CATHOLIC JUNIOR COLLEGE
JC2 PRELIMINARY EXAMINATIONS
Higher 2

CANDIDATE NAME	
CLASS	**2T**

CHEMISTRY

9647/03
Paper 3 Free Response
THURSDAY 25 AUGUST 2011
2 Hours

Candidates answer on separate paper.

Additional Materials: Answer Paper
Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name and class on all the work you hand in.
Write in dark blue or black pen on both sides of the paper. **[PILOT FRIXION ERASABLE PENS ARE NOT ALLOWED]**
You may use a soft pencil for any diagrams, graphs or rough working.
Do not use staples, paper clips, highlighters, glue or correction fluid.

Answer any **four** questions.
A Data Booklet is provided
You are reminded of the need for good English and clear presentation in your answers.

The number of marks is given in brackets [ ] at the end of each question or part of the question.
At the end of the examination, fasten all work securely together.

ANSWERS

Answer any **four** questions.

1 Nanochemistry is an important field of science that explores the use of extremely small particles that have diameters about thousand times thinner than the width of a human hair. Transition metals and its compounds are often the subject of interest in nanochemistry, as many useful properties are improved at this ultra small scale.

(a) Nano-sized iron(III) hydroxide, $Fe(OH)_3$ exists as a precipitate and can be used as a catalyst to remove aqueous arsenate(V) ions, AsO_4^{3-} from contaminated water. The $Fe(OH)_3$ with the adsorbed arsenate(V) ions are filtered off, and undergoes an ion-exchange with the arsenate(V) ions removed and $Fe(OH)_3$ precipitate recovered unchanged.

(i) State the electronic configuration of iron in $Fe(OH)_3$.

$1s^2 2s^2 2p^6 3s^2 3p^6 \mathbf{3d^5}$ **or** $[Ar]\mathbf{3d^5}$ **(ii)** State the type of catalysis and briefly explain why transition metal compounds are suitable for such catalysis.

$Fe(OH)_3$ act as a heterogenous catalyst. As transition metal compounds has **empty d orbitals** which can accept the lone pair of electrons from reactant species, and allow adsorption onto the transition metal compounds.

(iii) Suggest why the use of nano-sized particles will improve this catalytic property.

Nano-scaled particles have a **larger surface area**resulting in more\faster adsorption of the arsenate ions.

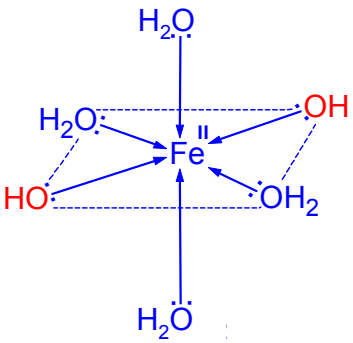
[4]

(b) Nano-sized iron(II) hydroxide exists as a complex solid with the formula $Fe(H_2O)_4(OH)_2$ and has no net dipole moment.

(i) State the colour and coordination number of the complex iron(II) hydroxide.

Green\Dirty Green\Grey Green. Coordination number is Six.

(ii) Suggest the structure of the complex solid, given that it is a non-polar species.



[4]

(c) Nano-sized iron(II) hydroxide, $Fe(OH)_2$ is often unstable, due to oxidation by water even though oxygen is not present. The pH of the solution remains largely unchanged, a reddish-brown precipitate and effervescence are observed.

(i) Identify the reddish-brown precipitate and suggest an equation for this reaction.

$Fe(OH)_3$ $2Fe(OH)_2 + 2H_2O \rightarrow 2Fe(OH)_3 + H_2$

(ii) The reaction is not expected to occur under standard conditions and can be considered reversible. Suggest a possible reason why it does in fact occur for an opened bottle of $Fe(OH)_2$ suspended in water.

As H_2 is formed, it is **constantly removed from the system**, hence the position of equilibrium will shift to the right, resulting in the reaction occurring.

[3]

(d) Nano-sized iron(II) hydroxide, $Fe(OH)_2$ is used for the purpose of removal of toxic selenite(IV) ions, SeO_3^{2-} from water, by reducing selenite(IV) ions to selenium, Se.

(i) Construct a half-equation for the reduction of SeO_3^{2-} to Se in an alkaline solution.

$4e^- + SeO_3^{2-} + 3H_2O \rightarrow Se + 6OH^-$

(ii) In water that is heavily contaminated with CN^- ions, iron(II) hydroxide appears to dissolve. State the type of reaction that is occurring and construct a balanced chemical equation for it.

Ligand displacement has occurred, forming soluble $[Fe(CN)_6]^{4-}$ ions.

$Fe(OH)_2 + 6\ CN^- \rightarrow [Fe(CN)_6]^{4-} + 2OH^-$
or $Fe(H_2O)_4(OH)_2 + 6\ CN^- \rightarrow [Fe(CN)_6]^{4-} + 2OH^- + 4H_2O$

(iii) By selecting $E^\ominus$ values from the *Data Booklet*, and given that the redox potential of the reaction in **(i)** is – 0.37 V, explain and justify if SeO_3^{2-} can be removed from water contaminated with CN^- ions.

