CATHOLIC JUNIOR COLLEGE
JC2 PRELIMINARY EXAMINATIONS
Higher 2

CHEMISTRY

9647/03

Paper 3 Free Response

Thursday 27 August 2015
2 hours

Additional Materials: Data Booklet
Answer Paper

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. Write your answers on the answer paper 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 question.

At the end of the examination, fasten all your work securely together.

ANSWER SCHEME & EXAMINERS' COMMENTS

[Turn over

Answer any **four** questions.

1 Butanone is an industrial organic solvent used in the manufacture of plastics, lacquers and varnishes.

(a) Butanone reacts with iodine in the presence of an acid according to the equation:

$$CH_3CH_2COCH_3 + I_2 \rightarrow CH_3CH_2COCH_2I + HI$$

In a series of experiments, the reaction was carried out with different concentrations of reagents, and the following initial rates were obtained:

Expt.	$[CH_3CH_2COCH_3]$ / mol dm^{-3}	$[I_2]$ / mol dm^{-3}	$[H^+]$ / mol dm^{-3}	Initial rate / mol dm^{-3} min^{-1}
1	0.010	0.010	0.010	8.31×10^{-8}
2	0.010	0.010	0.013	10.8×10^{-8}
3	0.013	0.010	0.013	14.0×10^{-8}
4	0.018	0.013	0.018	26.9×10^{-8}

(i) Using the data given, deduce the order of reaction with respect to each of the three reagents, clearly showing how you arrive at your answers. Hence, write a rate equation for the reaction.

Let rate = $k[CH_3CH_2COCH_3]^a[I_2]^b[H^+]^c$
Using data from experiments 1 and 2,

$$\frac{10.8\times10^{-8}}{8.31\times10^{-8}} = \frac{k(0.010)^a(0.010)^b(0.013)^c}{k(0.010)^a(0.010]^b(0.010)^c}$$

***c* = 1**
rate is first order with respect to H^+

Using data from experiments 2 and 3,

$$\frac{14.0\times10^{-8}}{10.8\times10^{-8}} = \frac{k(0.013)^a(0.010)^b(0.013)}{k(0.010)^a(0.010)^b(0.013)}$$

***a* = 1**
rate is first order with respect to $CH_3CH_2COCH_3$

Using data from experiments 3 and 4,

$$\frac{26.9\times10^{-8}}{14.0\times10^{-8}} = \frac{k[0.018][0.013]^b[0.018]}{k[0.013][0.010]^b[0.013]}$$

***b* = 0**
rate is zero order with respect to I_2

rate = $k[CH_3CH_2COCH_3][H^+]$

(ii) Explain how the rate of reaction would change if the solution was diluted with an equal volume of inert solvent, using ***r*** to represent the original rate before dilution.

Concentration of all solutions would be halved.
Since rate = k[$CH_3CH_2COCH_3$][H^+] = *r* (original rate)
New rate = k {[$CH_3CH_2COCH_3$]/2} {[H^+]/2} = *r* /4.
Hence, the rate would be ¼ the original rate.

(iii) The reaction can also be carried out in the presence of a strong base instead of an acid. State what would be observed when a strong base is used and write an equation for the reaction that occurs.

Yellow precipitate of CHI_3 observed.
$CH_3CH_2COCH_3 + 4OH^- + 3I_2 \rightarrow CH_3CH_2CO_2^- + CHI_3 + 3I^- + 3H_2O$
(OR $CH_3CH_2COCH_3 + OH^- + 3I_2 \rightarrow CH_3CH_2CO_2^- + CHI_3 + 3HI$) (Less accurate as HI further reacts with OH^-)

[7]

(b) Elemental iodine, I_2, has limited solubility in water. Its solubility is greatly increased in a solution containing iodide ion, I^-, due to the formation of triiodide ion, I_3^-, as shown:

$$I_2(aq) + I^-(aq) \rightleftharpoons I_3^-(aq)$$

(i) Write an expression for K_c for this reaction, stating its units.

$$K_c = \frac{[I_3^-]}{[I_2][I^-]} \text{ mol}^{-1} \text{ dm}^3$$

(ii) Experiments have shown that when $[I^-] = 1.4 \times 10^{-3}$ mol dm^{-3}, the concentrations of I_2 and I_3^- are equal. Use this information to calculate a value of K_c.

Since $[I_2] = [I_3^-]$,

$$K_c = \frac{[I_3^-]}{[I_2][I^-]} = \frac{[I_3^-]}{[I_2](1.4 \times 10^{-3})} = \frac{1}{(1.4 \times 10^{-3})} = 714 \text{ mol}^{-1} \text{ dm}^3$$

(iii) Using your answer from **(ii)**, calculate the concentration of iodide ions necessary for 99 % of the iodine to be dissolved.

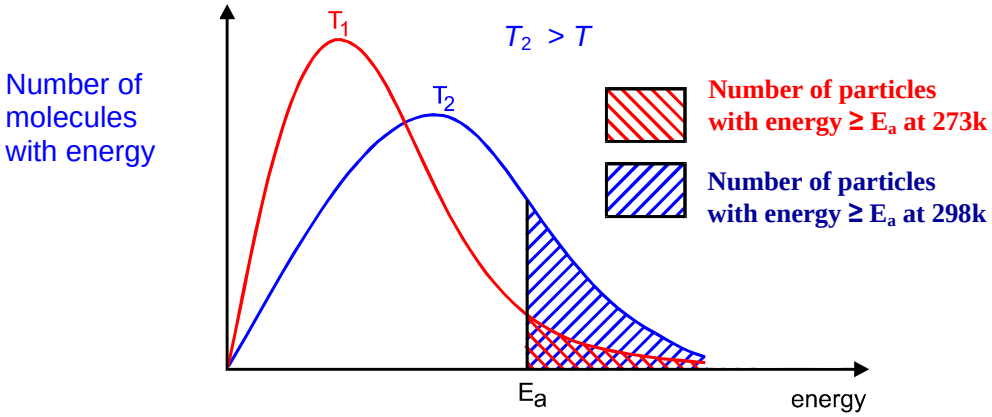
$$\frac{[I_3^-]}{[I_2]} = \frac{99}{1}$$

$$K_c = \frac{[I_3^-]}{[I_2][I^-]} = \frac{99}{[I^-]} = 714$$

$$[I^-] = \frac{99}{714} = 1.39 \times 10^{-1} \text{ mol dm}^{-3}$$

[4]

(c) Explain, using a Maxwell-Boltzmann distribution curve, how the rate of a reaction would change if the temperature was increased.

