Anglo-Chinese Junior College

JC2 Preliminary Examinations
Higher 2

A Methodist Institution
(Founded 1886)

CANDIDATE NAME	SUGGESTED SOLUTIONS	FORM CLASS	
TUTORIAL CLASS		INDEX NUMBER	

CHEMISTRY

9729/02

Paper 2 Structured Questions

22 August 2023
2 hours

Candidates answer on the Question Paper.
Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your index number and name in the spaces at the top of this page.
Write in dark blue or black pen.
You may use an HB pencil for any diagrams, graphs or rough working.
Do not use staples, paper clips, glue or correction fluid.

Answer **all** questions in the spaces provided on the Question Paper.
The use of an approved scientific calculator is expected, where appropriate.

A Data Booklet is provided.

The number of marks is given in brackets [ ] at the end of each question or part question.

For Examiners' use only	
1	/ 15
2	/ 9
3	/ 21
4	/ 14
5	/ 16
Total	/ 75

This document consists of **19** printed pages and **1** blank page.

1 This question examines the chemistry of Group 17 elements and their halides.

(a) **A_2** and **B_2** are halogens, and they are known to be more soluble in organic solvents.

In an experiment, excess **A_2** was mixed with $Na_2S_2O_3(aq)$. When cyclohexane was added, two immiscible layers were observed which were later separated using a separatory funnel. An orange-red organic layer was obtained, and the aqueous layer was divided into two portions.

To one portion of the aqueous layer, a solution of $Ba(NO_3)_2$ was added and a white precipitate formed which is insoluble in excess dilute nitric acid.

To another portion of the aqueous layer, **B_2**(aq) was added and shaken. When $CHCl_3$ was added, a purple organic layer was obtained.

(i) State the identities of **A_2** and **B_2**.

A_2: Bromine **B_2**: Iodine [1]

(ii) Write a balanced ionic equation for the reaction between $Na_2S_2O_3$ and **A_2**.

$4Br_2(l) + S_2O_3^{2-}(aq) + 5H_2O(l) \rightarrow 2SO_4^{2-}(aq) + 8Br^{-}(aq) + 10H^{+}(aq)$ [1]

(iii) Explain why halogens are more soluble in organic solvents than in water, in terms of the energy changes involved.

The energy evolved from forming id-id interactions btw halogen and organic solvent molecules is able to compensate the energy that is needed to overocome the id-id interactions btw halogen molecules and id-id interactions btw organic solvent molecules. Hence, it is energetically favourable.

Water is polar, energy released from forming id-id interactions btw water molecules and halogens is insufficient to overcome the energy needed to break the stronger hydrogen bonds btw water molecules.

[2]

(b) In another reaction, halogens can react with alkanes to form mono-substituted products. An example is the reaction of chlorine with 2-methylpentane.

(i) Alkanes are generally unreactive. Explain why this is so.

The C–H bonds are non-polar and very strong. [1]

(ii) This reaction is seldom used for synthesis as there are many associated problems. Firstly, several isomeric products are formed. The relative ratio of the isomeric products may be more accurately determined if relative rates of abstraction of H atoms are considered.

The relative rates of abstraction of H atoms are shown in Table 1.1.

Table 1.1

type of H atoms	relative rate of abstraction
primary	1
secondary	4
tertiary	6

By examining the difference in stability of the intermediates formed when different types of H atom are abstracted, explain the trend in the relative rate of abstraction.

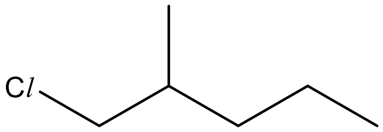
Tertiary radical is the most stable followed by secondary radical followed by primary radical. The tertiary radical is the most stable as it contains the most electron donating alkyl groups which help to stabilise the electron-deficient radical centre. Hence, it is abstracted more easily/faster.

……………………………………………………………………………………………

……………………………………………………………………………………………

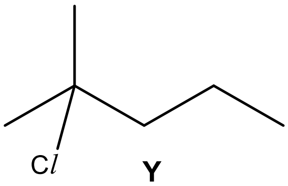
…………………………………………………………………………………… [2]

(iii) Predict the ratio of the following two products **X** and **Y**, from the reaction of chlorine with 2-methylpentane, taking into account the relative rates of abstraction given in Table 1.1. Explain your reasoning.

