CHEMISTRY

Write in dark blue or black pen.
You may use an HB pencil for any diagrams or graphs.
Do not use staples, paper clips, glue or correction fluid.

Answer **all** questions provided on the Question Paper.
The use of an approved scientific calculator is expected, where appropriate.

The number of marks is given in brackets [ ] at the end of each question, or part question.

This document consists a total of **16** printed pages.

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1 This Question tests up to, and mainly Chapter 20 (Electrochemistry).

(a) A student creates a simple electrolysis setup. 1 platinum anode and 1 platinum cathode was placed in a solution containing dilute sodium chloride, with a constant current of 0.500 A passed through the circuit.

(i) Using relevant standard electrode potentials from the *Data Booklet*, explain the effect of the electrolysis on the pH of the solution. [2]

$Cl_2 + 2e^- \rightleftharpoons 2\ Cl^-$ $E^\ominus = +1.36$ V – (1)

$2\ H_2O + 2e^- \rightleftharpoons H_2 + 2\ OH^-$ $E^\ominus = -0.83$ V – (2)

$O_2 + 4\ H^+ + 4e^- \rightleftharpoons 2\ H_2O$ $E^\ominus = +1.23$ V – (3)

B2 – All 6 points

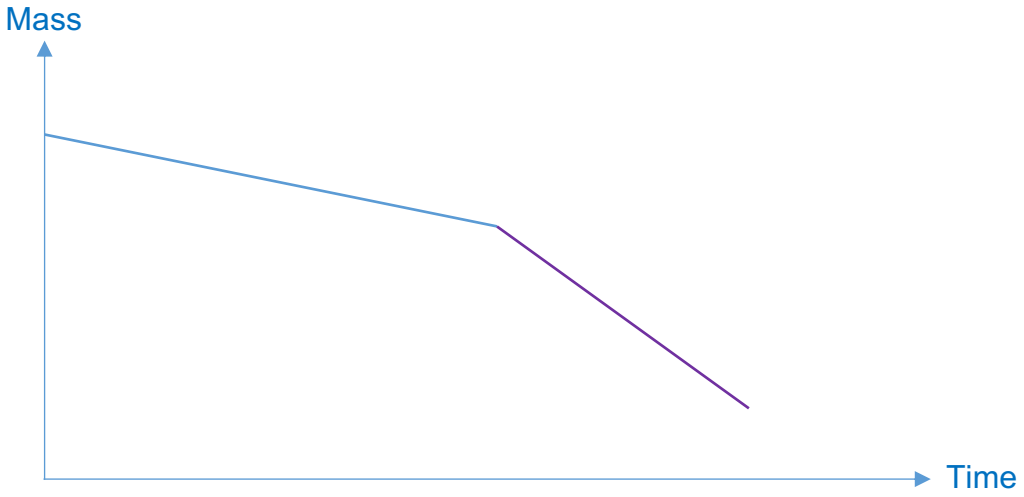
- All 3 standard electrode potential values shown as above
- Cathode: Water reduced to hydrogen which yields hydroxide ions
- Anode: Water preferentially oxidised to oxygen because standard electrode potential for (3) is more positive than (1). This produces hydrogen ions
- For every mole of electrons passed through the circuit, 1 mole of hydroxide ions are produced and 1 mole of hydrogen ions are produced.
- Meaning that they will neutralise each other
- So there's no net increase in concentration of hydrogen ions, so pH remains the same

