Past Papers Advanced Higher Chemistry

2016 Marking Scheme

Grade Awarded	Mark Required		% candidates achieving grade
	(/130)	%	
A	91+	70.0%	34.3%
B	78+	60.0%	27.8%
C	65+	50.0%	20.8%
D	58+	44.6%	8.2%
No award	<58	<44.6%	8.8%

Section:	Multiple Choice	Extended Answer	Investigation
Average Mark:	20.9 /30	42.2 /70	19.2 /30

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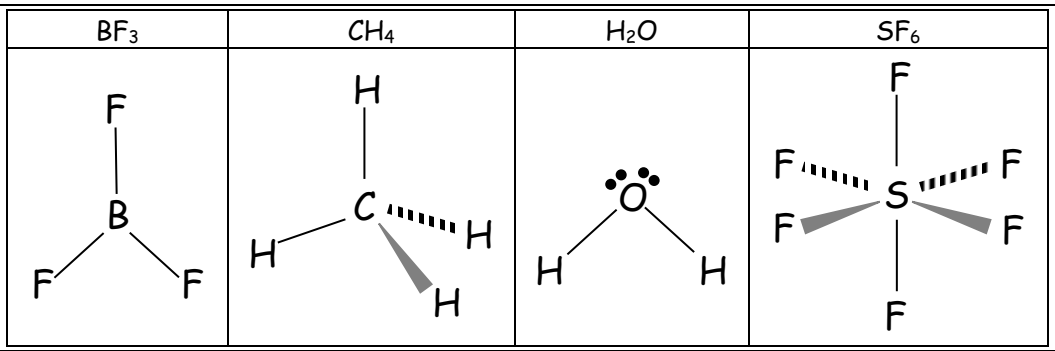
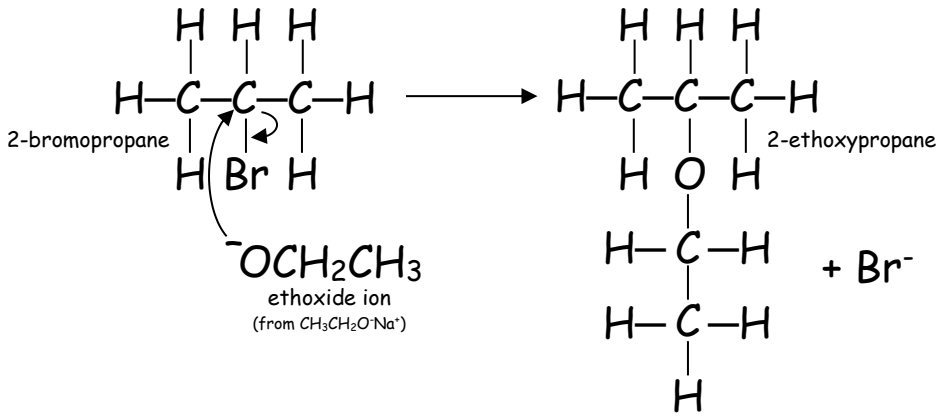
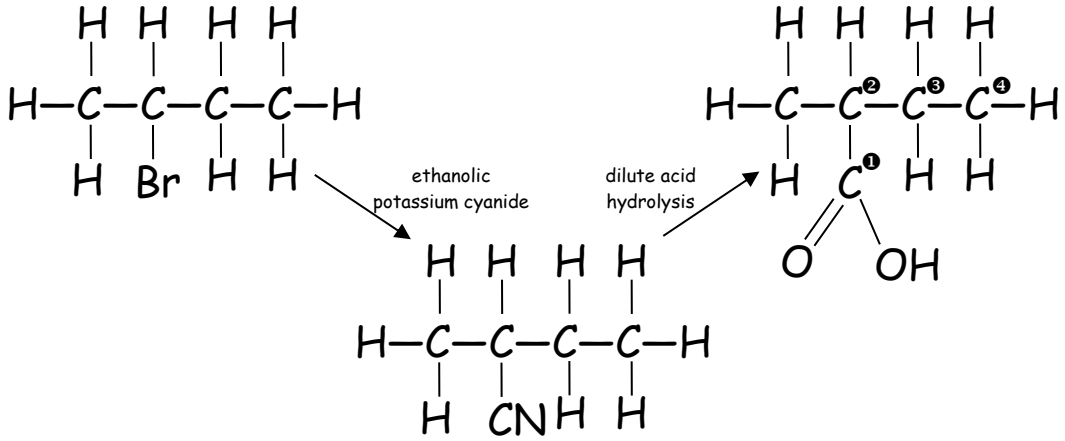
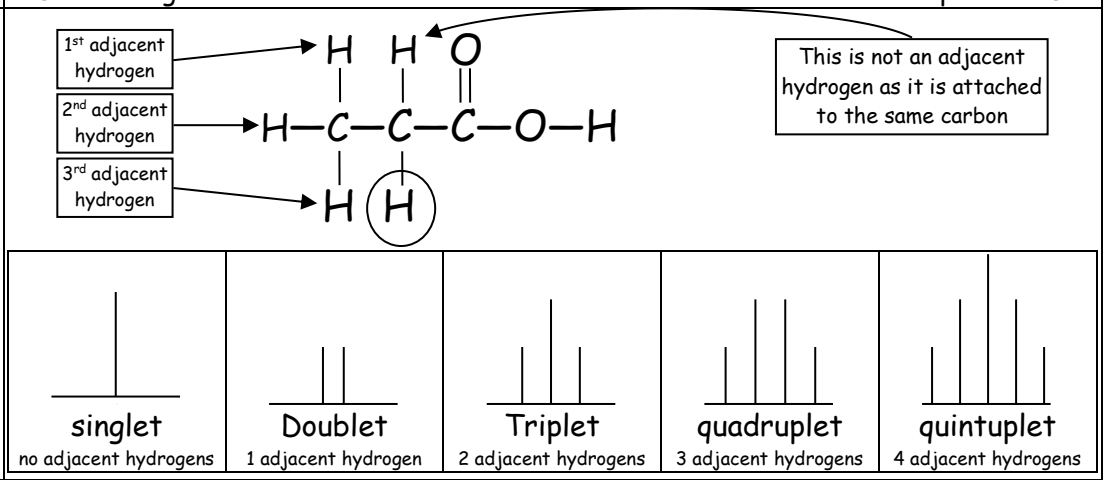
MC Qu	Answer	% Pupils Correct	Reasoning
1	C	85	<table><tr><td>EM Radiation</td><td>Gamma</td><td>X-ray</td><td>UV</td><td>Visible</td><td>Infrared</td><td>Microwave</td><td>Radio & TV</td></tr><tr><td>Velocity</td><td colspan="7">$3x10^8 m\ s^{-1}$</td></tr><tr><td>Wavelength</td><td>short</td><td colspan="6">→</td><td>long</td></tr><tr><td>Frequency</td><td>high</td><td colspan="6">←</td><td>low</td></tr></table>
2	B	92	☒A Hund's Rule: Electron half-fill degenerate orbitals before doubly-filling orbitals ☑B Aufbau Principle: Electrons fill in order of increasing energy ☒C Pauli Exclusion Principle: Orbital can hold 2 electrons only and they have opposite spins ☒D Valence Shell Electron Pair Repulsion Theory: predicts geometry of molecules
3	C	94	☒A s-block is group 1 → group 2 ☒B p-block is group 3 → group 0 ☑C d-block is the transition metals ☒D f-block is the Actinide and Lanthanides rows at the bottom of the Periodic Table
4	D	64	
5	C	67	☒A $[Cu(CN)_6]^{4-}$ complex is a negatively charged ∴ cuprate complex ☒B $[Cu(CN)_6]^{4-}$ complex is a negatively charged ∴ cuprate complex ☑C Cu^{2+} central ion and 6xCN^- ligands gives 4- charge over complex ☒D Cu^{4+} central ion and 6xCN^- ligands gives 2- charge over complex
