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2023 JC2 H2 Chemistry Preliminary Examination Paper 2 Suggested Solutions

1 The common chlorides of Period 3 elements are shown in Table 1.1.

Table 1.1

Period 3 chloride	$NaCl$	$AlCl_3$	$SiCl_4$	PCl_5
Bonding		C		
Structure		S		
pH of aqueous solution		3		

(a) A 3.30 g sample of a Period 3 chloride is heated to 500 K in a sealed flask of 250 cm^3. At this temperature, the chloride is a gas and the pressure in the flask is 323 kPa.

Assuming the gas behaves ideally, calculate the M_r of the Period 3 chloride. Hence, use the chlorides given in Table 1.1 to deduce its formula. [2]

$$n = \frac{3.23\times10^5 \times 250\times10^{-6}}{8.31\times500} = 0.0194$$

$$M_r = \frac{3.30}{0.0194} = 170.1 \quad [1]$$

$SiCl_4$ [1] matches the M_r from the table.

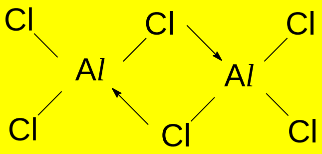
1 **(b)** **(i)** Complete Table 1.1 by

- identifying the bonding shown by each chloride under standard conditions. Use C = covalent, I = ionic, M = metallic
- identifying the structure shown by each chloride under standard conditions. Use G = giant, S = simple
- stating the pH of the aqueous solution of each chloride at 298 K.

[3]

Period 3 chloride	$NaCl$	$AlCl_3$	$SiCl_4$	PCl_5
Bonding [1]	I	C	C	C
Structure [1]	G	S	S	S
pH of aqueous solution [1]	7	3	1 or 2	1 or 2

(ii) At certain temperature, aluminium chloride exists as Al_2Cl_6 molecules. Draw the structure of Al_2Cl_6. State how the shape with respect to each Al atom changes from $AlCl_3$ to Al_2Cl_6. [2]



[1]

Trigonal planar about Al to tetrahedral about Al [1]

(iii) SCl_2 is also a chloride of Period 3 element.
It is a cherry-red liquid that reacts vigorously with water to form a strongly acidic solution.
Use this information to deduce the bonding and structure shown by SCl_2.

Structure: …………………………

Bonding: …………………………..

Explanation:……………………………………………………………………………….…

……………………………………………………………………………………………

……………………………………………………………………………………………[2]

Structure: simple / molecular, because it has a low melting / boiling point
Bonding: covalent, because it undergoes complete hydrolysis.
[1] for correct structure and bonding

Explanation: it has a low melting point (as it is a liquid) and it undergoes complete hydrolysis (reacts vigorously with water).
[1] for correct explanations on m.p. **and** hydrolysis

SCl_2 is formed when sulfur, S_8, reacts with an excess of chlorine in a series of steps.

step **1** $S_8(s) + 4Cl_2(g) \rightarrow 4S_2Cl_2(l)$ $\Delta H_r = -58.2$ kJ mol^{-1}
step **2** $S_2Cl_2(l) + Cl_2(g) \rightleftharpoons 2SCl_2(l)$ $\Delta H_r = -40.6$ kJ mol^{-1}

(iv) Calculate the enthalpy change of formation, ΔH_f, of $SCl_2(l)$. [2]

$$\frac{1}{8}S_8(s) + Cl_2 \rightarrow SCl_2(l) \qquad \Delta H_f$$

$1/8\ S_8(s) + Cl_2 \rightarrow SCl_2(l) \qquad \Delta H_f = ?$

$1/8\ S_8(s) + 1/2\ Cl_2(g) \rightarrow 1/2\ S_2Cl_2(l) \qquad \Delta H_r = (-58.2/8)$ kJ mol^{-1}
$1/2\ S_2Cl_2(l) + 1/2\ Cl_2(g) \rightleftharpoons SCl_2(l) \qquad \Delta H_r = (-40.6/2)$ kJ mol^{-1} [M1 for both]
$1/8\ S_8(s) + Cl_2 \rightarrow SCl_2(l) \qquad -27.6$ kJ mol^{-1} [1]

(v) State the effect of a decrease in pressure on the position of equilibrium in step **2**. Explain your answer. [1]

When pressure decrease equilibrium position will shift to the left to increase pressure by producing more gaseous molecules [1]

(c) Sulfur also reacts with chlorine to form S_2Cl_2.
Fig. 1.1 shows one of the constitutional isomers of S_2Cl_2

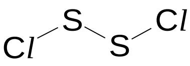


Fig. 1.1

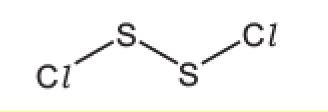
(i) Define the term *constitutional isomer*. [1]

Molecules / isomers with the same molecular formula but different structural formulae [1]

(ii) Using the isomer of S_2Cl_2 shown in Fig 1.1,

- State the oxidation state of S.
- Suggest a value for the *Cl*–S–S bond angle. Explain your answer. [3]

