Prelims Paper 2 Answers

1. (a) **P**, **Q**, **R and S** are consecutive elements in Period 4.

The table below shows the first four ionisation energies (in kJ mol^{-1}) of the elements.

Element	1st I.E.	2nd I.E.	3rd I.E.	4th I.E.	5th I.E.
P	908	1730	3828	5980	7970
Q	577	1980	2960	6190	8284
R	762	1540	3300	4390	9020
S	947	1798	2735	4837	6043

(i) Explain why the second ionisation energy of **Q** is higher than that of **R**. **[2]**

Q is in group 13, there is a great jump in IE from 3rd IE to 4th IE

Q: $4s^2 4p^1$ Q^+: $4s^2$

R: $4s^2 4p^2$ R^+ : $4s^2 4p^1$

Q: the second electron is removed from the **4s** orbital, whereas for R, the second electron is removed from the **4p** orbital. The **4p** orbital is **further** away from the nucleus than the 4s and **experiences additional shielding effect** by the two 4s electrons. These factors **outweigh the effect of increase in nuclear charge** from Q to R, resulting in a weaker attraction by nucleus. **Less energy** is required to **remove an electron** from 4p than the 4s orbital.

(ii) Explain why **P** is not considered to be a transition metal like most of the d-block metals. **[1]**

They **do not** form stable ions with a partially filled d subshell. **[1]**

(b) The idea of covalent bonding was first described in 1916 by an American physical chemist Gilbert Newton Lewis. HCOC*l* is an example of a polar covalent molecule.

(i) Explain what is *covalent bonding*. **[1]**

Covalent bonding is the electrostatic attraction between a shared pair of electrons and the positively charged nuclei.

(ii) State what is meant by the term *polar* when applied to a covalent bond. **[1]**

A polar covalent bond is one in which the electron density is unequally shared due to the difference in electronegativity of atoms bonded, resulting in $\partial+$ and $\partial-$ across bond.

(iii) State and explain with reference to the Valence Shell Electron Pair Repulsion theory, the shape of HCOC*l* molecule. **[2]**

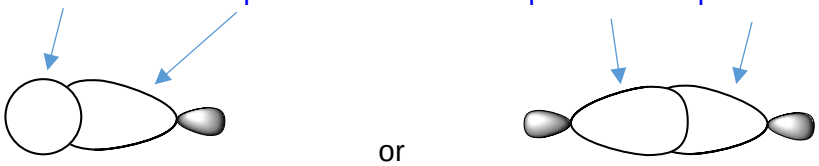
3 bond pair no lone pair so trigonal planar. The 3 electrons bond pairs arrange themselves to maximise stability and minimise electronic repulsion.

(iv) The molecule of HCOC*l* contains both σ (sigma) and π (pi) bonds. Draw labelled diagrams to show how orbitals overlap to form

- a σ (sigma) bond
- a π (pi) bond

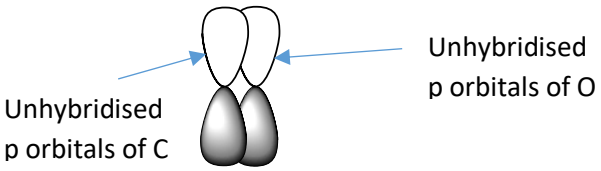
σ (sigma) bond is formed from **head-on overlap** of

s orbital of H and sp^2 of C or sp^2 of O and sp^2 of C **[2]**



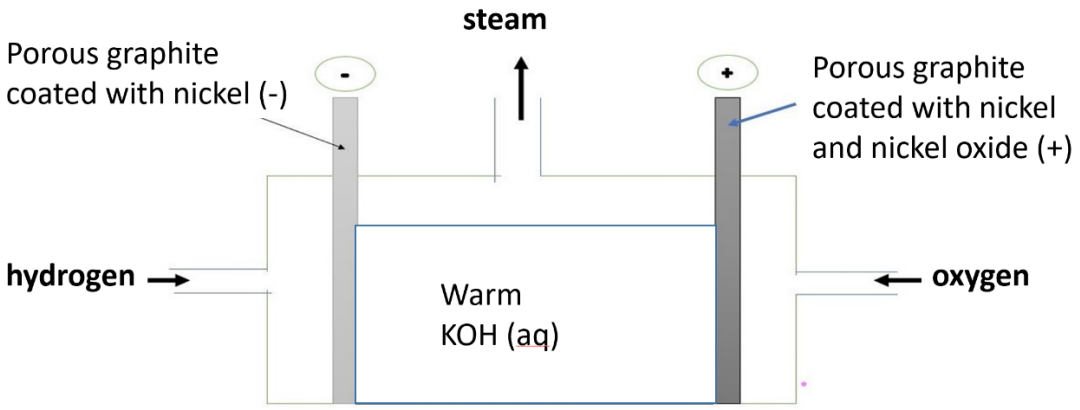
or

π (pi) bond is formed from **side-on overlap** of unhybridised p orbitals.



