525/2

S6 CHEMISTRY

Exam 12

PAPER 2

DURATION: 2 HOUR 30 MINUTES

For Marking guide contact and consultations: Dr. Bbosa Science 0776 802709.

INSTRUCTIONS TO THE CANDIDATES

Answer **five** questions including **three** questions in section **A** and any **two** questions in section **B**.

Write the answers in the answer booklet provided.

Mathematical tables and graph papers are provided.

Begin each question on a fresh page.

Non-programmable scientific electronic calculators may be used.

Illustrate your answers with equations where applicable.

Indicate the questions in the grid below.

Where necessary use C = 12, O = 16, H =1

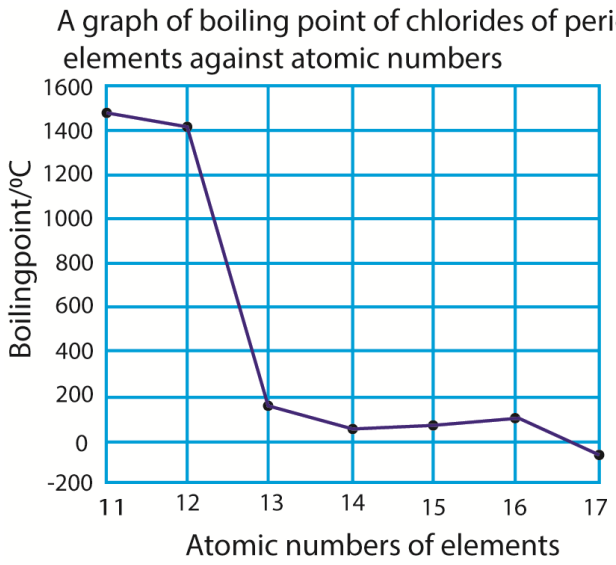
SECTION A

*Answer any **three** questions from this section.*

1. The table below shows the boiling points of the chlorides of period 3 elements.

Element	Na	Mg	Al	Si	P	S	Cl
Atomic number	11	12	13	14	15	16	17
Formula of the chloride	NaCl	$MgCl_2$	$AlCl_3$	$SiCl_4$	PCl_3	S_2Cl_2	Cl_2
Boiling point (^oC)	1465	1418	180	57	76	136	-35

(a)(i) Plot a graph of boiling points of the chlorides against atomic number of the elements. (3½marks)

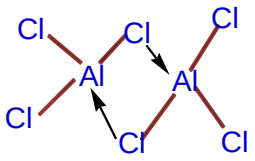


(ii) Explain the shape of the graph (7½marks)

NaCl and $MgCl_2$ have high boiling points due to strong the ionic bonding.

Aluminium chloride, silicon chloride, phosphorus chloride, disulphur dichloride and chlorine have low boiling points because their molecules are held by weak molecular forces.

$AlCl_3$ has a fairly high boiling point because in the liquid state, it consists of Al_2Cl_6 molecules and not simple $AlCl_3$. These molecules are produced through dative bonding between Al and Cl in the Al_2Cl_6 molecules.



Disulphur dichloride has relatively high boiling point due to its high molecular mass that increases the strength of the molecular forces

(b) Describe the reactions of the chlorides with water. (09marks)

$NaCl$ and $MgCl_2$ have no reaction with water but simply dissociate into ions.

$NaCl\ (s) + (aq) \rightarrow Na^+\ (aq) + Cl^-\ (aq)$

$MgCl_2\ (s) + (aq) \rightarrow Mg^{2+}\ (aq) + 2Cl^-\ (aq)$

$AlCl_3$, $SiCl_4$, PCl_5, Cl_2 are hydrolyzed by water.

$SiCl_4$, PCl_5, and S_2Cl_2 are hydrolyzed liberating hydrogen chloride.

$AlCl_3\ (aq) + 3H_2O(l) \rightarrow Al(OH)_3\ (s) + 3HCl(aq)$

$PCl_5\ (s) + 4H_2O\ (l) \rightarrow 5HCl\ (aq) + H_3PO_4\ (aq)$ [phosphoric acid]

$SiCl_4\ (l) + 3H_2O\ (l) \rightarrow 4HCl\ (aq) + H_2SiO_3\ (aq)$ [silicic (IV) acid]

$2S_2Cl_2 + 3H_2O\ (l) \rightarrow 4HCl\ (aq) + H_2SO_3\ (aq) + 3S\ (s)$

2. (a) Define the term buffer solution (01 mark)

A buffer is a solution that resist changes in pH when small amount of either acid or base are added.