Minimum number of points hit to score

0.5	2
1	4
1.5	5

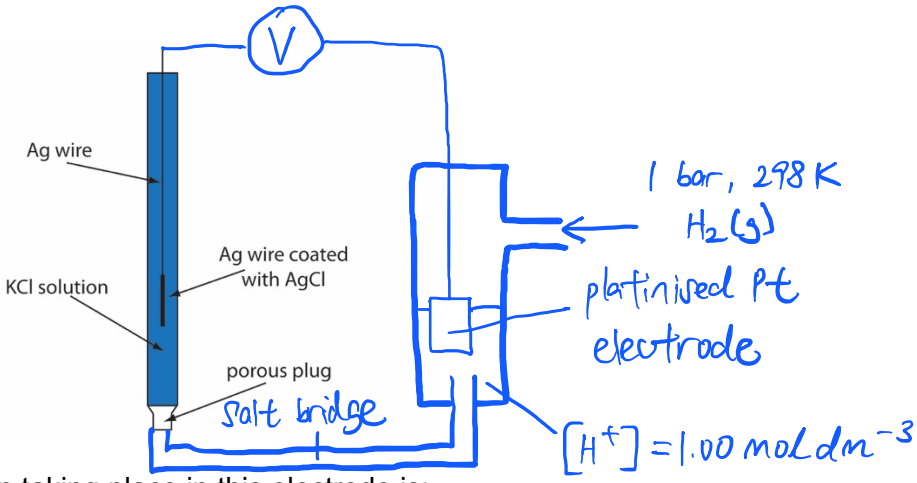
(ii) Sketch a graph of the mass of the solution against time elapsed since the current was passed through the circuit. [2]

B1 – Correct blue line (must be straight) and axes
B1 – Correct purple line (purple line must be steeper than the blue line at all times, need not be straight)
The concentration of chloride ions increases as water gets electrolysed, till the point that chloride ions are preferentially oxidised. The M_r of chlorine is higher than water, so the mass decreases faster.



(b) Apart from the standard hydrogen electrode, there are other standard electrodes used in analytical chemistry too.

One such electrode is the silver chloride electrode. A diagram of the silver chloride electrode is shown below.



The relevant half-equation taking place in this electrode is:

Equation 1: $AgCl\ (s) + e^- \rightleftharpoons Ag\ (s) + Cl^-\ (aq)$

(i) The porous plug is meant for a salt bridge to be connected to the analyte (solution to be tested).

Complete the diagram above to show how you would measure the potential of this electrode relative to the standard hydrogen electrode. [2]

B1 – miscellaneous items

- Salt bridge
- Voltmeter
- Platinised Pt electrode (or graphite electrode)
- The electrode must be in contact with the hydrogen gas and the solution.

B1 – Conditions

- Concentration of H^+ = 1.00 mol dm^{-3} and pressure of H_2 = 1 bar
- Temperature at 298 K

(ii) Given that the standard electrode (reduction) potential of **Equation 1** is +0.22249 V, using relevant data from the *Data Booklet*, calculate the change in the Gibbs' Free Energy of the dissolution of silver chloride at 25 degrees Celsius. [3]

M1 – Correct equation showing dissolution of silver chloride and half equation of the reduction of silver

The relevant equations are:

$$Ag^+ + e^- \rightleftharpoons Ag \text{ --- (2)}$$
$$AgCl \rightleftharpoons Ag^+ + Cl^- \text{ --- (3)}$$

M1 – Either correct Hess Law diagram (state symbols in this case can be omitted since it is fairly obvious) OR expressing (3) in terms of (1) and (2), with appropriate calculation or working of ΔG.

Since (3) = (1) - (2)
$\Delta G(3) = \Delta G(1) + \Delta G(2) = -0.22249F + 0.80F$

A1 – Correct answer
$\Delta G(3) = +55700$ J mol^{-1}

(iii) A modification of the silver chloride electrode is to use a saturated solution of potassium chloride instead of a concentration of 1.00 mol dm^{-3}.

Suggest a benefit of doing so. [1]

B1 – Touches on the practicality of using a saturated solution

- Not prone to any error in measuring the mass of potassium chloride to prepare a solution of an exact concentration since potassium chloride can simply be dissolved till excess; OR
- Since the solubility of potassium chloride is constant for a given temperature, potassium chloride can be simply added in excess. Excess undissolved potassium chloride can redissolve should chloride ions be depleted.

(iv) Compare the electrode potential of **Equation 1** when a saturated solution of potassium chloride is used as the aqueous media to when a solution of 1.00 mol dm^{-3} potassium chloride is used. Provide a reason for your answer. [1]