[Total:9]

2 Below is a labelled diagram of a hydrogen-oxygen fuel cell in an alkaline electrolyte.



(i) Write the half equations for both electrodes and hence the overall equation. **[2]**

Cathode: $O_2(g) + 2H_2O(l) + 4e^- \rightarrow 4OH^-(aq)$

Anode: $H_2(g) + 2OH^-(aq) \rightarrow 2H_2O(l) + 2e^-$

Overall equation : $2H_2(g) + O_2(g) \rightarrow 2\ H_2O(l)$

(ii) Calculate $\Delta G^\ominus$ for the above reaction and state whether it is spontaneous. **[3]**

$E^\ominus_{cell} = E^\ominus_{cathode} - E^\ominus_{anode}$

$= 0.40-(-0.83)$

$= +1.23$ V

$\Delta G^\ominus = -nFE^\ominus_{cell}$

$= -4 \times 96500 \times 1.23$

$= -474780$ Jmol^{-1}

$= -475$ kJmol^{-1}

It is spontaneous.

(iii) The hydrogen-oxygen fuel cell produces 1.5 A of current. Hydrogen gas is contained in a 1 dm^3 tank at a pressure and temperature of 200 atm and 20 ^{o}C respectively. Determine the number of days the fuel cell can operate before the hydrogen gas runs out. Give your answer to the nearest whole number. You may assume there is an unlimited supply of O_2. **[3]**

$PV = nRT$

$200 \times 1.01325 \times 10^5 \times 1 \times 10^{-3} = n \times 8.31 \times 293$

n (amt of H_2 gas) = 8.322 mol

no. moles of electrons given out = 2n = 16.64

Q = 16.64 x 96500 = 1605760C

Q = It

t = 1605760/1.5 = 1070506 s

=1070506/86400 = 12.39 days

12 days

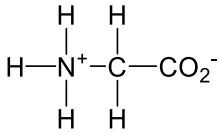
[Total:8]

3. Spider silk is a protein fiber. Major amino acids in the silk proteins are alanine and glycine. Serine and glutamine are also present in significant quantities in some types of silk.

The table below shows the typical amino acids present in spider silk.

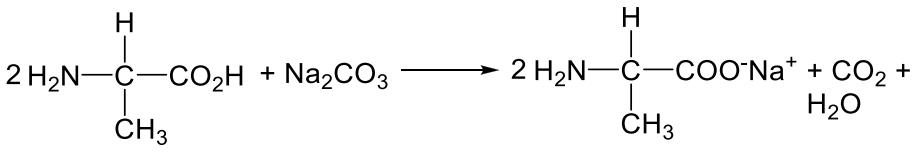
Amino Acid	Formula of side chain (R in $RCH(NH_2)CO_2H$)
Glycine	–H
Alanine	$–CH_3$
Serine	$–CH_2OH$
Glutamine	$–CH_2CH_2CONH_2$

(a) **(i)** Glycine exists as crystalline solids. Draw the zwitterionic structure of glycine and account for the high melting point of glycine. **[2]**



Crystalline solid of glycine has giant ionic lattice structure with strong electrostatic forces of attraction exists between the zwitterions. A lot of energy is required to overcome these strong ionic bonds between zwitterions.

(ii) Write an equation to show the reaction between alanine and aqueous sodium carbonate. **[1]**



(iii) Suggest a chemical test to distinguish between serine and glutamine. **[2]**

Test: $K_2Cr_2O_7(aq)$,$H_2SO_4(aq)$, heat

Observation:

For serine, orange dichromate turns green

For glutamine, orange solution remains

OR

Test: NaOH(aq), **heat**

Observation:

For serine, no pungent gas observed and moist litmus paper remained red.

For glutamine, pungent gas evolved turns **moist** red litmus blue

(b) Natural spider silk has excellent mechanical properties. In a recent study, researchers discovered that graphene-based materials can be used to boost the properties of spider's silk up to three times the strength and ten times the toughness of the unmodified silks.

Graphene is the thinnest material known to exist, yet it is stronger than steel. It is made from only carbon and is a single layer of graphite just one atom thick as shown in Figure **3.1** below.

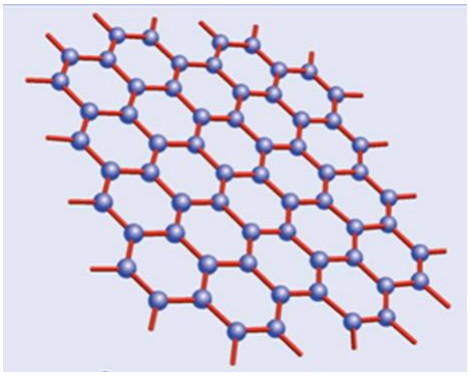


Figure **3.1**

(i) With reference to structure and bonding, explain why graphene is strong. **[1]**

Graphene is an allotrope of C and just like graphite it has giant covalent structure. Each layer of graphene is made of hexagonal "ring" of carbon atoms strongly covalently bonded. A lot of energy is required to break these strong covalent C-C bonds.