(b) Explain how a solution containing a mixture of sodium benzoate and benzoic acid acts as a buffer. (04 marks)

Sodium benzoate is fully hydrolyzed in water to for sodium and benzoate ions

$ArCOONa\ (aq) \rightarrow ArCOO^{-}\ (aq) + Na^{+}(aq)$

Presence of sodium benzoate suppresses ionization of benzoic acid

When a small amount of acid is added, the hydrogen ions are neutralized by the benzoate ions

$ArCOO\text{-}\ (aq) + H^{+}(aq) \rightarrow ArCOOH\ (aq)$

When a small amount of the base is added, the added hydroxyl ions are removed by benzoic acid

$ArCOOH + OH^{-}(aq) \rightarrow ArCOO^{-}\ (aq) + H_2O(l)$

In either case the pH of the solution is kept constant.

(c) $25cm^3$ of 0.2M sodium benzoate were mixed with $35cm^3$ of 0.1M benzoic acid.

(i) Calculate the pH of the resultant solution. State any assumptions made in your calculation.
(Ka for benzoic acid=$6.3\times10^{-5}moldm^{-3}$) (05marks)

Solution

Total volume = 25 + 35 = 60 cm^3

Moles of sodium benzoate = $\frac{25\ x\ 0.2}{1000} = 0.005 moles$

Concentration of sodium benzoate in $moldm^{-3}$ = $\frac{0.005\ x\ 1000}{60} = \frac{1}{12}$

Moles of benzoic acid = $\frac{35\ x\ 0.1}{1000} = 0.0035\ moles$

Concentration of benzoic acid = $\frac{0.0035\ x\ 1000}{60} = \frac{7}{120}$

$[H^{+}] = K_a \frac{(ArCOOH)}{(ArCOO^{-})} = 6.3\ x\ 10^{-5} \frac{7/120}{1/12} = 4.5 \times 10^{-5} moldm^{-3}$

$pH = -\log[H^{+}] = -\log 4.4 \times 10^{-5} = 4.3$

(ii) Determine the change in pH when 3.16×10^{-4} moles of sodium hydroxide were added to the mixture in (i). (04 marks)

When sodium hydroxide is added the concentration of the salt is increased by 3.16 x 10^{-4} while that of an acid is decreased by the same amount

$[H^+] = K_a \frac{(ArCOOH)}{(ArCOO^-)}$

$= 6.3\ x\ 10^{-5} \frac{(7/120)-3.16\ x\ 10^{-4}}{(1/12)+3.16\ x\ 10^{-4}}$

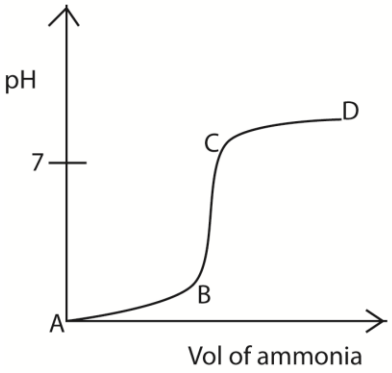
= 4.4 x 10^{-5}moldm^{-3}

pH = -log 4.4 x 10^{-5} = 4.3

Thus, the pH did not change because the volume of the base was very small.

(d) (i) Sketch a graph of pH against volume when hydrochloric acid is titrated against ammonia solution. (2marks)

A graph of pH against volume when hydrochloric acid is titrated against ammonia



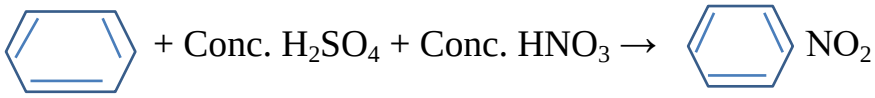
(ii) Explain the shape of the graph. (4marks)

- At A pH is low due to presence of a lot of H+ from ionization of HCl.
- Along AB pH increases due to neutralization of H+ by OH^- ions
  $H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$
- BC represent end point, it occurs below the pH 7 due to hydrolysis of salts
  $NH_4^+ \leftrightarrow NH_3(aq) + H^+(aq)$
- CD pH increases slowly due buffer effect of NH_4^+ and NH_3

3. (a) State what would be observed and write equation for the reaction when

(i) Benzene is warmed with a mixture of concentrated nitric acid and concentrated sulphuric acid. (1½marks)

Yellow oily liquid



(ii) chlorine gas is bubbled through benzene in the presence of ultra violet light. (1½marks)

Chlorine decolorized

$C_6H_6 + 3Cl_2 \rightarrow C_6Cl_{12}$

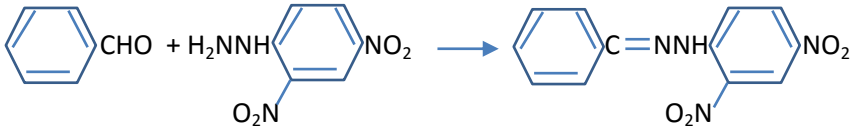
(iii) Ethanal is mixed with a saturated solution of sodium hydrogen sulphite. (1½marks)

White crystals

$$CH_3CHO + NaHSO_3 \rightarrow CH_3\underset{\displaystyle OH}{\underset{|}{C}}HSO_3$$

(iv) benzaldehyde is mixed with 2,4-dinitrophenylhydrazine in presence of dilute sulphuric acid. (1½marks)

Yellow ppt

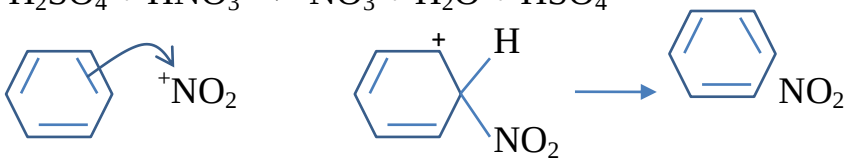


(b) Write the mechanisms for the reactions in (a)(i) , (a)(iii)and (a)(iv) (7½marks)

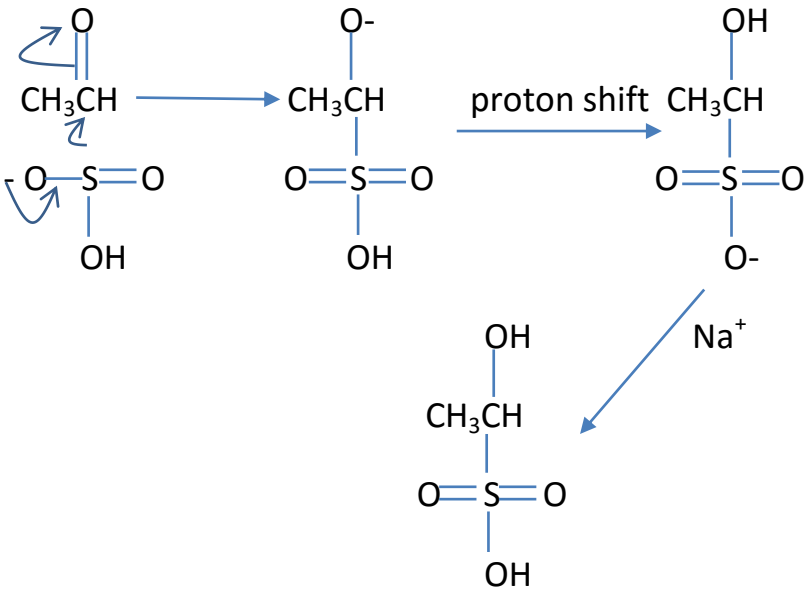
(b)(i)

Mechanism

$H_2SO_4 + HNO_3 \rightarrow {}^{+}NO_3 + H_2O + HSO_4^{-}$



(ii)



(c) Name the reagent that can used to distinguish between the following pairs of compounds. State what would be observed if the compound in each pair is treated with the reagent.

