☒ **C** $KCrO_2Cl$

☒ **D** $KCrO_4$

(Total for question = 1 mark)

Q10.

When concentrated ammonia solution is added to a green solution of chromium(III) sulfate, a green precipitate is formed which slowly dissolves in excess of the concentrated ammonia solution.

The chromium-containing species formed in these reactions are

	Green precipitate	Resulting solution
☒ **A**	$Cr(OH)_3$	$[Cr(OH)_6]^{3-}$
☒ **B**	$Cr(OH)_3$	$[Cr(NH_3)_6]^{3+}$
☒ **C**	$(NH_4)_2CrO_4$	$[Cr(OH)_6]^{3-}$
☒ **D**	$(NH_4)_2CrO_4$	$[Cr(NH_3)_6]^{3+}$

(Total for question = 1 mark)

Q11. When excess aqueous ammonia is added to a solution containing Zn^{2+}(aq) ions, a colourless solution is formed. This solution is colourless because

☒ **A** zinc does not form complex ions.

☒ **B** the d orbitals of Zn^{2+} in the complex formed are not split into different energy levels.

☒ **C** the energy difference between the d orbitals of Zn^{2+} in the complex formed does not correspond to the visible region of the spectrum.

☒ **D** the d orbitals of Zn^{2+} in the complex formed are full.

(Total for Question = 1 mark)

Q12.

The enthalpy changes of the reactions below are similar. The equilibrium constants for the two reactions are K_1 and K_2 respectively.

Reaction 1 $[Cu(H_2O)_6]^{2+}(aq) + EDTA^{4-}(aq) \rightleftharpoons [Cu(EDTA)]^{2-}(aq) + 6H_2O(l)$

Reaction 2 $[Cu(H_2O)_6]^{2+}(aq) + 4Cl^{-}(aq) \rightleftharpoons [CuCl_4]^{2-}(aq) + 6H_2O(l)$

The value of K_1 is greater than K_2 because

☒ **A** ΔS_{system} is much more positive in Reaction 1.

☒ **B** $\Delta S_{surroundings}$ is much more positive in Reaction 1.

☒ **C** the $EDTA^{4-}$ is more highly charged than Cl^{-}.

☒ **D** a lower concentration of $EDTA^{4-}$ is needed than Cl^{-}.

(Total for question = 1 mark)

Q13.

Copper(II) sulfate solution is blue. This is because

☒ **A** excited electrons emit light in the blue region of the spectrum as they drop back to the ground state.

☒ **B** excited electrons emit light in the red region of the spectrum as they drop back to the ground state.

☒ **C** electrons absorb light in the red region of the spectrum and the residual frequencies are observed.

☒ **D** electrons absorb light in the blue region of the spectrum and the residual frequencies are observed.

(Total for question = 1 mark)

Q14.

One method of manufacturing hydrazine (N_2H_4) involves the action of sodium chlorate(I) on excess ammonia at 443 K and 50 atm. The yield is normally around 80% but, if just 1 part per million of copper(II) ions is present, the yield drops to 30%.

The most likely explanation for this is the ability of copper(II) ions to

☒ **A** form complex ions with ammonia.

☒ **B** catalyse reactions producing other nitrogen compounds.

☒ **C** reduce the hydrazine as it is formed.

☒ **D** reduce the sodium chlorate(I).

(Total for question = 1 mark)

Q15. In aqueous solution, manganate(VI) ions disproportionate into manganate(VII) ions and manganese(IV) oxide when carbon dioxide is bubbled through the solution. The ionic equation for the reaction is

$$3MnO_4^{2-}(aq) + 4H^+(aq) \rightarrow 2MnO_4^-(aq) + MnO_2(s) + 2H_2O(l)$$

The role of the carbon dioxide is to

☒ **A** lower the pH of the solution.

☒ **B** raise the pH of the solution.

☒ **C** oxidize the manganate(VI) ions.

☒ **D** reduce the manganate(VI) ions.

(Total for Question = 1 mark)

Q16.

Which of the following is **not** a disproportionation reaction?

☒ **A** $2NaHCO_3 \rightarrow Na_2CO_3 + CO_2 + H_2O$

☒ **B** $6KOH + 3I_2 \rightarrow KIO_3 + 5KI + 3H_2O$

☒ **C** $2H_2O_2 \rightarrow 2H_2O + O_2$

☒ **D** $2CuI \rightarrow CuI_2 + Cu$

(Total for question = 1 mark)

Q17.