6	A	83	$HCN + H_2O \rightleftharpoons H_3O^+ + CN^-$ Acid Base Conjugate acid Conjugate base
7	C	49	☒A strong acid/weak base ∴ rapid area of pH change at neutralisation point ☒B strong acid/strong base ∴ rapid area of pH change at neutralisation point ☑C weak acid/weak base ∴ pH change at neutralisation point is gradual ☒D weak acid/strong base ∴ rapid area of pH change at neutralisation point
8	A	59	☑A ammonia forms the weak alkali ammonium hydroxide to complete the buffer ☒B ethanoic acid is a weak acid but a weak alkali (NH_4OH) required to complete butter ☒C potassium chloride is a second salt but there is no weak alkali to complete buffer ☒D ammonium sulphate is a second salt but there is no weak alkali to complete buffer
9	A	39	☑A $4Cl_{(l)}$ is not the natural state of chlorine $Cl_{2(g)}$ ☒B 1 mol of magnesium oxide MgO formed from its elements in their natural state ☒C 1 mol of methanol CH_3OH formed from its elements in their natural state ☒D I mol of ethane C_2H_6 formed from its elements in their natural state
10	C	69	☒A Gaseous neon (b.pt.=-246°C) has higher entropy (disorder) than solid sulphur ☒B Liquid mercury (m.pt.=-39°C) has higher entropy (disorder) than solid sulphur ☑C Solids have lower entropy/disorder than liquids or gases. (sulphur m.pt. =115°C) ☒D Liquid phosphorus (m.pt.=44°C) has higher entropy (disorder) than solid sulphur
11	B	70	Rate = k [A] $[B]^2$ ∴ Reactant A is first order and Reactant B is second order ∴ 1 particle of A and 2 particles of B participate in the (slow) rate determining step ∴ slow (rate determining) step is A + 2B → X

