HJI–S–CHEM

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

$N_A = 6 \cdot 022 \times 10^{23} \text{ mol}^{-1}$

Rydberg constant $= 2 \cdot 178 \times 10^{-18} \text{ J}$

$c = 2 \cdot 998 \times 10^8 \text{ ms}^{-1}$

$k_B = 1 \cdot 38 \times 10^{-23} \text{ JK}^{-1}$

$e = 1 \cdot 602 \times 10^{-19} \text{ C}$

$m_e = 9 \cdot 109 \times 10^{-31} \text{ kg}$

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

$R = 8 \cdot 314 \text{ JK}^{-1} \text{ mol}^{-1}$

$h = 6 \cdot 626 \times 10^{-34} \text{ Js}$

$\pi = 3 \cdot 142$

$1 \text{ amu} = 1 \cdot 66 \times 10^{-27} \text{ kg}$

$1 \text{ cal} = 4 \cdot 184 \text{ J}$

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

$1 \text{ Å} = 10^{-8} \text{ cm} = 10^{-10} \text{ m} = 0 \cdot 1 \text{ nm} = 100 \text{ pm}$

$1 \text{ atm} = 760 \text{ torr} = 1 \cdot 01325 \times 10^5 \text{ Pa}$

$1 \text{ bar} = 1 \times 10^5 \text{ Pa} = 0 \cdot 9869 \text{ atm}$

$1 \text{ eV} = 1 \cdot 602 \times 10^{-19} \text{ J}$

$1 \text{ L atm} = 101 \cdot 34 \text{ J}$

SECTION A

Q1. **Answer all of the following questions :** 5×16=80

(a) At the critical point on $P - V$ isothermal plot at critical temperature (T_c) of real gas $\left(\dfrac{\partial P}{\partial V}\right)_{n, T_c} = 0$ and $\left(\dfrac{\partial^2 P}{\partial V^2}\right)_{n, T_c} = 0$. What are the causes ? 5

(b) At Boyle temperature $\left(T_B = \dfrac{a}{Rb}\right)$ and inversion temperature $\left(T_i = \dfrac{2a}{Rb}\right)$ of van der Waals gas, it behaves ideally though values are not same. Explain with reasons. 5

(c) Prove that greater the diffraction angle, greater is the accuracy in determining the lattice parameters. 5

(d) Explain how thermodynamics relates non-expansion work to a change in composition of a system. 5

(e) Discuss van't Hoff plots for endothermic and exothermic reactions. 5

(f) Calculate ionic strength I, mean ionic activity coefficient r_+, and mean activity a_+, for a 0·0250 m solution of K_2SO_4 at 298 K. Assume complete ionisation. 5

(g) The rates of a reaction starting with initial concentration 2×10^{-3} mol L^{-1} and 1×10^{-3} mol L^{-1} are equal to $2\cdot40 \times 10^{-4}$ mol L^{-1} s^{-1} and $0\cdot6 \times 10^{-4}$ mol L^{-1} s^{-1}, respectively. Calculate the order of the reaction with respect to the reactant and the rate constant. 5

(h) The activation energy of a reaction is 75·2 kJ mol^{-1} in the absence of a catalyst and 50·14 kJ mol^{-1} in the presence of a catalyst. How many times does the rate of reaction increase in the presence of a catalyst if the reaction proceeds at 25°C ? 5

(i) Are chemical potential and electrochemical potential of Zn^{2+} (aq) same ? If not, write the expression for them. 5

(j) By potentiometer, we measure equilibrium or zero-current potential (E) of the galvanic cell. We know at equilibrium $\Delta G_{P,T} = 0$, but we write $-\Delta G = nFE$, where $E > 0$. How will you explain it ? 5

(k) Describe under what condition/s an operator is Hermitian. Prove that Hermitian operators have real eigenvalues.   5

(l) Consider a system whose state is given by $\psi = \dfrac{\sqrt{3}}{3}\phi_1 + \dfrac{2}{3}\phi_2 + \dfrac{\sqrt{2}}{3}\phi_3$, where ϕ_1, ϕ_2 and ϕ_3 are orthonormal.

   (i) Calculate the probability of finding the system in any of the states ϕ_1, ϕ_2 and ϕ_3.

   (ii) Consider an ensemble of 800 systems on which measurements are made. How many systems will be found in each one of the states ϕ_1, ϕ_2 and ϕ_3 ?   5

(m) Rigid H_2 molecule is rotational spectrum inactive but rotational Raman spectrum active. Explain with reasons.   5

(n) Does 'einstein' depend on wavelength of electromagnetic radiation ? If yes, how ? Give your answer with required expression.   5

(o) For the reaction :

$$UO_2^{2+}\,(aq.) + (COOH)_2\,(aq.) \rightarrow UO_2^{2+}\,(aq.) + CO\,(g) + CO_2\,(g) + H_2O\,(l)$$

   (i) What does the above reaction indicate ?