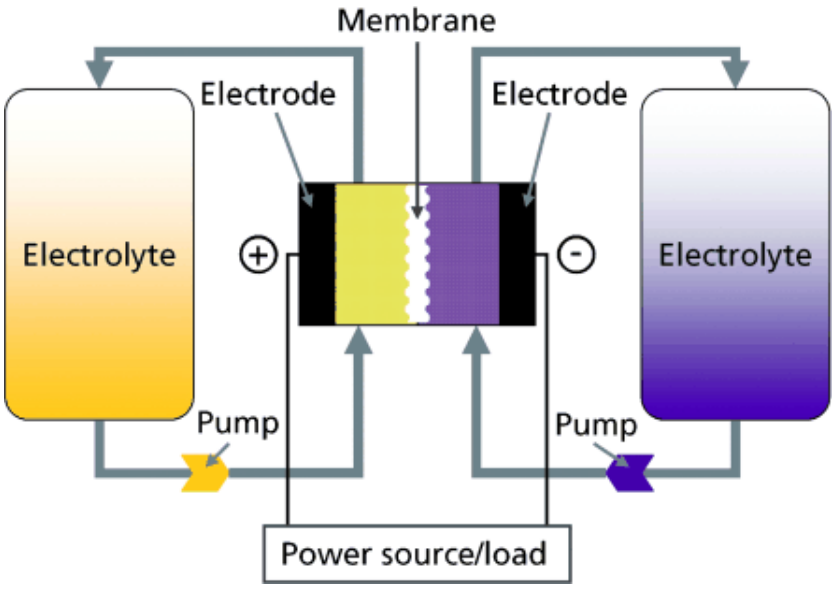
B1 – Less positive (reject more negative OR lower) because higher concentration of chloride ions shift the position of equilibrium of **Equation 1** to the left.

(v) Suggest a benefit of using the silver chloride electrode over the standard hydrogen electrode. [1]

B1 – Easy to setup because there's more difficulty in maintaining a constant pressure of 1 bar of hydrogen gas for the SHE compared to the SCE.

(c) Rechargeable batteries are now seen to be eco-friendly alternatives to conventional batteries made of manganese.

The diagram below illustrates the model of a rechargeable battery.



One such rechargeable battery is the zinc-cerium battery, developed in 2000 in the UK.

The solvent used in this system is methanesulfonic acid (CH_3SO_3H).

Relevant data is provided below:

$$Ce^{4+}(aq) + e^- \rightleftharpoons Ce^{3+}(aq) \qquad E^{\ominus} = +1.44\ V$$

The power source draws electricity from the setup.

(i) Based on the diagram above, state which electrode should be the zinc electrode. Calculate the discharge voltage at standard conditions. [1]

Ce(VI) will be reduced and Zn will be oxidised.
B1 – Negative electrode AND +2.20 V. (The sign can be omitted)

A scientist set up a small zinc-cerium battery with the following specifications.

Volume of negative electrolyte (Electrolyte at negative terminal)	20.0 dm^3
Volume of positive electrolyte (Electrolyte at positive terminal)	10.0 dm^3
Concentration of $Zn(CH_3SO_3)_2$ / mol dm^{-3}	1.500
Concentration of $Ce(CH_3SO_3)_3$ / mol dm^{-3}	1.050
Concentration of $Ce(CH_3SO_3)_4$ / mol dm^{-3}	0.840
Mass of zinc electrode	2.00 kg

(ii) Assume that this battery has no side reactions and is 100% efficient.

If this battery were to be charged to its fullest, how much charge needs to be supplied to the battery? Give your answer in mAh (milli-ampere hours). [3]

The negative electrolyte contains the Zn species
The positive electrolyte contains the Ce species

If the battery were to be charged, this means that instead, electrolysis occurs. That is, Ce(III) is oxidised to Ce(IV) and Zn(II) is reduced to Zn.

Hence, to fully charge the battery, we need to take the minimum of the amount of charge needed to convert all Ce(III) to Ce(IV) and that to convert all Zn(II) to Zn.

- This is because in the event where all Ce(III) is converted to Ce(IV), then no more Zn(II) can be converted to Zn since no more Ce(III) can be oxidised (or vice versa)

M1 – For Ce(III) to Ce(IV) and for Zn(II) to Zn

$$Ce^{3+} \rightarrow Ce^{4+} + e^-$$
$$n(e^-) = 10.0 \times 1.050 = 10.5 \text{ mol}$$

$$Zn^{2+} + 2\ e^- \rightarrow Zn$$
$$n(e^-) = 20.0 \times 1.500 \times 2 = 60.0 \text{ mol}$$

since 2 electrons are needed to reduce Zn(II) to Zn.

