

CHEMISTRY

9746/03

Paper 3 Free Response

12 September 2008

2 hours

Candidates answer on separate paper.

Additional Materials: Writing Papers
Data Booklet

READ THESE INSTRUCTIONS FIRST

DO NOT open this question booklet until you are told to do so.

Write your name, civics tutorial group and index number in the spaces provided on the cover page on page 10 and the writing papers.

Write in dark blue or black pen on both sides of paper.

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.

Begin each question on a fresh sheet of paper.

A Data Booklet is provided. Do not write anything on it.

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, with the cover page on top.

Answer any **four** questions. Begin each question on a fresh sheet of paper.

1 This question involves Period 3 elements and their compounds.

(a) An aqueous mixture of sodium hydrogencarbonate and sodium carbonate can act as a buffer solution.

(i) Define the term *buffer solution*.

(ii) With the aid of **two** equations, explain how a solution of sodium hydrogencarbonate and sodium carbonate can act as a buffer.

(iii) Calculate the pH range in which the buffer is most effective. Take the K_a for HCO_3^- to be $5.61 \times 10^{-11} \text{ mol dm}^{-3}$ at 25°C .

(iv) Calculate the change in pH of the solution if the ratio $\frac{[\text{CO}_3^{2-}]}{[\text{HCO}_3^-]}$ was increased from 0.30 to 0.96. [7]

(b) Explain, with the aid of equations, why

(i) a solution of aluminium sulphate turns blue litmus red.

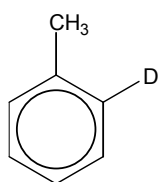
(ii) aluminium oxide dissolves on addition of excess aqueous sodium hydroxide. [4]

(c) Sketch the graph of the pH of the resulting mixture when the oxides of Na to S are separately added to water. [1]

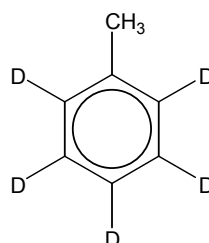
- (d) Deuterium (D or ^2H) is a heavy isotope of hydrogen.

Chlorine can react with deuterium to form deuterium chloride, DCl .

When DCl is dissolved in methylbenzene, no reaction occurs. However, if an anhydrous catalyst **W** is added to the solution, a reaction takes place, and a compound **X** is one of the products. If more DCl is present, a compound **Y** is formed.

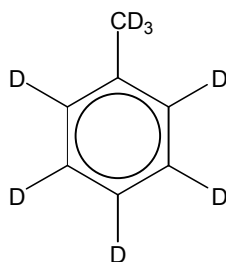


X



Y

- (i) Suggest a suitable identity for the catalyst **W**. Explain why **W** must be anhydrous and why it can act as the catalyst in the reaction.
- (ii) With the aid of equations, state and describe the mechanism involved in the formation of compound **X** from methylbenzene.
- (iii) In the presence of excess DCl , would compound **Z** be formed? Explain. [8]



Z

[Total: 20]

- 2 The halogens are elements in Group VII of the Periodic Table and display similar chemical properties. They are good oxidising agents and can exhibit variable oxidation states.

(a) Using relevant data from the *Data Booklet*, describe and explain the reactions of the

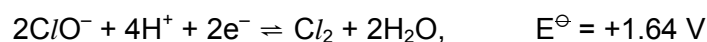
(i) elements, X_2 (where $X = Cl, Br$ and I), with aqueous sodium thiosulphate.

(ii) halide ions, X^- , with concentrated sulphuric acid.

Give an equation for any reaction that occurs.

[7]

Chlorine, which is a Group VII element, has been extensively used in the manufacture of many compounds. One such compound is household bleach, which contains sodium chlorate(I), $NaClO$. The chlorate(I) ion acts as a powerful oxidising agent in acid solution:



(b) (i) What do you understand by the term *standard electrode potential*?

(ii) Draw a labelled diagram to show how you could measure the standard electrode potential of the $ClO^-(aq)/Cl_2(g)$ electrode system. You are to indicate clearly the anode and cathode and to show the direction of the flow of electrons.

(iii) Predict whether a reaction will occur when chlorate(I) in acid solution is mixed with $H_2O_2(aq)$. Calculate E^\ominus_{cell} and write an equation for any reaction that occurs.

[7]

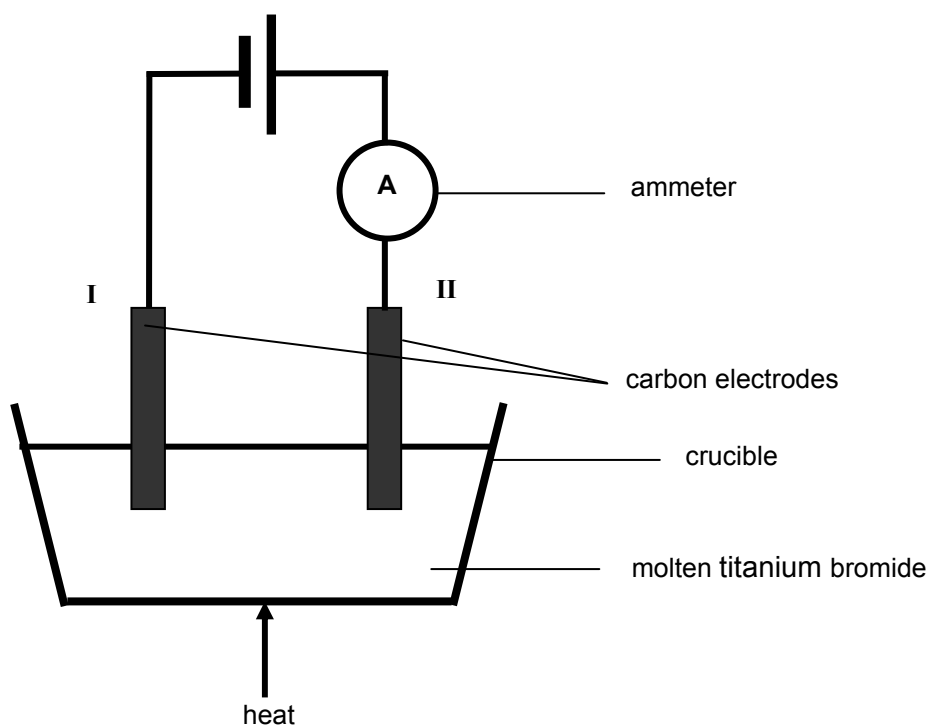
Bromine, which is another Group VII element, is used to manufacture silver bromide. Silver bromide is often found in photographic film.

