BP~613

HWA CHONG INSTITUTION
2025 C2 H2 CHEMISTRY PRELIMINARY EXAMINATION
MARK SCHEME / SUGGESTED SOLUTIONS

Paper 1

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

Comments

1 **D** The largest difference in consecutive ionisation energies occurs between the 5th and 6th ionisation energies, implying that the 6th electron is removed from an inner quantum shell and element **X** has 5 valence electrons. Since element **X** belongs to Group 15, it is likely to form a chloride of the formula **XCl_5**.

2 **D** Isotopes have the **same number of protons** but **different number of neutrons**.
The number of protons can be determined from the *number of electrons* and *charge*.
Once the number of protons are determined, the number of neutrons can be found from the nucleon number.
E.g., in **A**, H has 10 electrons and a charge of −2, so H has 8 protons. Thus, H has 10 neutrons.

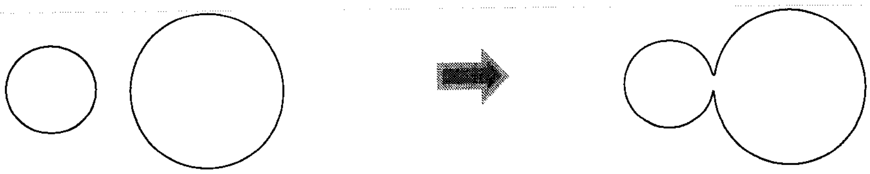
	G		H	
	no. of protons	no. of neutrons	no. of protons	no. of neutrons
A	8	10	8	10
B	18	19	16	18
C	16	20	18	20
D	20	22	20	20

In **D**, G and H have the same number of protons (20) but different number of neutrons (22 and 20).
Note that **A** is incorrect as G and H have the same number of protons and neutrons.

3 **D** The shape of a species depends on the **number of lone pairs and bond pairs of electrons** around the central atom. Refer to Topic 2 Chemical Bonding Sec. 6.1.

A	$AlCl_3$	PCl_3
	3 b.p. and 0 l.p. – trigonal planar	3 b.p. and 1 l.p. – trigonal pyramidal
B	BF_3	NH_3
	3 b.p. and 0 l.p. – trigonal planar	3 b.p. and 1 l.p. – trigonal pyramidal
C	SF_4	XeF_4
	4 b.p. and 1 l.p. – see saw (expanded octet)	4 b.p. and 2 l.p. – square pyramidal (expanded octet)
D	PH_4^+	BF_4^-
	4 b.p. and 0 l.p. – tetrahedral	4 b.p. and 0 l.p. – tetrahedral

4 **C**



n_s $V_s = 10\ m^3$ $P_s = 50\ kPa$

n_b $V_b = 30\ m^3$ $P_b = 120\ kPa$

$n_t = n_s + n_b$ $V_t = V_s + V_b$ $P_t = ??\ kPa$

Using $n_t = n_s + n_b$

Since T is constant, $P_tV_t = P_sV_s + P_bV_b$

After connection: $V_t = V_s + V_b$

$$P_t = \frac{(50)(10) + (120)(30)}{(10+30)} = 102.5\ kPa = 103\ kPa$$

5 **A** This question tests the definition of relative masses found in Topic 1 & 4.

Option B is wrong as the relative atomic masses must take into account all the isotopes of the element, hence the term 'average mass' must be used.

Option C is wrong as the reference should be ^{12}C & not ^{1}H.

Option D is wrong as the reference should be to 1/12 the mass of one atom of ^{12}C.

6 **B** Always check if the sum of the abundances of the isotopes add up to 100. In the case, they add up to 101.32.

$$Ar\ (Ge) = \left(\frac{19.01}{101.32}\times70\right) + \left(\frac{24.96}{101.32}\times72\right) + \left(\frac{7.76}{101.32}\times73\right) + \left(\frac{41.0}{101.32}\times74\right) + \left(\frac{8.59}{101.32}\times76\right) = 72.8$$

7 **A** Use the equation method to obtain the answer:

- Flip the first equation to get the MgO on the right side like in the combustion equation. Remember to flip the sign on its ΔH value.
- Half the third equation to ensure that the H_2 from the second equation and this third equation cancels off, and you get ½ O_2 as required in the combustion equation. Remember to halve its ΔH value.
- Add up all the equations to check that you get the combustion equation as given. And then add up all ΔH values to get the answer.

$MgCl_2(aq) + H_2O(l) \rightarrow MgO(s) + 2HCl(aq)$ +89
$Mg(s) + 2HCl(aq) \rightarrow MgCl_2(aq) + H_2(g)$ – 435
$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l)$ – 572 x ½ = – 286

$Mg(s) + \frac{1}{2}O_2(g) \rightarrow MgO(s)$ – 632 kJ mol^{-1}

8 **A** Option 1: ΔS increases as increasing the temperature at a fixed pressure increases the volume of the gas & increases the average kinetic energy of the gas particles and thus results in more ways to distribute the particles and energy.

Option 2: ΔS increases as doubling the number of moles of non-interacting gas particles at a fixed pressure increases the volume of the gas results in more ways to distribute the particles and energy.

Option 3: ΔS increases as doubling the number of moles of gas particles at a fixed pressure increases the volume of the gas results in more ways to distribute the particles and energy.

Option4: ΔS decreases as the number of moles of gas particles at a fixed pressure drops from 1 to 0 on the right-hand side of the equation.

9 **B** The rate equation can be written by inspecting the chemical equation of the slow step in the reaction mechanism. Hence it should look like: rate = $k[N_2O_2][H_2]$.

Rate equations should contain only reactants or product terms but not intermediates. In this case, N_2O_2 is an intermediate. To replace it, we see that N_2O_2 is related to a reactant NO by the reversible reaction which can be expressed in the form of the chemical equilibrium constant.

Thus $K=\frac{[N_2O_2]}{[NO]^2}$; rearranging gives $[N_2O_2] = K[NO]^2$.

Substituting $[N_2O_2]$ in rate = $k[N_2O_2][H_2]$ gives rate = $kK[NO]^2\,[H_2]$ or rate = $k'[NO]^2\,[H_2]$.

The units of the rate constant k' can be worked out as follows:

rate = $k'[NO]^2\,[H_2]$

$\text{mol dm}^{-3}\ \text{s}^{-1} = k' \times (\text{mol dm}^{-3})^2 \times (\text{mol dm}^{-3})$
Simplifying gives $k' = \text{mol}^{-2}\,\text{dm}^6\,\text{s}^{-1}$

10 **A** The area under the curve represent the total number of molecules. Thus this is represented by P + R. Since only the T is changed, the total number of molecule, P + R does not change. Thus the expression $\frac{R}{P+R}$ gives the fraction of molecules that have energy greater than the activation energy of the lower temperature. Note that the steeper curve represents the lower temperature while the shallower curve is for the higher temperature.

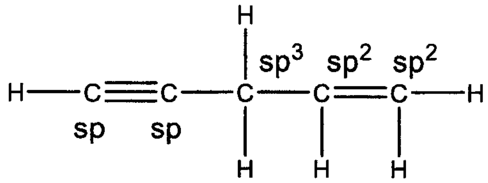
11 **B** Option A is wrong as the correct temperature is 450 °C.

Option C is wrong as the iron acts as an catalyst which speeds up the reaction but does not affect the yield.

Option D is wrong as removing NH_3 shifts the position of the equilibrium to the right but does not affect the rate of reaction.

12	D	$MnO_4^-(aq) + 8\,H^+(aq) + 5\,e^- \rightarrow Mn^{2+}(aq) + 4\,H_2O(l)$ $SO_2(g) + 2\,H_2O(l) \rightarrow SO_4^{2-}(aq) + 4\,H^+(aq) + 2\,e^-$ Obtain the overall equation through multiplying the first half-equation by 2 and the second half-equation by 5 in order to eliminate the electrons: $2MnO_4^- + 5SO_2 + 2H_2O \rightarrow 2Mn^{2+} + 5SO_4^{2-} + 4H^+$ Notice that there is a net production of H^+ so $[H^+]$ increases as the reaction proceeds. Since $pH = -lg\,[H^+]$, pH decreases over time.
13	D	Titration Curve 1 = strong acid-weak base curve (equivalence pH is acidic) Titration Curve 2 = weak acid-weak base curve (no vertical portion in the curve) Option A is wrong as there are no suitable indicators for weak acid-weak base titrations. Option B is wrong as give above. Option C is wrong as Titration Curve 1 involves a strong acid as depicted by the flat smooth curve at pH between 0 & 2. A weak acid will give a sharper rise in pH before flattening out shortly after and then rising sharply again near the equivalence point (i.e. a buffer region).
14	C	The decomposition of H_2O_2 is usually written as $2H_2O_2 \rightarrow 2H_2O + O_2$. In basic medium, it may be written as $2HO_2^- \rightarrow 2OH^- + O_2$, where a proton is lost from both H_2O_2 & H_2O. Re-writing it to make clear that two ions of HO_2^- are reacting with each other in the decomposition process: **$HO_2^- + HO_2^- \rightarrow 2OH^- + O_2$**. Thus $HO_2^- \rightarrow 2OH^-$ (reduction) ➔ $HO_2^- + H_2O + 2e \rightarrow 3OH^-$ $E^\ominus = +0.88$ V And $HO_2^- \rightarrow O_2$ (oxidation) ➔ $HO_2^- + OH^- \rightarrow O_2 + H_2O + 2e$ $E^\ominus = -0.08$ V Thus $E_{cell} = +0.96$ V The semi-permeable membrane allows ions to pass through to maintain electrical neutrality in both cells just like a salt bridge does.
15	B	The % composition of the alloy is a distractor and is not needed in the calculations. The total mass of metal deposited as the cathode represents the metal that was reduced. Use of the data booklet shows that both Cu & Ni may be both oxidized at the anode while the reduction potential for Cu^{2+} is positive and favorable while that for Ni^{2+} is negative and unfavorable, thus only Cu^{2+} is reduced at the cathode. Refer to the purification of copper in your notes for a similar analysis. Mass of Cu accumulated = 0.88 g No. of moles of Cu accumulated = 0.88 ÷ 63.5 = 0.013858 No. of moles of electrons passed through = 2 x 0.013858 = 0.027716 $Q = It = nF$ $0.50 \times 1.5 \times 60 \times 60 = 0.027716 \times F$ $F = 97416.654$ $F = Le$ $97416.654 = L \times 1.6 \times 10^{-19}$ $L = 6.088 \times 10^{23}$ or 6.09×10^{23}

16 **C**



Option A is correct as π bonds may be formed only side-on overlap of p orbitals. These bonds are found in the C≡C and C=C bonds.