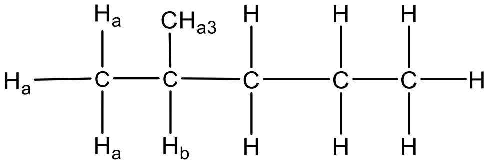


X

and



Y



$H_a{-}C(H_a)_2{-}C(CH_{a3})(H_b){-}CH_2{-}CH_2{-}CH_3$

6 possible (primary) hydrogens (H_a) can be substituted to form **X**
1 possible (tertiary) hydrogen (H_b) can be substituted to form **Y**

Assuming equal probability of abstraction,
Ratio of **X**:**Y** = 6:1
However, since a tertiary H is abstracted 6 times faster than a primary H,
Ratio of **X**:**Y** = 6:1 x 6 = 1:1

[2]

(iv) Describe how you can distinguish between compounds **X** and **Y** in **(b)(iii)** by chemical means.

Add NaOH(aq) to both compounds and heat (to form alcohols) followed by $KMnO_4$, NaOH(aq) and heat

Observation for **X**: Purple $KMnO_4$ is decolourised and brown ppt of MnO_2 is formed.

Observation for **Y**: Purple $KMnO_4$ remains

[2]

(v) Another problem of the reaction is poly-substitution.

Suggest the condition that will give rise to formation of poly-substituted products.

Excess chlorine or limited alkane [1]

(c) Hydrogen halides are dissociated at high temperatures according to the following equation:

$$2HX(g) \rightleftharpoons H_2(g) + X_2(g)$$

The approximate K_c values for the above equilibrium at various temperatures for the respective hydrogen halides are shown in Table 1.2.

Table 1.2

temperature / °C	K_c values for dissociation of HX		
	HC*l*	HBr	HI
800	10^{-13}	10^{-9}	10^{-5}
1000	10^{-10}	10^{-7}	10^{-4}
1200	10^{-9}	10^{-5}	10^{-3}
1400	10^{-7}	10^{-4}	10^{-2}

Using the information in Table 1.2 and relevant data from the *Data Booklet*, describe and explain the relative thermal stability of the hydrogen halides.

From the table, it is observed that at each temperature, decreasing order of K_c value is HI > HBr > HC*l*.

Since the larger the K_c values, the higher the degree of dissociation of HX, the order of degree of dissociation is HI > HBr > HC*l*.

From the Data Booklet, based on decreasing bond strength HC*l* > HBr > HI as shown:

	H – C*l*	H – Br	H – I
bond energy (kJ mol^{-1})	431	366	299

H–X bond energy decreases from HC*l* to HI due to increasing atomic size of X atom leading to decreasing H–X bond strength as degree of effective overlap between H and X atoms decreases from C*l* to I.

The H–I bond thus requires the least amount of energy to break, causing HI to be least thermally stable followed by HBr and then HC*l*.

Hence, order of thermal stability is HC*l* > HBr > HI.

[3]

[Total: 15]

2 **(a)** Write the electronic configuration of Mg^{2+} and explain why the ionic radius of Mg^{2+} is smaller than the atomic radius of Mg.

electronic configuration of Mg^{2+} ……$1s^2\ 2s^2\ 2p^6$…… [1]

explanation …… Mg^{2+} has **one less** occupied **principal quantum shell/ electron shell** than that of its parent atom Mg.

…… [1]

(b) Table 2.1 gives the melting points, in °C, of the fluorides and chlorides of two elements in Period 3.

Table 2.1

	magnesium	silicon
fluoride	1261	–90
chloride	714	–70

Explain, in terms of structure and bonding, the differences in melting point between

(i) $MgCl_2$ and $SiCl_4$

$MgCl_2$ has a giant ionic structure. $SiCl_4$ has a simple molecular structure. Large amount of energy is required to overcome the strong ionic bonds between Mg^{2+} and Cl^- as compared to the weak id-id interactions between $SiCl_4$ molecules. Thus, $MgCl_2$ has a higher melting point than $SiCl_4$.

…… [2]

(ii) $MgCl_2$ and MgF_2

Both $MgCl_2$ and MgF_2 have giant ionic structures. MgF_2 has a more exothermic lattice energy as the F^- is smaller in size than Cl^-. Hence, more energy is required to overcome the stronger ionic bonds between Mg^{2+} and F^- than that between Mg^{2+} and Cl^-. Thus, MgF_2 has a higher melting point than $MgCl_2$.

…… [1]

(c) The reaction scheme in Fig. 2.2 shows how a sample of anhydrous magnesium chloride is converted into a solution containing compound **F**.

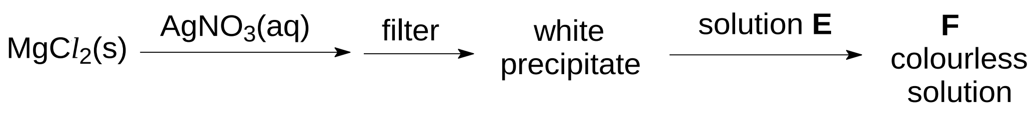


Fig. 2.2

Upon analysis, **F** is found to contain the following percentage composition by mass:

Ag, 52.6%; C*l*, 17.3%; N, 13.6%; C, 11.7%; H, 4.8%.