M1 – Expresses answer in C
Hence, the amount of charge needed to fully charge this battery is
Q = nF = 10.5 × 96500 = 1013250 C

MA1 – Converts answer from C to mAh.
Since 1 mAh = (1.00 × 10^{-3} C s^{-1}) × (3600 s) = 3.60 C,
Q = $\frac{1013250}{3.60}$ = 281458 mAh = 281000 mAh

(iii) Hence, calculate the charge capacity of this battery in mAh. [3]

Now, we need to suppose otherwise, that the whole battery is charged and going to be discharged.

From (ii), we know that at maximum charge, we have:

- Only Ce(IV) existing as all Ce species
- Some Zn(II) and Zn left

The amount of electrons that are produced from

- M1 – The conversion of all Ce(IV) to Ce(III)

$$n(e^-) = 10.5 + 0.840 \times 10.0 = 18.9 \text{ mol}$$

- M1 – The conversion of all Zn to Zn(II) (hypothetically)

$$n(e^-) = 60.0 + \frac{2000}{65.4} \times 2 = 121.2 \text{ mol}$$

OR

For the Zn present in the electrode initially,

$$n(e^-) = \frac{2000}{65.4} \times 2 = 61.2 \text{ mol}$$

So, Zn is always in excess. (Note: M1 mark awarded for convincingly showing that Zn is in excess)

MA1 – Converts limiting amount of electrons to their equivalent charge.
Q = nF = 18.9 × 96500 = 1823850 C = 506625 mAh = 507000 mAh

(iv) What is the percentage charge of this battery? [1]

MA1 – Correct answer

% charge = $\frac{10.5}{18.9} \times 100\% = 55.6\%$

2 (a) Explain why the hydrogen-halogen bond is weaker down the group for halogens. Hence describe the observations when the respective hydrogen halides are heated. [3]

B1 — For explaining the weaker H—X bond down the group for X

- Down the group for X, the valence orbital of X is more diffuse (or lower electron density)
- So there is less effective overlap of the 1s orbital of H and the valence orbital of X, consequently resulting in a weaker H—X bond

B2 — Observations (deduct 1 pt for each missing point up to 2 pts)

- HI decomposes under heat to yield violet iodine vapours
- HBr decomposes under strong heat to yield orange-brown bromine vapours
- HCl does not decompose

(b) Explain the trend in the boiling points of the hydrogen-halides. [3]

B3 – deduct 0.5 pts for each point missing until 3 pts

- HX (for X = F, Cl, Br or I) has a simple molecular structure

- Between molecules of HF exist hydrogen bonds
- But between molecules of HX (for X = C*l*, Br or I), much weaker permanent dipole-permanent dipole interactions and/or dispersion forces exists
    - Note: for the 2nd and 3rd bullet points, comparison between pd-pd or dispersion forces and hydrogen bonds must be already established. No comparison means that 1 bullet point is forgone
- So HF has the highest boiling point of the hydrogen halides.
- Between molecules of HX (for X = C*l*, Br or I), from X = C*l* to Br to I, stronger dispersion forces exist (optional: where the pd-pd interactions between HX molecules contribute to the minority of the strength of the intermolecular forces of attraction)
    - No comparison means that the 5th bullet point is forgone
- Hence, more energy is needed to overcome the stronger dispersion forces
- Which explains why the boiling point of HX increases from X = C*l* to Br to I.

(c) Explain the link between the trend of the decomposition temperature of the Group II carbonates and the disparity between their theoretically calculated and experimentally measured lattice energies. [5]

First 2 pts are for recognising that it's about the polarising power of the cation
B1 – Down the group, the ionic radius of the cation increases but the charge stays the same
B1 – Hence, the charge density and polarising power of the cation decreases.

B1 for stating the correct trends
Trend 1: The decomposition temperature of the Group II carbonates increases down the group
B1 - since the lower polarising power of the cation will lead to a smaller distortion of the electron cloud, thereby weakening the C—O bond to a lower extent.

B1 – Additionally, the lower polarising power down the group confers the ionic bond between the cation and the carbonate anion less covalent character
Trend 2: so the disparity between the theoretically calculated and experimentally measured lattice energies decreases down the group for the Group II carbonates

Recap that the disparity between the theoretical and experimental lattice energies lies in the assumption that the ionic bond only has pure ionic character, or there's no covalent character. More covalent character → larger disparity

(d) Element **E** is an element in the third period of the periodic table.

