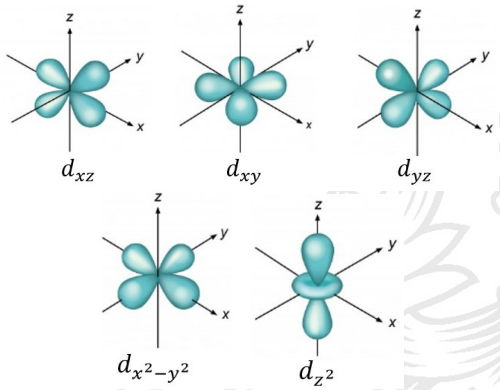
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
C	D	B	D	A	B	B	A	D	B	C	C	D	C	B
16	**17**	**18**	**19**	**20**	**21**	**22**	**23**	**24**	**25**	**26**	**27**	**28**	**29**	**30**
B	C	D	D	B	C	B	A	D	C	D	A	C	A	D

Q1 (C)

There are a total of five 3d orbitals. However, only the $3d_{x^2-y^2}$, $3d_{xy}$, $3d_{xz}$ and $3d_{yz}$ orbitals have four lobes.



Q2 (D)

Since there is a large jump from the 8th to 9th ionisation energy, the element has eight valence electrons and is a Group 18 element, i.e. Ar.

Q3 (B)

When nucleon number = 217,

	atomic number	no. of neutrons	no. of electrons
Po^{2+}	84	217 – 84 = 133	84 – 2 = 82
At^{3+}	85	217 – 85 = 132	85 – 3 = 82
Rn^{4+}	86	217 – 86 = 131	86 – 4 = 82
Fr^{5+}	87	217 – 87 = 130	87 – 5 = 82

From the above table, only At^{3+} has 50 more neutrons than electrons.

Q4 (D)

The three alkanes are constitutional isomers with the same M_r and number of electrons. All three are simple, non-polar molecules with only instantaneous dipole-induced dipole (id-id) interactions.

Since boiling involves overcoming the intermolecular forces of attraction (NOT covalent bonds), the differences in boiling points among the three alkanes are due to differences in the strength of their id-id interactions.

Pentane, a straight–chained hydrocarbon, has greater surface area for intermolecular interactions compared to its branched isomers, 2-methylbutane and 2,2-dimethylpropane. Thus, intermolecular id-id interaction is the strongest in pentane. As branching increases from 2-methylbutane to 2,2-dimethylpropane, the surface area for intermolecular interaction decreases.

Hence the boiling point decreases from pentane to 2–methylbutane to 2,2–dimethylpropane.

Q5 (A)

Both liquids are initially at 20 °C. Since stronger intermolecular forces between $CHCl_3$ and CH_3COCH_3 are formed (compared to their original intermolecular forces), energy is released upon mixing and initial temperature of the mixture will be above 20 °C.

Since the intermolecular forces between $CHCl_3$ and CH_3COCH_3 are stronger (than their original intermolecular forces) and require more energy to overcome, the boiling point of the mixture will be above 61 °C.

Q6 (B)

Since all four gases behave as ideal gases and temperature is kept constant,

$$pV = nRT = \text{constant}$$

Graph of pV against V is a horizontal straight line. Hence, the gas with a larger n will have a larger pV.

Since M_r of CH_4 < Ne < N_2 < Cl_2,
for equal masses of the four gases,
amount, n, of CH_4 > Ne > N_2 > Cl_2.

Hence, graph **B** corresponds to Ne.

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Q7 (B)

	$H_2(g)$	+	$I_2(g)$	⇌	$2HI(g)$
initial amt / mol	0		0		0.040
change in amt / mol	+x		+x		–2x
eqm amt / mol	x		x		0.040 – 2x

At equilibrium,
n_{total} = x + x + (0.040 – 2x) = 0.040 mol
P_{total} = 1.0 atm

$$K_p = \frac{P_{HI}^2}{P_{H_2}P_{I_2}} = \frac{(\frac{0.040 - 2x}{0.040} \times 1.0)^2}{(\frac{x}{0.040} \times 1.0)^2} = 54$$

x = 0.004279 mol

$$P_{HI} = \frac{0.040 - 2(0.004279)}{0.040} \times 1.0 = 0.79 \text{ atm}$$

Q8 (A)
Cationic radius of Mg^{2+} < Ca^{2+}, resulting in Mg^{2+} having a higher charge density and stronger polarising power than Ca^{2+}.

Consequently, there is greater extent of distortion of the electron cloud of the CO_3^{2-} anion and hence greater extent of weakening of covalent bonds within the CO_3^{2-} anion for $MgCO_3$. Less heat energy is required to break the covalent bonds within the CO_3^{2-} anion, causing the decomposition temperature of $MgCO_3$ to be lower.

Q9 (D)

$$n(B_2O_3) = \frac{2.50}{2(10.8) + 3(16.0)} = 0.03592 \text{ mol}$$

$$n(CO_2) = \frac{0.80}{12.0 + 2(16.0)} = 0.01818 \text{ mol}$$

ratio of B : C in boron carbide
= 2(0.03592) : 0.01818
= 4 : 1

Hence, the empirical formula of boron carbide is B_4C.

Q10 (B)
Since the reaction is zero order with respect to I_2, the rate of reaction is constant and independent of $[I_2]$.

Hence, the graph of $[I_2]$ against time is a downward sloping straight line with a constant gradient (since rate = – gradient).

Q11 (C)
$\Delta G = \Delta H - T\Delta S$
A reaction is spontaneous when $\Delta G < 0$.

statement	ΔH	ΔS	ΔG
1	> 0	< 0	> 0 at all temperatures
2	< 0	> 0	< 0 at all temperatures
3	< 0	< 0	< 0 at low temperatures (when the negative ΔH outweighs the positive – $T\Delta S$)

Q12 (C)
(This is an autocatalytic reaction where Mn^{2+} acts as the autocatalyst.)
For the graph of volume of CO_2 against time, the gradient of the graph at a particular time gives the instantaneous rate of the reaction.

Since the gradient of the graph at t_2 is greater than that at t_1, the reaction is occurring at a faster rate at t_2.

$n(MnO_4^-)$ added = $n(C_2O_4^{2-})$ added
= 25.0 / 1000 × 0.01
= 0.000250 mol

Since mole ratio of MnO_4^- : $C_2O_4^{2-}$ = 2 : 5, $C_2O_4^{2-}$ is the limiting reagent.

mole ratio of $C_2O_4^{2-}$: CO_2 = 5 : 10
$n(CO_2)$ = 0.000250 / 5 × 10 = 0.0005 mol

At s.t.p., z = 0.0005 × 22.7 = 0.0114 dm^3 = 11.4 cm^3

Q13 (D)
Since $t_{½}$ = 40 min, 120 min = 3 $t_{½}$

At r.t.p.,
$n(O_2)$ formed at 120 min = 6.00 / 24 = 0.250 mol

mole ratio of H_2O_2 : O_2 = 2 : 1
Let the initial amount of H_2O_2 be x mol.

	amt of H_2O_2 / mol	amt of O_2 / mol
t = 0 min	x	0
t = 40 min	$\frac{1}{2}$x	$\frac{1}{2}(x - \frac{1}{2}x)$
t = 80 min	$\frac{1}{4}$x	$\frac{1}{2}(x - \frac{1}{4}x)$
t = 120 min	$\frac{1}{8}$x	$\frac{1}{2}(x - \frac{1}{8}x)$ = 0.250