(c) Silver bromide is insoluble in water. Explain why silver bromide dissolves when concentrated aqueous ammonia is added.

[2]

[2]

Another bromine-containing compound is titanium bromide. An electrolysis experiment was conducted using the apparatus shown below to determine the correct formula for titanium bromide, TiBr_x .



Crystals of titanium bromide were placed in the crucible and heated. The molten bromide was then electrolysed using carbon electrodes. Results for the experiment were:

Ammeter reading	0.50 A
Duration of current flow	1 hour and 30 minutes
Mass of titanium produced	0.45 g

(d) (i) Identify the electrode (I or II) at which titanium is produced.

(ii) Determine the value of x .

[4]

[Total: 20]

3 Carbon is one of the most abundant elements on Earth. While it is found mainly in organic substances, carbon does exist as inorganic compounds such as carbon dioxide, carbonates and hydrogencarbonates.

(a) In order to determine the titration curve of the reaction between $\text{HCO}_3^-(\text{aq})$ and $\text{HCl}(\text{aq})$, a student took a 25.0 cm^3 of solution containing $0.100 \text{ mol dm}^{-3} \text{ HCO}_3^-$ ions and titrated it with standard $0.100 \text{ mol dm}^{-3}$ dilute HCl .

(K_b for $\text{HCO}_3^- = 2.34 \times 10^{-8} \text{ mol dm}^{-3}$ at 25°C)

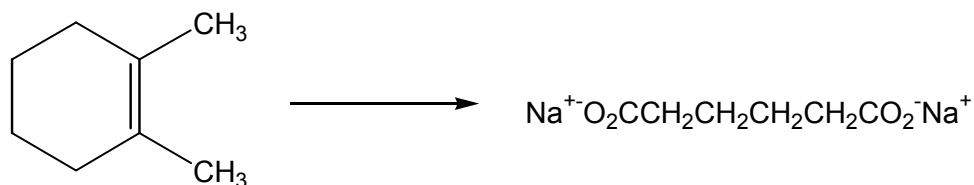
(i) Calculate the pH of the solution before the addition of dilute HCl .

(ii) Calculate the pH of the solution at the equivalence point.

(iii) Calculate the pH of the solution after 37.5 cm^3 of dilute HCl was added.

(iv) Using your answers from (i) to (iii), sketch the pH titration curve. [9]

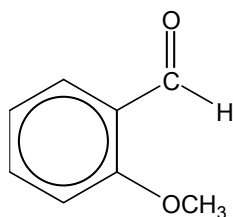
(b) Industrially, inter-conversions between organic compounds are common. Devise a **two**-step synthesis for the following conversion.



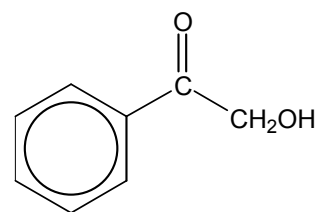
Indicate the reagents and conditions for each step, and draw the structure of the intermediate. [2]

(c) Organic compounds can be distinguished using simple chemical tests. Suggest how you can distinguish between the following pairs of isomers. State clearly the reagents and conditions used as well as the observations for each compound. (The $-\text{OCH}_3$ group is inert and can be disregarded in this question.)

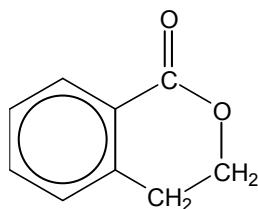
(i)



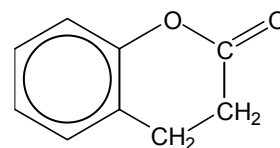
and



(ii)



and



[5]

(d) Observations from kinetics studies often allow scientists to deduce the mechanisms of organic reactions.

The hydrolysis of $(\text{CH}_3)_3\text{CBr}$ with aqueous sodium hydroxide is found to be first order with respect to $(\text{CH}_3)_3\text{CBr}$ and zero order with respect to OH^- . The half-life for the reaction is 5 minutes.

- (i) Write the rate equation. Calculate the value of the rate constant, giving its units.
- (ii) If the initial concentration of $(\text{CH}_3)_3\text{CBr}$ used is 1.6 mol dm^{-3} , sketch a graph of concentration of $(\text{CH}_3)_3\text{CBr}$ against time for the bromoalkane to decrease to 6.25 % of its original concentration. [4]

[Total: 20]

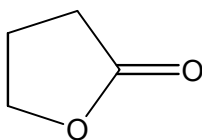
- 4 A neutral compound **P** has molecular formula, $C_{15}H_{20}O_3NCl$. When **P** is refluxed with aqueous sodium hydroxide, three compounds **Q**, **R** and **S** are obtained.

Upon analysis, **Q** is found to be a straight-chain molecule having a relative molecular mass of 59, and its composition by mass is as follows:

61.0% C, 15.3% H, 23.7% N

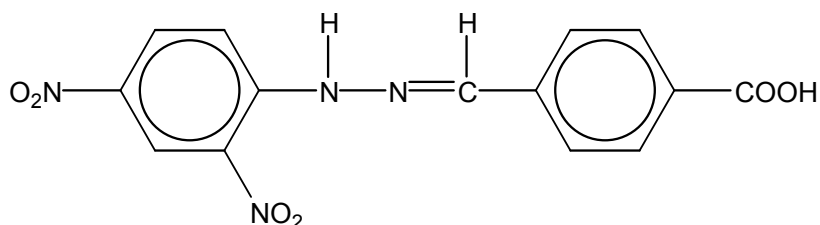
When **Q** is treated with excess iodomethane, **T** is formed. **T** has a relative formula mass of 229 and gives a yellow precipitate immediately when treated with aqueous silver nitrate.

