

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 ( $h$ )	:	$6.63 \times 10^{-34}$ Js
Speed of light ( $c$ )	:	$3.00 \times 10^8$ ms <sup>-1</sup>
Universal gas constant ( $R$ )	:	$8.31$ JK <sup>-1</sup> mol <sup>-1</sup>
$\pi$	:	3.14
Avogadro's number ( $N_A$ )	:	$6.02 \times 10^{23}$ mol <sup>-1</sup>

---

---

### Section – A

1. Answer *all* of the following questions :  $5 \times 16 = 80$

- (a) Derive the relationship  $TV^{\gamma-1} = \text{constant}$  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,  $\text{Mg} \mid \text{Mg}^{2+} \parallel \text{Ag}^+ \mid \text{Ag}$ , calculate the equilibrium constant at 25°C and also the maximum work that can be obtained by operating the cell. Given that  
 $E^\circ_{\text{Mg}^{2+} \mid \text{Mg}} = -2.37$  V and  $E^\circ_{\text{Ag}^+ \mid \text{Ag}} = +0.80$  V.
- (e) 0.001 kg of a water-insoluble substance of density  $0.8$  kg dm<sup>-3</sup> is dispersed in 1 dm<sup>3</sup> of water, forming a colloidal solution having  $10^{19}$  particles of spherical shape per dm<sup>3</sup>. Calculate the radius of the particles.

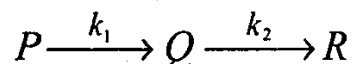
- (f) Which of the three vibrations of an  $AB_2$  molecule are infrared or Raman active if it is (i) linear (ii) angular.
- (g) The pH of a 0.10 M hydrocyanic acid solution is 5.2. What is the value of  $K_a$  for hydrocyanic acid ?
- (h) "While the viscosity of a gas increases with increase in temperature, 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  $0.25 \text{ m}^3$ .
- (k) Discuss the  $^1H$ -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 ( $d_{hkl}$ ) 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<sup>-1</sup> and that of the same reaction catalyzed by an enzyme is 25.10 kJ mol<sup>-1</sup>. Calculate the ratio of rate constants of the enzyme-catalyzed and non-catalyzed reactions. 4
- (c) For a reaction of the type

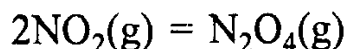


Given that  $[P]_0 = 1 \text{ M}$ ,  $k_1 = 1 \times 10^{-3} \text{ s}^{-1}$  and  $k_2 = 1 \times 10^{-4} \text{ s}^{-1}$ , find the time at which the concentrations of  $Q$  and  $R$  become 0.5966 and 0.03555 M, respectively. 3

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

5

- (b) Given the data below, calculate the equilibrium constant at  $25^\circ\text{C}$  for the reaction :



<i>Compound</i>	$\Delta G$ (kJ mol)	
$\text{NO}_2$	51.29	
$\text{N}_2\text{O}_4$	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  $25^\circ\text{C}$ , is compressed isothermally to half its initial value. Calculate  $W$ ,  $\Delta U$  and  $\Delta S$  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<sup>3</sup> of water,  $3.0 \times 10^{-3}$  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<sup>-1</sup> and 0.997 kg dm<sup>-3</sup>, 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  $1000 \text{ dm}^3$  of nitrogen at STP per kg in order to form a monolayer. The effective area occupied by a nitrogen molecule on the surface is  $0.162 \text{ nm}^2$ . 5

11. (a) Giving reasons, classify the following molecules into different categories exhibiting pure rotational, pure vibrational, rotational Raman and vibrational Raman spectra  
H<sub>2</sub>, HCl, CH<sub>4</sub>, H<sub>2</sub>O, CO<sub>2</sub>, N<sub>2</sub>, NO<sub>2</sub>, N<sub>2</sub>O. 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

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

- (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