Which is **not** a disproportionation reaction?

☒ **A** $3ClO^- \rightarrow 2Cl^- + ClO_3^-$

☒ **B** $I_2 + 5O_3 + H_2O \rightarrow 2HIO_3 + 5O_2$

☒ **C** $Br_2 + 2OH^- \rightarrow BrO^- + Br^- + H_2O$

☒ **D** $I_2 + H_2O \rightarrow HI + HIO$

(Total for question = 1 mark)

Q18.

(i) Cu^{+}(aq) ions are not stable in solution and undergo a disproportionation reaction.

Suggest an equation for this reaction, including state symbols.

(1)

(ii) Suggest in what way the **appearance** of CuI is similar to that of ZnI_2.

Give a reason for this similarity.

(2)

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Q19. The equation for the reaction of iron and nickel(II) ions in aqueous solution is

$$Fe(s) + Ni^{2+}(aq) \rightarrow Fe^{2+}(aq) + Ni(s)$$

Under standard conditions the value of the equilibrium constant, K_c, for this reaction is greater than 1. Hence, for this reaction,

☐ **A** $\Delta S^{\ominus}_{total}$ and $E^{\ominus}_{reaction}$ are both positive.

☐ **B** $\Delta S^{\ominus}_{total}$ is positive and $E^{\ominus}_{reaction}$ is negative.

☐ **C** $\Delta S^{\ominus}_{total}$ is negative and $E^{\ominus}_{reaction}$ is positive.

☐ **D** $\Delta S^{\ominus}_{total}$ and $E^{\ominus}_{reaction}$ are both negative.

(Total for Question = 1 mark)

Q20.

Which of the following statements about fuel cells is **not** true?

☒ **A** Reactants must constantly be fed into the cell when it is in use.

☒ **B** Fuel cells are 100% efficient.

☒ **C** Fuel cells convert chemical energy directly into electrical energy.

☒ **D** Fuel cells produce electricity more efficiently than a diesel generator.

(Total for question = 1 mark)

Q21.

This question is about the chemistry of chromium.

A solution containing Cr^{3+}(aq) ions is oxidized by hydrogen peroxide in the presence of hydroxide ions to form CrO_4^{2-} ions.

The half-equation for the reduction of hydrogen peroxide is

$$H_2O_2(aq) + 2e^- \rightarrow 2OH^-(aq)$$

(i) Write the half-equation for the oxidation of Cr^{3+}(aq) in the presence of hydroxide ions to form CrO_4^{2-} ions.

(1)

(ii) Hence write the overall equation for this reaction.

(1)

(Total for question = 2 marks)

Q22.

In the reaction of sodium thiosulfate solution with iodine, the half-equation for the reaction of the thiosulfate ions is

☒ **A** $S_2O_3^{2-}$ + $3H_2O$ → $2SO_3^{2-}$ + $6H^+$ + $4e^-$

☒ **B** $S_2O_3^{2-}$ + $3H_2O$ + $4e^-$ → $2SO_3^{2-}$ + $6H^+$

☒ **C** $2S_2O_3^{2-}$ + $2e^-$ → $S_4O_6^{2-}$

☒ **D** $2S_2O_3^{2-}$ → $S_4O_6^{2-}$ + $2e^-$

(Total for question = 1 mark)

Q23. Hydrogen combines rapidly with oxygen in the presence of a platinum catalyst:

$$H_2(g) + ½O_2(g) \rightarrow H_2O(l)$$

The reaction is highly exothermic.

(a) Use the thermochemical data from the data booklet to obtain the enthalpy change for this reaction under standard conditions.

(1)

.... kJ mol^{-1}

(b) The same reaction occurs, also with a platinum catalyst, in a fuel cell.

(i) Write the two ionic half equations which occur in an **alkaline** fuel cell. Include state symbols.

(3)

Equation 1

Equation 2

(ii) The alkali in an alkaline fuel cell serves the same purpose as the acid in an acid fuel cell. State this purpose.

(1)

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*(iii) Platinum catalyses both the direct combination of hydrogen with oxygen and the reactions in the fuel cell. By considering the way in which the catalyst lowers the activation energy, suggest two **similarities** in these processes.

