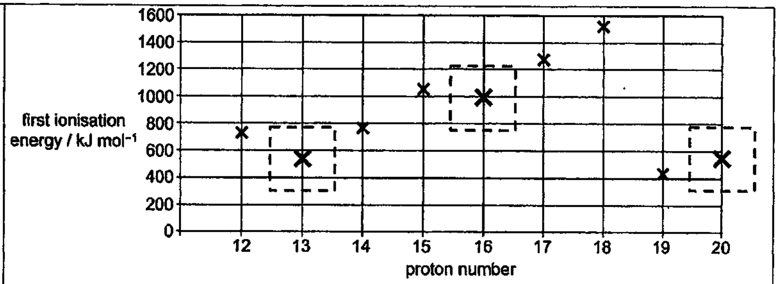
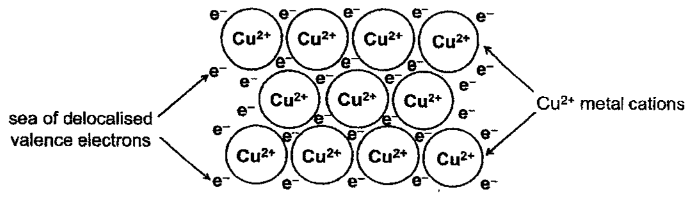
Paper 1 Answer Key

1	B	11	B	21	B
2	B	12	A	22	D
3	A	13	D	23	C
4	D	14	A	24	C
5	B	15	C	25	D
6	C	16	A	26	C
7	D	17	B	27	C
8	B	18	A	28	D
9	A	19	C	29	D
10	B	20	B	30	A

Paper 2 Answers

1 (a) (i)	 [1] for all 3 plots and ensure that the plot at proton number 20 is lower than proton number 12.
(ii)	• The number of protons increase and nuclear charge increase. • Successive electrons are added to the same valence shell, shielding effect remains approximately constant. • Effective nuclear charge increases and electrostatic attraction between the nucleus and valence electron increases. • More energy is required to remove the valence electron
(iii)	Proton number 15: $1s^2 2s^2 2p^6 3s^2 3p_x^1 3p_y^1 3p_z^1$ Proton number 16: $1s^2 2s^2 2p^6 3s^2 3p_x^2 3p_y^1 3p_z^1$ [1] for both electronic configurations. Reject students who write $1s^2 2s^2 2p^6 3s^2 3p_x^4$ for proton number 16. Element with proton number 16, the valence electron to be removed is from the paired electrons in $3p_x$ orbital. Hence, it experiences inter-electronic repulsion arising from the two electrons occupying the same $3p_x$ orbital and requires less energy to remove. [1]

(b) (i)	 [1] Copper has a giant metallic structure with strong metallic bonding (or electrostatic attraction) between copper ion and sea of delocalised electrons. The presence of sea of delocalised electrons acts as mobile charge carriers, hence making copper a good conductor of electricity. [1]
(ii)	• Both Na_2O and MgO have giant ionic structure held together by strong ionic bonding (or electrostatic attraction) between positively charged metal cations and negatively charged oxide anions. • $\|LE\| \propto \frac{\|q^+q^-\|}{r_+ + r_-}$ • Both Na_2O and MgO have the same oxide anion, but Mg^{2+} is doubly charged while Na^+ is singly charged. • The ionic radius of $Na^+ > Mg^{2+}$. The magnitude of LE is larger for MgO than Na_2O. • Ionic bonding of MgO is stronger than Na_2O. More energy is required to break the stronger ionic bonds between Mg^{2+} and O^{2-} in MgO than ionic bonds between Na^+ and O^{2-} in Na_2O. • Melting point of MgO is higher than Na_2O and hence able to withstand higher temperature in case of fire.
2 (a) (i)	The order of reaction with respect to a given reactant is the power to which the concentration of that reactant is raised in the experimentally determined rate equation. [1]
(ii)	When [NaOH] decreases, gradient remains constant, hence rate of reaction is constant. Rate of reaction is independent of [NaOH], hence the reaction is zero order wrt [NaOH]. [1] When $[CH_3CHBrCH_2CH_3] = 0.25$ mol dm^{-3} initial rate = 0.0048 / 30 = 1.60 x 10^{-4} mol dm^{-3} min^{-1} When $[CH_3CHBrCH_2CH_3] = 0.50$ mol dm^{-3} initial rate = 0.0095 / 30 = 3.16 x 10^{-4} mol dm^{-3} min^{-1} When $[CH_3CHBrCH_2CH_3]$ doubles (0.50/0.25), the gradient doubles, showing that the rate of reaction doubles from 1.60 x 10^{-4} to 3.16 x 10^{-4} mol dm^{-3} min^{-1}. [1] Hence the reaction is first order wrt $[CH_3CHBrCH_2CH_3]$.
(iii)	rate = $k[CH_3CHBrCH_2CH_3]$ 1.60 x 10^{-4} = k (0.25) k = 6.40 x 10^{-4} min^{-1} or 1.07 x 10^{-5} s^{-1} [1]