Oxidation state: +1 [1]



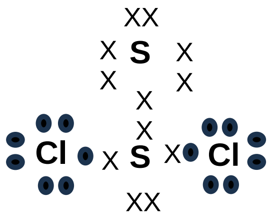
-1 +1 +1 -1

104.5^{o} or 105^{o} [1]

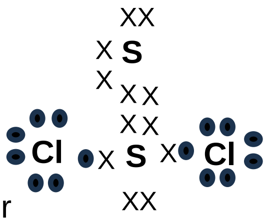
Sulfur has two bond pairs and two lone pairs of electrons **AND**
lone pair-lone pair repulsion is greater [1]

(iii) Draw the 'dot-and-cross' diagram of another isomer of S_2Cl_2, given that

- one of the S atom has an oxidation state of zero.
- the other S atom is the central atom. [1]



or

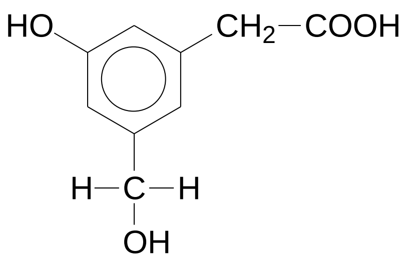


(d) SO_3 can react with SCl_2 to form liquid $SOCl_2$ and another gas which turns aqueous acidified potassium manganate(VII) from purple to colourless.

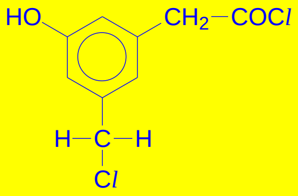
(i) Write a balanced chemical equation for the reaction between SO_3 and SCl_2. [1]

$SO_3 + SCl_2 \rightarrow SOCl_2 + SO_2$ [1]

(ii) Draw the organic product formed when compound **A** is reacted with $SOCl_2$. [1]



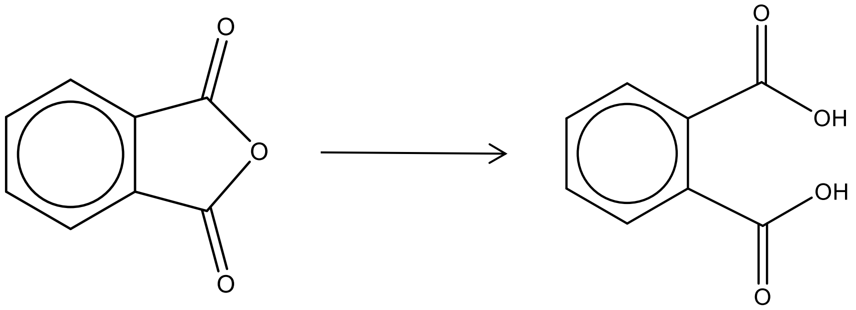
Compound **A**



[1]

[Total: 19]

2 **(a)** Phthalic anhydride is an important industrial chemical for the synthesis of phthalic esters, which are used as plasticisers to soften plastics.



Phthalic anhydride Phthalic acid ($C_8H_6O_4$)

The reactivity of phthalic anhydride is similar to that of acyl chloride. Hydrolysis of phthalic anhydride produces phthalic acid, which is an aromatic dicarboxylic acid that can ionise in two stages, each with its associated pK_a value as shown in Table 2.1.

Table 2.1

$C_8H_6O_4 \rightleftharpoons C_8H_5O_4^- + H^+$	pK_{a1} = 2.89
$C_8H_5O_4^- \rightleftharpoons C_8H_4O_4^{2-} + H^+$	pK_{a2} = 5.51

(i) Suggest reagents and conditions for hydrolysis of phthalic anhydride to form phthalic acid. [1]

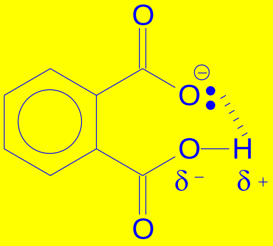
H_2O(l), room temperature [1]

(ii) Suggest two reasons why the pK_{a2} of phthalic acid is higher than its pK_{a1}. [2]

A higher pK_{a2} suggests that $C_8H_5O_4^-$ is a weaker acid than $C_8H_6O_4$.

For pK_{a1}, it involves removal of H^+ from a neutral $C_8H_6O_4$/molecule. For pK_{a2}, it is more difficult to remove H^+ from a negatively charged $C_8H_5O_4^-$/conjugate base / results in repulsion between two negatively charged $-CO_2^-$ in close proximity. [1]

(Intramolecular/internal) hydrogen bonding in $C_8H_5O_4^-$/conjugate base which stabilise it would be disrupted when it further dissociates. [1]



[1]: idea that pK_{a2} leads to the formation of a more negative conjugate base which made it harder for the H^+ to be removed (stronger attraction) / caused repulsion between the 2 negatively charged $-CO_2^-$
[1]: idea that pK_{a2} disrupts the (internal) hydrogen bonding within $C_8H_5O_4^-$

(b) A student pipetted 10 cm^3 of 0.50 mol dm^{-3} of phthalic acid into a conical flask and 20.00 cm^3 of 0.50 mol dm^{-3} of potassium hydroxide was required for complete neutralisation.