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x = 0.5714 mol

Initial concentration of H_2O_2 = 0.5714 / 200 × 1000
= 2.9 mol dm^{-3}

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Q14 (C)

$K_c = \frac{[R][S]^2}{[P][Q]}$ mol dm^{-3}

K_c for experiment 1 = 0.0375 mol dm^{-3}

K_c for experiment 2 = 0.0510 mol dm^{-3}

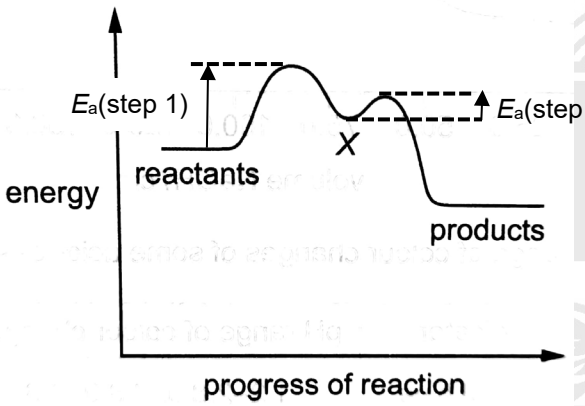
Comparing experiments 1 and 2, as temperature is increased from 300 K to 400 K, K_c increases. This shows that the equilibrium position shifted right with increasing temperature. Hence, the forward reaction must be endothermic.

Q15 (B)

A suitable indicator is one where its pH range coincides with the region of rapid pH change in the titration curve (i.e. the pH range of the indicator must fall on the vertical portion of the titration curve).

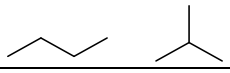
equivalence point	rapid change in pH occurs around	Suitable indicator
first	approx. 3 – 6	naphthyl red
second	approx. 8.5 – 10.5	thymol blue

Q16 (B)

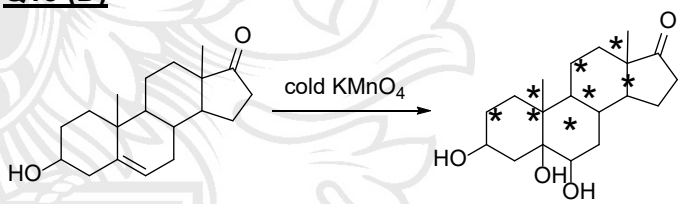


A	Incorrect. Point *X* is an intermediate. A transition state cannot be isolated (unstable) and exists at a potential energy maximum.
B	Correct. See above diagram.
C	Incorrect. Although step 1 is an endothermic process, the reaction involves both the breaking of C=O π bond and formation of C-C bond. Besides, bond formation is always an exothermic process.
D	Incorrect. The reaction pathway diagram does not give any conclusion about the reversibility of the reaction.

Q17 (C)

A	Incorrect. There are only two constitutional isomers of C_4H_{10}: 
B	Incorrect. Constitutional (Structural) isomers have the same molecular formula but different structural formula, i.e. different arrangement of atoms. But-1-ene (C_4H_8) and pen-1-ene (C_5H_{10}) are not constitutional isomers as they have different molecular formula.
C	Correct. Constitutional isomers with different functional groups can differ in their chemical properties. E.g. cyclobutane (C_4H_8) does not undergo electrophilic addition but but-1-ene (C_4H_8) does.
D	Incorrect. Refer to definition of constitutional isomers in option B.

Q18 (D)



M_r = 288

Z

M_r = 322

Q19 (D)

statement 1	Incorrect. •C*l* and •CC*l*F$_2$ should be the major free radical products formed in the initiation step as the C-C*l* bond is weaker and can be broken more easily than the C-F bond.
statement 2	Correct. X• is consumed in the first step and regenerated in the second step of the chain reaction.
statement 3	Incorrect. The termination step should involve the reaction between radicals instead. E.g. 2X• ⟶ X_2

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Q20 (B)

The reactions occurring in the catalytic converter are:

$2CO(g) + O_2(g) \longrightarrow 2CO_2(g)$

Carbon monoxide is oxidised to carbon dioxide.

Carbon dioxide is not further converted in the catalytic converter.

$2NO(g) + 2CO(g) \longrightarrow 2CO_2(g) + N_2(g)$

$NO_2(g) + 2CO(g) \longrightarrow 2CO_2(g) + ½N_2(g)$

Oxides of nitrogen are reduced to nitrogen.

$C_xH_y(g) + (x + \frac{y}{4}) O_2(g) \longrightarrow xCO_2(g) + \frac{y}{2}H_2O(g)$

Unburnt hydrocarbons are oxidised to carbon dioxide.

Q21 (C)

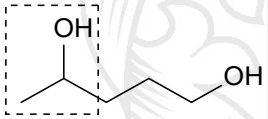
Order of reactivity towards nucleophilic substitution: acyl halides > alkyl halides > aryl halides

Benzoyl chloride, an acyl chloride, is the most reactive with ethanolic $AgNO_3$, followed by the chloroalkanes, 2-chloro-2-methylpropane and 1-chloropropane.

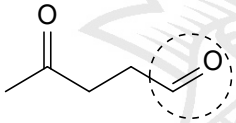
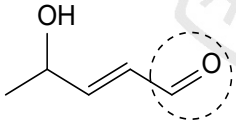
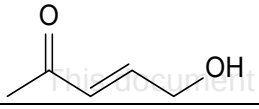
Chlorobenzene, an aryl halide, is the least reactive and does not undergo reaction with ethanolic $AgNO_3$.

Q22 (B)

All three structures can be reduced to form the following compound, which can react with alkaline aqueous I_2 due to the presence of the $–CH(OH)CH_3$ group.



W
$(C_5H_{12}O_2)$

	V $(C_5H_8O_2)$	reacts with Tollens' reagent
1		Yes
2		Yes
3		No

Only structures 1 and 2 contain the aldehyde group which will give a positive test with Tollens' reagent.

Q23 (A)

Information	Conclusion
$T \xrightarrow{NaBH_4} C_xH_{y+2}O_z$ only product ($C_xH_yO_z$)	• Addition of 2 H atoms • T has only one carbonyl group
$T \xrightarrow{\text{single reaction}} C_xH_yO_{z+1}$ ($C_xH_yO_z$)	• Addition of 1 O atom in a single reaction, i.e. oxidation, without any changes in the number of H atoms. • T has one aldehyde group
T gives orange ppt with 2,4-DNPH	• T has carbonyl group
T does not react with Na	• T has no -OH or -COOH group

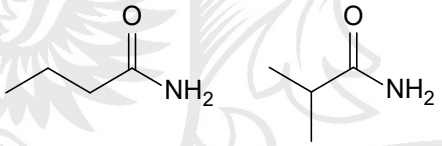
Q24 (D)

$C_2H_5NH_2$ is a primary amine with one electron-donating alkyl ($-C_2H_5$) group while $(C_2H_5)_2NH$ is a secondary amine with two electron-donating alkyl ($-C_2H_5$) groups. Hence, the electron density on the nitrogen atom of $(C_2H_5)_2NH$ is greater and its lone pair of electrons is more available for coordination with a proton.

As $(C_2H_5)_2NH$ is a stronger base, equilibrium position of (2) will lie further right that that of (1).

