MCQ worked solutions

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

Q1

(Ans: C)

Option **A** is incorrect.
$(NH_4)_2Fe(SO_4)_2$ has 5 ions per formula unit $\Rightarrow$ total number of ions = $5 \times 2 \times 6.02 \times 10^{23}$

Option **B** is incorrect.
$K_2Cr_2O_7$ has 3 ions per formula unit $\Rightarrow$ total number of ions = $3 \times 4 \times 6.02 \times 10^{23}$

Number of NO_2 molecules = $\dfrac{46}{14 + (16 \times 2)} \times 6.02 \times 10^{23}$

Option **C** is correct.
Number of electrons in 1 mol of N_2 = $(7 + 7) \times 6.02 \times 10^{23}$
Number of electrons in 1 mol of CO = $(6 + 8) \times 6.02 \times 10^{23}$

Option **D** is incorrect.
Let V_m be the molar volume of gas. At the same temperature and pressure,

number of atoms in 5 dm³ of O_2 = $\dfrac{5}{V_m} \times 2 \times 6.02 \times 10^{23}$

number of atoms in 10 dm³ of Ar = $\dfrac{10}{V_m} \times 6.02 \times 10^{23}$

Number of N_2 molecules = $\dfrac{14}{14 \times 2} \times 6.02 \times 10^{23}$

Q2

(Ans: C)

Let a be the fraction of ^{63}Cu and $(1 - a)$ be the fraction of ^{65}Cu in naturally occurring copper.

From the *Data Booklet*, the relative atomic mass of Cu is 63.5.

$63.5 = 63a + 65(1 - a) \Rightarrow a = 0.75$

Hence, in the sample of bronze,

% composition of ^{63}Cu = $\dfrac{d}{88 - d}$ = $\dfrac{0.75}{0.25}$

% composition of ^{65}Cu

$d = \underline{66}$

Q3

(Ans: A)

	$^{30}Si^{4+}$	$^{31}P^{3-}$	$^{32}S^{2-}$
Number of electrons	10	18	18
Number of neutrons	16	16	16
Number of protons	14	15	16

Statement 1 is correct. The ions have the same number of neutrons.

Statement 2 is incorrect. As the ions have different number of electrons, their electronic configurations are different.

Statement 3 is incorrect. The ionic radii increase in the order $^{30}Si^{4+} < ^{32}S^{2-} < ^{31}P^{3-}$.

The valence electrons of $^{30}Si^{4+}$ are found in the n=2 shell while the valence electrons of $^{31}P^{3-}$ and $^{32}S^{2-}$ are found in the n=3 shell. Hence the ionic radius of $^{30}Si^{4+}$ is smaller than that of $^{31}P^{3-}$ and $^{32}S^{2-}$.

Since $^{31}P^{3-}$ and $^{32}S^{2-}$ are isoelectronic with the same electronic configuration, their valence electrons experience the same shielding effect. However, nuclear charge of $^{32}S^{2-}$ is smaller than that of $^{32}S^{2-}$. Hence, the effective nuclear charge of $^{31}P^{3-}$ is smaller than that of $^{32}S^{2-}$, and therefore $^{31}P^{3-}$ has a larger ionic radius than $^{32}S^{2-}$.

Q4

(Ans: A)

Angle of deflection α $\dfrac{charge}{mass}$

ions	$^7Li^{2-}$	$^{15}O^{2+}$	$^{15}N^{4-}$	$^{11}C^{3+}$
$\dfrac{charge}{mass}$	0.286	0.133	0.267	0.273

Q ($^{11}C^{3+}$) should be a cation as it is attracted to the negatively charged plate, and its charge/mass ratio should be between that of the two anions P ($^7Li^{2-}$) and R ($^{15}N^{4-}$).

Q5

(Ans: A)

Indium is a Group 13 element with 3 valence electrons. Hence, there should be a large jump between the third and fourth IE as the fourth electron is removed from an inner electronic shell. Hence, option **A** is correct.

3

Q6 (Ans: B)

	G	H	Remarks
A	O=C=S net dipole	S=C=S no net dipole	G has a greater net dipole than H.
B	(P-F structure) net dipole	(P-Cl structure) net dipole	P-F bond is more polar than P-Cl bond. G has a smaller net dipole than H.
C	I-F net dipole	Br-Cl net dipole	I-F bond is more polar than Br-Cl bond. G has a greater net dipole than H.
D	XeF₄ no net dipole	PCl₅ no net dipole	Both G and H do not have a net dipole.

Q7 (Ans: B)

Statement 1 is correct. Since compounds M and N have the same electron cloud size, the strength of their intermolecular instantaneous dipole-induced dipole interactions is similar. However, the hydrogen bonds present between molecules of M are stronger than the permanent dipole-permanent dipole interactions between molecules of N. Hence, M would have a higher boiling point and lower volatility than N.

Statement 2 is correct. Compounds M and N are constitutional isomers as both have the same molecular formula $C_5H_{10}O$ but different structural formula.

Statement 3 is incorrect. M has 16 σ bonds whereas N has 15 σ bonds. (Note: Remember to include the C-H and O-H σ bonds.)

Q8 (Ans: B)

For ionic compounds, the extent of polarisation/distortion of the electron cloud of the anion and hence the degree of covalent character increases with:
- higher polarising power of the cation
- higher polarisability of the anion

Compared to Ca^{2+}, Mg^{2+} has a smaller ionic radius and hence a higher charge density and polarising power. Mg^{2+} is able to distort the electron cloud of the anion to a greater extent.

Compared to O^{2-}, S^{2-} has a larger and more polarisable electron cloud.

Hence, MgS has the greatest covalent character.

4

Q9 (Ans: D)

Δ After mixing at constant temperature
Applying $p_1V_1 = p_2V_2$ (since n and T are constant),

$(20 \text{ kPa})(1 \text{ m}^3) = (p_{He})(3 \text{ m}^3)$
p_{He} upon mixing = 6.67 kPa

$(10 \text{ kPa})(2 \text{ m}^3) = (p_{Ne})(3 \text{ m}^3)$
p_{Ne} upon mixing = 6.67 kPa

From the calculations,
$p_{He} = p_{Ne}$ upon mixing

Total pressure upon mixing = 6.67 + 6.67 = 13.3 kPa

Δ After decreasing temperature
- Total pressure will decrease below 13.3 kPa since p ∝ T (at constant V and n) ⇒ options **A** and **B** are incorrect.
- p_{He} will still be equal to p_{Ne} as the number of moles of each gas remains the same ⇒ option **C** is incorrect.

Q10 (Ans: B)

Element D is silicon as it has the highest melting point. Since the elements are consecutively arranged, B is sodium.

Q11 (Ans: A)

Option **A** is correct. The solubility of silver halides in aqueous ammonia decreases down the group (due to decreasing K_{sp} values). Since silver iodide is insoluble in aqueous ammonia, silver astatide is expected to be also insoluble in aqueous ammonia.

Option **B** is incorrect. The melting and boiling points of halogens increase down the group. Since iodine is a solid, astatine is expected to be also a solid at room temperature and pressure.

Option **C** is incorrect. H-X bond energy decreases down the group due to decreasing effectiveness of the valence orbital overlap. Hence the bond energy of HAt is expected to be smaller than that of HI.

Option **D** is incorrect. Oxidising power of halogens decreases down the group. Hence, a halogen can oxidise a halide below (but not above) it. Bromine is expected to be able to oxidise sodium astatide to give astatine.

Q12 (Ans: A)

$\Delta H_f^{\ominus} = \Sigma n\Delta H_c^{\ominus} \text{ (reactants)} - \Sigma m\Delta H_c^{\ominus} \text{ (products)}$

$= -3268 + 3(-286) - (-3754) = -372 \text{ kJ mol}^{-1}$

Q13 (Ans: D)

Option **A** is incorrect. The standard enthalpy change of atomisation of chlorine is the energy absorbed when 1 mole of gaseous Cl atoms is formed from $Cl_2(g)$ under standard conditions. The correct equation should be
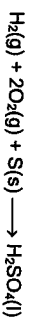
$$\tfrac{1}{2}Cl_2(g) \longrightarrow Cl(g)$$

Option **B** is incorrect. The standard enthalpy change of combustion of a substance is the energy released when 1 mole of the substance is completely burnt in excess oxygen under standard conditions. The correct equation should be

$$H_2S(g) + \tfrac{3}{2}O_2(g) \longrightarrow H_2O(g) + SO_2(g)$$

Note: H_2 cannot be the end product of a combustion reaction as it can be combusted to give H_2O.

Option **C** is incorrect. The standard enthalpy change of formation of a substance is the energy change when 1 mole of the pure substance in a specified state is formed from its constituent elements in their standard states under standard conditions. The correct equation should be

$$H_2(g) + 2O_2(g) + S(s) \longrightarrow H_2SO_4(l)$$

Note: The elements, hydrogen and oxygen, do not exist in the monoatomic form under standard conditions (i.e. 1 bar and 298 K).

Option **D** is correct. The standard enthalpy change of solution of a substance is the energy change when 1 mole of the substance (ionic compound) is completely dissolved in a solvent to form an infinitely dilute solution (containing aqueous ions) under standard conditions.

Q14 (Ans: D)

Comparing the first and third experiments,
When [R] × 3 while keeping [S] constant, initial rate × 3 ⇒ rate α [R].
Hence, order of reaction with respect to R is 1.

Comparing the first and second experiments,
When [R] × 2 and [S] × 2, initial rate × 8.
Since the order of reaction with respect to R is 1, rate α $[S]^2$.
Hence, order of reaction with respect to S is 2.

The rate equation is: rate = $k[R][S]^2$

Using data from the first experiment,
$k = 5.10 \times 10^{-4} \div (0.015 \times 0.010^2) = \underline{340}$ mol^{-2} dm^6 s^{-1}
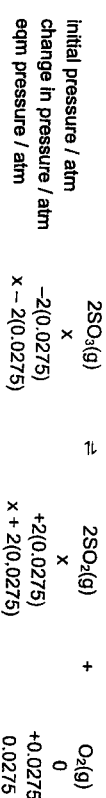
Q15 (Ans: C)

Statement 1	Correct. As there are no addition of any reactant or product to the system, the mole ratio of NH_3 : CO_2 should always stay the same at 2 : 1 (following the stoichiometric ratio of the balanced equation). Since p α n, P_{NH_3} : P_{CO_2} is also 2 : 1 at t_1.
Statement 2	Incorrect. Since the temperature at t_1 is higher than that at t_2, the rate of the forward (and backward) reaction at t_1 is greater than that at t_2. (Recall that at higher temperatures, a greater proportion of the reactant molecules have energy greater than or equal to the activation energy for reaction. Hence, the frequency of effective collisions increases resulting in an increase in rate of reaction.)
Statement 3	Incorrect. By Le Chatelier's Principle, a decrease in temperature will favour the backward exothermic reaction and a decrease in temperature (or increase in total pressure) will favour the backward reaction which reduces the number of gas particles. Hence at t_2, the degree of decomposition of NH_2COONH_4 is smaller than that at t_1.
Statement 4	Correct. Decreasing the volume of the vessel will cause the total pressure (and partial pressures of NH_3 and CO_2) to increase. By Le Chatelier's Principle, the equilibrium position will shift left to reduce the number of gas particles and the partial pressures of NH_3 and CO_2 will decrease. Since the equilibrium constant ($K_p = (P_{NH_3})^2(P_{CO_2})$) remains unchanged (as temperature is constant) and the P_{NH_3} : P_{CO_2} stays the same at 2 : 1, the equilibrium partial pressures of NH_3 and CO_2 at t_2 will be the same as that at t_1.

Q16 (Ans: C)

SO_3 and SO_2 are found in both reactions 1 and 2. For the forward reaction of reaction 2 to proceed, SO_3 and SO_2 must first be formed from reaction 1.

Since the mole ratio of SO_3 and SO_2 is 1 : 1 in reaction 1, let x atm be the initial partial pressures of SO_3 and SO_2 for reaction 2.

	$2SO_3(g)$	⇌	$2SO_2(g)$	+	$O_2(g)$
initial pressure / atm	x		x		x
change in pressure / atm	−2(0.0275)		+2(0.0275)		+0.0275
eqm pressure / atm	x − 2(0.0275)		x + 2(0.0275)		0.0275

Since total pressure at equilibrium is 0.836 atm,

$P_{SO_3} + P_{SO_2} + P_{O_2} = 0.836$ atm

x − 2(0.0275) + x + 2(0.0275) + 0.0275 = 0.836
x = 0.40425

P_{SO_3} = 0.40425 − 2(0.0275) = 0.34925 atm
P_{SO_2} = 0.40425 + 2(0.0275) = 0.45925 atm

$$K_2 = \frac{(P_{SO_2})^2(P_{O_2})}{(P_{SO_3})^2} = \frac{(0.45925)^2(0.0275)}{(0.34925)^2} = \underline{0.0476\ atm}$$

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Q17 (Ans: D)

Option A	Incorrect. The correct pH of the buffer solution is: $pH = pK_a + lg \dfrac{[lactate]}{[lactic\ acid]} = -lg(1.4 \times 10^{-4}) + lg\ \dfrac{0.5}{1.5} = 3.38$
Option B	Incorrect. Upon dilution with some water, the pH of the buffer solution should remain the same as the amount of lactic acid and sodium lactate in the buffer solution remains the same (although their concentrations decrease). $pH = pK_a + lg \dfrac{[lactate]}{[lactic\ acid]} = pK_a + lg\ \dfrac{n(lactate)\ /V_{buffer}}{n(lactic\ acid)\ /V_{buffer}} = pK_a + lg\ \dfrac{n(lactate)}{n(lactic\ acid)}$ *(If the buffer solution is infinitely diluted with water, the $[H^+]$ in the buffer solution tends towards that of pure water (i.e. 10^{-7} mol dm^{-3}) and pH increases and approaches 7.)* Hence, pH of the buffer solution will not decrease upon dilution with water.
Option C	Incorrect. For a given volume, a more diluted buffer solution will have a lower buffering capacity due to smaller amount of the lactic acid and lactate ions to remove any added OH^- and H^+ ions respectively.
Option D	Correct. Since the buffer solution has a greater amount of lactic acid (weak acid) than the lactate ions (conjugate base), the buffer solution is more effective in buffering the effect of addition of small amounts of base than acid.