Option B is correct as the H uses its 1s orbital to form the H–C bond in H–C≡

Option C is wrong as the sp C is bonded to a sp^3 C in ≡C–C

Option D is correct as the sp^3 C is bonded to a sp^2 C in C–C=

17 **B** It is helpful to refer to the reaction mechanisms in the notes.

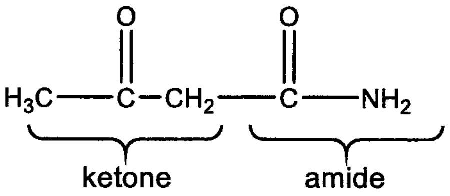
Option 1 is correct as the Cl_2 acts as the electrophile in the first step of the electrophilic addition reaction mechanism.

Option 2 is wrong as the Cl_2 acts as the electrophile while H_2O acts as the nucleophile in the second step of the electrophilic addition reaction mechanism.

Option 3 is correct as the Cl_2 undergoes homolytic cleavage to form $Cl\bullet$ radicals in uv light in the first step of the free radical substitution reaction mechanism.

18 **A**

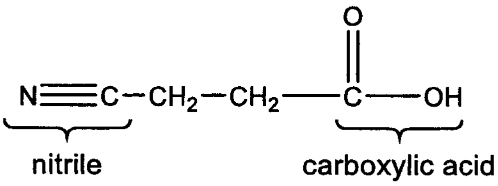
Option 1



$$\underbrace{H_3C-\overset{\overset{\displaystyle O}{\|}}{C}-CH_2}_{\text{ketone}}-\underbrace{\overset{\overset{\displaystyle O}{\|}}{C}-NH_2}_{\text{amide}}$$

The molecular formula is $C_4H_7O_2N$.

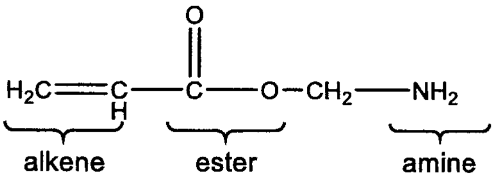
Option 2



$$\underbrace{N\equiv C}_{\text{nitrile}}-CH_2-CH_2-\underbrace{\overset{\overset{\displaystyle O}{\|}}{C}-OH}_{\text{carboxylic acid}}$$

The molecular formula is $C_4H_5O_2N$.

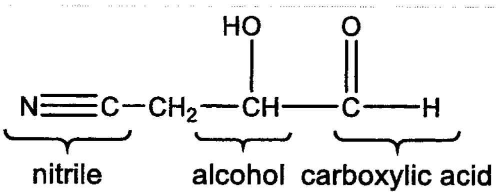
Option 3



$$\underbrace{H_2C=\underset{H}{C}}_{\text{alkene}}-\underbrace{\overset{\overset{\displaystyle O}{\|}}{C}-O}_{\text{ester}}-CH_2-\underbrace{NH_2}_{\text{amine}}$$

The molecular formula is $C_4H_7O_2N$.

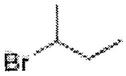
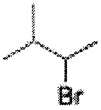
Option 4



$$\underbrace{N\equiv C}_{\text{nitrile}}-CH_2-\underbrace{\overset{\overset{\displaystyle HO}{|}}{CH}}_{\text{alcohol}}-\underbrace{\overset{\overset{\displaystyle O}{\|}}{C}-H}_{\text{carboxylic acid}}$$

The molecular formula is $C_4H_5O_2N$.

19 **C**

mono-brominated product				
no. of H atoms which can be substituted (probability)	6	3	2	1

20 **A** Recall what a catalytic converter does. A catalytic converter in cars reduces harmful emissions and its overall aim is to reduce CO, hydrocarbons, and oxides of nitrogen.

Option A is wrong as it shows CO_2 being reduced to CO, while the converter is meant to oxidise CO to CO_2.

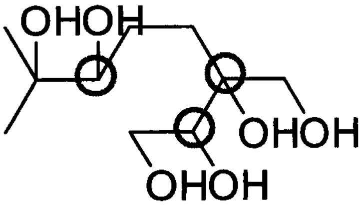
Option B is correct as CO is oxidized, and NO is reduced.

Option C is correct as it shows the complete combustion of hydrocarbons.

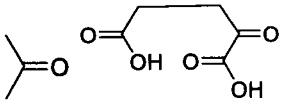
Option D is correct as hydrocarbons react with NO, reducing NO to N_2.

21 **A**

A The mild oxidation product is shown below with the chiral centres circled.

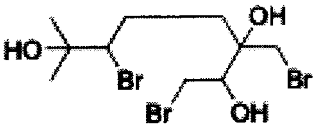


B Only two oxidative cleavage organic products:



CO_2 is <u>not</u> an organic product.

C Alkene C=C undergoes electrophilic addition with Br_2 or Cl_2 (halogens), and would react with aqueous Br_2 in a similar manner.

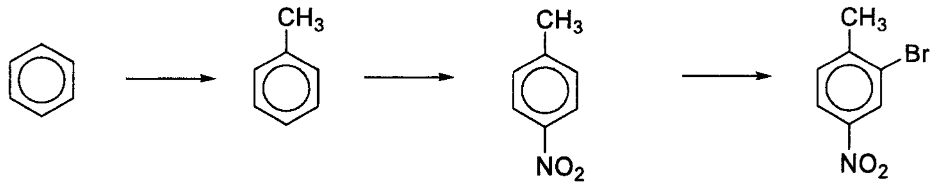


Major product contains one secondary alcohol and two tertiary alcohol functional groups.

D Hot ethanolic sodium hydroxide causes an elimination reaction, in which a halogenoalkane loses HX to form an alkene. Some possible products (which doesn't match the question context):

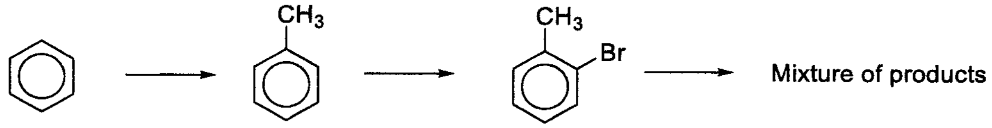
22 **A**

A



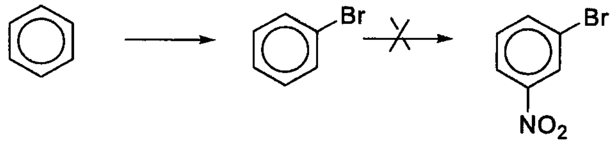
In the nitration step, $-CH_3$ directs $-NO_2$ to the 4-position since $-CH_3$ is 2,4-directing. In the bromination step, both methyl and nitro substituents direct the bromo group to the desired position (i.e. the directing effects mutually reinforce one another).

B



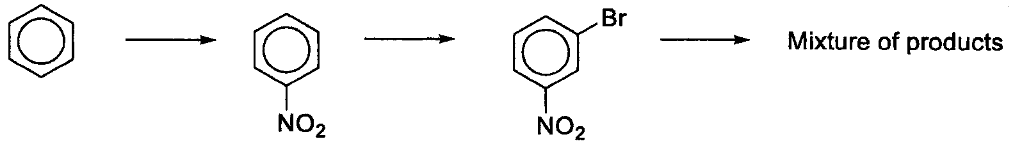
The methyl and bromo substituents are both 2,4-directing and hence in the nitration step, they direct the nitro group to different positions (i.e. the directing effects do not mutually reinforce one another). Thus, a mixture of products will be formed resulting in very low yield of the desired product.

C



The nitration step will not produce the desired product as the major product since bromine is 2,4-directing yet we need $-NO_2$ to be directed to the 3-position relative to Br.

D



The nitro substituent is 3-directing and the bromo substituent is 2,4-directing and hence in the alkylation step, they direct the methyl group to different positions (i.e. the directing effects do not mutually reinforce one another). Thus, a mixture of products will be formed resulting in very low yield of the desired product.

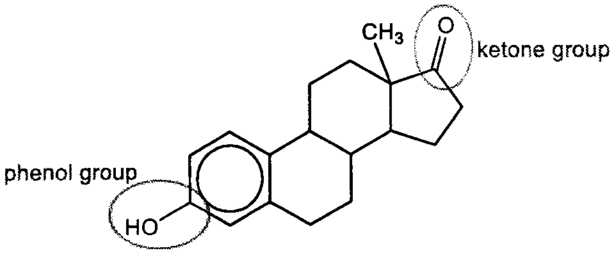
23 **B** Bromoalkanes and acyl bromides undergo hydrolysis by nucleophilic substitution, in which the C–Br bond breaks heterolytically to release Br^- ions. (Bromoarenes do not hydrolyse because the C–Br bond is strengthened by delocalisation of lone pair on Br into the benzene ring.) The Br^- ions formed can be identified by silver nitrate, which produces a cream precipitate of AgBr.