(i) Determine the empirical formula of **F** and hence suggest a possible identity for **F**.

$$\text{Molar ratio of Ag : Cl : N : C : H} = \frac{52.6}{107.9} : \frac{17.3}{35.5} : \frac{13.6}{14.0} : \frac{11.7}{12.0} : \frac{4.8}{1.0}$$

$$= 0.487 : 0.487 : 0.971 : 0.975 : 4.8$$

$$= 1 : 1 : 2 : 2 : 10$$

Hence the empirical formula of **F** is $AgClN_2C_2H_{10}$.
F is $[Ag(CH_3NH_2)_2]Cl$.

[2]

(ii) State the observation when excess dilute nitric acid is added to **F** and write a balanced equation for this reaction.

When dilute nitric acid is added to **F**, a white precipitate of AgC*l* forms.

$[Ag(CH_3NH_2)_2]Cl(aq) + 2HNO_3(aq) \longrightarrow AgCl(s) + 2CH_3NH_3^+(aq) + 2NO_3^-(aq)$
Or
$[Ag(CH_3NH_2)_2]^+ + Cl^- + 2H^+(aq) \longrightarrow AgCl(s) + 2CH_3NH_3^+(aq)$

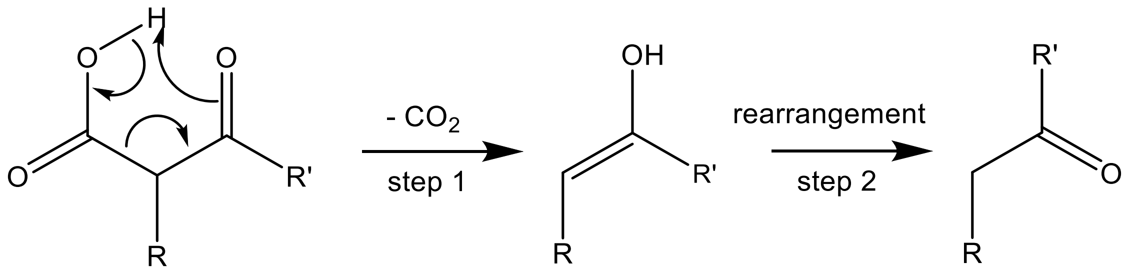
[2]

[Total: 9]

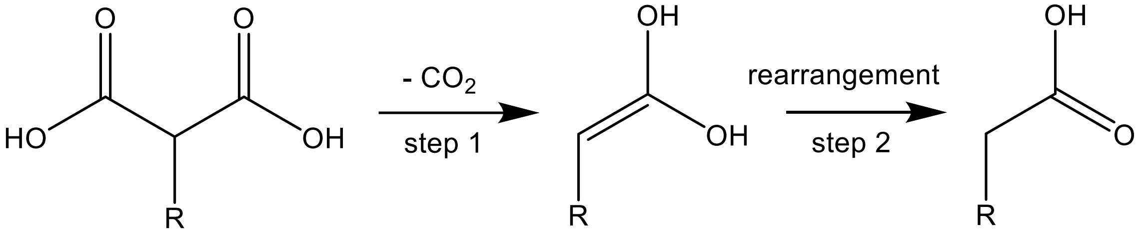
3 Decarboxylation is one of the oldest known organic reactions. It is a chemical reaction that releases carbon dioxide and requires a carbonyl or carboxylic acid to be two atoms away from a carboxylic acid.

Two examples of decarboxylation are shown below:

Example 1:

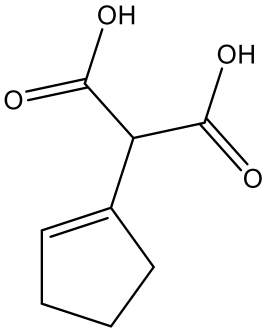


Example 2:

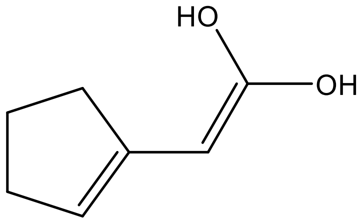


(a) **(i)** Draw the curly arrows to illustrate the mechanism for step 1 in the diagram above for **Example 1**.

(ii) Draw the structure of the intermediate when compound **J** undergoes decarboxylation.

