SERANGOON JUNIOR COLLEGE
General Certificate of Education Advanced Level
Higher 2

CANDIDATE NAME

CLASS

CHEMISTRY
9647/03

Preliminary Examination **21 August 2012**
Paper 3 Free Response Questions

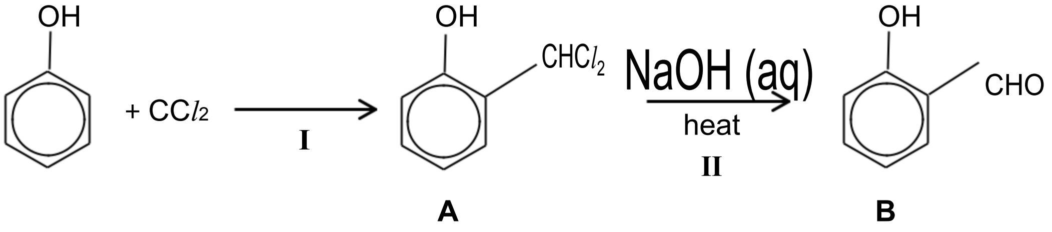
Suggested Solutions

1 **(a)** Aqueous sodium hydroxide is an important reagent in many organic reactions where the hydroxide ion can act as both a base and a nucleophile.

In the Reimer-Tiemann reaction, phenol is heated with chloroform in the presence of aqueous sodium hydroxide to give 2-hydroxybenzaldehyde, compound **B** . The reaction involves the formation of a reactive intermediate, CCl_2, through an acid-base reaction.

$CHCl_3 + OH^-$ ® $CCl_2 + H_2O + Cl^-$

chloroform



(i) State the type of reaction that occurred in reaction **I**.

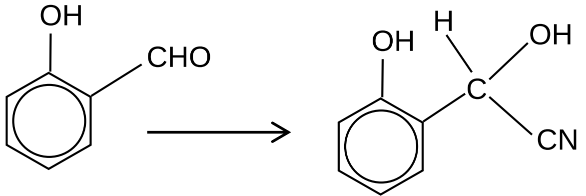
Electrophilic substitution

(ii) Suggest a chemical test to differentiate compounds **B** and **A** under room conditions.

Add **2,4-DNPH** to **B** and **A** separately.
B: **Orange precipitate** formed
A: **No orange precipitate** formed

Note: Tollens' reagent and aqueous NaOH tests are not allowed, as both require heating, which is not "room conditions"

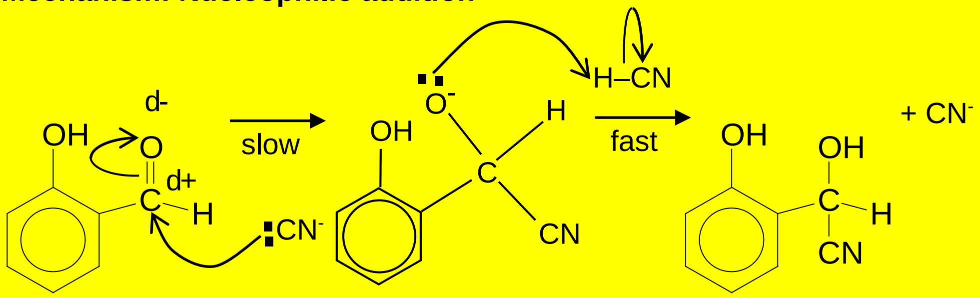
(iii) Compound **B** can undergo further reaction to form the product below.



B

Name and describe the mechanism involved, using curly arrows to show the movement of electrons and indicating all charges.

Mechanism: Nucleophilic addition



(iv) Comment on the relative acidity of phenol and compound **B**. **[9]**

Presence of **<u>electron withdrawing –CHO attached</u>** on the benzene ring.

<u>Negative charge of the phenoxide ion of compound B will be further dispersed</u>. **<u>Phenoxide ion of compound B is more stabilised</u>**.

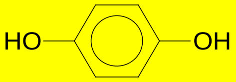
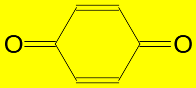
<u>Compound B is a stronger acid as compared to phenol</u>.

(b) Besides its extensive use in organic chemistry, aqueous sodium hydroxide is also used in photographic development.

The black-and-white (B/W) photography process involves four steps:

Step 1	Photo-taking: Interaction of light with silver halides (AgX) on film.
Step 2	Developing: Redox reactions to develop the actual image.
Step 3	Fixing: Changing the solubility of chemical compounds with different conditions to preserve the image on the film.
Step 4	Printing: Shining light through the film onto photosensitive paper, producing the final photograph using the same chemistry as step 1 to 3.

When light is shone on the film during the phototaking process, a very small number of X^- ions in AgX are oxidised.