K does not give any ppt, L gives 0.2 mol of ppt and M gives 0.3 mol of ppt.

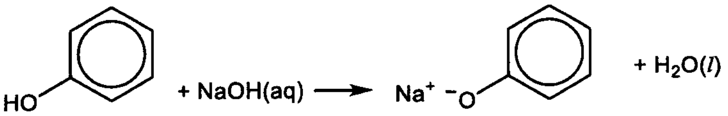
24 **D** V W X all react with Na to give H_2 ⇒ V W X contain alcohol &/or carboxylic acid &/or phenol group. ∴ A is **incorrect** ∵ the 2nd compound doesn't give such a reaction.

Only 1 of V W X reacts with Fehling's reagent. ∴ only one of them has aliphatic aldehyde group (i.e. an aldehyde but not benzaldehyde).
B is **incorrect** ∵ the 2nd and 3rd compounds have aliphatic aldehyde groups.
C is **incorrect** ∵ the 1st and 3rd compounds have aliphatic aldehyde groups.
D is **correct**, only the 2nd compound has aliphatic aldehyde group.

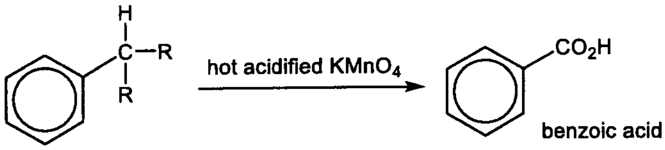
25 **D** The compound (oestrone) has a ketone group and a phenol group.



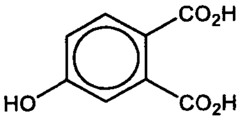
A is **correct**. The ketone group gives orange ppt with 2,4-DNPH.
B is **correct**. The phenol group gives an (ionic) salt with aq. NaOH, reaction illustrated below using phenol.



C is **correct**. Compounds with the following structure (e.g. methylbenzene) react with hot acidified $KMnO_4$ to give benzoic acid (side-chain oxidation for alkylbenzenes).

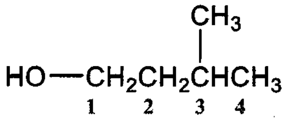


For oestrone (study its "side-chain" carefully), it indeed gives a dicarboxylic acid:



D is **incorrect**. Only alcohols and carboxylic acids give white (HC*l*) fumes with PC*l*$_5$.

26 **C** This question asks about making the ester, 3-methylbutyl ethanoate.
The "3-methylbutyl" part of this ester (look at the first part of its name) is derived from the alcohol: 3-methylbutan-1-ol:



$$HO{-}\underset{1}{CH_2}\underset{2}{CH_2}\underset{3}{\overset{\overset{\displaystyle CH_3}{|}}{C}H}\underset{4}{CH_3}$$

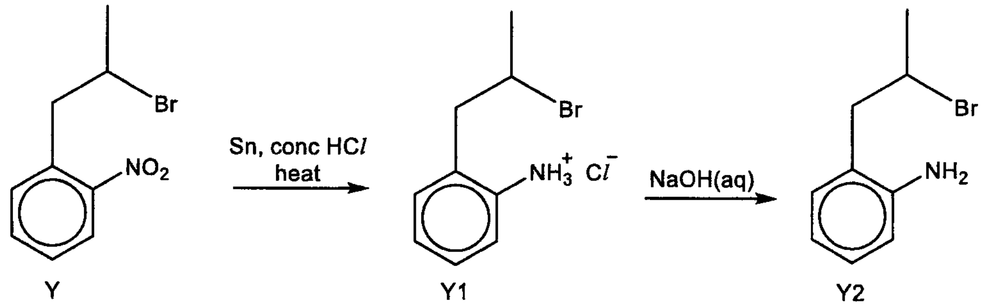
To make an ester of an alcohol, there are two methods:

$$\text{carboxylic acid} + \text{alcohol} \ \overset{\text{conc. } H_2SO_4 \text{ catalyst}}{\overset{\text{heat}}{\rightleftharpoons}} \ \text{ester} + H_2O$$

$$\text{acyl chloride} + \text{alcohol} \rightarrow \text{ester} + HCl$$

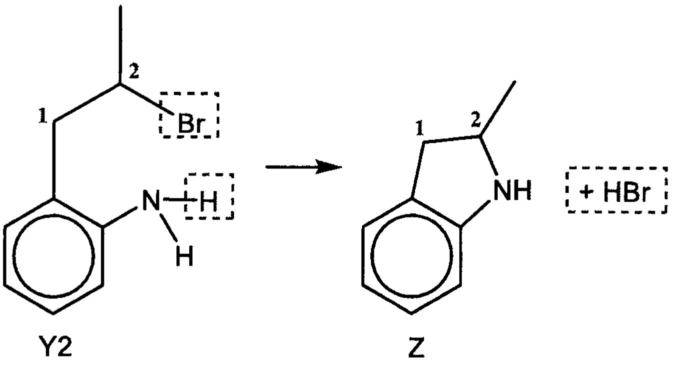
The "ethanoate" part of this ester (look at the last part of its name) is derived from ethanoic acid, CH_3CO_2H, or ethanoyl chloride, CH_3COCl. $\therefore$ A and B are **incorrect**.
Between C vs. D, C has the correct alcohol. (The alcohol in D is 2-methylbutan-1-ol.)

27 **A** The reaction described in the question should give compound Y2.



However, for the four given options, one H "disappeared" from the NH_2 group (in Y2), Br also "disappeared", and a new ring is formed.

We therefore deduce that the NH_2 and Br (in Y2) must have reacted together (while the mixture is still hot). We then deduce that this bromoalkane group (in Y2) has undergone nucleophilic substitution with the NH_2 group (in Y2) to give compound Z — similar to the reaction between a halogenoalkane and NH_3.



28 **B**

A Statement is **in**correct. Melting point of group 2 elements generally **de**creases down the group as less energy is required to overcome weaker metallic bonding between metal cations and sea of delocalised electrons. While the number of valence electrons contributed per metal atom remains as 2 and the charge of each metal cation remains as +2, the ionic radius increases down group 2 hence charge density of cation decreases resulting in weaker metallic bonding.

B Statement is correct. Down group 2 from Mg to Ba, reduction potential becomes more negative, increases tendency for group 2 elements to be oxidised, reducing power of group 2 elements increases as group 2 elements have higher tendency to reduce others when themselves undergo oxidation. From Data Booklet:

	E° / V
$Mg^{2+} + 2e^- \rightleftharpoons Mg$	−2.38
$Ca^{2+} + 2e^- \rightleftharpoons Ca$	−2.87
$Ba^{2+} + 2e^- \rightleftharpoons Ba$	−2.90

C Statement is **in**correct. Volatility of group 17 elements **de**creases (becomes less volatile) down the group as more energy is needed to overcome stronger dispersion forces between halogen molecules as size of electron cloud increases.

D Statement is **in**correct. Down group 17 from F_2 to I_2, reduction potential becomes less positive, decreases tendency for group 17 elements to be reduced, oxidising power of group 17 elements **de**creases as group 17 elements have lower tendency to oxidise others when themselves undergo reduction. From Data Booklet:

	E° / V
$F_2 + 2e^- \rightleftharpoons 2F^-$	+2.87
$Cl_2 + 2e^- \rightleftharpoons 2Cl^-$	+1.36
$Br_2 + 2e^- \rightleftharpoons 2Br^-$	+1.07
$I_2 + 2e^- \rightleftharpoons 2I^-$	+0.54

29 **C**

Students are expected to know that the density of vanadium is higher that of calcium. Density is defined as mass per unit volume. Both metals are in the same period.

1 Statement is correct. Vanadium (50.9) has a higher relative atomic mass than calcium (40.1), with heavier atoms per unit volume, the density of vanadium is higher.

2 Statement is **in**correct. A stronger shielding effect would result in weaker effective nuclear charge and larger atomic radius. Vanadium has a smaller atomic radius and a higher relative atomic mass compared to calcium which enables more and heavier atoms per unit volume. Hence, the density of vanadium is higher that of calcium.

3 Statement is correct. Vanadium (0.135 nm) has a smaller atomic radius compared to calcium (0.197 nm) because the outer shell electrons of vanadium experience greater attraction to the nucleus. The smaller atomic radius enables more efficient close packing of vanadium atoms, resulting in a greater number of atoms per unit volume. Hence, the density of vanadium is higher that of calcium.

30 **B**

In reactant platinum(IV) chloride and the product platinum(IV) compound, each platinum has an oxidation number of +4.

Since the central platinum ion in X^{2+} has an oxidation state of +4, there must be two Cl^- ions acting as ligands, so that the overall charge on the complex cation can be +2. The other four ligands, to make up the co-ordination number of 6, must therefore be ammonia that has no charge. Hence complex cation X^{2+} is $[Pt(NH_3)_4Cl_2]^{2+}$, containing a total of 4 ammonia molecules as ligands.