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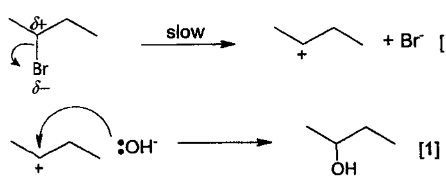
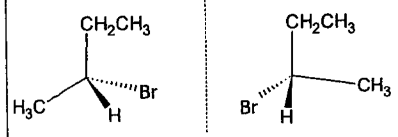
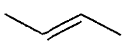
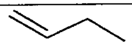
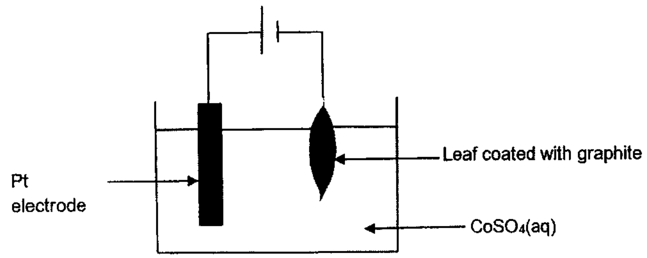
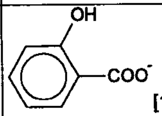
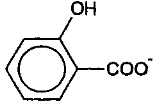
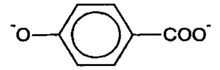
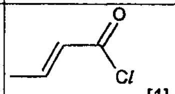
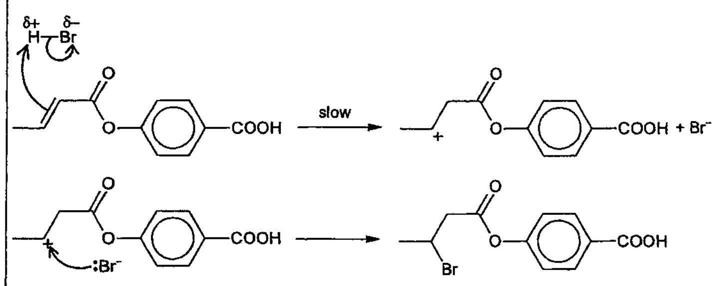
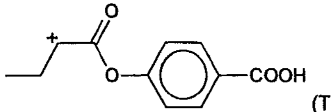
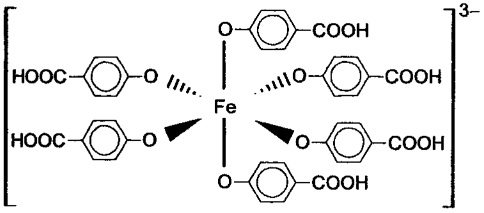
(iv)	Nucleophilic Substitution (S_N1)  [1] [1]
(v)	The OH⁻ nucleophile can attack the trigonal planar carbocation centre from either the top or bottom of the plane with equal probability, producing equal amounts of the pair of enantiomers (a racemic mixture). [1] The product mixture is optically inactive (i.e. does not rotate plane-polarised light) as each enantiomer rotate plane-polarised light in the opposite direction by the same magnitude hence the rotating powers of the enantiomers cancel out. [1]
(b) (i)	Stereoisomerism is defined as compounds having the same molecular formula but different spatial formulae / different spatial arrangement of atoms. [1]
(ii)	 mirror plane [1]
(iii)	  [1]
(iv)	
3 (a)	 [1]

(b)	Cathode: $Co^{2+}(aq) + 2e \rightarrow Co(s)$ [1] Anode: $H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e$ [1]
(c)	n(Co) coated = (8.90 x 0.2 x 10^{-1} x 10) / 58.9 = 0.0302 mol [1] n(O_2) = (0.0302) / 2 = 0.0151 mol Volume of gas = 0.0151 x 24 = 0.363 dm^3 (or 363 cm^3) [1]
(d)	$Co^{2+}(aq) + 2e \rightarrow Co(s)$ Q = It = nzF 0.5 × t = 0.0302 × 2 × 96500 t = 11657.2s = 3.24 h [1] unit must be in h
(e)	$Co^{2+} + 2e \rightleftharpoons Co$ –0.28 V $Pb^{2+} + 2e \rightleftharpoons Pb$ –0.13 V $O_2 + 4H^+ + 4e \rightleftharpoons 2H_2O$ +1.23 V The mass of the lead electrode will decrease. E°(Pb^{2+}/Pb) is more negative than E°(O_2/H_2O), Pb will be preferentially oxidised to form Pb^{2+} in aqueous solution. [1] Dull gray solid Pb will be deposited at the leaf. E°(Pb^{2+}/Pb) is less negative than E°(Co^{2+}/Co), Pb^{2+} will be preferentially reduced. [1]
4 (a) (i)	Acidity depends on the stability of the conjugate base. In phenoxide, the p-orbital of oxygen atom overlaps with the π electron cloud of the benzene ring. Lone pair of electrons of the oxygen atom delocalised into the benzene ring. The negative charge on the oxygen atom is dispersed into the benzene ring and stabilising the phenoxide. [1] In carboxylate ion, the p-orbital of oxygen atom overlaps with the π electron cloud of the C=O bond. Lone pair of electrons of the oxygen atom delocalised into the C=O bond. The negative charge on the oxygen atom is dispersed over the carbon atom and two electronegative oxygen atoms and stabilising the carboxylate ion. The charge dispersion is more effective than that in phenoxide due to the two electronegative oxygen atoms and hence carboxylate ion is more stable than phenoxide ion. [1] Hence, carboxylic acid is a stronger acid than phenol.
(ii)	 [1] Reject ⁻O-C_4H_6-COOH as the COOH should deprotonate first since it has a lower pK_a. Reject ⁻O-C_4H_6-COO⁻ as it differs from 2-hydroxybenzoic acid by 2 H^+ hence not a conjugate base of the acid. The conjugate base of 2-hydroxybenzoic acid can form intramolecular hydrogen bonding that helps to further stabilize the conjugate base. [1]