		(i)	A small amount of silver is produced as a result of the oxidation reaction of X^-. The silver produced catalyses the reduction of the surrounding AgX to black silver metal in the presence of a reducing agent, **D**, during the developing process. $2AgX + \mathbf{D} + 2OH^- \rightarrow 2Ag + \mathbf{E} + 2H_2O + 2X^-$ State and explain why the rate of reaction changes as the developing process proceeds.
			The reaction is autocatalytic. (Ag produced catalyses the reaction.) The rate of reaction **increases at first due to the formation of the Ag catalyst**, **then decreases as the reactants are used up**.
		(ii)	Under appropriate conditions, chloride can be oxidised to chlorine gas. With an aid of an equation, suggest how Cl_2 will react with hydroxide ions under room conditions.
			$2OH^- (aq) + Cl_2 (aq) \rightarrow Cl^- (aq) + ClO^- (aq) + H_2O (l)$
		(iii)	**E**, formed from the oxidation of **D**, has the molecular formula $C_6H_4O_2$. **E** forms an orange precipitate when warmed with 2,4-dinitrophenylhydrazine. One mole of **E** decolourises two mole of bromine dissolved in tetrachloromethane. Heating **E** with acidified potassium manganate(VII) produces only one product. **D** has the molecular formula $C_6H_6O_2$. It is insoluble in water but can dissolve in aqueous sodium hydroxide. Addition of sodium carbonate to **D** does not result in effervescence but addition of sodium metal to **D** gives mild effervescence. Suggest the structures of **D** and **E**, explaining your reasoning. (You are not required to explain the oxidation process of **E** from **D**) **[11]**
			E undergoes **condensation** with 2,4-DNPH $\Rightarrow$ **E** is a **carbonyl** compound 1 mol of **E** undergoes **electrophilic addition** with 2 mol of Br_2 $\Rightarrow$ **E** contains **two alkene** functional groups **E** undergoes **oxidation** with hot acidified $KMnO_4$ (aq) to give two identical compounds $\Rightarrow$ **E** is a **symmetrical** alkene **D** is insoluble in water due to **large hydrophobic benzene ring** but can undergo **neutralisation** with NaOH (aq) $\Rightarrow$ **D** contains **phenol or carboxylic acid** group **D** does not undergo **neutralisation** with Na_2CO_3 but undergoes **redox** reaction with Na $\Rightarrow$ **D** is not a carboxylic acid, so **D** contains **phenol** group **D**:  **E**: 
			Total 20 marks

2 Halogens are highly reactive and they are the only group in the Periodic Table which contains elements in all three familiar states of matter at 25°C and 1 atm.

The halogens form binary compounds with hydrogen and these compounds are known as hydrogen halides, all of which are strong acids with the exception of HF.

(a) Discuss the thermal stability trend of the hydrogen halides, HC*l*, HBr and HI and variation in volatility of the halogens from fluorine to iodine.

[5]

Order of thermal stability : HC*l* > HBr > HI

Down the group,

- Covalent bond length of H-X **increases**
- Covalent bond strength **decreases**
- Bond dissociation energy **decreases**

The number electrons in the halogen molecules increase, thus, **intermolecular van der Waals' forces of attraction become more extensive**. This leads to **increase in their boiling point**. **Volatility of halogens decreases** down the group

(b) Concentrated sulfuric acid will react with solid sodium halides NaX. (X = Cl^-, Br^- or I^-).

Using relevant data from the *Data Booklet*, describe and explain why hydrogen chloride can be prepared by the reaction between sodium chloride and concentrated sulfuric acid while hydrogen iodide cannot be synthesised using a similar method with sodium iodide and concentrated sulfuric acid. You are to include relevant chemical equation(s) in your discussion.

[5]

The **reducing power of the halides increases down the group** as shown by the stated E$^\ominus$ values.

$\mathbf{Cl_2 + 2e \rightleftharpoons 2Cl^-}$ **+1.36 V**

$\mathbf{Br_2 + 2e \rightleftharpoons 2Br^-}$ **+1.07 V**

$\mathbf{I_2 + 2e \rightleftharpoons 2I^-}$ **+0.54 V**

$NaCl\ (s) + H_2SO_4\ (l) \rightarrow HCl\ (g) + NaHSO_4$

HC*l* is produced as Cl^- is a weaker reducing agent.

$NaI\ (s) + H_2SO_4\ (l) \rightarrow NaHSO_4\ (s) + HI\ (g)$

$2\ HI\ (g) + H_2SO_4\ (l) \rightarrow I_2\ (g) + 2H_2O\ (l) + SO_2\ (g)$ *or*

$6HI\ (g) + H_2SO_4\ (l) \rightarrow 3I_2\ (g) + 4H_2O\ (l) + S\ (s)$ *or*

$8HI\ (g) + H_2SO_4\ (l) \rightarrow 4I_2\ (g) + H_2S\ (g) + 4H_2O$

HI is not produced as iodide is a stronger reducing agent and it will reduce the sulphur to a lower oxidation state.

(c) Halogens form many compounds with metals. These compounds range from ionic compounds such as lithium chloride, monomeric covalent compounds such as uranium hexafluoride, and polymeric covalent compounds like palladium chloride.

The Corey-Posner, Whitesides-House reaction is an organic reaction that involves the reaction of a lithium dialkyl cuprate with an alkyl halide to form a new alkane, an organocopper compound and a lithium halide.

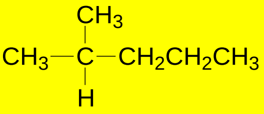
The formation of propane from a halogeno compound using the Corey-Posner, Whitesides-House reaction is as shown.

$$(CH_3)_2CuLi + CH_3CH_2X ® CH_3CH_2CH_3 + CH_3Cu + LiX$$

($X = Cl^-$, Br^- or I^-)

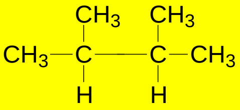
(i) Draw the structural formulae of the three alkanes produced when $(C_3H_7)_2CuLi$ and C_3H_7Br undergo the Corey–Posner, Whitesides–House reaction.