(i) Calculate the pH of 0.50 mol dm^{-3} solution of phthalic acid, ignoring the effect of pK_{a2}. [1]

$[H^+] = \sqrt{10^{-2.89} \times 0.50} = 0.02538$ mol dm^{-3}

pH = – lg 0.02538 = 1.60 [1]

(ii) Calculate the pH of a solution which contains both phthalic acid and potassium hydrogen phthalate, $C_8H_5O_4K$ in equal concentration. [1]

$C_8H_6O_4$ and $C_8H_5O_4K$ in equal concentration ⇒ maximum buffer capacity

pH = pK_{a1}
= 2.89 [1]

(iii) Determine the volume of potassium hydroxide that has been added when the solution in the conical flask contains only potassium hydrogen phthalate. [1]

Volume of KOH required = 20 ÷ 2 = 10 cm^3 [1]

(iv) Using information from Table 2.1,

- calculate the K_b of potassium hydrogen phthalate, $C_8H_5O_4K$.
- calculate the K_{a2} of phthalic acid.

Hence, suggest if an aqueous solution of potassium hydrogen phthalate is acidic or alkaline. [3]

pK_{a1} of $C_8H_6O_4$ = 2.89
pK_{a2} of $C_8H_6O_4$ = 5.51

$K_{a1} = 1.288 \times 10^{-3}$ mol dm^{-3}
$K_w = K_a \times K_b$ [$C_8H_6O_4$ and $C_8H_6O_4^-$ are conjugate pair]

$$K_b \text{ of } C_8H_5O_4^- = \frac{1 \times 10^{-14}}{1.288 \times 10^{-3}} = 7.76 \times 10^{-12} \text{ mol dm}^{-3}$$ [1]

K_{a2} of $C_8H_6O_4$ = K_a of $C_8H_5O_4^-$
$= 10^{-5.51}$
$= 3.09 \times 10^{-6}$ mol dm^{-3} [1]

Since K_a of $C_8H_5O_4^-$ is greater than its K_b, it is a stronger acid than a base/more likely to donate a proton than accepting one. Hence, aq. solution of $C_8H_5O_4K$ is acidic. [1]

(accept use of pH at 1st equivalence point = $\frac{pK_{a1} + pK_{a2}}{2}$ = 4.2 to conclude solution is acidic)

[Total: 9]

3 **(a)** Lucas Test is used to distinguish between primary, secondary and tertiary alcohols.

Table 3.1 shows the observations on adding reagents of Lucas Test (concentrated hydrochloric acid and zinc chloride as catalyst) to separate samples of three alcohols to form chloroalkanes.

Table 3.1

alcohol	observation on adding conc. HCl and $ZnCl_2$
$(CH_3)_3COH$	immediate cloudiness appears in the solution
$CH_3CH_2CH(OH)CH_3$	cloudiness apparent within 5 minutes
$CH_3CH_2CH_2CH_2OH$	no cloudiness apparent unless warmed

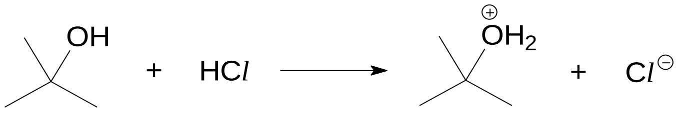
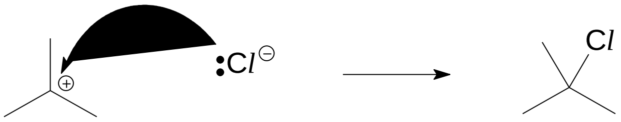
(i) The cloudiness is due to the formation of two immiscible layers. Suggest why cloudiness appears in the solution after the reaction is complete. [1]

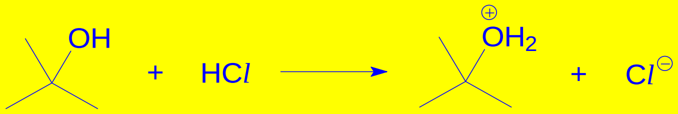
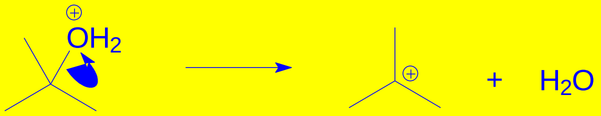
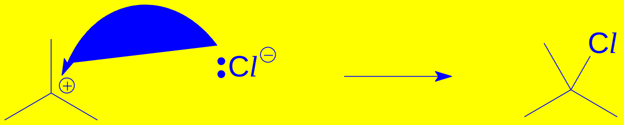
Chloroalkanes are less soluble in water than alcohols thus resulting in formation of two immiscible layers (which appears cloudiness). [1]

(ii) The three stages of the Lucas test using $(CH_3)_3COH$ are described in Table 3.2.