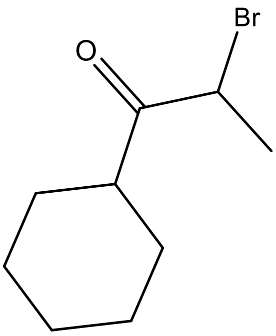


J



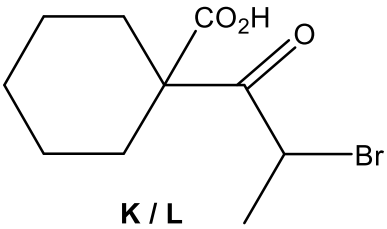
intermediate

(iii) Two different keto-acids, **K** and **L**, can undergo decarboxylation to give **M**.

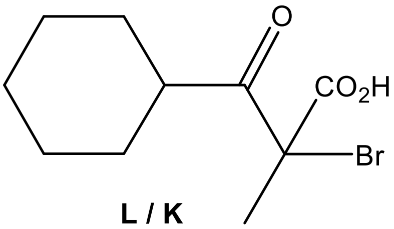


M

Suggest possible structures of **K** and **L**.

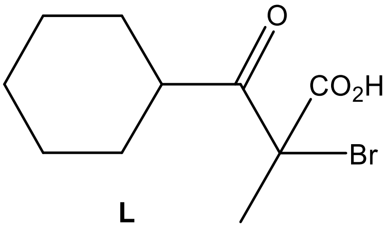


K / L



L / K

(iv) Given that **L** is more acidic than **K**, suggest the structure of **L**. Explain your answer.



L

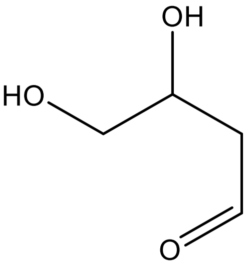
The conjugate base of L is more stable than that of K.

The distance between the electron-withdrawing bromine and the $-CO_2^-$ is larger in the conjugate base of K than in the conjugate base of L.

Therefore, L is the stronger acid.

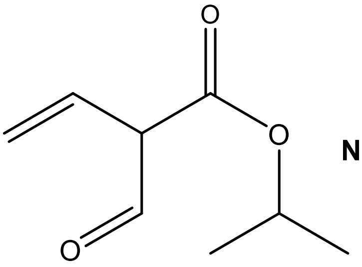
[2]

(b) Compound **N** has the molecular formula $C_8H_{12}O_3$. When heated with dilute acid, it produces **O**, C_3H_8O and **P**, $C_5H_6O_3$. **O** gives a yellow precipitate when warmed with aqueous alkaline iodine. **P** undergoes decarboxylation to give **Q**. When **Q** is reacted with cold alkaline $KMnO_4$, **R** is produced.

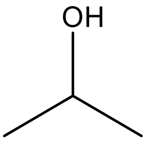


R

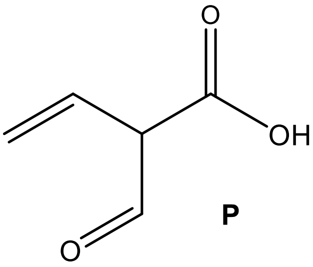
(i) Draw the structures of **N**, **O**, **P** and **Q.**



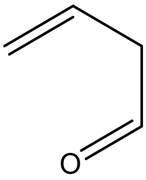
N



O



P



Q

(ii) Write the balanced ionic equation for the reaction between **R** and an alkaline solution of copper(II) tartrate (Fehling's reagent).
You may use RCHO to represent **R**.

$RCHO + 2Cu^{2+} + 5OH^{-} \longrightarrow RCO_2^{-} + Cu_2O + 3H_2O$ [1]

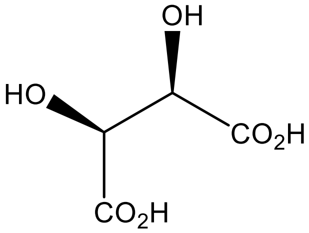
(iii) Suggest the function of tartrate in Fehling's reagent.

It is to form a complex with Cu^{2+}, otherwise $Cu(OH)_2$ will be precipitated out and affect the experimental observations.

[1]

(iv) Tartrate is the di-anionic form of tartaric acid. The condensed structural formula of tartaric acid is $HO_2CCH(OH)CH(OH)CO_2H$. Tartaric acid exists in three stereoisomeric forms.

Draw the stereoisomer of tartaric acid which has no effect on plane-polarised light.



[1]

(c) Prussian Blue (PB) played an important role in the historical development of dyes. PB has high colouring ability and has been widely used to colour paints, inks, textiles, and other commercial products.

There are various members in the family of pigments containing iron(II), iron(III) and cyanide – for instances, Turnbull's Blue (TB), Prussian Brown (PBr) and William White (WW).