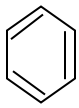
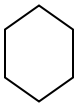
(i) HCOOH and CH_3COOH (2marks)

Reagent: ammoniacal silver nitrate

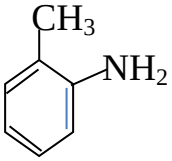
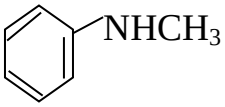
Observation:

HCOOH - black ppt

CH_3COOH - no observable change

(ii)  and  (2marks)

Reagent: concentrated nitric acid and concentrated sulphuric acid
Benzene: yellow oily liquid of nitrobenzene formed
Cyclohexane: no observable change

(iii)  and  (2½marks)

Reagent: Sodium nitrite in presence of hydrochloric acid at temperatures below 5^0C
Observation: 2-methylaminobenzene- no observable change
Methylphenylamine – yellow oily liquid

4. Both camphor and naphthalene are solids at room temperature with melting points 179.5^oC and 80.2^oC respectively. In colligative properties they are used as non- volatile solutes and solvents.

(a) (i) Explain why naphthalene is preferred to camphor as a solvent in determination of relative formula masses of compounds in the laboratory by freezing point depression method. (02marks)
it has low melting point measurable by common thermometer

(ii) Describe an experiment to determine the relative formula mass of mannitol by method of freezing point depression method using naphthalene as a solvent. (09marks)

Procedure
The freezing point t^0C of a mixture containing a g of mannitol in b g of naphthalene is determined

Treatment of results

Mass of naphthalene = b

Mass of mannitol = a

Δt = (t-80.2)

Mass of mannitol in 1000g of naphthalene $= \frac{1000a}{b}$

Let the freezing point depression constant for 1000g of naphthalene be K_f and molecular mass of mannitol be Mr

$\frac{1000a}{b}$ g of mannitol cause a depression of $(t\text{-}80.2)^0$

Mr g of mannitol cause K_f

$Mr = \frac{1000a}{b} \; x \; \frac{K_f}{(t-80.2)}$

(iii) State **four** limitations of the method in (a)(ii) above. (02marks)

- Solution must be dilute
- Solute should not react with solvent
- Solute should not associate in solvent
- Solute should not dissociate in the solvent
- Solute should not have very high molecular mass as this leads to negligible freezing point depression.

(b) (i) When 4.2g of mannitol was added to 50g of naphthalene, the mixture had a freezing point of 77.03°C.Calculate the relative molecular mass of mannitol.

(Kf for naphthalene = $6.87^oCkg^{-1}mol^{-1}$) (04marks)

Freezing point depression = 80.2 – 77.03 = 3.17^0C

Mass of mannitol in 1000g of naphthalene = $\frac{4.2 \; x \; 1000}{50}$ = 84g

Formula mass of mannitol

3.17^0 is caused by 84 g

6.87^0 is caused by RFM of mannitol

Thus RFM of mannitol $= \frac{84 \; x \; 6.87}{3.17}$ = 182

(ii) Explain how the relative molecular mass of mannitol would be affected if it associated in naphthalene. (03marks)

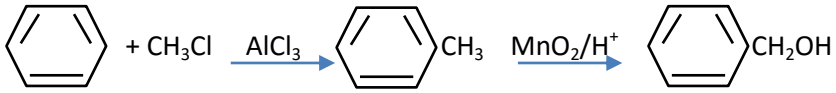
The molecular mass of mannitol would increase because association reduces the number of particles in solution and thus the apparent molecular mass increases

SECTION B

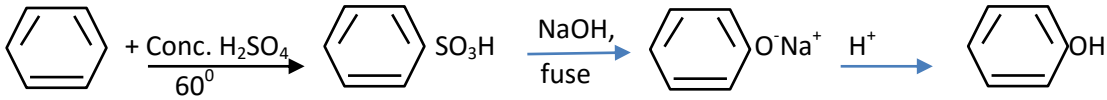
*Attempt any **two** questions from this section.*

5. Write equations to show how the following conversions can be effected. Indicate the reagents and conditions.

(a) Phenyl methanol from benzene (04marks)



(b) Phenol from benzene . (04marks)



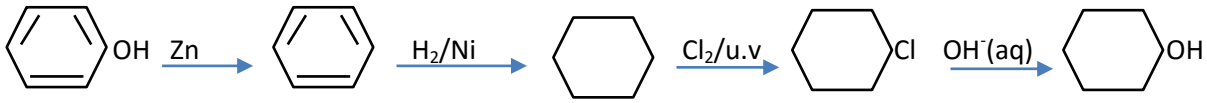
(c) Propanoic acid from propyne (04marks)

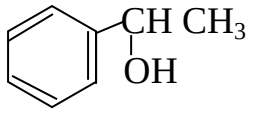
$CH3C{\equiv}CH \xrightarrow{Pd/H_2} CH_3CH{=}CH_2 \xrightarrow{HBr/peroxide} CH_3CH_2CH_2Br \xrightarrow{OH^-} CH_3CH_2CH_2OH$

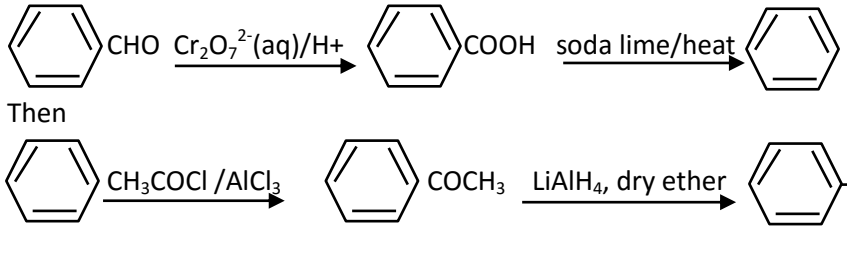
Then

$CH_3CH_2CH_2OH \xrightarrow{Cr_2O_7^{2-}/H^+} CH_3CH_2COOH$

(d) Cyclohexanol from phenol. (04marks)



(e)  from benzaldehyde (04marks)

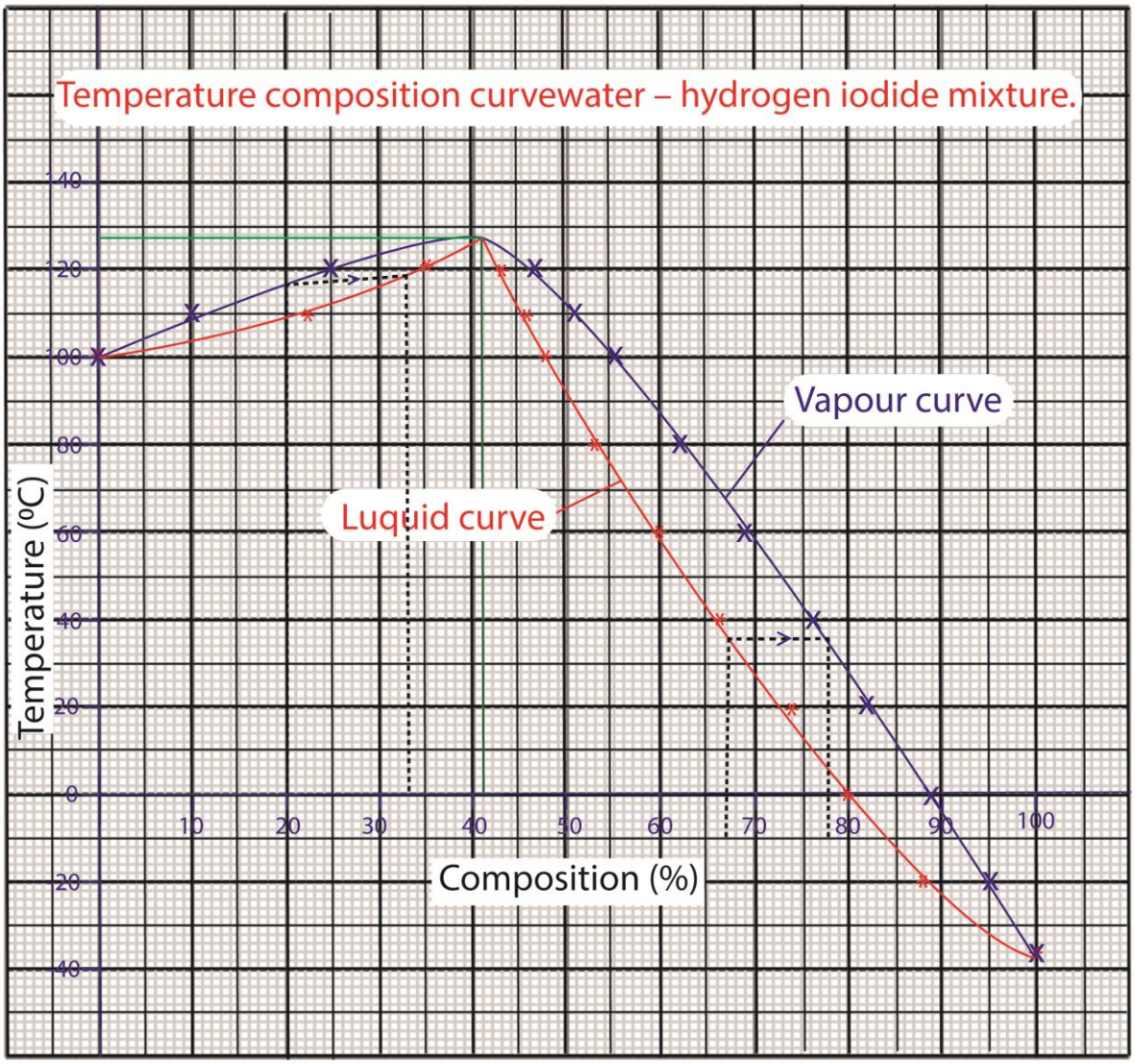


6. The table below shows the mole fraction of hydrogen iodide in the liquid mixture and in the vapour varying with temperature in water – hydrogen iodide mixture.

Temperature (^oC)		-20	0	20	40	60	80	100	110		120	
% Mole fraction of hydrogen iodide	in liquid mixture	88	80	72	66	60	54	48	46	22	36	44
	in vapor	95	89	82	76	69	63	55	52	10	25	47

The boiling points of pure water and pure hydrogen iodide are 100^0 C and -36^oC respectively.

Draw a well labelled temperature – composition diagram for water – hydrogen iodide mixture. (05marks)



(a) Use your graph to determine

(i) temperature and composition of the azeotropic mixture. (02marks)

Temperature: 128^0C

Composition: 41% water

(ii) the composition of the vapour when a liquid mixture containing 67% hydrogen iodide was boiled. (01marks)

78% HI

(iii) the composition of the liquid mixture which when boiled produced a vapour of containing 80% water. (02marks)
33% HI

(b) Explain the shape of the graph. (04marks)
The graph show negative deviation from Raoult's law because there are stronger attraction due to hydrogen bonds between hydrogen iodide and water molecules than those between like molceules

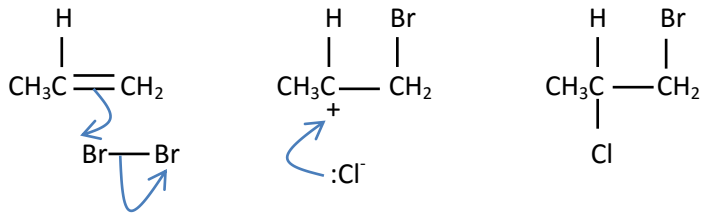
(c) Describe how

(i) a liquid mixture containing 40% water was fractionally distilled. (04marks)
filtrate is water
Residue - azeotrope

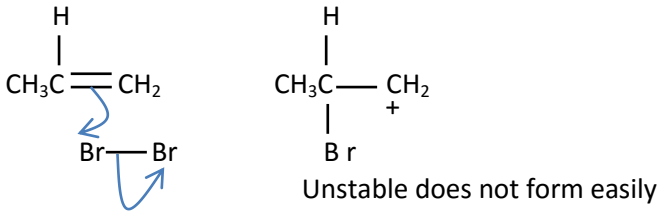
(ii) pure water can be obtained from the azeotropic mixture in (b)(i) above.
Add lead oxide and distil
(02marks)

7. Explain the following observations.

(a) When propene gas was bubbled through bromine liquid containing brine, 1-bromo-2-chloropropane is formed rather than
1- chloro-2-bromopropane (05marks)
1-bromo-2-chloropropane is formed instead 1-chloro-2-bromopropane because 1-bromo-2-chloropropane is formed through a stable intermediate (secondary caarbonium ion) as shown in the mechanism below



While
1-chloro-2-bromopropane would be formed unstable intermediate- a primary carbonium ion



Unstable does not form easily

(b) When excess cold concentrated hydrochloric acid is added to lead (IV) oxide, brown solid dissolves to a bright yellow liquid which formed a pale yellow precipitate on addition of concentrated solution of ammonium chloride. (05marks)

Lead (IV) oxide reacts with cold concentrated hydrochloric acid to form a yellow liquid of Lead (IV) chloride

$PbO_2(s) + 4HCl\ (aq) \rightarrow PbCl_4(l) + 2H_2O(l)$

Lead(IV) chloride react with ammonium chloride to form a yellow solid of ammonium hexachloridoplumbate(IV*).*

$PbCl_4 + 2NH_4Cl \rightarrow (NH_4)_2[PbCl_6]$

(c) When sulphur was warmed separately with concentrated nitric acid and concentrated sulphuric acid, sulphuric acid and sulphur dioxide were respectively formed as one of the products. (05marks)

- Nitric acid oxidizes sulphur to sulphuric acid

$S(s) + 6HNO_3(aq) \rightarrow H_2SO_4\ (aq) + 6NO_2(aq) + 2H_2O\ (l)$

- Concentrated sulphuric acid oxidizes sulphur to sulphur dioxide

$S\ (s) + 2H_2SO_4\ (l) \rightarrow 3SO_2\ (g) + 2H_2O\ (l)$

(d) The second ionization energy of sodium is much higher than the first ionization energy than the third ionization energy to the second ionization energy. (05marks)

The second ionization energy is very high compared the first ionization energy because

(i) removal of the first electron increases the effective nuclear charge on the remaining electrons

(ii) the second electron is removed from a full thermodynamically stable electrons shell

Increase in ionization energy from the second to the third is not very high because the third electron is removed unstable less than full energy level

8. (a) What is meant by the term **electrode potential**? (01mark)

Electrode potential is a potential difference that is set up between a metal and its solution containing metal ions.

(b) The electrode potentials of $S_2O_8^{2-}(aq) / SO_4^{2-}(aq)$ and $I_2(aq) / I^-(aq)$ are +2.01V and +0.54V respectively.

Write an equation for the reaction that occur at the

(i) anode (1½marks)

$2I^-(aq) - 2e \rightarrow I_2(aq)$

(ii) cathode (1½marks)

$S_2O_8^{2-}(aq) + 2e \rightarrow 2SO_4^{2-}(aq)$

(c) Write the overall cell reaction in (b) above. (1½marks)

$S_2O_8^{2-}(aq) + 2I^-(aq) \rightarrow 2SO_4^{2-}(aq) + I_2(aq)$

(d) Calculate the e.m.f and Gibbs free energy for the cell reaction in (b) above. (04marks)

$E^0_{cell} = E^0_{R.H.E} - E^0_{L.H.E}$

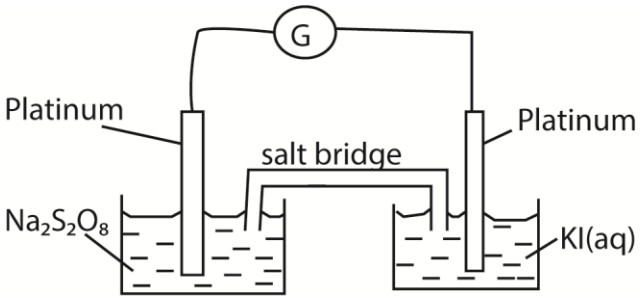
$= +2.01 - (+0.54) = 1.47V$

$\Delta G^0 = -nFE^0$

$=2 \times 96500 \times 1.47 = 283.17kJ$

(e) Draw a well labeled cell diagram for the cell in (b) above.

(03½marks)



(f) State what would observed when the two half cells in(b) above are connected. (02marks)

L.H.S: no observable change

R.H.S: brown color develops

(g) Distinguish between electrolytic cell and e.m.f cell. (04marks

Electrolytic cell	E.m.f. cells
Uses single electrolyte	Uses two electrolytes
Changes electrical energy into chemical energy	Changes chemical energy into electrical energy
Cathode is negative electrode	Cathode is positive electrode
Anode is positive electrode	Anode is negative electrode

END