Complete Table 3.2 by suggesting the mechanism involved in stage 2 **only**. Show the structure of the intermediate and movement of electron pairs by using curly arrows in your answer. [2]

Table 3.2

stage	description of stage	equation
1	acid–base reaction between alcohol and conc. HCl to form protonated alcohol	
2	heterolytic fission of C–O bond in protonated alcohol to form a carbocation intermediate	
3	reaction of intermediate carbocation with Cl^- to form the chloroalkane	

stage	description of stage	equation
1	acid–base reaction between alcohol and conc. HC*l* to form protonated alcohol	
2	heterolytic fission of C–O bond in the conjugate acid to form a carbocation intermediate	 [1] correct arrow, charge on -OH_2 (ignore position), correct carbocation with right placement of +ve charge [1] for balancing with water
3	reaction of carbocation intermediate with Cl^- to form the chloroalkane	

(iii) Suggest why primary alcohol such as $CH_3CH_2CH_2CH_2OH$ does not give cloudiness in Lucas test. [1]

Does not form chloroalkane as reaction goes through primary carbocation which are unstable. [1]

(iv) Beside using Lucas Test, suggest how $(CH_3)_3COH$ and $CH_3CH_2CH_2CH_2OH$ can be differentiated using another chemical test. Include reagents and condition and state the observation that will be made. [2]

Test : Add $KMnO_4$ in dilute H_2SO_4, heat [1]
Observation: [1]
$(CH_3)_3COH$ will not decolourise purple $KMnO_4$
$CH_3CH_2CH_2CH_2OH$ will decolourise purple $KMnO_4$.

OR

Test : Add $K_2Cr_2O_7$ in dilute H_2SO_4, heat
Observation:
Orange $K_2Cr_2O_7$ remains orange in $(CH_3)_3COH$
Orange $K_2Cr_2O_7$ change from orange to green in $CH_3CH_2CH_2CH_2OH$

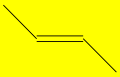
(b) One of the alcohols listed in Table 3.1 undergoes elimination to form three isomeric alkenes **B**, **C** and **D** of molecular formula, C_4H_8.

(i) Identify the alcohol and draw the skeletal formula of alkenes **B**, **C** and **D**. [3]

Identity of alcohol: $CH_3CH_2CH(OH)CH_3$ [1]

Alkenes:

cis

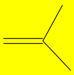


trans

Cis & trans [1] [1]

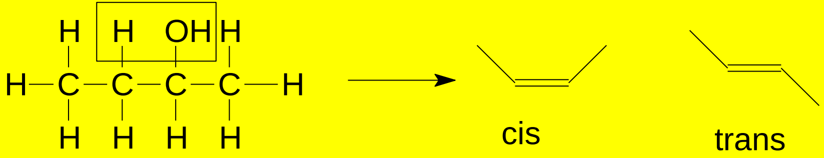
Thinking process:

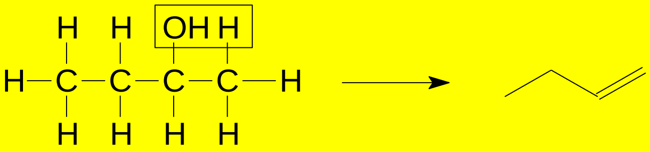
Cannot be $(CH_3)_3COH$ as it undergo elimination to form only one alkene:



Cannot be $CH_3CH_2CH_2CH_2OH$ as it undergo elimination to form only one alkene:

Thus, it boils down to $CH_3CH_2CH(OH)CH_3$. Upon elimination it will produce





which explains why there are three alkenes generated.

(ii) 20 cm^3 of alkene with formula C_4H_8 underwent complete combustion in an oxygen-rich environment. There was a reduction in volume of *x* cm^3. When the residual gaseous mixture was treated with sodium hydroxide solution, there was a further reduction in volume of *y* cm^3.

Determine the values of *x* and *y*.

(All measurement of volumes was done at room temperature and pressure.) [2]

$C_4H_8 + 6O_2 \rightarrow 4CO_2 + 4H_2O$
Sodium hydroxide absorbs CO_2 gas ➔ ***y* = 80** [1]

Total volume before combustion – Total volume after combustion = *x*
(20 + unreacted O_2 + reacted O_2) – (unreacted O_2 + CO_2) = *x*
(20 + unreacted O_2 + 120) – (unreacted O_2 + 80) = *x*
140 – 80 = *x*
***x* = 60** [1]

OR

	C_4H_8	+ $6O_2$	$\rightarrow$	$4CO_2$	+ $4H_2O$
Initial vol /cm^3	20	Unreacted O_2 + 120		0	–
Change in vol /cm^3	-20	-120		+80	–
Final vol /cm^3	0	Unreacted O_2		80	–

From Table above,
Total decrease in volume due to gas reacted = 20 + 120
Total increase in volume due to gas produced = 80
Net reduction in volume = 140 – 80 = 60 = x

[Total: 11]

4 Silver forms a series of halides of general formula AgX. The chloride, bromide and iodide of silver are sparingly soluble in water at room temperature.