(i) The typical method for the preparation of PB is by the reaction of ferric cations, Fe^{3+}, with potassium hexacyanoferrate(II), $K_4[Fe(CN)_6]$.
The chemical equation below is **not** balanced.

$$Fe^{3+} + Fe(CN)_6^{4-} \longrightarrow PB$$

State the molecular formula of PB, given that this form of PB is an uncharged compound which does not contain K^+, and its formula mass is 858.6.

$Fe_4[Fe(CN)_6]_3$
.... [1]

(ii) The typical method for the preparation of WW is by the reaction of ferrous cations, Fe^{2+}, with potassium hexacyanoferrate(II), $K_4[Fe(CN)_6]$.
The chemical equation below is **not** balanced.

$$K^+ + Fe^{2+} + Fe(CN)_6^{4-} \longrightarrow WW$$

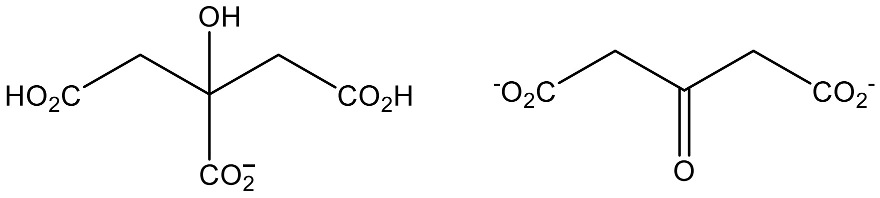
State the molecular formula of WW, given that this form of WW is an uncharged compound, and its formula mass is 345.8.

$K_2Fe[Fe(CN)_6]$
.... [1]

In the presence of citrate, during irradiation, especially those involving ultra-violet radiation, the Fe(III) in PBr is partially reduced, producing PB. If the exposure time is too long, PB will be further converted into WW.

The citrate ion functions as the reducing agent in both stages, undergoing decarboxylation to form 3-oxopentanedioate.

The structural formulae of citrate and 3-oxopentanedioate are given below.



citrate $C_6H_7O_7^-$

3-oxopentanedioate $C_5H_4O_5^{2-}$

(iii) Write the half-equation of the conversion of citrate to 3-oxopentanedioate. You may use their molecular formulae to represent them.

$C_6H_7O_7^- \longrightarrow 3H^+ + CO_2 + 2e^- + C_5H_4O_5^{2-}$ [1]

(d) Sodium nitroprusside, $Na_2[Fe(CN)_5NO]$, is used to treat hypertension.

The nitroprusside complex, $[Fe(CN)_5NO]^{2-}$, is formed in the reaction between $[Fe(CN)_6]^{4-}$, nitrite and water, in which water functions as a Brønsted acid. This reaction is non-redox.

(i) Define the term *Brønsted acid*.

A species which donates a proton/H^+. [1]

(ii) Write the balanced ionic equation of the synthesis of nitroprusside from hexacyanoferrate(II).

$Fe(CN)_6^{4-} + H_2O + NO_2^- \longrightarrow [Fe(CN)_5NO]^{2-} + CN^- + 2OH^-$ [1]

(e) Explain why transition metal compounds are often coloured.

When ligands approach a transition metal ion, the degenerate 3d orbitals split into two non-degenerate levels. When light of a certain wavelength in the visible region of the electromagnetic spectrum corresponding to the energy gap is absorbed, an electron in the lower level is promoted to the higher level. The colour seen is complementary to the wavelength of light absorbed.

[3]

[Total: 21]

4 This question is about silver and its compounds.

The solubility of silver(I) chloride, AgCl, at different concentrations of Cl^- is expressed by the two equilibria.

equation 1 $AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$ $K_1 = 1.8 \times 10^{-10}$ mol^2 dm^{-6}
equation 2 $Ag^+(aq) + 2Cl^-(aq) \rightleftharpoons AgCl_2^-(aq)$ $K_2 = 1.8 \times 10^{5}$ mol^{-2} dm^{6}

Fig. 4.1 shows the solubility of AgCl against concentration of Cl^-.

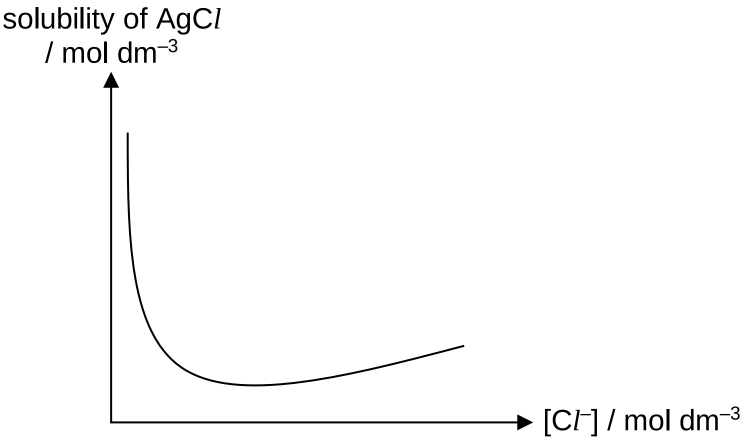


Fig. 4.1

(a) Use the information and equilibria concepts to explain the shape of the graph in Fig. 4.1.