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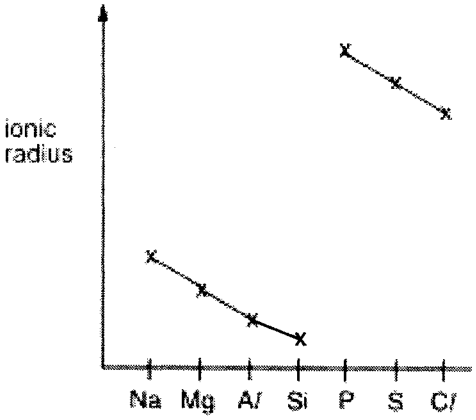
2025 C2 H2 CHEMISTRY PRELIMINARY EXAMINATION
MARK SCHEME

Paper 2

1 (a)



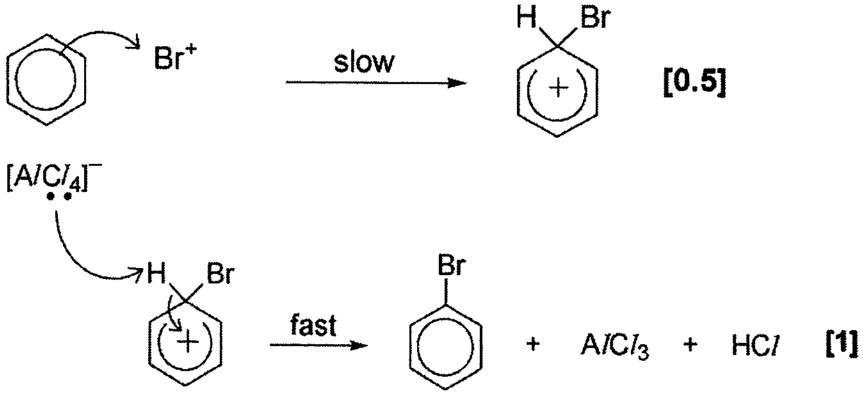
Na^+, Mg^{2+}, Al^{3+} and Si^{4+} are isoelectronic (or have the same number of electrons) and P^{3-}, S^{2-} and Cl^- are isoelectronic, hence **shielding effect** is the **same**. Across each series, number of protons and thus **nuclear charge** increases. **[1]**
Thus, **effective nuclear charge** increases, attraction of the nucleus on the **valence/outermost** electrons become stronger (*or* outermost electrons pulled closer to the nucleus), and ionic radius decreases.
There is a sharp increase in radius from Si^{4+} to P^{3-}, as anions have one more **quantum/electron shell** than cations. **[1]**

(b) $P_4O_{10(s)} + 6H_2O_{(l)} \rightarrow 4H_3PO_{4(aq)}$ **[0.5]**
pH of resulting mixture is 2 (*accept 1 – 3*). **[0.5]**

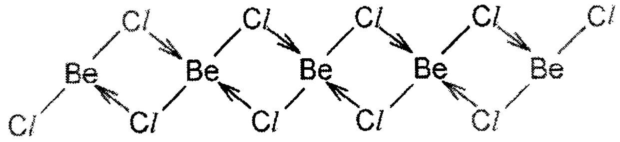
(c) Al_2O_3 is amphoteric. **[0.5]**
$Al_2O_{3\,(s)} + 3H_2SO_{4(aq)} \rightarrow Al_2(SO_4)_{3(aq)} + 3H_2O_{(l)}$ **[0.5]**
$Al_2O_{3\,(s)} + 2NaOH_{(aq)} + 3H_2O_{(l)} \rightarrow 2Na[Al(OH)_4]_{(aq)}$ **[1]**

(d) (i) A Lewis acid is a species that accepts an **electron pair**. **[1]**

(ii) $AlCl_3 + BrCl \longrightarrow Br^+ + [AlCl_4]^-$ **[0.5]**



(iii)



[1]

2 (a) (i) The heat evolved when 1 mole of water is formed from an acid-base reaction at 298 K and 1 bar. **[1]**

(ii) $q = mc\Delta T = [(25+45) \times 1.00](4.18)(30.5 - 27.8) = 733.6$ J **[1]**

no. of moles of H_2O = no. of moles of LiOH (limiting reagent)
= 25/1000 × 0.5 = 0.0125 mol

$$\Delta H^\ominus_{neut} = -\frac{q}{n_{H2O}} = -\frac{733.6}{0.0125} = -58688 \text{ J mol}^{-1} = \mathbf{-58.7} \text{ kJ mol}^{-1} \text{ (3 s.f.)}$$ **[1]**

(b) (i)

$$\begin{tikzcd}
2HCl(aq) + 2LiOH(s) + CO_2(g) \arrow[r, "\Delta H^\ominus_2"] \arrow[d, "2(-21)"'] & Li_2CO_3(s) + H_2O(l) + 2HCl(aq) \arrow[d, "-29.0"] \\
2HCl(aq) + 2Li^+(aq) + 2OH^-(aq) + CO_2(g) \arrow[r, "2(-58.7)"'] & 2LiCl(aq) + CO_2(g) + 2H_2O(l)
\end{tikzcd}$$

[2]

$\Delta H^\ominus_2 = 2(-21) + 2(-58.7) + 29.0 = -130.4$ kJ mol^{-1} = -130 kJ mol^{-1} (3 s.f.) **[1]**

If used suggested value in question ($\Delta H^\ominus_{neut} = -48.2$ kJ mol^{-1})
$\Delta H^\ominus_2 = 2(-21) + 2(-48.2) + 29.0 = -109.4 = -109$ kJ mol^{-1} **[1]**

(ii) Since the no. of moles of gas decreases from 1 to 0 in this reaction, the entropy change of reaction is negative. **[1]**

$\Delta G = \Delta H - T\Delta S$
When temperature increases, $-T\Delta S$ becomes more positive. Since ΔH is negative, ΔG becomes less negative, and reaction is less spontaneous. **[1]**

(iii) Volume of CO_2 exhaled per crewmember per day
= 25 × 15 × 60 × 24 = 540000 cm^3/CM-d = 540 dm^3/CM-d **[1]**

Mass of CO_2 exhaled = 1.98 × 540 = 1069.2 g/CM-d = **1.07** kg/CM-d **[1]**

(iv) No. of moles of CO_2 /CM-d = 1069.2 / (12+16+16) = 24.3 mol
No. of moles of LiOH/ CM-d = 24.3 × **2** = **48.6 mol [0.5]**
Mass of LiOH /CM-d = 48.6 × (6.9+16+1) = 1161.54 g = 1.16 kg **[0.5]**
Mass of LiOH brought on trip = 250 × 5.2 = 1300 kg **[0.5]**
No. of days = 1300 / (**8** × 1.16) =139.9 = 139 days **[0.5]**

Alternative method:
Total no. of moles of LiOH supplied = 5.2 × 1000 (6.9+16+1) = 54393 mol
Total no. of moles of CO_2 can be absorbed = 54393/2 = 27196.5 mol
Total mass of CO_2 that can be absorbed = 27196.2 × (12+16+16) = 1196600 g
= 1196.6 kg
Max no. of days = 1196.6/(1.07 × 8) = 139.8 = 139 days

(v) For the same number of moles, the mass of LiOH is smallest hence it is easier to transport in a space craft. **[1]**

(c) **(i)** $Li_2CO_3(s) \rightarrow Li_2O(s) + CO_2(g)$ **[1]**

Li^+ is a cation with small ionic radius and high charge density **[1]**, it polarises the electron cloud of carbonate to a large extent, hence weakening the C-O bonds **[1]**. Hence less energy is needed to break the C-O bonds and it decomposes easily when heated.

(ii)

ion	Li^+	Na^+	Mg^{2+}	Ca^{2+}
ionic radius / nm	0.06	0.095	0.065	0.099
$\frac{q^+}{r^+}$	16.7	10.5	30.7	20.2

Marking points **[2]**

- quote **ionic** radius for all 4 ions
- suggest a temperature **between 635 and 851** (excluding the two numbers)
- correct explanation in terms of charges and ionic radii: calculate $\frac{q^+}{r^+}$ and conclude that charge density of Li^+ is between those of Na^+ and Ca^{2+}

3 **(a)** **(i)** 50%. The optically inactive mixture of **P** contains equal proportions of two enantiomers **[0.5]**. Enzyme amidase has specific activity and only one enantiomer can bind to the active sites of the enzyme **[0.5]**.

(ii) Amidase is a biological catalyst which is regenerated during the reaction / remains chemically unchanged / not used up / lower E_a **[0.5]**. Hence, its concentration stays constant **[0.5]**.

H_2O is a solvent and is present in large excess **[0.5]**. Hence, its concentration can be treated as a constant (or differs very slightly or pseudo-zeroth order) **[0.5]**.

(iii) **At lower concentrations of P**

From experiments 1 and 2 (*accept* if compare expt 2 and 3), when [P] doubles from 0.50 to 1.00 mmol dm^{-3}, the initial rate doubles from 1.25 to 2.50 × 10^{-4} mol dm^{-3} s^{-1}.**[1]** Reaction is first order with respect to [P]. **[0.5]**

At higher concentrations of P

From experiments 5 to 6, when [P] doubles from 8.00 to 16.00 mmol dm^{-3}, the initial rate remains constant at 8.00 × 10^{-4} mol dm^{-3} s^{-1}.**[1]** Reaction is zeroth order with respect to [P]. **[0.5]**

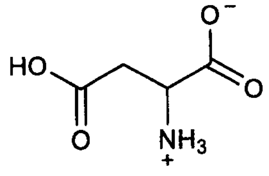
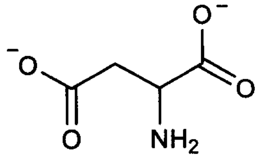
or

From experiments 4 to 5, when [P] doubles from 4.00 to 8.00 mmol dm^{-3}, the initial rate remains almost constant at 7.50 × 10^{-4} mol dm^{-3} s^{-1} (*accept* increases slightly). Reaction is zeroth order with respect to [P].