Q25 (C)

$C_3H_7CONH_2$ can be either of the following structures:



Considering the straight-chain isomer:

A	Incorrect. The name is butanamide.
B	Incorrect. Alkaline hydrolysis of the amide group will form sodium butanoate.
C	Correct. Acidic hydrolysis of the amide group will form butanoic acid.
D	Incorrect. Butanoic acid will undergo acid-base reaction with $NH_3(aq)$ to form a salt instead of an amide.

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Q26 (D)

statement 1	Alcoholic OH group is too weak an acid to react with cold NaOH(aq).
statement 2	Amide group will only undergo basic hydrolysis when heated with NaOH(aq). Hence, the amide group will not react with cold NaOH(aq).
statement 3	Phenolic OH group, which is a stronger acid then alcoholic OH group, will undergo acid-base reaction with cold NaOH(aq).

Q27 (A)

$2H_2O + 2e^- \rightleftharpoons H_2 + 2OH^-$ $E^\ominus = -0.83$ V
$O_2 + 2H_2O + 4e^- \rightleftharpoons 4OH^-$ $E^\ominus = +0.40$V

Hence, for the hydrogen-oxygen fuel cell,
cathode: oxygen electrode ($E^\ominus = +0.40$V)
anode: hydrogen electrode ($E^\ominus = -0.83$ V)

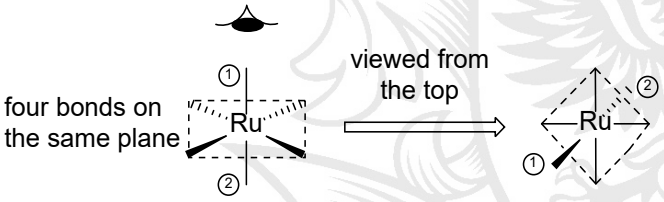
Electrons will flow from X to Y.
Note: Standard conditions should be 1 bar, instead of 1atm.

Q28 (C)

$Q = It = n_eF$
$n_e = It / F$
$= 20.0 \times 3.00(60) / 96500$
$= 0.03731$ mol

Anode: $2H_2O \longrightarrow O_2 + 4H^+ + 4e^-$
mole ratio of $O_2 : e^- = 1 : 4$
$n(O_2) = 0.03731 / 4 = 9.33 \times 10^{-3}$ mol

Q29 (A)



Q30 (D)

Vanadium, a transition metal, has a higher density and melting point than strontium, a Group 2 metal.

From the options, we can conclude that:

metal	density / g cm^{-3}	melting point / °C
vanadium	6.0	1900
strontium	2.6	770

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Hence, row D shows two properties of vanadium.

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Question 1

(a)(i) $HCN(aq) + H_2O(l) \rightleftharpoons CN^-(aq) + H_3O^+(aq)$

(a)(ii) $CN^-(aq) + H_2O(l) \rightleftharpoons HCN(aq) + OH^-(aq)$

Note: An equation for the reaction between NaCN and H_2O is required (not the dissociation of NaCN in water).

(a)(iii) acid H_2O conjugate base OH^-
base CN^- conjugate acid HCN

(a)(iv) $K_a = 10^{-4.79} = 1.62 \times 10^{-5}$ mol dm^{-3}

(a)(v) pK_b of $CN^-(aq) = 14 - 4.79 = 9.21$

(b)(i) Nucleophilic addition

(b)(ii) Unlike HCN which undergoes partial dissociation in water, KCN is a soluble salt that undergoes complete dissolution in water to form the CN^- nucleophile needed in the rate-determining step of the nucleophilic addition reaction.

Also, the acidic condition provides the H^+ ions required for the protonation of the intermediate to form the hydroxynitriles.

(b)(iii)

(b)(iv) In CN^-, the negative charge is on the carbon atom. This makes the carbon atom more electron rich and more nucleophilic than the nitrogen atom. Hence, the carbon atom, and not the nitrogen atom, attacks the electron deficient carbonyl carbon in the nucleophilic addition reaction.

(c)(i) The CN^- ions act as ligands by donating a lone pair of electrons on the carbon atom into the low-lying vacant orbital of the Au^+ central metal ion forming a dative covalent/co-ordinate bond.

(c)(ii) $[Au(CN)_2]^-$

Question 2

(a) Due to the high charge of Al^{3+} and O^{2-} ions and the small interionic distance/ionic radii of both ions, Al_2O_3 has strong ionic bonds/highly exothermic lattice energy. As a result, the energy required to overcome the strong ionic bonds cannot be compensated by the hydration energy released upon hydration of the ions. Hence, dissolution of Al_2O_3 is energetically unfavourable and Al_2O_3 is insoluble in water.

(b)(i) $Al_2O_3(s) + 2NaOH(aq) + 3H_2O(l) \longrightarrow 2Na^+[Al(OH)_4]^-(aq)$

or

$Al_2O_3(s) + 2OH^-(aq) + 3H_2O(l) \longrightarrow 2[Al(OH)_4]^-(aq)$

(b)(ii) $2Al(s) + 2OH^-(aq) + 6H_2O(l) \longrightarrow 2[Al(OH)_4]^-(aq) + 3H_2(g)$

After the insoluble oxide layer is removed, the Al is exposed and undergoes redox reaction with hydroxide ions to form $[Al(OH)_4]^-$ and bubbles of H_2 gas.

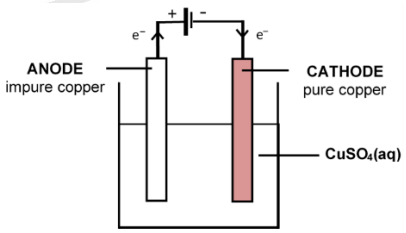
(c)(i) Aluminium objects are highly reactive and not resistant to corrosion. Anodising them will form the protective layer of aluminium oxide which protects the underlying aluminium metal from water and any further chemical attack. The oxide layer is also hard, resistant to wear and a good electrical insulator.

Note: Avoid the use of the term 'rust' as this is specific to the corrosion of iron.

(c)(ii)

	type of reaction occurring	half-equation(s)
anode	oxidation	$2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$
cathode	reduction	$2H^+(aq) + 2e^- \rightarrow H_2(g)$

(d)



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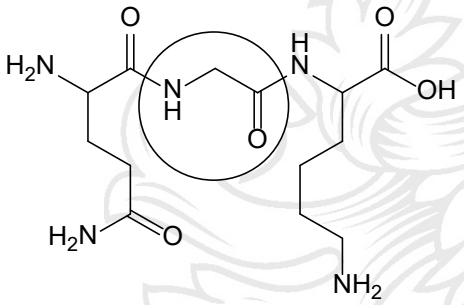
(e)(i) Al^{3+}: $1s^2\ 2s^2\ 2p^6$
Cr^{3+}: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^3$

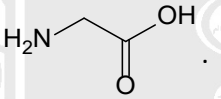
(e)(ii) Compared to Al^{3+}, Cr^{3+} has one more electronic shell, this results in greater shielding effect in Cr^{3+} as it has more electrons. However, Cr^{3+} has a higher nuclear charge than Al^{3+}. Hence, the electrostatic attraction between the nucleus and the outermost electron in both Cr^{3+} and Al^{3+} are similar, resulting in their similar ionic radii.

Question 3

(a) Condensation

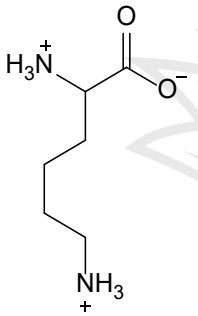
(b)



Since **X** does not rotate plane-polarised light, **X** has a plane of symmetry/does not contain a chiral carbon. Hence, **X** is  .