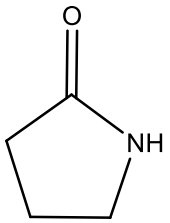
(ii) Since its discovery in 2004, graphene has been widely studied and manufactured as replacement materials for many touchscreen products. Suggest why graphene is a suitable touchscreen material in mobile phones. **[1]**

It is two-dimensional which makes it thin/light/transparent, suitable as touchscreen material.

Or it has high electrical conductivity due to presence of delocalized electrons that serve as mobile charge carriers.

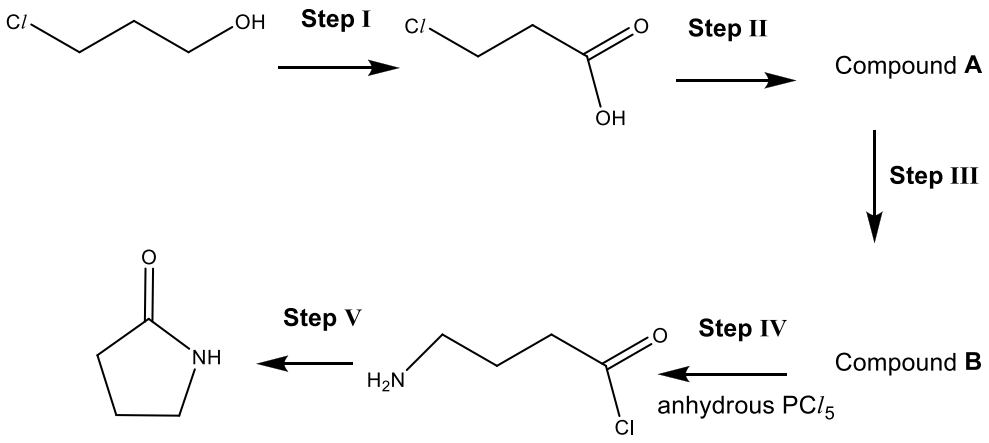
(c) Spiders are excellent treats for colonies of marauding ants. To protect their homes, spiders coat their webs using a chemical called 2-pyrrolidone, which acts as a deterrent to many insects.

2-Pyrrolidone is a 5-membered cyclic amide (commonly known as lactam). It is a colourless liquid that is miscible with water and most common organic solvents.



2-Pyrrolidone

2-pyrrolidone can be synthesised using 3-chloropropan-1-ol as the starting organic compound as shown in the reaction scheme below:



(i) State the type of reaction in **Step V**. **[1]**

(Intramolecular) condensation

(intramolecular) nucleophilic (acyl) substitution)

(ii) Suggest reagents and conditions for **Step I**, **II** and **III**. **[3]**

Step I : .....

Step II : .....

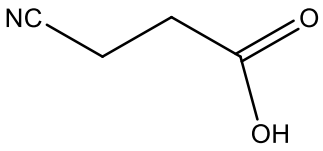
Step III : .....

Step I: $KMnO_4(aq)$, $H_2SO_4(aq)$, heat OR $K_2Cr_2O_7$, $H_2SO_4(aq)$, heat

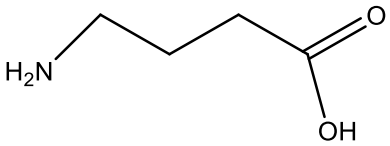
Step II: ethanolic KCN, heat

Step III: H_2, Ni, heat

(iii) Draw the structures of intermediate compounds **A** and **B.** **[2]**



A



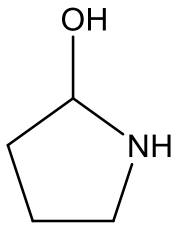
B

(iv) With the aid of an equation, explain why anhydrous condition is necessary for the reaction in **Step IV**. **[1]**

PCl_5 will hydrolyse readily in water as follows:

$PCl_5 + 4H_2O \rightarrow H_3PO_4 + 5HCl$

(v) 2-pyrrolidirol can be synthesised from 2-pyrrolidone.



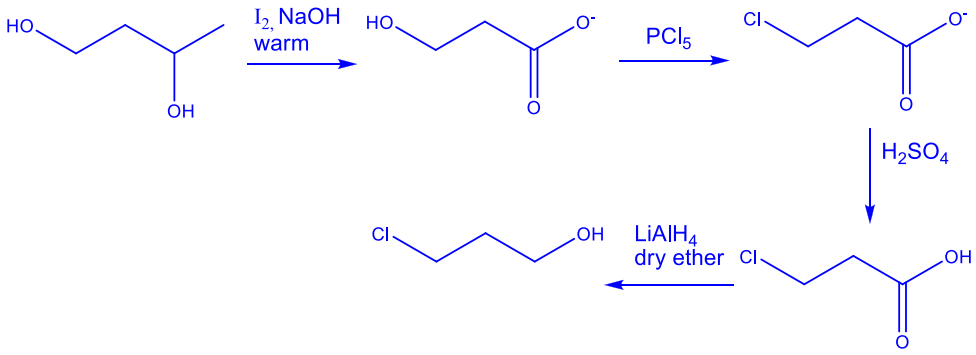
[2]

2-pyrrolidirol

Deduce whether 2-pyrrolidone or 2-pyrrolidirol has a higher pK_b.

