Part A - Structured essay

Answer all four questions on this paper itself. (Each question carries 10 marks)

1. (a) Arrange the following in the increasing order of the property indicated in parenthesis. Reasons are not required.

(i) CO, CO_2, CO_3^{2-} (C- O bond distance)

..... < ..... < .....

(ii) NO_2^+ NO_3^-, NH_3 (electronegativity of N atom)

..... < ..... < .....

(iii) $BeSO_4$, $MgSO_4$, $CaSO_4$ (decomposition temperature $MSO_4 \rightarrow MO + SO_3$, M = metal)

..... < ..... < .....

(iv) Ne, Ar, Kr (boiling point)

..... < ..... < .....

(v) S, F, Si, Cl (atomic radius)

..... < ..... < .....

(05 × 5)

1 (a) 25 marks.

(b) Nitramide ($H_2N - NO_2$) is a weak acid. It decomposes to N_2O and H_2O in the presence of a base. answer the parts (i) to (v) which are based on niramide. Its skeleton is given below:

(i) draw the most acceptable Lewis structure for this molecule.

(ii) Draw the resonance structures for this molecule. Giving reasons, comment on their stabilities.

(10)

(iii) State the following

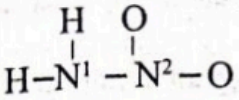
I. electron pair geometry (arrangement of electron pairs) around the atoms.
II. Shape around the atoms.
III. Hybridization of the atoms.

given in the table below

		The N attached to two H atoms	The N attached to two O atoms
I.	electron pair geometry		
II.	shape		
III.	hybridization		

(iv) Is this molecule polar or nonpolar?

(v) Identify the atomic/hybrid orbitals involved in the formation of the following bonds in the Lewis structure drawn in part (i) above. N atoms are labelled 1 and 2 as given below:



I. N^1 and N^{-2} .....

II. N^1 and H .....

Note: type of orbital need not be specified. For hydrogen only Is accepted.

1(b) 65 Marks.

(v) Xe, CH_3Cl, HF

Of the substances given above, which one / ones will have the forces given below?

(i) dipole - dipole forces .....

(ii) Hydrogen bonding forces .....

(iii) London dispersion forces .....

10 marks.

2. *(a)* Element A belongs to the s-block. Its first ionization energy is the highest in the groups. A reacts with water liberating a gas B. The resulting solution from this reaction gives a red colouration to a Bunsen burner flame, and the metal oxide on evaporation. A reacts with $N_2(g)$ to give compound C. The reaction of A with $H_2(g)$ gives a salt-like basic compound D. On treatment with H_2O, C gives a gas E which turns red litmus blue.

(i) Identify A, B, C, D and E giving their chemical formulae.

A = ... B = ... C = ... D = ... E = ...

(03 × 5)

(ii) Give balanced chemical equations for the reactions described above.

.....

.....

.....

.....

.....

..... *(03 × 5)*

..... *2 (a) 03 marks*

.....

.....

(b) The following questions are based on the transition metals, V and Cr and their compounds

(i) Give the ground sate electronic configuration of V. ..... (01)

(ii) State the positive oxidation states of V. ..... (02 × 4)

(iii) Give the chemical formulae of the oxides formed by V in the positive oxidation sates given in

(ii) above. Indicate whether each of these oxides is acidic, amphoteric or basic.

.....

.....

.....

..... (02 × 3)

.....

(iv) Write the chemical formulae of two oxocations formed by V. State their colours in aqueous acidic medium.

..... (01 × 4)

.....

(v) What is the simplest ion that chromium forms in aqueous solution? State its colour. Predict what you would expect to observe when solid Na_2CO_3 is added to an aqueous solution of this ion. (04 + 04)

..... (04)

.....

Note: No mark for colour if species is incorrect.

(vi) Give one use of the metal V.