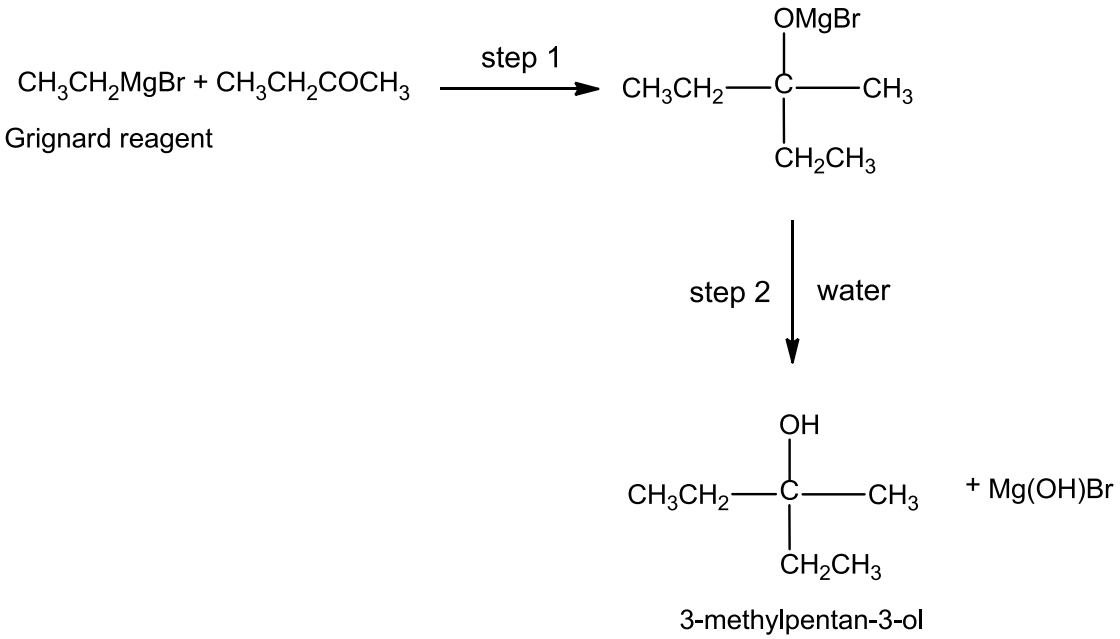


From the Maxwell-Boltzmann distribution of molecular energies, an increase in temperature results in more molecules having greater kinetic energy. This means that the fraction of particles with energy ≥ E_a would increase.
Thus, more molecules would have sufficient energy to overcome the energy barrier. Hence, the frequency of effective collisions increases, leading to increase in rate.

[3]

(d) Grignard reagents are organo-magnesium halides, commonly used in synthesis to prepare a variety of organic compounds.

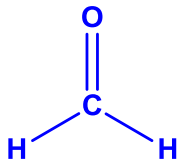
The carbon-magnesium bonds in Grignard reagents are highly polar and this makes it extremely useful in organic synthesis as it is able to react with other polar organic molecules to form carbon-carbon bonds. An example of the use of a Grignard reagent is the two-step reaction of CH_3CH_2MgBr with butanone, $CH_3CH_2COCH_3$, to form 3-methylpentan-3-ol.



(i) Suggest the type of reaction that has taken place in step 1.

Nucleophilic Addition

(ii) Suggest the structural formula of the organic compound to be used with CH_3CH_2MgBr to form propan-1-ol, if the reaction undergoes a similar two-step process.



methanal

(iii) Suggest a suitable Grignard reagent and another organic compound to be used if propan-2-ol is to be prepared using a similar two-step process.

CH_3MgBr $HCOCH_3$ (ethanal)

[4]

(e) There are certain practical issues with the use of Grignard reagents, notably slow formation of the Grignard reagent and its susceptibility to water in air.

The slow formation of the Grignard reagent may be offset by cutting the precursor magnesium into smaller pieces or scraping the sides of the metal before use. Using a balanced equation, explain why magnesium, which has been stored in dry ambient conditions, may not react as quickly as expected.

$Mg(s) + ½ O_2(g) \rightarrow MgO(s)$

Mg reacts with the oxygen in air to form magnesium oxide which acts as a protective layer and so, prevents the magnesium from reacting with the organic compounds.

[2]

2 The direct oxidation of alcohols in a fuel cell represents potentially the most efficient method of obtaining useful energy from renewable fuel.

The diagram below illustrates the functional parts of a direct-ethanol fuel cell (DEFC). The anode and cathode compartments are separated by the proton exchange membrane. The protons are transported across the proton exchange membrane to the cathode where they react with oxygen to produce water.

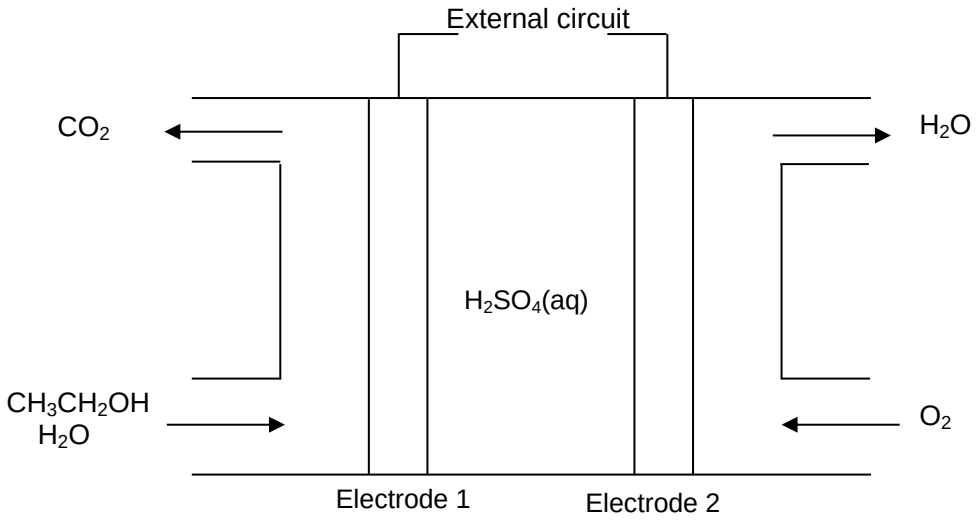


Diagram of a DEFC

(a) (i) Explain, in terms of the change in **average** oxidation number of the carbon atoms, whether electrode 1 or 2 acts as the anode.

Electrode 1 acts as the anode as oxidation occurs since there is an increase in average oxidation state for carbon from -2 to +4.

(ii) Write the half-equations for the reactions which take place at the electrodes of the DEFC, and hence an overall equation for the cell reaction.

Anode: $CH_3CH_2OH + 3H_2O \rightarrow 2CO_2 + 12H^+ + 12e^-$
Cathode: $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$
Overall: $CH_3CH_2OH + 3O_2 \rightarrow 2CO_2 + 3H_2O$

(iii) The cell is capable of producing an e.m.f. of 1.47 V. By using suitable data from the *Data Booklet*, calculate a value for the $E^{\ominus}$ of the CO_2/CH_3CH_2OH electrode reaction.

$E^{\ominus}_{O2/H2O}$ = +1.23 V

$E^{\ominus}_{cell} = E^{\ominus}_{O2/H2O} - E^{\ominus}_{CO2/\ CH3CH2OH}$
$1.47 = 1.23 - E^{\ominus}_{CO2/\ CH3CH2OH}$

$E^{\ominus}_{CO2/C2H5OH} = -0.24$ V

(iv) By quoting relevant $E^{\ominus}$ values from the *Data Booklet*, explain why an acidic electrolyte is preferred to an alkaline electrolyte in the DEFC.

In an acidic medium, $E^{\ominus}_{O_2/H_2O}$ = +1.23 V while in an alkaline medium, $E^{\ominus}_{O_2/OH^-}$ = +0.40 V.

Since $E^{\ominus}_{cell} = E^{\ominus}_{reduction} - E^{\ominus}_{oxidation}$ and $E^{\ominus}_{reduction}$ becomes more positive, $E^{\ominus}_{cell}$ would be more positive and hence a higher emf is obtained.