(c) A zwitterion is an electrically neutral molecule with oppositely charged ends.

(d)(i)



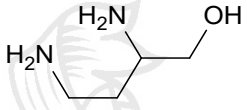
(d)(ii) pH = ½ (9.16 + 10.67)
= 9.92 (accept: 9.16 < pH <10.67)

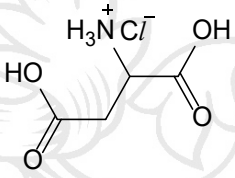
(e)(i) side-chain of **Y**: primary amine
side-chain of **Z**: primary amine

(e)(ii) The amide side-chain in **Z** is neutral. This is because the orbital containing the lone pair of electrons on the nitrogen atom overlaps with the π electron cloud of the adjacent C=O bond and is delocalised. Hence, this lone pair of electrons on the nitrogen atom is not available for coordination to a proton to form an acidic group. Hence the side-chain in **Z** does not have a K_a value.

The amine side-chain in **Y** is basic as the lone pair electrons on the nitrogen atom is available for protonation to form an acidic $-NH_3^+$ group which has a K_a value.

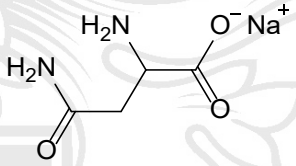
(f) **T :**





U :

V :



(g) step a: $K_2Cr_2O_7$(aq), H_2SO_4(aq), heat with immediate distillation
step b: H_2SO_4(aq)/HCl(aq)/HNO_3(aq), heat

Question 4

(a) $C_6H_6O_2 + 2NaOH \longrightarrow Na_2C_6H_4O_2 + 2H_2O$

(b) All three compounds contain the -OH group and will react with Na to form effervescence of H_2 gas. However, the rate of formation of H_2 will be the slowest for ethanol as ethanol is a weaker acid than phenol and hydroquinone. Between phenol and hydroquinone, hydroquinone will produce more H_2 gas as it contains one more -OH group than phenol. Once reaction has ceased, only the reactions with ethanol and phenol will contain excess unreacted Na metal.

Note: Na is only present in excess for ethanol and phenol.

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(c)(i) Silver bromide has a <u>giant ionic lattice structure</u> with <u>strong ionic bonds/ electrostatic forces of attraction</u> between the Ag^+ and Br^- ions. As <u>large amount of energy</u> is required to overcome the strong ionic bonds, silver bromide has a relatively high melting point.

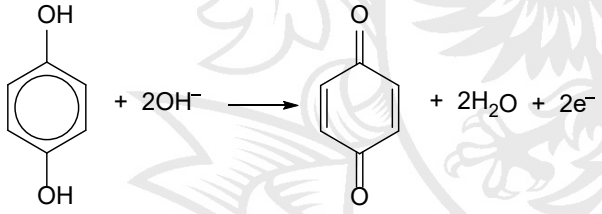
(c)(ii) $AgBr \longrightarrow Ag + Br$

(c)(iii) $Br^- \longrightarrow Br + e^-$
$Cl^- \longrightarrow Cl + e^-$

Although Br^- has a <u>higher nuclear charge</u>, Br^- also has one <u>more electronic shell</u> than Cl^-. Hence, the <u>distance between the nucleus and valence electrons in Br^- is larger</u> and the outermost electron experiences greater <u>shielding effect</u>. This results in <u>weaker electrostatic attraction</u> between the nucleus and outermost electrons. Hence, <u>less energy</u> is required to remove the outermost electron from Br^- than Cl^- ions. Thus, Br^- ions are more affected by light of a lower energy/frequency.

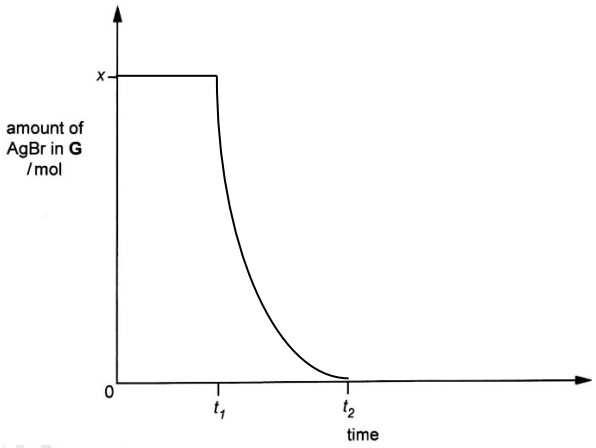
(c)(iv) Photographic film is developed in the dark to <u>prevent stage 1</u> from occurring which will <u>turn more AgX to Ag</u>, resulting in the <u>loss of the original hidden image</u>.

(d)



(e)(i) Ag acts as the <u>autocatalyst</u> in step 4.

(e)(ii)



Note:
The autocatalyst, Ag, is already formed in stage 1 (after brief exposure to light).

Upon addition of excess alkaline aqueous hydroquinone at t_1, the reaction in stage 2 will immediately be catalysed by Ag (i.e. initial rate will not be slow).

<u>Question 5</u>

(a)(i) For every 100 g of reaction mixture,
mass of $C_6H_6O_2$ = 10 g
mass of H_2O_2 = 25 g

$$n(C_6H_6O_2) = \frac{10}{6(12.0)+6(1.0)+2(16.0)} = 0.09091 \text{ mol}$$

$$n(H_2O_2) = \frac{25}{2(1.0) + 2(16.0)} = 0.7353 \text{ mol}$$

From equation 1,
mole ratio of $C_6H_6O_2 : H_2O_2 = 1 : 1$
Since $n(H_2O_2) > n(C_6H_6O_2)$, H_2O_2 is present in excess in the reaction mixture.

(a)(ii) The <u>excess unreacted H_2O_2 is decomposed by catalase to form O_2 gas</u>, which <u>increases the number of gas particles</u> inside the reaction chamber, resulting in an increase in pressure.

(b)

reaction	ΔH / kJ mol^{-1}
equation 3: $C_6H_6O_2(aq) \rightarrow C_6H_4O_2(aq) + H_2(g)$	+177.2
equation 2 × ½: $H_2O_2(aq) \rightarrow H_2O(l) + ½O_2(g)$	½(–189.0)
equation 4: $H_2(g) + ½O_2(g) \rightarrow H_2O(l)$	–285.5

Summing the above equations gives equation 1:
$C_6H_6O_2(aq) + H_2O_2(aq) \rightarrow C_6H_4O_2(aq) + 2H_2O(l)$

$\therefore y$ = +177.2 + ½(–189.0) + (–285.5)
= –202.8 = <u>–203</u>

(c) For 1.0×10^{-3} g of reaction mixture,

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$n(C_6H_6O_2) = (0.09091 / 100) \times 10^{-3}$
$= 9.091 \times 10^{-7}$ mol

Energy released from equation 1
$= 9.091 \times 10^{-7} \times 202.8$
$= 1.844 \times 10^{-4}$ kJ

Remaining amount of H_2O_2
$= [(0.7353 - 0.09091) / 100] \times 10^{-3}$
$= 6.444 \times 10^{-6}$ mol

Energy released from decomposition of unreacted H_2O_2
$= (6.444 \times 10^{-6}) \times ½(189.0)$
$= 6.089 \times 10^{-4}$ kJ

total energy released
$= (1.844 \times 10^{-4}) + (6.089 \times 10^{-4})$
$= \underline{7.93 \times 10^{-4} \text{ kJ}}$

Note:
- *The total energy released will need to include both the energy released from the reaction between H_2O_2 and hydroquinone AND the energy released from the decomposition of the unreacted H_2O_2.*
- *ΔH_{eqn2} involves 2 moles of H_2O_2 undergoing decomposition.*

(d)(i) Given that $\underline{\Delta G_{eqn1} = -206.5 \text{ kJ mol}^{-1} < 0}$, the reaction between hydroquinone and hydrogen peroxide (shown in equation 1) is spontaneous.