The solubility products of the chloride, bromide and iodide of silver are given in Table 4.1.

Table 4.1

Salt	value of solubility product at 298 K
Ag*Cl*	2.0×10^{-10}
AgBr	5.0×10^{-13}
AgI	to be calculated

(i) Write an expression for the solubility product, K_{sp} of silver iodide. [1]

$K_{sp} = [Ag^+][I^-]$ [1]

(ii) Given the solubility of silver iodide, AgI is 8.9×10^{-9} mol dm^{-3}, calculate a value for K_{sp} of silver iodide. Leave your answer to **two** significant figures. [1]

$[Ag^+] = [I^-] = [AgI(aq)]$

$K_{sp} = (8.9 \times 10^{-9})^2$
$= \underline{7.9 \times 10^{-17}}$ mol^2 dm^{-6}

[1]: correct answer to 2 s.f.

When a precipitate is formed, $\Delta G^{\ominus}_{ppt}$ is given by the following expression.

$$\Delta G^{\ominus}_{ppt} = 2.303\, RT \log_{10} K_{sp}$$

(iii) Use the data above to calculate $\Delta G^{\ominus}_{ppt}$, for silver chloride. [1]

$\Delta G^{\ominus}_{ppt} = 2.303\, RT \log_{10} K_{sp}$
$= 2.303(8.31)(298)(\log 2.0 \times 10^{-10})$ J mol^{-1}
$= \underline{-5.53 \times 10^4 \text{ J mol}^{-1}}$ [1]

(iv) For silver fluoride, AgF, $K_{sp} = 1.006$ mol^2 dm^{-6} at 298 K.
Use the $\Delta G^{\ominus}_{ppt}$ expression given to determine whether silver fluoride is soluble in water at 298 K.

Explain your answer. [2]

$\Delta G^{\ominus}_{ppt} = 2.303\, RT \log_{10} K_{sp}$
$= 2.303(8.31)(298)(\log_{10} 1.006)$
$= \underline{+14.8 \text{ J mol}^{-1}}$ [1]

Since $\Delta G^{\ominus}_{ppt}$ is +ve, precipitation will <u>not occur</u> [1]
i.e. <u>AgF is soluble</u>

[1]: $\Delta G^{\ominus}_{ppt}$ calculated [1]: conclusion (ecf)

(b) **(i)** When silver nitrate is added to solution containing chloride ions, a white precipitate is observed. The white precipitate dissolves when aqueous ammonia was added.

With the aid of suitable equations only, explain the chemistry that is occurring during these reactions. Include state symbols in your equations. [2]

$Ag^+ (aq) + Cl^- (aq) \rightleftharpoons AgCl(s)$ [1]
White ppt is formed due to the formation of insoluble AgC*l*.

$Ag^+(aq) + 2NH_3(aq) \rightleftharpoons [Ag(NH_3)_2]^+ (aq)$ [1]

When NH_3 is added, $[Ag(NH_3)_2]^+$ is formed. $[Ag^+]$ decreases. POE shifts left. AgCl White ppt dissolves.

(ii) Aqueous sodium bromide was added to the resultant mixture from **(b)(i)**, a cream precipitate is obtained. Explain the observation made using information from Table 4.1. [1]

$Ag^+ (aq) + Br^- (aq) \rightarrow AgBr(s)$ or $NaBr (aq) + AgCl(s) \rightarrow AgBr (s) + NaCl (aq)$

Cream ppt is AgBr

Since **K_{sp} of AgBr < K_{sp} of AgC*l***, **AgBr is less soluble than AgCl**. Hence, addition of NaBr will cause **AgBr (cream ppt) to be precipitated out from AgCl.** [1]

(c) Silver bromide dissolves in an aqueous solution of $S_2O_3^{2-}$ ions to form the complex ion $[Ag(S_2O_3)_2]^{3-}$. The $S_2O_3^{2-}$ ions act as monodentate ligands here.

equilibrium 1 $AgBr(s) + 2S_2O_3^{2-}(aq) \rightleftharpoons [Ag(S_2O_3)_2]^{3-}(aq) + Br^-(aq)$

(i) Define the term *ligand*. [1]

Molecule / anion that uses a lone pair of electrons to form a coordinate bond to a metal atom / ion. [1]

(ii) Write an expression for the equilibrium constant, K_c, for equilibrium 1. [1]

$$K_c = \frac{\left[Ag(S_2O_3)_2^{3-}\right][Br^-]}{[S_2O_3^{2-}]^2}$$ [1]

Stability constant of a complex, K_{stab}, is the equilibrium constant for its formation as shown below. It is a measure of the relative stability of complex compared to its aqua complex.

$$[Ag(H_2O)_2]^+(aq) + 2L^{m-}(aq) \rightleftharpoons [AgL_2]^{(1-2m)}(aq) + 2H_2O(l) \qquad K_{stab}$$

(where m = 0, 1 or 2)

Table 4.2 lists the numerical values for the stability constant of three silver(I) complexes with 3 different ligand, L^{m-}.