When element **E** is left in open air, its oxide **A** is formed. The oxidation state of **E** in **A** is its maximum. When **A** is dissolved in water, a solution of a different pH is formed due to formation of **B**. When potassium carbonate is slowly added into the solution until no further change, no precipitate is observed, but **C** is formed.

Dissolving the salt **C** in water results in an alkaline solution being formed.

E can be heated in chlorine gas to form **D**. Increasing the pressure of chlorine gas will result in **F** being formed. **F** also dissolves in water to form **B**, but a solution of a low pH results instead.

(i) Deduce the element **E**, and species **A** to **D** and **F**. [7]

B2 – Deductions and correct element **E**

- **E** is not a metal since **E** has 2 different oxidation states
- **E** is not sulfur since the sulfate ion cannot alter the pH of the solution
- **E** is not silicon because its oxide is not soluble in water
- **E** is phosphorous

B5 – Correct **A** to **D** and **F**

A: P_4O_{10}
B: H_3PO_4
C: K_3PO_4 (or K_2HPO_4)
D: PCl_3
F: PCl_5
Note: **C** is not KH_2PO_4 because the second deprotonation is still viable. It's not an exam-smart thing to write KH_2PO_4.

(ii) Write balanced chemical equations for all reactions taking place in the description. [7]

B1 each
Accept stoichiometric multiples of the equation
Accept phosphorous written as "P"
Ionic equations are accepted, but compounds **A** to **F** must match with that written in **(i)**.
Award ECF only for:

- **C**, where the candidate has omitted the potassium ion (or writes the wrong cation) and writes the anionic species only with the correct charge.
- OR where **C** is written as KH_2PO_4

When element **E** is left in open air, its oxide **A** is formed.	$P_4 + 5\ O_2 \rightarrow P_4O_{10}$
When **A** is dissolved in water, a solution of a different pH is formed due to formation of **B**.	$P_4O_{10} + 6\ H_2O \rightarrow 4\ H_3PO_4$
When potassium carbonate is slowly added into the solution, no precipitate is observed, but **C** is formed.	$3\ K_2CO_3 + 2\ H_3PO_4 \rightarrow 2\ K_3PO_4 + 3\ H_2O + 3\ CO_2$ (accept K_2HPO_4 variant)
Dissolving the salt **C** results in an alkaline solution being formed.	$K_3PO_4 + H_2O \rightleftharpoons K^+ + K_2HPO_4 + OH^-$ (reversible sign is required)
E can be heated in chlorine gas to form **D**.	$P_4 + 6\ Cl_2 \rightarrow 4\ PCl_3$

Increasing the pressure of chlorine gas will result in **F** being formed.	$PCl_3 + Cl_2 \rightarrow PCl_5$
F also dissolves in water to form **B**, but a solution of a low pH results instead.	$PCl_5 + 4\ H_2O \rightarrow H_3PO_4 + 5\ HCl$

(e) Aluminium isopropoxide is a reducing and oxidising agent in organic chemistry. To prepare aluminium isopropoxide, some aluminium is dissolved in a solution of isopropanol.

Analysis discovers that aluminium isopropoxide contains Al—O bonds.

(i) Explain why aluminium can form covalent bonds with oxygen. [2]

B1 – Al^{3+} cation has a small ionic radius but high charge of 3+, so it has a high charge density and high polarising power
B1 – The high polarising power of the Al^{3+} cation results in significant distortion of the electron cloud of the oxygen atom, resulting in covalent character of the aluminium-oxygen bond.

(ii) Aluminium isopropoxide can also be formed through aluminium chloride. Describe what happens when a few drops of water is added to anhydrous aluminium chloride. [1]

B1 – White fumes that turn moist blue litmus red, with a white residue left behind.

(iii) When aluminium is added into a solution of sodium hydroxide, a gas is evolved after some time. The gas extinguishes a lighted splint with a 'pop'. The aluminium dissolves and forms a colourless solution.