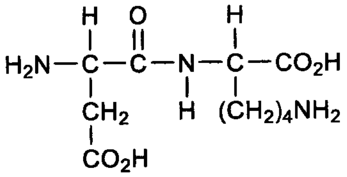
(iii) At low [P], rate of reaction increases **proportionally** with increasing [P] (or follow first order kinetics) **[0.5]** as [amidase] is greater than [P] / [P] is the limiting factor (*accept* there are many active sites available on the enzyme amidase / binds->reaction->released / form enzyme-substrate complex). **[0.5]**

At high **[P]**, rate of reaction remains constant with increasing **[P]** (or follow zeroth order kinetics) **[0.5]** as the active sites on the enzyme amidase are saturated (*accept* all active sites are filled) with **P** molecules. **[0.5]**

(b)

 **[1]** pH 3	 **[1]** pH 14

(c)

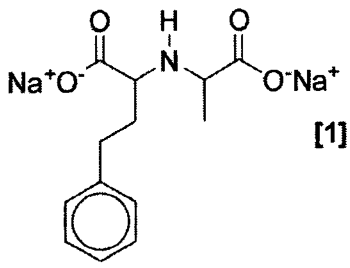


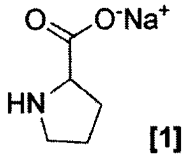
$$H_2N-\underset{\underset{\displaystyle CO_2H}{|}}{\underset{CH_2}{\underset{|}{\overset{\overset{H}{|}}{C}}}}-\overset{\overset{O}{||}}{C}-\underset{\underset{H}{|}}{N}-\underset{\underset{(CH_2)_4NH_2}{|}}{\overset{\overset{H}{|}}{C}}-CO_2H$$

[1]

(d)

 **[1]**

 **[1]**

 **[1]**

4 (a) (i) disproportionation **[1]**

(ii) **3** Cl_2 + **6** NaOH → **5** NaCl + **1** $NaClO_3$ + **3** H_2O **[1]**

(b) (i) $E^\ominus(Cl_2/Cl^-) = +1.36$ V, $E^\ominus(O_2/H_2O) = +1.23$ V **[1]**

Since $E^\ominus(O_2/H_2O)$ is less positive than $E^\ominus(Cl_2/Cl^-)$ **[1]**, H_2O will be selectively oxidised.

(ii) The high concentration of Cl^- (5.0 mol dm^{-3}) **[0.5]** causes the position of equilibrium $Cl_2 + 2e^- \rightleftharpoons 2Cl^-$ to shift to the left. **[0.5]** This causes $E(Cl_2/Cl^-)$ to become less positive than +1.23 V, resulting in the selective oxidation of Cl^- over H_2O. **[1]**

(c) total charge passed = 5000 × 60 × 60 = 18 000 000 C **[0.5]**

actual charge to produce Cl_2 = 18 000 000 × 0.88 = 15 840 000 C **[0.5]**

$$\text{amount of } e^- = \frac{15\,840\,000}{96500} = 164.145 \text{ mol}$$ **[0.5]**

$$\text{amount of } Cl_2(g) = \frac{164.145}{2} = 82.07 \text{ mol}$$ **[0.5]**

$$\text{volume} = \frac{(82.07)(8.31)(70 + 273)}{10^5} = 2.34 \text{ m}^3$$

(d) **(i)** $NaHg + H_2O \rightarrow NaOH + \frac{1}{2}H_2 + Hg$ **[1]**

(ii) It can be used in fuel cells / to hydrogenate alkenes / in the Haber Process. **[1]**

(e) **(i)** The electronegativity of an atom is a measure of its ability to attract the electrons in a covalent bond to itself. **[1]**

(ii)

chemical bond	explanation
ionic	There is a transfer of electrons from the less electronegative Na to more electronegative Hg to form Na^+ and Hg-rich polyanions like Hg_4^{4-} and Hg_2^{2-}.
metallic	Electrons are lost from low electronegativity Na atoms to form a sea of delocalised electrons.

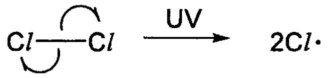
[1] each correct explanation

5 **(a)** The order of thermal stability is: H–C*l* > H–Br > H–I **[0.5]**. Down the group, atomic radius (or size of halogen atom) increases, hence orbital overlap (with H atom) is less effective **[0.5]**, resulting in a longer/weaker H–X bond **[0.5]** (*accept* if quoted BE values from *Data Booklet*), hence less energy is needed to break the H–X bond.

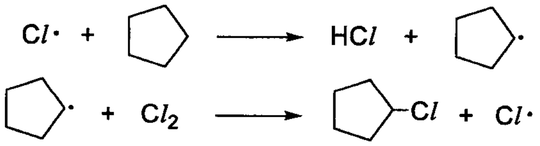
HC*l* does not decompose even on strong heating. **[0.5]**
HBr yields reddish-brown (accept "brown") fumes of Br_2 under strong heating. **[0.5]**
HI gives violet fumes of I_2 when red-hot rod is plunged into jar of HI. **[0.5]**

(b) Free radical substitution **[0.5]**
Correct stages labelled: initiation + propagation + termination **[0.5]**

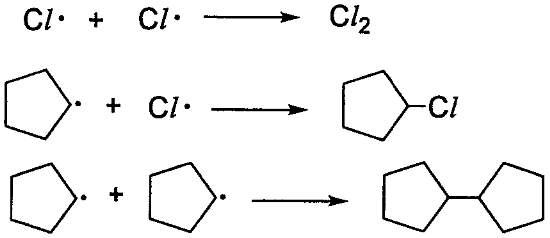
initiation



propagation

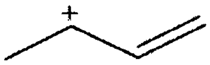
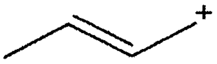


termination



Total 6 equations for 2 marks:

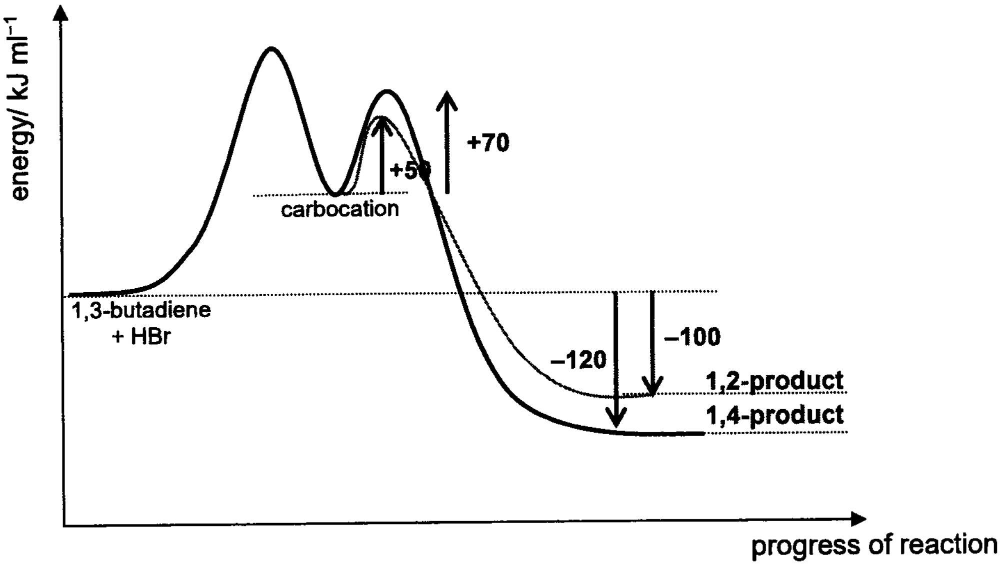
(c) (i)

carbocation structure that forms 1,2-product	carbocation structure that forms 1,4-product
	

The continuous overlap of p orbitals **[0.5]**, causes the delocalisation of π electrons. Hence the positive charge can be delocalised to C4. **[0.5]**

(ii) The bulky I atom on the carbocation on C-1 causes steric hindrance for the attack of Br^- on C-2, hence reducing the % of 1,2-product. **[1]**

(iii)



[2]

(iv) At low temperatures, a greater proportion of the reacting particles would possess sufficient (kinetic) energy to overcome E_{a1} which is lower compared to E_{a2}. Hence the 1,2-product dominates. **[1]**

At high temperatures, the particles have sufficient energy to overcome both E_a and hence the more stable 1,4-product dominates. **[1]**

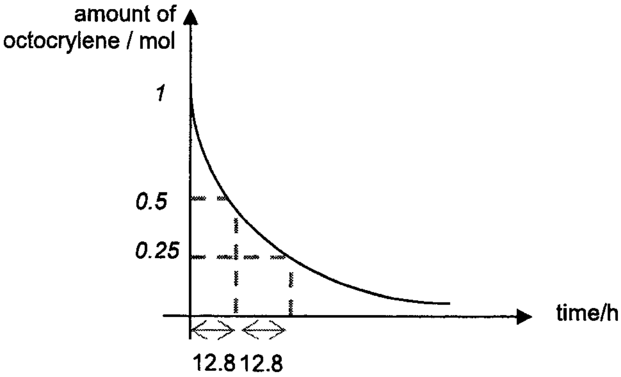
(d) (i) Ti^{4+} and Zn^{2+} have electronic configurations d^0 and d^{10} (or fully-filled and empty d subshell) **[0.5]** respectively, hence no d-d transition can occur. **[0.5]**

(iii) X is the best as octocrylene covers UVB (280–320) while avobenzone covers UVA (310–400) **[1]** (or it contains both octocrylene and avobenzone which together covers the whole range of UVA and UVB).