..... (04)

(vii) What would you observe when a green coloured aqueous solution of $CrCl_3$ is subjected to the following

I. Addition of a few drops of dilute NaOH

..... (03)

II. Addition of excess dilute NaOH followed by H_2O_2 and then heated.

..... (03)

(viii) When a concentrated solution of $K_2Cr_2O_7$ is treated with conc H_2SO_4 the bright red acidic oxide X of chromium is precipitated On heating X, the green amphoteric oxide Y is obtained Y could also be obtained on heating $(NH_4)\ Cr_2\ O_2$
Give the chemical formulae of X and Y.

X = ... Y = ... (03 + 03)

(ix) What would you observe when dil NaOH is added to a solution of $K_2Cr_2O_7$?

..... (03)

.....

(x) Give on advantage and one disadvantage of using $K_2Cr\ O_7$ in titrations.

Advantage : ..... (03)

Disadvantage: ..... (03)

3. Chlorine gas is used as an oxidizing agent to oxidize the metal ion $M^{2+}_{(aq)}$ The following data are given.

Reaction	Standard enthalpy change ΔH° at 25 °C(kj mol-1)
$M(s) \rightarrow M^{+}(aq) + e$	-32.5
$M(s) \rightarrow M^{2+}(aq) + 2e$	- 48.5
$M(s) \rightarrow M^{3+}(aq) + 3e$	- 82.5
$Cl_2(g) + 2e \rightarrow 2Cl^{-}(aq)$	-334.0

$E^{\theta}_{M^{3+}/M^{2+}} = +0.77$ $E^{\theta}_{Cl_2/Cl^-} = +1.36V$

The above oxidation is carried out electrochemically.

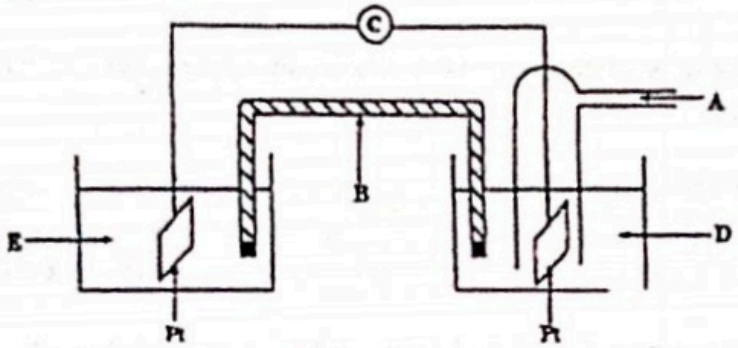
(i) Write half reactions for oxidation and reduction processes and derive the cell reaction.

Oxidation reaction : ..... *(05)*

Reduction reaction : ..... *(05)*

Cell reaction : ..... *(05)*

(ii) The following diagram shows the experimental setup needed to measure E^{θ}_{cell} of the above reaction. Identify A - E, Giving physical state, concentration/pressure where applicable.



A : ..... B : ..... C : .....

D : ..... E : .....

(iii) Calculate E_{cell} for the above cell

.....

.....

.....

(iv) Calculate the standard enthalpy change (ΔH^{θ}) at 25 °C, for the cell reaction given in part (i)

.....

(v) The relationship between standard Gibbs energy change, ΔG^0 for the reaction and E^0_{cell} is given by

$$\Delta G^0 = - kE^0_{cell}$$

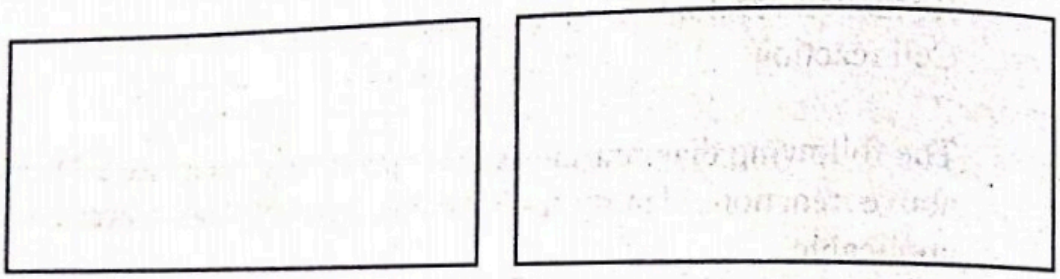
where, $k = 1.93 \times 10^5$ J mol^{-1} V^{-1}

Calculate the standard Gibbs energy change ((ΔG^0) at 25 ^{0}C for the above cell reaction.