At low concentrations of Cl^-, as its concentration increases, equilibrium position of equation 1 will shift left to counteract the effects of the change and solubility decreases.

As concentration of Cl^- increases, equilibrium in equation 2 dominates and shifts position of equilibrium to the right to counteract the effects of the change and solubility increases.

[2]

(b) **(i)** Write an expression for the equilibrium constant, K_2.

$$K_2 = \frac{[AgCl_2^-]}{[Ag^+][Cl^-]^2}$$

[1]

(ii) Hence, use equations 1 and 2 to show that the concentration of $AgCl_2^-$ is expressed as $[AgCl_2^-] = 3.24 \times 10^{-5} \times [Cl^-]$.

$[AgCl_2^-] = K_2 [Ag^+] [Cl^-]^2$
$= K_2 K_1 [Cl^-]$
$= (1.8 \times 10^5)(1.8 \times 10^{-10}) [Cl^-]$
$= 3.24 \times 10^{-5} \times [Cl^-]$

[1]

(c) The solubility of AgC*l* is expressed as the sum of the concentrations of Ag^+ and $AgCl_2^-$.

Solubility of AgC*l* is lowest when $[Ag^+] = [AgCl_2^-]$.

(i) Use your answer in **(b)(i)** to calculate the concentration of Cl^- when $[Ag^+] = [AgCl_2^-]$.

$K_2 = \frac{[AgCl_2^-]}{[Ag^+][Cl^-]^2}$

$[Cl^-] = \sqrt{\frac{1}{K_2}}$

$[Cl^-] = \sqrt{\frac{1}{1.8\times10^5}}$

$[Cl^-] = 0.00236 \text{ mol dm}^{-3}$

[2]

(ii) Hence, calculate the lowest solubility of AgC*l*.

$[Ag^+]\,[Cl^-] = 1.8 \times 10^{-10}$

$[Ag^+] = 1.8 \times 10^{-10} \div 0.00236$

$[Ag^+] = 7.63 \times 10^{-8}$

Lowest solubility of AgC*l* $= 2 \times 7.63 \times 10^{-8}$

$= 1.53 \times 10^{-7} \text{ mol dm}^{-3}$

[2]

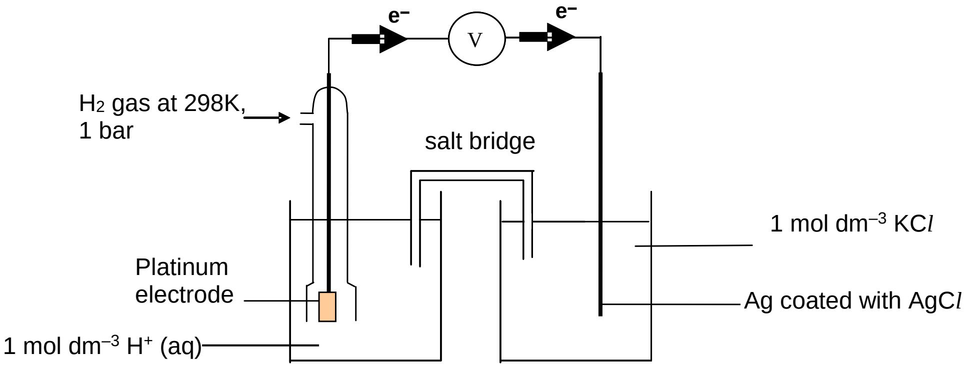
(d) One of the uses of silver(I) chloride is found in the silver chloride electrode used in electrochemical measurements. The electrode consists of a metallic silver wire coated with a thin layer of silver(I) chloride in aqueous potassium chloride and its standard electrode potential is +0.23 V when measured against the standard hydrogen electrode.

(i) Define the term *standard electrode potential*.

It is defined as the potential difference between a standard hydrogen electrode

and a half-cell under standard conditions. [1]

(ii) Draw a labelled diagram to illustrate the setup used to measure the standard electrode potential of the silver chloride electrode. Include the direction of electron flow.



standard condition: temp, pressure, and concentration
identity of electrodes and electrolytes
salt bridge + electron flow

[3]

(iii) Use relevant information in the *Data Booklet* to calculate the standard electrode potential of the $Ag^+(aq)\,|\,Ag(s)$ half-cell when referenced against the silver chloride electrode.