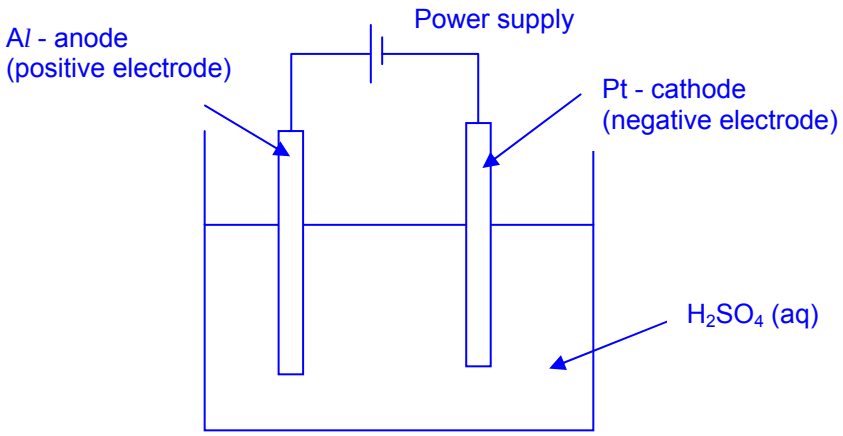
$[Fe(CN)_6]^{3-} + e^- \rightleftharpoons [Fe(CN)_6]^{4-}$ $E^\ominus = +0.36V$

$E^\ominus_{reaction}$ = – 0.37 – (+0.36V) = –0.73 V < 0, hence the reaction is not spontaneous. Thus removal of SeO_3^{2-} ions cannot occur.

[5]

(e) Electrochemistry is also widely used in the synthesis of nano-sized materials. For instance, anodising of aluminium can be conducted to produce extremely small aluminium oxide.

Describe with the aid of a labelled diagram, the set-up used during anodising of aluminium, and the reactions occurring at each electrode. [4]



At the Cathode:
$2e^- + 2H^+ \rightarrow H_2$
At the Anode:
$H_2O \rightarrow O_2 + 4e^- + 4H^+$
$3O_2 + 4Al \rightarrow 2Al_2O_3$

[Total: 20]

2 (a) ***Vitamin C***, $C_6H_8O_6$, is also known as ascorbic acid. It is a monobasic acid and has a pK_a of 4.10. When a 500 mg tablet of ***Vitamin C*** is swallowed, it dissolves in the stomach before being absorbed into the bloodstream. The stomach may be assumed to contain 1.0 dm^3 of 0.10 mol dm^{-3} hydrochloric acid

(i) Estimate the percentage of ***Vitamin C*** that is ionised in the stomach under these conditions. State the assumptions made during the calculation.

$$[C_6H_8O_6] = \frac{500 \times 10^{-3}}{176} \text{ mol dm}^{-3}$$
$$= 2.84 \times 10^{-3} \text{ mol dm}^{-3}$$
$$pK_a = -\log K_a = 4.10$$
$$\therefore K_a = 10^{-4.10} = 7.94 \times 10^{-5}$$

Vitamin C is a weak, monobasic acid, HA;

$$HA \overset{K_a}{\rightleftharpoons} H^+ + A^-$$
$$(2.84 \times 10^{-3} - x) \quad x \quad x$$
$$\approx 2.84 \times 10^{-3} \text{ mol dm}^{-3}$$
$$HCl \rightarrow H^+ + Cl^-$$
$$0.1 \text{ mol dm}^{-3}$$

Assumptions: Vitamin C is a ***weak acid***, only ***partially ionised*** in solution, so that; $(2.84 \times 10^{-3} - x) \approx 2.84 \times 10^{-3}$ mol dm^{-3},
$(0.1 + x) \approx 0.1$ mol dm^{-3},

since x is very small.

$$K_a = \frac{[H^+][A^-]}{[HA]} = \frac{(x+0.1)(x)}{2.84\times10^{-3}-x}$$

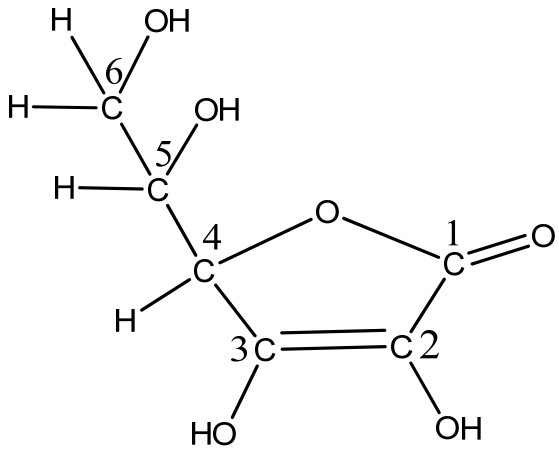
$$7.94 \times 10^{-5} = \frac{(0.1)x}{2.84\times10^{-3}}$$

$\therefore$ $x = [H^+] = 2.25 \times 10^{-6}$ mol dm^{-3}

$$\% \text{ of Vitamin C that is ionised} = \frac{2.25\times10^{-6}}{2.84\times10^{-3}} \times 100$$

$$= 0.0794\ \%$$

(ii) The structure of ***Vitamin C*** is



State which hydrogen atom in the molecule is likely to be acidic, and justify your choice.

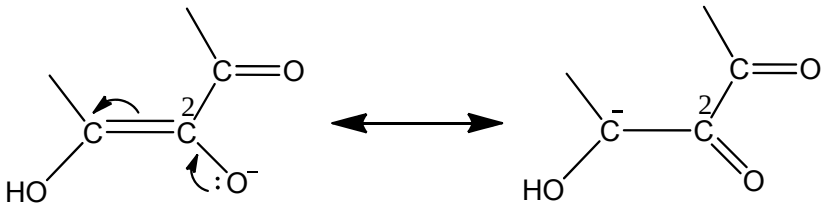
The H atom of the OH group attached to ***Carbon 2*** is likely to be acidic.