Table 4.2

m	silver(I) complex	numerical value of K_{stab}
0	$[Ag(NH_3)_2]^+$	1.6×10^7
1	$[Ag(CN)_2]^-$	5.3×10^{18}
2	$[Ag(S_2O_3)_2]^{3-}$	2.9×10^{13}

(iii) Use your answer from **(c)(ii)** and relevant data from Table 4.1 and 4.2 to calculate the K_c for equilibrium 1.
(Note that $[Ag(H_2O)_2]^+(aq)$ is equivalent to $[Ag^+]$) [1]

$$K_c = \frac{\left[Ag(S_2O_3)_2^{3-}\right]}{[Ag^+]\,[S_2O_3^{2-}]^2} \times [Ag^+]\,[Br^-]$$

$\boldsymbol{K_c = K_{stab}\ ([Ag(S_2O_3)_2]^{3-}) \times K_{sp}\ (AgBr)}$

$= 2.9 \times 10^{13} \times 5.0 \times 10^{-13}$

$= \underline{14.5}$ [1]

(iv) An aqueous solution containing Ag^+ is added to a solution containing equal concentrations of $CN^-(aq)$, $NH_3(aq)$ and $S_2O_3^{2-}(aq)$. The mixture is left to reach equilibrium.

Deduce, in decreasing order, the relative concentrations of $[Ag(NH_3)_2]^+$, $[Ag(CN)_2]^-$ and $[Ag(S_2O_3)_2]^{3-}$ present in the resulting mixture. Explain your answer. [2]

decreasing order: $[Ag(CN)_2]^-$, $[Ag(S_2O_3)_2]^{3-}$, $[Ag(NH_3)_2]^+$ [1]

$\underline{K_{stab}}$ for the complex formed by CN^- and Ag^+ ions is largest;
$\underline{[Ag(CN)_2]^-}$ is most stable and its concentration will be the highest. [1]

(d) **(i)** State the electronic configuration of a Ag^+ ion. [1]

Ag^+: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^6\ 4d^{10}$ [1]

(ii) Suggest why the silver(I) complexes in Table 4.2 are colourless. [1]

Ag^+ has a fully-filled 4d subshell/orbital

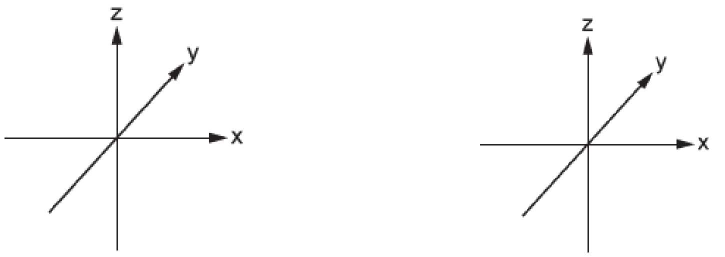
AND

hence no d-d transition can occur. [1] (ignore if write 3d, 5d)

(e) In an octahedral complex, the d subshell of a transition metal ion is split into two energy levels.

Using the axes in Fig. 4.1, draw **fully-labelled** diagrams of the following.

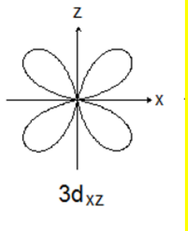
- One of the d orbitals at the lower energy level in an octahedral complex.
- One of the d orbitals at the higher energy level in an octahedral complex.



lower energy level higher energy level

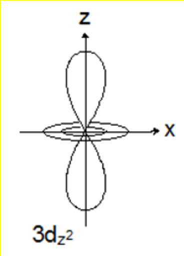
Fig. 4.1 [2]

Lower energy level (in between axes) [1]



Comment: aligning with the axis provided, $3d_{xz}$ is the easiest to draw.

Higher energy level (on the axes) [1]



Comment: aligning with the axis provided, $3d_{z^2}$ is the easiest to draw.

[Total: 17]

5 **(a)** NH_3 is produced from N_2 and H_2 in the presence of a catalyst. When N_2 and H_2 is heated in a sealed reactor, the following equilibrium is established.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

(i) Write an expression for K_p for this equilibrium. [1]

$$K_p = \frac{(p_{NH_3})^2}{(p_{N_2})(p_{H_2})^3} \text{ [1]}$$

(ii) In an experiment, N_2 and H_2 are placed in a sealed reactor in the molar ratio 1:3. Fig. 5.1 shows the variation in the amounts of N_2 and NH_3 in the system with time. The reactor is maintained at a temperature of 750 K and the total pressure is 200 atm.