2-pyrrolidone is less basic hence a higher pK_b as it is an amide. The lone pair of electrons on N are delocalised over the O-C-N bond and not available for protonation.

(vi) Suggest a synthesis to form 3-chloropropan-1-ol from 1,3-butanediol.



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4 (a) Copper and iron are examples of native metals, which are found pure in its metallic form on its own or in alloys in nature.

Copper and iron form many complexes with a range of colours as shown in the table:

complex	colour	complex	colour
$[Cu(NH_3)_4]^{2+}$	dark blue	$[Fe(H_2O)_6]^{3+}$	yellow
$[Cu(H_2O)_6]^{2+}$	blue	$[Fe(CN)_6]^{3-}$	red

(i) Explain why $[Cu(H_2O)_6]^{2+}$ is blue. **[3]**

In the isolated gas phase, all partially filled 3d orbitals of the transition metal ions are degenerate. In the presence of ligand such as NH_3 or CN^-, the 3d orbitals split into 2 energy level with a small energy gap between them.

An electron from the lower energy d orbital absorbs energy from the visible region (or visible spectrum) of the electromagnetic spectrum with wavelength corresponding to the energy gap is absorbed and get promoted to a higher energy d orbital.

The orange light energy is absorbed and the complementary blue colour is observed.

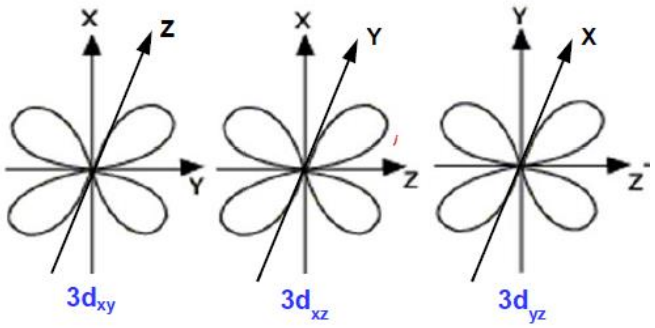
(ii) The oxidation state of iron in both $[Fe(CN)_6]^{3-}$ and $[Fe(H_2O)_6]^{3+}$ complexes is the same. However, they have different colours. Explain this observation. **[1]**

Different ligands (CN^- and H_2O) split the energy gap between the d orbitals differently. Hence different wavelength of light is absorbed and colour reflected is different.

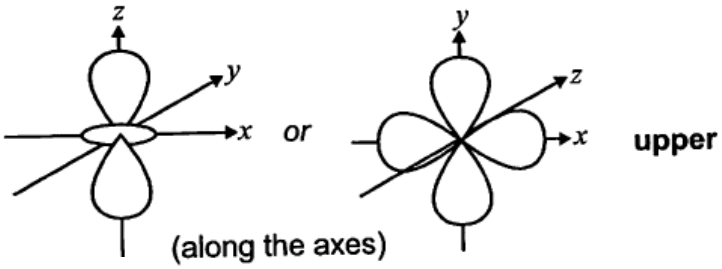
(iii) Draw **fully labelled** diagrams of the following:

- One of the d-orbitals at the lower energy level in $[Cu(H_2O)_6]^{2+}$. Label the diagram "lower".
- One of the d-orbitals at the upper energy level in $[Cu(H_2O)_6]^{2+}$. Label this diagram "upper". **[2]**

Lower: any



Upper: either



3dz^2 3dx^2 – y^2

(b) *Use of the Data Booklet is relevant to this question.*

Fe^{2+} is commonly used to catalyse the reaction between $S_2O_8^{2-}$and I^-. In another similar reaction, peroxodisulfate(VI), $S_2O_8^{2-}$, reacts with tartrate ion, $[CH(OH)CO_2]_2^{2-}$, to give carbon dioxide and methanoate as shown in the following equation.

$$[CH(OH)CO_2]_2^{2-} + 3S_2O_8^{2-} + 2H_2O \rightarrow 2CO_2 + 2HCO_2^- + 6H^+ + 6SO_4^{2-}$$

The reaction is very slow, even when heated, hence a catalyst is used to speed up the reaction.

(i) Explain why the reaction is slow. **[1]**

It involved two negative ions ($S_2O_8^{2-}$ and tartrate ion) which repel each other.