12	D	92	<table><tr><td>Bond</td><td></td><td>C – C</td><td>C = C</td><td>C – H</td></tr><tr><td>Sigma</td><td>σ</td><td>1</td><td>1</td><td>1</td></tr><tr><td>Pi</td><td>π</td><td>0</td><td>1</td><td>0</td></tr></table> 12xC-H + 4xC-C + 2xC=C = (12σ) + (4σ) + (2σ+2π) = 18σ + 2π
13	C	71	☒A molecule drawn is cis-3-methylhept-4-ene-2-one ☒B molecule drawn is trans-3-methylhept-4-ene-2-one ☑C molecule drawn is trans-5-methylhept-3-ene-2-one ☒D molecule drawn is cis-5-methylhept-3-ene-2-one
14	D	85	☒A ethanol C_2H_5OH has an –OH hydroxyl group which has hydrogen bonding ☒B ethylamine $C_2H_5NH_2$ has an $-NH_2$ amine group which has hydrogen bonding ☒C ethanoic acid CH_3COOH has a –COOH carboxyl group which has hydrogen bonding ☑D ethoxyethane is an ether which shows no hydrogen bonding between molecules (but will exhibit hydrogen bonding when mixed with water due to the similar shape to water molecules)
15	B	67	☒A longer chain length has lower volatility due to increased London Dispersion Forces ☑B longer chain length has lower volatility and lower solubility ☒C longer chain length has lower volatility due to increased London Dispersion Forces ☒D longer chain length has lower solubility due to longer non-polar hydrocarbon chain
16	D	42	
17	A	83	☑A Methanal (R′ = H) would produce ethanol (primary alcohol) ☒B Ethanal (R′ = CH_3) would produce propan-2-ol (secondary alcohol) ☒C Propanal (R′ = C_2H_5) would produce butan-2-ol (secondary alcohol) ☒D Butanal (R′ = C_3H_7) would produce pentan-2-ol (secondary alcohol)
18	D	77	☒A hydration: adding water across a C=C double bond ☒B hydrolysis: adding water across the break as molecule splits into two ☒C dehydration: removing water and creating a C=C double bond ☑D condensation: two molecules join together and water is removed as they join
19	A	73	Markovnikov's Rule states the hydrogen mostly add to the side of the double bond which already contains the most hydrogen atoms. • In but-1-ene, C_1 contains 2 hydrogens and C_2 contains 1 hydrogen • H of H-Cl mostly adds to C_1 and Cl of H-Cl mostly adds to C_2 • 2-chlorobutane is main product and 1-chrlorobutane is the minor product.
20	C	60	