(iii)	[4-hydroxybenzoic acid] = $\frac{2.76}{138.0} \div \frac{100}{1000}$ = 0.2000 mol dm^{-3} [1] $[H_3O^+] = \sqrt{10^{-4.58} \times 0.2000}$ = 2.293 × 10^{-3} mol dm^{-3} pH = -lg (2.293 × 10^{-3}) = 2.639 = 2.64 [1]
(iv)	$n_{\text{4-hydroxybenzoic acid}} = \frac{2.76}{138}$ = 0.02000 mol $n_{NaOH} = \frac{0.35}{40.0}$ = 8.750 × 10^{-3} mol [1] Since the neutralisation between 4-hydroxybenzoic acid and NaOH is 1:1 mole ratio, NaOH is a limiting reagent. $n_{\text{4-hydroxybenzoic acid}}$ left = 0.02000 – (8.750 × 10^{-3}) = 0.01125 mol $n_{\text{4-hydroxybenzoate}}$ formed = 8.750 × 10^{-3} mol [1] Since there is a mixture of 4-hydroxybenzoic acid and 4-hydroxybenzoate, solution **Q** is an acidic buffer. pH = pK_a + lg $\frac{[\text{4-hydroxybenzoate}]}{[\text{4-hydroxybenzoic acid}]}$ = 4.58 + lg $\frac{8.750 \times 10^{-3} / \frac{100}{1000}}{0.01125 / \frac{100}{1000}}$ = 4.470 = 4.47 [1]
(v)	 2-hydroxybenzoic acid at pH 12 position on Fig. 4.1: 3  4-hydroxybenzoic acid at pH 12 position on Fig. 4.1: 4 [1] for each correct structure and position
(vi)	Any pH between 4.58 and 9.51. [1]
(b) (i)	 [1]
(ii)	Electrophilic Addition  [1] for step 1 [1] for step 2

(iii)	Formation of T involves a less stable carbocation that is adjacent to an electron withdrawing ester group, which destabilises the carbocation. Hence, a smaller amount of that carbocation intermediate is formed, and T is a minor product. [1]  (T forms a less stable carbocation than S)
(c) (i)	$Fe(OH)_3$ [1]
(ii)	A complex is a species that contains a central metal atom/ion surrounded by molecules or anions (known as ligands) which form coordinate bonds (dative bonds) to the metal centre. [1]
(iii)	The phenoxide ion is a stronger ligand as the lone pair on the O atom is less delocalised compared to that in the carboxylate ion, and hence more available to form dative bonds. OR In the carboxylate ion, the lone pair of electrons of the O atom is delocalised into the C=O bond more effectively due to the electronegative oxygen atom, hence it is less available to form dative bonds. [1]
(iv)	 • correct shape • overall charge (overall charge = +3 + 6 (– 1) = –3) • correct structure
5 (a) (i)	When NaOH is added, OH$^-$ reacts with H$^+$, decreasing [H$^+$]. By Le Chatelier's Principle, the position of equilibrium for the dissociation of H_2S shifts to the right to increase [H$^+$], resulting in higher [S^{2-}]. [1] Precipitation of metal sulfides occurs as the ionic product of metal sulfides becomes greater than the K_{sp}. [1]
(ii)	Volume of 100 g of lake water sample = 100 g / 1.02 g cm^{-3} = 98.03 cm^3 = 0.09803 dm^3 [Cu^{2+}] in g dm^{-3} = 6.54 / 0.09803 = 66.71 g dm^{-3} [Cu^{2+}] in mol dm^{-3} = 66.71 / 63.5 = 1.050 = 1.05 mol dm^{-3} [1] [Zn^{2+}] in g dm^{-3} = 1.25 / 0.09803 = 12.75 g dm^{-3} [Zn^{2+}] in mol dm^{-3} = 12.75 / 65.4 = 0.1949 = 0.195 mol dm^{-3} [1]
(iii)	K_{sp} for ZnS = [Zn^{2+}][S^{2-}] mol^2 dm^{-6} [1]