Construct an ionic equation accounting for the observations. [2]

B1 – Correct species in equation that accounts for the description
B1 – Balanced equation (accept another stoichiometric multiple of this equation where the stoichiometric coefficient of aluminium is 1)

$2\ Al + 6\ H_2O + 2\ OH^- \rightarrow 2\ Al(OH)_4^- + 3\ H_2$

There are 2 stages to this reaction
The first is where aluminium reacts with water to form hydrogen gas and aluminium hydroxide.
As heat is evolved through this reaction, the aluminium hydroxide dissolves in the presence of the alkaline environment to form the aluminium complex.

3 (a) The peroxysulfate ($S_2O_8^{2-}$) ion is a very strong oxidising agent.

When a solution of potassium peroxysulfate is added into a solution of potassium iodide, a yellow colouration is observed. After some time, the solution turns brown.

When a drop of dilute iron(II) sulfate is added, the solution immediately turns brown.

Using relevant standard electrode potential values, explain the above observations. [3]

B3 for all pointers (deduct 0.5 pts up to 3 pts for each missing marking point)
Explain why the reaction happens without a catalyst in the first place, with appropriate calculations and a chemical equation AND why the reaction is slow

- $2\ I^- + S_2O_8^{2-} \rightarrow I_2 + 2\ SO_4^{2-}$
- $E_{cell}^{\ominus} = 2.01 - 0.54 = 1.47$ V is positive, so reaction is thermodynamically feasible and occurs without a catalyst
- Iodine gives the brown colouration at high concentrations, and yellow colouration at low concentrations.
- Reactants are negatively charged which will repel each other → high activation energy

Explain how iron(II) sulfate catalyses the reaction

- $2\ Fe^{2+} + S_2O_8^{2-} \rightarrow 2\ SO_4^{2-} + 2\ Fe^{3+}$ where $E_{cell}^{\ominus} = 2.01 - 0.77 = +1.24$ V
- $2\ Fe^{3+} + 2\ I^- \rightarrow I_2 + 2\ Fe^{2+}$ where $E_{cell}^{\ominus} = 0.77 - 0.54 = +0.23$ V
- Since both E_{cell} values are positive, reaction is thermodynamically feasible.
- Oppositely charges attract each other → lower activation energy
- So iodine forms much faster which results in the immediate brown colouration

(b) A dilute solution of iron(II) sulfate is light green in colour. In contrast, a solution of iron(III) is yellow in colour.

Explain why these solutions are coloured using the crystal field theory, and why solutions of iron(II) and iron(III) ions are different in colour. [3]

B2 for explanation of the crystal field theory.

- Under the presence of water ligands
- The initially degenerate d orbitals of the Fe centre will split into 2 different levels (in the case of an octahedral ligand field)
- Solution absorbs light of a certain wavelength, with an energy that corresponds with the energy gap between the 2 levels
- Promoting 1 electron from an orbital of a lower energy level to an orbital of a higher energy level
- So the colour observed is the complementary colour of that wavelength of light absorbed.

B1 for explanation of different colours

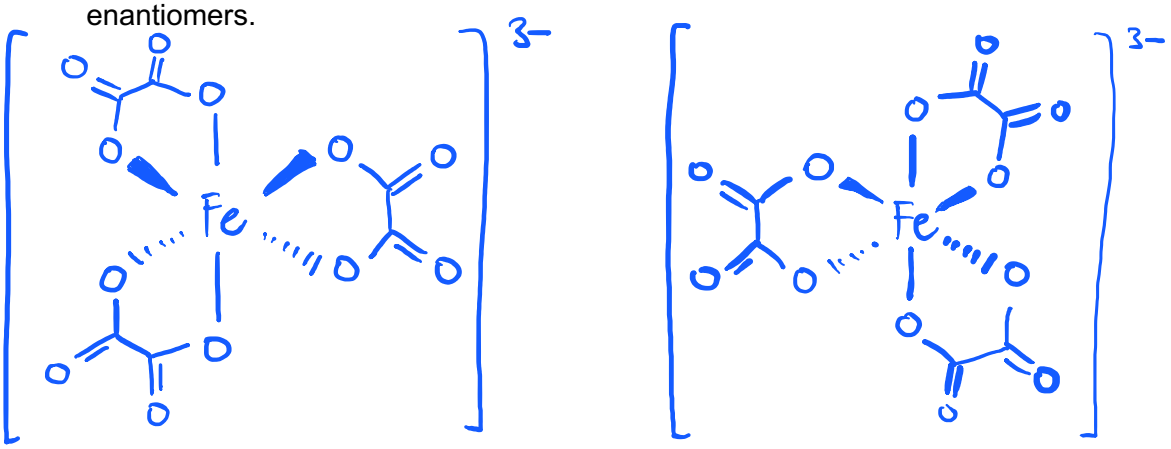
- Since Fe2+ and Fe3+ have different charges
- The splitting of d orbitals occurs to a different extent
- The energy gap is different, so the wavelength of light absorbed, and its complementary colour, is different.