(vi) Calculate the standard entropy change (ΔS^0) at 25 ^{0}C, for the above cell reaction.

4. (a) (i) Compound A exhibits optical isomerism and has the molecular formula C_7H_{16}

I. Draw two possible structures for A which are not enantiomers of each other, in the boxes given below.



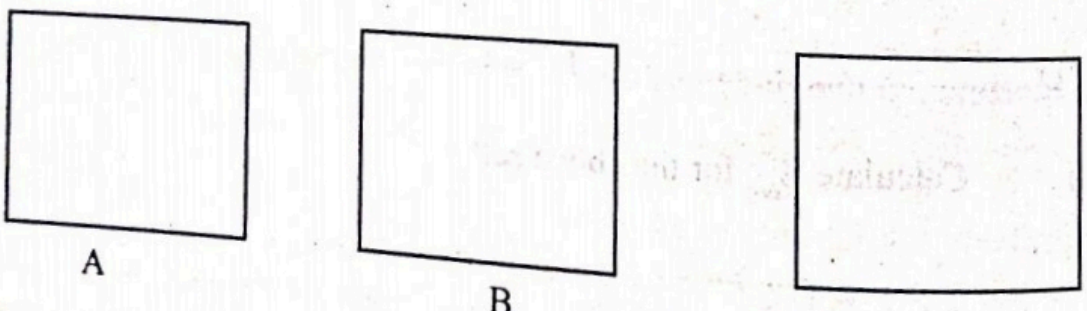
(10 + 10)

II State the isomeric relationship between the two structures you have drawn.

..... *(03)*

(ii) B and C are optically inactive compounds with the molecular formula C_7, H_{14} Both B and C exhibit geometric isomerism. B and C are not geometric isomers of each other Catalytic hydrogenation of either B or C yields are same compound A

I Draw the structures of A, B and C in the boxes given below (It is not necessary to draw the stereoisomeric forms)



A B C

II Write the IUPAC names of B and C

B: .....

C: .....

(b) Consider the following reaction sequence:

$CH_2=CH-CH_2Br \xrightarrow[\text{Reaction 1}]{HBr} P \xrightarrow[\text{Reaction 2}]{\text{alcoholic KOH}} Q \xrightarrow[\text{Reaction 3}]{NaNH_2,\ \text{liq. } NH_3} R \xrightarrow[\text{Reaction 4}]{CH_3CH_2Br} S$

(i) Draw the structures of P, Q, R and S in the boxes given below.

P

Q

R

S

(03 + 04)

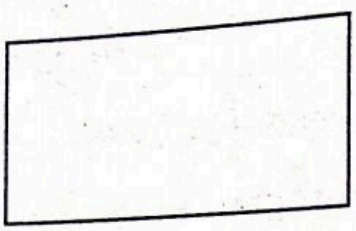
(ii) Classify each of the reactions in the above sequence as nucleophilic addition (A_N), electrophilic addition (A_g) nucleophilic substitution (S_N) electrophilic substitation (S_E) elimination (E) or acid-base (AB), by writing A_N, A_E, S_N, S_E, E, AB in the appropriate cages.

Reaction	1	2	3	4
Reaction type				

(iii) Write the mechanism for Reaction I. *(03 + 04)*

(12)

(iv) Draw the structure of the product T obtained when Reaction 1 is carried out in the presence of peroxide.



T

(03)

(v) It has been found that T is also formed in Reaction 1 as a minor product. By considering the mechanism of the reaction, explain why the major product in Reaction 1 is P and not T.