R has the molecular formula $C_4H_7O_3Na$. Upon acidification, it yields **U**. **U** is also obtained when **P** is refluxed with dilute sulphuric acid. Heating **U** with a small amount of concentrated sulphuric acid produces a compound known as gamma-butyrolactone, which has the following structure:



gamma-butyrolactone

S ($C_8H_7O_3Na$), upon addition of acidified potassium dichromate(VI) and heating with immediate distillation, yields **V**. Treating **V** with 2,4-dinitrophenylhydrazine gives an orange precipitate which has the following structure:



- (a) Determine the empirical and molecular formula of **Q**. Show your working clearly. [2]
- (b) Deduce, with reasoning, the structures of **P** to **V**. [15]

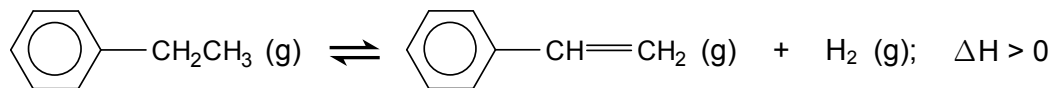
Compound **U** can be used as a precursor of 4-aminobutanoic acid, which is also known as GABA (Gamma-AminoButyric Acid). GABA is the chief inhibitory neurotransmitter in the central nervous system and in the human retina. It also regulates muscle tone and other functions.

- (c) Both GABA and **U** have similar relative molecular masses. However, GABA is found to have a much higher melting point than **U**. Explain. [3]

[Total: 20]

- 5 Styrene, $\text{C}_6\text{H}_5\text{CH}=\text{CH}_2$, which occurs naturally in foods like beef, peanuts and strawberries, is the raw material used to make plastics such as polystyrene. Industrially, styrene can be synthesized from ethylbenzene.

- (a) The most common method of manufacturing styrene is by the catalytic dehydrogenation of ethylbenzene:



In a pilot study, ethylbenzene gas is mixed with steam in a 1000 m^3 reactor, maintained at 600°C , in the presence of an iron(III) oxide catalyst. The steam does not take part in the above reaction but acts like a gaseous solvent. The equilibrium constant, K_p , is found to be 0.242 atm .

- (i) Write an expression for the equilibrium constant, K_p .
- (ii) Given that the initial pressure of ethylbenzene gas is $p \text{ atm}$, and that the conversion to styrene was 65% , calculate the value of p .
- (iii) Draw a sketch graph showing how the **rates** of the forward and reverse reactions change, from the time ethylbenzene was mixed with steam in the presence of the catalyst, to the time the reaction reaches equilibrium. Label the two lines clearly.
- (iv) State and explain how the yield of styrene would change if there was an increase in temperature.

In the above reactor system, all the gases present can be treated as exhibiting ideal behaviour.

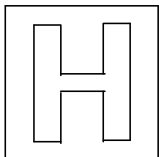

- (v) State **two** assumptions of the kinetic theory of gases.
- (vi) Based on your answer in (ii), calculate the amount of styrene present at equilibrium. [12]

- (b) Both styrene and ethylbenzene share similar reactions although the actual mechanisms usually differ.

- (i) When styrene and ethylbenzene are brominated via different electrophilic mechanisms, a **total** of three isomers ($\text{C}_8\text{H}_9\text{Br}$) in significant quantities are formed. For each hydrocarbon, state the reagents/conditions used and give the structural formula of the product(s).
- (ii) When styrene and ethylbenzene are oxidised vigorously, the same compound **K** is formed. By slightly modifying the conditions, **one** of the hydrocarbons reacts to form compound **L**. Both **K** and **L** contain two oxygen atoms. Give the structural formulae of **K** and **L** and state the reagents/conditions needed to produce **L**. [8]

[Total: 20]

Name	()	CT Group
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	RAFFLES JUNIOR COLLEGE PRELIMINARY EXAMINATION 2008	
	HIGHER 2 CHEMISTRY 9746	

Attach this cover page to the top of your answer scripts.

Question <i>(Please circle the questions you have attempted.)</i>	For Examiners' Use Only Parts			Marks
1				/ 20
2				/ 20
3				/ 20
4				/ 20
5				/ 20

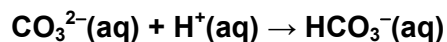
Paper 1	/ 40
Paper 2	/ 60
Paper 3	/ 80
Total Marks	/180
Percentage	%
Grade	

Suggested Solutions to 2008 RJC Prelim Paper 3:

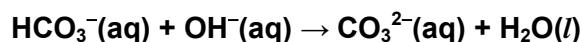
Question 1 :

- (a) (i) A buffer solution can resist small change in pH when a small quantity of acid or base is added.

- (ii) When a small amount of H^+ is added:



When a small amount of OH^- is added:



The high concentration of the $\text{CO}_3^{2-}(\text{aq})$ and $\text{HCO}_3^-(\text{aq})$ ions can resist a change in pH.

- (iii) The buffer action would be most effective in the range of **9.3 to 11.3 (or 10.3 ± 1)**.