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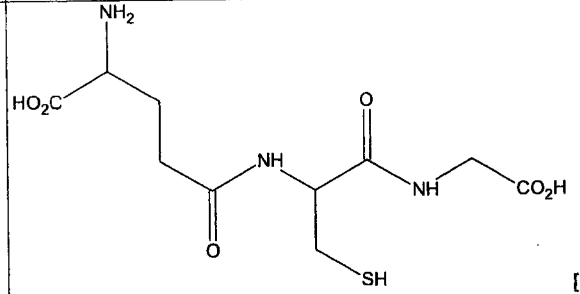
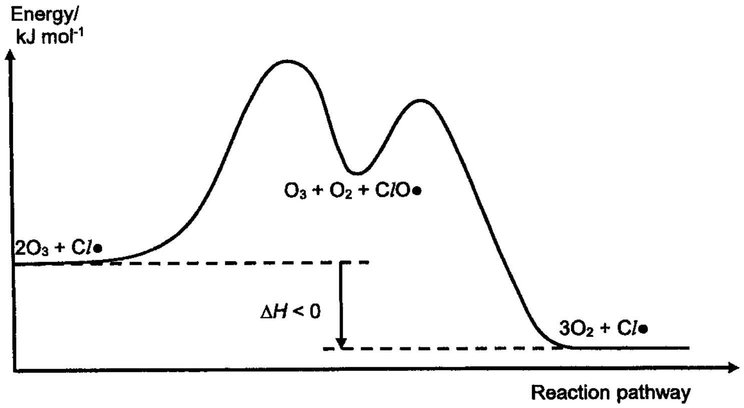
(iv)	For precipitation of metal to occur, ionic product > K_{sp} $[M^{2+}][S^{2-}] > K_{sp}$ Minimum $[S^{2-}]$ required for precipitation of CuS = $6.3 \times 10^{-36} / 1.050$ $= 6.00 \times 10^{-36}$ mol dm^{-3} [1] allow ecf Minimum $[S^{2-}]$ required for precipitation of ZnS = $1.6 \times 10^{-24} / 0.1949$ $= 8.21 \times 10^{-24}$ mol dm^{-3} [1] allow ecf Black precipitate of CuS would appear first, followed by appearance of white precipitate of ZnS. [1]
(v)	$Cu(NO_3)_2(s) + aq \rightarrow Cu^{2+}(aq) + 2NO_3^-(aq)$ -----(1) $CuS(s) + aq \rightleftharpoons Cu^{2+}(aq) + S^{2-}(aq)$ -------(2) On addition of solid $Cu(NO_3)_2$, concentration of the common ion Cu^{2+} increases (1). By Le Chatelier's Principle, position of equilibrium of dissolving of CuS(s) (2) shifts to the left to reduce the added Cu^{2+}. Hence, solubility of CuS will decrease and student's suggestion is right. [1] However, solubility product of CuS will remain unchanged since it is affected only by temperature changes and so student's suggestion is wrong. [1]
(b) (i)	SiO_2 has a giant molecular structure [1] where each Si atom is covalently bonded to 4 other O atoms and each O atom is covalently bonded to 2 other Si atoms. [1]
(ii)	The energy released during the formation of instantaneous dipole–induced dipole attraction between water and the Si or O atoms [1] is not enough to overcome the energy needed to break strong covalent bonds between Si and O atoms. [1]
(c) (i)	2GSH → GSSG + $2H^+$ +2e [1] Oxidation. GSH loses electron to transform into GSSG. [1]
(ii)	 [1]
(d) (i)	High temperature. High kinetic energy results in faster motion of halogen molecules. Hence intermolecular forces of attraction between halogen molecules become less significant. [1] Low pressure. Volume of container is large. Volume occupied by halogen molecules becomes negligible as compared to the volume of container. [1]

(ii)	$Cl\bullet$ acting as a catalyst. It is used in step 1 and regenerated in step 2. [1]
(iii)	 [1] correct shape of diagram showing 2 steps and overall exothermic reaction [1] label axis, balanced chemical species, and enthalpy change correctly Note: 1st step is likely to be endothermic as more energy was taken in to break a stronger O→O bond in ozone (O=O→O) than energy released to form a weaker Cl-O bond. 2nd step has to be exothermic in order for overall ΔH to be exothermic. Optional for first peak to be higher than second peak i.e. $E_{a1} > E_{a2}$.
(e) (i)	[R] $I_2 + 2e \rightarrow 2I^-$ [O] $2S_2O_3^{2-} \rightarrow S_4O_6^{2-} + 2e$ Overall equation: $I_2 + 2S_2O_3^{2-} \rightarrow S_4O_6^{2-} + 2I^-$ $E^\theta_{cell} = +0.54 - (+0.09) = +0.45$ V [1] balanced equation and E^θ_{cell} value.
(ii)	[R] $Cl_2 + 2e \rightarrow 2Cl^-$ [O] $S_2O_3^{2-} + 5H_2O \rightarrow 2SO_4^{2-} + 10H^+ + 8e$ [1] correct half equations Overall: $4Cl_2 + S_2O_3^{2-} + 5H_2O \rightarrow 8Cl^- + 2SO_4^{2-} + 10H^+$ [1] correct balanced overall equation

Paper 3 Answers

1 (a) (i)

NaCl has a giant ionic structure, it undergoes hydration to form a neutral solution of hydrated ions with pH = 7.
$NaCl(s) + aq \rightarrow Na^+(aq) + Cl^-(aq)$

$AlCl_3$ has a simple covalent structure with ionic character thus it undergoes hydration to give the hydrated ions.
$AlCl_3(s) + 6H_2O(l) \rightarrow [Al(H_2O)_6]^{3+}(aq) + 3Cl^-(aq)$

$[Al(H_2O)_6]^{3+}$ then undergoes further hydrolysis to give $[Al(H_2O)_5OH]^{2+}$. Al^{3+} in $[Al(H_2O)_6]^{3+}$ has a high charge density and is highly polarising. It is able to polarise one of the O–H bond in H_2O, causing H^+ to be released to give a slightly acidic solution of pH = 3.
$[Al(H_2O)_6]^{3+}(aq) + H_2O(l) \rightleftharpoons [Al(H_2O)_5OH]^{2+}(aq) + H_3O^+(aq)$

PCl_5 has a simple covalent structure and undergoes hydrolysis to give a highly acidic solution of pH = 1 and white fumes of HCl gas.
$PCl_5(s) + 4H_2O(l) \rightarrow H_3PO_4(aq) + 5HCl(g)$

[1] for each point

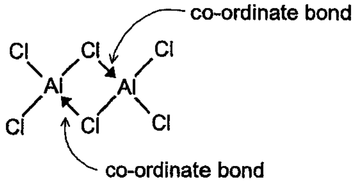
(ii)

- pH value of $BeCl_2$: Below 3
- Quote the ionic radius of Al^{3+} and Be^{2+}:

Ion	Ionic radius / nm	Charge density
Al^{3+}	0.050	3/0.050 = 60
Be^{2+}	0.031	2/0.031 = 64.5

- Charge density of Be^{2+} is higher than Al^{3+}; its degree of hydrolysis is higher than Al^{3+}, hence, the pH of $BeCl_2$ lower than $AlCl_3$.