(v) Describe and explain the effect on the cell potential when the concentration of ethanol is increased.

When [ethanol] is increased, position of equilibrium for the following reaction shifts to the left. There is greater tendency for ethanol to be oxidised and thus $E_{CO2/\ CH3CH2OH}$ becomes more negative.

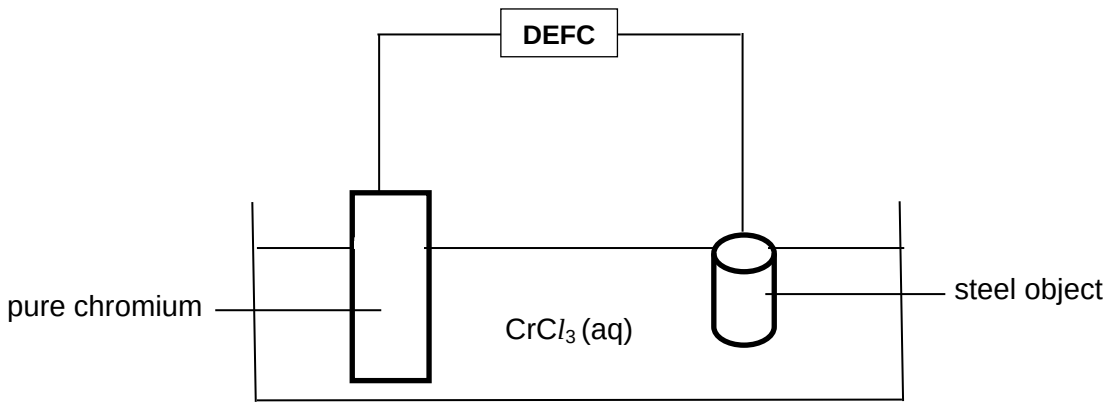
$2CO_2 + 12H^+ + 12e^- \rightleftharpoons CH_3CH_2OH + 3H_2O$ $E_{CO2/\ CH3CH2OH}$

Since $E_{cell} = E_{O2/H2O} - E_{CO2/\ CH3CH2OH}$
A more negative $E_{CO2/\ CH3CH2OH}$ will cause E_{cell} to be more positive.

[9]

(b) Chromium plating is an important industrial application of electrolysis, where a steel object is plated with a thin layer of chromium to make it resistant to rusting and scratches.

In an electroplating experiment, a researcher connected the DEFC to an electrolytic cell as shown below. The aqueous solution containing chromium(III) chloride was electrolysed using a piece of pure chromium and the steel object to be electroplated as the electrodes.



(i) The total time taken for 10 g of chromium to be plated was 4 hours. Calculate the current produced by the DEFC.

$Cr^{3+} + 3e^- \rightarrow Cr$
Amount of Cr = $\frac{10}{52.0}$ = 0.192 mol
Amount of e^- = 0.192 x 3 = 0.577 mol
Q = 0.577 x 96500 = 55700 C

Q = It
55700 = I x (4 x 60 x 60)
I = 3.87 A

(ii) Calculate the volume of ethanol used when 10 g of chromium metal was plated onto the steel object at room conditions, given that the density of ethanol is 0.789 g cm^{-3}.

$Cr^{3+} + 3e^- \rightarrow Cr$
$CH_3CH_2OH + 3H_2O \rightarrow 2CO_2 + 12H^+ + 12e^-$ (from aii)
$Cr \equiv 3e^- \equiv \frac{1}{4} CH_3CH_2OH$
No of mol of CH_3CH_2OH = 0.192 x ¼ = 0.0480 mol
Mass of CH_3CH_2OH = 0.0480 x 46 = 2.208 g
Volume = $\frac{2.208}{0.789}$ = 2.80 cm^3

[3]

(c) Chromium is a *transition element*.

(i) Explain what is meant by the term *transition element*.

A transition element is defined as a d-block element which forms at least one stable ion with partially filled d-subshell of electrons (or incompletely filled d-orbitals).

(ii) Chromium(III) chloride, $CrCl_3$, reacts with water to form a violet hydrate $[Cr(H_2O)_6]Cl_3$. This violet hydrate is isomeric to the dark green $[CrCl_2(H_2O)_4]Cl.2H_2O$ and the pale green $[CrCl(H_2O)_5]Cl_2.H_2O$

Based on the above information, give one property of transition elements or its compounds that is **not** shown by s-block elements.

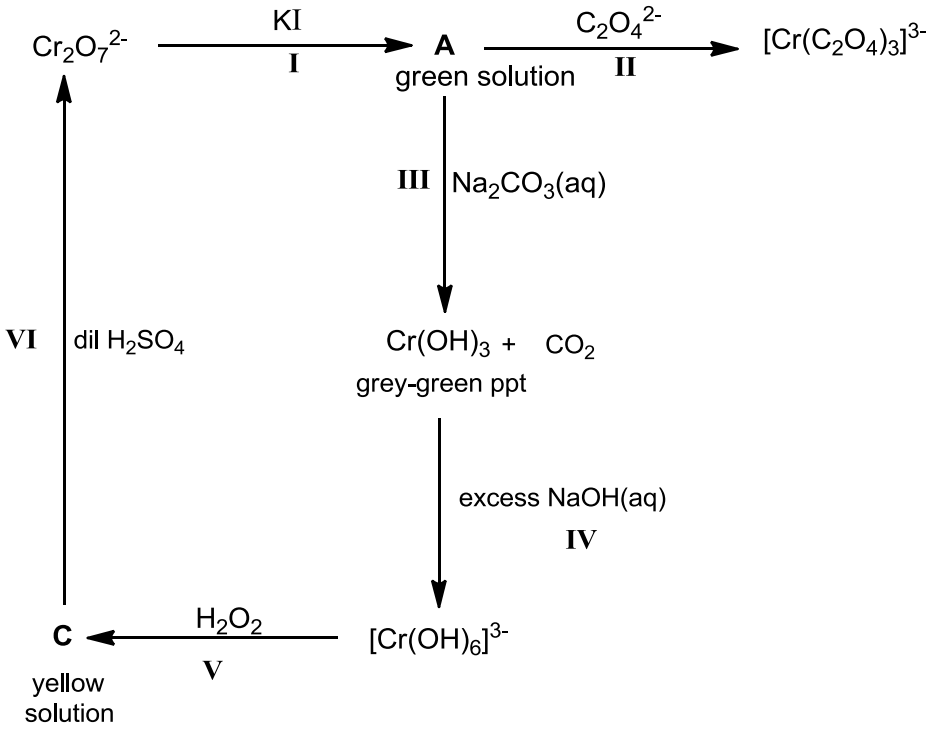
Transition elements form complexes that are coloured.

(iii) When 0.03 mol of aqueous silver nitrate is added to 0.01 mol of one of the chromium-containing compounds in **(ii)**, a white precipitate weighing 1.44 g is formed. Deduce the formula of the compound that the silver nitrate was added to.

Amt of AgCl = Amt of Cl^- = $\frac{1.44}{108+35.5}$ = 0.0100 mol
There is 1 mol of free Cl^- per mol of the compound.
Formula of the compound: $[CrCl_2(H_2O)_4]Cl.2H_2O$

[3]

(d) The following reaction scheme shows the chemistry of some chromium-containing species in aqueous solution.