$CH_3CH_2CH_2CH_2CH_2CH_3$:



$CH_3-CH(CH_3)-CH_2CH_2CH_3$

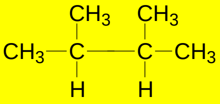
:



$CH_3-CH(CH_3)-CH(CH_3)-CH_3$

(ii) Suggest with reasoning which of the alkanes in **(c)(i)** has the lowest boiling point.

[6]

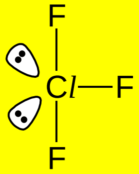


$CH_3-CH(CH_3)-CH(CH_3)-CH_3$

Alkanes has simple molecule structure **has the lowest boiling point** as the **extensiveness of VDW is reduced due to the branched structure**.

(d) Chlorine and fluorine react exothermically to form an interhalogen compound, ClF_3.

(i) With the help of a Lewis structure, state the shape of the ClF_3 molecule.



\ T-shape molecule

		(ii)	The interhalogen compounds are very strong oxidising agents. When gaseous ClF_3 is added to water, a vigorous reaction occurs, giving three gases as the only products. The gaseous product mixture appears as white fumes which forms a weak acid. The gaseous mixture not only turns moist blue litmus paper red but also bleaches it. In addition, it relights a glowing splint. State the three gases in the gaseous mixture. Hence, construct a balanced equation, including state symbols, for the reaction. **[4]**
			O_2, Cl_2 and HF $6H_2O(l) + 4ClF_3(g) \rightarrow 3O_2(g) + 2Cl_2(g) + 12HF(g)$
			Total 20 marks

3 **(a)** Nitrous acid is an unstable, weakly acidic compound. It can easily be prepared by acidifying a solution of a nitrite. Barium nitrite, $Ba(NO_2)_2$ is often used since the insoluble barium sulfate can be easily filtered off.

$$Ba(NO_2)_2\,(aq) + H_2SO_4\,(aq) \rightarrow 2HNO_2\,(aq) + BaSO_4\,(s)$$

Nitrite ion can be oxidised by $KMnO_4$ to form nitrate ion:

$$5NO_2^-\,(aq) + 2MnO_4^-\,(aq) + 6H^+\,(aq) \rightarrow 5NO_3^-\,(aq) + 2Mn^{2+}\,(aq) + 3H_2O\,(l)$$

The following are some thermochemistry data pertaining to the experiment.

	$\Delta H^{\ominus}$ / kJ mol^{-1}
enthalpy change of atomisation of barium	+175
enthalpy change of $Ba\,(s) \rightarrow Ba^{2+}\,(aq) + 2e$	+286
enthalpy change of hydration of NO_3^-	-325
lattice energy of barium nitrate	-1395

(i) Using the above data, and relevant data from the *Data Booklet*, construct an energy cycle to calculate the enthalpy change of hydration of the barium ion.

$$\begin{tikzcd}
Ba(s) \arrow[r, "\Delta H_{rxn} = +286\ kJ\ mol^{-1}"] \arrow[d, "\Delta H_a(Ba) = +175\ kJ\ mol^{-1}"] & Ba^{2+}(aq)\ +2e \\
Ba(g) \arrow[r, "1^{st}\ IE + 2^{nd}\ IE = +502 + 966 = 1468\ kJ\ mol^{-1}"] & Ba^{2+}(g)\ \ +2e \arrow[u, "\Delta H_{hyd}"']
\end{tikzcd}$$

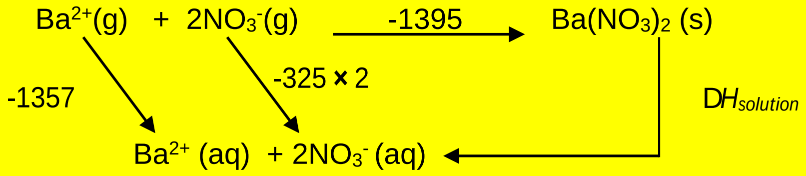
$\Delta H_{hyd}\,(Ba^{2+}) = -1468 - 175 + 286$
$= \underline{\mathbf{-1360\ kJ\ mol^{-1}}}$

(ii) The $\Delta S^{\ominus}_{hydration}$ of barium ion is -188 J mol^{-1} K^{-1}. Explain why the sign of $\Delta S^{\ominus}_{hydration}$ is negative.

When Ba^{2+} is hydrated, the **ions are surrounded by water molecules**. There is an **increase in orderliness** of the water molecules. Hence, $\Delta S_{hydration}$ is negative.

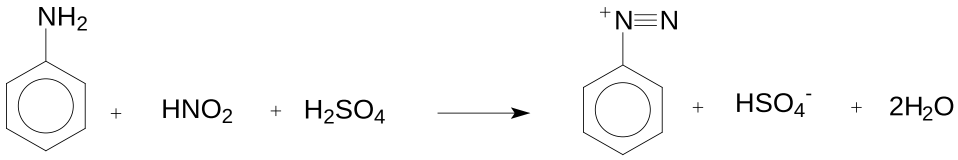
(iii) Hence, calculate $\Delta G^{\ominus}_{hydration}$ of barium ion at 298K.