21	C	95	❸ propanone (Ketone) —reduction→ ❷ propan-2-ol (Secondary Alcohol) —dehydration→ ❹ propene (Alkene) —addition→ ❶ 1-chloropropane (Halogenalkane)
22	D	68	☒A Benzene is a flat planar molecule ☒B Benzene takes part is electrophilic substitution reactions ☒C All carbon to carbon bonds are the same length in benzene ☑D Benzene has no C=C double bonds to react with bromine by addition reaction.
23	A	61	☑A In S_N1 reactions, there is only one molecule in the rate determining step $(CH_3)_3CBr$ ☒B No change to reaction rate as OH^- ion is zero order and does not take part in RDS ☒C No change to reaction rate as OH^- ion is zero order and does not take part in RDS ☒D No change to reaction rate as OH^- ion is zero order and does not take part in RDS
24	C	45	
25	D	70	☒A –OH group at top of molecule required in both noradrenaline and phenylephrine ☒B 2nd H atom on N not required as phenylephrine lacks this H atom (has $-CH_3$ instead) ☒C –OH group on benzene ring required to directly stimulate the receptor ☑D pharmacophore (structural fragment) for directly stimulating the receptor
26	B	66	200ppm = 200 particles in every million particles $\therefore$ mass = $\frac{200}{1000000} \times 134g = 0.0268g \quad 26.8mg$
27	D	82	☒A corrosive substances can be used as a primary standard with care ☒B primary standards should be readily soluble in water ☒C primary standards must have a high degree of purity ☑D if a substance readily absorbs water then its changing mass makes it unsuitable as a primary standard
28	B	44	**n**o. of mol NO_3^- = **v**olume x **c**oncentration = 0.5 litre x 0.1 mol l^{-1} = 0.05mol NO_3^- ions but 2 NO_3^- ions per $Ca(NO_3)_2$ f.u. $\therefore$ 0.05mol NO_3^- ions $\rightarrow$ 0.025mol $Ca(NO_3)_2$ f.u. **v**olume = $\frac{\textbf{n}\text{o of moles}}{\textbf{c}\text{oncentration}} = \frac{0.025 \text{ mol}}{0.25 \text{ mol } l^{-1}} = 0.1 \text{ litres} = 100cm^3$
29	A	63	1mol $BaSO_4$ = (1x137.3)+(1x32.1)+(4x16) = 137.3+32.1+64 = 233.4g **n**o. of mol = $\frac{\textbf{m}\text{ass}}{\textbf{gfm}} = \frac{2.33}{233.4} = 0.010mol$ $CuSO_4 + BaCl_2 \longrightarrow BaSO_4 + CuCl_2$ 1mol 0.010mol — 1mol 0.010mol 1mol $CuSO_4$ = (1x63.5)+(1x32.1)+(4x16) = 63.5+32.1+64 = 159.6g **m**ass = **n**o. of mol x **gfm** = 0.01mol x 159.6g mol^{-1} = 1.59g
30	B	79	**n**o. of mol = **v**olume x **c**oncentration = 0.02litres x 4.0 mol l^{-1} = 0.08mol $NH_3 + HNO_3 \longrightarrow NH_4NO_3$ 1mol 1mol — 1mol 0.08mol — 0.08mol 0.02mol $Pt(NH_3)_xCl_2$ contains 0.08 mol of NH_3 $\therefore$ x=4