(ii) Given that the standard electrode potential for the following half-equation is

$$2CO_2 + 2HCO_2^- + 6H^+ + 6e^- \rightleftharpoons [CH(OH)CO_2]_2^{2-} + 2H_2O \qquad E^\theta = +0.56\ V$$

Using suitable equations, explain why Mn^{2+} is a suitable catalyst for this reaction. **[2]**

$S_2O_8^{2-} + 2e^- \rightleftharpoons 2SO_4^{2-}$ $E^\theta = +2.01$ V

$Mn^{3+} + e^- \rightleftharpoons Mn^{2+}$ $E^\theta = +1.54$ V

(Catalysed reaction using Mn^{2+})

$2Mn^{2+} + S_2O_8^{2-} \rightarrow 2Mn^{3+} + 2SO_4^{2-}$

$E^{\theta}_{cell} = 2.01 - (1.54) = + 0.47\ V$

$6Mn^{3+} + [CH(OH)CO_2]_2^{2-} + 2H_2O \rightarrow 6Mn^{2+} + 2CO_2 + 2HCO_2^- + 6H^+$

$E^{\theta}_{cell} = 1.54 - 0.56 = + 0.98\ V$

Alternative answer:

$S_2O_8^{2-} + 2e^- \rightleftharpoons 2SO_4^{2-}$ $\quad E^{\theta} = +2.01\ V$

$MnO_4^- + 8H^+ + 5e^- \rightleftharpoons Mn^{2+} + 4H_2O$ $\quad E^{\theta} = +1.52\ V$

$5S_2O_8^{2-} + 2Mn^{2+} + 8H_2O \rightarrow 10SO_4^{2-} + 2MnO_4^- + 16H^+$

$E^{\theta}_{cell} = 2.01 - (1.52) = + 0.49\ V$

$6MnO_4^- + 18H^+ + 5[CH(OH)CO_2]_2^{2-} \rightarrow 6Mn^{2+} + 14H_2O + 10CO_2 + 10HCO_2^-$

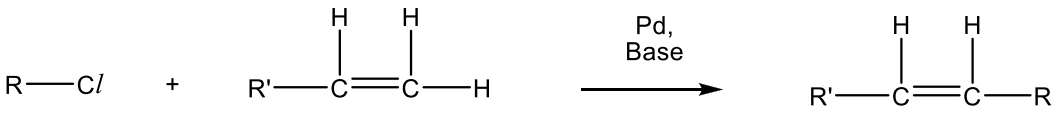
$E^{\theta}_{cell} = 1.52 - 0.56 = + 0.96\ V$

(iii) State the property of transition metal ions that enable them to function as a homogenous catalyst in the reaction. **[1]**

Transition metal ions are able to exhibit a variety of oxidation states due to the similar energy of the 3d and 4s orbitals and hence both are able to be shared or lost.

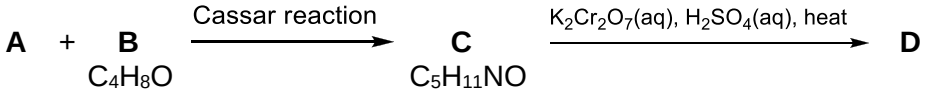
(c) Palladium is a transition element that is used as a catalyst in the Cassar reaction.

The Cassar reaction is a type of substitution reaction between an alkyl chloride and a terminal alkene in the presence of a base and a palladium catalyst.



[R can be a substituted alkyl group containing –OH, –NH_2, –NO_2 –COOH]

The following scheme shows the synthesis of **D** using Cassar reaction in one of the steps.



The table below shows the observations when **A**, **B** and **D** reacts with various reagents.

reaction		observations
1	**A** + HC*l*(aq)	colourless solution
2	**B** + Br_2(aq)	colourless solution
3	**D** + Na_2CO_3(aq)	Gas forms white ppt with $Ca(OH)_2$

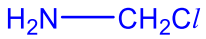
(i) Name the functional group that reaction **1** shows to be present in **A** **[1]**

(Primary) amine

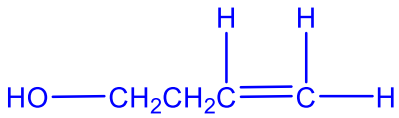
(ii) State the type of reaction that takes place in reaction **2** and name the functional group present in **B** **[1]**

Electrophilic addition. Alkene

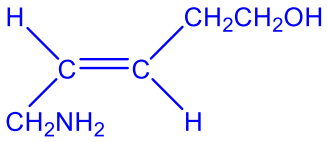
(iii) **C** is able to exhibit cis-trans isomerism. Draw the structures of **A**, **B**, **C** and **D**. **[4]**



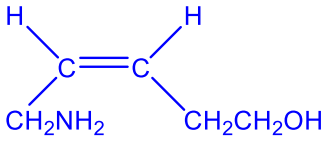
Compound A



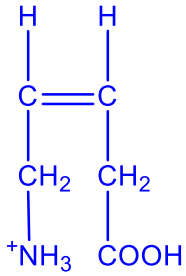
Compound B



Trans isomer of compound C EITHER

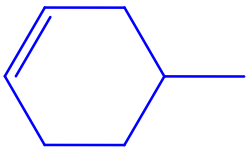


Cis isomer of compound C



Compound D

(iv) Draw the structure of the product when $CH_3CH(CH_2Cl)CH_2CH_2CH{=}CH_2$ undergoes the Cassar reaction. **[1]**



(d) A solution containing Cu^{2+} and Zn^{2+} can be separated by selective precipitation.