(03)

(03)

4(b) 45 marks

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අධ්‍යයන පොදු සහතික පත්‍ර (උසස් පෙළ) විභාගය, 2013 අගෝස්තු
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General Certificate of Education (Adv. Level) Examination, August 2013

නව නිර්දේශය
புதிய பாடத்திட்டம்
New Syllabus

රසායන විද්‍යාව II
இரசாயனவியல் II
Chemistry II

02 E II

Universal gas constant $R = 8.314\ J\ K^{-1}\ mol^{-1}$

Avogadro constant $N_A = 6.022 \times 10^{23}\ mol^{-1}$

PART B — ESSAY

Answer two questions only. (*Each question carries* **15** *marks.*)

5. (*a*) **A** and **B** are volatile and completely miscible liquids which form an ideal solution when mixed. A mixture containing 1.0 mol of liquid **A** and 1.0 mol of liquid **B** was placed in a closed container. When the system reached equilibrium, the pressure and volume of the gaseous phase, and the mole ratio of **A**/**B** in this phase were found to be 1.0×10^3 Pa, 0.8314 m^3 and 2/3 respectively. The system was maintained at 200 K.

Calculate the following.

(i) the total number of moles in the gas phase.

(ii) the mole fractions of **A** and **B** in the liquid phase.

(iii) the saturated vapour pressures of **A** and **B**.

(5.0 *marks*)

(*b*) In a saturated solution of $Mn(OH)_2$ at 25 °C, the concentration of Mn^{2+} is 1.0×10^{-5} mol dm^{-3}. The solubility product of $Mg(OH)_2$ at 25 °C is 1.0×10^{-10} $mol^3\ dm^{-9}$. K_b of NH_4OH at 25 °C is 1.6×10^{-5} mol dm^{-3}

(i) Calculate the solubility product of $Mn(OH)_2$ at 25 °C.

(ii) Calculate the concentration of hydroxide ions in a 0.01 mol dm^{-3} NH_4OH solution at 25 °C.

(iii) Determine the concentration of NH_4OH necessary to start precipitation of $Mn(OH)_2$ from a 0.001 mol dm^{-3} solution of $MnSO_4$.

(iv) If 5.35 g of NH_4Cl is dissolved in 1.00 dm^3 of 1.00 mol dm^{-3} NH_4OH solution, calculate the concentration of hydroxide ions in the solution. (H = 1.0, N = 14.0, Cl = 35.5)

(v) Calculate the number of moles of solid NH_4Cl required to prevent the precipitation of $Mg(OH)_2$ in a solution to be made by mixing 0.50 dm^3 of a 0.02 mol dm^{-3} solution of $Mg(NO_3)_2$ and 0.50 dm^3 of a 0.20 mol dm^{-3} solution of NH_4OH.

(vi) Explain the use of NH_4Cl in group analysis.

(10.0 *marks*)

6 (a) Consider the reaction,

$$mM + nN \longrightarrow cC$$

where m, n and c are stoichiometric coefficients of M, N and C respectively.