Q18 (Ans: B)

① $Cu^+(aq) + Cl^-(aq) \rightleftharpoons CuCl(s)$ $\qquad\qquad K_1 = 8.33 \times 10^5$

② $CuCl(s) + Cl^-(aq) \rightleftharpoons CuCl_2^-(aq)$ $\qquad K_2 = 0.104$

③ $Cu^+(aq) + 2Cl^-(aq) \rightleftharpoons CuCl_2^-(aq)$ $\qquad K_3 = z$

③ = ① + ②

$K_3 = \dfrac{[CuCl_2^-]}{[Cu^+][Cl^-]^2} = \dfrac{1}{[Cu^+][Cl^-]} \times \dfrac{[CuCl_2^-]}{[Cl^-]} = K_1 \times K_2 = 86632\ mol^{-2}\ dm^6$

Hence, $z = \underline{8.66 \times 10^4}$

Solubility product, K_{sp} of $CuCl(s) = [Cu^+][Cl^-] = \dfrac{1}{K_1} = \dfrac{1}{(8.33 \times 10^5)} = \underline{1.20 \times 10^{-6}\ mol^2\ dm^{-6}}$

Q19 (Ans: A)

From the *Data Booklet*: $E^\ominus(Cr_2O_7^{2-}/Cr^{3+}) = +1.33\ V$ and $E^\ominus(O_2/H_2O_2) = +0.68\ V$

For this electrochemical cell, $E_{cell} = E(Cr_2O_7^{2-}/Cr^{3+}) - E(O_2/H_2O_2)$. Hence, an <u>increase in $E(Cr_2O_7^{2-}/Cr^{3+})$</u> or a <u>decrease in $E(O_2/H_2O_2)$</u> will lead to an increase in E_{cell}.

The reduction half-equations of the two half-cells are shown below.
$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightleftharpoons 2Cr^{3+}(aq) + 7H_2O(l)$ —— (1)
$O_2(g) + 2H^+(aq) + 2e^- \rightleftharpoons H_2O_2(aq)$ —— (2)
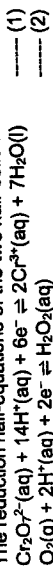
For option **A**, addition of water to O_2/H_2O_2 half-cell favours the side with more aqueous species so position of equilibrium of (2) shifts left and <u>decreases $E(O_2/H_2O_2)$</u>. Thus, E_{cell} increases.
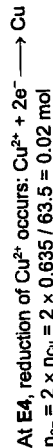
For option **B**, $E^\ominus_{cell}$ for the reaction between I^- and $Cr_2O_7^{2-} = +1.33 - 0.54 = +0.79\ V$ Hence the reaction is spontaneous and the addition of KI(s) to the $Cr_2O_7^{2-}/Cr^{3+}$ half-cell decreases $[Cr_2O_7^{2-}]$ so that position of equilibrium of (1) shifts left and <u>decreases $E(Cr_2O_7^{2-}/Cr^{3+})$.</u> Thus, E_{cell} decreases. (Note: KI(s) is soluble in water and dissolves to form $K^+(aq)$ and $I^-(aq)$.)

For option **C**, 1 atm of O_2 has a higher pressure than 1 bar of O_2. The increase in P_{O_2} shifts position of equilibrium of (2) to the right and <u>increases $E(O_2/H_2O_2)$</u>. Thus, E_{cell} decreases.

For option **D**, using $[Cr^{3+}]$ of 2.0 mol dm^{-3} increases $[Cr^{3+}]$ so that position of equilibrium of (1) shifts left and <u>decreases $E(Cr_2O_7^{2-}/Cr^{3+})$</u>. Thus, E_{cell} decreases.

Q20 (Ans: B)

At **E4**, reduction of Cu^{2+} occurs: $Cu^{2+} + 2e^- \longrightarrow Cu$
$n_{e^-} = 2 \times n_{Cu} = 2 \times 0.635 / 63.5 = 0.02\ mol$

Since $Q = n_{e^-} \times F = I \times t$,
$t = (n_{e^-} \times F) / I = (0.02 \times 96500) / 5 = 386\ s = 6.43\ min \Rightarrow$ Option **A** is incorrect

As Cu^{2+} is reduced to Cu at **E4**, $[Cu^{2+}]$ decreases and the colour intensity of the solution in cell 2 decreases $\Rightarrow$ Option **D** is incorrect.

At **E2**, H_2O is reduced to H_2: $2H_2O + 2e^- \longrightarrow H_2 + 2OH^-$ Since OH^- is produced and the electrolyte contains Mg^{2+}, a white precipitate of $Mg(OH)_2$ is formed around **E2** $\Rightarrow$ Option **B** is correct.

At **E1** and **E3**, H_2O is oxidised to O_2 and effervescence is observed. At **E2**, H_2O is reduced to H_2 and effervescence is also observed $\Rightarrow$ Option **C** is incorrect.

Q21 (Ans: D)

half-cell of V species	VO_2^+/VO^{2+}	VO^{2+}/V^{3+}	V^{3+}/V^{2+}	V^{2+}/V
$E^\ominus$/V	+1.00	+0.34	-0.26	-1.20

Since the metal is oxidised, $E^\ominus_{cell}$ = $E^\ominus$(species containing V) – $E^\ominus$(species containing V).

To be thermodynamically feasible, $E^\ominus_{cell} > 0$. Hence, $E^\ominus(M^{n+}/M)$ need to be less positive or more negative than $E^\ominus$(species containing V).

half-cell of M^{n+}/M	Mg^{2+}/Mg	Ag^+/Ag	Sn^{2+}/Sn	Zn^{2+}/Zn
$E^\ominus$/V	-2.38	+0.80	-0.14	-0.76

As the resultant solution is violet, the final vanadium-containing species is V^{2+}.

Thus, $E^\ominus(M^{n+}/M)$ must be <u>more negative than -0.26 V but less negative than -1.20</u> so that the metal will not further reduce V^{2+} to V.

Since $E^\ominus(Zn^{2+}/Zn)$ is more negative than -0.26 V but less negative than -1.20 V, Zn reduces VO_2^+ to VO^{2+} then to V^{3+} and finally to V^{2+} ⇒ option **D** is correct.

Q22 (Ans: C)

Statement 1 is incorrect. Since **S2** consists of $[CrY_6]^{3+}$ and absorbs orange-red light strongly, $[CrY_6]^{3+}$(aq) cannot be orange in colour as the colour observed is complement of the colour absorbed.

Statement 2 is correct. In **S3**, [X]$_{initial}$ and [Y]$_{initial}$ are reduced by half compared to **S1** and **S2**. The concentration of $[CrY_6]^{3+}$ formed is greater than $[CrX_6]^{3+}$, as can seen by the absorbance peak of $[CrY_6]^{3+}$ being reduced to a smaller extent in **S3**. Hence, **Y** forms the complex with Cr^{3+} more readily and **Y** forms stronger bond with Cr^{3+}.

Statement 3 is correct. Compared to $[CrY_6]^{3+}$, the absorbance peak of $[CrX_6]^{3+}$ is at a shorter wavelength with higher energy. Hence, d-orbital splitting is larger in $[CrX_6]^{3+}$.
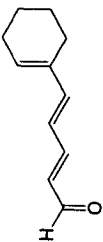
Q23 (Ans: C)

An example of a 11 carbon-containing compound with an aldehyde group, a cyclohexene ring and a straight chain is shown below.
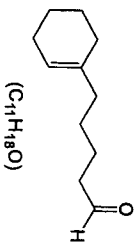
$(C_{11}H_{18}O)$

Since compound A ($C_{11}H_{14}O$) has 4 fewer H atoms than the above structure, compound A must have two more C=C bonds than the above structure ⇒ total of 2 + 2 = 4 double bonds.

A possible structure of compound A:

With 4 double bonds in the structure, there should be <u>4 π bonds</u>.

Q24 (Ans: D)

Statement 1 is correct. The initiation step involves the homolytic fission of the Cl-Cl bond. The propagation steps can involve the homolytic fission of C-H and Cl-Cl bonds.

Statement 2 is correct. Ignoring stereoisomers, the eight possible mono-chlorinated products are as follows.
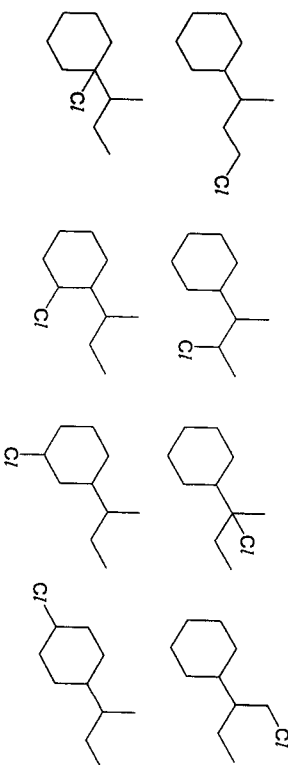
Statement 3 is correct. In the termination step, two alkyl radicals (•$C_{10}H_{19}$) can react together to form the product ($C_{20}H_{38}$) in small quantities. Example:
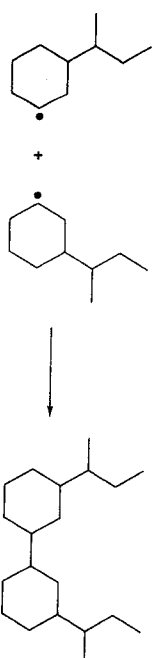
Q25 (Ans: C)

Cars are fitted with catalytic converters to remove three main pollutants (CO, NO_x, and unburnt hydrocarbons) from exhaust gases. The harmful gases are converted into CO_2, N_2 and H_2O.

The following reactions occur in the catalytic converter. Each reaction is a <u>redox</u> reaction.

Reaction	Remarks
$2CO(g) + O_2(g) \longrightarrow 2CO_2(g)$	Reaction 1 is correct. • CO is oxidised. • O_2 is reduced.
$2NO(g) + 2CO(g) \longrightarrow 2CO_2(g) + N_2(g)$	Reaction 2 is correct. • CO is oxidised. • NO is reduced.
$NO_2(g) + 2CO(g) \longrightarrow 2CO_2(g) + \frac{1}{2}N_2(g)$	Reaction 3 is correct. • CO is oxidised. • NO_2 is reduced.
$C_xH_y(g) + (x + \frac{y}{4})O_2(g) \longrightarrow xCO_2(g) + \frac{y}{2}H_2O(g)$	Reaction 4 is correct. • C_xH_y is oxidised. • O_2 is reduced.

Reaction 4 is incorrect as <u>both hydrocarbons and carbon monoxide needs to be oxidised</u>. Hence, they do not react together in the catalytic converter.

Q26 (Ans: D)

The sequence of reactions that would give the highest yield of compound C is given below.
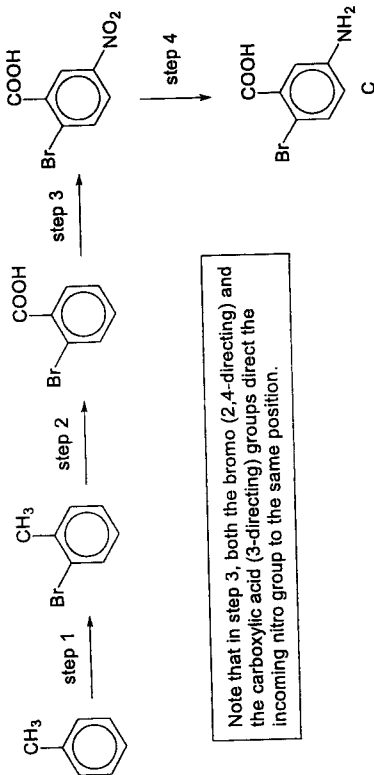
Note that in step 3, both the bromo (2,4-directing) and the carboxylic acid (3-directing) groups direct the incoming nitro group to the same position.

Option **A** is incorrect. The major product, NO₂, formed in step 3 does not lead to the eventual formation of C.

Option **B** is incorrect. In step 4, the amino (2,4-directing) and the carboxylic acid (3-directing) groups do not direct the incoming bromo group to the same position.

Option **C** is incorrect. In step 2, the methyl (2,4-directing) and the bromo (2,4-directing) groups do not direct the incoming nitro group to the same position.

Q27 (Ans: B)

To oxidise the aldehyde group (–CHO) in J to carboxylic acid group (–COOH) in K (without oxidative cleave of the C=C bond), only K₂Cr₂O₇ with H₂SO₄ and heating can be used. If J is heated with KMnO₄ and H₂SO₄, the C=C bond will undergo oxidative cleavage, in addition to the oxidation of the –CHO to –COOH.

For the reduction of both alkene (C=C) and aldehyde (–CHO) groups in J to –CH₂CH₂– and primary alcohol (–CH₂OH) groups respectively in L, only H₂ with Ni and heating can be used. If NaBH₄ is used, only –CHO will be reduced to –CH₂OH and the C=C bond will remain unreacted.

Q28 (Ans: B)

(1-Bromoethyl)benzene reacts with methylamine via nucleophilic substitution. As the rate of the reaction is independent of the concentration of the nucleophile, CH₃NH₂, the reaction proceeds via Sₙ1 mechanism. The following carbocation will be formed when the C–Br bond breaks in the rate-determining step:
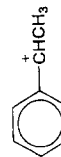
Q29 (Ans: A)

Option **A** is correct. When heated with NaOH, CH₃CH₂NH₃⁺ will undergo acid-base reaction to form CH₃CH₂NH₂ gas which will turn damp red litmus paper blue. For (CH₃CH₂)₄N⁺, there is no acid-base reaction with NaOH, and no gas will be evolved.

Option **B** is incorrect. Fehling's solution forms brick-red ppt of Cu₂O only with underlined aliphatic aldehyde.

 is an aromatic aldehyde and is a ketone. Hence, both compounds will not form brick-red ppt.