(d)(ii) Though spontaneous, the reaction has a <u>significantly high E_a</u> and hence does not occur in the reservoir. However, once the reaction mixture enters the reaction chamber containing the enzymes catalase and peroxidase, the <u>enzymes catalyse the reaction by providing an alternative reaction pathway with a lower E_a</u>. Hence, the reaction occurs quickly in the reaction chamber.

(e) At high $[H_2O_2]$, <u>all the active sites</u> on the enzyme catalase are <u>occupied</u> / the active sites of the enzyme catalase become <u>saturated</u> with the substrate H_2O_2. Any increase in $[H_2O_2]$ will not have any effect on the reaction rate and the reaction is <u>zero order with respect to H_2O_2</u>.

(f) $\Delta G_{eqn1} = \Delta G^{\ominus}_{eqn1}$
$= -n_e F E^{\ominus}_{cell}$
$= -2 \times 96500 \times E^{\ominus}_{cell}$
$= -206.5 \text{ kJ mol}^{-1}$
$= -206500 \text{ J mol}^{-1}$

$E^{\ominus}_{cell} = +1.070$ V

$E^{\ominus}_{cell} = E^{\ominus}_{cathode} - E^{\ominus}_{anode}$
$= E^{\ominus}(H_2O_2/H_2O) - E^{\ominus}(C_6H_4O_2/C_6H_6O_2)$
$= +1.77 - E^{\ominus}(C_6H_4O_2/C_6H_6O_2)$
$= +1.070$

$E^{\ominus}(C_6H_4O_2/C_6H_6O_2) = +1.77 - (+1.070)$
$= \underline{+0.70 \text{ V}}$

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Question 1

(a)(i) A transition element is a d-block element which can form one or more stable ions with a partially filled d subshell.

(a)(ii) Let x be the percentage abundance of ^{63}Cu and (100 – x) be the percentage abundance of ^{65}Cu.

$$\left(\frac{x}{100} \times 62.930\right) + \left(\frac{100 - x}{100} \times 64.928\right) = 63.546$$

percentage abundance of
^{63}Cu = x = 69.2 %
^{65}Cu = 100 – x = 30.8 %

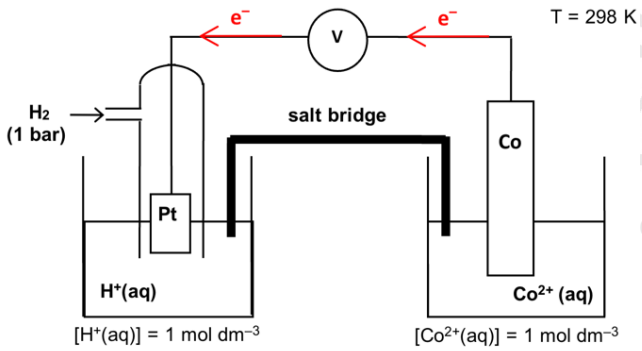
Note: Use the accurate isotopic masses in the calculation.

(b)(i) The presence of ligands in the transition element complexes causes the splitting of the five d orbitals into two sets of slightly different energy levels. Since the d subshell of these transition elements are usually partially filled, electrons from the lower-energy d orbital can absorb energy corresponding to certain wavelengths from the visible spectrum and get promoted to the higher-energy d orbitals (d-d transitions). This results in the complexes being coloured, and the colour observed is the complement of the colour absorbed.

(b)(ii) electronic configurations of
Cu^{2+}: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^9$
Cu^{+} : $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10}$

Compounds containing Cu^{2+} are often coloured as Cu^{2+} has a partially filled 3d subshell and d-d transition is possible. However, compounds containing Cu^{+} are colourless as Cu^{+} has a fully filled 3d subshell and d-d transition cannot occur.

(c)(i)



(c)(ii) $Co^{2+}(aq) + 2e^- \rightleftharpoons Co(s)$ $\quad E^{\ominus} = -0.28$ V
$Fe^{3+}(aq) + e^- \rightleftharpoons Fe^{2+}(aq)$ $\quad E^{\ominus} = +0.77$ V

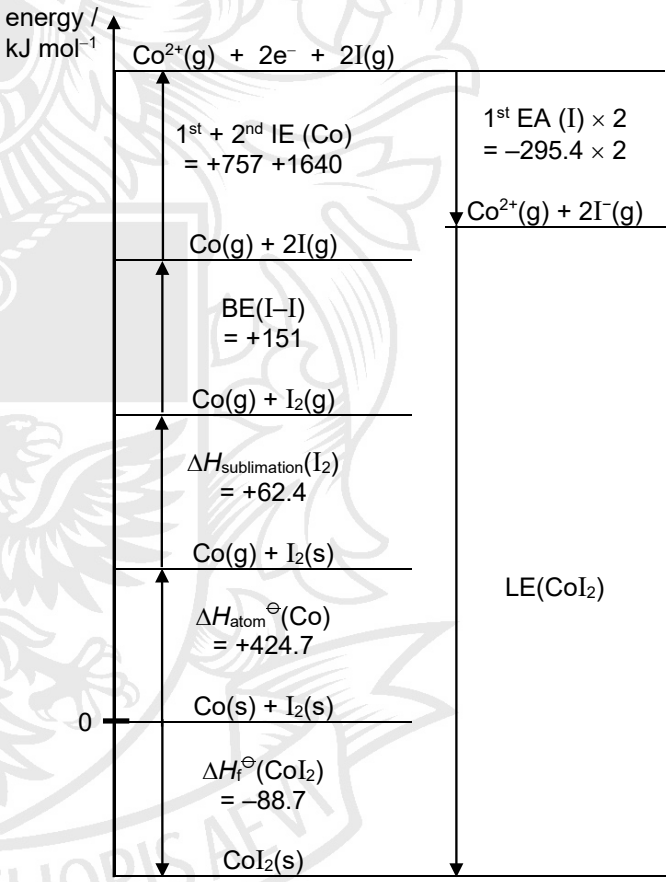
$E^{\ominus}_{cell} = E^{\ominus}_{cathode} - E^{\ominus}_{anode}$
$= E^{\ominus}(Fe^{3+}/Fe^{2+}) - E^{\ominus}(Co^{2+}/Co)$
$= +1.05$ V > 0 (spontaneous reaction)

$Fe^{3+}(aq)$ will be reduced to $Fe^{2+}(aq)$ and Co(s) will be oxidised to $Co^{2+}(aq)$.

Equation:
$2Fe^{3+}(aq) + Co(s) \longrightarrow 2Fe^{2+}(aq) + Co^{2+}(aq)$

(d)(i) Lattice energy of an ionic compound is the energy released when one mole of the solid ionic compound is formed from its constituent gaseous ions at 298 K and 1 bar.