- (iv) Use $\text{pH} = \text{pK}_a + \log[\text{CO}_3^{2-}]/[\text{HCO}_3^-]$

When $[\text{CO}_3^{2-}]/[\text{HCO}_3^-] = 0.30$, $\text{pH} = 9.728$

When $[\text{CO}_3^{2-}]/[\text{HCO}_3^-] = 0.96$, $\text{pH} = 10.233$

Therefore, change in $\text{pH} = 10.233 - 9.728 = \mathbf{0.505}$

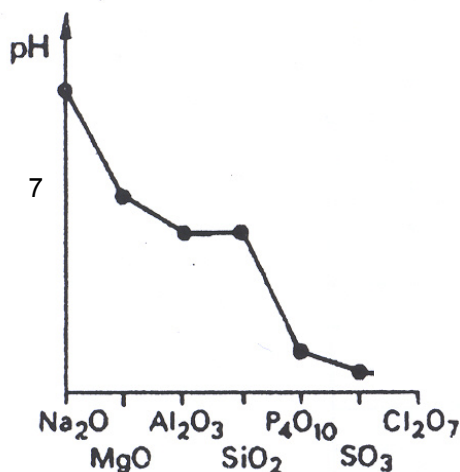
- (b) (i) $[\text{Al}(\text{H}_2\text{O})_6]^{3+}(\text{aq}) \rightleftharpoons [\text{Al}(\text{H}_2\text{O})_5(\text{OH})]^{2+}(\text{aq}) + \text{H}^+(\text{aq})$

The hydrolysis of the $[\text{Al}(\text{H}_2\text{O})_6]^{3+}(\text{aq})$ would release H^+ ions which would turn blue litmus red.

- (ii) $\text{Al}_2\text{O}_3(\text{s}) + 2\text{OH}^-(\text{aq}) + 3\text{H}_2\text{O}(\text{l}) \rightarrow 2\text{Al}(\text{OH})_4^-(\text{aq})$

Al_2O_3 is predominantly ionic with some covalent character. Hence it is amphoteric and is able to react with alkali.

- (c)

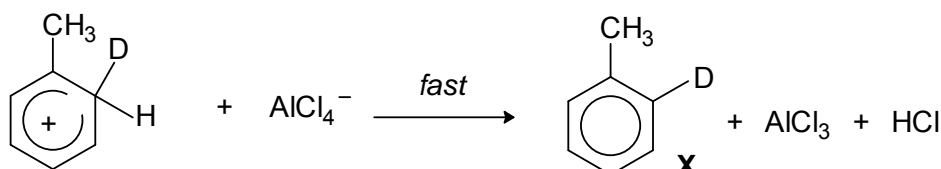
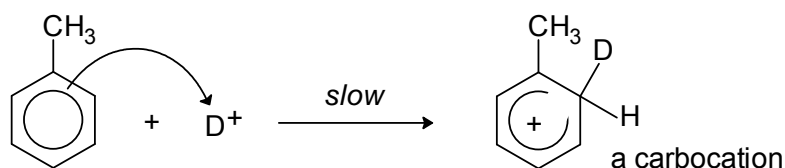
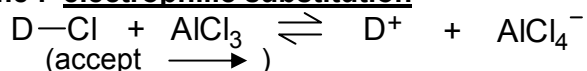


(d) (i) **W** can be **AlCl₃/ FeCl₃**

AlCl₃ (FeCl₃) is able to act as a catalyst for the reaction because the Al (Fe) atom is **electron-deficient** and has a **low-lying vacant orbital** to accept an electron pair from Cl of the DCl molecule.

AlCl₃ (FeCl₃) has to be anhydrous because it **hydrolyses** in / **reacts** with water to yield [Al(H₂O)₆]³⁺ ([Fe(H₂O)₆]³⁺) and Cl⁻ ions. Al atom in [Al(H₂O)₆]³⁺ is **coordinatively saturated** (has **no low-lying vacant orbitals**) and cannot function as a catalyst.

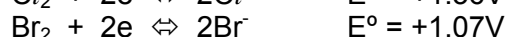
(ii) Name : **electrophilic substitution**



(iii)

Z would **not** be formed.

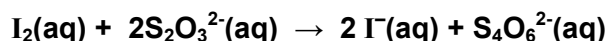
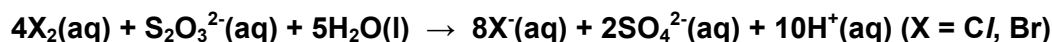
The D⁺ electrophile would not be attracted to the carbon atom in the -CH₃ group since this carbon atom is **not electron-rich**. (or it would require a **D• radical** to react with the **non-polar** CH₃ side-chain)

Question 2 :**(a) (i)**

Down the group, $E^\circ (\text{X}_2/\text{X}^-)$ becomes **less positive** (decreases)

Oxidising power of the halogens **decreases** down Group VII.

(or Cl_2 is the strongest oxidizing agent, I_2 is the weakest oxidizing agent.)

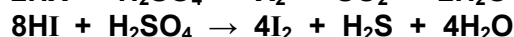
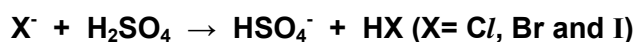


Both Cl_2 and Br_2 can oxidise $\text{S}_2\text{O}_3^{2-}$ (oxidation state of S = **+2**) to SO_4^{2-} (oxidation state of S = **+6**)

I_2 can only oxidise $\text{S}_2\text{O}_3^{2-}$ (oxidation state of S = **+2**) to $\text{S}_4\text{O}_6^{2-}$ (oxidation state of S = **+2.5**)

(ii) Down the group,

Reducing power of the **halide ions increases** or reducing power of $\text{I}^- > \text{Br}^- > \text{Cl}^-$



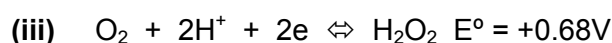
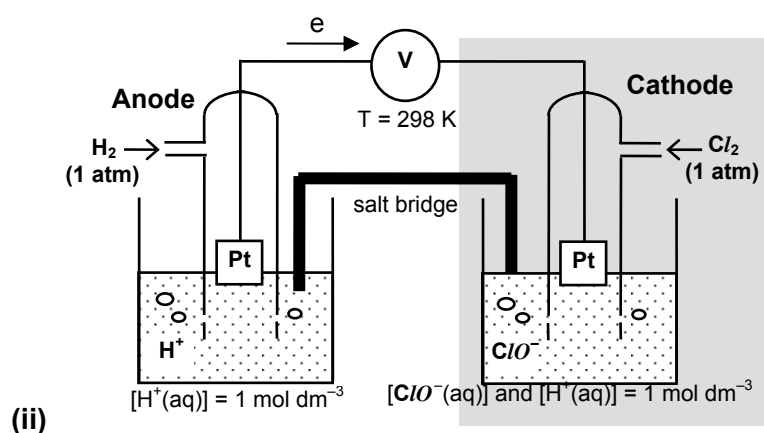
The halide ions react with concentrated H_2SO_4 to give the hydrogen halide. HX can reduce the concentrated H_2SO_4 , depending on the reducing power of the halides.