(iii)



(b)

Both BeO and Al_2O_3 are amphoteric and reacts with both acids and bases.
BeO and Al_2O_3 react similarly as Be and Al have similar effective nuclear charge. [1]

$BeO(s) + 2HCl(aq) \rightarrow BeCl_2(aq) + H_2O(l)$
$BeO(s) + 2NaOH(aq) + H_2O(l) \rightarrow Na_2Be(OH)_4(aq)$ [1]

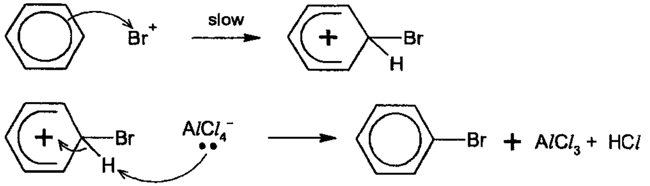
(c) (i)

Br is less electronegative than Cl, hence will react with $AlCl_3$ to form the electrophile Br^+ which undergoes electrophilic substitution with benzene.

(ii)

Electrophilic substitution

$BrCl + AlCl_3 \rightleftharpoons Br^+ + AlCl_4^-$

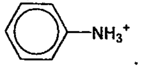


3 correct steps – 2 marks
2 correct steps – 1 mark

(iii)

- Least: Isomer 3-position Most: Isomer 4-position
- Electron donating $-C(CH_3)_3$ group is directly bonded to the carbocation centre hence it disperses the positive charge on the carbocation centre in the intermediates for isomer 2-position and isomer 4-position more effectively than for isomer 3-position, forming a more stable carbocation. Hence, isomer 3-position will be formed the least.
- However, the incoming Br^+/electrophile will experience steric hindrance from the bulky $-C(CH_3)_3$ group as it approaches the 2-position. Hence, isomer 4-position will be formed the most.

(iv)

- Under acidic conditions, phenylamine undergoes acid-base reaction to produce a high proportion of  .

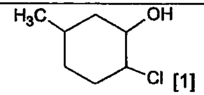
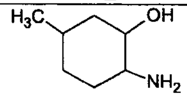
- The $-NH_3^+$ is 3-directing and hence a large proportion of the 3-isomer is produced.

(d)

B, A, C

- In **B**, the p orbital of Cl atom overlaps with π electron cloud of benzene ring resulting in the delocalisation of lone pair of electrons on the Cl atom into the benzene ring, strengthening the C–Cl bond, and is least susceptible to attack by water nucleophile. [1]
- In **A**, C atom in **C–Cl** is attached to only one electronegative atom, Cl. It is less electron deficient / carries a smaller partial positive charge δ+ than the carbon atom in **–COCl** and is less susceptible to attack by water nucleophile. [1]
- In **C**, the C atom in **–COCl** is attached to two highly electronegative atoms, O and Cl. It is more electron deficient / carries a larger partial positive charge δ+. This C atom is most highly susceptible to attack by water nucleophile. [1]

(e) (i)

D	E
 [1]	 [1]

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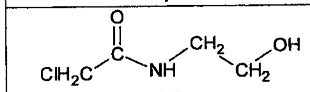
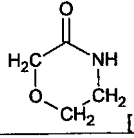
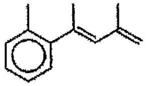
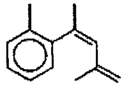
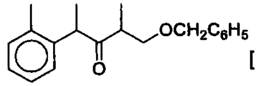
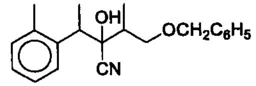
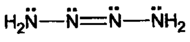
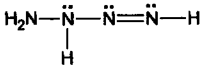
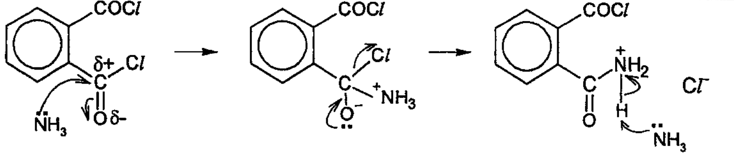
(ii)	**F**  [1] **G**  [1]
2 (a)	heat energy from heating coil = heat absorbed by water + heat absorbed by calorimeter 10000 = (300 x 4.18 x 7.5) + (C x 7.5) [1] 10000 = (9405) + (7.5C) 7.5C = 10000 – 9405 = 595 J Heat capacity of calorimeter, C = $\frac{595}{7.5}$ = 79.3 J K^{-1} [1]
(b) (i)	$K_{sp} = [Ag^+]^2[CO_3^{2-}] = (2.57\times10^{-4})^2(2.57\times10^{-4}/2) = 8.49 \times 10^{-12}$ [1] $mol^3\ dm^{-9}$ [1]
(ii)	$K_{sp} = [Ag^+]^2[CO_3^{2-}]$ $8.49 \times 10^{-12} = [Ag^+]^2 \times (2.50 \div (23.0 \times 2 + 12.0 + 16.0 \times 3) \div (100/1000))$ $[Ag^+] = 6.00 \times 10^{-6}$ mol dm^{-3} [1] Solubility of Ag_2CO_3 = ½ × $6.00 \times 10^{-6} = 3.00 \times 10^{-6}$ mol dm^{-3} [1]
(c) (i)	$P_{Al_2I_6} = \frac{nRT}{V} = \frac{(\frac{10.0}{816})(8.31)(673)}{2 \times 10^{-3}}$ = 34300 Pa [1]
(ii)	$P_{Al_2I_6}$ (after dissociation) = 0.65 x 34300 = 22300 Pa P_{AlI_3} = 2 x 0.35 x 34300 = 24000 Pa [1] $K_p = \frac{(P_{AlI_3})^2}{P_{Al_2I_6}} = \frac{24000^2}{22300}$ = 25800 [1] Pa [1] allow ecf
(iii)	ΔS is positive and Δ*H* is positive. When temperature decreases, <u>|–TΔ*S*| will be smaller than |Δ*H*|</u>. [1] <u>Δ*G* will become more positive</u> and <u>less spontaneous</u>. Hence <u>degree of dissociation decreases</u>. [1] OR When the temperature is decreased, by Le Chatelier's Principle, the <u>backward exothermic reaction is favoured</u> to <u>produce more heat</u>. [1] Hence, the <u>position of equilibrium will shift to the left</u> and <u>degree of dissociation decreases</u>. [1]