Option **C** is incorrect. Both and CH₃CH₂OH do not react with aqueous Na₂CO₃ to form CO₂ gas. (Note: Aqueous Na₂CO₃ reacts only with carboxylic acid functional group.)

Option **D** is incorrect. In both and , the lone pair of electrons in the p orbital of the chlorine is able to delocalise into the benzene ring and C=C bond respectively. As there is partial double bond character in the C–Cl bond, the bond is strengthened and will not be easily broken to form chloride ions when heated with ethanolic AgNO₃. Hence, no AgCl (white ppt) will be observed for both compounds.

Q30 (Ans: D)

In options **B** and **C**, the compounds contain the –CH(CH₃)OH group which will give a yellow ppt with hot alkaline aqueous I₂ ⇒ Options **B** and **C** are incorrect.

(Note: In option **D**, the –N(CH₃)COCH₃ group is an amide which will not form a yellow ppt with hot alkaline aqueous I₂.)

Option **A** is incorrect. The –CN group will be reduced by LiAlH₄ in dry ether to form a primary amine (–CH₂NH₂). The product contains the –CH₂NH₂ and –C(CH₃)₂OH groups which will react with ethanoyl chloride to form an amide and ester respectively, and hence the product will react with ethanoyl chloride in a 1:2 ratio.

Option **D** is correct. The –N(CH₃)COCH₃ group will be reduced by LiAlH₄ in dry ether to form a tertiary amine (–N(CH₃)CH₂CH₃) which does not react with ethanoyl chloride. Since only –C(CH₃)₂OH group will react with ethanoyl chloride, the product will react with ethanoyl chloride in a 1:1 ratio.

2022 RI H2 Chemistry Prelim Paper 2 – Suggested Solutions

1(a)

Amount of iodine reacted = $\dfrac{65}{22700} \times \dfrac{1}{3} \times \dfrac{3}{2} = 1.432 \times 10^{-3}$ mol

Mass of iodine = $1.432 \times 10^{-3} \times 126.9 \times 2 = \underline{0.363 \text{ g}}$

1(b)(i)

The boiling points increase from HCl to HBr to HI as the size of electron cloud for polarisation increases, resulting in stronger instantaneous dipole-induced dipole (id-id) interactions, and hence requiring more energy to overcome.

The boiling point decreases from HF to HCl (or HF has the highest boiling point) due to the presence of stronger hydrogen bonding between HF molecules which requires more energy to overcome.

1(b)(ii)

Down Group 17, the valence orbital of the halogen atom becomes increasingly diffuse and the orbital overlap between the halogen and hydrogen atoms becomes less effective / electronegativity difference between the halogen and hydrogen decreases, resulting in a decrease in bond polarity.

Hence, the H–X bond strength decreases from HCl to HBr to HI and the thermal stability decreases from HCl to HBr to HI.

1(c)(i)
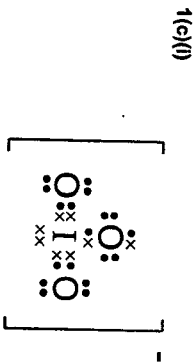
1(c)(ii)

In IO_3^-, there are 3 bond pairs and 1 lone pair of electrons around the central I atom. To minimise electronic repulsion between the bond pairs and lone pair electrons, the shape about the I atom is trigonal pyramidal.

As the lone pair-bond pair repulsion is greater than the bond pair-bond pair repulsion, the bond angle is 107°.
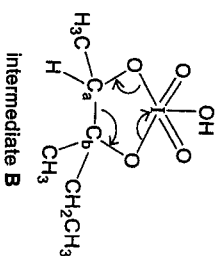
1(c)(iii)

Method 1: Oxidation number method
Oxidation number of I in I_2 = 0
Oxidation number of I in IO_3^- = +5
Oxidation number of I in I^- = –1

1 mol of I atom loses 5 mol of e⁻ to form 1 mol of IO_3^-.
1 mol of I atom gains 1 mol of e⁻ to form 1 mol of I^-.

Since no. of e⁻ lost = no. of e⁻ gained, mole ratio of $IO_3^- : I^- = 1 : 5$

$$6OH^- + 3I_2 \rightarrow IO_3^- + 5I^- + 3H_2O$$

Method 2: Half-equation method
Half equation from I_2 to I^-:
$I_2 + 2e^- \rightarrow 2I^-$ (1)

Half equation from I_2 to IO_3^-:
$I_2 + 12OH^- \rightarrow 2IO_3^- + 6H_2O + 10e^-$ (2)

Balancing equation (1) and (2):
$$6OH^- + 3I_2 \rightarrow IO_3^- + 5I^- + 3H_2O$$

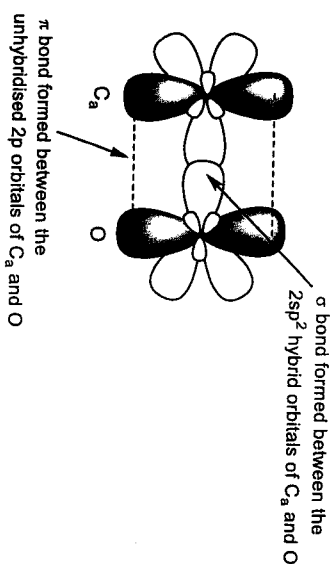**1(d)(i)**
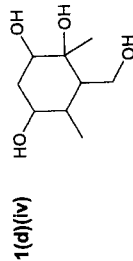
The C_a–H bond in ethanal is stronger than that in glycol A.

The $2sp^2$ orbital of C_a in ethanal has higher s character and is less diffuse than the $2sp^3$ orbital of C_a in glycol A. Hence, the $2sp^2$ orbital of C_a in ethanal has a more effective overlap with the 1s orbital of H leading to a stronger bond.
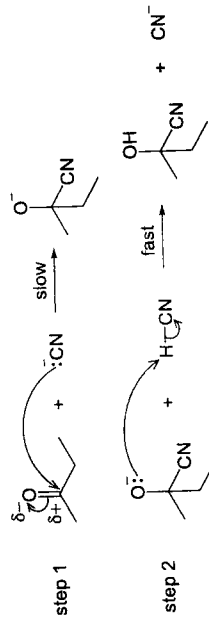
1(d)(ii)

intermediate B

1(d)(iii)

π bond formed between the unhybridised 2p orbitals of C_a and O

σ bond formed between the $2sp^2$ hybrid orbitals of C_a and O

3

1(d)(iv)

1(d)(v) Nucleophilic addition

$$HCN + OH^- \longrightarrow CN^- + H_2O$$


step 1 — slow

step 2 — fast → + CN⁻

2(a)(i) Any three of the following:
- An ideal gas consists of particles of negligible volume.
- The gas particles exert negligible attractive forces on one another.
- The gas particles are in constant random motion.
- Collisions between the gas particles are perfectly elastic.
- The average kinetic energy of particles in a gas is constant at constant temperature. OR The average kinetic energy is proportional to the absolute temperature.

2(a)(ii)
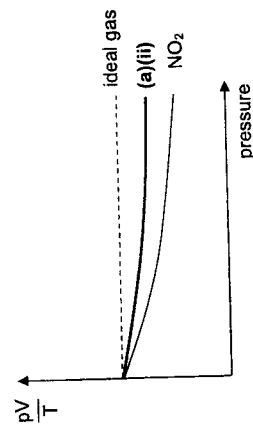
At higher temperature of T_2 K, the NO_2 gas molecules have higher kinetic energy and are better able to overcome the intermolecular attractive forces. Hence it would exhibit less deviation from an ideal gas as compared to at a lower temperature of T_1 K.

4

2(b)(i)

At t = 200 s, [NOCl] = 0.032 mol dm⁻³

	$2NO_2(g)$ +	$HCl(g)$	$\longrightarrow$ $NOCl(g)$ +	$HNO_3(g)$
initial conc / mol dm⁻³	1.00	0.05	0	0
change in conc / mol dm⁻³	-0.064	-0.032	+0.032	+0.032
conc at 200 s / mol dm⁻³	0.936	0.018	0.032	0.032

mole fraction of NOCl $= \dfrac{0.032}{0.936 + 0.018 + 0.032 + 0.032} = \underline{0.0314}$

2(b)(ii)

$pV = nRT$

$p_{NOCl}V = n_{NOCl}RT$

$p_{NOCl} = \dfrac{n_{NOCl}}{V} RT$

$= \dfrac{0.032}{10^{-3}} (8.31)(500)$

$= 1.3296 \times 10^5$ Pa

$p_{NOCl} = x_{NOCl} \times p_{total}$

$p_{total} = \dfrac{1.3296 \times 10^5}{0.0314}$

$= \underline{4.23 \times 10^6 \text{ Pa}}$
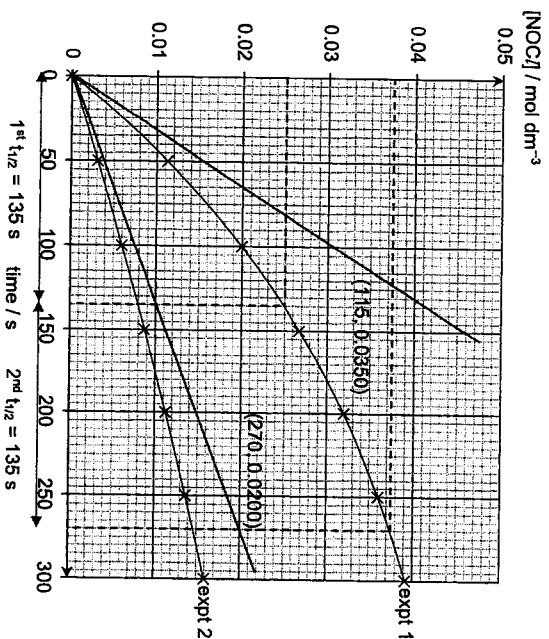
Alternative method:

$pV = nRT$

$p_{total}V = n_{total}RT$

$p_{total} = \dfrac{n_{total}}{V} RT$

$= \dfrac{0.936 + 0.018 + 0.032 + 0.032}{10^{-3}} (8.31)(500)$

$= \underline{4.23 \times 10^6 \text{ Pa}}$

2(b)(iii)

[NOCl] / mol dm⁻³

y-axis values: 0.05, 0.04, 0.03, 0.02, 0.01, 0

x-axis: time / s — 0, 50, 100, 150, 200, 250, 300

1st t₁/₂ = 135 s   2nd t₁/₂ = 135 s

(115, 0.0350)   (270, 0.0200)

expt 1   expt 2

initial rate of reaction for experiment 1 = $\dfrac{0.0350-0}{115-0}$ = 3.04 × 10⁻⁴ mol dm⁻³ s⁻¹

initial rate of reaction for experiment 2 = $\dfrac{0.0200-0}{270-0}$ = 7.41 × 10⁻⁵ mol dm⁻³ s⁻¹

$\dfrac{\text{initial rate of expt 1}}{\text{initial rate of expt 2}}$ = $\dfrac{3.04 \times 10^{-4}}{7.41 \times 10^{-5}}$ = 4.10 ≈ 4 (to nearest integer)

Comparing experiments 1 and 2, when [NO₂] × 2, rate × 4.
⇒ rate ∝ [NO₂]²,
⇒ reaction is <u>second order with respect to NO₂</u>.

2(b)(iv)

Final [NOCl] = <u>0.0500 mol dm⁻³</u>

2(b)(v)   For experiment 1, final [NOCl] = 0.05 mol dm⁻³.

1st t₁/₂ ⇒ time taken for [HCl] to decrease from 0.05 mol dm⁻³ to 0.025 mol dm⁻³
⇒ time taken for [NOCl] to increase from 0 mol dm⁻³ to 0.025 mol dm⁻³
⇒ 135 s

2nd t₁/₂ ⇒ time taken for [HCl] to decrease from 0.025 mol dm⁻³ to 0.0125 mol dm⁻³
⇒ time taken for [NOCl] to increase from 0.025 mol dm⁻³ to 0.0375 mol dm⁻³
⇒ 135 s

Since t₁/₂ is constant, reaction is first order with respect to HCl.

2(b)(vi)

Since NO₂ is in large excess, rate = k'[HCl] where k' = k[NO₂]².
Hence $t_½$ = $\dfrac{\ln 2}{k'}$ = $\dfrac{\ln 2}{k[NO_2]^2}$.

OR

Since NO₂ is in large excess, the overall reaction is <u>pseudo first-order with respect to HCl</u>. Hence $t_½$ is <u>independent of [HCl]</u>.

As <u>initial [NO₂] of experiment 3 is the same as that of experiment 2</u>, $t_½$ would remain the same at 540 s even though [HCl] is different.

2(c)(i)

N₂O₄ + CH₂CH₂ ⟶ O₂NCH₂CH₂NO₂

2(c)(ii)

<u>Addition</u> reaction

2(c)(iii)

The N₂O₄ molecules diffuse to the surface of the Pt catalyst and they become <u>adsorbed</u> onto the active sites of the Pt surface.

The adsorption <u>weakens the covalent bonds</u> in the N₂O₄ molecules and <u>lowers the activation energy</u>.

Once the NO₂ molecules are formed, they <u>desorb</u> from the surface and diffuse away from the Pt catalyst, freeing up the active sites for adsorbing other N₂O₄ molecules.

2(c)(iv)

K_c = $\dfrac{[NO_2]^2}{[N_2O_4]}$

[NO₂] = $\sqrt{K_c\,[N_2O_4]}$ OR $K_c^{¼}\,[N_2O_4]^{½}$

2(c)(v)

rate = k_2[NO₂][CH₂=CH₂]
rate = k'[N₂O₄]^½[CH₂=CH₂]   where k' = $k_2\,K_c^{¼}$

3(a)(i)

Upon heating with NaOH, the <u>amide in the side chain</u> of glutamine was <u>hydrolysed</u> to form –CH₂CH₂COO⁻. Upon acidification, the –CH₂CH₂COO⁻ undergoes protonation to form –CH₂CH₂COOH which is the side chain of glutamic acid.