(i) Identify the chromium-containing species present in **A**. Describe how this species accounts for the formation of carbon dioxide in Step **III**. Include any relevant equations in your answer.

Cr^{3+} ion has a high charge density and high polarising power. Hence $[Cr(H_2O)_6]^{3+}$ can undergo hydrolysis in water, polarising and weakening the O-H bonds of surrounding H_2O molecules, to release H^+ ions. H^+ ions react with carbonate ions via acid-base reaction to form CO_2.

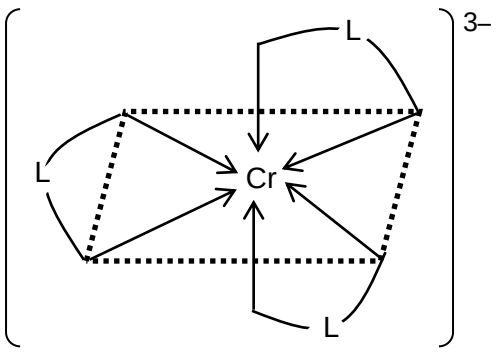
$[Cr(H_2O)_6]^{3+}(aq) \rightleftharpoons [Cr(OH)(H_2O)_5]^{2+}(aq) + H^+(aq)$

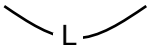
$2H^+(aq) + CO_3^{2-}(aq) \rightarrow CO_2(g) + H_2O(l)$

(ii) Give a balanced equation for step **VI**.

$2CrO_4^{2-} + 2H^+ \rightleftharpoons Cr_2O_7^{2-} + H_2O$

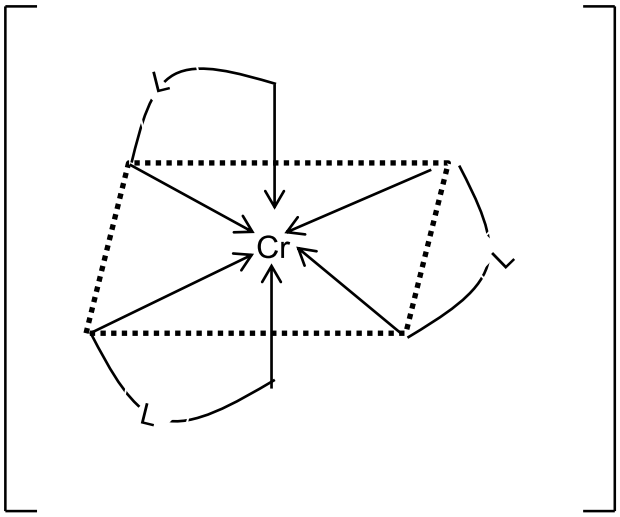
(iii) Similar to some organic molecules, the complex $[Cr(C_2O_4)_3]^{3-}$ formed in step **II** can exist as a pair of optical isomers. One of the isomers is as shown below:





is used to represent the $C_2O_4^{2-}$ ion.

Draw the structure of the other optical isomer.

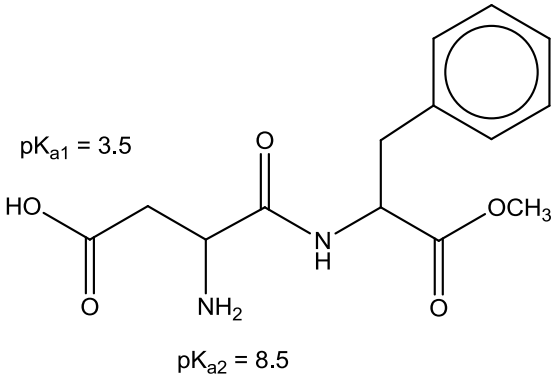


3-

[5]

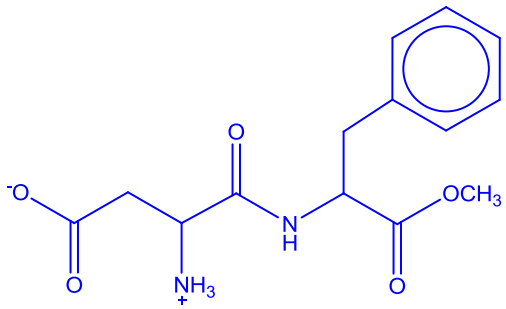
[Total: 20]

3(a) Aspartame is made from the amino acids aspartic acid and phenylalanine. It is one of the most commonly used artificial sweeteners as it is about 200 times sweeter than sugar so lesser amount is required to achieve the same level of sweetness. A molecule of aspartame is shown below:



aspartame

(i) Aspartame can exist as a zwitterion. Using the information given above, draw the structure of the zwitterion and suggest one possible pH value at which aspartame exists predominantly as a zwitterion.

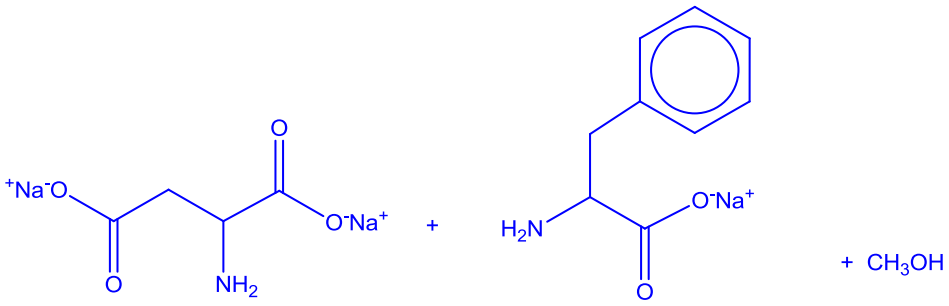


zwitterion

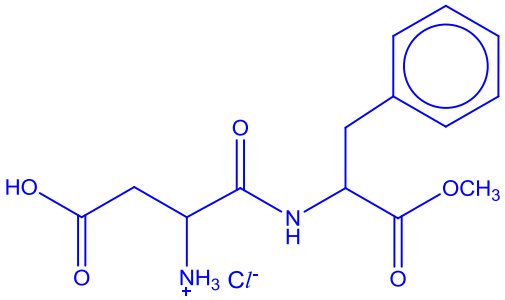
For aspartame to exist as a zwitterion, the pH of the solution should be between 3.5 and 8.5. Acceptable range: 3.5 ≤ pH ≤ 8.5.

(ii) Draw the structural formulae of the organic products formed when aspartame reacts with

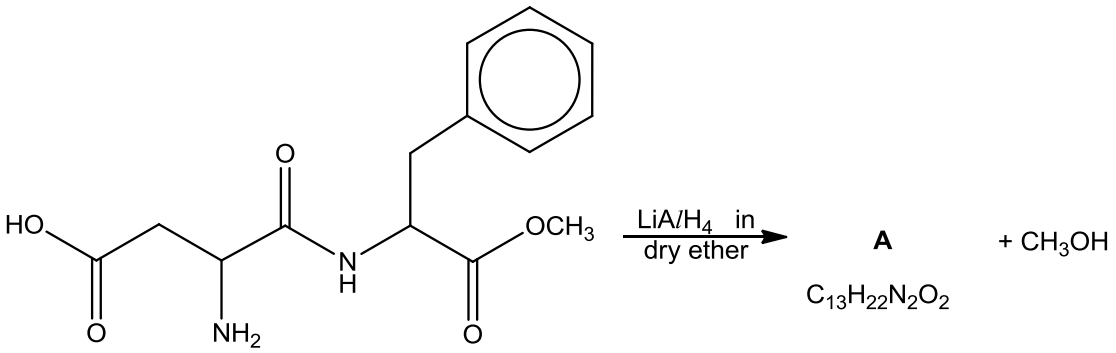
I an excess of hot NaOH(aq).