(d) (i)	P:  [1] Q:  [1]
(ii)	Nucleophilic Substitution [1]
(iii)	Step 2: $K_2Cr_2O_7$, H_2SO_4(aq), heat [1] [do not accept $KMnO_4$, H_2SO_4(aq)] **B:**  [1] Step 3: HCN, trace amount of NaOH(aq), 10–20 °C [1] **C:**  [1] Step 4: H_2SO_4(aq), heat [1]
3 (a)	Most stable structure:  or  [1]
(b)	Both compounds have simple molecular structures. On average, tetrazene is able to form 4 hydrogen bonds per molecule as compared to 1 hydrogen bond per molecule for hydrogen azide. More energy is required to overcome the more extensive hydrogen bonding in tetrazene. Hence, the high boiling point of hydrazine. [1]
(c) (i)	Ammonia is acting as a Bronsted Lowry acid as it donates H^+ to $CH_2{=}CH^-$ to form $CH_2{=}CH_2$. [1]
(ii)	Ammonia is acting as a Lewis base as the N atom donates a lone pair of electrons to the electron deficient B atom. [1]
(iii)	Ammonia is acting as a reducing agent as it reduces the oxidation number of chlorine from +1 in NaOC*l* to –1 in NaC*l*. [1]
(iv)	Ammonia is acting as a nucleophile as it contains a lone pair of electrons which attacks the electron deficient carbon of the two acyl chlorides. [1]
(d)	Condensation/ nucleophilic acyl substitution [1]



[1] for 2 correct sets [2] for all 3 correct sets

(e) (i) There are 5 electrons in the 2nd shell of the sp^2 hybridised N.

- In the three sp^2 hybrid orbitals of N atom, each hybrid orbital has an unpaired electron.
- Sigma bonds are formed when two sp^2 hybrid orbitals of N atom overlaps head-on with the sp^2 hybrid orbitals of each carbon atom and when one sp^2 hybrid orbital of N atom overlaps head on with the 1s orbital of H atom.
- The unhybridised p orbital are filled with a lone pair of electrons.

(ii) 4-methylphenylamine is (1) more basic than phthalimide.

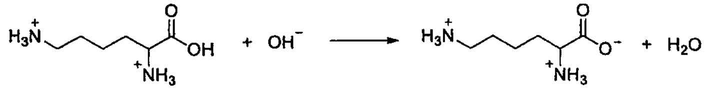
For 4-methylphenylamine, the (2) p orbital of N atom overlaps with the π electron cloud of the benzene ring, causing the lone pair on N atom to be delocalised into the benzene ring. This (3) decreases the availability of the lone pair of electrons on N atom but lone pair is still available for dative bonding with a H^+. [1]

While in phthalimide, (4) p orbital of N atom overlaps effectively with the π electron cloud of the 2 C=O due to the electronegative O atoms, allowing the lone pair of electrons on N atom to be delocalise into the π electron cloud of C=O, making (5) lone pair not available to form a dative bond with a H^+. [1]

(f) (i) $pK_{a1} = 2.2$

$K_{a1} = 10^{-2.20} = 6.31 \times 10^{-3}$ mol dm^{-3} [1]

(ii) When small amount of base is added,



- Balanced eqn, with correct structural formula of the protonated lysine and product,
- full arrow for equation (reaction is a neutralisation reaction)

[1] for both points

When a small amount of OH^- is added, it is removed by the large reservoir of protonated lysine, hence keeping pH fairly constant. [1]

(iii) Fig 3.2 shows that end point is achieved when 10cm^3 of 1.00 mol dm^{-3} NaOH was added to 10cm^3 of fully protonated lysine, HA. Hence [HA] = 1.00 mol dm^{-3}

$$n(HA) \text{ at point } \mathbf{A} = 1.00 \times \frac{10}{1000} = 1.00 \times 10^{-2} \text{ mol}$$

At point **B** (MBC) $n_{HA} = n_{A^-}$

$$= \frac{1.00 \times 10^{-2}}{2}$$

$$= 5.00 \times 10^{-3} \text{ mol}$$

$$n(NaOH) \text{ added} = 0.0200 \times \frac{10.0}{1000} = 2.00 \times 10^{-4} \text{ mol}$$