Take note that light is NOT “emitted”.

(c) Potassium ferrioxalate ($K_3[Fe(C_2O_4)_3]$) crystals are green in colour. The ferrioxalate ion has an octahedral geometry with respect to the iron(III) centre.

The oxalate ion contains 1 C—C bond and is symmetrical. It acts as a bidentate ligand.

(i) The ferrioxalate ion has 2 enantiomers. Draw the 3 dimensional structures of the 2 enantiomers. [3]



B1 for each enantiomer
Charge and usage of wedges and dashes must be present (penalise overall 1 pt otherwise)

(ii) To make a solution of potassium ferrioxalate, ferric oxalate ($Fe_2(C_2O_4)_3$) needs to be prepared first. Ferric oxalate is yellow in colour.

Explain why there is a difference in colour between both iron(III) and oxalate containing species. [1]

B1 – Correct explanation

- Ferrioxalate has 3 ligands of oxalate ions about the iron centre, whereas ferric oxalate has both water and oxalate ligands (or only water ligands) about the iron centre
- Different ligands results in different extent of splitting of d orbitals. So different wavelengths of light will be absorbed, resulting in different complementary colours.

(d) When iron(III) hydroxide is treated with sodium hypochlorite (NaOC*l*) in aqueous sodium hydroxide, a violet colouration is observed. Subsequently, the violet solution is treated with barium chloride, in which a brown precipitate is formed.

The brown precipitate contains 3 elements.

(i) Given that the brown precipitate contains 53.4% barium and 24.9% oxygen by mass, determine the empirical formula of this brown precipitate. [2]

M1 – Correct mole ratio

A1 – Correct answer

Since the brown precipitate contains 3 elements, the third element must be iron.

	Ba	Fe	O
Mass	53.4	21.7	24.9
Convert to moles	0.3889	0.3889	1.556
Ratio	1	1	4

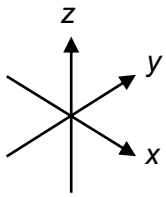
Empirical formula is $BaFeO_4$

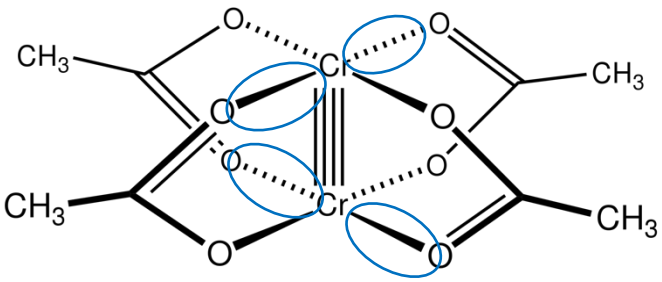
(ii) Hence, construct 2 equations for the reactions taking place above. [2]

The oxidation state of iron in the brown precipitate is +6.
B1 for each reaction
First reaction: $2\ Fe(OH)_3 + 3\ OCl^- + 4\ OH^- \rightarrow 2\ FeO_4^{2-} + 5\ H_2O + 3\ Cl^-$
OCl^- is reduced to Cl^- not Cl_2 in basic conditions. Do verify it with the Data Booklet.
Second reaction: $FeO_4^{2-} + Ba^{2+} \rightarrow BaFeO_4$

(e) Chromium(II) acetate is a non-ionic compound despite its name. Its molecular formula is $Cr_2(CH_3CO_2)_4$.

The structure of chromium(II) acetate is shown below.