(2)

Similarity 1

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Similarity 2

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(c) The use of hydrogen as a fuel, both in fuel cells and in direct combustion reactions, is seen as an important potential alternative to fossil fuels.

(i) State what is considered to be the main advantage of hydrogen compared with fossil fuels, bearing in mind that most hydrogen is obtained from fossil fuels.

(1)

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*(ii) Explain the main advantage of using a fuel cell over direct combustion of hydrogen.

(2)

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(iii) State a disadvantage of using a hydrogen fuel cell compared with direct combustion of hydrogen.

(1)

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(iv) Suggest **two** advantages of using an ethanol fuel cell rather than a hydrogen fuel cell.

(2)

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(Total for Question = 13 marks)

Q24. Hydrogen-oxygen fuel cells can operate in acidic or alkaline conditions. One such commercial cell uses porous platinum electrodes in contact with concentrated aqueous potassium hydroxide solution, KOH(aq).

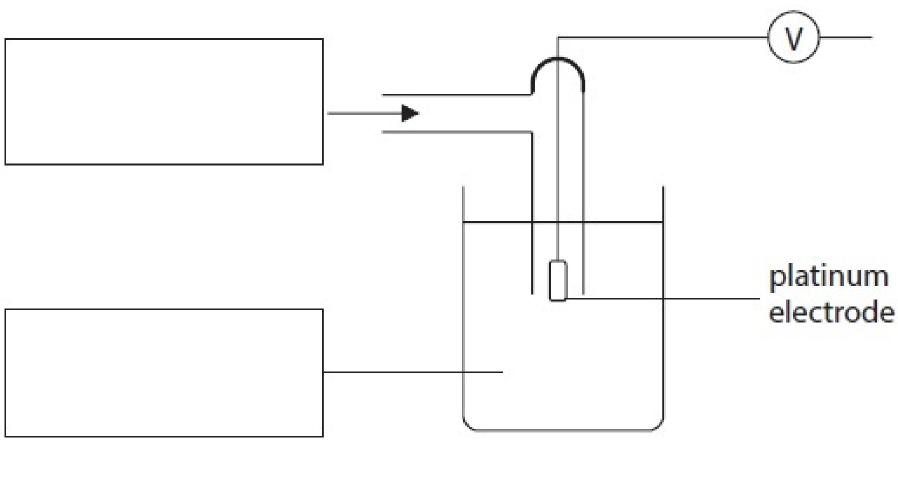
(a) Use relevant standard electrode potential values, on pages 15 and 17 of the Data Booklet, to complete the table below in which two $E^{\ominus}$ values are missing.

(2)

Half-equation	$E^{\ominus}$ / V
$2H_2O(l) + 2e^- \rightleftharpoons 2OH^-(aq) + H_2(g)$	−0.83
$2H^+(aq) + 2e^- \rightleftharpoons H_2(g)$	0.00
$O_2(g) + 2H_2O(l) + 4e^- \rightleftharpoons 4OH^-(aq)$	
$O_2(g) + 4H^+(aq) + 4e^- \rightleftharpoons 2H_2O(l)$	

(b) (i) Fill in the boxes to identify, by name or formula, the substances used in the **standard** hydrogen electrode.

(2)



(ii) State **three** conditions that are necessary for a standard hydrogen electrode.

(2)

1. ....

2. ....

3. ....

(c) Write appropriate half-equations and use them to derive an overall equation for the reaction which occurs when an **alkaline** hydrogen-oxygen fuel cell operates.

(2)

(d) Use the $E^{\ominus}$ values from the table in part (a) to calculate the $E^{\ominus}_{cell}$ for a hydrogenoxygen fuel cell operating in alkaline conditions.

(1)

(e) Suggest why the $E^{\ominus}_{cell}$ cell for a hydrogen-oxygen fuel cell, operating in **acidic** conditions, is identical to that of an alkaline fuel cell.

(1)

....

....

(f) Give **one** reason (other than cost implications) why the platinum electrodes are made by coating porous material with platinum rather than by using platinum rods.

(1)

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(g) Suggest **one** disadvantage of using a hydrogen-oxygen fuel cell compared with a rechargeable battery when providing electrical energy for a motor vehicle.

(1)

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(Total for Question = 12 marks)