HI can reduce H_2SO_4 (oxidation state of S = **+6**) to H_2S (oxidation state of S = **-2**) and itself oxidized to I_2 .

HBr reduce H_2SO_4 (oxidation state of S = **+6**) to SO_2 (oxidation state of S = **+4**) and itself oxidized to Br_2 .

HCl cannot reduce H_2SO_4 .

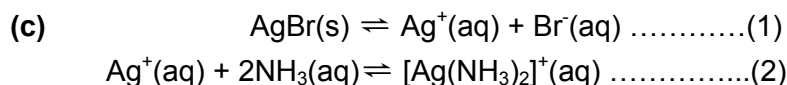
- (b) (i)** The *standard electrode potential* of a half-cell is the electromotive force, measured at **298K and 1 atm**, between the **half-cell and the standard hydrogen electrode**, in which the reacting species in solution are at **molar concentrations**.



$$E^\circ_{\text{cell}} = 1.64 - (+0.68) = +0.96\text{V} > 0$$

=> reaction is thermodynamically feasible

$$2\text{ClO}^- + \text{H}_2\text{O}_2 + 2\text{H}^+ \rightarrow \text{Cl}_2 + \text{O}_2 + 2\text{H}_2\text{O}$$



When concentrated $\text{NH}_3(\text{aq})$ is added to AgBr(s) in water, there is formation of the soluble $[\text{Ag}(\text{NH}_3)_2]^+$ complex ion as shown by reaction (2).

This **causes the $[\text{Ag}^+(\text{aq})]$ to decrease** and forces the **equilibrium position of reaction (1) to shift right in accordance to LeChatelier's principle**. Hence AgBr(s) dissolves to form $\text{Ag}^+(\text{aq})$ ions. With sufficient concentrated $\text{NH}_3(\text{aq})$ added, all the AgBr dissolves.

or

This **causes the $[\text{Ag}^+(\text{aq})]$ to decrease** and hence momentarily **causes the ionic product of AgBr to drop below its K_{sp} value**. To restore the ionic product to this K_{sp} value, AgBr(s) dissolves i.e. the equilibrium position of reaction (1) shifts right. With sufficient concentrated $\text{NH}_3(\text{aq})$ added, all the AgBr dissolves.

(d)(i)
Electrode I.

(ii)
Amount of Ti = $0.45/47.9 = 9.39 \times 10^{-3}$ mol
Quantity of charge, $Q = It = (0.50)(90 \times 60) = 2700$ C
Amount of electrons = $2700/96500 = 2.80 \times 10^{-2}$ mol

Molar ratio of e^- to Ti = $2.80 \times 10^{-2} : 9.39 \times 10^{-3} = 2.98 : 1 = 3 : 1$

Reaction at the cathode: $\text{Ti}^{x+}(\text{l}) + \text{x}\text{e}^- \longrightarrow \text{Ti}(\text{l})$
Molar ratio of e^- to Ti: $x : 1$
Hence $x = 3$

Question 3:**(a)(i)** HCO_3^- is a weak base.

concentration/mol dm ⁻³	$\text{HCO}_3^-(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}_2\text{CO}_3(\text{aq}) + \text{OH}^-(\text{aq})$		
initial	0.100	–	–
equilibrium	$(0.100 - y)$ ≈ 0.100 (since HCO_3^- has a relatively small K_b such that $y \ll 0.1.00$)	y	y

$$K_b \text{ of } \text{HCO}_3^- = \frac{[\text{H}_2\text{CO}_3][\text{OH}^-]}{[\text{HCO}_3^-]} = \frac{y^2}{(0.100)} = 2.34 \times 10^{-8} \text{ mol dm}^{-3}$$

$$y = (2.34 \times 10^{-8})^{1/2} = 4.84 \times 10^{-5}$$

$$[\text{OH}^-] = 4.84 \times 10^{-5} \text{ mol dm}^{-3}$$

$$\text{pOH} = -\lg(4.84 \times 10^{-5}) = 4.32$$

$$\text{pH} = 14 - 4.32 = 9.68$$

Hence pH of the HCO_3^- solution = **9.68****(ii)**Reaction upon addition of $\text{HCl}(\text{aq})$: $\text{HCO}_3^-(\text{aq}) + \text{HCl}(\text{aq}) \longrightarrow \text{H}_2\text{CO}_3(\text{aq}) + \text{Cl}^-(\text{aq})$ Volume of $0.100 \text{ mol dm}^{-3} \text{ HCl}(\text{aq})$ needed to reach equivalence point = 25.0 cm^3 Total volume of resultant solution = $25.0 + 25.0 = 50.0 \text{ cm}^3$ At the equivalence point, the resultant solution contained $\text{H}_2\text{CO}_3(\text{aq})$.Assumption: $\text{H}_2\text{CO}_3(\text{aq})$ did not decompose to yield $\text{CO}_2(\text{g})$ and $\text{H}_2\text{O}(\text{l})$.Amount of H_2CO_3 = Amount of HCO_3^- reacted = $(25.0/1000)(0.100) = 2.50 \times 10^{-3} \text{ mol}$ $[\text{H}_2\text{CO}_3]$ in solution = $2.50 \times 10^{-3} / 0.050 = 0.0500 \text{ mol dm}^{-3}$

$$K_a \text{ of } \text{H}_2\text{CO}_3 = \frac{K_w}{K_b \text{ of } \text{HCO}_3^-} = \frac{1.0 \times 10^{-14}}{2.34 \times 10^{-8}} = 4.27 \times 10^{-7} \text{ mol dm}^{-3}$$

concentration/mol dm ⁻³	$\text{H}_2\text{CO}_3(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{HCO}_3^-(\text{aq}) + \text{H}_3\text{O}^+(\text{aq})$		
initial	0.0500	–	–
equilibrium	$(0.0500 - w)$ ≈ 0.0500	w	w