$E^\ominus = +0.80 - (+0.23) = +0.57$ V

[1]

(iv) Suggest a reason why the silver chloride electrode is more commonly used as a reference electrode than the standard hydrogen electrode.

Easier to setup c.f. SHE where H_2 gas needs to be supplied under pressure. or

Silver/Silver chloride is cheaper than platinum. or

Hydrogen gas is flammable and may be a safety hazard. or

[1]

Accept any other logical explanation.

[Total: 14]

5 The World Health Organisation has recently classified aspartame, an artificial sweetener, as a possible carcinogen. Even though it has the same energy and caloric content by mass compared with table sugar (4 kcal g^{-1}), it is 200 times as sweet and is thus beneficial for use as a sugar substitute in foods and beverages.

A typical canned soda contains 40 g of table sugar.

(a) Drinks sweetened with aspartame to the same sweetness as table sugar are commonly marketed as "zero calories".

Show, with calculations, that the caloric content, in kcal, in a canned soda sweetened with aspartame is negligible. Leave your answer to 1 decimal place.

Caloric content = $\frac{40\times 4}{200}$ = 0.8 kcal

[1]

(b) The acceptable daily intake of aspartame was determined to be 40 mg per kg of body weight per day.

(i) Calculate the maximum number of canned sodas sweetened with aspartame a man weighing 72 kg can consume a day to stay within the acceptable daily intake.

Number of cans = $\frac{0.040\times 72}{\frac{40}{200}}$ = 14.4 ≈ 14 cans (round down for max no.)

[1]

The daily recommended calorie intake for a man is 2400 kcal.

(ii) The man considered consuming the number of canned sodas sweetened with aspartame calculated in **(b)(i)** to meet his daily recommended calorie intake.

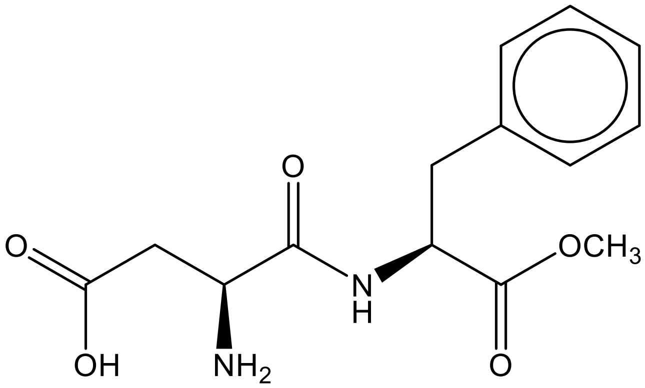
Evaluate, with calculations, if he will meet his daily recommended calorie intake.

Calories consumed = 14 x 0.8 = 11.2 kcal < 2400 kcal

He will not meet his daily recommended calorie intake.

[1]

Aspartame is a methyl ester of a dipeptide consisting of two amino acids, aspartic acid, and phenylalanine. Like many other peptides, aspartame is prone to hydrolysis, and this takes place in the stomach as well.

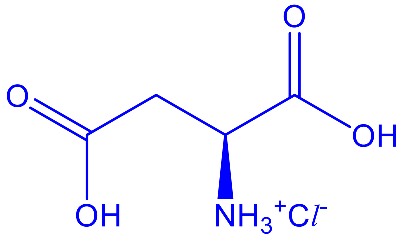


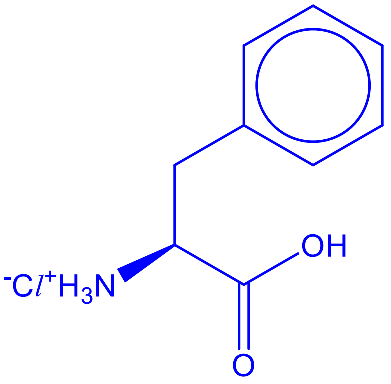
aspartame

(c) **(i)** State the number of stereoisomers for aspartame.

4 .... [1]

(ii) Consider the stomach to contain only hydrochloric acid, draw the structures of the hydrolysed products.





CH_3OH

[3]

The pK_a values associated with aspartic acid are 2.0, 3.9 and 9.9.

(iii) Assign, with explanation, the pK_a value to the side chain of aspartic acid.