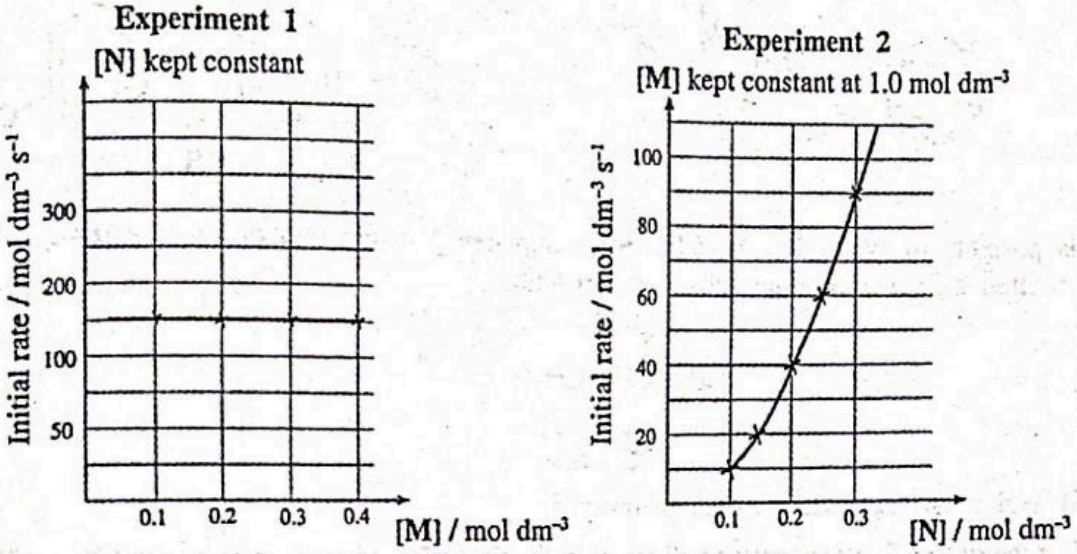
(i) Considering the above reaction to be an elementary reaction, write an expression for the rate of reaction. (The rate constant of the reaction = k.)

(ii) Two experiments were conducted to find the order of the reaction.

Experiment 1 : Initial rate was measured varying the concentration of M while keeping the concentration of N constant.

Experiment 2 : Initial rate was measured varying the concentration of N while keeping the concentration of M constant at 1.0 mol dm^{-3}

Both experiments were conducted at the same temperature. The results of the experiments are shown in the graphs below.



I. Find the order of the reaction with respect to M.

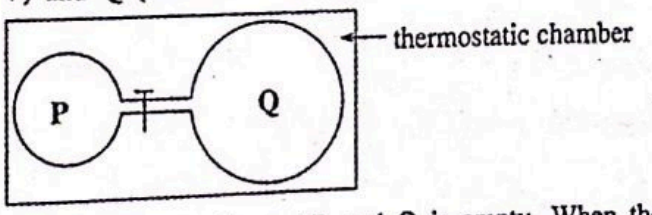
II. Find the order of the reaction with respect to N.

III. What is the overall order of the reaction?

IV. Find the rate constant, k of the reaction.

(6.0 *marks*)

(b) Two rigid bulbs **P** (volume = V) and **Q** (volume = 2V) connected by a tap are placed in a thermostatic chamber as shown below.



Initially the tap is closed. **P** contains 1.0 mol of gas **AB** and **Q** is empty. When the temperature of the system was increased to 400 K, AB(g) dissociated into A(g) and B(g) according to the equilibrium reaction given below.

$$AB(g) \rightleftharpoons A(g) + B(g)$$

The equilibrium constant for the above equilibrium is K_c. When the system has reached equilibrium (first equilibrium) the amount of A(g) was found to be x mol. The tap was opened and the system was allowed to reach equilibrium again (second equilibrium). The amount of A(g) formed was found to be y mol.

(i) Show that $K_cV(1-x) = x^2$ and $3K_cV(1-y) = y^2$.

(ii) If $y = 0.5$ mol, calculate the value of x.

(iii) Explain your answer in (ii) above using the Le Chatelier's principle.

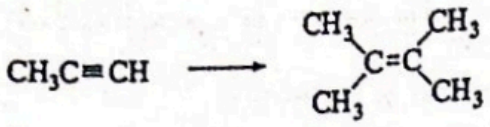
(iv) The temperature of the system was increased to 600 K. When the system reached equilibrium (third equilibrium) the pressure of the system was 1.7 times that at the second equilibrium. The amount of A(g) at the third equilibrium was z mol. Calculate the value of z.

(v) Show that the decomposition of AB(g) is endothermic.

(vi) State any assumption/s made in your calculations.

(9.0 *marks*)

7. (*a*) Using **only** the chemicals given in the list, show how you would carry out the following conversion.