3(a)(ii)

$$H_2N-\overset{H}{\underset{O}{C}}-\overset{H}{\underset{CH_2}{C}}-\overset{O}{\underset{OH}{C}}-\overset{H}{N}-\overset{H}{\underset{CH_2}{C}}-COO^-$$

3(a)(iii)

leu–arg–ser–tyr
arg–ser–tyr–ser
tyr–ser–phe–arg
leu–arg–ser–tyr–ser–phe–arg

3(b)(i)
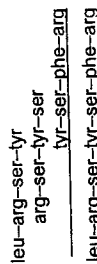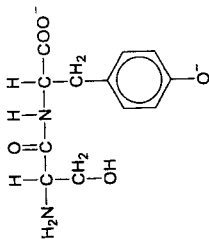
$(CH_3)_3N$ is more basic as it has 2 more electron-donating alkyl groups, which increase the electron density on the N atom, making the lone pair of electrons on N more available for coordination to an electron deficient species / a proton.
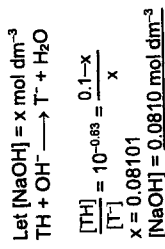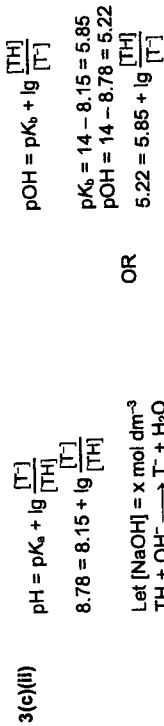
3(b)(ii)

ion–dipole interactions

3(b)(iii)

Due to its smaller ionic radius/size, $CH_3NH_3^+$ has a higher charge density compared to $(CH_3)_3NH^+$. Hence, $CH_3NH_3^+$ forms stronger ion-dipole interactions with water.
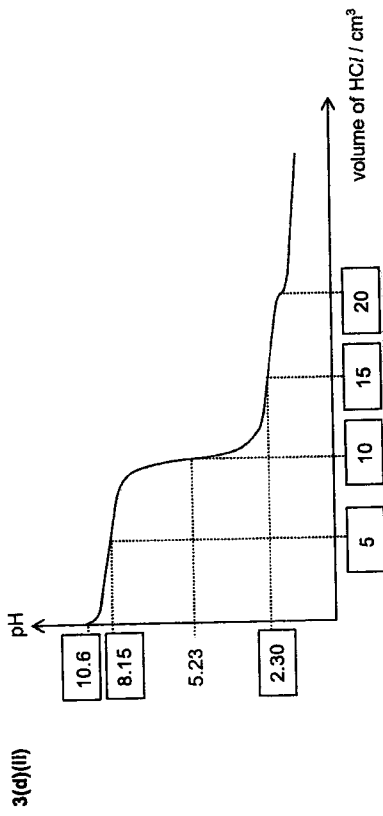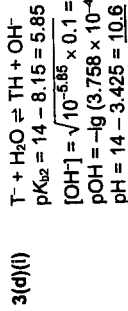
3(b)(iv)

The stronger interaction between $CH_3NH_3^+$ and water leads to greater stability and causes the position of equilibrium of equation 3.2 to lie more to the right / greater extent of ionisation of CH_3NH_2 as compared to $(CH_3)_3N$. Hence, CH_3NH_2 is a stronger base with a lower pK_b.

3(c)(i)

$$HO-\overset{OH}{\underset{OH}{\underset{\overset{+}{NH_2}}{C}}}-\overset{O}{\underset{O^-}{C}}$$
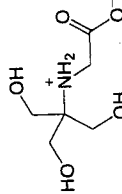
TH exists as a zwitterion with oppositely charged ends. It has a giant ionic lattice structure consisting of strong ionic bonds between the oppositely charged ends of neighbouring zwitterions. The strong ionic bonds require a large amount of heat energy to overcome. Hence, TH has a high melting point and exists as a solid at room temperature.


3(c)(ii)

$$pH = pK_a + lg\frac{[T^-]}{[TH]}$$

$$8.78 = 8.15 + lg\frac{[T^-]}{[TH]}$$

Let [NaOH] = x mol dm^{-3}

$$TH + OH^- \longrightarrow T^- + H_2O$$

$$\frac{[T^-]}{[TH]} = 10^{0.63} = \frac{x}{0.1-x}$$

x = 0.08101
[NaOH] = 0.0810 mol dm^{-3}

OR

$$pOH = pK_b + lg\frac{[TH]}{[T^-]}$$

$$pK_b = 14 - 8.15 = 5.85$$
$$pOH = 14 - 8.78 = 5.22$$

$$5.22 = 5.85 + lg\frac{[TH]}{[T^-]}$$

Let [NaOH] = x mol dm^{-3}

$$TH + OH^- \longrightarrow T^- + H_2O$$

$$\frac{[TH]}{[T^-]} = 10^{-0.63} = \frac{0.1-x}{x}$$

x = 0.08101
[NaOH] = 0.0810 mol dm^{-3}

3(c)(iii)

With lower concentrations of T^- and TH, the buffering capacity will decrease as there is less amount of T^- and TH to react with added H^+ or OH^- respectively.

3(d)(i)

$$T^- + H_2O \rightleftharpoons TH + OH^-$$

$$pK_{b2} = 14 - 8.15 = 5.85$$

$$[OH^-] = \sqrt{10^{-5.85} \times 0.1} = 3.758 \times 10^{-4}\ mol\ dm^{-3}$$

$$pOH = -lg\,(3.758 \times 10^{-4}) = 3.425$$

$$pH = 14 - 3.425 = 10.6$$

3(d)(ii)

pH axis values: 10.6, 8.15, 5.23, 2.30

volume of HCl / cm^3 axis values: 5, 10, 15, 20

3(d)(iii)

The pH range of methyl red coincides with the region of rapid pH change in the first equivalence point. At the first end-point, the colour change is from yellow to orange.

3(d)(iv)

There is no region of rapid pH change at the second equivalence point.

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4(a)(i) Since the proportion of **G** to **F** increases with temperature, the <u>forward reaction is favoured by an increase in temperature</u>. As <u>increase in temperature favours the endothermic reaction</u> which absorbs heat, the forward reaction is endothermic and hence χ is a positive value.
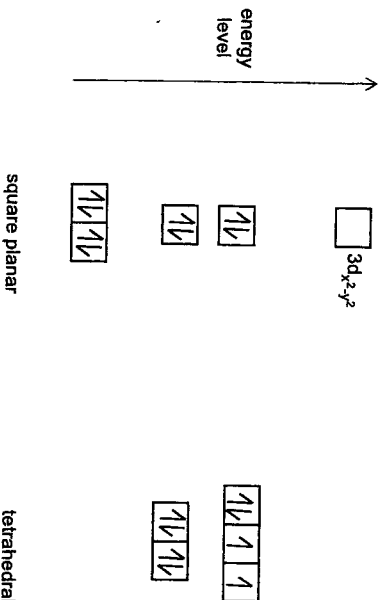
4(a)(ii) $1s^2 2s^2 2p^6 3s^2 3p^6 3d^8$
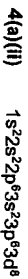
4(a)(iii)
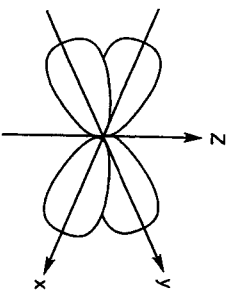
In **F** (a square planar complex), the <u>four ligands approach Ni²⁺ (the central metal ion)</u> along the x and y axes.
Since $3d_{x^2-y^2}$ orbital has its lobes along the x and y axes, any electron in the $3d_{x^2-y^2}$ orbital would be repelled most greatly by the lone pair of electrons in the ligands, causing $3d_{x^2-y^2}$ orbital to have the highest energy.

4(a)(iv)

4(a)(v) In **F** and **G**, the 3d orbitals are split differently, causing the <u>energy gap between the higher and lower energy levels to be different</u>.
<u>The energy required to promote an electron from the lower energy to the higher energy d orbital corresponds to different wavelengths of light.</u>
The different colours observed of **F** and **G** are the complement of the colour absorbed.

4(a)(vi)
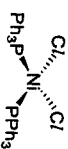
H has <u>two large PPh₃ groups</u> which are <u>close to each other</u>. This results in <u>great repulsion / steric strain between the two groups</u>, causing **H** to be less stable than **F**. Hence, **G** is converted to the more stable **F** rather than **H**.

4(b)(i) X⁻ must have a large <u>non-polar/ hydrophobic</u> portion to enable CuX_2 to interact well with oil rather than with water.

4(b)(ii) Concentration of CuX_2(oil) at equilibrium = 0.045 mol dm⁻³

4(b)(iii)

$$K_c = \frac{[CuX_2(oil)][H^+(aq)]^2}{[Cu^{2+}(aq)][HX(oil)]^2}$$

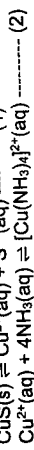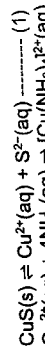$$2.1 \times 10^{-2} = \frac{(0.045)(10^{-3})^2}{[Cu^{2+}(aq)](0.20)^2}$$

[Cu²⁺(aq)] at equilibrium = 5.36 × 10⁻⁵ mol dm⁻³

Initial amount of Cu²⁺ in 2.0 dm³ = eqm amt of Cu²⁺(aq) + eqm amt of CuX₂(oil)
= (2 × 5.36 × 10⁻⁵) + (1 × 0.045) mol
= 0.0451 mol

Percentage of copper extracted = $\dfrac{\text{eqm amount in oil}}{\text{initial amount}}$
= $\dfrac{0.045}{0.0451}$ × 100% = <u>99.8 %</u>

4(b)(iv) Cu²⁺ can be released from the CuX₂ molecules in the oil solution by <u>adding H₂SO₄ to increase [H⁺(aq)]</u>. This shifts the <u>position of equilibrium in equation 4.2 to the left</u>, converting CuX₂(oil) to Cu²⁺(aq).

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4(c)

$CuS(s) \rightleftharpoons Cu^{2+}(aq) + S^{2-}(aq)$ ----------- (1)

$Cu^{2+}(aq) + 4NH_3(aq) \rightleftharpoons [Cu(NH_3)_4]^{2+}(aq)$ ----------- (2)

Cu^{2+} reacts with NH_3 in the metal polish to form a soluble complex $[Cu(NH_3)_4]^{2+}$, thus <u>decreasing</u> $[Cu^{2+}]$.

This causes the <u>position of equilibrium in (1) to shift to the right</u> so that the tarnish, CuS, <u>dissolves and can be removed</u>.
OR
If there is <u>sufficient</u> NH_3, the <u>ionic product, $[Cu^{2+}][S^{2-}]$, will be less than the K_{sp}</u> and hence <u>all the CuS dissolves.</u>

Section A

1(a)(i)

$[CO_3^{2-}] = \dfrac{0.010 \times \frac{20}{1000}}{\frac{20+20}{1000}} = 5.00 \times 10^{-3} \text{ mol dm}^{-3}$

As maximum amount of AgCl have been precipitated without precipitating Ag_2CO_3, the solution is saturated with Ag_2CO_3. Hence,

ionic product = $K_{sp}(Ag_2CO_3)$

$[Ag^+]^2[5.00 \times 10^{-3}] = 8.1 \times 10^{-12}$

$[Ag^+] = 4.025 \times 10^{-5} \text{ mol dm}^{-3}$

As the solution is also saturated with AgCl,

$[Ag^+][Cl^-]_{remaining} = (4.025 \times 10^{-5})[Cl^-]_{remaining} = 2.0 \times 10^{-10}$

$[Cl^-]_{remaining} = 4.97 \times 10^{-6} \text{ mol dm}^{-3}$

1(a)(ii)

Initial $[Cl^-]$ in mixture = $\dfrac{0.010 \times \frac{20}{1000}}{\frac{20+20}{1000}} = 5.00 \times 10^{-3} \text{ mol dm}^{-3}$

Percentage of Cl^- precipitated

$= \dfrac{(5.00 \times 10^{-3}) - (4.97 \times 10^{-6})}{5.00 \times 10^{-3}} \times 100\%$

$= 99.9\%$

This is an effective method.

1(b)(i)

Co-ordination number is the number of nearest neighbouring ions that surrounds an ion of opposite charge.

1(b)(ii)

As the Ba^{2+} ion is larger than the Ca^{2+} ion, the Ba^{2+} ion is able to accommodate a greater number of chloride ions surrounding it.
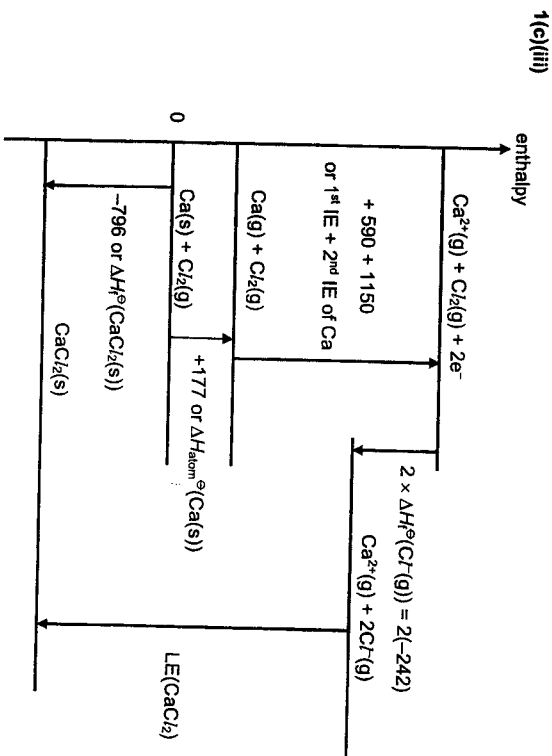
1(b)(iii)

The ions in $CaCl_2$ are less tightly packed in the lattice structure. Hence, less energy is required to overcome the weaker electrostatic forces of attraction between Ca^{2+} and Cl^- ions.