$HA + OH^- \rightarrow A^- + H_2O$

n_{HA} present after NaOH is added= $(5.00 \times 10^{-3}) - (2.00 \times 10^{-4})$
$= 4.80 \times 10^{-3}$ mol

n_{A^-} present after NaOH is added $= (5.00 \times 10^{-3}) + (2.00 \times 10^{-4})$
$= 5.20 \times 10^{-3}$ mol [1]

$$K_a = \frac{[H^+][A^-]}{[HA]}$$

$$6.31 \times 10^{-3} = \frac{[H^+] \times 5.20 \times 10^{-3}}{4.80 \times 10^{-3}}$$

$[H^+] = 5.82 \times 10^{-3}$ mol dm^{-3}
pH = 2.24 [1]

OR

ICE table for understanding (not necessary to draw for answer)

	HA (acid)	+ NaOH	→	NaA (salt)	+ H_2O
n(Initial)	5.00×10^{-3}	2.00×10^{-4}		5.00×10^{-3}	-
n(Change)	-2.00×10^{-4}	-2.00×10^{-4}		$+ 2.00 \times 10^{-4}$	-
n(Eqm)	0.0048	0		0.0052	-

$$pH = pK_a + \lg\frac{[salt]}{[acid]}$$

$$= 2.2 + \lg\left(\frac{0.0052/V}{0.0048/V}\right) \quad [1]$$

$$= 2.23$$

4 (a) (i) Ionic radius (Pb^{2+}) = 0.120nm
Ionic radius (Mg^{2+}) = 0.065nm
Ionic radius of the Pb^{2+} is larger than that of Mg^{2+} but ionic charge remains as 2+.
Charge density of the Pb^{2+} is lower and its polarising power is also lower. [1]

Pb^{2+} is less able to polarise the electron cloud of the CO_3^{2-} ion in $PbCO_3$.
C–O bonds in CO_3^{2-} is polarised and weakened to a smaller extent.
More energy is needed to break the C–O bond.
$PbCO_3$ has the higher decomposition temperature. [1]

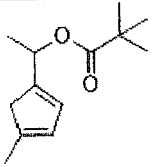
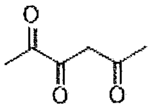
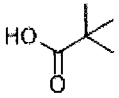
(b) (i) I: Electrophilic Substitution [1]

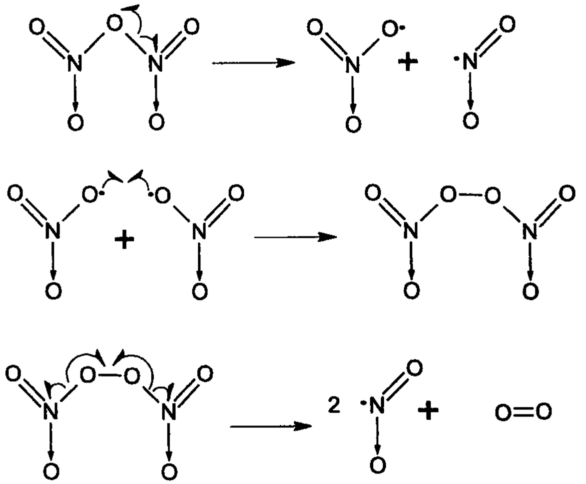
(ii) +2
$1s^2 2s^2 2p^6 3s^2 3p^6 3d^6$
[1] for both

(iii) In the presence of ligands, the partially filled 3d orbitals split into two energy levels, with a small energy gap, ΔE.
An electron in the lower energy d orbital absorbs energy in the visible spectrum corresponding to ΔE and becomes excited to a vacant d orbital at the higher energy level (d-d transition). [1]

