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PART A — Structured Essay

Answer all four questions. Each question carries 10 marks.

1. (*a*) (i) Define the term, **'Avogadro constant'**.

(Basic)

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(ii) Write the numerical value of the Avogadro constant.

(iii) If there is a unit pertaining to the above value, indicate it below.
If there is no unit, state that fact below, specifically.

(*b*) Name the following compounds appropriately.

(Inorganic)

compound	name
FeS_2O_3	
$Cr_2(MnO_4)_3$	

(*c*) (i) Indicate **specifically, in the usual manner**, the arrangement of electrons in **the last two sub-energy levels** of the element, **X** of atomic number 40.

(Inorganic)

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(ii) Write the chemical formula of the nitride of **X** derived from its highest oxidation state.

2. (*a*) (i) Write a balanced chemical equation for the complete precipitation reaction occurring between aqueous H_3PO_4 and aqueous $Ba(OH)_2$.

(ii) Calculate the volume of 0·2 mol dm^{-3} aqueous $Ba(OH)_2$ solution required for the complete precipitation of PO_4^{3-} ions obtainable from 25 cm^3 of 0·12 mol dm^{-3} aqueous H_3PO_4 solution.

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(*b*) Indicate briefly how you would use an acidified solution of $K_2Cr_2O_7$ for the purpose of distinguishing between a dilute aqueous solution of HBr and a dilute aqueous solution of HI.

N.B. You are not supplied with organic solvents or other reagents. However, you are provided with the normal facilities available in the laboratory.

(*c*) Name the factors that influence the rate of a chemical reaction.

(*d*) Assume that you are supplied with only H_2S gas and chlorine water as reagents. Propose a suitable method to distinguish between an ammoniacal solution of $CuSO_4$ and an ammoniacal solution of $NiSO_4$, using the above two substances.

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3. (*a*) **Y** is a gaseous hydrocarbon. 15 cm^3 of **Y** was mixed with an excess of oxygen gas. This mixture was ignited by an electrical method, and it was allowed to attain normal temperature and pressure. Then it was observed that the volume of the gaseous mixture decreased by 30 cm^3. When this gaseous mixture was treated with a solution of concentrated KOH, the volume of the gaseous mixture decreased further by 45 cm^3. Calculate the molecular formula of **Y** in the usual manner.

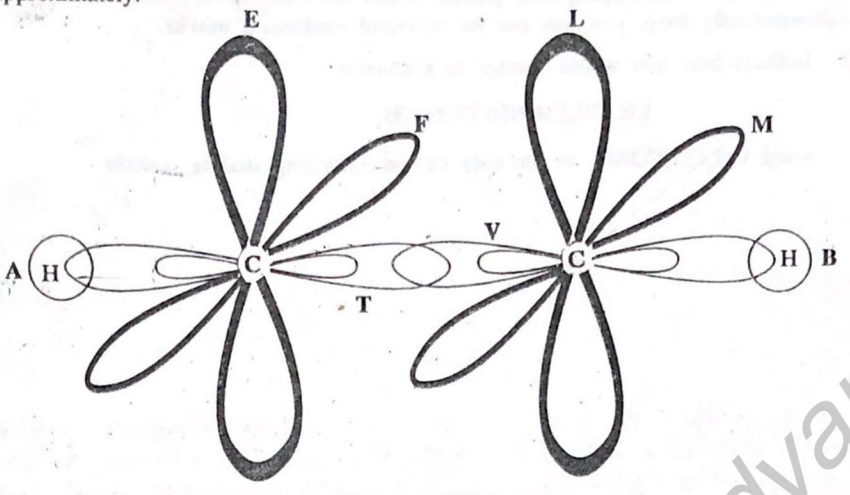
N.B. Assume that all of the above volumes were measured at s.t.p.