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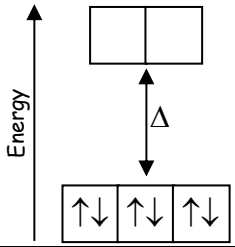
Long Qu	Answer	Reasoning
1a(i)	-44 kJ mol^{-1}	$\Delta H^\circ = \Sigma\Delta H_f^\circ{}_{(products)} - \Sigma\Delta H_f^\circ{}_{(reactants)}$ $= (1x\text{-}278) - (1x52)+(1x\text{-}286)$ $= -278 - 52 + (-286)$ $= -278 - (-234)$ $= -44$ kJ mol^{-1}
1a(ii)	-128 J K^{-1} mol^{-1}	$\Delta G^\circ = \Sigma G^\circ{}_{(products)} - \Sigma G^\circ{}_{(reactants)}$ $= (1x\text{-}175) - (1x68)+(1x\text{-}237)$ $= -175 - 68 + (-237)$ $= -175 - (-169)$ $= -6$ kJ mol^{-1} $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \therefore T\Delta S^\circ = \Delta H^\circ - \Delta G^\circ \therefore \Delta S^\circ = \frac{\Delta H^\circ - \Delta G^\circ}{T}$ $\Delta S^\circ = \frac{-44 - (6)}{298}$ $= -0.128$ kJ K^{-1} mol^{-1} $= -128$ J K^{-1} mol^{-1}
1b	344K	The reaction becomes thermodynamically feasible when $\Delta G^\circ = 0$ $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = 0 \therefore T\Delta S^\circ = \Delta H^\circ \therefore T = \frac{\Delta H^\circ}{\Delta S^\circ} = \frac{-44 \times 1000 \text{ J mol}^{-1}}{-128 \text{ J K}^{-1} \text{ mol}^{-1}} = 343.75K$
2a	$1s^2 2s^2 2p^6$	Neon atoms have 10 electrons. (2+2+6=10) Neon is a Noble Gas has full orbitals (s holds 2 electrons and p holds 6 electrons)
2b	∞	Angular Momentum Quantum Number has value of l=0, 1, 2 or 3 for s, p, d and f respectively. When l=1 the shape of the orbital is the p orbital. p_x, p_y and p_z orbitals all have a *figure of 8* shape (∞).
2c	-1,0,+1	10^{th} electron is a p orbital electron where l=1 • l is angular momentum quantum number • magnetic quantum number **m** has values –l through to +l If l=1 then $\mathbf{m}_l$ can have values -1,0,+1
3a(i)		Fe electronic configuration $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^6\ 4s^2$ $\therefore Fe^{2+}$ has electronic configuration $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^6$ To be paramagnetic there needs to be unpaired electrons. As $[Fe(CN)_6]^{4-}$ is not paramagnetic $\therefore$ it has no unpaired electrons Only formation of the six electrons in the 3d orbital without any unpaired electrons would be 3 electron pairs in the lower orbitals.
3a(ii)	Answer to include:	1st Mark: Smaller energy gap (due to H_2O being lower in spectrochemical series) 2^{nd} Mark: electrons are promoted to higher d-orbitals by absorbing energy from visible spectrum
3a(iii)	Fe^{3+} has five electrons in d-orbital	Fe^{3+} has electronic configuration $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^5$. With an odd number of d-orbital electrons there will always be at least one unpaired electron in any formation of electrons.
3b(i)	4	The haemoglobin structure has four nitrogen atoms whose lone pairs of electrons are attracted to the central Fe^{2+} ion.
3b(ii)	One answer from:	Flame test | Atomic absorption | Atomic emission

3b(iii) — Open question answer to include

3 mark answer	2 mark answer	1 mark answer
Demonstrates a **good understanding** of the chemistry involved. A good comprehension of the chemistry has provided in a logically correct, including a statement of the principles involved and the application of these to respond to the problem.	Demonstrates a **reasonable understanding** of the chemistry involved, making some statement(s) which are relevant to the situation, showing that the problem is understood.	Demonstrates a **limited understanding** of the chemistry involved. The candidate has made some statement(s) which are relevant to the situation, showing that at least a little of the chemistry within the problem is understood.

4a(i) — The exact mass should be measured accurately and should be close to 4.25g.

The mass does not have to be exactly 4.25g for the experiment and depending on the particle size of the solid it may not be possible to exactly measure out 4.25g on the balance. It is vitally important that the actual mass measured is recorded and used to calculate the number of moles of silver nitrate for use in the calculation.

4a(ii) — Answer to include:

1st Mark: Dissolve silver nitrate in deionised water in a beaker. Transfer solution and beaker rinsings to standard flask

2nd Mark: Make solution up to the mark on standard flask with deionised water.

4a(iii) — One answer from:

Use lower concentration of silver nitrate solution	Titrate a larger sample of seawater	Use a microburette
Dilute the standard silver nitrate solution	Dilute the sea water less	Use class A glassware

4b(i) — Filtration under suction

A Buchner funnel is used with suction pump to assist the movement of the liquid through the filter leaving the precipitate on the filter paper. Your answer must mention suction

4b(ii) — One Answer from:

To check reaction is complete	To check all chloride ions have reacted	To check no more precipitate is formed	If there is a precipitate then the reaction is not complete

4c — Titrations suitable for lower concentrations of chloride ions

The gravimetric method would produce very little precipitate and the errors involved in such small quantities would be large. Volumetric methods are much more accurate with smaller quantities.