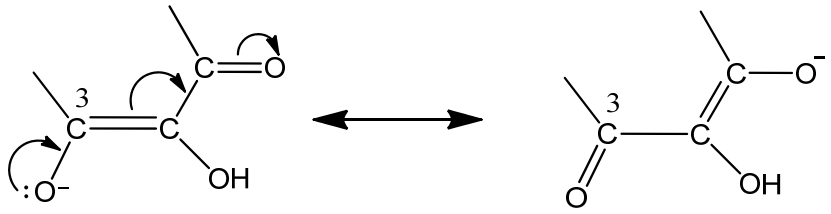
The C=O group attached to Carbon 2 withdraws electrons due to the electronegative O atom, thus making the O-H bond more polar so that dissociation of the O-H bond can take place more readily.

OR

The H atom of the OH group attached to ***Carbon 2/3*** is likely to be acidic.

Ion formed is stabilized by delocalization of electrons / resonance stabilized.





(iii) Blood has a pH of 7.35 and is saturated with carbon dioxide of concentration 3.2 x 10^{-3} mol dm^{-3}. The equilibrium reaction,

$$H_2O + CO_2 \rightleftharpoons H^+ + HCO_3^- \; ; \; K_a = 4.5 \times 10^{-7} \text{ mol dm}^{-3}$$

acts as a buffer.

(I) Explain clearly how this buffering action minimizes the change in pH on the addition of either acid or alkali.

On addition of small amounts of H^+, HCO_3^- consumes it,

$$H^+ + HCO_3^- \rightarrow H_2O + CO_2 \text{ (or } H_2CO_3)$$

So, pH hardly changes.

OR

On addition of small amounts of OH^-, CO_2 consumes it,

$$OH^- + CO_2 \rightarrow HCO_3^-$$

So, pH hardly changes.

(II) Calculate the concentration of HCO_3^- ions in blood.

pH = 7.35; $\quad -\log [H^+] = 7.35$

$[H^+] = 10^{-7.35} = 4.47 \times 10^{-8}$ mol dm^{-3}

$$K_a = \frac{[H^+][HCO_3^-]}{[CO_2]} = 4.5 \times 10^{-7}$$

$$[HCO_3^-] = \frac{[CO_2](4.5 \times 10^{-7})}{[H^+]} = \frac{(3.2 \times 10^{-3})(4.5 \times 10^{-7})}{4.47 \times 10^{-8}}$$

$= 3.22 \times 10^{-2}$ mol dm^{-3}

(III) Explain ***qualitatively*** how the extent of ionisation of ***Vitamin C*** changes as it moves from the stomach to the bloodstream.

Conditions in the blood stream are basic.

Increased ionisation as equilibrium position, ($C_6H_8O_6 \rightleftharpoons H^+ + C_6H_7O_6^-$) shifts right as the H^+ is removed in the basic medium to form water.

[8]

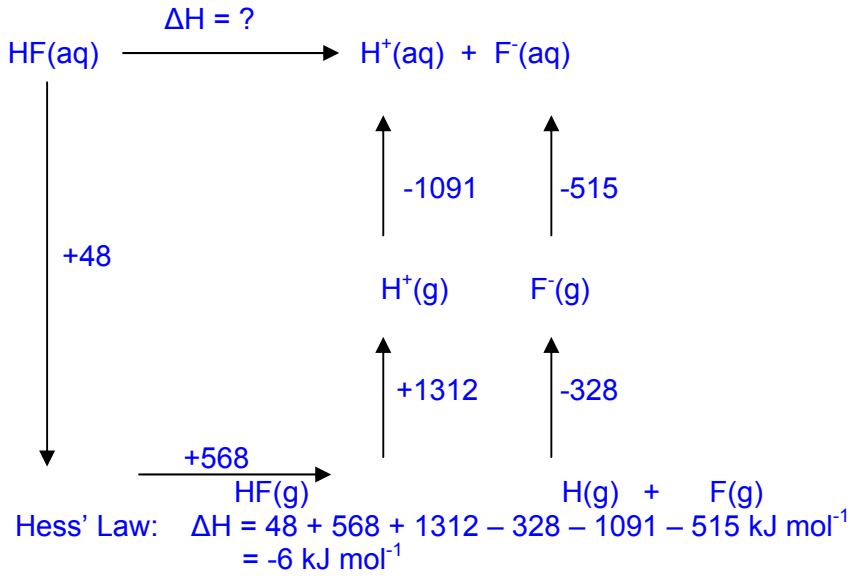
(b) The acid strength of the hydrogen halides in aqueous solution may be related to the enthalpy change for the process,

$$HX(aq) \rightarrow H^+(aq) + X^-(aq)$$

where X is a halogen.

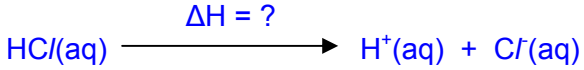
(i) By constructing a suitable energy cycle and using the data in the following table, calculate the enthalpy change of this process for hydrofluoric acid.

Reaction	$\Delta H^{\ominus}$ / kJ mol^{-1}	
	X = F	X = C*l*
$HX(aq) \rightarrow HX(g)$	+48	+18
$HX(g) \rightarrow H(g) + X(g)$	+568	+432
$H(g) \rightarrow H^+(g) + e^-$	+1312	+1312
$X(g) + e^- \rightarrow X^-(g)$	-328	-349
$H^+(g) \rightarrow H^+(aq)$	-1091	-1091
$X^-(g) \rightarrow X^-(aq)$	-515	-381



Hess' Law: $\Delta H = 48 + 568 + 1312 - 328 - 1091 - 515$ kJ mol^{-1}
$= -6$ kJ mol^{-1}

(ii) Hence calculate the enthalpy change of this process for hydrochloric acid.