(d)(ii)



By Hess' law,
LE (CoI_2)
$= -(-295.4 \times 2) - (+757 + 1640) - (+151)$
$- (+62.4) - (+424.7) + (-88.7)$
$= -2533$ kJ mol^{-1}
$= -2530$ kJ mol^{-1}

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(d)(iii) Order of lattice energy (in decreasing magnitude): $CoO > CoF_2 > CoI_2$

All three ionic compounds have the same cation, Co^{2+}.

$$|LE| \propto \left|\frac{q_+ q_-}{r_+ + r_-}\right|$$

Since O^{2-} has a higher charge than F^- and I^-, CoO has the greatest magnitude of lattice energy. As the ionic radius of F^- is smaller than that of I^- / interionic distance in CoF_2 is smaller than that in CoI_2, the magnitude of lattice energy of CoF_2 is greater than that of CoI_2.

(e)

compound	formula	M_r
A	$[Co(NH_3)_3(NO_2)_3]$	247.9
B	$[Co(NH_3)_6]^{3+}[Co(NO_2)_6]^{3-}$	495.8

Since the oxidation number of the cobalt is the same in **A** and **B**, using formula of **A**:

overall oxidation number
= oxidation number of cobalt + 3(0) + 3(–1)
= 0

∴ oxidation number of cobalt = +3

*(Since the M_r of $CoH_9N_6O_6$ is 247.9, **A** has molecular formula $CoH_9N_6O_6$. As there are only 9 H atoms and 6 O atoms, there must be 3 NH_3 and 3 NO_2^- in **A**. Since **A** is not an ionic salt, the 3 NH_3 and 3 NO_2^- must be ligands bound to the cobalt ion center.*

*Since **B** is an ionic salt with an M_r twice that of **A**, the molecular formula of **B** must be $Co_2H_{18}N_{12}O_{12}$. **B** is likely to contain one complex cation and one complex anion, both of which have charges of equal magnitude.)*

(f)(i) Overall ionic equation:
$2MnO_4^- + 6H^+ + 5NO_2^- \rightarrow 2Mn^{2+} + 3H_2O + 5NO_3^-$

(f)(ii) $n(S_2O_3^{2-}) = \frac{22.40}{1000} \times 0.0150 = 0.000336$ mol

$n(I_2) = \frac{1}{2} \times 0.000336 = 0.000168$ mol

mole ratio of $I_2 : e^- : MnO_4^-$
1 : 2
5 : 1
= 5 : 10 : 2

$n(MnO_4^-)$ that reacted with I^-
$= \frac{0.000168}{5} \times 2 = 0.0000672$ mol

$n(MnO_4^-)$ that reacted with NO_2^-
$= (\frac{50.00}{1000} \times 0.00500) - 0.0000672$
= 0.0001828 mol

$n(NO_2^-)$ in 1.00 g sample of preserved meat
$= \frac{0.0001828}{2} \times 5$
= 0.0004570 mol

mass of $NaNO_2$ in 1.00 g sample of preserved meat
= 0.0004570 × (23.0 + 14.0 + 2(16.0))
= 0.03153 g

percentage by mass of $NaNO_2$
$= \frac{0.03153}{1.00} \times 100\%$
= 3.15%

Question 2

(a) Relative basicity:
$CH_3CH_2NH_2 > C_6H_5NH_2 > CH_3CONH_2$

In $CH_3CH_2NH_2$, the $-CH_2CH_3$ group is electron-donating and increases the electron density at the nitrogen atom, making the lone pair of electrons on the nitrogen atom more readily available for coordination to a proton.

In phenylamine, the orbital containing the lone pair of electrons on the nitrogen atom overlaps with the π electron cloud of the benzene ring. Thus the lone pair of electrons on the nitrogen atom is delocalised into the benzene ring and is less available for coordination to a proton.

CH_3CONH_2 is the least basic/neutral because the orbital containing the lone pair of electrons on the nitraogen atom overlaps with the π electron cloud of the adjacent C=O bond and is delocalised. Hence, this lone pair of electrons on the nitrogen atom is least/not available for coordination to a proton.

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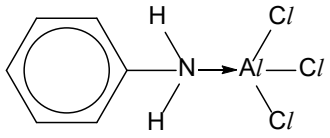
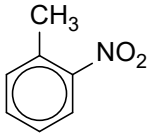
(b)

Structure of **C**:

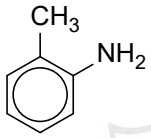


(Phenylamine acts as a Lewis base, donating its lone pair of electrons on the N atom to a low-lying vacant orbital of Al atom in $AlCl_3$.)

(c)(i)



D



E

(c)(ii)

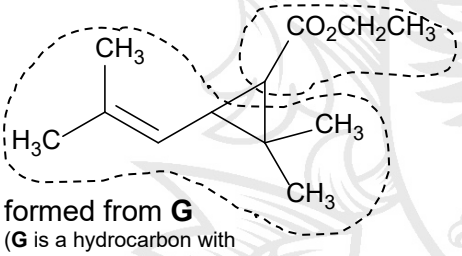
step 1:	concentrated HNO_3, concentrated H_2SO_4, 30 °C
step 2:	Sn, concentrated HC*l*, heat, followed by NaOH(aq)
step 3:	limited CH_3CH_2Cl, heat (in sealed tube) *(using limited CH_3CH_2Cl will help to prevent polysubstitution)*

(d) Two possible non-cyclic structures:

$N{\equiv}C{-}NH_2$ and $HN{=}C{=}NH$

(e)(i) Using information from Fig. 2.2,

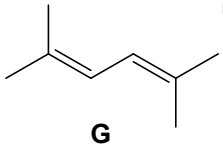
formed from **H**



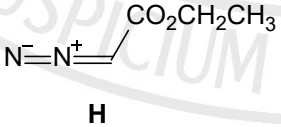
formed from **G**

(**G** is a hydrocarbon with only C and H atoms)

Structures of **G** and **H**:

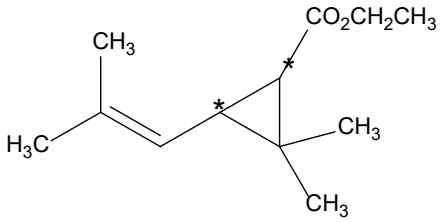


G



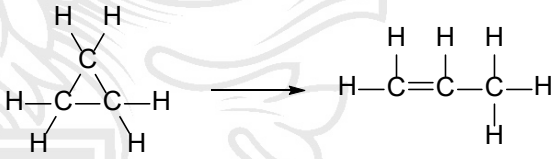
H

(e)(ii) There are a total of 2^2 = 4 stereoisomers of **J** due to the presence of 2 chiral carbons. The C=C bond in **J** does not exhibit cis-trans isomerism as one of the doubly bonded C atom has two identical $–CH_3$ bonded to it.



(f)(i) The C–C bond energy in cyclopropane is lower than that in propane as the ring strain in the three-membered ring of cyclopropane weakens the C–C bond / smaller bond angle (60°) in cyclopropane results in greater repulsion between the bond pairs or less effective overlap of orbitals that weakens the C–C bond.

(f)(ii)



ΔH = 6BE(C–H) + 3(289) – 6(410) – 350 – 610

= –31 kJ mol^{-1}

6BE(C–H) = +2522 kJ mol^{-1}

average C–H bond energy = $\frac{2522}{6}$

= +420 kJ mol^{-1}

(f)(iii) Using the results, plot the graph of concentration of cyclopropane against time for each experiment. Draw a tangent to the graph at t = 0 min and calculate the gradient of the tangent ⇒ initial rate = –gradient

Compare the initial rates and the initial concentrations of cyclopropane. If the initial rate is directly proportional to the initial concentration of cyclopropane, then the reaction is first order with respect to cyclopropane.