II cold HC*l*(aq).



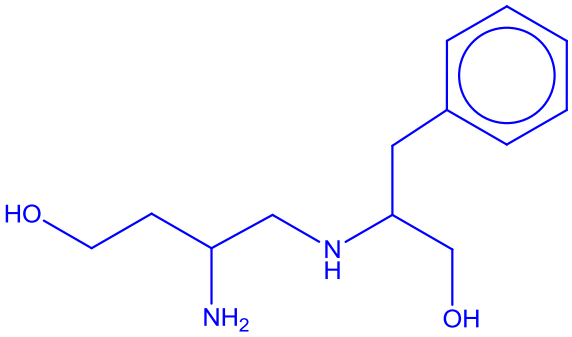
(iii) Draw the structure of compound **A** in the following reaction.



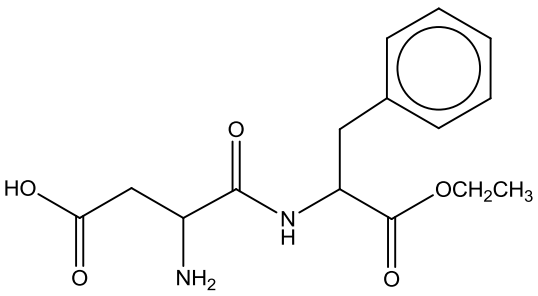
aspartame

$C_{14}H_{18}N_2O_5$

Compound **A**



(iv) Describe a simple chemical test to distinguish between aspartame and compound **B**, clearly stating the reagents, conditions and observations for each compound.



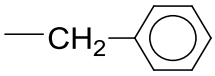
Compound **B**

To separate test tubes containing aspartame and compound B, add aqueous alkaline Iodine and heat.

For the test tube containing aspartame, no yellow crystals of CHI_3 will be formed while for the test tube containing compound B, yellow crystals of CHI_3 (CH_3CH_2OH is produced upon hydrolysis of ester) will be seen.

[9]

(b) Aspartic acid and phenylalanine can also be found in insulin**,** which consists of two polypeptide chains. It is responsible for the regulation of blood glucose level in the human body. The following table shows some amino acid residues that can be found in insulin:

Amino acid	Abbreviation	R group
aspartic acid	asp	$-CH_2CO_2H$
phenylalanine	phe	
lysine	lys	$-(CH_2)_4NH_2$
cysteine	cys	$-CH_2SH$
glycine	gly	$-H$

(i) When mercury ions, Hg^{2+}, are added to a sample of insulin, the protein is found to be denatured. State which aspects of the protein structure are affected during this denaturation.

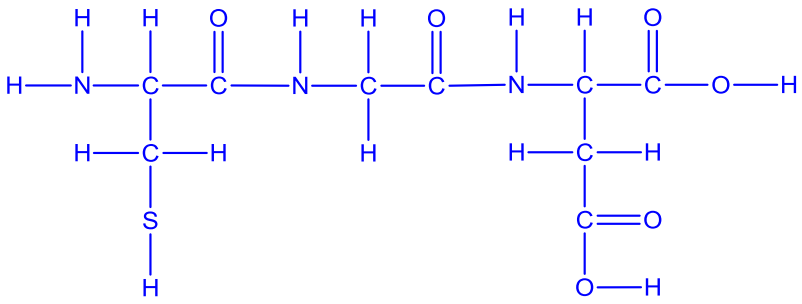
The tertiary and quaternary structures of insulin protein will be affected as the R-group interactions will be disrupted.

(ii) By considering all the interactions formed by the above amino acid residues, explain clearly how Hg^{2+} can interact with the insulin protein to bring about denaturation.

Addition of Hg^{2+} which disrupts the ionic interaction formed between $-CO_2^-$ in asp and $-NH_3^+$ in lys as Hg^{2+} will form ionic interactions with $-CO_2^-$ in asp instead.

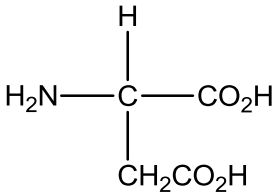
Addition of Hg^{2+} will also disrupts the disulfide linkages as Hg^{2+} binds permanently with S, thus breaking the covalent disulfide linkages formed between 2 cysteine residues.

(iii) Upon partial hydrolysis of insulin, the polypeptide chain is broken down into several fragments. One of the fragments formed is **cys-gly-asp.** Draw the displayed structure of this tripeptide.



[4]

c)



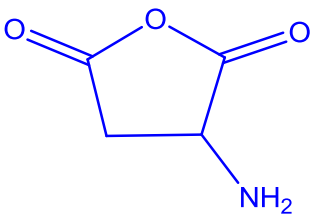
aspartic acid

Aspartic acid, $C_4H_7NO_4$, is heated gently to produce a cyclic compound **C**, $C_4H_5NO_3$, and H_2O as by-product. **C** does not react with PCl_5 and does not give any orange precipitate with 2,4-dinitrophenylhydrazine. The addition of water to **C** re-forms aspartic acid. In a similar reaction, **C** reacts with methanol in the presence of an organic solvent to give compound **D**, $C_5H_9NO_4$. 2 moles of **D** reacts completely with 1 mole of Na_2CO_3 to produce effervescence of CO_2.

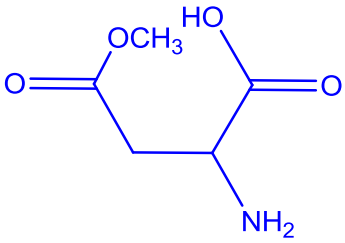
(i) Deduce structures **C** and **D** and give your reasoning.

(ii) Write a balanced equation for the reaction of **D** with sodium carbonate.

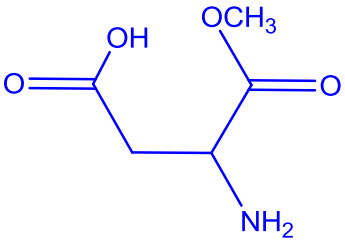
Observation	Type of reaction	Deduction
Aspartic acid, $C_4H_7NO_4$, is heated gently to produce compound **C**, $C_4H_5NO_3$, and H_2O as by-product.	-	A cyclic compound is formed after condensation
C does not react with PCl_5	No nucleophilic substitution	No alcohol group and $-CO_2H$ present in **C**.
C does not give any orange precipitate with 2,4-dinitrophenylhydrazine.	No condensation	No carbonyl group present in **C**. **C** could be an acid anhydride
C reacts with methanol in the presence of an organic solvent to give compound **D**, $C_5H_9NO_4$.	-	An ester bond and a $-CO_2H$ group is formed.
2 moles of **D** reacts completely with 1 mole of Na_2CO_3 to produce effervescence of CO_2	Acid-base reaction of carbonate and acid	1 $-CO_2H$ group is present in **D**.