The reagent used is hydrogen sulfide which behaves as a dibasic (diprotic) weak acid when in aqueous solution.

Aqueous hydrogen sulfide behaves as a dibasic acid.

$H_2S\,(aq) \rightleftharpoons H^+\,(aq) + HS^-\,(aq) \quad K_{a1} = 8.9 \times 10^{-8}\ mol\ dm^{-3}$

$HS^-\,(aq) \rightleftharpoons H^+\,(aq) + S^{2-}\,(aq) \quad K_{a2} = 1.2 \times 10^{-13}\ mol\ dm^{-3}$

Metal sulfides are precipitated by the following reaction.

$$M^{2+}(aq) + S^{2-}(aq) \rightleftharpoons MS(s)$$

Relevant K_{sp} values are given in the table below.

Salt	K_{sp} / mol^2 dm^{-6}
CuS	6.3×10^{-36}
ZnS	1.6×10^{-24}

(i) Given that a solution contains 0.0010 mol dm^{-3} Zn^{2+} and 0.0010 mol dm^{-3} Cu^{2+}, determine the maximum sulfide concentration for each cation so that no precipitation occurs. **[1]**

$[S^{2-}]_{max}$ for ZnS= $\frac{1.6 \times 10^{-24}}{0.0010}$ = 1.6 x 10^{-21} mol dm^{-3}

$[S^{2-}]_{max}$ for CuS = $\frac{6.3 \times 10^{-36}}{0.0010}$ = 6.3 x 10^{-33} mol dm^{-3}

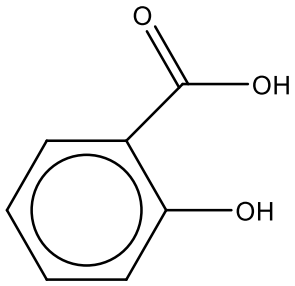
(ii) Given that $[H^+] = \sqrt{\frac{K_{a1}K_{a2}[H_2S]}{[S^{2-}]}}$ and using your answer in **(d)(i)**, calculate the maximum pH that must be maintained to separate Zn^{2+} and Cu^{2+} ions, given that the concentration of H_2S in the solution is 0.0010 mol dm^{-3}. **[2]**

K_{a1} K_{a2} = 1.068 × 10^{-20} mol^2 dm^{-6}

$[H^+] = \sqrt{\frac{1.068 \times 10^{-20} \times 0.0010}{1.6 \times 10^{-21}}}$ = 0.08170 mol dm^{-3}

pH = – log 0.08170 = 1.09

(e) The Trinder spot test is a diagnostic test used in medicine to determine exposure to salicylates, in particular, salicylic acid. The test involved the Trinder reagent which is mixed with a patient's urine. A coloured complex is formed if salicylates are present.



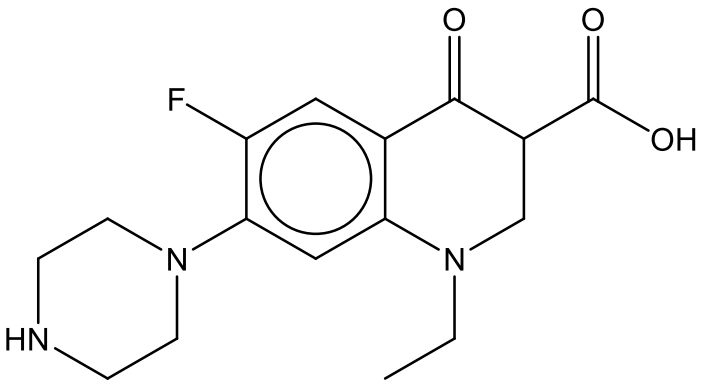
Salicylic acid

(i) Suggest the compound that is present in the Trinder reagent added to salicylic acid and state the observation when if the test is positive. **[2]**

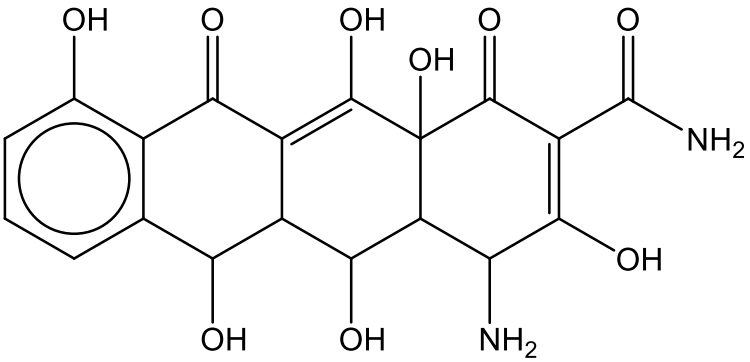
Neutral aq $FeCl_3$. [1]

Violet [1] coloration is observed.