Similarly, using Hess' Law,
$\Delta H = 18 + 432 + 1312 - 349 - 1091 - 381$ kJ mol^{-1}
$= -59$ kJ mol^{-1}

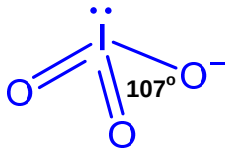
(iii) Comment on your answers in relation to the strength of hydrofluoric acid ($K_a = 6.7 \times 10^{-4}$ mol dm^{-3}) and hydrochloric acid.

ΔH(HF) is very much less exothermic than ΔH(HC*l*) indicating lesser tendency for HF to ionise, therefore HF is the weaker acid.

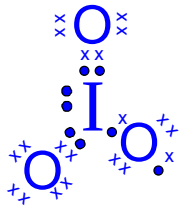
[4]

(c) Each Group II element forms an iodate(V) with the formula $M(IO_3)_2$. The iodates(V) have many uses, for example, calcium iodate is an oxidant added to lotions and ointments as an antiseptic and deodorant.

(i) Draw the structural formula of the iodate(V) ion, indicating the likely bond angle.



(ii) Draw a dot-and-cross diagram corresponding to this structure.



(iii) The iodates(V) readily decompose on heating giving oxygen gas as one of the two products formed.

(I) Write a likely equation for the decomposition of $M(IO_3)_2$.

$M(IO_3)_2(s) \rightarrow MI_2(s) + 3O_2(g)$

(II) Predict and explain how the thermal decomposition of these iodates(V) varies down the group. The decomposition of the iodates(V) is similar to the decomposition of the nitrates(V).

The thermal decomposition temperature increases/thermally more stable down the group
Size of cation increases
Charge density of cation decreases
Cation polarizes / distorts electron cloud of IO_3^- less readily

(iv) The percentage purity of a sample of barium iodate(V), $Ba(IO_3)_2$ can be determined by the following method.

0.105 g of $Ba(IO_3)_2$ (M_r = 487) is added to excess aqueous potassium iodide, KI in acidic medium. The iodine liberated is then titrated against aqueous sodium thiosulfate pentahydrate, $Na_2S_2O_3.5H_2O$ (M_r = 248.2) of concentration, 24.8 g dm^{-3}.

25.00 cm^3 of the thiosulfate is used for the titration. By using the reactions given below, and the information described above, calculate the percentage purity of the sample of barium iodate(V).

[In the presence of acid and the iodide ions, the following reaction takes place quantitatively: $IO_3^- + 5\ I^- + 6\ H^+ \rightarrow 3\ I_2 + 3\ H_2O$. The reaction between iodine and thiosulfate is given by the equation: $I_2 + 2\ S_2O_3^{2-} \rightarrow 2\ I^- + 2\ S_4O_6^{2-}$].

$Ba(IO_3)_2 \equiv 2IO_3^- \equiv 6I_2 \equiv 12S_2O_3^{2-}$

No of mol of $S_2O_3^{2-} = \frac{25.00}{1000} \times \frac{24.8}{248.2}$

$= 2.50 \times 10^{-3}$ mol

No of mol of $Ba(IO_3)_2 = \frac{1}{12} \times 2.50 \times 10^{-3}$ mol

$= 2.08 \times 10^{-4}$ mol

Mass of $Ba(IO_3)_2 = 2.08 \times 10^{-4} \times 487$ g

$= 0.101$ g

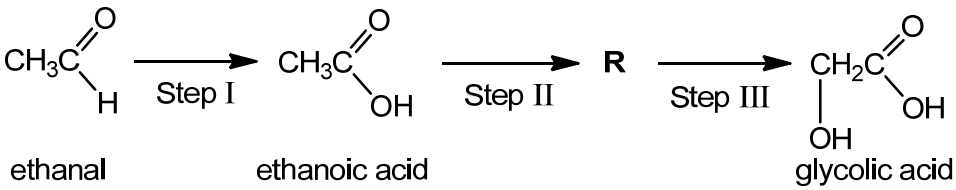
% purity of $Ba(IO_3)_2 = \frac{0.101}{0.105} \times 100$ %

$= 96.5$ %

[Total: 20]

3 Ethanal occurs commonly in coffee and fruits. In humans, ethanal is formed by oxidation of ethanol consumed from alcoholic drinks and is believed to cause hangovers. Ethanal can be used as precursors of other important organic compounds. In addition, ethanal can also be used to synthesize glycolic acid, which is used in various skin-care products.

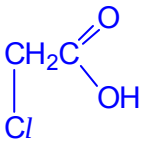
(a) In the synthesis of glycolic acid as shown below,



(i) state the reagents and conditions for Step II and Step III, and identify the intermediate **R**, and

Step II: Cl_2, uv light
Step III: NaOH(aq), heat under reflux

R:

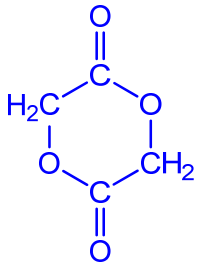


(ii) explain the difference in acidity between glycolic acid and ethanoic acid.

Glycolic acid is a stronger acid than ethanoic acid.The electron withdrawing –OH group in glycolic acid increases the polarization of the O-H bond, thus making it easier to break and hence a stronger acid than ethanoic acid. OR
The electron withdrawing –OH group reduces the negative charge on $–COO^-$ of the conjugate base of glycolic acid, thus making it more stable and hence a stronger acid.