(e) (i) The half-life, $t_{1/2}$, of a reaction is the time taken for the concentration of a reactant to decrease to half its initial value. **[1]**

(ii) $t = 12.8 \times 3 = 38.4$ hours **[1]**

(iii)



[1]

HWA CHONG INSTITUTION
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MARK SCHEME

Paper 3

1 **(a)** **(i)** Let the solubility of $MgCO_3$ and $Mg(OH)_2$ be x and y respectively, in mol dm^{-3}.

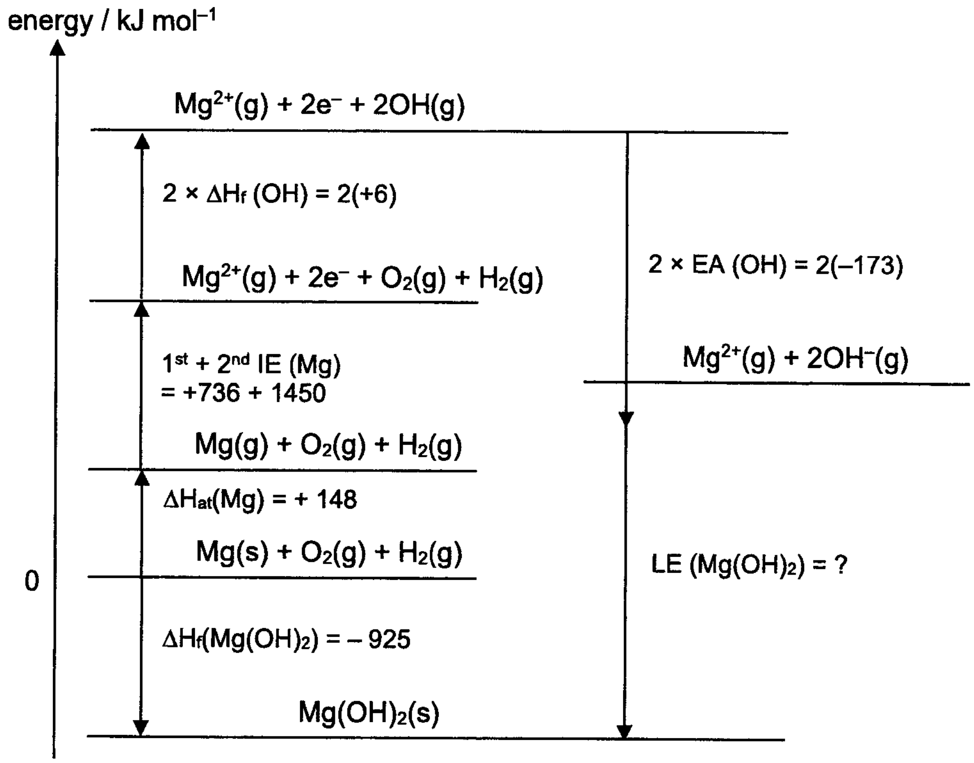
For $MgCO_3$	For Mg(OH)2
$K_{sp} = [Mg^{2+}][CO_3^{2-}]$ **[0.5]**	$K_{sp} = [Mg^{2+}][OH^-]^2$ **[0.5]**
$1.0 \times 10^{-5} = (x)(x)$	$1.1 \times 10^{-11} = (y)(2y)^2$
$x = 3.16 \times 10^{-3}$ **[0.5]** mol dm^{-3}	$y = 1.40 \times 10^{-4}$ **[0.5]** mol dm^{-3}

(ii) $[Mg^{2+}][OH^-]^2 = 1.1 \times 10^{-11}$ **[0.5]**
$(3.0 \times 10^{-5})[OH^-]^2 = 1.1 \times 10^{-11}$
$[OH^-] = 6.06 \times 10^{-4}$ mol dm^{-3} **[0.5]**

(iii) **[0.5]** CO_3^{2-} ions are added first to precipitate Ca^{2+} as $CaCO_3$
[0.5] such that the filtrate contains mainly Mg^{2+} / very little Ca^{2+}.
[1] This must be controlled to prevent precipitation of Mg^{2+} as $MgCO_3$

(b) **(i)** Lattice energy is the heat evolved when 1 mole of solid ionic compound is formed from its constituent gaseous ions. **[1]**

(ii)



[3] total for correct Born-Haber cycle
ΔH_{at} (Mg) + 1st + 2nd IE (Mg) + ΔH_f (OH) + EA (OH) x 2 + LE ($Mg(OH)_2$) = ΔH_f ($Mg(OH)_2$)
148 + 736 + 1450 + (6 x 2) – (173 x 2) + LE ($Mg(OH)_2$) = –925
LE ($Mg(OH)_2$) = –2925 (or 2900 or 2930) kJ mol^{-1} **[1]**

(iii) **[1]** *correct trend:*
decreasing magnitude of LE: MgO > $Mg(OH)_2$ > $Ca(OH)_2$
or LE for MgO is larger than for $Mg(OH)_2$ + LE for $Mg(OH)_2$ is larger than for $Ca(OH)_2$

[1] ***explain why LE of MgO > LE of $Mg(OH)_2$:***
The cation Mg^{2+} is the same for both compounds.

- O^{2-} anion has larger charge [0.5]
- but smaller ionic radius than OH^- [0.5]

[0.5] ***explain why LE of $Mg(OH)_2$ > LE of $Ca(OH)_2$:***
The anion OH^- is the same for both compounds and Mg^{2+} cation has the same charge as Ca^{2+} but Mg^{2+} has smaller ionic radius than Ca^{2+}

[0.5] ***link between ionic radius and charge with magnitude of LE*** (e.g. quote LE eqn or link to strength of ionic bond / attraction bet. oppositely-charged ion ***at least once***)

(c) **(i)** Al : $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^1$ **[0.5]**
Mg: $1s^2\ 2s^2\ 2p^6\ 3s^2$ **[0.5]**

[0.5] The 3p subshell of Al is further away from the nucleus than the 3s subshell (or at higher energy level).
[0.5] There is weaker attraction between the nucleus and the outermost electron of Al (or less energy is needed to remove the 3p electron) resulting in lower ionisation energy.

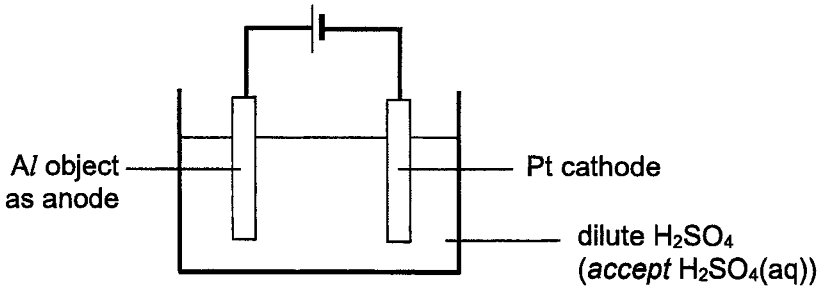
(ii) $MgCl_2$ dissolves in water to form aqueous ions.
$MgCl_2(s) + 6H_2O(l) \rightarrow [Mg(H_2O)_6]^{2+}(aq) + 2Cl^-(aq)$
or $MgCl_2(s) + aq \rightarrow Mg^{2+}(aq) + 2Cl^-(aq)$ **[1]**

Mg^{2+} has slightly high charge density. Slight hydrolysis occurs, forming a slightly acidic solution of pH 6.5.
$[Mg(H_2O)_6]^{2+}(aq) + H_2O(l) \rightleftharpoons [Mg(H_2O)_5(OH)]^{+}(aq) + H_3O^+(aq)$ **[1]**

$AlCl_3$ dissolves in water to form aqueous ions.
$AlCl_3(s) + 6H_2O(l) \rightarrow [Al(H_2O)_6]^{3+}(aq) + 3Cl^-(aq)$
or $AlCl_3(s) + aq \rightarrow Al^{3+}(aq) + 3Cl^-(aq)$ **[1]**

Al^{3+} having high charge density, undergoes hydrolysis **to a greater extent** to give an acidic solution with pH 3. (*must compare extent of hydrolysis with Mg^{2+}*)
$Al(H_2O)_6]^{3+}$ (aq) + H_2O (*l*) $\rightleftharpoons$ $[Al(H_2O)_5(OH)]^{2+}$ (aq) + H_3O^+ (aq) **[1]**

(d)



[1] diagram
- label anode, cathode and electrolyte
- battery in correct orientation

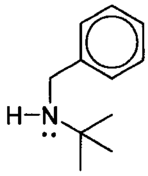
anode: $2Al\ (s) + 3H_2O\ (l) \rightarrow Al_2O_3\ (s) + 6H^+\ (aq) + 6e^-$ **[1]**
cathode: $2H^+\ (aq) + 2e^- \rightarrow H_2\ (g)$ **[1]**

2 (a) The negative charge on O atom in phenoxide ion is delocalised into the benzene ring, hence negative charge is dispersed, stabilising the phenoxide ion **[1]**. So phenol is a stronger acid than alcohol.

Alkyl group is electron-donating, alkyl group intensifies the negative charge on the alkoxide ion through inductive effect, destabilising the alkoxide ion **[1]**.

(b) (i) step 1: electrophilic substitution **[1]**
step 2: nucleophilic substitution **[1]**

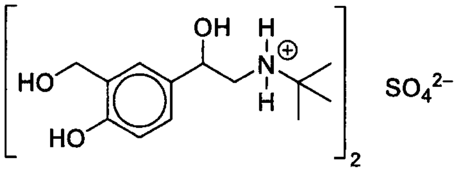
(ii)



[1]

(iii) Amine in **C** has **one more** electron-donating ($-CH_2C_6H_5$) group **[1]** that increases the electron density on N, making the lone pair of electrons on N more available for donation to form a dative bond with a Lewis acid **[1]**.