OR

Due to its smaller size/radius, Ca^{2+} has a higher charge density and polarising power than Ba^{2+}. As such, $CaCl_2$ has a greater covalent character than $BaCl_2$, resulting in an unexpectedly lower melting point than that of $BaCl_2$.

1(c)(i)

As the process occurs readily (or is spontaneous), ΔG is negative. Since there is a decrease in the number of ways the water particles can be arranged, ΔS is negative. $\Delta G = \Delta H - T\Delta S$. Since $-T\Delta S$ is positive, ΔH_f must be negative.

1(c)(ii)

The lattice energy (LE) of calcium chloride is the energy released when 1 mole of solid $CaCl_2$ is formed from $Ca^{2+}(g)$ and $Cl^-(g)$ at 1 bar and 298 K.

1(c)(iii)

$Ca^{2+}(g) + Cl_2(g) + 2e^-$

$+590 + 1150$ or 1st IE + 2nd IE of Ca

$Ca(g) + Cl_2(g)$

$+177$ or $\Delta H_{atom}^\ominus (Ca(s))$

$Ca(s) + Cl_2(g)$

0

-796 or $\Delta H_f^\ominus (CaCl_2(s))$

$2 \times \Delta H_f^\ominus (Cl^-(g)) = 2(-242)$

$Ca^{2+}(g) + 2Cl^-(g)$

$LE(CaCl_2)$

$CaCl_2(s)$

$+177 + 590 + 1150 + 2(-242) + LE(CaCl_2) = -796$

$LE(CaCl_2) = -2230 \text{ kJ mol}^{-1}$

1(d)

$AlCl_3$ exists as simple covalent molecules but dissolves in water to form $[Al(H_2O)_6]^{3+}$ ions.

$AlCl_3(s) + 6H_2O(l) \longrightarrow [Al(H_2O)_6]^{3+}(aq) + 3Cl^-(aq)$
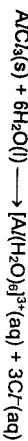
In $[Al(H_2O)_6]^{3+}$, the high charge density of Al^{3+} polarises and weakens the O–H bond of the water molecules, allowing the complex ion to undergo hydrolysis to form H_3O^+. A weakly acidic solution of pH 3 results.

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

PCl_5 exists as simple covalent molecules, which hydrolyses in water as the low-lying d-orbitals of the central P atom accepts a lone pair of electrons from H_2O. The reaction produces HCl as a product which dissolves in water to form a strongly acidic solution of pH 2.

$PCl_5(s) + 4H_2O(l) \longrightarrow H_3PO_4(aq) + 5HCl(aq)$
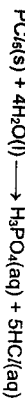
2(a)(i) Cyclopentadienyl anion consists of a ring of five sp² hybridised carbon atoms. Each carbon atom has an unhybridised p orbital that overlaps continuously.

The C atom bearing the negative charge contains a lone pair of electrons in its unhybridised p orbital. Hence, together with the 4 π electrons from the two C=C bonds, the cyclopentadienyl anion has a total of 6 delocalised π electrons.

2(a)(ii) When naphthalene undergoes substitution reaction, the product formed retains its aromaticity (of the entire molecule) as there are 10 delocalised π electrons in the continuously overlapping p orbitals.

However, if naphthalene undergoes addition reaction, the product formed is no longer aromatic (across the entire molecule) due to the absence of continuously overlapping p orbitals (or absence of 4n + 2 delocalised π electrons).

**2(b)(i)** $SO_3 + H_2SO_4 \rightleftharpoons HSO_3^+ + HSO_4^-$

2(b)(ii) Electrophilic substitution
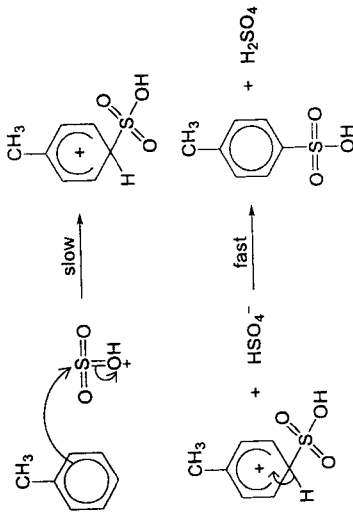
2(b)(iii) concentrated H_2SO_4, concentrated HNO_3, heat (under reflux)

2(c) Nitrogen is less electronegative than oxygen and its lone pair of electrons is more readily delocalised into the benzene ring. Hence, $-NH_2$ group is more activating than the $-OH$ group and directs the electrophilic substitution to occur more at the 2-position relative to $-NH_2$.
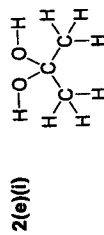
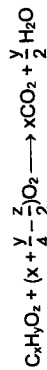**2(d)(i)** (excess) benzene, $FeBr_3$ (or $A\ell Br_3$)

2(d)(ii)

Structure of **X**:
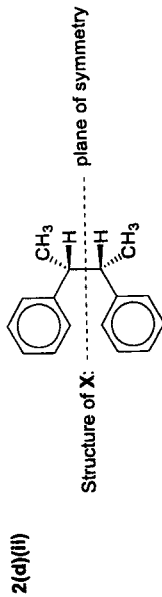
plane of symmetry

As **X** has a plane of symmetry / is a meso compound, **X** is optically inactive.

Structures of **Y** and **Z**:

mirror plane
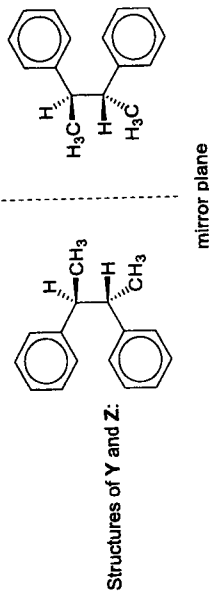
Y and **Z** are a pair of enantiomers and hence rotates plane-polarised light in equal but opposite directions.

2(e)(i)

2(e)(ii) Let the molecular formula of **K** be $C_xH_yO_z$.

$C_xH_yO_z + (x + \frac{y}{4} - \frac{z}{2})O_2 \longrightarrow xCO_2 + \frac{y}{2} H_2O$

$n(H_2O)$ collected $= \dfrac{0.090}{18.0} = \underline{0.005\ mol}$

Vol of gases (after cooling) = V(unreacted O_2) + V(CO_2) = 202 cm³

$V(CO_2) = 144\ cm^3$

$n(CO_2)$ evolved $= \dfrac{144}{24000} = \underline{0.006\ mol}$

V(unreacted O_2) = 202 – 144 = 58 cm³
V(reacted O_2) = 250 – 58 = 192 cm³
$n(reacted\ O_2) = \dfrac{192}{24000} = \underline{0.008\ mol}$

5

2(e)(iii)

|	$C_xH_yO_z$	O_2	CO_2	H_2O
amount / mol	0.001	0.008	0.006	0.005
mole ratio	1	8	6	5

x = 6

$\frac{y}{2}$ = 5, hence y = 10

$x + \frac{y}{4} - \frac{z}{2} = 6 + 2.5 - \frac{z}{2}$ = 8, hence z = 1

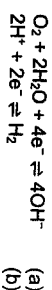Molecular formula for **K** is $C_6H_{10}O$.

Evidence / Information	Deduction / Explanation
K gives an orange ppt with 2,4-DNPH but does not form silver mirror with Tollens' reagent.	Condensation with 2,4-DNPH but no oxidation with Tollens' reagent. **K** is a carbonyl compound but not an aldehyde. **K** is a ketone.
When **K** is heated with acidified KMnO₄, **L** and propanone are formed.	Strong oxidation. **K** is an alkene that contains =C(CH₃)₂ group.
When **L** is heated with aqueous I₂ in dilute NaOH followed by acidification, **M** and a yellow ppt are formed.	Oxidation and acid-base reaction. **L** has 3 C atoms and contains —C(=O)—CH₃ group. Yellow ppt is CHI₃. **L** contains a —COOH group.
When **M** is heated with acidified KMnO₄, the only product form is a gas that gives a white precipitate with limewater.	Oxidation. **M** contains a —COOH group. Gas is CO₂.

K	**L**	**M**
$(CH_3)_2C=CH-C(=O)-CH_3$	$CH_3-C(=O)-C(=O)-OH$	$HO-C(=O)-C(=O)-OH$

6
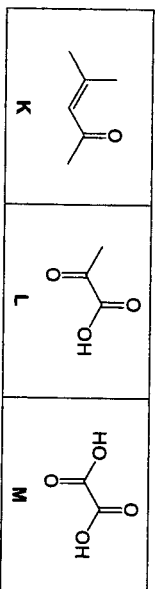
3(a)(i) From the *Data Booklet*, $E^\ominus_{cathode}$ = +0.40 V and $E^\ominus_{anode}$ = 0.00 V.
Hence, $E^\ominus_{cell} = E^\ominus_{cathode} - E^\ominus_{anode}$ = **+0.40 V**

$$O_2 + 2H_2O + 4e^- \rightleftharpoons 4OH^- \quad (a)$$
$$2H^+ + 2e^- \rightleftharpoons H_2 \quad (b)$$

3(a)(ii) Hence, E_{cell} of the EDCS is more positive than that of the hydrogen-fuel cell in (a).

The higher the CO_2 concentration, the more positive the E_{cell} and the current increases. Since I = n_eF/t, the amount of electrons transferred per second increases and hence increases the rate of removal of CO_2.

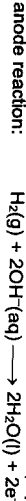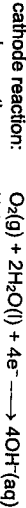**3(a)(iii)** At the anode, the CO_3^{2-} which migrates from the cathode removes H⁺ formed, causing a decrease in [H⁺]. The position of equilibrium for reaction (b) shifts to the left and this causes E_{anode} to be more negative.

At the cathode, CO_2 removes OH⁻ formed, causing a decrease in [OH⁻]. The position of equilibrium for reaction (a) shifts to the right and this causes $E_{cathode}$ to be more positive.

3(b)(i) From the *Data Booklet*,
If a typical hydrogen-oxygen fuel cell operates under acidic conditions:
cathode reaction: $O_2(g) + 4H^+(aq) + 4e^- \longrightarrow 2H_2O(l)$
anode reaction: $H_2(g) \longrightarrow 2H^+(aq) + 2e^-$
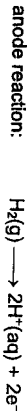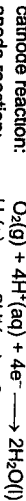
$E^\ominus_{cathode}$ = +1.23 V and $E^\ominus_{anode}$ = 0.00 V
Hence, $E^\ominus_{cell}$ = +1.23 − 0.00 = **+1.23 V**

3(b)(ii) If a typical hydrogen-oxygen fuel cell operates under alkaline conditions:
cathode reaction: $O_2(g) + 2H_2O(l) + 4e^- \longrightarrow 4OH^-(aq)$
anode reaction: $H_2(g) + 2OH^-(aq) \longrightarrow 2H_2O(l) + 2e^-$

$E^\ominus_{cathode}$ = +0.40 V and $E^\ominus_{anode}$ = −0.83 V
Hence, $E^\ominus_{cell}$ = +0.40 − (−0.83) = **+1.23 V**

Under acidic conditions, there will not be any H⁺ ions at the cathode to react with and to convert atmospheric CO_2 to CO_3^{2-}. Hence, the CO_2 in air cannot be captured by the EDCS.

Under alkaline conditions, there will not be any H⁺ ions at the anode to convert CO_3^{2-} ions back to CO_2 to be removed into a separate storage.

Hence, a typical hydrogen-oxygen fuel cell cannot be used in the EDCS.

7

3(c)(i) Volume of CO_2 removed per minute = $0.99 \times 3000 \times \dfrac{400}{10^6}$ = 1.188 cm³

Amount of CO_2 removed per second = $\dfrac{1.188}{24000} \div 60$ = 8.25×10^{-7} mol

From equations (1) – (4),
amount of electrons passed per second
= $2 \times 8.25 \times 10^{-7}$
= 1.65×10^{-6} mol per second

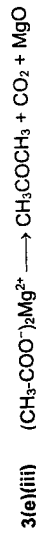Hence, current = $1.65 \times 10^{-6} \times 96500$ = 0.159 A

3(c)(ii) The CO_3^{2-} and electrons can diffuse more quickly across a larger surface area and hence increase the rate of CO_2 removal.

3(d) Similar to graphite, CNTs have an **extended** delocalised π electron cloud, which allows CNTs to conduct electricity.

Thus, it is likely that CNTs help conduct electricity across the membrane and increases the membrane's electrical conductivity.

3(e)(i) Mg^{2+} has a smaller ionic radius than Ca^{2+}. Hence, with the same charge, Mg^{2+} has a higher charge density and hence greater polarizing power than Ca^{2+}. As a result, Mg^{2+} distorts the electron cloud of R-COO⁻ to a greater extent. The covalent bonds within R-COO⁻ are weakened to a greater extent as compared to that in (R-COO⁻)₂Ca²⁺. Therefore, less heat energy is needed to decompose (R-COO⁻)₂Mg²⁺. Hence (R-COO⁻)₂Mg²⁺ has lower thermal stability.

3(e)(ii) $MgCO_3 \longrightarrow MgO + CO_2$

**3(e)(iii)** $(CH_3\text{-}COO^-)_2Mg^{2+} \longrightarrow CH_3COCH_3 + CO_2 + MgO$

8

Section B

4(a) Nitrogen has a higher number of protons and hence higher nuclear charge than carbon. Although there is one more electron in nitrogen than carbon, this electron is added to the same outermost shell, and hence shielding effect remains approximately constant. Thus, nitrogen has a higher effective nuclear charge and stronger electrostatic attraction between the nucleus and the valence electrons than carbon, resulting in an increase in the amount of energy required to remove the valence electron from nitrogen. Hence, the first ionisation energy of nitrogen is higher than carbon.

The first ionisation energy of oxygen is lower than that of nitrogen. This is because the 2p electron to be removed from oxygen is a paired electron while that to be removed from nitrogen is an unpaired electron. Due to inter-electronic repulsion between paired electrons in the same orbital, less energy is required to remove the paired 2p electron from oxygen.

4(b) The stronger the acid, the lower the pK_a value and the more stable the conjugate base.

