Sl. No. 0011812

A-IGQ-O-FGB

CHEMISTRY

Paper II

Time Allowed : Three Hours	*Maximum Marks : 200*

INSTRUCTIONS

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

There are THIRTEEN questions divided under THREE sections.

Candidate has to attempt TEN questions in all.

The ONLY question in Section A is compulsory.

Attempt any SIX questions from Section B.

Attempt any THREE questions from Section C.

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

All parts and sub-parts of a question are to be attempted together in the answer book.

Attempts of questions shall be counted in chronological 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 answer book must be clearly struck off.

Answers must be written in ENGLISH only.

Neat sketches are to be drawn to illustrate answers, wherever required.

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

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

Constants which may be needed

Planck's constant (h)	:	$6{\cdot}63\times10^{-34}$ Js
Speed of light (c)	:	$3{\cdot}00\times10^{8}$ ms^{-1}
Universal gas constant (R)	:	$8{\cdot}31$ JK^{-1} mol^{-1}
π	:	$3{\cdot}14$
Avogadro's number (N_A)	:	$6{\cdot}02\times10^{23}$ mol^{-1}

Section – A

1. Answer ***all*** of the following questions : $5\times16=80$

(a) Derive the relationship $TV^{\gamma-1}$ = constant for a reversible adiabatic expansion.

(b) Show that, for a van der Waals gas, the Boyle temperature $T_b = a/Rb$.

(c) The half-life period of a first order reaction is 3 min. Calculate the time taken to complete 75% of the reaction.

(d) For the cell, $Mg \mid Mg^{2+} \parallel Ag^{+} \mid Ag$, calculate the equilibrium constant at 25°C and also the maximum work that can be obtained by operating the cell. Given that

$E^{\circ}_{Mg^{2+}|Mg} = -2{\cdot}37$ V and $E^{\circ}_{Ag^{+}|Ag} = +0{\cdot}80$ V.

(e) 0·001 kg of a water-insoluble substance of density 0·8 kg dm^{-3} is dispersed in 1 dm^3 of water, forming a colloidal solution having 10^{19} particles of spherical shape per dm^3. Calculate the radius of the particles.

(f) Which of the three vibrations of an AB_2 molecule are infrared or Raman active if it is (i) linear (ii) angular.

(g) The pH of a 0·10 M hydrocyanic acid solution is 5·2. What is the value of K_a for hydrocyanic acid ?

(h) "While the viscosity of a gas increases with increase in temperature, that of a liquid decreases with increase in temperature". How do you account for this ?

(i) State and explain the term 'quantum yield'. How do you explain the fact that the quantum yield of the photochemical reaction

$H_2(g) + Br_2(g) \rightarrow 2HBr(g)$ is low ($\sim$ 0·01), while that of the reaction

$H_2(g) + Cl_2(g) \rightarrow 2HCl(g)$ is very high ($\sim 10^5$) ?

(j) Calculate the thermal de Broglie wavelength of a hydrogen atom at 3000 K confined to move in a box of volume 0·25 m^3.

(k) Discuss the ^{1}H-NMR of pure ethanol and acidified ethanol.

(l) Justify the following statements :

(i) Fluorescence is favoured at very low pressures.

(ii) Phosphorescence, unlike fluorescence, cannot be studied in the liquid phase.

(m) Derive an expression for the variation of fugacity with temperature.

(n) Why is a bathochromic shift observed with increasing conjugation in electronic spectra ?

(o) Calculate the interplanar spacing (d_{nkl}) between the following set of planes : (i) 110 (ii) 111 (iii) 222 for cubic systems.

(p) Calculate the root mean square velocity of helium gas at 25°C.