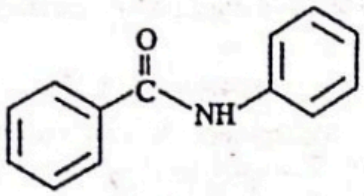


List of chemicals

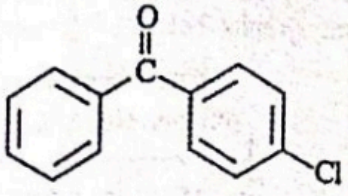
$NaBH_4$, $HgSO_4$, dil. H_2SO_4, conc. H_2SO_4, PCl_5, Mg, ether

(4.0 *marks*)

(*b*) Show how you would synthesize compound **B** using compound **A** as the **only** organic starting material.



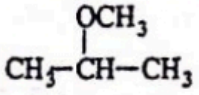
A



B

(6.0 *marks*)

(*c*) It is possible to synthesize the following compound **X** using two different pathways. Each pathway can be written as a nucleophilic substitution reaction.



X

(i) Write the reactants for each pathway.

(ii) One of the above pathways will result in the formation of another compound **Y** in additon to **X**. Identify the reactants involved in this pathway and write the structure of **Y**.

(iii) State what **type of reaction** is involved in the formation of **Y**.

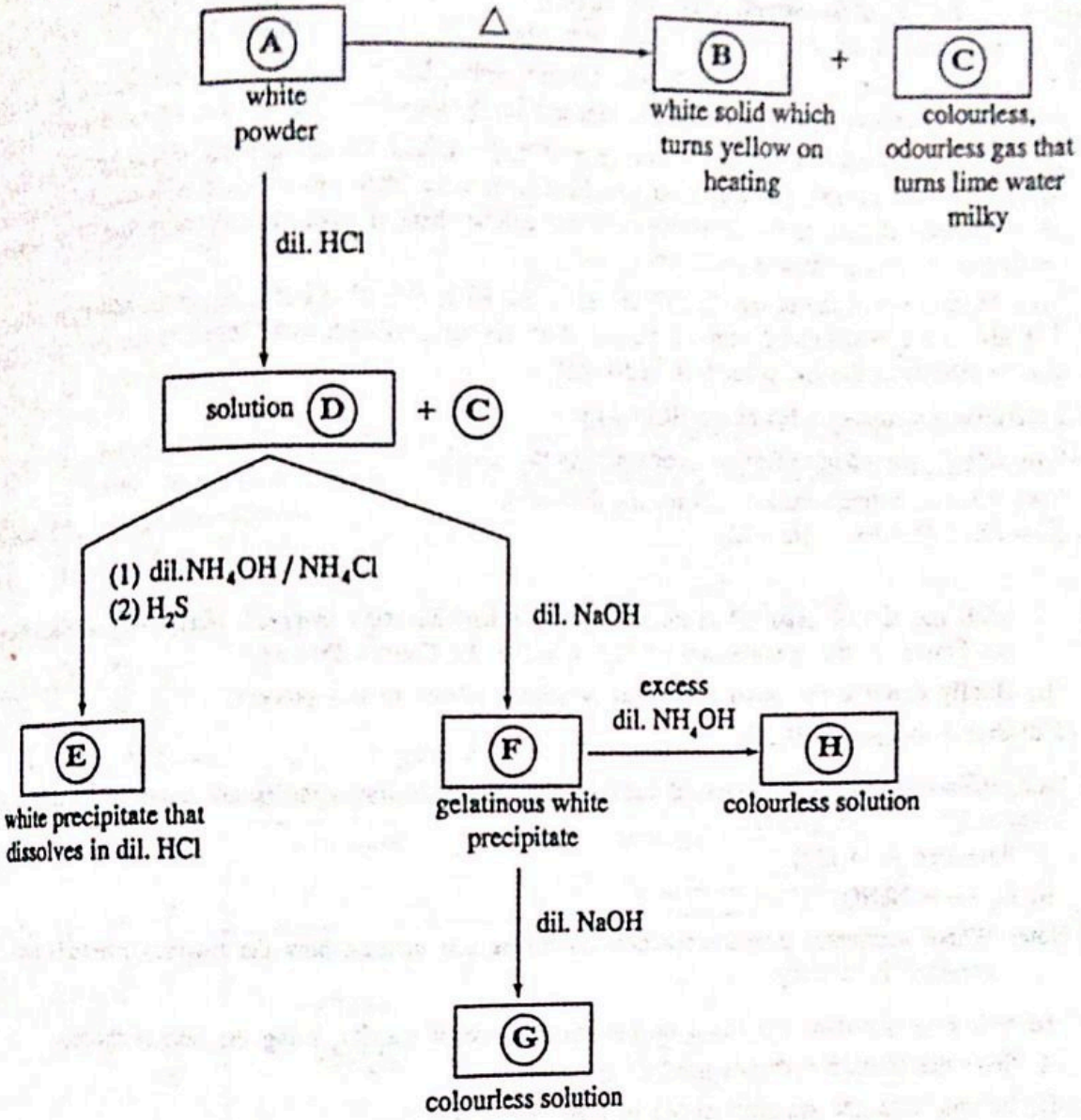
(iv) Assume that the reactants identified in (ii) above, form **X**, by a two step reaction. Show how **X** is formed by writing these two steps. Use curved arrows to indicate movement of electrons.