$\Delta G^{\ominus}_{hydration} = \Delta H_{hydration} - T\Delta S_{hydration}$
$= -1360 - (298)(-188 \times 10^{-3})$
$= \underline{\mathbf{-1300\ kJ\ mol^{-1}}}$

		(iv)	Predict the effect of high temperature on the spontaneity of the above reaction.
			ΔH = -ve ΔS= -ve Since $\Delta G^{\theta}_{hydration} = \Delta H_{hydration} - T\Delta S_{hydration}$ $\Delta G^{\theta}_{hydration}$ = -ve – (-ve) = -ve + TΔS As temperature increases, $\Delta G^{\theta}_{hydration}$ will become more positive; **<u>reaction will become less spontaneous</u>** at high temperature.
		(v)	Using your answer in **(a)(i)**, and relevant data from the table, calculate the enthalpy change of solution of barium nitrate.
			 $\Delta H_{solution} = \Delta H_{hyd}(Ba^{2+}) + 2\Delta H_{hyd}(NO_3^-)$ - LE = - 1360 + 2(-325) – (-1395) = **<u>-615 kJ mol^{-1}</u>**
	(b)	**(i)**	Write an equation to represent the thermal decomposition of barium nitrate.
			$2Ba(NO_3)_2$ (s) $\rightarrow$ 2BaO (s) + $4NO_2$ (g) + O_2 (g) or **$Ba(NO_3)_2$ (s) $\rightarrow$ BaO (s) + $2NO_2$ (g) + ½O_2 (g)**
		(ii)	Group II iodates decomposed according to the following equation. $2Mg(IO_3)_2$ (s) $\rightarrow$ 2MgO (s) + $2I_2$ (g) + $5O_2$ (g) Describe and explain how the thermal stabilities of Group II iodates vary down the group. **[10]**
			For Group II cations when **going down the group**, · **Cationic radius** of M^{2+} **increases.** · **Charge remains constant.** **Charge density of cation decreases.** · **Polarising power <u>of</u> cation decreases** and M^{2+} is less able to distort the electron cloud of anion · **Polarising effect <u>on</u> anion decreases** · **Higher temperature** (more energy) is required to decompose the compound. · Hence, **<u>stability</u>** of nitrates **<u>increases</u>**.

(c) Nitrous acid is useful in converting amines into diazonium compounds:

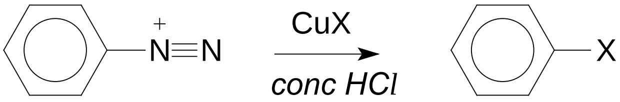
Reaction 1



diazonium salt

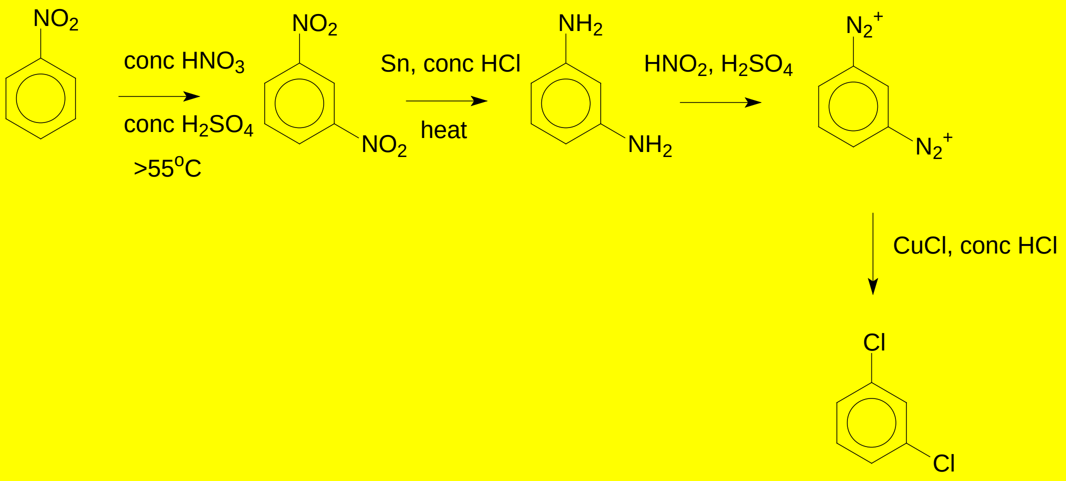
In a process named the Sandmeyer reaction, the –$\overset{+}{N}\equiv N$ is replaced by –C*l* or –Br using the corresponding cuprous halide, CuX, together with concentrated HC*l*.

Reaction 2



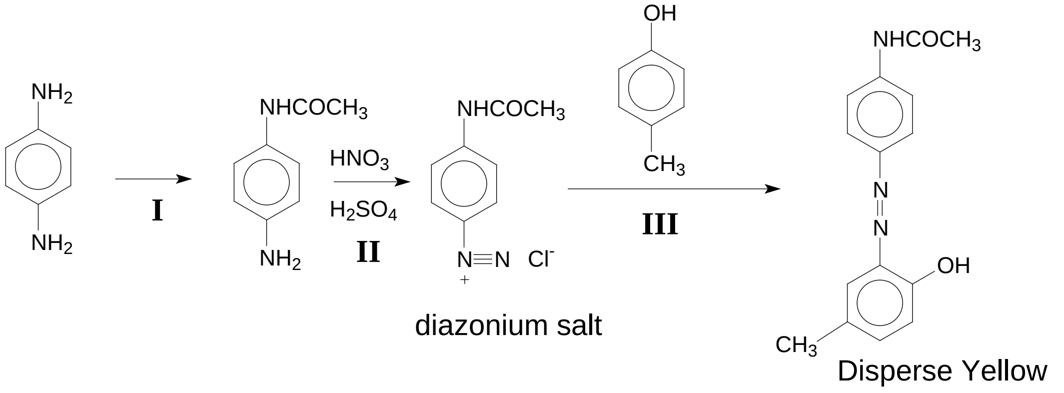
Outline how you could convert nitrobenzene into 1,3-dichlorobenzene in a **four steps synthesis**, using both reactions 1 and 2 in your synthesis. In your answer, you are to clearly state the reagents and conditions used and the intermediates formed.