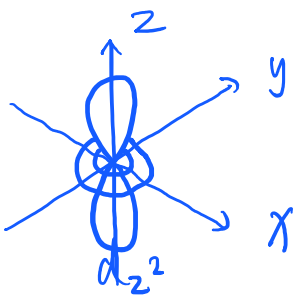


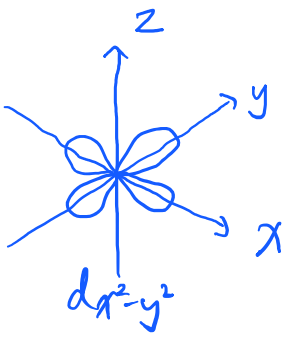
(i) On the structure above, indicate the co-ordinate bond(s) by circling the bond(s). [1]

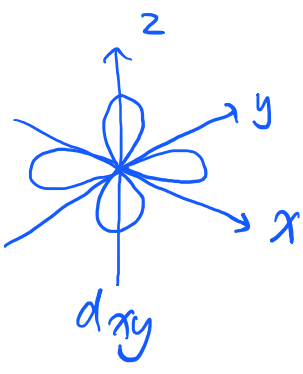
(ii) Copy and use the x-y-z axes printed on the top right of the structure in its given orientation. On separate axes, draw all the 5 *d* orbitals of chromium. [2]

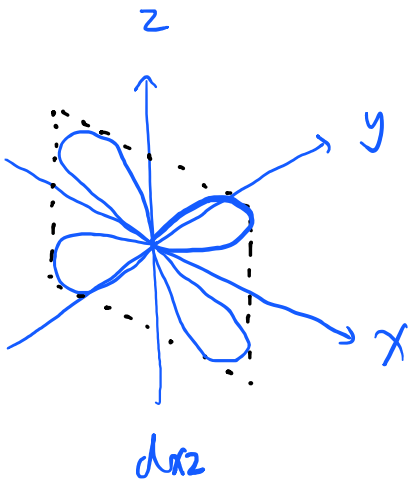
You must not change the orientation of the axes.

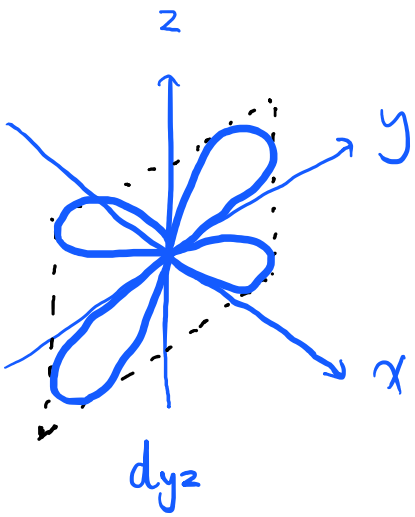
B2 for all 5 correct. Award 1 pt for 3 correct.











(iii) The chromium-chromium bond has 4 covalent bonds, containing 1 sigma bond, 2 pi bonds, and 1 delta bond.

The delta bond is formed through a side-on overlap of 2 orbitals with 4 lobes.

By considering the given orientation of the axes in the structure and your answer in **(ii)**, state which orbital(s) in the chromium atom are involved in:

- the sigma bond,
- the 2 pi bonds, and
- the delta bond of the Cr—Cr bond. [2]

B1 – Correct orbital for sigma and delta bond
Sigma: d_{z^2}
Delta: d_{xy} (accept $d_{x^2-y^2}$)

B1 – Correct orbitals for the 2 pi bonds
d_{xz} and d_{yz}

(iv) Chromium(II) acetate is insoluble in water. It can be prepared through a precipitation reaction between the chromium(II) ion and acetate ion. State how you would obtain the chromium(II) ion from a solution of chromium(III) sulfate. [1]

B1 – Add zinc metal to the solution
Take note that $E^{\ominus}(Cr^{3+}/Cr^{2+})$ = -0.41 V and $E^{\ominus}(Cr^{2+}/Cr)$ = -0.91 V so a reducing agent must have $E^{\ominus}$(oxidised form/reduced form) in the range of -0.41 V to -0.91 V.
One such reducing agent is zinc.
While other reducing agents like iron(II) hydroxide and hydrogen gas (in alkaline conditions) from the data booklet are valid, chromium(III) will be precipitated out as its hydroxide first. The reduction potential of chromium(III) hydroxide to chromium(II) may be different, so it's not the best answer.
For this question, chromium metal and iron metal can be accepted.