Another variation of the Trinder spot test has also been used to determine the presence of norfloxacin and oxytetracycline.



norfloxacin



oxytetracycline

(ii) State the number of stereoisomers present in oxytetracycline. **[1]**

……..……

$2^6 = 64$

(iii) Suggest a chemical test to distinguish between oxytetracycline and norfloxacin. **[2]**

……..……

……..….

$K_2Cr_2O_7(aq)$, $H_2SO_4(aq)$, heat. Orange $K_2Cr_2O_7$ turns green for oxytetracycline but remained orange for norfloxacin.

Or

Na_2CO_3(aq). Effervescence observed and gas evolved formed white ppt in limewater for norfloxacin but no effervescence for oxytetracycline.

Or

Neutral $FeCl_3$ (aq). Violet colouration for oxytetracycline but no violet colouration for norfloxacin.

[Total:25]

5 Sodium alginate is a natural polymer extracted from brown seaweed. Figure **5.1** shows the simplified representation of a sodium alginate polymer.

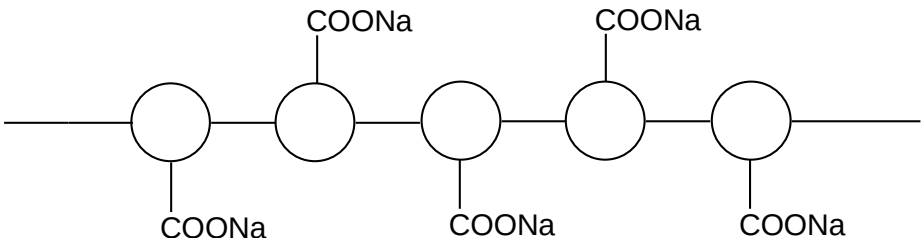


Figure **5.1** : simplified representation of sodium alginate polymer

In food chemistry, sodium alginate serves as a gel-forming agent as it can react with calcium salts to make “popping boba” in the bubble tea industry. This process is commonly known as spherification.

During spherification, a solution of sodium alginate is added to a solution of calcium salt. Na^+ ions are exchanged with Ca^{2+} ions and the cross linked calcium alginate polymers forms as shown in Figure **5.2**.

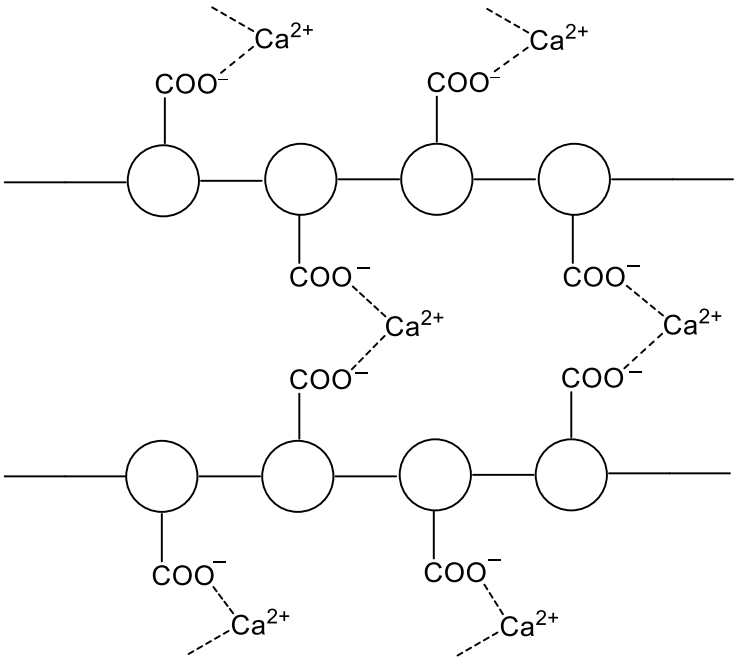


Figure **5.2**: simplified representation of cross-linked calcium alginate polymer.

(a) **(i)** Cross-linking is the general term for the process of forming chemical bonds to join two polymer chains together. Explain, in terms of bonding, why Ca^{2+} ions are able to cross-link the alginate polymers but Na^{+} ions are unable to do so. **[1]**

The divalent Ca^{2+} ions are able to cross-link the alginate polymers because they can form two ionic bonds, while monovalent Na^{+} ions can only form one bond. [1]

(ii) Explain why calcium alginate has low solubility in water. **[1]**

The energy released from the ion-dipole interactions between calcium alginate and the water molecules [1] is insufficient to overcome the strong ionic bonds between calcium ions and alginate ions and hydrogen bonds between the water molecules.[1]

(b) During spherification, the pH of the flavoured liquid used is important. Below a pH of 3.6, sodium alginate tends to react and the resultant solution will thicken which makes it difficult to form spheres.

Although Ca^{2+} is crucial in helping the alginate to gel, excess Ca^{2+} present can also cause the liquid to gel prematurely which is undesirable.

Table **5.3** shows the pH of various flavoured liquids.