5a — Answer showing:

$$K_a = \frac{[C_6H_5CH(OH)COO^-]\,[H_3O^+]}{[C_6H_5CH(OH)COOH]}$$

NB: H_2O is both a reactant and the solvent so $[H_2O] = 1$

5b(i) — 0.658

1mol $C_6H_5CH(OH)COOH$ = (8x12)+(8x1)+(3x16) = 96+8+48 = 152g

$$\textbf{n}\text{o. of mol} = \frac{\textbf{mass}}{\textbf{gfm}} = \frac{10g}{152\ g\ mol^{-1}} = 0.0658\ mol$$

$$\textbf{c}\text{oncentration} = \frac{\textbf{n}\text{o. of mol}}{\textbf{v}\text{olume}} = \frac{0.0658mol}{0.1\ litres} = 0.658\ mol\ l^{-1}$$

5b(ii) — 1.97

$$\begin{aligned} pH &= \tfrac{1}{2}pK_a - \tfrac{1}{2}\log_{10} c \\ &= \tfrac{1}{2}(-\log_{10}K_a) - \tfrac{1}{2}\log_{10} c \\ &= \tfrac{1}{2}(-\log_{10}1.78\times10^{-4}) - \tfrac{1}{2}\times\log_{10}(0.658) \\ &= \tfrac{1}{2}(3.750) - \tfrac{1}{2}(0.182) \\ &= 1.875 - (-0.0909) \\ &= 1.97 \end{aligned}$$

6a — 196.3 kJ mol^{-1}

$$E = \frac{L \times h \times c}{\lambda} = \frac{6.02\times10^{23}\ mol^{-1} \times 6.63\times10^{-34}\ J\ s \times 3\times10^{8}\ m\ s^{-1}}{610 \times 10^{-9} m}$$

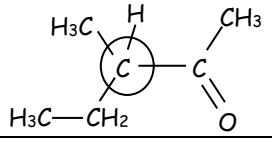
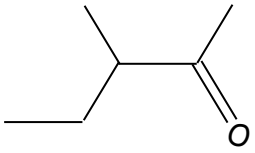
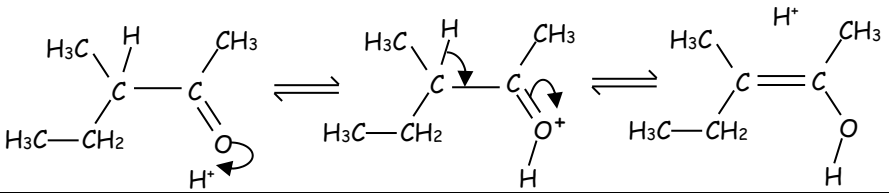
$$= 196291\ J\ mol^{-1}$$

$$= 196.3\ kJ\ mol^{-1}$$

6b(i) Part A — 2nd order

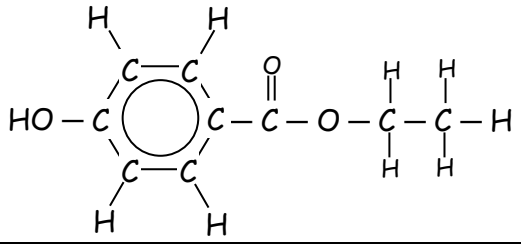
6b(i) Part B — 1st order

Experiment	$[ClO_2]$	$[OH^-]$	Effect on Rate	Order of Reactant
❶+❷	x2	no change	x4	$[ClO_2]^2$
❷+❸	no change	x3	x3	$[OH^-]^1$

