

CHEMISTRY

Paper II

Time Allowed : Three Hours

Maximum Marks : 200

QUESTION PAPER SPECIFIC INSTRUCTIONS

Please read each of the following instructions carefully before attempting questions.

There are **FIFTEEN** questions divided under **THREE** Sections.

Candidate has to attempt **TEN** questions in all.

The **ONLY** question in Section 'A' is compulsory. In Section 'B', **SIX** out of **NINE** questions are to be attempted. In Section 'C', **THREE** out of **FIVE** questions are to be attempted.

The number of marks carried by a question/part is indicated against it.

Neat sketches are to be drawn to illustrate answers, wherever required. These shall be drawn in the space provided for answering the question itself.

Unless otherwise mentioned, symbols and notations have their usual standard meanings.

Assume suitable data, if necessary, and indicate the same clearly.

Attempts of questions shall be counted in sequential order. Unless struck off, attempt of a question shall be counted even if attempted partly.

Any page or portion of the page left blank in the Question-cum-Answer Booklet must be clearly struck off.

Answers must be written in **ENGLISH** only.

Some useful fundamental constants and conversion factors

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

$$\text{Rydberg constant} = 2.178 \times 10^{-18} \text{ J}$$

$$c = 2.998 \times 10^8 \text{ ms}^{-1}$$

$$k_B = 1.38 \times 10^{-23} \text{ JK}^{-1}$$

$$e = 1.602 \times 10^{-19} \text{ C}$$

$$m_e = 9.109 \times 10^{-31} \text{ kg}$$

$$F = 96485 \text{ C mol}^{-1}$$

$$R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}$$

$$h = 6.626 \times 10^{-34} \text{ Js}$$

$$\pi = 3.142$$

$$1 \text{ amu} = 1.66 \times 10^{-27} \text{ kg}$$

$$1 \text{ cal} = 4.184 \text{ J}$$

$$1 \text{ J} = 1 \text{ kg m}^2 \text{ s}^{-2}$$

$$1 \text{ \AA} = 10^{-8} \text{ cm} = 10^{-10} \text{ m} = 0.1 \text{ nm} = 100 \text{ pm}$$

$$1 \text{ atm} = 760 \text{ torr} = 1.01325 \times 10^5 \text{ Pa}$$

$$1 \text{ bar} = 1 \times 10^5 \text{ Pa} = 0.9869 \text{ atm}$$

$$1 \text{ eV} = 1.602 \times 10^{-19} \text{ J}$$

$$1 \text{ L atm} = 101.34 \text{ J}$$

$$1 \text{ eV} = 23060 \text{ cal}$$

- 1.(n) Citing the case of rotation of HCl molecule, explain how the photon-molecule interaction takes place. You may draw pictures or scheme to establish yourself. 5
- 1.(o) Radiative transitions (both absorption and emission) are displayed by vertical lines in Jablonski diagram. Explain why these lines are kept vertical. 5
- 1.(p) Calculate the relative energies of one einstein of photon of wavelength 600 nm to that of wavelength 300 nm. 5

SECTION 'B'

- 2.(a) Derive the reduced equation of state from van der Waals equation. 5
- 2.(b) Show that the excluded volume is four times the actual volume of the gas molecule. 5
3. Establish the relative order of compactness between simple cubic, body centered cubic and face centered cubic crystals. Draw diagrams, if needed. 10
4. How does chemical potential vary with temperature and pressure? Derive the relevant equations. 10
5. Derive an equation relating the effect of ionic strength on the rate constant of an ionic reaction. Discuss the effect of ionic product on rate constants. 6+4
- 6.(a) In lead acid storage cell write down the electrode reactions and the total cell reaction during discharging. 6
- 6.(b) Specific gravity of the sulfuric acid used in a lead acid storage cell gives an assessment about the performance of the cell — justify or criticise. 4
7. Solution of a two-dimensional box problem gives the following for wave function and energy :
- $$\psi_{n_1, n_2}(x, y) = \frac{2}{L} \sin\left(\frac{n_1 \pi x}{L}\right) \sin\left(\frac{n_2 \pi y}{L}\right) \text{ for } 0 \leq x \leq L \text{ and } 0 \leq y \leq L$$
- $$\psi_{n_1, n_2}(x, y) = 0 \text{ outside the box and } E_{n_1, n_2} = (n_1^2 + n_2^2) \frac{h^2}{8mL^2}.$$
- Show that if the 2D box becomes a square there arises the case of degeneracy. 10
- 8.(a) Homonuclear diatomic molecules like H₂, N₂, O₂ are insensitive to microwave spectroscopy. Hence their bond lengths cannot be determined from microwave spectroscopy. How are their bond lengths determined? — Logically explain your answer. 5