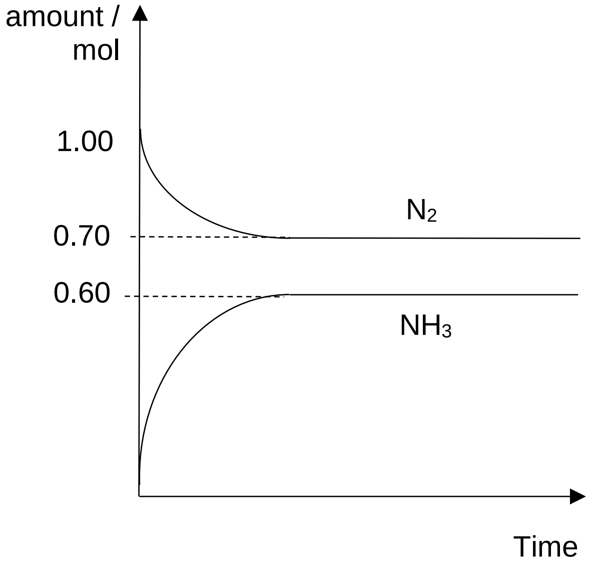


Fig. 5.1

Use the information provided above and data from Fig. 5.1 to calculate the value of K_p for the equilibrium at 750 K, stating its units. [3]

n	$N_2(g)$	+	$3H_2(g)$	⇌	$2NH_3(g)$
Initial / mol	1		3		0
Change / mol	– 0.30		– 0.90		+ 0.60
Equilibrium / mol	0.70		2.10		0.60

Total amount at eqm = 3.40 mol

$$p_{N_2} = \frac{0.70}{3.40} \times 200 = 41.18 \text{ atm}$$

$$p_{H_2} = \frac{2.10}{3.40} \times 200 = 123.5 \text{ atm}$$

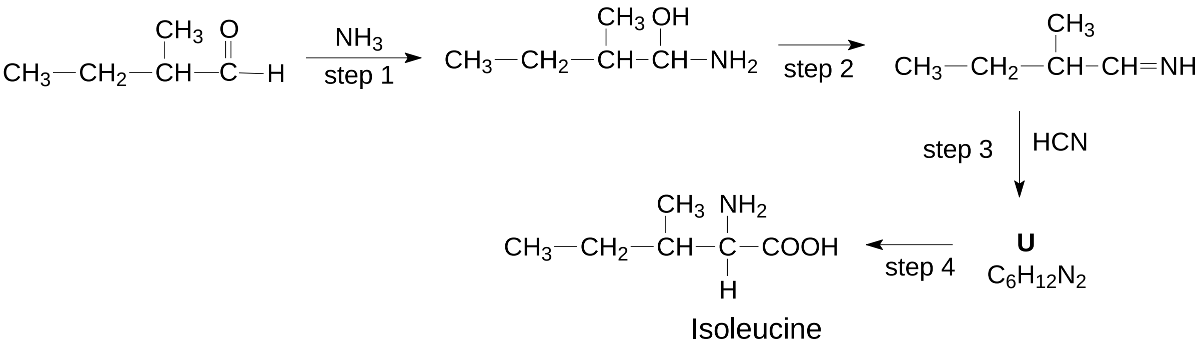
$$p_{NH_3} = \frac{0.60}{3.40} \times 200 = 35.29 \text{ atm}$$

[1] equilibrium partial pressures

$$K_p = \frac{(p_{NH_3})^2}{(p_{N_2})(p_{H_2})^3} = \frac{35.29^2}{(41.18)(123.5)^3} = 1.61\times10^{-5} \text{ atm}^{-2}$$

[1] K_p value (allow ecf) [1] for units

(b) The Strecker amino acid synthesis, is a method for the synthesis of amino acids by the reaction of an aldehyde with ammonia is shown below. Isoleucine can be prepared via Strecker synthesis as shown below.



(i) Suggest the type of reaction occurring in steps 1 and 2. [2]

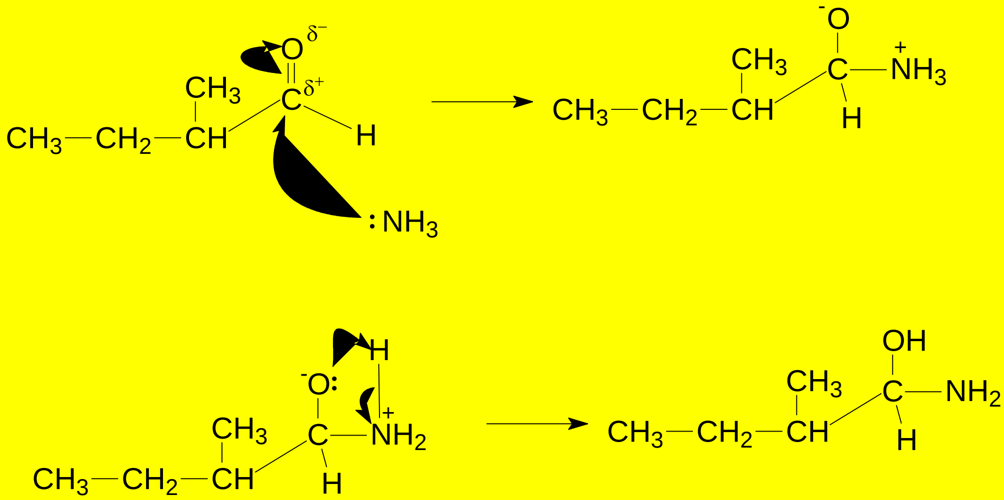
Step 1: Nucleophilic Addition [1]
Step 2: Elimination [1]

(ii) The mechanism of the reaction in step 1 proceeds via the following stages:

1. Nucleophilic attack of ammonia on the carbonyl carbon forming an intermediate (with a negative charge on O atom and a positive charge on N atom).
2. The intermediate abstract a proton from the neighboring nitrogen and form the product.