Compound **C**: $C_4H_5NO_3$

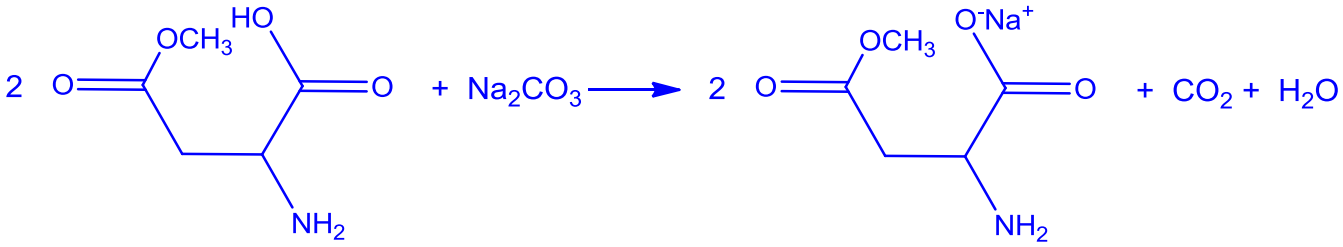


or



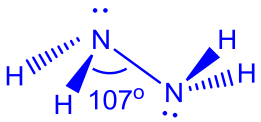
Compound **D**: $C_5H_9NO_4$

(i) Write a balanced equation for the reaction of **D** with sodium carbonate.



4 Hydrazine is a hydride of nitrogen with the formula N_2H_4. It is a colourless, flammable liquid with an ammonia-like odour. It behaves as a weak monoacidic base, forming salts with the common mineral acids.

(a) Draw the structure of hydrazine molecule to show the shape of the molecule and indicate the bond angle.



Trigonal pyramidal about N

[2]

(b) Write a balanced equation for the reaction between hydrazine and sulfuric acid.

$2N_2H_4 + H_2SO_4 \rightarrow [N_2H_5]^+{}_2SO_4^{2-}$ [OR]
$N_2H_4 + H_2SO_4 \rightarrow [N_2H_5]^+ HSO_4^-$

[1]

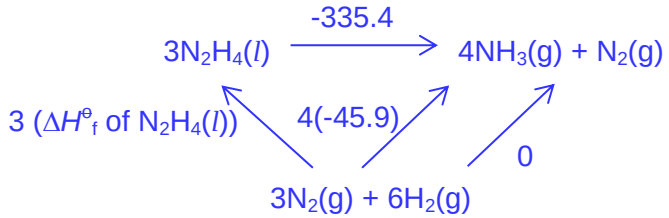
(c) One of the industrial uses of hydrazine is as a low-power monopropellant in spacecraft. In all hydrazine monopropellant engines, the hydrazine is passed by a catalyst which causes it to decompose into ammonia, nitrogen and hydrogen according to the following reactions:

reaction 1: $3N_2H_4(l) \rightarrow 4NH_3(g) + N_2(g)$ $\Delta H^{\ominus} = -335.4$ kJ mol^{-1}

reaction 2: $4NH_3(g) + N_2H_4(l) \rightarrow 3N_2(g) + 8H_2(g)$

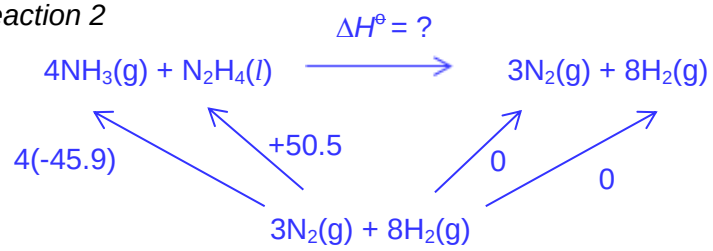
Given that $\Delta H^{\ominus}_f$ of $NH_3(g) = -45.9$ kJ mol^{-1}, calculate

(i) $\Delta H^{\ominus}_f$ of $N_2H_4(l)$



$-335 = -3(\Delta H^{\ominus}_f \text{ of } N_2H_4(l)) + 4(-45.9) + 0$
$\Delta H^{\ominus}_f \text{ of } N_2H_4(l) = (4(-45.9) + 335) / 3 = \underline{+ 50.5 \text{ kJ mol}^{-1}}$

(ii) $\Delta H^{\ominus}$ for *reaction 2*



$\Delta H^{\ominus}$ = 4(+45.9) - 50.5 = + 133 kJ mol^{-1}

[3]

(d) By considering the entropy and enthalpy changes during *reaction 1* and *reaction 2*, suggest how the standard Gibbs free energy change of the two reactions will compare in sign and in magnitude.
Hence predict which reaction will be more spontaneous. Explain your reasoning.

[3]

Entropy changes during *reaction 1* and *reaction 2* are positive due to increase in disorder of the systems as there is an increase in the number of moles of gaseous molecules formed in both reactions.

reaction 1: $\Delta G = \Delta H - T\Delta S$ (Thus, $\Delta G < 0$ at all T values)
(-) (-)(+)
reaction 2: $\Delta G = \Delta H - T\Delta S$ (Thus, $\Delta G < 0$ only at higher T values)
(+) (-)(+)

As ΔH for *reaction 2* is positive, its ΔG would only become negative at a higher temperatures whereas since the ΔH for *reaction 1* is negative, the ΔG for this reaction is negative at all temperatures.
Hence *reaction 1* will be more spontaneous.

(e) Diphosphine, P_2H_4 is the phosphorus analogue of hydrazine. Unlike hydrazine, diphosphine is not basic. It disproportionates into phosphine, PH_3 and phosphorus, P_4 in *UV* light. Both phosphine and diphosphine have lower boiling points than their nitrogen analogues.

Compound	b.p./ °C	compound	b.p./ °C
NH_3	-33	PH_3	-87
N_2H_4	113	P_2H_4	(decompose at 30)

(i) Suggest, with a reason, the bond angle in diphosphine.

The bond angle in P_2H_4 is _____ (accept any angle < 107.5° but > 90°).
P atoms in P_2H_4 are less electronegative than N atoms in hydrazine. Hence bond pair-bond pair repulsion in P_2H_4 will be less than that in N_2H_4, resulting in a smaller bond angle in P_2H_4 as compared to that in N_2H_4.

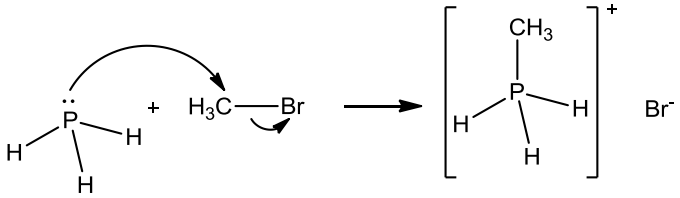
(ii) Estimate what the boiling point of diphosphine would be if it did not decompose. Explain your answer.

[3]

Boiling point of diphosphine would be (any value quoted between 30°C & 113°C acceptable).

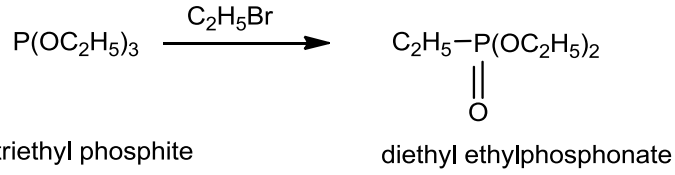
Diphosphine would have a lower b.p. than hydrazine due to less energy required to overcome its weaker intermolecular permanent dipole-permanent dipole attractions than the stronger intermolecular hydrogen bonding in hydrazine.