6b(ii)	Rate = $k[ClO_2]^2[OH^-]$	Rate = k x $[ClO_2]^2$ x $[OH^-]^1$ = $k[ClO_2]^2[OH^-]$
6b(iii)	230 l^2 mol^{-2} s^{-1}	$rate = k[ClO_2]^2[OH^-]$ $k = \frac{rate}{[ClO_2]^2 \times [OH^-]}$ $= \frac{2.48\times10^{-2} \text{ mol } l^{-1} s^{-1}}{(6.0\times10^{-2} \text{ mol } l^{-1})^2 \times 3.0\times10^{-2} \text{ mol } l^{-1}}$ = 230 l^2 mol^{-2} s^{-1}
7a	Ethanal (keto form)	As the value of K is well below 1 the equilibrium must lie well to the left.
7b(i)		A chiral carbon centre is a carbon with four different groups attached to the same carbon
7b(ii)	A racemic mixture is formed over time	The keto form converts into the enol form due to the equilibrium but will then convert back to the keto form again. When the enol form converts back to the keto form both enantiomers are formed an the previously optical-activity is lost as a racemic mixture forms.
7b(iii)		Skeletal structures have a carbon atom at the end of every line and corner unless another atom/group is indicated in the structure.
7c	Diagram showing:	
8a	Produces response similar to the body's natural active compound	Every pharmacologically-active substance has a part of the molecule which has a specific shape which fits the receptor. • Agonists and the natural substrate cause a biological response inside the cell. • Antagonists fit the binding site of the receptor but do not cause the biological response and prevent any other chemical doing so.
8b	Catalyst	$AlCl_3$ is not a reactant in the reaction. It must be acting as a catalyst.
8c	ultra violet (U.V.)	Free radical chain reaction mechanism for the substitution reaction of a bromine atom requires u.v. light for the initiation step of $Br_2 \rightarrow 2Br^{\bullet}$
8d	nucleophilic substitution	The C-Br bond is polar with the δ-charge on the bromine end of the bond. The δ-charge on the N of the incoming molecule is attracted to the C atom of the C-Br and the Br atom leaves the bond as a Cl^- ion.
8e	Lithium aluminium hydride	Lithium Aluminium Hydride $LiAlH_4$ is a reducing agent which will carry out reduction reactions: aldehyde → primary alcohol | ketone → secondary alcohol | carboxylic acid → aldehyde
8f	Open Question to include:	**3 mark answer**: Demonstrates a **good understanding** of the chemistry involved. A good comprehension of the chemistry has provided in a logically correct, including a statement of the principles involved and the application of these to respond to the problem. **2 mark answer**: Demonstrates a **reasonable understanding** of the chemistry involved, making some statement(s) which are relevant to the situation, showing that the problem is understood. **1 mark answer**: Demonstrates a **limited understanding** of the chemistry involved. The candidate has made some statement(s) which are relevant to the situation, showing that at least a little of the chemistry within the problem is understood.

9a(i)

$C_9H_{10}O_3$



9a(ii)

sp^2

Aromatic rings have sp^2 hybridisation as the 2s and two of the three 2p orbitals hybridise. The remaining 2p orbital is unhybridised and the electron in this orbital delocalises into the ring of 6 electrons.

9a(iii)

orbitals overlap sideways

The unhybridised p orbital on either side of the central sigma bond bend and overlap to form a Pi bond (second bond in a double bond)

9b(i)

Diagram showing:

Cross-sectional diagram showing inner wall of condenser	Be an open system	Sealed around the flask neck	Have water going into the bottom and out at the top

9b(ii)

Products are soluble

The products of hydrolysing an ester are soluble as the both contain polar groups that make the products soluble. When all the ester is hydrolysed then there is only the water soluble layer left.

9b(iii)

Answer to include:

<u>1st Mark</u>: 4-hydroxybenzoate ion removes H^+ by joining together to form molecules of 4-hydroxybenzoic acid

<u>2nd Mark</u>: water equilibrium shift to right to replace H^+ ions and this increases the OH^- ions making pH>7

9b(iv)

Any two from:

Doesn't react with solute	More soluble in hot solvent than cold solvent	Impurities to be soluble /insoluble in hot/cold solvents	Boiling point	polarity

9b(v)

3.85g

Percentage yield 77.5% ⟷ 2.48g 4-hydroxybenzoic acid

Percentage yield 100% ⟷ 2.48g x $^{100}/_{77.5}$

= 3.20g

ethylparaben ⟶ 4-hydroxybenzoic acid

1mol 1mol

166g 138g

166g x $^{3.20}/_{138}$ 3.20g

= 3.85g

10a

$C_3H_4O_2$

Element	C	H	O
%	50.0	5.60	44.4
No. of moles (divide % by gfm)	$\frac{50.0}{12}$ = 4.167	$\frac{5.60}{1}$ = 5.60	$\frac{44.4}{16}$ = 2.775
Mole ratio (divide through by smallest value)	$\frac{4.167}{2.775}$ = 1.50	$\frac{5.60}{2.775}$ = 2.02	$\frac{2.775}{2.775}$ 1.00
Double to get rid of .5	3.00	4.04	2.00
Round to Whole Number	3	4	2

10b

C=O Carbonyl

The peak at 1710 cm^{-1} is caused by C=O within a carboxyl group.

10c(i)

$C_3H_4O_2$

Heaviest peak is the original molecule: $C_3H_4O_3$ = (3x12)+(4x1)+(2x16) = 36+4+32 = 72

10c(ii)

$[C_2H_3]^+$

Positive charge must be shown. C_2H_3 = (2x12)+(3x1) = 24+3 = 27

10d

Structure shown: