PART A — STRUCTURED ESSAY

*Answer **all four** questions. Each question carries **10** marks.*

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1. (*a*) (i) Define the term, **'atomic mass unit' (amu)**.

(ii) It is possible that the mass of a certain molecule of carbon dioxide supplied to you is **not** equal to 44·0 amu. Give **two** reasons for this possibility.

(*b*) (i) The element, **X** belongs to the 4th Period of the Periodic Table. An atom of **X** forms an anion. The highest valency-state oxide formed by **X** is XO_3. Identify **X**.

(ii) The compound, XCl_4 formed by the above element **X** is reduced with $LiAlH_4$. Write the molecular formula of the hydride of **X** that is most likely to be formed in this reaction.

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(c) Can the hydride referred to in (b)(ii) above, act as an oxidizing agent? If so, give an example for that. If not, give reasons for that.

(Inorganic)

2. (a) Assume that $Na_2S_2O_3$ reacts with HNO_3 under a certain condition forming NO_2, $NaHSO_4$ and water only. Write a balanced chemical equation for this reaction, either by considering the relevant oxidation numbers or by another method.

(Basic)

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(b) A finely powdered mixture has been prepared so that the $CaCO_3$: $MgCO_3$ mole ratio is 1 : x. It contains no other substances. 1·30 g of this mixture was heated strongly, until it was converted completely into CaO and MgO. The mass of the mixture of oxides thus obtained was 0·640 g.

The relative atomic masses relevant here are as follows:

Ca = 40·0; Mg = 24·0; O = 16·0; C = 12·0.

(i) Now consider P, Q, R and S in the mathematical expression given below.

$$\frac{100 + P \times x}{Q + R \times x} = \frac{1{\cdot}30\ \text{g}}{S}$$

Write the values appropriate for P, Q, R and S in the Table provided below.

P	
Q	
R	
S	

(ii) Substitute these values appropriately in the mathematical expression given above, and calculate the value of x.

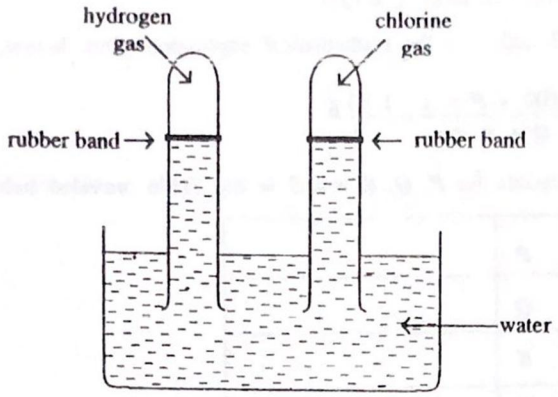
(c) (i) State **Gay Lussac's Law.**

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(ii) Direct your attention now to the experiment that you carried out in the laboratory for the purpose of demonstrating Gay Lussac's Law, using equal volumes of hydrogen gas and chlorine gas under constant temperature and pressure.

Assume that you are supplied with a sample of hydrogen gas and a sample of chlorine gas as shown below.



Describe briefly how you would demonstrate in the laboratory that Gay Lussac's Law is true, using the two gas samples shown above.

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(Organic)

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3. (*a*) The organic compound, **Y** contains C, H and O only. When **Y** is subjected to complete combustion, CO_2 and H_2O are obtained in the mole ratio of 2 : 1, respectively. The accurate relative molecular mass of **Y** is equal to 152. The percentage of O in **Y** is less than 40%, by weight. Determine the molecular formula of **Y**.

The relevant relative atomic masses are as follows: C = 12·0; H = 1·00; O = 16·0

(*b*) **A** and **B** are two alkynes. **A** and **B** were reacted as shown below, and **C** and **D** were obtained, respectively.

$$\mathbf{A} \xrightarrow{H_2/Pd} \mathbf{C}$$

$$\mathbf{B} \xrightarrow{H_2/Pd} \mathbf{D}$$

The molecular formulae of both **C** and **D** were C_4H_8.

C and **D** reacted as follows:

$$\mathbf{C} + HBr \xrightarrow[\text{conditions}]{\text{under polar}} \text{An equi-molar mixture of optically active compounds}$$

$$\mathbf{D} + HBr \xrightarrow[\text{conditions}]{\text{under polar}} \text{The same equi-molar mixture of optically active compounds mentioned above}$$

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(i) You are supplied with a mixture containing both **A** and **B**. How would you attempt to obtain either pure **A** or pure **B** from this mixture by a chemical method?

(ii) Draw the structures possible for the compounds **C** and **D**.

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(iii) Draw the structure of one of the optical isomers formed in the reaction with HBr, in the usual manner, so that its three-dimensional nature is clearly apparent.

(c) Consider the following series of reactions.

$$\mathbf{E} \xrightarrow{\mathbf{L}} \mathbf{F} \xrightarrow{\text{heating}} \mathbf{G} \xrightarrow{LiAlH_4} \mathbf{H} \xrightarrow[\text{heating}]{M/H_3O^+} CH_3CH=CHCH_2OCOCH_3$$

(i) Draw appropriately the structures of **E**, **F**, **G** and **H** in the cages provided below.

E

F

G

H

(ii) Identify **L** and **M** and appropriately indicate them in the cages provided below.

L	
M	

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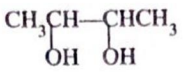
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(*d*) Assume that you are supplied with

$$CH_3CH_2CH_2CH_2OH$$

as the **only** organic compound.

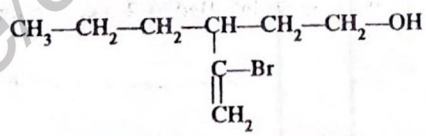
Indicate how you would synthesize



using the above compound.

N.B. Disregard the isomerism of the products. If the method of synthesis proposed by you is unnecessarily long, you will not be awarded the maximum marks.

4. (*a*) Name the compound with the following structure, in accordance with IUPAC nomenclature.

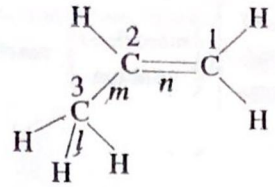


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(*b*) Consider the structure shown below. The three carbon atoms of the structure are labelled as 1,2 and 3. Three of its bonds are labelled as *l*, *m* and *n*.



Now, write clearly the words and/or symbols appropriate for the vacant spaces at the relevant places in the description presented below.

Description:

The C—H σ-bond designated as *l* is formed by the _____ _____ of the _____ orbital of the relevant H atom with an _____ _____ orbital of the relevant C atom."

"The C—C bond designated as *m* is formed by the _____ _____ of an _____ _____ orbital of the C atom labelled as 3, with an _____ _____ orbital of the C atom labelled as 2."

In the formation of the π–bond of C=C designated as *n*, the _____ _____ of the C atom labelled as 2, containing one unpaired _____ _____ _____ with the _____ _____ of the C atom labelled as 1, containing one _____ _____."

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(*c*) (i) A brief description pertaining to the reaction between aqueous KCN and the bromoalkane, $R_1R_2R_3CBr$ is given below.

"This reaction is called { **a free radical / an electrophillic / a nucleophillic** } { **substition / addition** } **reaction.**"

Clearly cross out the **inappropriate** words out of the five words within the brackets.

N.B. The appropriate words should be clearly visible. If your responses are not clear, you will not be awarded marks.

(ii) Present clearly the mechanism of the reaction given in 4 (*c*)(i) above.

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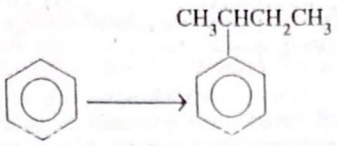
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(*d*) Propose a method for effecting the following conversion.

N.B. If the method of conversion proposed by you is unnecessarily long, you will not be awarded the maximum marks.

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கல்விப் பொதுத் தராதரப்பத்திர(உயர் தர)ப் பரீட்சை, 1999 ஒகஸ்ற்
General Certificate of Education (Adv. Level) Examination, August 1999

රසායන විද්‍යාව II
இரசாயனவியல் II
Chemistry II

02
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PART B — ESSAY

Answer two questions only. Each question carries 15 marks.

5. (*a*) Using the equation, $PV = \frac{1}{3}mN\overline{c^2}$ pertaining to the Kinetic Theory of gases, derive Dalton's Law of partial pressures.

(*b*) A mixture of gases contains 75.0% of N_2 gas and 25.0% of O_2 gas, by volume. The pressure of the mixture of gases is 1.00×10^5 N m^{-2} and the temperature is 300 K. Assuming ideal behaviour calculate the following:

(i) The partial pressure of O_2 in this mixture of gases.

(ii) The relative molecular mass relevant for this mixture of gases. (The relative atomic masses of N and O are 14·0 and 16·0 respectively.)

(iii) The density of this mixture of gases.

(*c*) You are supplied with a real gas. You are not informed of its relative molecular mass. Explain how you would attempt to show that this real gas does not behave ideally.

(*d*) You would have performed an experiment in the laboratory for the purpose of determining the molar volume of oxygen gas. Describe that experiment briefly, and explain how the molar volume of O_2 at s.t.p. is determined.

6. (*a*) At a certain temperature, the K_C value for the equilibrium, $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ is about 25. Assume that this reaction was started with equi-molar amounts of $H_2(g)$ and $I_2(g)$. Draw a diagram of the graphs which shows the variation of $H_2(g)$ concentration and HI(g) concentration with time, for this reaction at the above temperature.

(*b*) 0·200 mol NO, 0·100 mol H_2 and 0·200 mol H_2O were placed initially in a closed vessel of volume 0·0200 m^3. At 500 K the following equilibrium occurred.

$$2NO(g) + 2H_2(g) \rightleftharpoons N_2(g) + 2H_2O(g)$$

At equilibrium, the amount of NO(g) present was 0·150 mol.

(i) Calculate the K_C for this equilibrium.

(ii) Using the value obtained above for K_C, calculate the K_P for this equilibrium.

(*c*) (i) Derive the relationship between K_b of NH_3 and K_a of NH_4^+, in aqueous solution.

(ii) At 25 °C, the concentration of an aqueous solution of a mono-basic weak acid is 0·10 mol dm^{-3}.
Calculate the OH^- concentration in this aqueous solution.

K_a at 25 °C = 9.0×10^{-9} mol dm^{-3}.
K_w at 25 °C = 1.0×10^{-14} mol^2 dm^{-6}.

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(*d*) The ionic compound, FeX_2 is only slightly soluble in water. The anion, X^- is not oxidi... solution by chemical means. The amount of FeX_2 dissolving in water cannot be directly d... by methods involving weighings. However, there is a measurable Fe^{2+} ion concentration in a sa... aqueous solution at 25 °C. Explain how you would attempt to determine the solubility product of ... at 25 °C, under these conditions.

7. (*a*) (i) Consider the following data:

The standard enthalpy of formation of $CH_4(g) = -75{\cdot}0$ kJ mol^{-1}

The standard enthalpy change for the reaction, $2H(g) \rightarrow H_2(g) = -432$ kJ mol^{-1}

The standard enthalpy change for the reaction, $C(graphite) \rightarrow C(g) = +715$ kJ mol^{-1}

Using these data, calculate the standard mean bond dissociation enthalpy of C–H pertaining to $CH_4(g)$.

(ii) Three standard bond dissociation enthalpies are given below.

bond	**standard bond dissociation enthalpy**
H — H	+ 432 kJ mol^{-1}
F — F	+ 158 kJ mol^{-1}
H — F	+ 569 kJ mol^{-1}

Using these values, calculate the standard enthalpy of formation of HF(g).

(*b*) (i) Describe briefly what is meant by '**the standard hydrogen electrode**'.

(ii) Describe briefly what is meant by '**the standard zinc electrode**'.

(*c*) (i) A certain electrochemical cell which is at 25 °C is represented below.

$$Sn(s) \left| Sn^{2+}(aq,\ 1\ mol\ dm^{-3}) \right\| Cu^{2+}(aq,\ 1\ mol\ dm^{-3}) \left| Cu(s) \right.$$

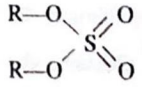
Using the data given below, calculate the e.m.f. of the above cell.