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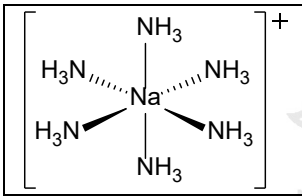
(f)(iv) A catalyst increases the rate of a reaction by providing an alternative reaction pathway with lower activation energy, without itself undergoing any permanent chemical change.

Hence, the presence of a catalyst will increase the magnitude of the rate constant, k, and decrease the magnitude of the activation energy, E_a.

Question 3

(a)(i)

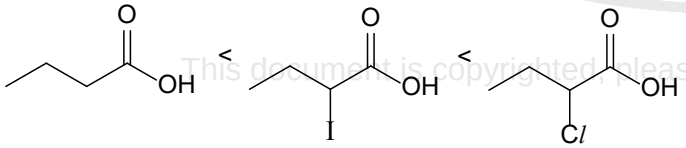
	
There are 6 bond pairs and 0 lone pairs. To minimise repulsion between the electron pairs, the shape is octahedral.	There are 2 bond pairs and 2 lone pairs. To minimise repulsion between the electron pairs, the shape is bent.
The bond angle is 90°.	As lone pairs exert greater repulsion than bond pairs, the bond angle is 105°. (90° < bond angle <109.5°)

(a)(ii) S_N2

(Since step 2 involves an intramolecular nucleophilic substitution of a primary chloroalkane, the reaction is likely to proceed via the S_N2 mechanism.)

(a)(iii) $2NaNH_2 + \frac{5}{2} O_2 \longrightarrow Na_2O + 2NO + 2H_2O$

(b) Order of increasing Bronsted-Lowry acidity:



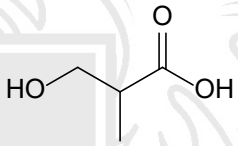
The more stable the conjugate base, the stronger the acid.

2-chlorobutanoic acid and 2-iodobutanoic acid have the electronegative C*l* and I atoms which disperses the negative charge on the $–COO^-$. This stabilises their corresponding conjugate bases and hence they are stronger acids than butanoic acid.

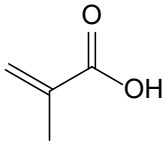
As C*l* is more electronegative than I, it disperses the negative charge on the $–COO^-$ and stabilises the conjugate base to a greater extent. Hence 2-chlorobutanoic acid is more acidic than 2-iodobutanoic acid.

(c)

step 1	NaOH(aq), heat followed by HC*l*/HNO_3/H_2SO_4(aq) *Note: acidification is required as a carboxylate salt would be obtained after heating **N** with NaOH(aq).*
step 2	excess concentrated H_2SO_4, heat
step 3	dry HBr



P ($C_4H_8O_3$)



Q

(d) As HA is a weak acid with partial dissociation,

$[H^+] = \sqrt{K_a \times [HA]}$

$10^{-3.28} = \sqrt{(1.38 \times 10^{-5}) \times [HA]}$

$[HA] = 0.01996$ mol dm^{-3}

Since 1 dm^3 contains 1.76 g sample of HA,

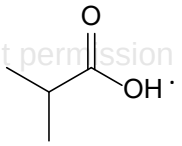
M_r of HA $= \frac{1.76}{0.01996} = 88.2$

Let HA be $C_nH_{2n+1}COOH$.

$(n+1)(12.0) + (2n+2)(1.0) + 2(16.0) = 88.2$

$n = 3$

Hence, HA is C_3H_7COOH.

Since HA is a branched-chain carboxylic acid, structure of HA is  .

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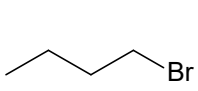
Question 4

(a)(i)



1-bromobutane

2-bromo-2-methylpropane

1) Reaction of 1-bromobutane with $OH^-(aq)$

Predominant mechanism: S_N2

1-bromobutane is a primary bromoalkane with little steric hindrance around the C bonded to Br for nucleophilic attack, making S_N2 mechanism favourable. S_N1 mechanism will be less preferred as the primary carbocation formed will be unstable as there is only one electron-donating alkyl group to disperse the positive charge.

2) Reaction of 2-bromo-2-methylpropane with $OH^-(aq)$:

Predominant mechanism: S_N1

2-bromo-2-methylpropane is a tertiary bromoalkane with greater steric hindrance around the C bonded to Br, making S_N2 mechanism less favourable. S_N1 mechanism is preferred as the tertiary carbocation formed is stabilised by three electron-donating alkyl groups.

(a)(ii) For the S_N2 mechanism, a single enantiomer (with inversion of configuration if the C bonded to halogen is a chiral carbon) is formed. This is due to the backside attack of the nucleophile on the C bonded to halogen.

For the S_N1 mechanism, a racemic mixture is formed. In the reaction, the carbocation intermediate formed has a trigonal planar shape around the positively charged C. The subsequent attack by the nucleophile on either side of the plane with equal probability results in the formation of a pair of enantiomers in a 1:1 ratio.

(b) $\Delta H_{sol}^{\ominus} = \Sigma n\Delta H_f^{\ominus}(pdts) - \Sigma m\Delta H_f^{\ominus}(rxts)$
$= +64.8 + 2(-230.0) - (-449.8)$
$= +54.6 \text{ kJ mol}^{-1}$

$\Delta G_{sol}^{\ominus} = \Delta H_{sol}^{\ominus} - T(\Delta S_{sol}^{\ominus})$
$= (+54.6) - (298)(\frac{-196.2}{1000})$
$= +113 \text{ kJ mol}^{-1}$

$Cu(OH)_2(s)$ is only sparingly soluble in water at 25 °C (298 K) as the $\Delta G_{sol}^{\ominus} > 0$, showing that the dissolution process is non-spontaneous.

(c)(i) A buffer solution is a solution which is able to resist pH changes when a small amount of an acid or a base is added.

(c)(ii) When a small amount of base is added:
$HSO_3^-(aq) + OH^-(aq) \longrightarrow SO_3^{2-}(aq) + H_2O(l)$

When a small amount of acid is added:
$SO_3^{2-}(aq) + H^+(aq) \longrightarrow HSO_3^-(aq)$

(c)(iii) $n(NaHSO_3)$ added $= \frac{50.0}{1000} \times 0.500 = 0.0250$ mol

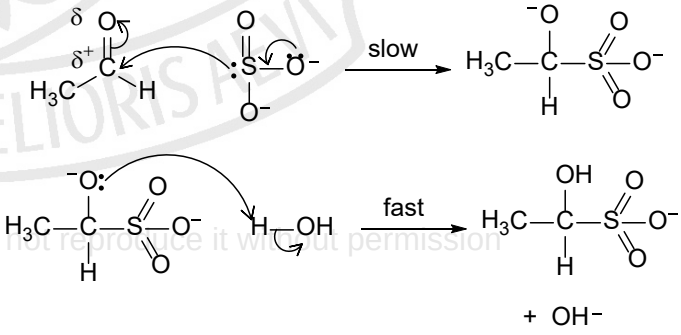
$n(NaOH)$ added $= \frac{25.0}{1000} \times 0.600 = 0.0150$ mol

Upon mixing, $NaHSO_3$ reacts with NaOH:
$HSO_3^-(aq) + OH^-(aq) \longrightarrow SO_3^{2-}(aq) + H_2O(l)$