Assumptions:
 (1) H_2CO_3 has a relatively small K_a such that $w \ll 0.0500$.
 (2) H^+ (or H_3O^+) from the second dissociation of H_2CO_3 (i.e. from the hydrolysis of HCO_3^-) is negligible and is ignored.

$$K_a \text{ of } \text{H}_2\text{CO}_3 = \frac{[\text{HCO}_3^-][\text{H}_3\text{O}^+]}{[\text{H}_2\text{CO}_3]} = \frac{w^2}{0.0500} = 4.27 \times 10^{-7} \text{ mol dm}^{-3}$$

$$\Rightarrow w = 1.46 \times 10^{-4}$$

$$[\text{H}_3\text{O}^+] = 1.46 \times 10^{-4} \text{ mol dm}^{-3}$$

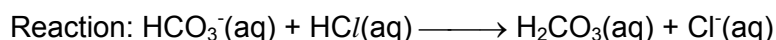
$$\text{pH} = -\lg(1.46 \times 10^{-4}) = 3.84$$

Hence pH of the solution at the equivalence point = **3.84**

(iii)

Volume of HCl needed to reach equivalence point = 25.0 cm^3

Excess volume of HCl added = $37.5 - 25.0 = 12.5 \text{ cm}^3$



The resultant solution contained both **$\text{H}_2\text{CO}_3(\text{aq})$** and **unreacted $\text{HCl}(\text{aq})$** .

Note:

HCl(aq) is a strong acid. The presence of H^+ from the complete dissociation of HCl(aq) suppressed the dissociation of H_2CO_3 (a weak acid) by common ion effect such that any contribution of H^+ from H_2CO_3 can be ignored. All the H^+ in the solution can be assumed to come from HCl(aq).

Amount of H^+ from HCl(aq) = Amount of HCl = $(12.5/1000)(0.100) = 1.25 \times 10^{-3} \text{ mol}$

Total volume of resultant solution = $25.0 + 37.5 = 62.5 \text{ cm}^3$

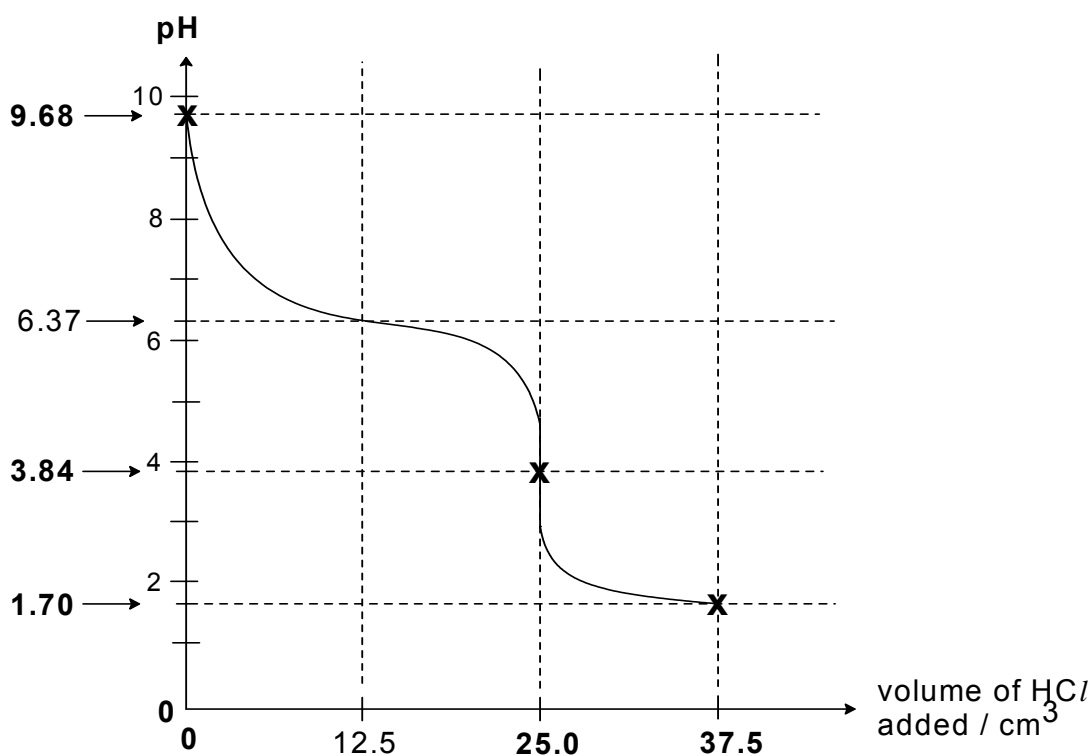
$$[\text{H}^+] = 1.25 \times 10^{-3} / 0.0625 = 0.0200 \text{ mol dm}^{-3}$$

$$\text{pH} = -\lg [\text{H}^+] = -\lg(0.0200) = \mathbf{1.70}$$

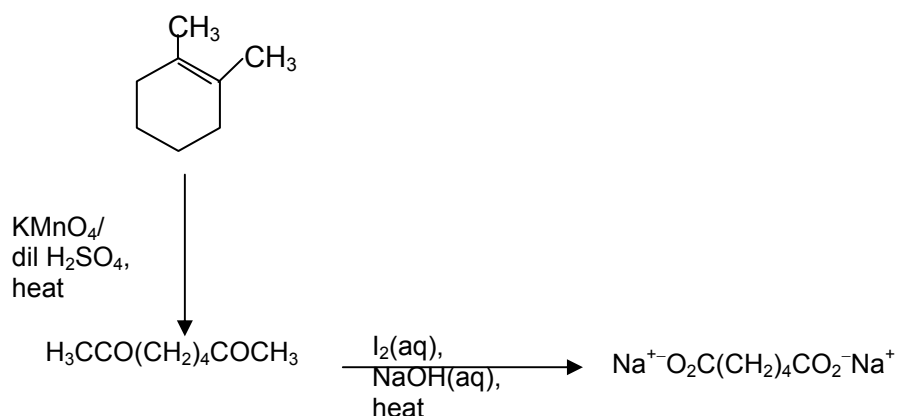
(iv)