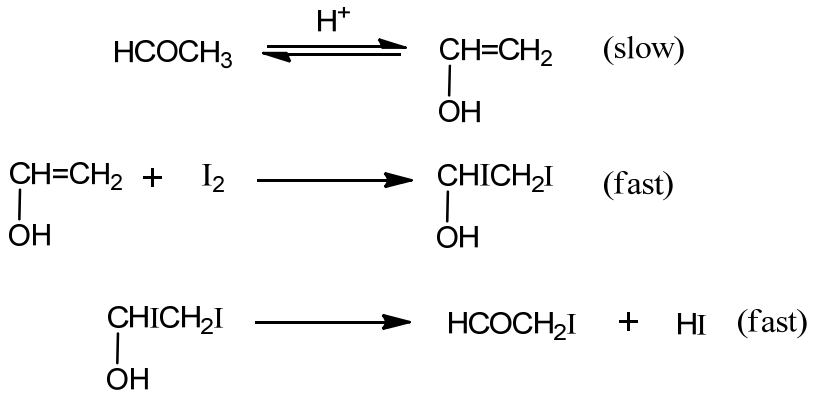
Two molecules of glycolic acid can react with one another under suitable conditions with the loss of two water molecules.

(iii) Suggest a possible structure for the compound formed.



[6]

(b) Ethanal and iodine reacts in an acidic medium according to the mechanism as shown.



(i) State the type of reaction that occurs in each of the fast step.

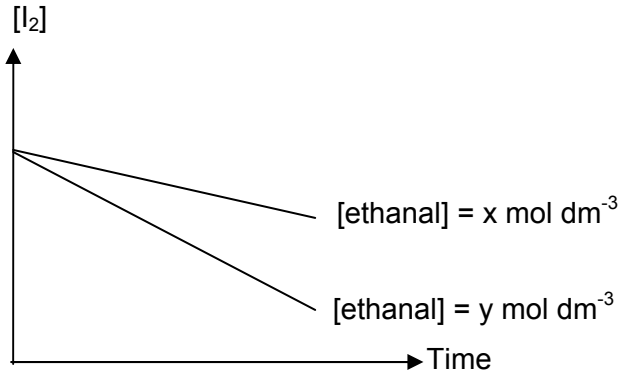
(ii) Electrophilic addition, Elimination Suggest the rate equation for the reaction, and hence the units of the rate constant.

Rate =k[$HCOCH_3$][H^+]

(iii) Units: $mol^{-1}dm^3s^{-1}$ Suggest how the rate of reaction between ethanal and iodine can be determined experimentally.

-Measure time taken for the brown colour of iodine to disappear.-Quench the reaction with water at fixed time intervals and titrate the iodine with sodium thiosulfate.

(iv) Sketch an appropriate graph and show how the order of reaction with respect to ethanal can be obtained experimentally.



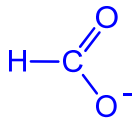
(v) Explain how the rate of reaction would change if bromine is used instead of iodine.

Rate would remain constant.Rate is independent of the halogen used.

[9]

(c) Ethanol can first be oxidised to ethanal by the mild oxidising agent formed when iodine reacts with the hydroxide ions in the alkaline medium. The ethanal formed then reacts with iodine in an alkaline medium via a different mechanism.

(i) Draw the structure of all organic compounds formed in the reaction when ethanal reacts with iodine in an alkaline medium.



CHI_3

(ii) Write an ionic equation to show how iodine reacts with the hydroxide ions and state the type of reaction that is occurring. Hence, suggest the identity of the oxidising agent.

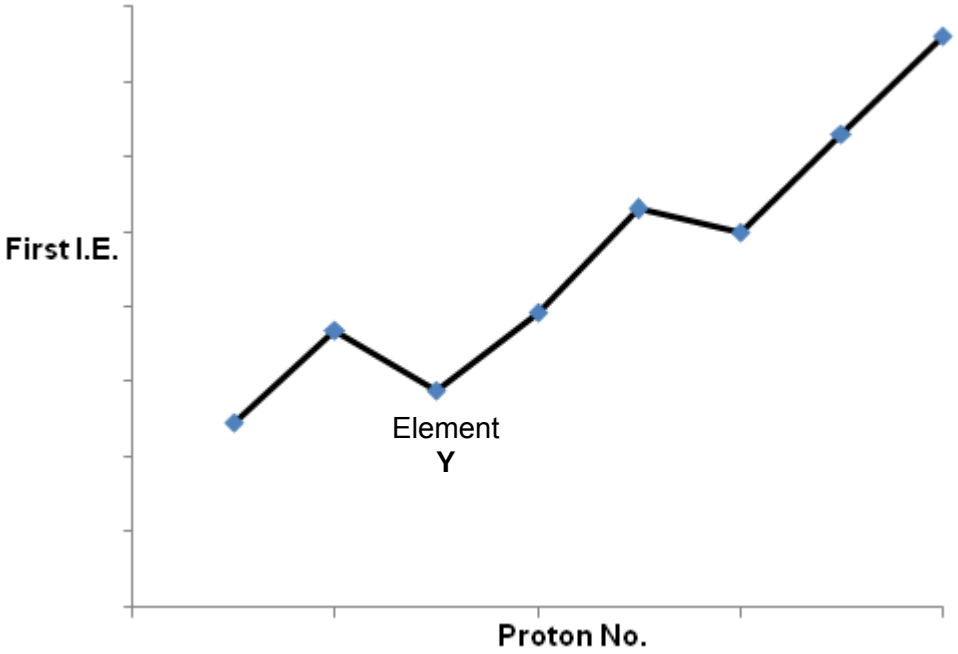
$I_2 + 2OH^- \rightarrow I^- + IO^- + H_2O$ Disproportionation Oxidising agent: IO^-

[5]

[Total: 20]

4 (a) The elements **Y** and **Z** are in Period 3 and can be one of the following: Mg, A*l*, Si and P.