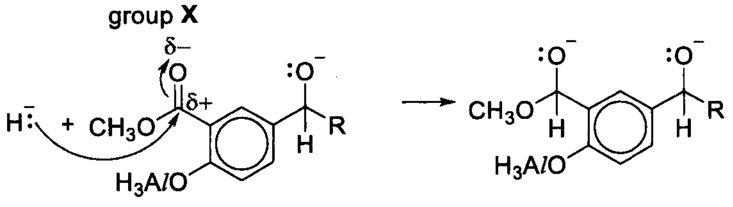
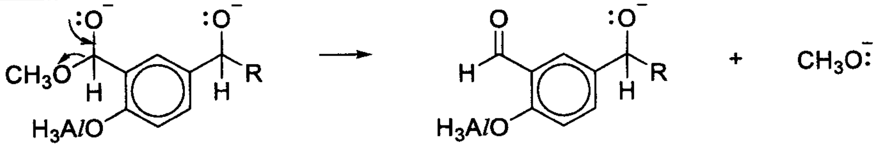
(c) (i)



[1] cation structure, minus 0.5 if structure of SO_4^{2-} was incorrect
[1] cation:anion ratio = 2:1

(ii) Salbutamol sulfate forms strong ion-dipole interactions **[1]** and hydrogen bonding **[1]** with water molecules.

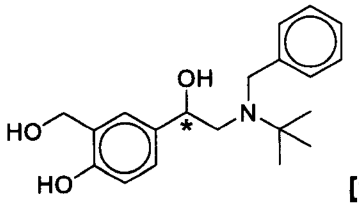
(d) **(i)**

stage	equation
2	 **[0.5] for two arrows [0.5] dipoles**
3	 **[1] for two arrows**

(ii) Lone pair on O of OCH_3 delocalises into C=O in group **X** (ester) making ester carbon of group **X** less electron-deficient **[1]** than aldehyde carbon of group **Y**, hence ester carbon attracts electron-rich hydride ion less well as compared to aldehyde carbon.

Ester carbon of group **X** is more sterically hindered than aldehyde carbon of group **Y** for the approach of the hydride ion as OCH_3 is larger than H atom **[1]**.

(iii)



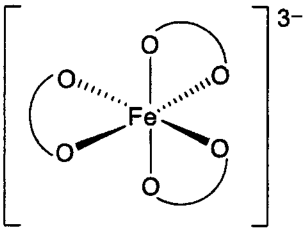
[1]

(iv) In stage 1, the ketone carbon is trigonal planar, there is equal probability for the hydride ion to attack the ketone carbon from the top and bottom **[1]** of the plane.

3 **(a)** Iron is a *d*-block element that forms one or more stable ions (or forms a stable Fe^{3+} ion) with partially filled *d* subshells. **[1]**

(b) **(i)** The phenoxide groups in Cat^{2-} donate their lone pair of electrons on O to the partially-filled 3d orbitals of Fe^{3+} ion, forming coordinate/dative bonds. **[1]**

(ii)



[2]

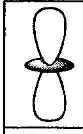
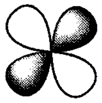
(iv) ligand exchange **[1]**

$[Fe(H_2O)_6]^{3+}$ + $3Cat^{2-}$ → $[Fe(Cat)_3]^{3-}$ + $6H_2O$ **[1]**

(c) $Fe(OH)_3$ (s) ⇌ Fe^{3+}(aq) + $3OH^-$(aq) --------- (1) **[0.5]**

The catechin in tea leaves could form a complex with Fe^{3+} ions, hence concentration of Fe^{3+}(aq) decreases **[0.5]** and shifts the position of equilibrium (1) to the right **[0.5]** and increases its solubility into the mixture **[0.5]** to be discarded.

(d) **(i)** **[0.5]** for each correct shape (no need for axes or labels of orbitals)

	
d_{z^2}*orbital*	$d_{x^2-y^2}$, d_{xy}, d_{xz}, d_{yz}*orbitals*

In an octahedral complex, the ligands approach the central metal ion along the x, y and z axes. Hence the electrons in the d_{z^2} and $d_{x^2-y^2}$ orbitals experience stronger repulsion from the direct approach of the ligands, causing the energies of d_{z^2} and $d_{x^2-y^2}$ orbitals to be at a higher level than the d_{xy}, d_{xz} and d_{yz} orbitals. This results in *d* orbital splitting, where the originally degenerate five d orbitals are split into two groups with a small energy gap ΔE between them.

The lobes of the d_{z^2} and $d_{x^2-y^2}$ orbitals lie along the axes, while those of d_{xy}, d_{xz} and d_{yz} orbitals lie in between the axes.

[1] states the 2 different orientations of lobes for the 2 groups of d orbitals

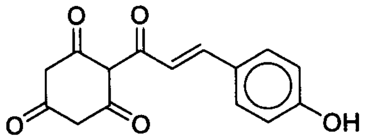
[0.5] states how the ligands approach in an octahedral complex
[0.5] recognizes 1 group experiences stronger repulsion due to direct approach of ligands

[1] states correct group of orbitals in each level

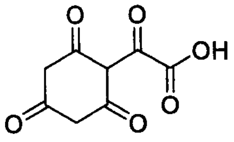
(ii) When white light shines on the complex, an electron from the lower energy *d* orbitals absorbs energy DE and is promoted to vacancies in the higher energy *d* orbitals. The energy absorbed in this *d-d* transition corresponds to wavelength of the visible region of the electromagnetic spectrum. Hence, we observe colours complementary to the colours absorbed.

[0.5] electron in lower E level absorb energy ΔE to promote to higher level
[0.5] vacancies in higher level
[0.5] energy absorbed/ΔE corresponds to visible region
[0.5] color observed is complementary of that absorbed

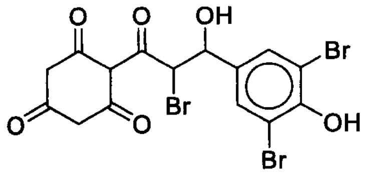
(e) **P** undergoes oxidative cleavage of alkene/C=C with acidified $KMnO_4$.
P undergoes electrophilic addition of alkene and electrophilic substitution of phenol group to give **R**.
P undergoes reduction of alkene/C=C and ketone groups with H_2



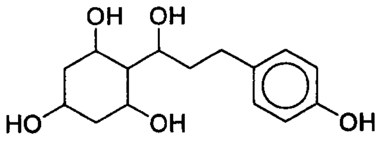
P



Q



R (accept if OH and Br swapped)



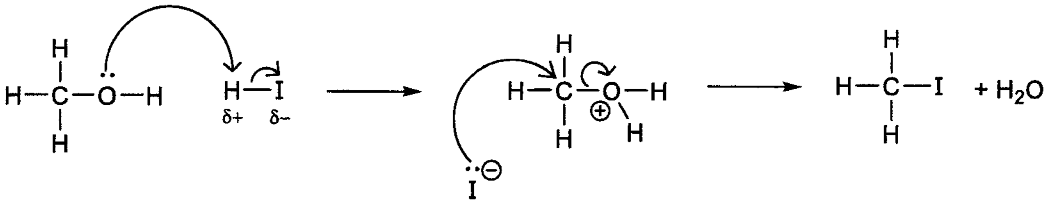
S

[1] for each correct compound
[1] for each correct type of reaction
Total **[8]**, award max **[7]**

4 **(a)** $CH_3OH + CO \rightarrow CH_3CO_2H$ **[1]**

(b) **(i)** (nucleophilic) substitution **[1]**

(ii)



[1] for each step

(c) **(i)** When temperature increased, the position of equilibrium shifts to the left. As the system will try to absorb the additional heat / by favouring the backward endothermic reaction **[1]**.

When a catalyst is added, the position of equilibrium is unaffected. As the catalyst just shortens the time taken to reach equilibrium / increases the rates of both forward and backward reactions **by the same extent**. **[1]**

(ii) $K_c=\frac{[CH_3COI]}{[CH_3I][CO]}$ **[1]**

	$CH_3I(aq)$	+	$CO(aq)$	⇌	$CH_3COI(aq)$
I / mol	0.400		0.300		–
C / mol	–0.105		–0.105		+0.105
E / mol	**0.295**		**0.195**		**0.15 × 0.7 = 0.105 [1]**

$K_c=\frac{(\frac{0.105}{0.7})}{(\frac{0.295}{0.7})(\frac{0.195}{0.7})}$ **[1]**

$= 1.28\ mol^{-1}\ dm^3$ **[1] ecf**

(d) **(i)** Homogeneous catalyst acts in the same phase as the reactants, while heterogeneous catalyst acts in a different phase from the reactants. **[1]**
Homogeneous catalyst forms an intermediate with one of the reactants, providing an alternative pathway with lower activation energy. Heterogeneous catalyst has active sites on its surface for reactants to adsorb on, weakening the bonds in the reactants, hence lowering the activation energy. **[1]**

(ii) In the rhodium(I) complex, the Rh^+ is coordinated by two CO ligands and two I^- ligands and is still able to accomodate two more ligands to form an intermediate. **[1]**
OR
vacant *d* orbitals to accept up to 6 electron pairs / coordination number can vary from 4 to 6
OR
C–I bond breaks, forming CH_3^+ and I^- ligands which can dative bond to rhodium

Rhodium being a transition element can have variable oxidation states. Its oxidation state can increase (*accept* changes) from +1 to +3 (then regenerated back to +1). **[1]**