Note:

	(i)	"half-equivalence point"	(ii)	(iii)
Volume of HCl added/ cm^3	0	12.5	25.0	37.5
Species present	weak base HCO_3^-	acidic buffer $\text{HCO}_3^- + \text{H}_2\text{CO}_3$	weak acid H_2CO_3	strong acid & weak acid $\text{HCl} + \text{H}_2\text{CO}_3$
pH of resultant solution	9.68	$\text{pOH} = \text{p}K_b = 7.63$ $\text{pH} = 6.37$	3.84	1.70



(b)



(c) (i) Add **Tollens' reagent** to both compounds separately with **warming**.
For the 1st compound (aldehyde), there would be a **silver mirror formed**.
For the 2nd compound, there would be **no silver mirror formed**.

(ii) First, **add dil H₂SO₄ (aq)** to both compounds **separately**, and **heat**.
Then, **cool** and add **aqueous bromine** to both samples.

For the 1st compound, the **reddish-brown bromine remains**, with the absence of the formation of any ppt.

For the 2nd compound, there would be a **decolourisation of reddish-brown bromine**, with the formation of a **white ppt**.

Or

Add **K₂Cr₂O₇ (aq), dil H₂SO₄, heat**

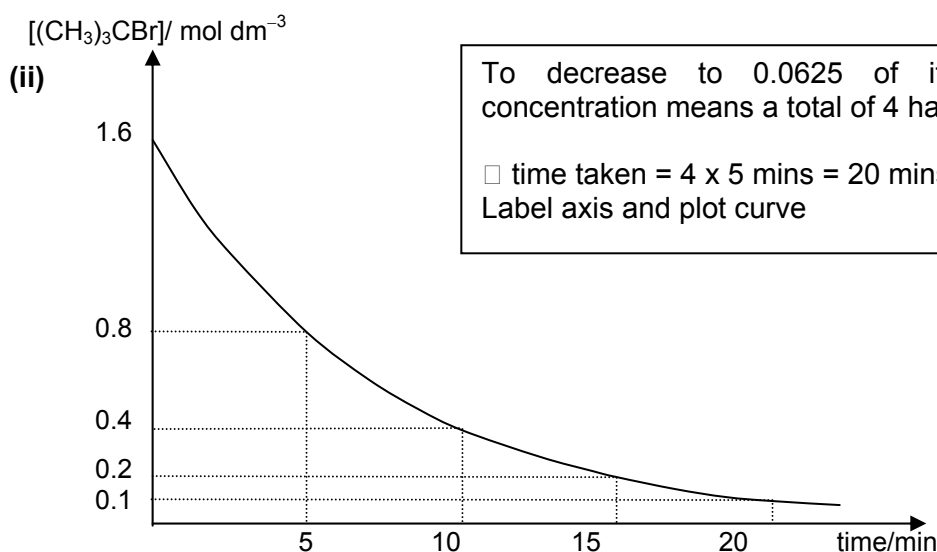
For the 1st compound, **orange** solution turns **green**.

For the 2nd compound, orange solution does **not** turn green.

(d) (i) **rate = k[(CH₃)₃CBr]**

$$kt_{1/2} = \ln 2$$

$$k = (\ln 2) / 5 = \mathbf{0.139 \text{ min}^{-1} \text{ or } 2.31 \times 10^{-3} \text{ s}^{-1}}$$



Question 4 :

(a)

Mole ratio of C to H to N in compound Q			
=	61.0/12.0	15.3/1.0	23.7/14.0
=	5.08	15.3	1.7
=	3	9	1

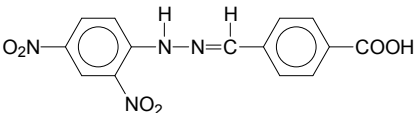
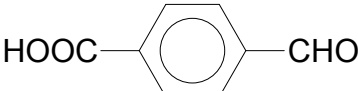
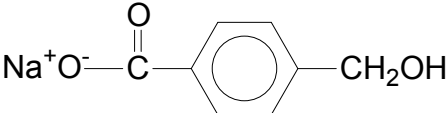
Hence the empirical formula of **Q** is **C₃H₉N**.

The M_r of **Q** is 59.

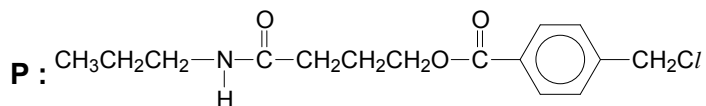
Let **Q** be (C₃H₉N)_n. Then M_r of **Q** = (3n)(12.0) + (9n)(1.0) + (n)(14.0) = 59
 $59n = 59$ i.e. **n = 1**

Hence the molecular formula of **Q** is **C₃H₉N**.