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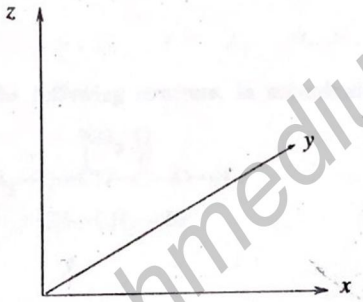
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(*b*) Consider the diagram shown below, pertaining to the formation of chemical bonds in the C_2H_2 molecule. In this diagram the various atomic orbitals relevant to the C_2H_2 molecule are drawn approximately.



atomic orbitals



axes

Examine the diagram given above, and fill the blanks in the following sentences appropriately. **N.B. You should pay attention to the axes. In naming the various atomic orbitals specifically, follow the method usually accepted for that purpose.**

(i) **A** is ..... orbital.

(ii) **T** is .....orbital.

(iii) **L** is ..... orbital.

(iv) **M** is ..... orbital.

(v) Between **T** and **V**, ... takes place.

(vi) Between **F** and **M**, ... takes place.

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(c) **N.B. In the following syntheses, the necessary reagents and reaction conditions should be shown clearly at the appropriate places. When the method of synthesis proposed by you is unnecessarily long, you will not be awarded maximum marks.**

(i) Indicate how you would attempt to synthesize

$$CH_3CH_2CH_2NHCOCH_2CH_3$$

using $CH_3CH_2CONH_2$ as the only carbon-containing starting material.

(ii) Indicate how you would attempt to synthesize

$$(CH_3)_2CHCOOCH(CH_3)_2$$

using $CH_3CH_2CH_2OH$ as the only carbon-containing starting material.

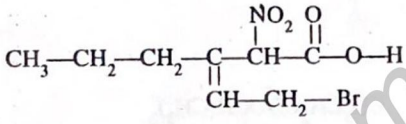
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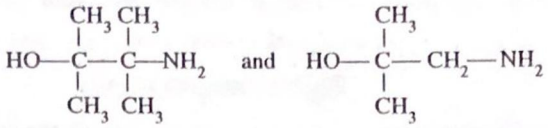
4. (*a*) Name the compound with the following structure, in accordance with IUPAC nomenclature.



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(*b*) Indicate how you would distinguish between the two compounds in each of the following pairs.

(i)  and

(ii) $(CH_3)_2CHCOOCH_2CH_3$ and $CH_3CH_2COOCH(CH_3)_2$

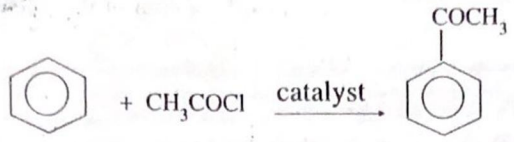
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(c) Consider the following acylation reaction.



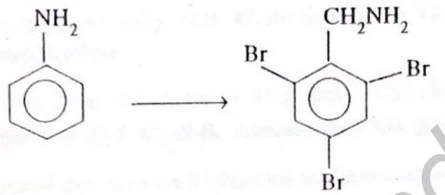
Now, fill the blanks in the following sentences appropriately.

(i) For this reaction, ... is a suitable catalyst.

(ii) In this reaction, ... is the ionic species that attacks the benzene ring.

(iii) This attack is called ..... reaction.

(d) Indicate how the following conversion could be effected. **N.B. The necessary reagents and reaction conditions should be shown clearly at the appropriate places. If the method of conversion proposed by you is unnecessarily long, you will not be awarded maximum marks.**



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முழுப் பதிப்புரிமையுடையது)
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අධ්‍යයන පොදු සහතික පත්‍ර (උසස් පෙළ) විභාගය, 1998 අගෝස්තු (නව නිර්දේශය)
கல்விப் பொதுத் தராதரப்பத்திர(உயர் தர)ப் பரீட்சை, 1998 ஒகஸ்ற் (புதிய பாடத்திட்டம்)
General Certificate of Education (Adv. Level) Examination, August 1998 (New Syllabus)

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இரசாயனவியல் II
Chemistry II

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PART B — Essay

Answer two questions only. Each question carries 15 marks.

5. (*a*) (i) Assuming the equation $PV = \frac{1}{3} mNc^2$, derive the equation $PV = nRT$ pertaining to an ideal gas.

(ii) Explain how the equation $PV = nRT$ has been modified so as to be appropriate for a gas that does not behave ideally. **N.B. Write clearly the Van der Waals equation obtained after effecting this modification.**

(*b*) The molar mass of a certain gas is 16 g mol^{-1}. Calculate the density of this gas under a pressure of $30{\cdot}4 \times 10^5$ Nm^{-2} at 29·5 °C. **N.B. Assume that the gas is behaving ideally under these conditions.**

(*c*) You are informed that chlorine in aqueous medium **cannot be directly** titrated with a solution of $Na_2S_2O_3$. You are provided with chlorine gas, CCl_4 and a standard solution of $Na_2S_2O_3$. You are also supplied with **other materials** and facilities normally available in the laboratory. Explain, with the essential details, how you would attempt to determine the distribution coefficient of chlorine between CCl_4 and water, using the above $Na_2S_2O_3$ solution.

6. (*a*) (i) The two ions X^{5+} and Y^{2-} react together and form the solid, X_2Y_5 which is sparingly soluble in water. At a certain temperature, a saturated aqueous solution of X_2Y_5 exists in equilibrium with solid X_2Y_5. Derive an equation for the equilibrium constant, K_C, for this equilibrium.

(ii) Write an equation for the K_{sp} of X_2Y_5. If there are any assumptions that you make in writing this equation, state those assumptions **clearly in words**.

(iii) Assume that the cation M^{3+} forms the hydroxide, $M(OH)_3$ which is sparingly soluble in water. The pH of a saturated aqueous solution of $M(OH)_3$, in equilibrium with solid $M(OH)_3$, at 25 °C is 9·301. Calculate the K_{sp} of $M(OH)_3$ at 25 °C. $K_w = 1{\cdot}0 \times 10^{-14}$ mol^2 dm^{-6} at 25 °C.

(*b*) (i) Describe clearly how the colour-change pH interval of an acid-base indicator, supplied to you, can be experimentally determined.

(ii) The colour-change pH intervals of some acid-base indicators are given in the following Table.

indicator	pH interval
P	9·0 – 10·0
Q	4·0 – 5·0
R	12·0 – 13·0
S	2·0 – 3·0
T	6·0 – 8·0

Now, consider the following titrations **A**, **B**, **C** and **D**, carried out between 0·1 mol dm^{-3} aqueous acid and 0·1 mol dm^{-3} aqueous base.

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A	The titration between $HClO_4$ and $Ba(OH)_2$.
B	The titration between HI and CH_3NH_2.
C	The titration between CH_3COOH and $[(CH_3)_4N]^+OH^-$.
D	The titration between CH_3CH_2COOH and $CH_3CH_2NH_2$.

Select and mention clearly, **the most suitable indicator**, out of **P**, **Q**, **R**, **S** and **T**, for the purpose of obtaining the correct burette reading in the case of each of the above titrations. **If none of the above indicators is suitable for a particular titration, mention that fact also clearly.**

N.B. If you mention more than one indicator for a particular titration, you will not be awarded marks for that answer.

7. (*a*) (i) Indicate clearly how the natural occurrence of the metals can be related to the various positions of the metals in the electrochemical series.

(ii) Indicate clearly how the general methods of extraction of the metals can be related to the various positions of the metals in the electrochemical series.

(*b*) (i) Explain how an aqueous solution of the compound, $HOOCCH_2CH_2COONa$ exhibits buffer action.

(ii) Explain how proteins exhibit buffer action.

(*c*) (i) Consider the following reaction which is in a state of equilibrium.

$$aA(g) + bB(g) \rightleftharpoons cC(g) + dD(g)$$

Derive the relationship between K_P and K_C for this equilibrium.

(ii) Consider the following equilibrium

$$QR_3(g) + R_2(g) \rightleftharpoons QR_5(g).$$

5 mol of QR_3 and 3 mol of R_2 are kept in a closed vessel. When the temperature was 469 K, the pressure inside the vessel was $10{\cdot}13 \times 10^5$ Nm^{-2}. Under these conditions, 30% of the initial amount of $QR_3(g)$ had taken part in the above reaction. Calculate the K_P for this reaction.

8. (*a*) (i) State Hess's Law.

(ii) Explain how the standard enthalpy change for the reaction,

$$3C(s) + 4H_2(g) \longrightarrow C_3H_8(g)$$

can be experimentally determined.

(*b*) (i) Describe clearly and briefly an experiment that you have done in the laboratory for the purpose of examining the variation of the rate of the reaction between $S_2O_3^{2-}$ and H_3O^+ with the concentration of $S_2O_3^{2-}$.

(ii) Consider the reaction

$$L(g) + M(g) \longrightarrow S(g) + T(g).$$

The rate of decrease of the partial pressure of L(*g*) in this reaction was studied at 30 °C. Some data obtained in this study are given in the Table below.

experiment number	**initial partial pressure of L(*g*), mm Hg**	**initial partial pressure of M(*g*), mm Hg**	**rate of decrease of the partial pressure of L(*g*), mm Hg s^{-1}**
1	400	375	0·762
2	400	152	0·125
3	291	400	0·780
4	147	400	0·395

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Assume that in this reaction the rate of decrease of the partial pressure of $L(g)$ varies as follows:

$$\text{Rate} \propto \{p_{L(g)}\}^x \times \{p_{M(g)}\}^y$$

Using the data supplied to you, calculate the values appropriate for x and y.

(iii) Calculate the rate of decrease of the partial pressure of $L(g)$ when the partial pressure of $L(g)$ and the partial pressure of $M(g)$ are both 300 mm Hg, and the temperature is 30 °C.

PART C — Essay

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

9. (*a*) Consider the simplest hydrides of the elements, nitrogen, oxygen and phosphorus.

(i) Indicate clearly and separately whether each one of the above hydrides

acts as an acid, or
acts as a base, or
acts both as an acid and as a base, or
does not act as either an acid or as a base.

(ii) Indicate clearly and separately whether each one of the above hydrides

acts as an oxidizing agent, or
acts as a reducing agent, or
acts both as an oxidizing agent and as a reducing agent, or
does not act as either an oxidizing agent or as a reducing agent.

(*b*) (i) Explain what is meant by the **'hardness of water'**.

(ii) Explain briefly **four** methods used in removing the hardness of water.

(*c*) You are supplied with an aqueous solution containing SO_3^{2-} ions and SO_4^{2-} ions. Propose a method suitable for the quantitative determination of the concentration of SO_3^{2-} ions and the concentration of SO_4^{2-} ions in the solution.

10. (*a*) Write a brief description of the manufacture of nitric acid by the **'Ostwald Process'**.

(*b*) How and under what conditions does nitric acid react with the following elements?

(i) copper
(ii) carbon
(iii) sulphur

N.B. You should write balanced chemical equations for the above reactions.

(*c*) Draw the structure of the compound, $H_4P_4O_{12}$.

(*d*) Propose a suitable method for obtaining zinc and sulphur from zinc sulphide.
N.B. It is not necessary to write balanced chemical equations.

11. (*a*) Name the compound with the chemical formula, $[Ni(H_2O)_6][CoCl_4]$ in accordance with IUPAC nomenclature.

(*b*) (i) Moderately concentrated hydrochloric acid is gradually added to solid $CuCO_3$. Indicate clearly **three** changes that you would expect to see in this instance. **N.B. Disregard the heat changes.**

(ii) Explain the reactions that occur in the above **three** changes. **N.B. You should write balanced chemical equations for these changes.**

(*c*) Present **five** important facts pertaining to the environmental pollution that occurs in the manufacture of sulphuric acid by the **'Contact Process'**.

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12. (*a*) **"In our march towards progress, we have to burn petroleum fuels. This action damages the environment."**

Give **five** reasons pertaining to the above environmental damage.

(*b*) You are supplied with a mixture consisting of barium carbonate, dolomite, potassium carbonate and silicon dioxide. Explain how you would attempt to determine quantitatively each of the constituents present in this mixture.

(*c*) You are given a sample of cinnamon oil with some kerosene oil dissolved in it. Propose a method to determine **at least approximately** the percentage of kerosene oil present in this sample, **by volume**.

N.B. **(i) You are not provided with facilities for various types of distillation.**

(ii) Clue: Think of the chemical nature of the principal constituents of cinnamon oil. Recollect that eugenol is a phenol and that camphor is a ketone.

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