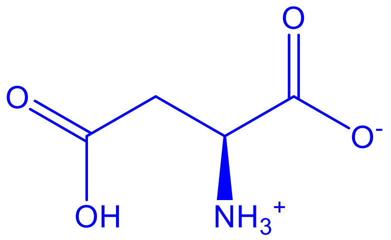
3.9. The side chain is farther from the electron withdrawing groups (NH_2/NH_3^+) and CO_2H and is thus less acidic due to (1) less polarisation/weakening of the O–H bond OR (2) less charge dispersal on the conjugate base.

....

....

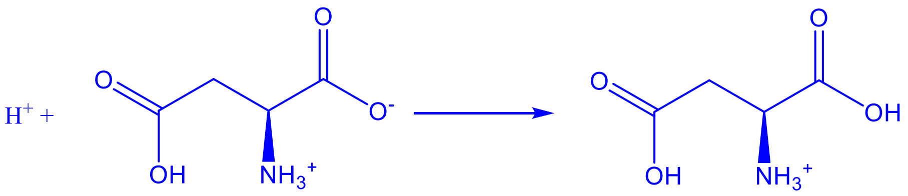
.... [2]

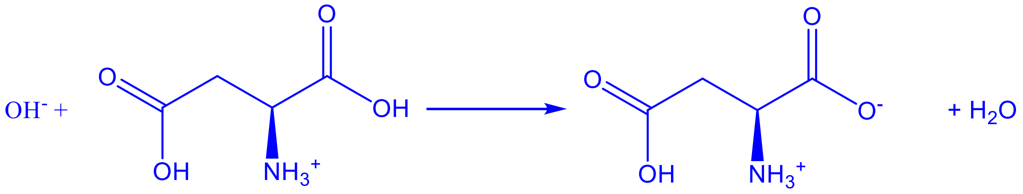
(iv) Hence, draw the zwitterionic form of aspartic acid.



[1]

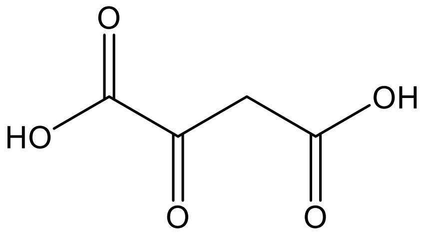
(v) Write two equations to show how aspartic acid may function as a buffer at pH 2.0.





[2]

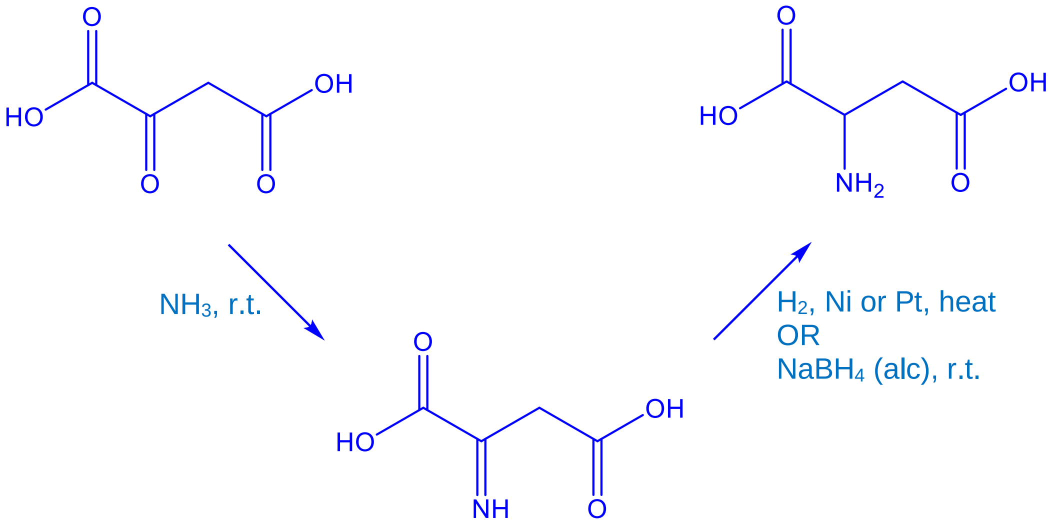
(d) Aspartic acid can be synthesised in two steps from oxaloacetic acid in a process known as reductive amination.



oxaloacetic acid

The first step involves a condensation reaction with the ketone and a nitrogen containing molecule to form an imine containing a C=N bond, and the second step involves reduction of the imine to form the amine.

(i) Suggest the reagents and conditions needed for this synthesis. Include the structure of the intermediate.



[3]

(ii) Comment on the optical activity of the synthesised aspartic acid.

It should be optically inactive as a racemic mixture is formed in step 2 due to

(1) the possibility of BH_4^- ions attacking from either side of the trigonal plane OR

(2) the planar imine being able to be reduced on either side with the catalyst.

OWTTE

[1]

[Total: 16]

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