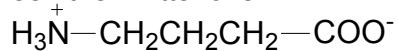
(b)

Description	Deductions
P , C ₁₅ H ₂₀ O ₃ NC/	6 degrees of unsaturation / high C:H ratio . Benzene ring may be present since P has at least 6 C atoms
P is neutral compound	Amines, carboxylic acids, phenols absent OR amides, esters present
Q reacted with excess iodomethane to give T (M_r = 229). T gives a yellow precipitate with aqueous silver nitrate. Q is straight-chain.	T is a quarternary ammonium iodide OR quarternary ammonium salt T can be [CH ₃ CH ₂ CH ₂ N(CH ₃) ₃] ⁺ I ⁻ T has M_r = (6)(12.0)+(16)(1.0)+(1)(14.0)+127 = 229 which agrees with the given value (show working) OR Since M_r of T is 229, three -CH ₃ groups must be substituted on Q (show working : 229-127-57 = 45 = 3 x 15) Hence Q is a primary amine Since Q is a straight-chain amine, Q can be CH₃CH₂CH₂NH₂ .
R on acidification yields U , which is also obtained from acidic hydrolysis of P .	R is the sodium carboxylate U is a carboxylic acid
U reacts with a small amount of concentrated sulphuric acid to give γ -butyrolactone	U undergoes esterification (or intra-esterification) U must be a hydroxy acid U must be HO₂C-CH₂CH₂CH₂OH R must be Na⁺O₂C-CH₂CH₂CH₂OH
S (C ₈ H ₇ O ₃ Na), reacts with acidified potassium dichromate(VI) and heating with immediate distillation, to give V . Treating V with 2,4-DNPH gives an orange precipitate which has the following structure: 	Since V undergoes condensation with 2,4-DNPH to give the hydrazone, V must be an aldehyde with the structure  Since V is obtained from (controlled) oxidation of S S must be a primary alcohol with the structure 
When P is refluxed with aqueous sodium hydroxide, three compounds Q , R and S are	P undergoes alkaline hydrolysis of the ester and amide groups and nucleophilic substitution of the Cl . P must be an ester, amide and chloroalkane .

obtained.



(c) Solid GABA, 4-aminobutanoic acid, exists as **zwitterions** in a **giant ionic structure** with **strong ionic bonds** between the zwitterions.



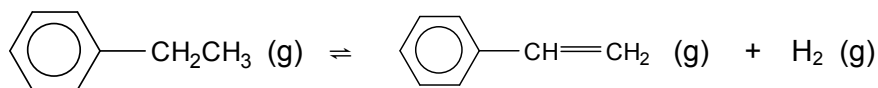
zwitterionic form of GABA (4-aminobutanoic acid)

U has a **simple molecular structure** with **intermolecular H-bonds**. The ionic bonds in GABA are **much stronger** than the H-bonds in **U**. Thus, a **larger amount** of heat energy is required to melt GABA and hence GABA has a much higher melting point.

Question 5 :

5(a)(i) $K_p = \frac{p_{\text{C}_6\text{H}_5\text{CH}=\text{CH}_2} p_{\text{H}_2}}{p_{\text{C}_6\text{H}_5\text{CH}_2\text{CH}_3}}$

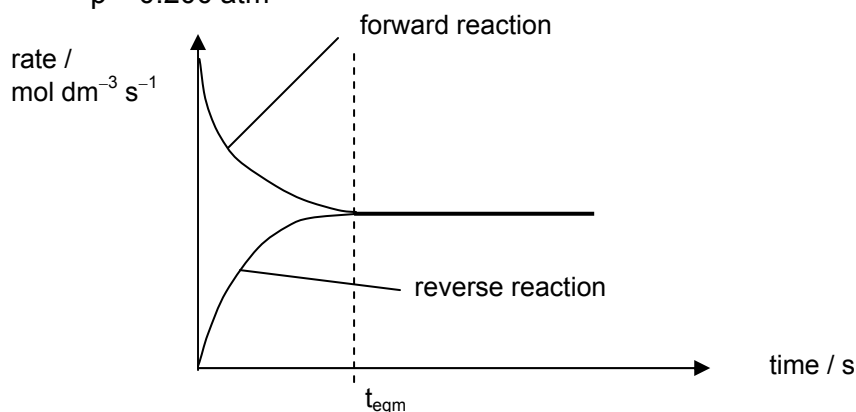
(ii)



initial pressure / atm	p	—	—
eqm pressure / atm	0.35 p	0.65 p	0.65 p

$$K_p = \frac{p_{\text{C}_6\text{H}_5\text{CH}=\text{CH}_2} p_{\text{H}_2}}{p_{\text{C}_6\text{H}_5\text{CH}_2\text{CH}_3}}$$
$$0.242 = \frac{(0.65p)(0.65p)}{(0.35p)}$$
$$p = 0.200 \text{ atm}$$

(iii)



(iv)

The yield of styrene will **increase**.

Since the forward reaction is **endothermic**, when the temperature increases, by Le Chatelier's principle, the **forward reaction is favoured as it absorbs heat and removes excess heat** and thus the position of equilibrium will shift to the **right** and **more** styrene will be formed.

(v)

There are **negligible forces of attraction between gas particles**.

The **volume of gas particles is negligible** compared to the **volume of the vessel** / container.

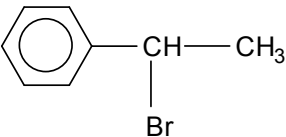
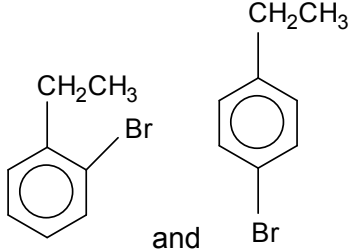
(vi)

$$pV = nRT$$

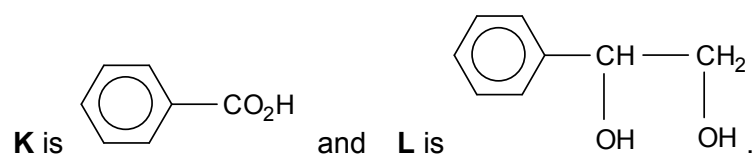
$$(0.65 \times 0.200 \times 10^5)(1000) = n(8.31)(600 + 273)$$

$$n = 1.79 \times 10^3 \text{ mol}$$

(b)(i)

	styrene	ethylbenzene
reagents/conditions	HBr(g)	Br ₂ / FeBr ₃ dark
product		

(ii)



reagents/conditions: **cold**, alkaline **KMnO₄** (aq)