(f) In a similar reaction to that of ammonia, phosphine can react with bromoethane as follows.



Use this information to help explain the following reaction.

When heated with a catalytic quantity of bromoethane, triethylphosphite isomerises to diethylethylphosphonate:



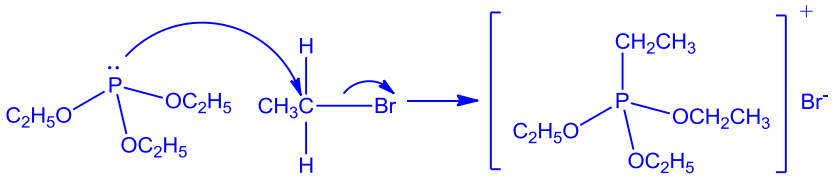
triethyl phosphite — diethyl ethylphosphonate

The isomerisation of triethyl phosphite in the presence of bromoethane is thought to proceed in two steps.

- The first step involves the formation of an intermediate upon reaction with bromoethane.
- The second step involves the cleavage of a C–O bond in the intermediate to form the final product, diethyl ethylphosphonate. Bromoethane is also regenerated.

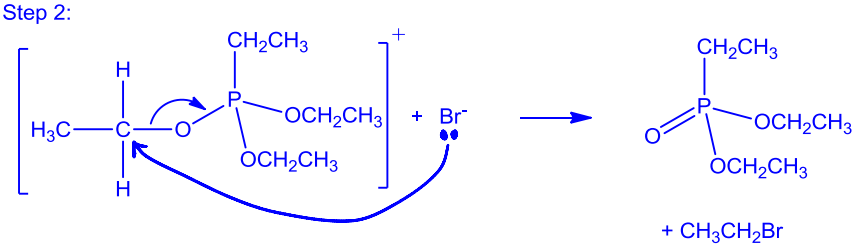
Use the information given above to draw out the full mechanism for the isomerisation of triethylphosphite. You are advised to use the structural formulae for all species so that it is clear which bonds are broken and which are formed. Include all charges and use curly arrows to show the movement of electron pairs. [3]

Step 1:



Intermediate

Step 2:



+ CH_3CH_2Br
(regenerated)

(g) Bromoethane is formed when ethane and bromine are irradiated with light at room temperature. Outline the mechanism of this reaction. [3]

Free-radical substitution

Initiation

Propagation

$CH_3CH_3 + Br\cdot \longrightarrow CH_3\dot{C}H_2 + HBr$

$CH_3\dot{C}H_2 + Br_2 \longrightarrow CH_3\dot{C}H_2Br + Br\cdot$

Termination

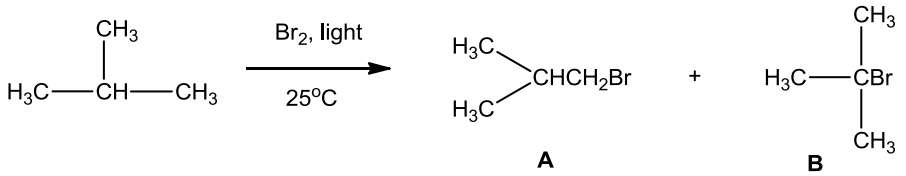
$Br\cdot + Br\cdot \longrightarrow Br_2$

$CH_3\dot{C}H_2 + Br\cdot \longrightarrow CH_3CH_2Br$

$CH_3\dot{C}H_2 + CH_3\dot{C}H_2 \longrightarrow CH_3CH_2CH_2CH_3$

butane

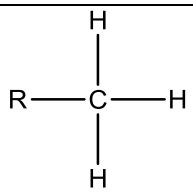
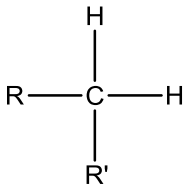
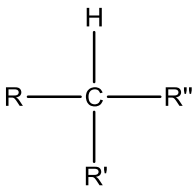
(h) The reaction described in **(g)** is seldom used for synthesis of halogenoalkanes as it results in the formation of several isomeric products.
It was observed that methylpropane reacts with bromine to form a mixture of two monobrominated alkanes, **A** and **B**, as shown below.



(i) State the expected ratio of products **A** and **B** in the mixture, assuming equal rate of substitution of H atom.

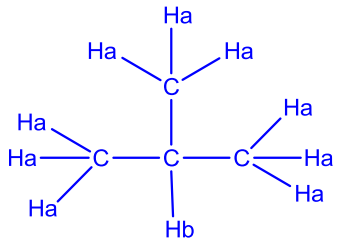
Expected ratio of **A**: **B** = 9 : 1

The ratio of the isomeric products is more accurately determined if the relative rates of substitution of H atoms are taken into account. The types of hydrogen atoms in alkanes, together with their relative rates of substitution, are shown in the following table.

Types of H atoms	**Structure**	**Relative rate of substitution**
Primary		1
Secondary		4
Tertiary		6

(ii) By taking into account the relative rates of substitution of H atoms given above, show that the products **A** and **B** are formed in the ratio of 3:2.

[2]



9 possible (primary) hydrogen (H_a) can be substituted to form **A**
1 possible (tertiary) hydrogens (H_b) can be substituted to form **B**

Assuming equal probability of substitution,
Ratio of **A : B** = 9:1

However since a tertiary H is substituted 6 times faster than a primary H,
Ratio of **A : B** = 9×1 :1×6 = 9 : 6 = 3: 2

[Total: 20]

5 (a) Explain the following observation and give balanced equations, where appropriate, to support your answers.

When chlorine is bubbled through cold sodium hydroxide and acidified silver nitrate solution is added, only half of the chlorine which has dissolved is precipitated as silver chloride. When the sodium hydroxide is hot, up to five-sixth of the chlorine can be precipitated. [3]

- **When Cl_2 is bubbled through cold NaOH,**

  $Cl_2 + 2NaOH \rightarrow NaCl + NaClO + H_2O$

  The products, NaCl and NaClO, are formed in the ratio of 1:1. Thus, only one-half of the chlorine can be precipitated as AgCl from the NaCl formed.

- **When Cl_2 is bubbled through hot NaOH,**

  $3Cl_2 + 6NaOH \rightarrow 5NaCl + NaClO_3 + 3H_2O$

  The products, NaCl and $NaClO_3$, are formed in the ratio of 5:1. Thus, only five-sixth of the chlorine can be precipitated as AgCl from the NaCl formed.

(b) In film photography, light strikes an emulsion containing silver bromide grains. The grains which are exposed turn partially into silver.

$$AgBr \xrightarrow{h\nu} Ag + \tfrac{1}{2} Br_2$$

A ***developer*** is then added to turn all the silver bromide in the affected grains to silver.