Based on the given pK_a values, acidity increases in the order:
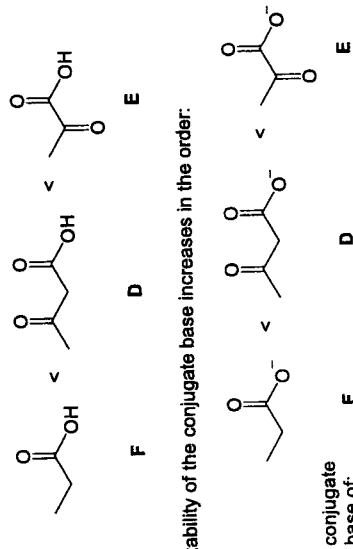
and the stability of the conjugate base increases in the order:

Compared to the conjugate base of **F**, the conjugate bases of **D** and **E** are more stable due to the presence of the electron-withdrawing carbonyl group to disperse the negative charge and hence stabilising the anions.

The conjugate base of **E** is more stable than that of **D** as the electron-withdrawing carbonyl group is nearer to the –COO⁻, and can better disperse the negative charge, thus stabilising the conjugate base of **E** to a greater extent.
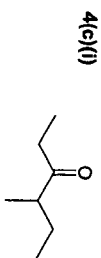
4(c)(i) step 1: ethanolic KOH, heat (under reflux)

4(c)(ii) I: [structure]

4(c)(iii) step 1: [structure]

step 2: KMnO$_4$(aq), H$_2$SO$_4$(aq), heat (under reflux)
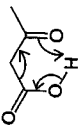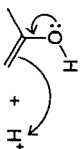
step 2: [structure] + H$^+$

4(d)(i) J: HO–N(H)–... –COOH [structure]

4(d)(ii) KMnO$_4$(aq), H$_2$SO$_4$(aq), heat   OR   K$_2$Cr$_2$O$_7$(aq), H$_2$SO$_4$(aq), heat

4(d)(iii) Acidic hydrolysis and oxidation
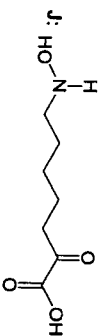
4(e)(i) High dilution or low concentration of reactant

4(e)(ii) A catalytic amount of H$^+$ is not sufficient as H$^+$ is <u>consumed stoichiometrically in step 6</u> to protonate the NH$_3$ hydrolysis product.

4(f)(i) In conjugate acid **X**, the <u>lone pair of electrons on the N atom interacts with the π electron cloud of the adjacent C=O bond and is delocalised, hence dispersing the positive charge on the O atom and stabilising **X**.</u>

4(f)(ii) In conjugate acid **Y**, there is <u>no continuous side-on overlap of p orbitals and hence **Y** is not resonance stabilised.</u>

4(f)(iii) [structure: ^{18}O ... OH] and [structure: O ... ^{18}OH]

5(a)(i) Cyclohexanone and compound **P** are <u>constitutional (or structural) isomers.</u>

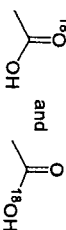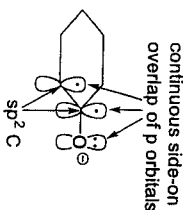**5(a)(ii)** Compound **Q** is more stable than pentane-2,4-dione because:
- the H atom of the –OH group can form <u>intramolecular hydrogen bond</u> with the O atom of the nearby carbonyl group.
- there is <u>resonance stabilisation / delocalisation</u> of lone pair of electrons on the O atom of –OH group with the π electron cloud of the C=C and C=O groups.

5(b)(i) The carbon atoms in the C=C bond are sp^2 hybridised, each with an unhybridised p orbital containing one electron. The p orbital of the adjacent O atom can overlap <u>continuously side-on</u> with the p orbitals of the sp^2 carbon atoms, resulting in <u>delocalisation of the negative charge on the O atom into the C=C bond. Hence, **R** is resonance stabilised.</u>

5(b)(ii)

[diagram: sp^2 C, continuous side-on overlap of p orbitals]

[reaction: cyclohexanone + B base ⇌ R + BH$^+$ conjugate acid]

Unlike conjugate acids of **I** and **II**, the pK_a of the conjugate acids of **III** and **IV** are higher than the pK_a of cyclohexanone. This means that the conjugate acids of **III** and **IV** are weaker acids than cyclohexanone. Hence, the acid-base reaction of **III** and **IV** with cyclohexanone lie further right compared to that of **I** and **II** with cyclohexanone.

Compared to **IV**, **III** is more suitable as the <u>presence of bulky alkyl groups in **III** prevents it from acting as a nucleophile</u> to react with the carbonyl group in cyclohexanone, resulting in the formation of side/addition product.

Hence, **III** is the most suitable base to deprotonate cyclohexanone to form **R**.

5(e)(i)   Step 1 is a <u>condensation reaction</u>.

5(e)(ii)   Compound **V** <u>does not exhibit cis-trans isomerism</u>. Although there is restricted rotation about the C=N bond, the <u>C atom in the C=N bond has two identical groups</u> bonded to it.

5(e)(iii) H_2SO_4(aq) / HCl(aq) / HNO_3(aq), heat
OR
NaOH(aq), heat

5(c)(i)

step 1
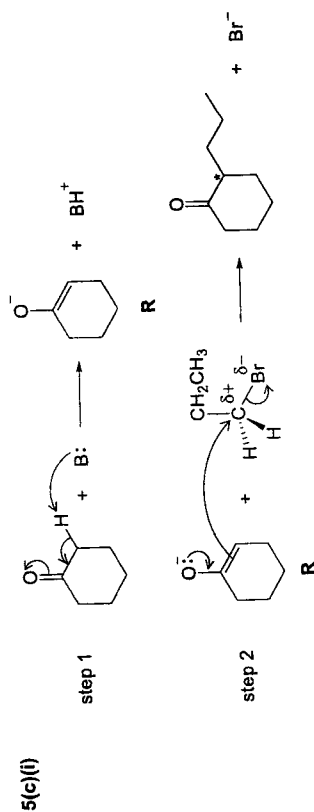
step 2

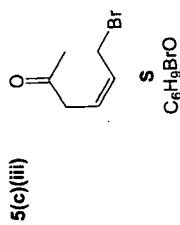**5(c)(ii)**   In step 2, the S_N2 reaction can occur with 1-bromopropane on <u>either side of the trigonal planar carbon</u> of C=C in **R** with <u>equal probability</u>, hence forming a <u>racemic mixture / equal amounts of a pair of enantiomers which does not rotate the plane of polarised light.</u>

5(c)(iii)

S
C_6H_9BrO

5(c)(iv)   step 2: H_2, Ni, heat

step 3: $KMnO_4$(aq), H_2SO_4(aq), heat (under reflux)
OR
$K_2Cr_2O_7$(aq), H_2SO_4(aq), heat (under reflux)

5(d)

potential energy

U

T

+ base

progress of reaction

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2022 RI H2 Chemistry Prelim Paper 4 – Suggested Solutions

1(a)

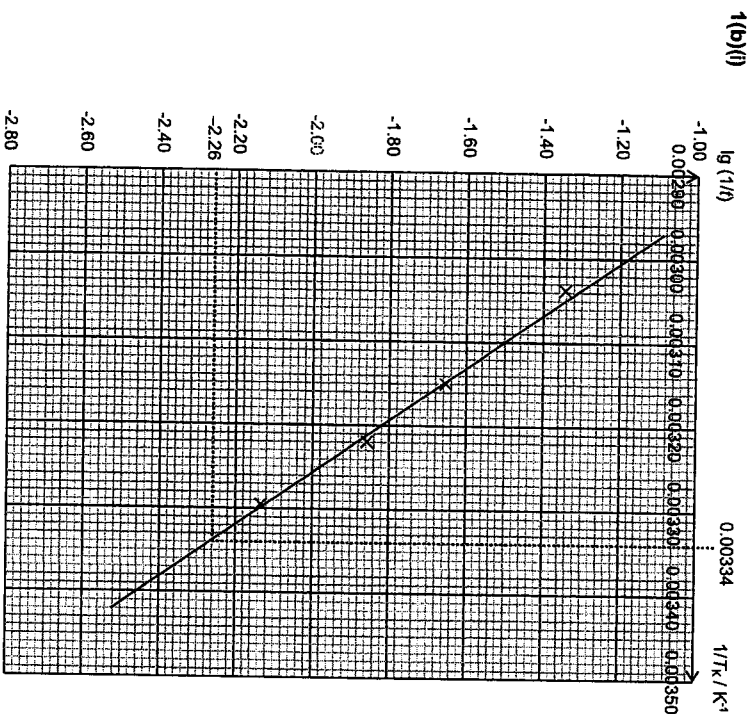| Expt	$T_{initial}$ /°C	T_{final} /°C	t /s	$1/t$ /s^{-1}	$\lg (1/t)$	T_{ave} /°C	T_K /K	$1/T_K$ /K^{-1}
1	30.4	30.6	136	0.00735	-2.13	30.5	304	0.00329
2	62.4	50.0	22	0.0455	-1.34	56.2	329	0.00304
3	39.2	36.0	72	0.0139	-1.86	37.6	311	0.00322
4	48.2	40.8	45	0.0222	-1.65	44.5	318	0.00315

1(b)(i)

1(b)(ii)

$t = 3 \times 60 = 180$ s

$\lg (1/t) = \lg (1/180) = -2.26$

From the graph, $1/T_K = 0.00334$ K^{-1}

$T_{ave} = \underline{26.4}$ °C

(c)(i)

Mole ratio of MnO_4^- : D-glucose : $e^- = 1 : 2.5 : 5$

Hence, mole ratio of D-glucose : $e^- = 1 : 2$

1 mol of D-glucose loses $\underline{2 \text{ mol of } e^-}$.

-1-

(c)(ii) Structure of **P**:

O=C—OH
H—C—OH
HO—C—H
H—C—OH
H—C—OH
CH₂OH
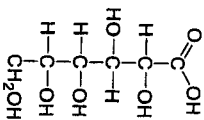
Since 1 mol of D-glucose loses 2 mol of e^- and only one carbon atom in each glucose molecule is oxidised, the oxidation state of this carbon must have increased by 2. Hence, the aldehyde group of D-glucose is oxidised to carboxylic acid as the oxidation state of carbon increases from +1 in aldehyde to +3 in carboxylic acid.

(d)(i)

Maximum total percentage uncertainty $= (\dfrac{2(\pm 0.05)+(\pm 0.5)+(\pm 0.5)}{60}) \times 100\% = \pm 1.83\%$

(d)(ii)

Although T_{ave} was calculated, the difference between $T_{initial}$ and T_{final} was quite significant, especially for experiments conducted at temperatures above room temperature. This in turn resulted in inaccuracy in the measurement of the temperature of the reaction/measurement of the time required for the reaction to complete at T_{ave}.

A modification to the experimental procedure would be to use a water bath maintained at a fixed temperature for each experiment, to equilibrate the reactants at the same fixed temperature before starting the reaction, and to ensure that the temperature of the reaction mixture stayed constant throughout the reaction.

OR

The human perception of when the reaction mixture turned colourless may be inconsistent/vary across different experiments, hence resulting in inaccuracy in the measurement of the time required for the reaction to complete at T_{ave}.

A modification to the experimental procedure would be to use a colorimeter to monitor the absorbance of the reaction mixture, and stopping the stopwatch only when there was no more absorbance (i.e. reaction mixture had turned colourless).

2(a)(i)

Mass of capped weighing bottle and **FA 4** / g	9.135
Mass of capped weighing bottle after emptying **FA 4** / g	5.211
Mass of **FA 4** used / g	3.924

2(a)(ii)

Titration number	1	2
Final burette reading / cm³	19.90	39.80
Initial burette reading / cm³	0.00	19.90
Volume of **FA 1** used / cm³	19.90	19.90
Values used	✓	✓

Average volume of **FA 1** used = (19.90 + 19.90) / 2 = $\underline{19.90 \text{ cm}^3}$

-2-

3(b)

	test	observations with FA 6	observations with FA 7
(i)	Add about 2 cm depth of FA 6 to a test-tube. To this test-tube, add 2 cm depth of dilute sulfuric acid, followed by 1 drop of potassium manganate(VII) solution and shake well.		no observable change.
	Leave the test-tube to stand in a beaker of hot water for about 5 minutes.	Decolourisation of purple $KMnO_4$	
(ii)	Add 1 cm depth of aqueous silver nitrate to a test-tube. Then slowly add 1 cm depth of aqueous sodium hydroxide.		
	Add aqueous ammonia slowly, with shaking, until the precipitate just dissolves. You may use a clean glass rod to stir the mixture and help dissolve the precipitate. Add 1 cm depth of FA 6 to this mixture, shake the tube and place it in the test-tube rack to stand.	Silver mirror formed.	no observable change.
(iii)	Add about 1 cm depth of FA 7 to a test-tube. To this test-tube, add 4 drops of sodium hydroxide solution followed by iodine solution, dropwise, until a permanent orange/red colour is present.		Yellow ppt formed in orange / red solution.
	Warm the mixture in a beaker of hot water for about 2 minutes.		
	Add sodium hydroxide solution using a teat pipette until no further change is seen.		Solution turns colourless. Yellow ppt remained.

-4-

2(b)(i)

$n(MnO_4^-) = \dfrac{19.90}{1000} \times 0.0100 = 0.0001990$ mol

$n(Fe^{2+})$ in 25.0 cm³ of FA 5 = $5(MnO_4^-) = 5 \times 0.0001990 = 0.0009950$ mol

$[Fe^{2+}] = \dfrac{0.0009950}{0.025} = \underline{0.0398 \text{ mol dm}^{-3}}$

2b(ii)

$n(Fe^{2+})$ in 250 cm³ of FA 5 = $0.25 \times 0.0398 = 0.009950$ mol

$n(\text{FA 4})$ in 250 cm³ of FA 5 = $n(Fe^{2+}) = 0.009950$ mol

M_r of FA 4 = $\dfrac{3.924}{0.00995} = \underline{394}$

2(b)(iii)

Total number of positive charge = total number of negative charge

$(+1)a + 2 = 2b$

$\underline{a = 2b - 2}$

2(b)(iv)

Using the formula $(NH_4)_aFe(SO_4)_b.6H_2O$,

M_r of FA 4 = $a(14.0 + 4 \times 1.0) + 55.8 + b(32.1 + 16.0 \times 4) + 6(2 \times 1.0 + 16.0)$ ----------(1)

$= 18.0a + 96.1b + 163.8$

From (b)(ii), M_r of FA 4 = 394.4 $\Rightarrow 18.0a + 96.1b + 163.8 = 394.4$ --------(1)

Substitute $a = 2b - 2$ in (1).