Draw the mechanism for step 1. Show relevant lone pairs and dipoles and use curly arrows to indicate the movement of electron pairs.

[2]

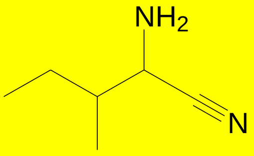


[2]

(iii) Suggest why step 1 produces a mixture which is optical inactive. [2]

The **structure** has a **trigonal planar** shape with respect to the carbon and **nucleophile** NH_3 has **an equal chance of attacking it from the top or bottom** of the plane. [1]
This produces an **equimolar** mixture of **both enantiomers** of compound **U** which makes the mixture optically inactive. [1]

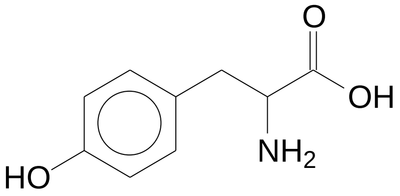
(iv) Draw the structure of compound **U,** $C_6H_{12}N_2$. [1]



[1] (no need skeletal)

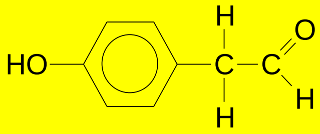
Thinking process: work back from isoleucine.

(v)



Tyrosine

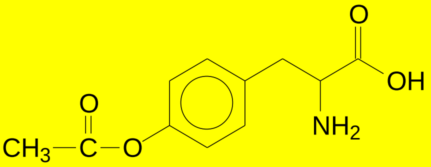
An amino acid, Tyrosine can be prepared from aldehyde **V** via Strecker synthesis.
Draw the structure of aldehyde **V**. [1]



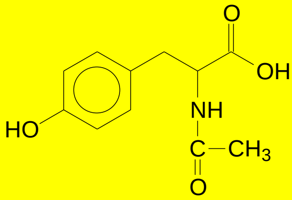
[1]

Modify HCI 2019 P3 1b

(vi) When one mole of CH_3COCl is added to one mole of tyrosine, two different isomeric products, **X** and **Y**, are formed.
Y forms violet complex with neutral $FeCl_3$ while **X** does not.
Draw the structures of **X** and **Y**. [2]

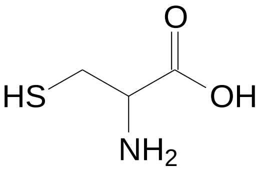


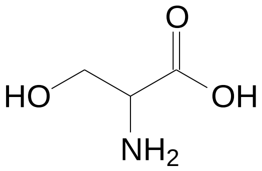
X [1]



Y [1]

(c) Cysteine and serine are naturally occurring amino acids found in proteins with the following structures.



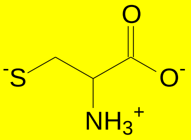


cysteine serine

Thiols having the structure R−SH, undergoes similar reactions as alcohols but are generally more acidic than alcohols.

(i) The thiol group in cysteine has a pK_a value of 8.18. The remaining pK_a values of cysteine are 1.96 and 10.28.

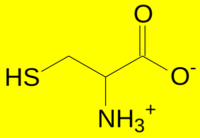
Draw the structure of the predominant species of cysteine at pH 9.0. [1]



[1]

(ii) Suggest a pH at which the predominant species of cysteine is a zwitterion. Draw the structure of the zwitterion. [2]

Any value between 1.96 but less than 8.18 [1]



[1]

(iii) The pK_a value of the alcohol group in serine is 13.00.

Suggest a reason why the pK_a value for the thiol group in cysteine is lower than that for the alcohol group in serine. [1]

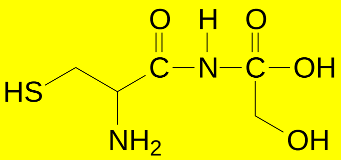
CH_3CH_2SH is a stronger acid (lower *pK_a*) because the sulfur atom is larger than the oxygen atom AND (*any of the following reason*)

- it makes the S–H bond weaker than the O–H bond and so favours dissociation of CH_3CH_2SH to give out H^+.

OR

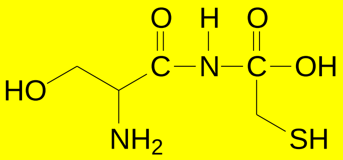
- the conjugate base of the CH_3CH_2SH is more stable than that of the CH_3CH_2OH because the negative charge is spread out over a larger surface area so lowering the charge density in the thiolate (RS^-) compared to the alkoxide (RO^-). [1]

(iv) Cysteine and serine can form a dipeptide. Draw the structure of this dipeptide. [1]



cys-ser

or



ser-cys

[1]

[Total: 19]