(5.0 *marks*)

PART C — ESSAY

Answer two questions only. (Each question carries 15 marks.)

8. (a) Reactions of compounds of an element in the 3*d* block of the Periodic Table are given below. Identify the species A, B, C, D, E, F, G and H.



(5.0 *marks*)

(b) Tests (1) and (2) were carried out with an aqueous solution Z produced by passing the colourless gas P into water. The tests and observations are given below.

Test	Observation
(1) Added an acidified solution of $K_2Cr_2O_7$ to the solution.	A clear green solution was obtained.
(2) Added H_2O_2 to the solution and warmed. Then added a solution of $BaCl_2$.	A white precipitate insoluble in dil. HCl was formed.

(i) Identify gas P. (Reasons are not required.)

(ii) Give balanced chemical equations for the reactions that occur in tests (1) and (2).

(iii) When gas Q was passed through solution Z, a pale yellow (could be seen as white) turbidity resulted.

I. Identify gas Q. (Reasons are not required.)

II. Give the balanced chemical equation for this reaction.

(5.0 *marks*)

(c) A sample given for analysis was found to contain NaOH, Na_2CO_3 and an inert water soluble substance. The following procedure was used to determine the percentage of Na_2CO_3 in the sample.

Note: The inert substance **does not** participate in the reactions in the procedure given below.

Procedure:

A weight of 42.40 g of the sample was transferred quantitatively to a 500 cm^3 volumetric flask and made upto the mark with distilled water. The flask was shaken thoroughly (**solution X**).

(1) A 25.00 cm^3 portion of **solution X** was titrated with dil. HCl solution using methyl orange as the indicator, until the colour changed from orange to red. The burette reading at the end point was 32.00 cm^3.

(2) A 25.00 cm^3 portion of **solution X** was warmed to 70 °C and 1% $BaCl_2$ solution was added in slight excess. The $BaCO_3$ precipitate formed was filtered, and the filtrate was titrated with dil. HCl solution using phenolphthalein as the indicator until the colour changed from pink to colourless. The burette reading at the end point was 24.00 cm^3.

(3) To a 25.00 cm^3 volume of the dil. HCl solution, 5% KIO_3 and 5% KI solutions were added in excess. The liberated I_2 was titrated with a 0.50 mol dm^{-3} $Na_2S_2O_3$ solution using starch as the indicator. The burette reading at the end point was 12.50 cm^3.

(i) Determine the concentration of the HCl solution.

(ii) Calculate the percentage of sodium carbonate in the sample.

(iii) State any assumption/s made in calculating the above.

(C = 12, O = 16, Na = 23)

(5.0 marks)

9. (*a*) (i) I. With the aid of balanced chemical equations list the steps involved, along with the reaction conditions, in the manufacture of H_2SO_4 using the Contact Process.