$18.0(2b - 2) + 96.1b + 163.8 = 394.4$

$36.0b - 36.0 + 96.1b + 163.8 = 394.4$

$132.1b = 266.6 \Rightarrow b = 2.018 = \underline{2}$ (whole number)

$a = 2(2) - 2 = \underline{2}$

2(c)

The student's titre value would be <u>higher</u>.

Due to insufficient amount of H_2SO_4, <u>MnO_4^- is reduced to MnO_2 instead of Mn^{2+}</u>. As MnO_4^- <u>accepts 3 e⁻</u> when it is reduced to MnO_2 compared to <u>accepting 5 e⁻</u> when it is reduced to Mn^{2+}, more MnO_4^- is needed to oxidise the same amount of Fe^{2+}, so titre value to reach end-point is higher.

3(a)

test	observations
Using a 10 cm³ measuring cylinder, add 5.0 cm³ of FA 3 to a boiling tube.	
To this boiling tube, add 5.0 cm³ of FA 8 using the same 10 cm³ measuring cylinder.	No observable change.
Leave this boiling tube in the hot water bath for about 3 minutes.	Red/brown ppt formed.
Filter the reaction mixture into another boiling tube.	Brown filtrate.
Wash the residue with some deionised water.	Red/brown residue.
The residue is FA 9.	
Retain the filter funnel containing FA 9 for 3(c)(iii).	

-3-

3(b)(iv)

	functional group	evidence
FA 6	aldehyde	In test (b)(ii), FA 6 gives a silver mirror with Tollens' reagent. In test (b)(ii), FA 6, FA 7 did not decolourise purple acidified KMnO₄.
FA 7	ketone	In test (b)(iii), FA 7 gave yellow ppt, CHI₃, with alkaline aq iodine.

3(c)

	test	observations
(i)	Test solution FA 8 with Universal Indicator paper.	Universal indicator turns dark blue, pH is 12.
(ii)	Add about 1 cm depth of FA 8 to a test-tube. Then add 1 cm depth of dilute nitric acid.	Solution FA 8 turns from dark blue to light blue. No effervescence.
	To this test-tube, add about 1 cm depth of aqueous barium nitrate slowly, with shaking, until no further change is seen.	White ppt formed in light blue solution.
(iii)	Place the filter funnel containing FA 9 into a clean test-tube.	
	Using a 10 cm³ measuring cylinder, carefully add 2.0 cm³ of dilute sulfuric acid to the filter funnel. The filtrate will collect in the test-tube.	The residue turned from red/brown to red-brown/dark brown/black.
	The residue is FA 10.	Red-brown/dark brown/black residue.
	The filtrate is FA 11.	Blue filtrate.
(iv)	Add 1 cm depth of FA 11 to a test-tube.	
	Add aqueous ammonia slowly, with shaking, until no further change is seen.	Blue ppt formed, soluble in excess NH₃(aq) to form a dark blue solution.

3(c)(v)

Cu^{2+}

3(c)(vi)

Oxidation state of element X: +1

3(c)(vi)

Type of reaction: Disproportionation

3(c)(vii)

SO_4^{2-} is present. In test (c)(ii), FA 8 reacted with Ba(NO₃)₂ in the presence of HNO₃(aq) to form white ppt of BaSO₄.

4(a)(i)

Let V_{neut} cm³ be the volume of barium hydroxide and (100 - V_{neut}) cm³ be the volume of hydrochloric acid used at which stoichiometric amount of barium hydroxide and hydrochloric acid react.

Assuming [Ba(OH)₂] = 0.080 mol dm⁻³,

mole ratio of HCl : Ba(OH)₂ = 2 : 1

$n(HCl) = 2 \times n(Ba(OH)_2)$

$$\frac{100 - V_{neut}}{1000} \times 0.200 = 2 \times \frac{V_{neut}}{1000} \times 0.080$$
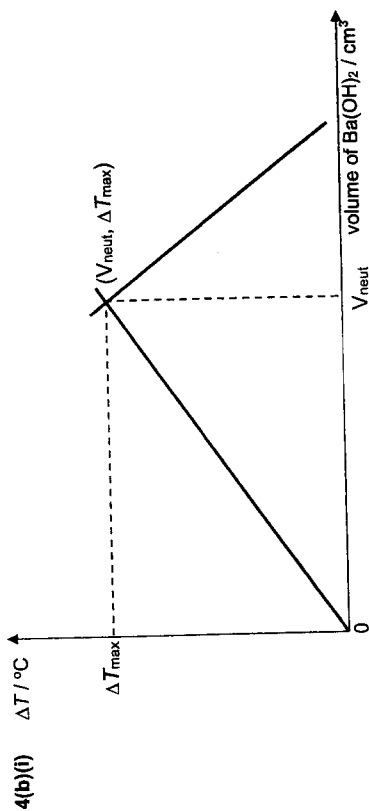
$20 - 0.2V_{neut} = 0.16V_{neut}$

$0.36V_{neut} = 20$

$V_{neut} = 55.6$ cm³

4(a)(ii)

Procedure

1. Using a 100 cm³ measuring cylinder, transfer 10.0 cm³ of Ba(OH)₂ into a clean and dry Styrofoam cup supported in a 250 cm³ beaker.
2. Use a thermometer to measure and record the steady initial temperature of Ba(OH)₂.
3. Using another 100 cm³ measuring cylinder, measure 90.0 cm³ of 0.200 mol dm⁻³ HCl. Ensure that both Ba(OH)₂ and HCl have the same initial temperature.
4. Add HCl from the measuring cylinder into the Styrofoam cup containing Ba(OH)₂ and cover the Styrofoam cup with a lid. Use the thermometer to stir the mixture gently. Measure and record the highest temperature of the mixture.
5. Empty, wash and carefully dry the Styrofoam cup.
6. Repeat steps 1 to 5 using volumes of HCl and Ba(OH)₂ in the table below so that the total volume of the mixture is 100 cm³.
7. Record all measurements of volume, highest temperature after mixing and temperature change, ΔT, in the table below.

volume of Ba(OH)₂ / cm³	volume of HCl / cm³	initial temperature of Ba(OH)₂ /°C	highest temperature after mixing /°C	ΔT /°C
10	90			
20	80			
30	70			
40	60			
50	50			
60	40			
65	35			
70	30			
75	25			
80	20			

4(b)(i)

Graph axes: ΔT / °C (vertical), volume of Ba(OH)$_2$ / cm^3 (horizontal). Point marked $(V_{neut}, \Delta T_{max})$ with ΔT_{max} and V_{neut} indicated by dashed lines.

4(b)(ii)

$$\frac{[Ba(OH)_2] \times V_{neut}}{0.200 \times (100 - V_{neut})} = \frac{1}{2}$$

$$[Ba(OH)_2] \times V_{neut} = \frac{1}{2} \times 0.200 \times (100 - V_{neut})$$

$$[Ba(OH)_2] = \frac{0.100 \times (100 - V_{neut})}{V_{neut}} \text{ mol dm}^{-3}$$

Heat released $= \dfrac{100 \times 4.18 \times \Delta T_{max}}{1000}$ kJ $\qquad$ (accept q $= + \dfrac{100 \times 4.18 \times \Delta T_{max}}{1000}$ kJ)

$n(H_2O)$ produced $= n(HCl)$ reacted $= 0.200 \times \dfrac{(100 - V_{neut})}{1000} = 0.0002 \times (100 - V_{neut})$

$$\Delta H_{neut} = - \frac{\frac{100 \times 4.18 \times \Delta T_{max}}{1000}}{0.0002 \times (100 - V_{neut})} = - \frac{2090 \times \Delta T_{max}}{100 - V_{neut}} \text{ kJ mol}^{-1}$$

4(c)

When a bottle of barium hydroxide solution is left standing in the air for some time, <u>barium hydroxide reacts with carbon dioxide in the air to form barium carbonate</u>. <u>The enthalpy change of neutralisation of barium hydroxide and hydrochloric acid is different from that of barium carbonate and hydrochloric acid, this results in an inaccurate determination of</u> ΔH_{neut} of barium hydroxide and hydrochloric acid.

RIVER VALLEY HIGH SCHOOL
JC 2 PRELIMINARY EXAMINATION

CANDIDATE
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CLASS | 2 | 1 | J |

CENTRE
NUMBER   S

INDEX
NUMBER

H2 CHEMISTRY

Paper 1 Multiple Choice   9729/01

22 September 2022

1 hour

Additional Materials: Multiple Choice Answer Sheet
Data Booklet

READ THESE INSTRUCTIONS FIRST

Write in soft pencil.

Do not use staples, paper clips, glue or correction fluid.

Write your name, class, centre number and index number on the Answer Sheet in the spaces provided.

There are **thirty** questions on this paper. Answer **all** questions. For each question there are four possible answers **A**, **B**, **C** and **D**.

Choose the **one** you consider correct and record your choice in **soft pencil** on the separate Answer Sheet.

Read the instructions on the Answer Sheet very carefully.

Each correct answer will score one mark. A mark will not be deducted for a wrong answer.

Any rough working should be done in this booklet.

The use of an approved scientific calculator is expected, where appropriate.

---

1   Which particle has more protons than electrons and more protons than neutrons?
($D = {}_1^2H$)

   A NO_2^+ B ND_2H C NDH^- D ND_3H^+

2   Which particle would, on gaining an electron, have a half-filled subshell?

   A V^- B N C Se^+ D Ti

3   The first six ionisation energies (I.E.) of a Period 3 element, M, in kJ mol^{-1} are shown.

	1st	2nd	3rd	4th	5th	6th
I.E./ kJ mol^{-1}	1012	1907	2914	4964	6274	21267

   Which equations show the formation of the chloride of M?

   1   $M + 2Cl_2 \rightarrow MCl_4$

   2   $2M + 3Cl_2 \rightarrow 2MCl_3$

   3   $2M + 5Cl_2 \rightarrow 2MCl_5$

   A   1 and 3 only   B   2 and 3 only   C   1 only   D   2 only

4   The boiling point of water (100 °C) is greater than that of HF (20 °C).
   Which statement is a correct explanation of this?

   A   The H_2O molecule has a larger net dipole moment than the HF molecule.

   B   Each hydrogen bond formed between H_2O molecules is stronger than that formed between HF molecules.

   C   There are more electrons in a H_2O molecule than there are in a HF molecule, so the instantaneous dipole-induced dipole interactions are stronger in H_2O.

   D   On average, there are two hydrogen bonds between H_2O molecules compared to one hydrogen bond between HF molecules.

5 Which molecule contains a dative bond?

A BF_3

B NO

C CO

D SiO_2

6 Which gas shows the greatest deviation from ideality?

A CH_4 B SO_3 C C_2H_2 D CO_2

7 When a sample of gas is compressed at constant temperature from 20 atm to 80 atm, its volume changes from 67.0 cm^3 to 15.5 cm^3.

Which of the following is **not** a possible explanation of this behaviour?

A   Gas is adsorbed onto the vessel walls.

B   Gas begins to liquefy at 80 atm.

C   The gas dissociates.

D   The gas dimerises.

8 The titration curve shows how pH changes when 20.0 cm^3 of 0.20 mol dm^{-3} acid is titrated against 0.10 mol dm^{-3} base.
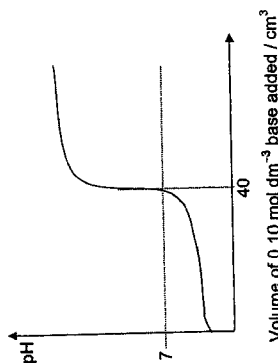
Which of the following statements regarding this titration is **incorrect**?

A   The identity of the acid and base could be CH_3COOH and $Ba(OH)_2$ respectively.

B   A buffer solution is formed when 15 cm^3 of the base is added.

C   The solution at equivalence point is alkaline.

D   This is a weak acid–strong base titration.

9 Self-heating cans offer benefits to campers without access to a stove or campfire. These soup cans have double walls with an ionic compound such as CaO in a packet and water between the walls. Upon opening the can, the packet breaks, allowing CaO to react with water and warm up the soup.

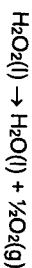$$CaO(s) + H_2O(l) \rightarrow Ca(OH)_2(s)$$

What are the signs of ΔH, ΔS and ΔG for the overall process?

	ΔH	ΔS	ΔG
A	−	−	−
B	−	+	−
C	+	+	−
D	+	+	+

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10 Hydrogen peroxide is thermodynamically unstable and decomposes over time to form water and oxygen gas.

The following data are provided:

$$H_2O_2(l) \rightarrow H_2O(l) + \tfrac{1}{2}O_2(g)$$
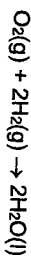
$O_2(g) + 2H_2(g) \rightarrow 2H_2O(l)$	$\Delta H_1 = -572$ kJ mol^{-1}; $\Delta S_1 = -325$ J mol^{-1} K^{-1}
$O_2(g) + H_2(g) \rightarrow H_2O_2(l)$	$\Delta H_2 = -188$ kJ mol^{-1}; $\Delta S_2 = -225$ J mol^{-1} K^{-1}

What is the value of ΔG, in kJ mol^{-1}, for the decomposition of hydrogen peroxide at 25 °C?

A −79 **B** −100 **C** −117 **D** −354

11 The enthalpy change of reaction between calcium and water is measured in the laboratory and found to be x kJ mol^{-1}.

$$Ca(s) + 2H_2O(l) \rightarrow Ca(OH)_2(aq) + H_2(g) \qquad \Delta H = x \text{ kJ mol}^{-1}$$

What information is needed to calculate the value of x?