Table **5.3**

Flavoured Liquid	pH
cranberry juice	2.3
blueberry juice	3.4
tomato juice	4.6
watermelon juice	5.2
aloe vera juice	6.1

(i) Cranberry juice is not suitable for spherification to work. **[2]**

Suggest the type of reaction that takes place when sodium alginate is added to cranberry juice and hence explain why spherification will not occur in presence of cranberry juice.

Acid-base reaction.[1]

The sodium alginate will be protonated and converted to the covalent conjugate acid molecule (alginic acid). Without Na^+, ion-exchange does not take place readily with Ca^{2+} to make the cross-linked polymer. [1]

(ii) A bubble tea shop wanted to make a "popping boba" by mixing 250 cm^3 of aloe vera juice with 300 cm^3 of blueberry juice. By determining the pH of the mixture, deduce if the spherification would happen. **[3]**

$[H^+]_{aloe\ vera} = 10^{-6.1} = 7.943 \times 10^{-7}$ mol dm^{-3}

Amt of H^+ in aloe vera = $7.943 \times 10^{-7} \times 250/1000$

$= 1.986 \times 10^{-7}$ mol

$[H^+]_{blueberry} = 10^{-3.4} = 3.981 \times 10^{-4}$ mol dm^{-3}

Amt of H^+ in blueberry juice = $3.981 \times 10^{-4} \times 300/1000$

$= 1.194 \times 10^{-4}$ mol [1 for both amount of H^+]

$[H^+]_{mixture} = (1.986 \times 10^{-7} + 1.194 \times 10^{-4})/0.55 = 2.175 \times 10^{-4}$ mol dm^{-3}

pH = 3.66 [1] > 3.6

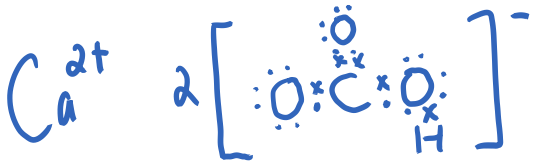
Since pH > 3.6, spherification would happen. [1]

(iii) Hard water is water that has a high mineral content. It is formed when water percolates through deposits of limestone which are made up of calcium and magnesium carbonates and bicarbonates. **[1]**

Suggest why spherification does not work well in hard water.

The presence of high concentration of calcium in hard water will solidify/gel in the sodium alginate solution **immediately/prematurely** to form calcium alginate. [1]

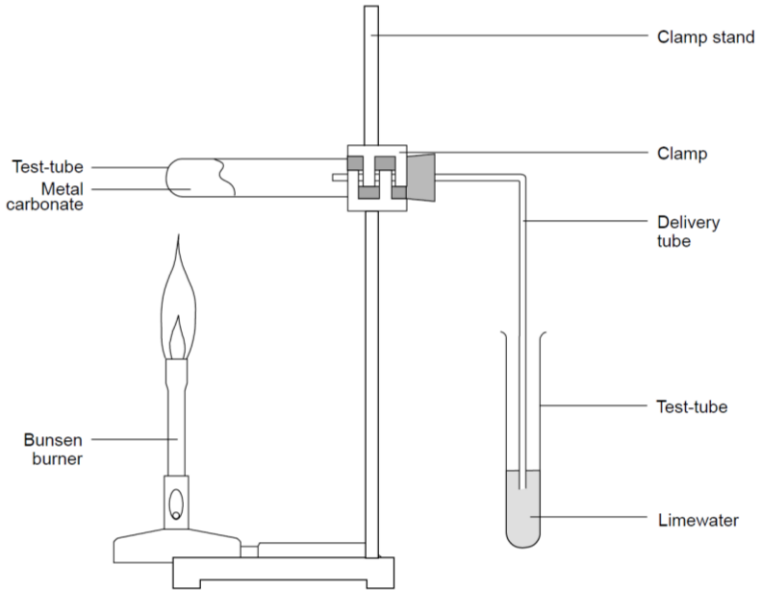
(iv) Draw the dot-cross diagram for calcium bicarbonate $Ca(HCO_3)_2$. **[2]**



[1] for ionic structure

[1] for HCO_3^{2-}

(c) A student set up the following experiment to investigate the thermal stability of magnesium and calcium carbonates:



Each of the metal carbonate is heated strongly for 5 min and the time taken for a white precipitate to form in limewater is recorded in the following table:

Metal carbonate	Time taken (s)
X	70
Y	40

(i) What is the identity of **X** and **Y**? **[1]**

X: Calcium carbonate

Y: Magnesium carbonate

(ii) Explain the results. **[2]**

Magnesium carbonate decomposes more easily and releases CO_2 faster to form white ppt in limewater because size of Mg^{2+} is smaller than Ca^{2+} but charge remains. Hence charge density of Mg^{2+} is larger than Ca^{2+} [1]. Electron cloud of carbonate in $MgCO_3$ will be distorted to a larger extent/polarising power of Mg^{2+} is more, weakening the C-O bond more [1].

[Total:13]