(e) **(i)** $CH_3CO_2H + OH^- \rightarrow CH_3CO_2^- + H_2O$ **[1]**

(ii)

	CH_3CO_2H	$+ OH^-$	$\rightarrow CH_3CO_2^-$	$+ H_2O$
amt after adding NaOH / mol	$0.4 - 0.15 = 0.25$	–	0.15	
conc after reaction / mol dm^{-3}	$\frac{0.25}{0.8} = 0.313$ **[0.5]**		$\frac{0.15}{0.8} = 0.188$ **[0.5]**	

$CH_3CO_2H + H_2O \rightleftharpoons CH_3CO_2^- + H_3O^+$

$K_a = \frac{(0.1875)[H^+]}{(0.3125)} = 1.8 \times 10^{-5}$ **[1]**

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

pH $= -\lg (3 \times 10^{-5}) = 4.52$ **[1] ecf**

(iii) In the buffer: $CH_3CO_2H + H_2O \rightleftharpoons CH_3CO_2^- + H_3O^+$ ----- (1) When H^+ is added, the position of equilibrium (1) shifts to the left to form more CH_3CO_2H. **[1]**

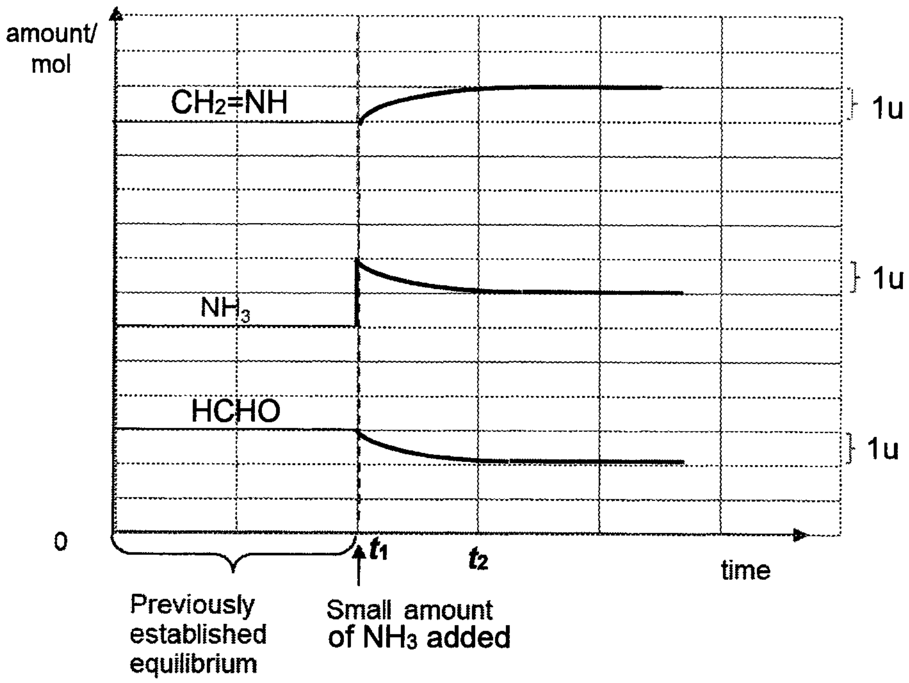
As the original amounts of CH_3CO_2H and $CH_3CO_2^-$ are **large** (or large reservoir of both species) compared to the **small** amount of H^+ ions added, the ratio $[CH_3CO_2^-] / [CH_3CO_2H]$ remains **almost** constant. Since $K_a = [H^+][CH_3CO_2^-] / [CH_3CO_2H]$, and K_a is a constant, so $[H^+]$ and pH remains **almost** constant. **[1]**

5 **(a)** **(i)** Le Chatelier's Principle states that if the conditions of a system at equilibrium are changed, the position of equilibrium shifts so as to reduce that change. **[1]**

(ii) When temperature is increased, the system will try to absorb the additional heat by favouring the backward endothermic reaction, hence the position of equilibrium shifts to the left. **[1]**

The number of moles of gas on both sides of the equation are the same. Hence when pressure is increased, the position of equilibrium is unaffected. **[1]**

(b) **(i)**



[1] correct shapes of CH_2=NH and HCHO graphs (increase for CH_2=NH and decrease for HCHO)

[1] correct shape of NH_3 graph (sharp increase at t_1, followed by decrease)

[1] correct relative amounts of increase/decrease according to 1:1:1 mole ratio + new equilibrium established at **t_2.**

(ii) $K_p = \frac{(P_{CH_2=NH})(P_{H_2O})}{(P_{NH_3})(P_{HCHO})}$ **[0.5]** no unit **[0.5]**

(iii)

	$NH_3(g)$	+	HCHO(g)	$\rightleftharpoons$	CH_2=NH(g)	+	$H_2O(g)$
initial amount/mol	5		5		0		0
change/mol	-(1-0.09)(5) =-4.55		-4.55		+4.55		+4.55
final amount/mol	0.45		0.45		4.55		4.55

Total amount present at equilibrium = 0.9 + 0.9 + 4.1 + 4.1 = 10.0 mol

$K_p = \frac{(P_{CH_2=NH})(P_{H_2O})}{(P_{NH_3})(P_{HCHO})} = \frac{(4.55/10 \times P_T)(4.55/10 \times P_T)}{((0.45/10 \times P_T))((0.45/10 \times P_T))}$ = **102** (to 3 s.f.)

where P_T is the total pressure of the system.

[1] calculate the equilibrium amount of each species

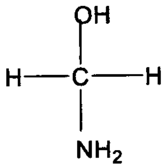
[1] correct substitution into the K_p expression

[1] calculates K_p correctly

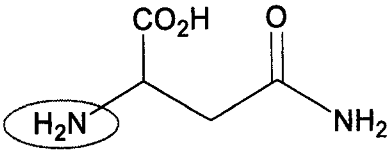
(iv) $K_p >> 1$, which means that at equilibrium, there are much more products than reactants. Hence, the sign for the Gibbs free energy of the forward reaction is negative and the position of equilibrium lies to the right. **[1]**

(c) **(i)** condensation **[1]**

(ii)

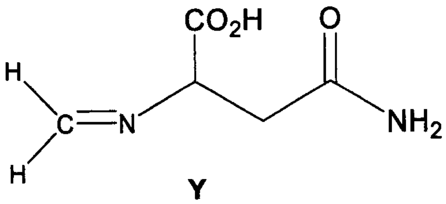
X is  . **[1]**

(iii)



asparagine **[1]**

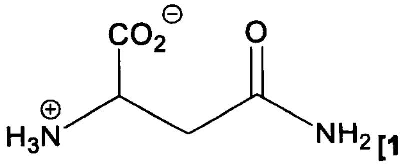
(iv)



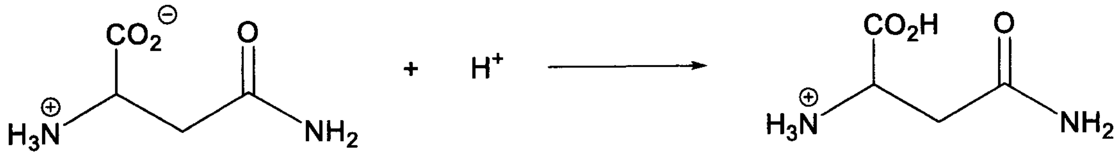
Y

(v) In acidic medium, the $-NH_2$ group gets protonated to $-NH_3^+$ **[0.5]**, reducing its nucleophilicity **[0.5]** and reactivity in the formation of acrylamide. *no ecf*

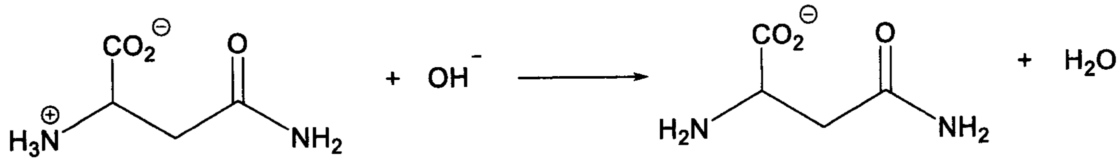
(d) **(i)**

 **[1]**

(ii) When a small amount of acid is added:

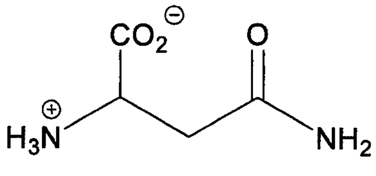


When a small amount of base is added:



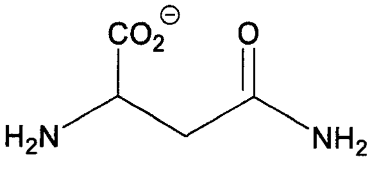
[1] for each equation

(iii) At pH 8, the predominant species of asparagine present are its zwitterionic form and its deprotonated conjugate base.



A

and



B

A and B are conjugate acid-base pairs

$$K_a = \frac{[\mathrm{H^+}][\mathrm{B}]}{[\mathrm{A}]}$$

$$\frac{[\mathrm{B}]}{[\mathrm{A}]} = \frac{K_a}{[\mathrm{H^+}]}$$

$$\frac{[\mathrm{B}]}{[\mathrm{A}]} = \frac{10^{-8.8}}{10^{-8}}$$

$\frac{[B]}{[A]}$ = **0.158** (to 3 s.f.) **[1]**

Also accept

$\frac{[\mathrm{A}]}{[\mathrm{B}]} = \frac{[\mathrm{H^+}]}{[K_a]} = \frac{10^{-8}}{10^{-8.8}}$ = **6.31** (to 3 s.f.)

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