Section – B

(Answer any ***six*** questions. Each question carries 10 marks)

2. (a) Can the activation energy of a reaction be zero or negative ? Explain. 3

(b) The activation energy of a non-catalyzed reaction at 37°C is 83·68 kJ mol^{-1} and that of the same reaction catalyzed by an enzyme is 25·10 kJ mol^{-1}. Calculate the ratio of rate constants of the enzyme-catalyzed and non-catalyzed reactions. 4

(c) For a reaction of the type

$$P \xrightarrow{k_1} Q \xrightarrow{k_2} R$$

Given that $[P]_0$ = 1 M, $k_1 = 1\times10^{-3}$ s^{-1} and $k_2 = 1\times10^{-4}$ s^{-1}, find the time at which the concentrations of Q and R become 0·5966 and 0·03555 M, respectively. 3

3. (a) For a certain reaction, $\Delta G° = +45$ kJ mol^{-1} and $\Delta H° = +90$ kJ mol^{-1} at 0°C. At what temperature (K) is $\Delta G° = 0$, assuming that $\Delta H°$ and $\Delta S°$ are independent of temperature. 5

(b) Given the data below, calculate the equilibrium constant at 25°C for the reaction :

$$2NO_2(g) = N_2O_4(g)$$

Compound	*ΔG (kJ mol)*
NO_2	51·29
N_2O_4	97·82

5

4. (a) At 460 nm, a blue filter transmits 72·7% of light and a yellow filter 40·7% of light. What is the transmittance at the same wavelength if the two filters are in combination. 5

(b) In a cell of a certain length and a pressure of 100 mm Hg, gaseous acetone transmits 25·1% of incident radiation of wavelength 265 nm. Assuming Beer's law to apply, calculate the pressure at which 98% of the incident radiation will be absorbed. 5

5. (a) One mole of an ideal gas, initially at 25°C, is compressed isothermally to half its initial value. Calculate W, ΔU and ΔS for the process. 4

(b) A Carnot cycle operates at a temperature difference of 200 K, one-third of the heat absorbed from the source is discharged as waste heat to the sink at T_1. The cycle does 400 J of work. Calculate the values of q_1, q_2, T_1 and T_2. 3

(c) Determine the mean ionic mobility of a 0·5 molal solution of ferric chloride. 3

6. Show that eigenfunctions corresponding to different eigenvalues are orthogonal. 10

7. What is sacrificial protection of iron from corrosion ?

Explain the following :

(i) Passivation of kinetic protection.

(ii) Impressed current cathodic protection. 10

8. (a) To 0·5 dm^3 of water, $3{\cdot}0\times10^{-3}$ kg of acetic acid is added. If 23% of the acetic acid is dissociated, what will be the depression in freezing point ? K_f and density of water are 1·86 K kg mol^{-1} and 0·997 kg dm^{-3}, respectively. 6

(b) Which colligative property is preferred for the molar mass determination of macromolecules and why ? 2

(c) Explain why doctors advise persons suffering from high blood pressure to take less quantity of common salt. 2

9. (a) The g value for the proton is 5·5854. Calculate the energy difference between the two levels of protons in a field of 1 Tesla. In what range of electromagnetic radiation does the above difference lie ? 5

(b) Why does the magnetic moment vector execute Larmor precession instead of alignment with the magnetic field ? 5

Section – C

(Answer any ***three*** questions. Each question carries 20 marks)

10. (a) Outline the assumptions made for the derivation of the Langmuir adsorption equation and derive it. 10

(b) Show that at low surface coverage, the Langmuir isotherm corresponds to the Freundlich expression with $n = 1$, and at high surface coverage, it corresponds to the Freundlich expression with n equal to infinity. 5

(c) Calculate the surface area of a catalyst that adsorbs 1000 dm^3 of nitrogen at STP per kg in order to form a monolayer. The effective area occupied by a nitrogen molecule on the surface is 0·162 nm^2. 5

11. (a) Giving reasons, classify the following molecules into different categories exhibiting pure rotational, pure vibrational, rotational Raman and vibrational Raman spectra

H_2, HCl, CH_4, H_2O, CO_2, N_2, NO_2, N_2O. 10

(b) Show that the rotational level whose quantum number is given by the expression

$$J = \sqrt{\frac{kT}{2\tilde{B}hc}} - \frac{1}{2}$$

has the maximum population. 10

12. Derive the limiting equation of Debye and Hückel activity coefficients of strong electrolytes. 20

13. (a) Set up the Schrödinger equation for a particle in a one-dimensional box. Show that the solution of the Schrödinger equation leads to quantization of translational motion and hence derive the expression

$$E = \frac{n^2h^2}{8\text{m}\,L^2}$$ 10

(b) What are the permitted values of the quantum number n? Explain why a zero value of n is not permitted. 5

(c) Show that, for a free particle moving in an unbounded region of space, the translational energy is virtually unquantized. 5