The following graph depicts the variation in first ionization energy (I.E.) of the elements across Period 3.



(i) Based on the above data, identify element **Y**. Explain why the first ionization energy of **Y** is lower than that of the element preceding it.

A*l*. The first I.E. is lower since it involves removal of an electron from the 3p orbital which is of a higher energy.

When NaOH is added to a solution containing ions of **Y**, a white precipitate is formed initially. When an excess of NaOH is added, the precipitate dissolves to give a colorless solution.

The oxide of **Y** reacts with both aqueous hydrochloric acid and sodium hydroxide.

Element **Z** has a chloride and an oxide and both react vigorously with water to form a solution of pH = 2.

(ii) By identifying the white precipitate, construct ionic equations for the formation of this precipitate and its subsequent dissolving in NaOH.

$Al(OH)_3$ $Al^{3+} + 3OH^- \rightarrow Al(OH)_3$ $Al(OH)_3 + OH^- \rightarrow [Al(OH)_4]^-$

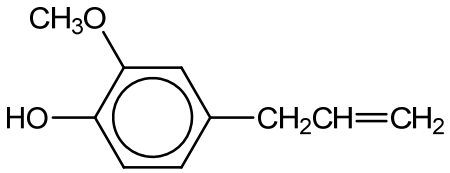
(iii) State the identity the element **Z** and hence give the equation for the reaction between the chloride of **Z** and water.

P

$PCl_5 + 4H_2O \rightarrow H_3PO_4 + 5HCl$ $PCl_3 + 3H_2O \rightarrow H_3PO_3 + 3HCl$

Either equation given will be accepted. [7]

(b) ***Eugenol*** is an important compound in spices like cinnamon and cloves.
[The CH_3O group is inert and can be disregarded in this question.]



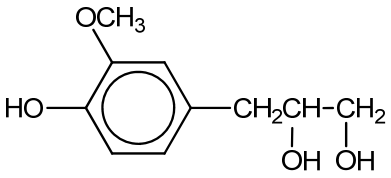
Eugenol

(i) Explain why ***Eugenol*** is more soluble in aqueous sodium hydroxide than in water.

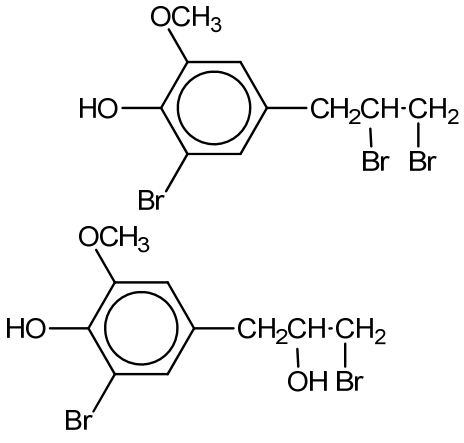
The acidic phenol group will react with NaOH to form phenoxide ions. Large amount of energy is released due to the ion-dipole interaction with water.

(ii) Draw the structures of **all** the possible organic products formed when ***Eugenol*** reacts with each of the following reagents.

(I) cold, dilute manganate(VII) ions



(II) aqueous bromine



[4]

(c) A hydrocarbon **A** has the molecular formula of $C_{10}H_{14}$. When **A** is treated with hot aqueous acidified $KMnO_4$, benzoic acid is formed. When reacted with bromine in the presence of ultraviolet light, **A** produced **four** isomeric monobromo compounds with the formula $C_{10}H_{13}Br$. Upon heating with alcoholic NaOH, two of the monobromo compounds **B** and **C** gave the **same** compound which can exist as a pair of geometric isomers, **D** and **E**. Heating **B** with aqueous NaOH produces compound **F** which does not react with acidified potassium dichromate(VI). Suggest the structures of **A**-**F**, explaining your reasoning. [9]

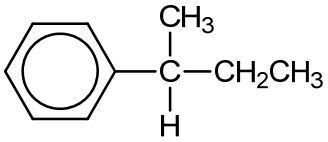
A undergoes side-chain oxidation to give benzoic acid => only 1 alkyl side-chain is present

The alkyl group present in **A** undergoes free radical substitution with Br_2 & ultraviolet light

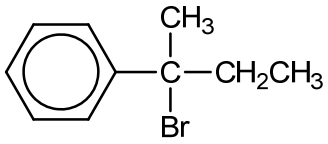
The monobromo compounds undergo elimination in the presence of ethanolic NaOH to give alkenes. OR the monobromo compound undergoes nucleophilic substitution in the presence of aqueous NaOH

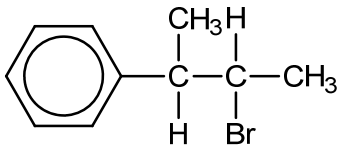
Compound **F** does not react with potassium dichromate => tertiary alcohol

A:

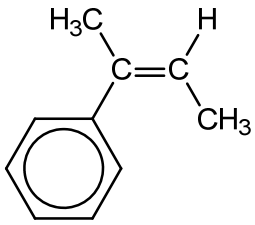


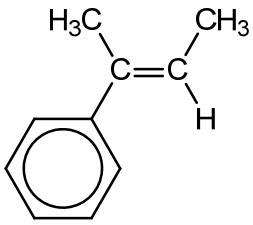
B and **C**:





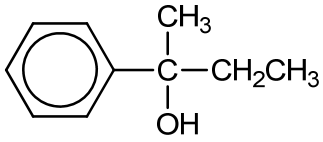
D and **E**





For **D** and **E**: Students need to show clearly whether the isomer is cis/trans.
Only is awarded if student gave the correct compound but did not show the geometry

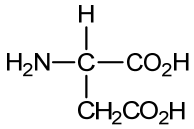
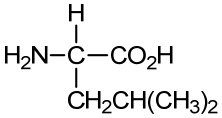
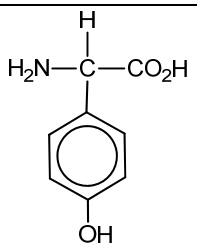
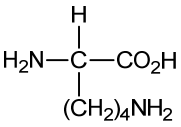
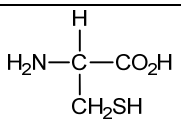
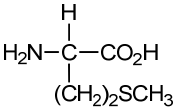
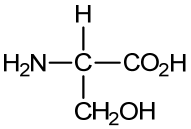
F:



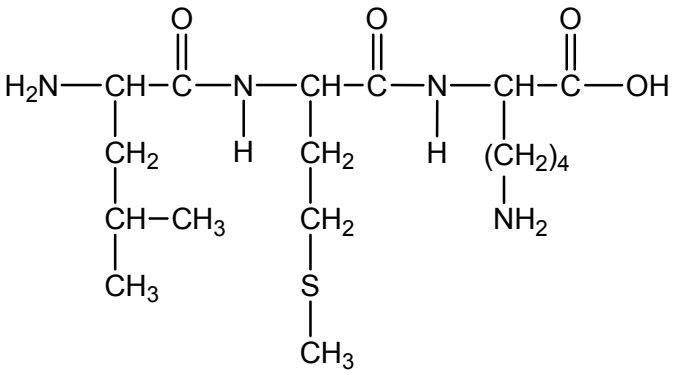
for each correct structure. If student draws A wrongly, D-F can be given ECF if the chemistry is correct (i.e. D and E are geometric isomers, F is a tertiary alcohol).

[Total: 20]

5 Proteins are found in every living organism and are made up of many amino acids linked together in a long chain.
Below are some of the naturally occurring amino acids.

Amino Acid	Abbreviated name	Structure
Aspartic acid	Asp	
Leucine	Leu	
Tyrosine	Tyr	
Lysine	Lys	
Cysteine	Cys	
Methionine	Met	
Serine	Ser	

(a) Draw the structural formula of the tripeptide *leu-met-lys*, stating clearly the type of linkage formed. [2]



(b) Proteins structures can be classified into primary, secondary, tertiary and quartenary structures. The tertiary structure of proteins enables it to adopt a 3-dimensional shape which allows it to be soluble in water and be mobile within the cell.

(i) Identify 2 amino acids from the list above which would be present in proteins enabling it to dissolve in water.

Any two: lys, asp, ser, tyr, cys

(ii) Hence, state the interactions between the selected amino acids and water molecules.

Lys, asp and cys form ion-dipole interactions with water,
Ser and try forms H-bonding with water [2]

(c) Compound **X** is one of the amino acids shown in the table. 1 mol of **X** reacts with solid sodium to form 1 mol of hydrogen gas. In addition, 1 mol of **X** reacts only with 1 mol of aqueous NaOH. Compound **X** has pK_a values of 2.21 and 9.15. When acidified potassium dichromate(VI) is added to compound **X** and distilled, the product formed gives an orange precipitate, compound **Y** with 2,4-DNPH.

(i) Explain, with the aid of an equation if applicable, why the amino acid **CANNOT** be cysteine.

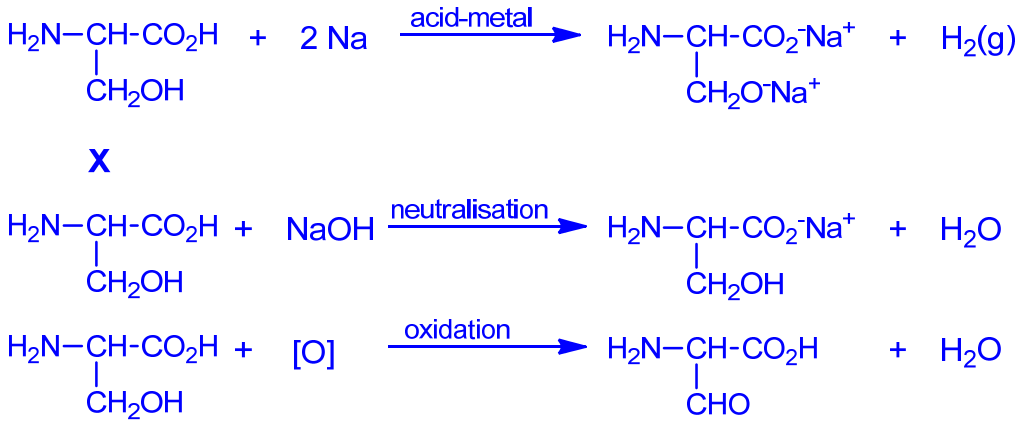
The –SH group, **S being a larger atom** than O, the **S-H bond is more polarised** and releases the H^+ ion more easily than –OH. Hence, cys is more acidic than the –OH group in ser.