(i) Name the type of reaction taking place in the action of light on AgBr.
redox/decomposition

The remaining silver bromide in the unaffected grains is then removed by a ***fixer***, containing thiosulfate ions, which is a monodentate ligand.

$$AgBr(s) + 2S_2O_3^{2-}(aq) \rightarrow [Ag(S_2O_3)_2]^{x-}(aq) + Br^-(aq)$$

(ii) State the value of x in $[Ag(S_2O_3)_2]^{x-}(aq)$ and suggest the shape of this ion. [1]

3, linear

(iii) A student suggests adding concentrated sulfuric acid to the photographic emulsion to test for the presence of bromide ions. Describe and explain, with the aid of balanced equations, what the student would observe as a result of a successful test. [3]

- **red/reddish brown fumes/red liquid of Br_2 and some steamy fumes of HBr**
- **Br^- reacts with conc. H_2SO_4 to give HBr, which is further oxidised by conc. H_2SO_4 to Br_2.**
- **$Br^- + H_2SO_4 \rightarrow HBr + HSO_4^-$**
  $2HBr + H_2SO_4 \rightarrow Br_2 + SO_2 + 2H_2O$

(iv) If a photographic film is over-exposed, a ***reducer*** is used to diminish the intensity of the image. One such reducer is 'Farmer's reducer' which contains aqueous hexacyanoferrate(III), $[Fe(CN)_6]^{3-}$. This dissolves some of the silver metal and hexacyanoferrate(II) ions, $[Fe(CN)_6]^{4-}$, are formed.

Write an **ionic** equation to represent the action of 'Farmer's reducer'. Hence explain why, to a chemist, 'reducer' is a wrong word in view of what happens to the silver. [2]

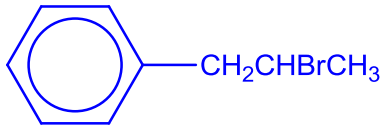
- **$Ag + [Fe(CN)_6]^{3-} \rightarrow Ag^+ + [Fe(CN)_6]^{4-}$**
- **Ag is <u>oxidised</u> to Ag^+**

(c) An organic compound **A**, $C_9H_{11}Br$, on treatment with hot aqueous potassium hydroxide gave compound **B**, $C_9H_{12}O$.

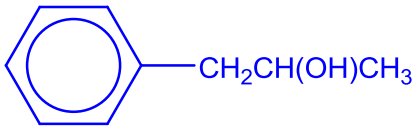
B responded to oxidation in three different ways. With acidified potassium dichromate(VI), it yielded **C**, $C_9H_{10}O$. With sodium hydroxide and iodine, it yielded **D**, $C_8H_7O_2Na$, and a yellow precipitate. With hot, acidic potassium manganate(VII) it yielded **E**, $C_7H_6O_2$.

(i) Identify compounds **A** to **E**. [5]

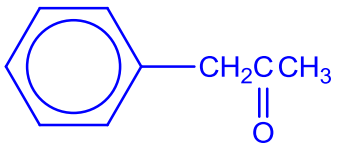
A



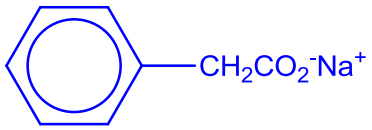
B



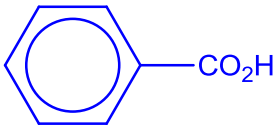
C



D



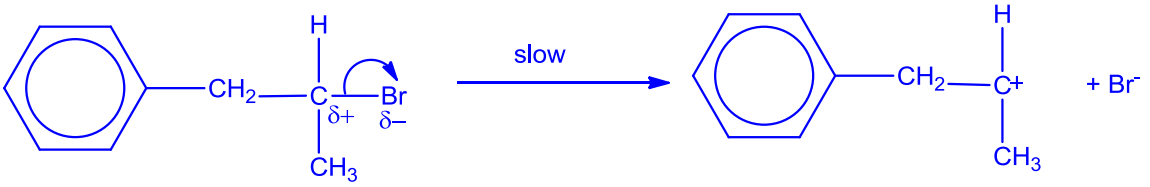
E



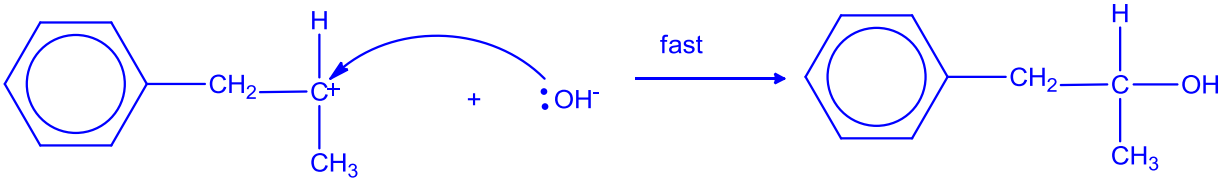
(ii) Suggest a possible mechanism for the formation of compound **B** from compound **A**, include all charges and curly arrows to show movement of electrons. [3]

Accept S_N1 or S_N2 mechanism

S_N1 Nucleophilic Substitution

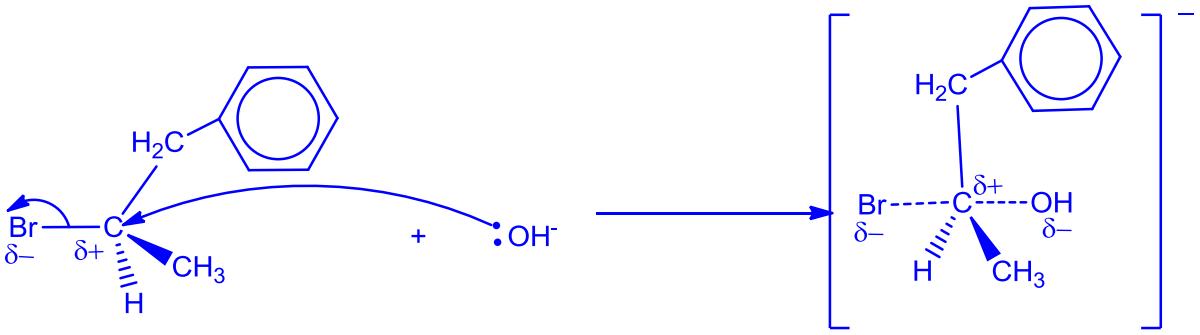


A

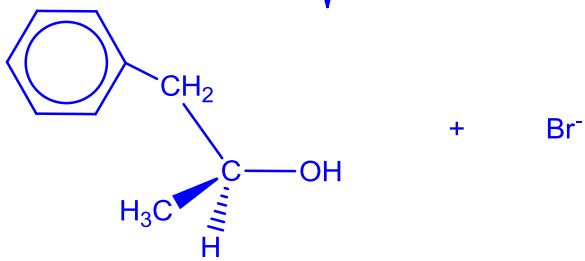


B

S_N2 Nucleophilic Substitution



A **transition state**

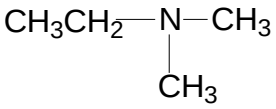


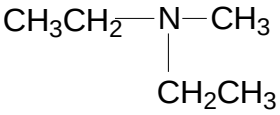
B

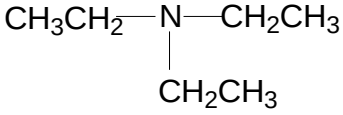
(d) Bromoethane and bromomethane, present in 1:1 molar ratio, can both react with ethylamine to form three different tertiary amines.

Suggest the structures of these three tertiary amines and hence state the ratio in which they are formed. [2]

The three tertiary amines are:







ratio 1 2 1

[Total: 20]