II. Briefly describe the physicochemical principles related to this process.

III. Give two uses of H_2SO_4.

(ii) Using balanced chemical equations, indicate how the following conversions could be carried out industrially:

I. limestone $\longrightarrow C_2H_2$

II. $N_2 \longrightarrow NaNO_2$

Note: Where applicable give the reaction conditions and indicate how the reagents/reactants are obtained industrially.

(iii) The following questions are based on the manufacture of Na_2CO_3 using the Solvay Process.

I. State the starting materials used in this process.

II. Indicate how the materials stated in I are obtained.

III. Give the final by-product of this process.

IV. Give two reasons as to why low temperatures are used in this process.

V. Give two uses of Na_2CO_3.

VI. Propose a method to convert the final by-product stated in III to gypsum, using sea water as a natural resource.

(7.5 marks)

(*b*) As an alternative to chlorofluorocarbons (CFCs), hydrochlorofluorocarbons (HCFCs) were introduced to reduce the ozone layer depletion. However, both these groups of compounds not only deplete the ozone layer but also contribute to other environmental problems.

(i) Draw the chemical structures of all the CFCs and HCFCs with a single C atom. Label each of them as a CFC or HCFC.

(ii) "Under normal atmospheric conditions, HCFCs are more reactive than CFCs." Comment on this statement.

(iii) Name another environmental problem that is associated with CFCs and HCFCs. Comment on their relative contribution towards this environmental problem.

(iv) Identify three properties of CFCs that make them suitable for use as refrigerants.

(v) Explain how CFCs contribute to the depletion of the ozone layer.

(vi) Briefly describing the consequence of the depletion of the ozone layer, identify three problems associated with it.

(7.5 marks)

10. (a) Predict the products and give balanced chemical equations for the following reactions. State the action of the species underlined, in the reaction.

(i) $\underline{H_2O_2}(aq) + PbS(s) \longrightarrow$

(ii) $MnO_4^-(aq) + \underline{H_2O_2}(aq) + H^+(aq) \longrightarrow$

(iii) $Cr_2O_7^{2-}(aq) + \underline{H_2S}(aq) + H^+(aq) \longrightarrow$

(iv) $Cu(s) + \underline{H_2S}(g) \xrightarrow{\Delta}$

(v) $C(s) + \underline{\text{conc. } HNO_3} \xrightarrow{\Delta}$

(2.5 *marks*)

(b) A solution **T** has been prepared by dissolving 0.300 g of FeC_2O_4 in dilute H_2SO_4. The solution was heated to 65 °C. Calculate the volume of 0.025 mol dm^{-3} $KMnO_4$ solution required to react completely with FeC_2O_4 under these conditions.

(C = 12, O = 16, Fe = 56)

Note : Consider FeC_2O_4 to exist as Fe^{2+} and $C_2O_4^{2-}$ in solution **T**.

(5.0 *marks*)

(c) Liquefied-petroleum gas (LP gas) is commonly used as a fuel for cooking purposes in Sri Lanka. It is a mixture of liquefied propane and butane, under high pressure. The following data are provided.

Substance	Standard enthalpy of formation ΔH_f° at 25 °C (kJ mol^{-1})
$H_2O(l)$	−286
$CO_2(g)$	−394
$C_3H_8(g)$	−104
$C_4H_{10}(g)$	−126

(i) Calculate the standard enthalpies of combustion of propane and butane gases at 25 °C.

(ii) Calculate the amount of heat needed to increase the temperature of 400 g of water from 25 °C to 85 °C. (Heat capacity of water is 4.2 J g^{-1} $°C^{-1}$).

(iii) Assuming complete combustion would take place, calculate the mass of CO_2 emitted in each case when the above process (ii) is carried out using:

I. propane as the fuel.

II. butane as the fuel.

(iv) Based on your calculations in (iii) above, identify which fuel is more environmentally friendly and explain why it is so.

(7.5 *marks*)

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