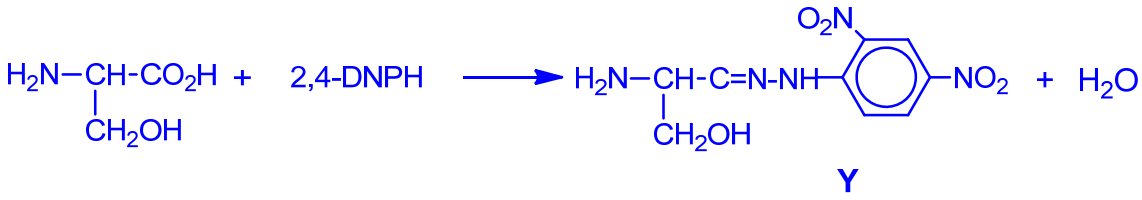
$-CH_2SH + OH^- \rightarrow CH_2S^- + H_2O$

OR
Although -SH can be **oxidized**, it **does not form a compound that will form an orange ppt with 2,4-DNPH**.

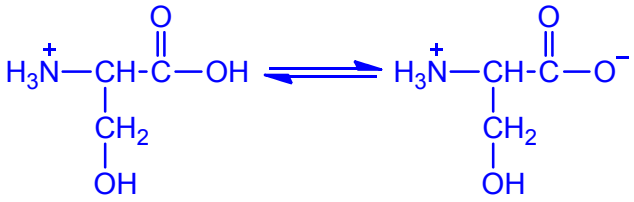
(ii) Deduce the structures of compound **X** and **Y**, explaining the reactions involved by writing appropriate equations.

X is serine.





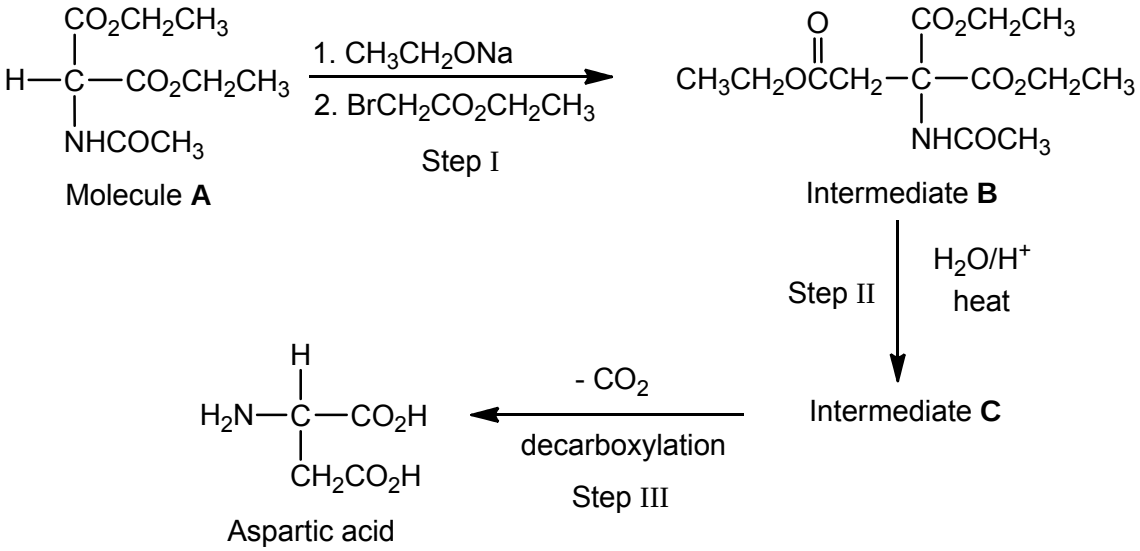
(iii) Draw the two forms of compound **X** which exist at pH 2.21.



[8]

(d) A general method for the preparation of α-amino acids is the amidomalonate synthesis.

Below is an example of the synthesis of aspartic acid using this method:

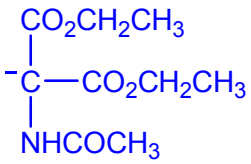


In Step I, the reaction begins with a treatment of molecule **A** with a base, followed by the attack of a primary alkyl halide by a nucleophile. Step II is an acid hydrolysis to form intermediate **C**, followed by decarboxylation in Step III.

(i) Identify the base used to attack molecule **A** in Step I, explaining its property as a base.

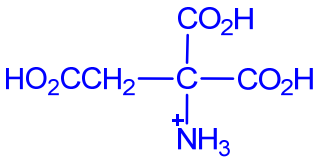
$CH_3CH_2O^-$ The lone pair on the O atom is a proton acceptor.

(ii) By determining the nucleophile, suggest the type of reaction undergone in Step I.

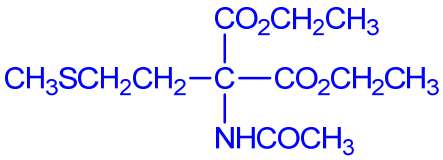
Nucleophile: 

Type of reaction: Nucleophilic substitution (S_N2)

(iii) Draw the structure of intermediate **C**.



(iv) By using the amidomalonate method described above, the amino acid, methionine can also be produced. State the appropriate intermediate formed after Step I and the halogenoalkane which can be used to form methionine.



(v) This method usually yields an optically inactive mixture. Explain why the mixture is optically inactive.

The product is produced as **racemic mixture**, with an equimolar of each enantiomer, making the mixture optically inactive.

[8]

[Total: 20]