1 enthalpy change of neutralisation of calcium hydroxide

2 enthalpy change of reaction of calcium with acid

3 enthalpy change of formation of water

A 1, 2 and 3 **B** 1 and 2 only **C** 1 and 3 only **D** 2 and 3 only

12 When 10 cm³ of a hydrocarbon was burnt in 100 cm³ of excess oxygen, the volume of residual gas mixture contracted by 20 cm³ after passing through a solution of aqueous sodium hydroxide. The remaining volume of gas was just sufficient to completely burn exactly 30 cm³ of the same hydrocarbon.

All gas volumes were measured at room temperature and pressure.

What is the formula of the hydrocarbon?

A C_2H_2 **B** C_2H_3 **C** C_2H_4 **D** C_2H_6

---

13 50.0 cm³ of a 0.10 mol dm^{-3} metallic salt solution was found to react exactly with 25.0 cm³ of 0.10 mol dm^{-3} aqueous sodium sulfite. In this reaction, the sulfite ion is oxidised as follows:

$$SO_3^{2-}(aq) + H_2O(l) \rightarrow SO_4^{2-}(aq) + 2H^+(aq) + 2e^-$$
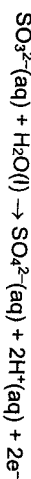
The oxidation state of metal in the salt solution is +3. What is the oxidation state of metal in the product?

A +1 **B** +2 **C** +4 **D** +5

14 Ethyl ethanoate undergoes acid-catalysed hydrolysis where the concentration of acid in the solution remains constant.

$$CH_3CO_2CH_2CH_3 + H_2O \xrightarrow{H^+} CH_3CO_2H + CH_3CH_2OH$$
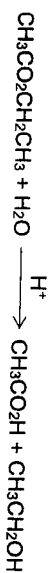
The rate equation is found to be

$$\text{rate} = k\,[CH_3CO_2CH_2CH_3]\,[H^+]$$

In experiment **1**, the half-life was found to be 31 minutes when 0.2 mol dm^{-3} of HCl was reacted with 0.2 mol dm^{-3} of ethyl ethanoate.

In experiment **2**, 0.1 mol dm^{-3} of HCl was reacted with 0.2 mol dm^{-3} of ethyl ethanoate.

How long does it take for the concentration of ethyl ethanoate in experiment **2** to fall to 0.05 mol dm^{-3}?

A 31 min **B** 62 min **C** 93 min **D** 124 min

15 The reaction between NO and H$_2$ is thought to involve the following mechanism:

$2NO = N_2O_2$	(fast)
$N_2O_2 + H_2 \rightarrow N_2O + H_2O$	(slow)
$N_2O + H_2 \rightarrow N_2 + H_2O$	(fast)
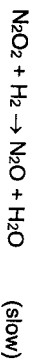
Which of the following conclusions can be drawn from this information?

A N$_2$O acts as a catalyst.

B The overall order of reaction is 3.

C The order of reaction with respect to H$_2$ is 2.

D The rate is independent of the concentration of NO.

16 In a closed system, the reaction between steam and hot iron to form ferroso-ferric oxide is an example of an equilibrium. The reaction is investigated by mixing 3.0 mol of Fe with 2.0 mol of H_2O and allowing the equilibrium to establish.

$$3Fe + 4H_2O \rightleftharpoons Fe_3O_4 + H_2$$

initial moles	3.0	2.0	0	0
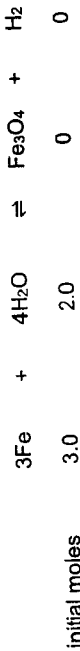
At equilibrium, x mol of H_2O has reacted with Fe.
What are the amounts, in moles, of each of the components of the equilibrium mixture?

	Fe	H_2O	Fe_3O_4	H_2
A	$3.0 - \dfrac{3x}{4}$	$2.0 - \dfrac{x}{4}$	$4x$	$4x$
B	$3.0 - \dfrac{4x}{3}$	$2.0 - x$	$4x$	$4x$
C	$3.0 - \dfrac{3x}{4}$	$2.0 - x$	$\dfrac{x}{4}$	$\dfrac{x}{4}$
D	$3.0 - \dfrac{4x}{3}$	$2.0 - x$	$\dfrac{x}{4}$	$\dfrac{x}{4}$

17 0.1 mol solid sodium sulfide was added to a 1 dm^3 sample containing Ag^+, Cu^{2+} and Sn^{4+} to obtain saturated solutions for all 3 sulfides.
Relevant K_{sp} values are given in the table.

salt	K_{sp}
Ag_2S	6.8×10^{-50}
CuS	6.3×10^{-36}
SnS_2	1.0×10^{-70}

What are the concentrations, in mol dm^{-3}, for each of the cations?

	$[Ag^+(aq)]$	$[Cu^{2+}(aq)]$	$[Sn^{4+}(aq)]$
A	8.25×10^{-49}	6.3×10^{-35}	1.0×10^{-68}
B	8.25×10^{-25}	6.3×10^{-35}	1.0×10^{-68}
C	8.25×10^{-25}	6.3×10^{-37}	1.0×10^{-69}
D	8.25×10^{-49}	6.3×10^{-37}	1.0×10^{-69}

18 The pK_a values of ethanoic, bromoethanoic and fluoroethanoic acids are given in the table.

	CH_3COOH	$CH_2BrCOOH$	CH_2FCOOH
pK_a	4.76	2.86	2.57

Which statements explain these data?

1 Bromine and fluorine are both electronegative and draw electrons away from the O#H bond in the carboxyl group.

2 Bromine and fluorine are both electronegative and stabilise the carboxylate anion.

3 Methyl groups are electron donating and destabilise the carboxylate anion.

A 1 and 2 only   B 1 and 3 only   C 2 and 3 only   D 1, 2 and 3

19 Which conditions are necessary when an electrode potential is measured using a standard hydrogen electrode as the reference electrode?

1 the use of hydrogen gas at 1 bar

2 measurement of e.m.f when the current delivered by the cell is effectively zero

3 a pH of 1.0 for the solution at the hydrogen electrode

A 1 and 2 only **B** 1 and 3 only **C** 2 and 3 only **D** 1, 2 and 3

20 β-carotene is a red-orange pigment found in carrots.
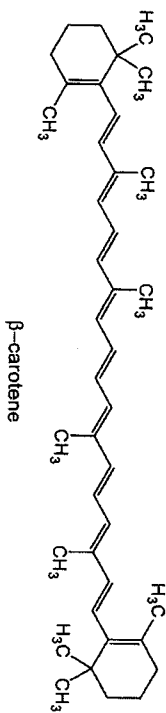

β–carotene

β-carotene reacts with hot, acidified $KMnO_4$.

Which statements are correct?

1 Two organic products are obtained.

2 All organic products react with warm aqueous alkaline iodine.

3 Some of the products are isomeric.

A 2 only **B** 3 only **C** 1 and 2 only **D** 1, 2 and 3

21 Equal amounts of compound **W**, **X**, **Y** and **Z** are heated separately with excess ethanolic silver nitrate for the same duration. Any precipitate formed is filtered, dried and weighed.

What are the possible masses of the precipitates obtained for each halogen-containing compound?

	CH_3CH_2COCl	C_6H_5Cl	$(CH_3)_3CCl$	$(CH_3)_3CBr$
	W	X	Y	Z
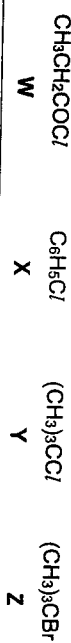
|	mass of precipitate/ g			
	W	**X**	**Y**	**Z**
A	1.434	0	1.256	1.388
B	1.434	0	1.256	1.723
C	1.723	0	1.434	1.256
D	1.434	1.434	1.434	1.878

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22 Which are the products formed when compound **P** reacts with the following reducing agents?
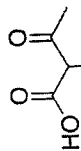
compound **P**

H₂, Ni, heat	LiAlH₄ in dry ether
A	
B	
C	
D	

23 Which statement is true about the reaction between propanone and hydrogen cyanide?

A The sp² hybridised carbon is electrophilic and accepts a pair of electrons.

B The π bond in the carbon-oxygen bond is weak and undergoes homolytic fission.

C All carbon atoms in the product are sp³ hybridised.

D Nucleophilic attack on the trigonal planar carbon centre forms a racemic mixture.

24 Estradiol is an estrogen steroid hormone and daidzein is a natural isoflavone with estrogen-like activity.
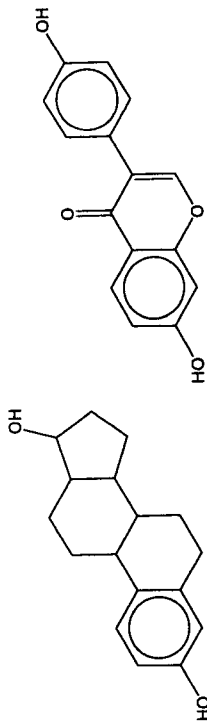

estradiol

daidzein

You may assume that the C≡O≡C bond in daidzein is unreactive.

Which reagent **cannot** be used as a distinguishing test?

A acidified potassium dichromate(VI), heat

B phosphorous pentachloride

C 2,4-dinitrophenylhydrazine

D aqueous bromine

25 Which statements best describe the reaction mechanism involved in the conversion of chloroethane to ethanol?

1 The reaction mechanism involves a carbocation.

2 The rate determining step involves both the chloroethane and the nucleophile.

3 The reaction mechanism involves heterolytic fission of the C≡Cl bond.

4 The activation energy of the first step of the mechanism is greater than that of the second step.

A 2 only   **B** 2 and 3 only   **C** 1, 3 and 4 only   **D** 2, 3 and 4 only

26   Compound **Y** is formed from the partial hydrolysis of a biomolecule.

CH(CH₃)OH

H₂NCHCONHCHCONHCHCONHCHCOOH

CH₂COOH   CH₂   CH₂CONH₂

OH
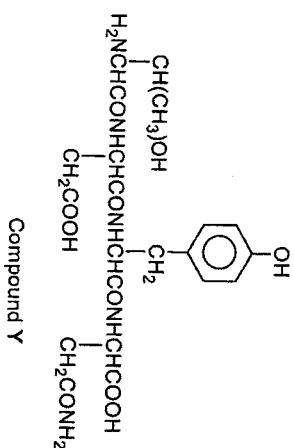
Compound **Y**

Which of the following statements is **incorrect**?

A   Two moles of Br₂ are needed for complete reaction with one mole of compound **Y**.

B   Two moles of Na₂CO₃ are needed for complete reaction with one mole of compound **Y**.

C   Prolonged heating of compound **Y** with dilute NaOH liberates an alkaline gas.

D   Prolonged heating of compound **Y** with dilute NaOH produces three carbon-containing products.

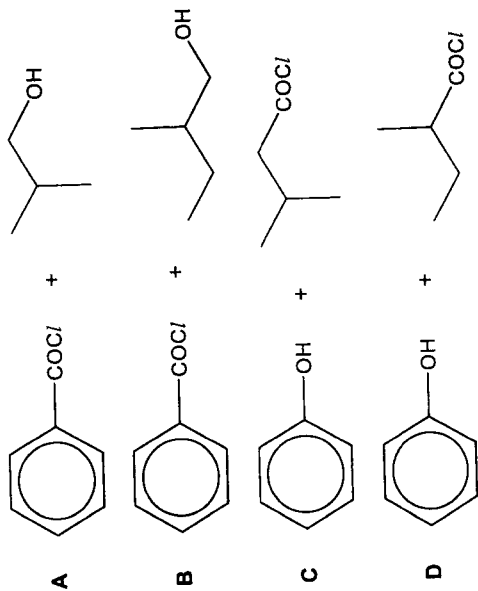27   The set-up below is commonly used in the synthesis of organic compounds in the laboratory.
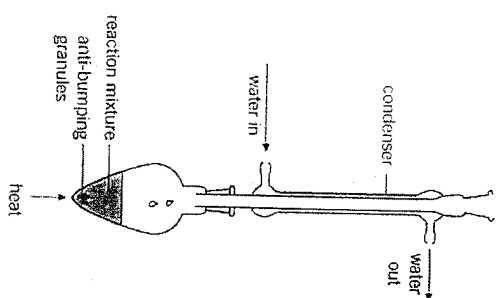
Which reaction requires the above set-up for synthesis?

A   CH₃CH₂NH₂ + CH₃COCl → CH₃CONHCH₂CH₃ + HCl

B   CH₃COCl + H₂O → CH₃COOH + HCl

C   CH₃CH₂OH + [O] → CH₃CHO + H₂O

D   CH₃CONH₂ + NaOH → CH₃COONa + NH₃

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2022 Preliminary Examination

9729/01/PRELIMS/22

[Turn over

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BP~273

28 Which reaction will produce phenyl 2-methylbutanoate under suitable conditions?

A [structure: benzene-COCl + OH-CH2-CH(CH3)-]

B [structure: benzene-COCl + CH2OH-CH2-CH(CH3)-]

C [structure: benzene-OH + ClOC-CH2-CH(CH3)-]

D [structure: benzene-OH + ClOC-CH(CH2CH3)-]

29 When drops of $NH_3(aq)$ are added to $Cu(NO_3)_2(aq)$, a pale blue precipitate is formed. This precipitate dissolves when an excess of $NH_3(aq)$ is added, giving a dark blue solution.

Which of the following process does **not** occur?

A ligand exchange

B acid-base reaction

C reduction of Cu^{2+} ions

D formation of a complex ion

30 Iron, a transition metal, is used in the Haber process. Which of the following statements best explains the role of iron in this application?

A Iron has partially filled 3d orbitals for adsorption of reactant molecules.

B Iron exhibits variable oxidation states in its compounds as 3d and 4s electrons have similar energies.

C Iron has a very high melting point as both 3d and 4s electrons contribute to forming strong metallic bonds.

D Iron forms coloured ions due to absorption of energy in the visible light region to promote an electron from a lower energy to a higher energy 3d orbital.

- End of paper -