8.(b) We have the following spectral data for N₂O molecule.

$\bar{\nu}(\text{cm}^{-1})$	<i>Infra-red</i>	<i>Raman</i>
589	Strong; PQR Contour	—
1285	Very strong; PR Contour	Very strong; polarized
2224	Very strong; PR Contour	Strong; depolarized

From this data logically comment on the structure of the linear N₂O molecule. 5

9.(a) Using the relative method how can you determine the fluorescence quantum yield of a fluorophore in solution? 5

9.(b) On which factors does fluorescence quantum yield of a fluorophore in a solution depend? 5

10. CO₂ is a linear triatomic molecule. How many lines do you expect to have in its vibrational spectrum?

Compare this with the observed IR spectrum of CO₂. 6+4

SECTION 'C'

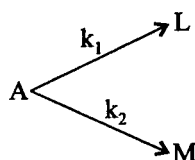
11.(a) From the concept of “particle in a box”, how would you predict the relative positions of the absorption bands of linear conjugated alkenes as the chain length increases. 10

11.(b) A metallic element exists as a cubic lattice. Each edge of the unit cell is 2.88 Å. The density of the metal is 7.20 g cm⁻³. How many unit cells will be there in 100 g of the metal? 10

12.(a) A buffer solution contains 0.2 mole of acetic acid and 0.25 mole of potassium acetate per litre. Calculate the change in pH of the solution if 0.5 mL of 1 M HCl is added to it. The dissociation constant of acetic acid at room temperature is 1.75×10^{-5} . (The volume change on the addition of HCl may be neglected). 10

12.(b) An aqueous solution at 25°C is 0.005 molal in sodium chloride and 0.001 molal in potassium sulphate. Calculate activities of Na⁺ and SO₄²⁻ ions. At 25°C the Debye-Huckel constant *A* is equal to 0.509. 10

13.(a) Derive the rate equation for the overall reaction of type,



How can we evaluate individual rate constants k_1 and k_2 ? 10

- 13.(b) The equilibrium constant of the reaction $X \rightleftharpoons Y$ is doubled when temperature is raised from 25°C to 35°C. Calculate the enthalpy of the reaction. 10
- 14.(a) Without derivation, write down the BET equation giving the meanings of the terms.
Using BET equation how can one measure the total surface area of a solid catalyst in powder state. Given: cross sectional area of each adsorbed gas molecule is A and m g of solid adsorbent is present. 3+7
- 14.(b) Using the law of corresponding state for a van der Waals gas, calculate pressure exerted by one mole of carbon dioxide at 40°C confined to a volume of 0.107 dm³. (For carbon dioxide $P_c = 73.0$ atm; $V_c = 0.0957$ dm³; $T_c = 304$ K) 10
- 15.(a) On irradiation of propionaldehyde at 30°C with light of 302 nm, the quantum yield of formation of CO is found to be 0.54. The intensity of incident light is 15000 erg s⁻¹. Find out the rate of formation of CO. 10
- 15.(b) What are 1st overtone and hot band in IR spectroscopy? How can these two be differentiated experimentally? 6+4
-