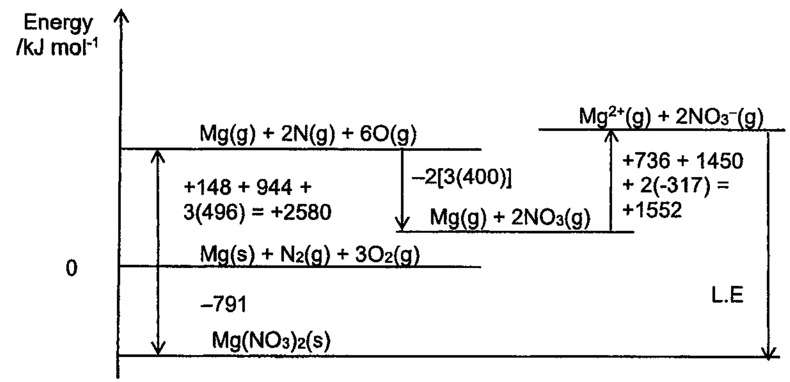
BP-73

BP~74

	Unabsorbed wavelengths are transmitted and the colour observed is complementary to the colour absorbed. [1]
(iv)	With water as the ligand, electromagnetic waves with energy corresponding to red is absorbed which has a lower energy than blue, which is absorbed when $C_5H_5^-$ is the ligand. [1] $C_5H_5^-$ causes a larger 3d orbital split. [1]
(v)	$E^\circ(Fe(C_5H_5)_2^+\|Fe(C_5H_5)_2)$ is less positive than $E^\circ(Fe^{3+}\|Fe^{2+})$. In reaction (**II**), ferrocene has been oxidised by Fe^{3+}, thus $E^\circ(Fe(C_5H_5)_2^+\|Fe(C_5H_5)_2)$ has a less positive E° value than $E^\circ(Fe^{3+}\|Fe^{2+})$ since $E^\circ_{cell} = E^\circ_{reduced} - E^\circ_{oxidised} > 0$. [1]
(vi)	$2Fe(C_5H_5)_2 + S_2O_8^{2-} \rightarrow 2Fe(C_5H_5)_2^+ + 2SO_4^{2-}$ [1] $2Fe(C_5H_5)_2^+ + 2I^- \rightarrow 2Fe(C_5H_5)_2 + I_2$ [1] Without the catalyst, the reaction has a high activation energy due to collisions between ions of the same charge. In the presence of catalyst, collisions between ions of the same charge are avoided hence it lowers the activation energy. [1]
(vii)	$+0.54V < E^\circ(Fe(C_5H_5)_2^+\|Fe(C_5H_5)_2) < +0.77V$ [1]
(c)	 G  H  J [1] for each correct structure. Maximum [3]. **G** contains an ester and undergoes acid hydrolysis to form a carboxylic acid and an alcohol. **G** contains an alkene and undergoes oxidative cleavage with acidified MnO_4^- to give **H**, **J** and CO_2. **G** contains two alkenes and undergoes electrophilic addition with two Br_2 to form alkylbromide due to the addition of four Br atoms. **J** contains a carboxylic acid and undergoes neutralisation with $NaHCO_3$. **J** contains a carboxylic acid and undergoes reduction with $LiAlH_4$ to give a primary alcohol. Primary alcohol cannot undergo elimination with conc H_2SO_4 as the C atom next to C with –OH group has no available H atom.

	H conatins a ketone and undergoes condensation with 2,4-DNPH to give an orange ppt. **H** contains a ketone since there is no reaction with Tollen's reagent. **H** contains two CH_3CO– and undergoes oxidation with alkaline aqueous iodine to give two moles of yellow ppt of CHI_3. [4]
5 (a) (i)	BE(C–C) + 2×BE(C–O) = 350 + 2×360 = +1070 kJ mol^{-1} [1]
(ii)	$\Delta H_r^\ominus = \sum BE(\text{bonds broken}) - \sum BE(\text{bonds formed})$ –354 = [4×BE(C–H) + BE(C=C)] – [BE(C–C) + 4×BE(C–H) + 2×BE(C–O)] –354 = [(4×410) + 610] – [BE(C–C) + (4 × 410) + 2×BE(C–O)] –354 = 610 – [BE(C–C) + 2×BE(C–O)] BE(C–C) + 2×BE(C–O) = +964 kJ mol^{-1} [1] The actual bond energy is less endothermic as it takes lesser energy to break the weaker covalent bonds in the 3 member ring. [1]
(iii)	ΔS is negative. Entropy of the system decreases and there is an decrease in the total number of gaseous particles in the system (i.e. from 2 mol of gaseous reactant to 1 mol of gaseous product). [1] There are less ways of arranging the particles in the system, resulting in a more disordered system to a less disordered system. [1]
(iv)	$\Delta H^\ominus$ and $\Delta S^\ominus$ are both negative. For reaction to be feasible, ΔG < 0 (negative). Since ΔG = ΔH – TΔS, |TΔS| factor would be smaller in magnitude at lower temperature than |ΔH|. The reaction is feasible at low temperature. [1]
(b)	 [3] total [1] for each correct step

(c)

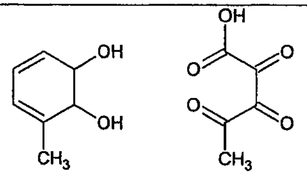


By Hess' Law:
$-791 = (+2580) + (-2400) + (1552) + \text{L.E.}$

L.E. = -2523 kJ mol^{-1}
= -2520 kJ mol^{-1} [1]

(d) (i) 2,3-dioxobutanedioic acid

(ii)



J **K**

1 mark for each correct structure

Observations	Deductions
J, $C_7H_{10}O_2$ decolourises bromine water	**J** could be alkene or phenol. An alkene undergoes electrophilic addition reaction with $Br_2(aq)$ to form bromohydrin.
22.7 dm^3 of hydrogen is formed at s.t.p when **J** is reacted with sodium metal	2 moles of secondary alcohol in **J** undergoes reduction with Na to form 1 mol of H_2. $n(H_2) = \frac{22.7}{22.7} = $ 1 mol of H_2 is formed. $ROH + Na \rightarrow RO^-Na^+ + \frac{1}{2}H_2$ Since 1 FG produces ½ mole of H_2, there must be 2 –OH groups present. –COOH group is absent as it will only produce only ½ mole of H_2 and 2 –COOH groups or 1 –OH & 1 –COOH groups cannot be present as it will not correspond to the molecular formula of **J**.
On heating with acidified $KMnO_4$, **K**, $C_5H_4O_5$, is the only organic product formed	Secondary alcohol and the alkene in **J** undergoes oxidation with $KMnO_4$ to form ketones and carboxylic acid. There is a decrease in 2C atoms – which suggest that ethane-1,2-dioic acid was oxidised to form CO_2. From the given structure of **L**, it can be seen that **K** is unlikely a phenol and should not contain benzene as there will not be oxidation that leads to a reduction of 2 C atoms.
K reacts with sodium carbonate and 2,4 DNPH	Carboxylic acid in **K** undergoes acid-base with Na_2CO_3 to form salt and water. Ketone in **K** undergoes condensation with 2,4 DNPH to give an orange ppt of hydrazone.
K reacts with alkaline aqueous iodine to form **L**	Methyl ketone in **K** undergoes oxidation with alkaline $I_2(aq)$ to give a carboxylate salt and yellow ppt of CHI_3. The carboxylate ion undergoes acid-base reaction with acid to form COOH in **L**.

[4]