$E^{\ominus}$ values at 25 °C are as follows:

$$E^{\ominus}_{Sn^{2+}/Sn} = -0{\cdot}136\ V\ ;\ E^{\ominus}_{Cu^{2+}/Cu} = +0{\cdot}337\ V$$

(ii) At which electrode does the reduction take place when a current of electricity is drawn from this cell? Write the electrode reaction that takes place at that electrode.

(*d*) (i) When the temperature increases slightly, the rate of a chemical reaction increases considerably. Explain this fact by considering the distribution of the velocities of the molecules (Boltzmann Curve).

(ii) Assume that the solid organic compound,  dissolves in water. Assume also that one molecule of this compound, in aqueous solution, hydrolyses slowly giving two molecules of R—O—H and another product, and also that the two molecules of R—O—H are formed simultaneously. Describe briefly how you would attempt to determine the order of this reaction.

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PART C — ESSAY

Answer two questions only. Each question carries 15 marks.

8. (*a*) (i) Write an expression which will describe in a generalized form the electronic configurations of all of the following elements: Be, Mg, Ca and Sr.

(ii) Write an expression which will describe in a generalized form the electronic configurations of all of the following elements: F, Cl, Br and I.

(*b*) (i) Predict what products would be formed when CuCl is reacted with caesium.

(ii) Explain the above reaction on the basis of ionization energies.

(*c*) (i) Write a balanced chemical equation for the reaction that occurs between H_2O_2, $KMnO_4$ and an exess of dilute H_2SO_4.

(ii) How would you explain the action of H_2O_2 as a reducing agent under the above conditions?

(*d*) An aqueous solution supplied to you contains the two compounds Na_2CO_3 and NaOH. You are also supplied with a standard 0·100 mol dm^{-3} H_2SO_4 solution. However, you are not supplied with other acids or bases. As the indicator you are given only phenolphthalein. Explain how you would determine **volumetrically** the NaOH concentration present in the original solution supplied to you, under these conditions.

N.B. You are provided with the other materials and facilities available in the Chemistry Laboratory.

9. (*a*) This part of the question pertains to the industrial production of caustic soda.

(i) Making use of a labelled diagram, indicate clearly the essential parts and all the relevant materials used in a diaphragm cell.

(ii) What is the principal purpose served by the diaphragm?

(iii) Write the chemical reaction that takes place at the anode.

(iv) Write the chemical reaction that takes place at the cathode.

(v) Write, **in the balanced form**, the **overall** chemical reaction that takes place in the formation of NaOH in the diaphragm cell.

(*b*) Name the following compounds in accordance with IUPAC nomenclature.

(i) $[Cu(NH_3)_4]Br_2$

(ii) $(NH_4)_3[Fe(CN)_6]$

(*c*) Explain the following facts pertaining to the Periodic Table.

(i) In comparison with the melting points of the elements in the *s*–block, the melting points of the elements in the *d*–block are very high.

(ii) The elements manganese and bromine both belong to the same period in the Periodic Table. The total number of electrons in the two outermost sub-energy levels of the atoms of both these elements is equal to seven. However, manganese is a good conductor of electricity, while bromine does not conduct electricity.

(*d*) You are supplied with several samples of a solution containing $CuCl_2$, $FeCl_3$ and $NiCl_2$. How would you demonstrate clearly that the cations, Cu^{2+}, Fe^{3+} and Ni^{2+} are present in this solution?

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10. (*a*) Write a brief description of how the environment could be polluted by the industrial production of ammonia by the Haber Process.
N.B. It is sufficient to present five important facts.

(*b*) (i) The thinning of the ozone layer is harmful to man. Explain why this is so.

(ii) Explain, with essential details, how the ozone layer is destroyed.

(*c*) (i) Indicate clearly the organic compounds necessary for the production of each of the materials, '**polyester**' and '**nylon**'.
N.B. You may use either words or structures for this purpose.

(ii) You are supplied a sample of polyester and a sample of nylon. Indicate clearly how you would attempt to chemically distinguish between these two samples.

(*d*) Propose **three** chemical tests that could be performed easily for the purpose of clearly demonstrating that P—H bonds are present in H_3PO_2. You should also give the relevant observations along with each of the tests.

Clue: Think of oxidation numbers.

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