$n(SO_3^{2-})$ formed $= n(NaOH) = 0.0150$ mol
$n(HSO_3^-)$ left $= 0.0250 - 0.0150 = 0.0100$ mol

$pH = pK_a + \lg \frac{[SO_3^{2-}]}{[HSO_3^-]}$
$= -\lg (6.73 \times 10^{-8}) + \lg \frac{0.0150 / V_T}{0.0100 / V_T}$
$= 7.35$

(c)(iv) Nucleophilic addition



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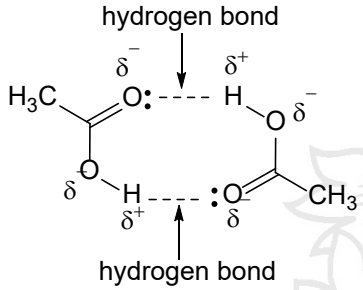
(d)(i) Dynamic equilibrium refers to a state in a reversible system in which the rates of the forward and backward reactions are continuing at the same rate, resulting in no net change in the macroscopic properties (e.g. concentrations, partial pressure) of the reactants and products.

(d)(ii)



(d)(iii)

	$2CH_3CO_2H$	$\rightleftharpoons$	$(CH_3CO_2H)_2$
initial conc / mol dm^{-3}	0.100		0
change in conc / mol dm^{-3}	–2(0.0417)		+0.0417
eqm conc / mol dm^{-3}	0.0166		0.0417

ratio of $[(CH_3CO_2H)_2]$ / $[CH_3CO_2H]$
= 0.0417 / 0.0166
= 2.51

(d)(iv) $\Delta G^{\ominus} = -RT \ln K_c$

In an aqueous solution, the equilibrium position will lie further left as the system favours the formation of the monomer, which can form more extensive hydrogen bonding with surrounding water molecules. As a result, K_c will be smaller in an aqueous solution.

Hence, $\Delta G^{\ominus}$ in an aqueous solution will be less negative (or more positive) than that in a non-polar solvent.

Question 5

(a) Across Period 3, the number of protons increases and hence nuclear charge increases. Although the number of electrons also increases, these electrons are added to the same outermost shell, and hence shielding effect remains approximately constant. Electrostatic attraction between the nucleus and the valence electrons increases, resulting in an increase in the energy required to remove the valence electron from an atom. Hence the first ionisation energies of the elements generally increase across a period.

However, there are two irregularities in the trend.

The first ionisation energy of Al is lower than that of Mg. This is because the 3p electron to be removed from Al is at a higher energy level than the 3s electron to be removed from Mg. Hence less energy is required to remove the 3p electron in Al than the 3s electron in Mg.

Also, the first ionisation energy of S is lower than that of P. This is because the 3p electron to be removed from S is a paired electron while that to be removed from P is an unpaired electron. Due to inter–electronic repulsion between paired electrons in the same orbital, less energy is required to remove the paired 3p electron from S.

(b)(i) Al_2O_3 does not react with water as it does not dissolve in water. pH of the resulting mixture is 7.

$AlCl_3$ dissolves in water to form the complex ion, $[Al(H_2O)_6]^{3+}$, which then undergoes appreciable hydrolysis in water to form an acidic solution with an approximate pH of 3.

(equations are not required by question)
$AlCl_3(s) + 6H_2O(l) \rightarrow [Al(H_2O)_6]^{3+}(aq) + 3Cl^-(aq)$

$[Al(H_2O)_6]^{3+}(aq) \rightleftharpoons [Al(H_2O)_5(OH)]^{2+}(aq) + H^+(aq)$
OR
$[Al(H_2O)_6]^{3+}(aq) + H_2O(l) \rightleftharpoons [Al(H_2O)_5(OH)]^{2+}(aq) + H_3O^+(aq)$

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(b)(ii)

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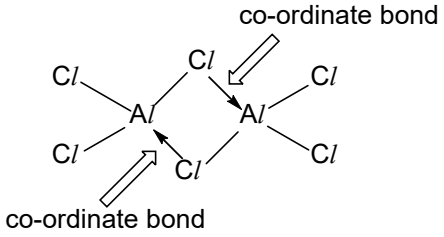


(c)(i) K_{sp} of $Zn(OH)_2 = [Zn^{2+}]\,[OH^-]^2$ mol^3 dm^{-9}

(c)(ii) Let s be the solubility of $Zn(OH)_2$ at 25 °C.

$K_{sp} = [Zn^{2+}]\,[OH^-]^2$
$= (s)(2s)^2$
$= 4s^3$
$= 2.0 \times 10^{-17}$ mol^3 dm^{-9}

$s = 1.710 \times 10^{-6}$ mol dm^{-3}

$[OH^-] = 2s = 3.420 \times 10^{-6}$ mol dm^{-3}
$pOH = -\lg [OH^-] = 5.466$
$pH = 14 - pOH = 8.53$

(c)(iii) In a saturated solution of $Zn(OH)_2$, the following equilibrium is established.

$Zn(OH)_2(s) \rightleftharpoons Zn^{2+}(aq) + 2OH^-(aq)$ ---- (1)

Addition of HCl(aq):
H^+ from HCl will undergo acid-base reaction with OH^-. This decreases the concentration of $OH^-(aq)$. To counteract the decrease in concentration of $OH^-(aq)$, the equilibrium position of reaction (1) shifts right, resulting in the dissolution of $Zn(OH)_2(s)$ and hence solubility of $Zn(OH)_2$ increases.

Addition of $ZnCl_2(aq)$:
Zn^{2+} is the common ion and addition of $ZnCl_2(aq)$ increases the concentration of $Zn^{2+}(aq)$. To counteract the increase in concentration of $Zn^{2+}(aq)$, the equilibrium position of reaction (1) shifts left, resulting in precipitation of some $Zn(OH)_2(s)$. Hence, the solubility of $Zn(OH)_2$ decreases.

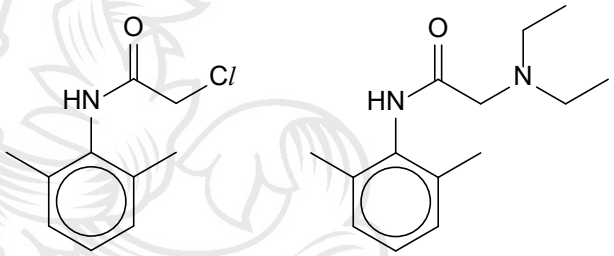
(d)(i) Overall equation:
$2MnO_2(s) + Zn(s) \longrightarrow Mn_2O_3(s) + ZnO(s)$

$E^{\ominus}_{cell} = E^{\ominus}_{cathode} - E^{\ominus}_{anode}$
$= E^{\ominus}(MnO_2/Mn_2O_3) - E^{\ominus}(ZnO/Zn)$
$= +0.15 - (-1.28)$
$= +1.43$ V

(d)(ii) $\Delta G^{\ominus} = -n_e F E^{\ominus}_{cell}$
$= -(2)(96500)(+1.43)$
$= -275990$ J mol^{-1}
$= -276$ kJ mol^{-1}

(e)(i) 2,6-dimethylphenylamine

(e)(ii)



T ($C_{10}H_{12}NOCl$) **U**

(e)(iii)

step 1	$ClCH_2COCl$ (room temperature)
step 2	excess $(CH_3CH_2)_2NH$, heat (in sealed tube)

(e)(iv) acid-base reaction

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