[5]



(d) The diazonium salt can undergo a coupling reaction with activated aromatic rings to obtain brightly coloured azo compounds which can be used as dyes.

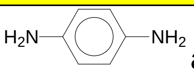
The dye, Disperse Yellow, is formed as follows:



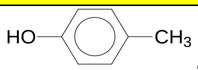
(i) Identify a reagent which might be used for step **I**.

CH_3COCl

(ii) Propose a chemical test to differentiate



and



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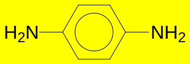
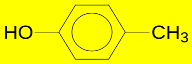
In your answer, state clearly the reagents and conditions required and any observations made.

Test: Add **<u>neutral FeCl$_3$</u>** or $KMnO_4$ in H_2SO_4, heat

Observations:

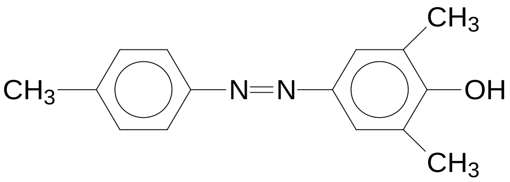


: **<u>No violet complex observed</u>** (Purple solution remains)



: **<u>Violet complex observed</u>** (Purple solution decolourised)

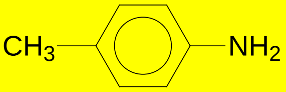
(iii) Another azo dye, **H**, can be obtained from an amine and a phenol under suitable conditions.

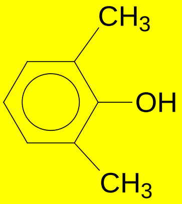


azo dye, **H**

Draw the structural formulae of the amine and of the phenol used to make **H**.

[5]

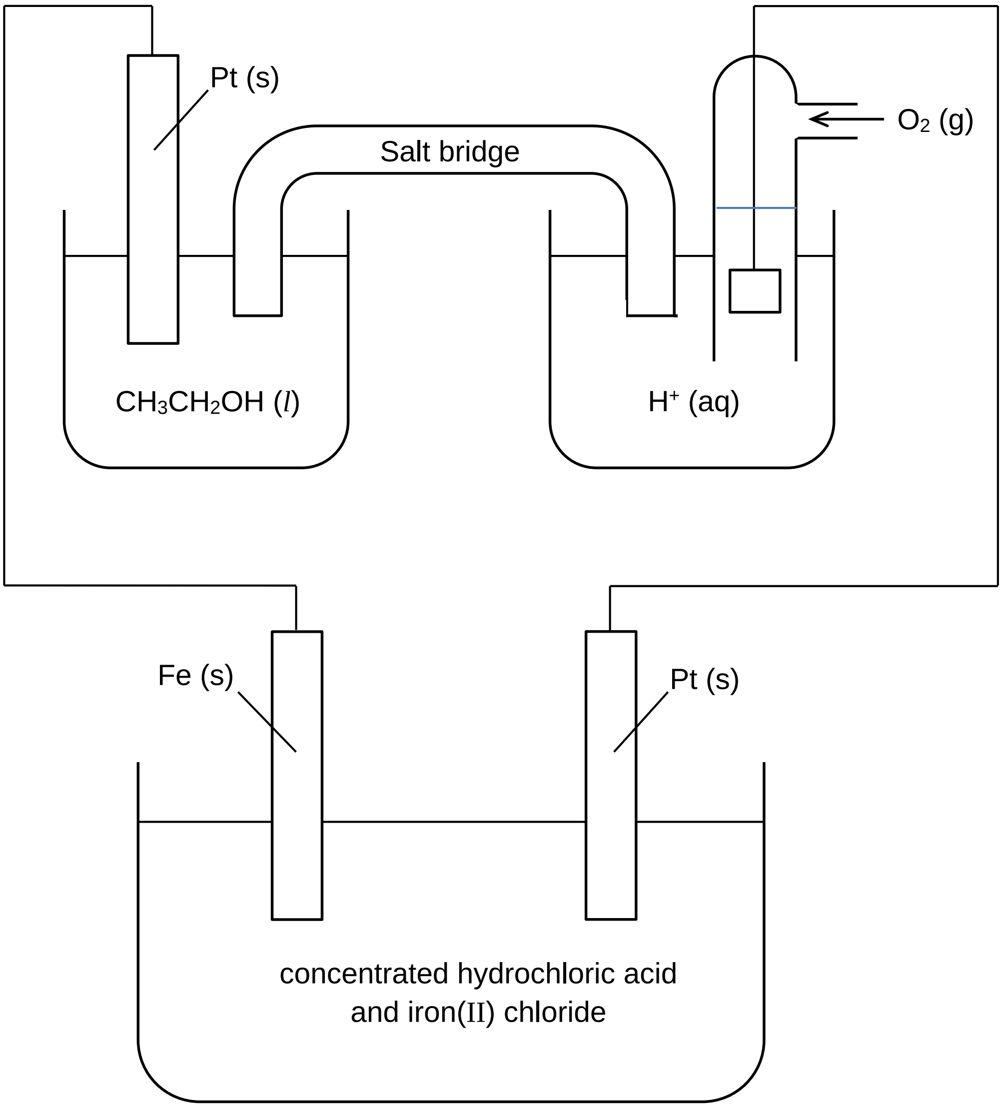




Total 20 marks

4 The pickling of steel is the process of removing rust, or iron(III) oxide, from steel by using excess concentrated hydrochloric acid to react with layers of the oxide and iron metal. The reaction produces a solution of iron(II) chloride.

A chemist used the set-up shown below to investigate if the resulting solution which consists of concentrated hydrochloric acid and iron(II) chloride, from the pickling of steel, can be used to produce iron metal via electrolysis.



(a) An organic fuel cell, the direct ethanol fuel cell, is used to drive the electrolysis. The reaction that takes place at one of the electrodes involves the reduction of oxygen gas as follows:

$O_2 + 4H^+ + 4e^-$ ® $2H_2O$

(i) Construct the overall equation for the fuel cell reaction, given that carbon dioxide is produced at the anode.

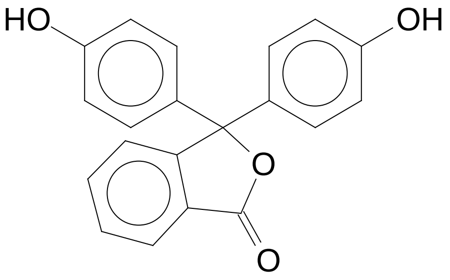
$CH_3CH_2OH + 3O_2$ à $2CO_2 + 3H_2O$

		(ii)	Write the cell diagram for the direct ethanol fuel cell, stating the polarity of the respective electrodes. **[3]**
			$Pt\ (s) \mid CH_3CH_2OH\ (l) \mid CO_2\ (g) \parallel O_2\ (g) \mid H_2O\ (l) \mid Pt\ (s)$ Negative Positive
	(b)	**(i)**	Construct a balanced equation for the reaction that takes place during the pickling of steel, indicating the state symbols clearly.
			$Fe_2O_3\ (s) + Fe\ (s) + 6HCl\ (aq) \rightarrow 3FeCl_2\ (aq) + 3H_2O\ (l)$
		(ii)	Write half-equations for the reactions taking place at the cathode and anode of the electrolytic cell and state all observations made within the cell.
			Fe (s) cathode: $Fe^{2+} + 2e^- \rightarrow Fe$ Observation: Fe (s) cathode increases in mass or pale green solutions fade off Anode: $2Cl^- \rightarrow Cl_2 + 2e^-$ (high concentration of Cl^- ions from conc. HC*l*) Observation: Effervescence observed.
		(iii)	Suggest the observation made at the anode when nitric acid is used in the pickling of steel instead of hydrochloric acid. **[6]**
			Effervescence observed. Oxygen is evolved instead of chlorine gas.
	(c)	Upon addition of cyanide ions, the colour of the electrolyte changes from pale green to “Prussian blue”.	
		Explain why iron complexes are coloured. **[3]**	
			The d orbitals are split into two groups due to the ability of the ligands to split them into two energy levels. **The d electron undergoes d-d transition** and **is promoted to a higher energy d orbital**. **The d electron absorbs a certain wavelength of light energy from the visible region of the electromagnetic spectrum and transmits the remaining wavelength, which appear as the colour observed**.
	(d)	Another chloride of iron, $FeCl_3$, has similar characteristics as aluminium chloride. Both form dimers at low temperatures, produce acidic solutions when dissolved in water and are used in the electrophilic substitution reactions of benzene rings.	
		(i)	Using suitable data from the *Data Booklet*, explain the acidic nature of $FeCl_3$ in water.
			From the *Data Booklet*, Fe^{3+} has a **small cationic radius** of 0.064 nm and **high charge** of +3. Thus, Fe^{3+} ion has **high charge density and high polarising power**. **Hydrolysis of water molecules occurs, thus releasing H^+** ions in aqueous

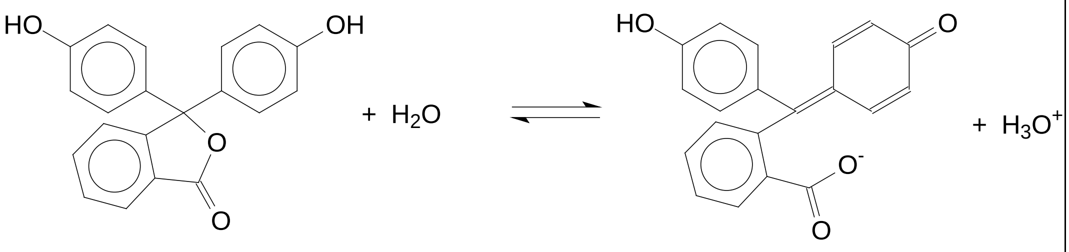
			solution. Or $[Fe(H_2O)_6]^{3+} \rightleftharpoons [Fe(H_2O)_5(OH)]^{2+} + H^+$
		(ii)	State what role does iron(III) chloride play in the electrophilic substitution reaction of benzene ring with chlorine. **[4]**
			FeC*l*$_3$ acts as a **catalyst or halogen carrier or Lewis acid** or f**orm** the **electrophile C*l*$^+$** catalysing the reaction.
	(e)	**(i)**	Haemoglobin, which contains iron(II) ions is a protein found in the red blood cells that carries oxygen. Describe the protein components of haemoglobin.
			Haemoglobin consists of 4 polypeptide chain: **2 α-sub-units** and **2 β-sub-units**, with each sub-unit being **non-covalently** bonded to a **haem** (iron) group. Each heme group consists of a central Fe^{2+} ion that can bond to one O_2 oxygen. Each haemoglobin is able to carry a maximum of four O_2 oxygen. **All four components** (4 sub-units and 4 haem groups) **must be present** to form haemoglobin.
		(ii)	In World War II, the use of cyanide pills were frequently recorded. Pilots of B-29 Superfortress bombers sent to drop atomic bombs on Japan were issued with the lethal pills. Fortunately, all aircraft returned safely and none of the pills were used. These pills contain a concentrated solution of potassium cyanide and the release of the fast-acting poison causes brain death within minutes. Suggest why brain death occurs within minutes after the poison is administered. **[4]**
			In the presence of **cyanide**, the CN^- bonds **irreversibly** with haemoglobin to form a stable complex. This **prevents haemoglobin from transporting oxygen** and cells die of oxygen starvation
			Total 20 marks

5 **(a)** The Kastle-Meyer test is often used to test for the presence of blood at a crime scene. It relies on the peroxidase-like activity of haemoglobin in blood to catalyse the oxidation of colourless phenolphthalein into its bright pink conjugate base.

Phenolphthalein has the following structure:



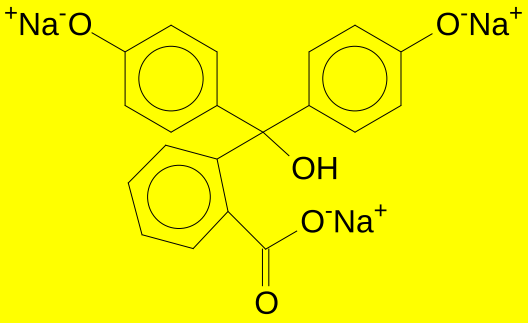
Phenolphthalein is a *weak acid* which dissociates in water according to the following equation:



colourless (acid) pink (conjugate base)

The pK_a of phenolphthalein is 9.7.

(i) Draw the structure of the compound formed when phenolphthalein is heated with aqueous sodium hydroxide.



(ii) Using Le Chatelier's principle, explain why phenolphthalein appears colourless in an acidic solution.

In acidic solution, **the concentration of H_3O^+ is high**, hence the above **equilibrium position is shifted to the left** and the concentration of the conjugate base is too low for the pink colour to be observed.

(iii) Calculate the ratio of the concentration of the conjugate base to the concentration of the acid at pH 10.
Using this ratio, predict and explain the colour of phenolphthalein at pH 10.

$$[H_3O^+] = 10^{-10}\, mol dm^{-3}$$

$$K_a = \frac{[H_3O^+][conjugate\ \text{base}]}{[acid]}$$

$$= \frac{[10^{-10}][conjugate\ \text{base}]}{[acid]} = 10^{-9.7}$$

$$\frac{[conjugate\ \text{base}]}{[acid]} = \frac{10^{-9.7}}{10^{-10}} = 1.995 \approx 2.00$$

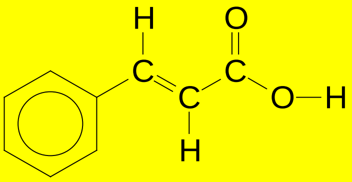
Since the **<u>concentration of the conjugate base is much more than the acid</u>** (2 times), the **<u>solution will appear pink</u>** (the colour of the conjugate base).

(b) Cinnamic acid, commonly found in cinnamon, has a molecular formula of $C_9H_8O_2$.

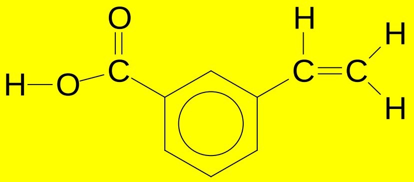
It is known that cinnamic acid can react with liquid bromine in the dark. It also undergoes oxidation to form benzoic acid and in the process, carbon dioxide gas was released.

An isomer of cinnamic acid also reacts with liquid bromine in the dark. Upon oxidation with potassium manganate(VII),1 mol of this isomer reacts with 1 mol of sodium carbonate.

Suggest the displayed formulae of cinnamic acid and its isomer.
State the type of isomerism exhibited by cinnamic acid. **[3]**



Cinnamic acid

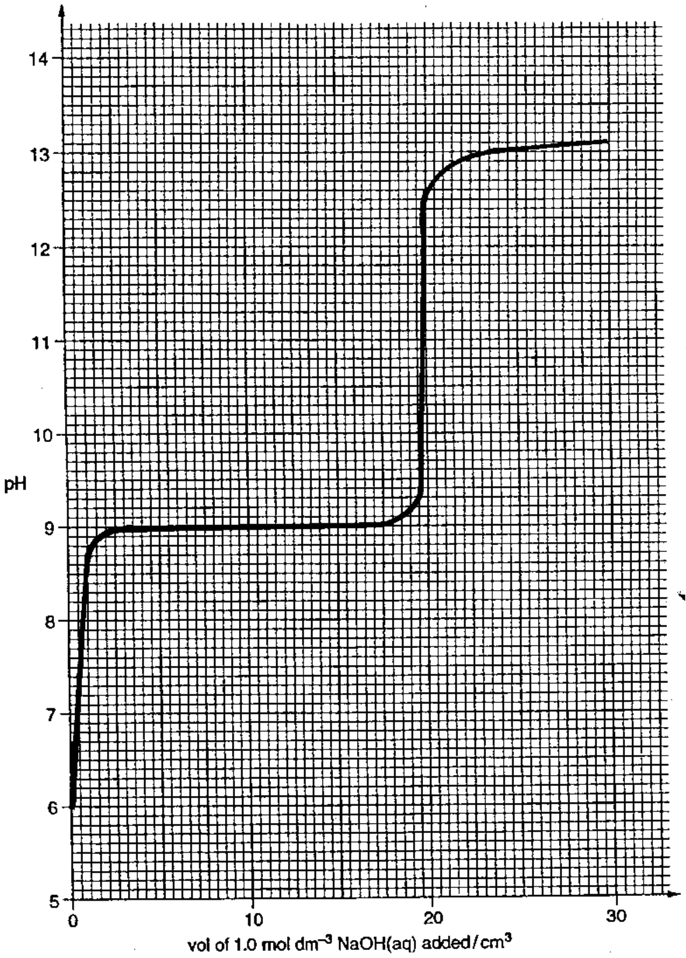


isomer of cinnamic acid

Both undergo electrophilic addition with liquid bromine.

1 mol of this isomer reacts with 1 mol of sodium carbonate. Indicates there are 2 carboxylic acid group ⇒ 2 side chains

Cinnamic acid exhibits **<u>geometric isomerism (cis-trans isomerism)</u>**

	(c)	Phenolphthalein is usually used as an indicator in a strong base and weak acid titration. Aqueous magnesium chloride can act as a weak monobasic acid. In an experiment, 50.0 cm^3 of aqueous magnesium chloride was titrated with 1.00 mol dm^{-3} sodium hydroxide. The variation of pH of the solution is as shown in the diagram.  	
		(i)	Explain what is meant by the term *weak acid.*
			A **weak acid** is one which **dissociates partially** in solution to give **protons (H^+)**
		(ii)	Write an equation showing hydrated magnesium ion acting as an acid.
			$[Mg(H_2O)_6]^{2+} \rightleftharpoons [Mg(H_2O)_5OH]^{2+} + H^+$

(iii) Using the graph above, calculate the initial concentration of magnesium ions.

V_{NaOH} for equivalence = 20.00 cm^3

$$\therefore\ [Mg^{2+}]\text{ initial} = \frac{\frac{20.00}{1000} \times 1}{\frac{50.00}{1000}} = 0.4\ \text{mol dm}^{-3}$$

(iv) Calculate the K_a value for aqueous magnesium chloride.

initial pH = 6 $\Rightarrow$ $[H^+] = 1 \times 10^{-6}$

$$K_a = \frac{[Mg(H_2O)_5OH]^+\ [H^+]}{[Mg^{2+}]}$$

$$= \frac{(10^{-6})^2}{(0.4)}$$

$$= 2.5 \times 10^{-12}\ \text{mol dm}^{-3}$$

(v) At the point where 10.0 cm^3 of sodium hydroxide has been added to the solution, a saturated solution of a sparingly soluble salt, magnesium hydroxide, $Mg(OH)_2$, is formed.

Calculate the solubility product, K_{sp} of $Mg(OH)_2$.

[7]

At 10 cm^3, pH = 9

pOH = 5 $\Rightarrow$ $[OH^-] = 1 \times 10^{-5}$

$$[Mg^{2+}] = \frac{10.00 \times 1}{60.00} = 0.167$$

$$K_{sp} = [Mg^{2+}]\,[OH^-]^2 = (0.167)\,(1 \times 10^{-5})^2 = 1.67 \times 10^{-11}\ \text{mol}^3\ \text{dm}^{-9}$$

(d) Iodine reacts with propanone in acid solution as follows.

$$I_2 + CH_3COCH_3 \xrightarrow{H^+} CH_3COCH_2I + HI$$

Kinetics studies have shown that the reaction is second order overall, and it has been suggested that the mechanism involves the following three steps.

$$CH_3COCH_3 + H^+ \rightleftharpoons CH_3\overset{+}{C}(OH)CH_3 \qquad \text{(fast)}$$

$$CH_3\overset{+}{C}(OH)CH_3 \rightleftharpoons H_2C{=}C(OH)CH_3 + H^+ \qquad \text{(slow)}$$

$$H_2C{=}C(OH)CH_3 + I_2 \longrightarrow CH_3COCH_2I + HI \qquad \text{(fast)}$$

(i) Explain the meaning of *order of reaction.*

Order of reaction with respect to a reactant is the power to which its concentration is raised in the rate equation.

.

(ii) Construct the rate equation for this reaction.

Rate = k $[CH_3COCH_3]\,[H^+]$

(iii) An experiment was carried out at 60 °C using the reagents of the following concentrations.

[4]

Initial concentration / mol dm^{-3}		
$[I_2]$	$[CH_3COCH_3]$	$[H^+]$
0.002	0.050	0.050

The initial rate of reaction was found to be 1.25×10^{-6} mol dm^{-3} s^{-1} under these conditions. Calculate the rate constant for this reaction, stating its units.

$$k = \frac{\text{Rate}}{[CH_3COCH_3]\,[H^+]} = \frac{1.25 \times 10^{-6}}{0.05 \times 0.05} = \underline{\mathbf{5.00 \times 10^{-4}\ mol^{-1}\ dm^{3}\ s^{-1}}}$$

Total 20 marks

END