   (ii) What is the role of UO_2^{2+} here ?

   Give reasons in support of your answer.   5

(p) Photodecomposition of HI (g) follows the following mechanism :

   $HI + h\nu \rightarrow H + I$

   $H + HI \rightarrow H_2 + I$

   $I + I \rightarrow I_2$

   Find its quantum yield, ϕ.   5

SECTION B

Attempt any *six* questions :

10×6=60

Q2. Gases A, B, C and D are van der Waals gases. Its van der Waals constants ('a' and 'b') values (in SI units) are :

	A	**B**	**C**	**D**
'a'	0·6	0·6	0·2	0·005
'$10^3 b$'	0·025	0·15	0·10	0·02

(i)   Which gas has highest critical temperature ?

(ii)   Which gas molecule has highest molecular volume ?

(iii) Which gas has highest $\left(\dfrac{\theta}{\pi}\right)$ value at 273 K and 1·0 atm ? (θ and π are the reduced temperature and pressure respectively)

(iv)   Which gas is most nearly ideal behaviour at 273 K and 1·0 atm ? Explain with reason.

10

Q3. Potassium chloride (rock salt structure) crystal has a density of 1·98 g cm^{-3}. The first order (200) reflections were observed at 6·5° when X-rays of 70·8 pm (Mo source) were used. Calculate the number of KCl molecules in a unit cell.

10

Q4. $BaSO_4$ is not very soluble in water.

(i)   Calculate the solubility product equilibrium constant, K_{sp} for $BaSO_4$ from the following molar free energies of formation, expressed as $\Delta_f G°/RT$ at 298 K.

$$BaSO_4 \,(s) \quad Ba^{2+}\,(aq) \quad SO_4^{2-}\,(aq)$$

$$\Delta_f G°/RT \quad -549·53 \quad -226·21 \quad -300·34$$

(ii)   Experimentally, 0·246 mg of $BaSO_4$ (molar mass of $BaSO_4$ = 233·38 g mol^{-1}) is dissolved in 0·1 L of water at 298 K. What K_{sp} does this fact predict, assuming that all activity coefficients are equal to 1 ?

(iii) Why is there difference in the values of K_{sp} as calculated in (i) and (ii) ?   *10*

Q5. Consider the following opposing reaction :

$$A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} B \quad \text{(Both are first order)}$$
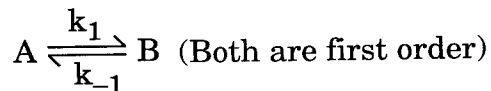
Derive : $(k + k_{-1})\, t = ln\left(\dfrac{x_e}{x_e - x}\right)$

where x = concentration of B at time 't', and

x_e = its equilibrium concentration.   10

Q6. (a) Discuss the variation of molar conductivity of an aqueous solution of surfactant with the increase in concentration of surfactant solution.   5

(b) Why does critical micelle concentration of sodium dodecyl sulphate decrease as the concentration of added sodium chloride salt increases ? Explain this effect.   5

Q7. (a) For a galvanic cell reaction, how will you determine its thermodynamic parameters ($\Delta_r G$, $\Delta_r S$ and $\Delta_r H$) ? Derive the required expressions.   5

(b) The emf (E) of the cell :

$(Pt)\,|\,H_2\,(g)\,|\,HCl\,(aq)\,|\,AgCl\,(s)\,|\,Ag\,(s);$ is 0·265 V at

25°C and 0·260 V at 35°C. Calculate the $\Delta_r H$ of the cell reaction at 25°C.   5

Q8. Evaluate the expectation values of p and p^2 for a particle confined in the region − a/2 < x < +a/2 of a one-dimensional box.   10

Q9. The energy equivalent wave numbers, obtained from vibrational spectra of HD, D_2, HCl and DCl in their ground level are 3627, 2990, 2885 and 1990 cm^{-1} respectively. Calculate the energy change (in J mol^{-1}) of the following reaction in the ground level.   10

$HD + DCl = D_2 + HCl$
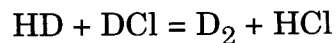
Q10. (a) Fluorescence and phosphorescence are photophysical phenomena, not photochemical ones. Explain with reason.   5

(b) Glowing of fireflies is a result of combination of chemical and physical processes. Explain with reasons.   5

SECTION C

Attempt any _three_ questions :   *20×3=60*

Q11. (a)   Express van der Waals equation in virial form (in terms of molar volume, V_m). From this, derive the expression of Boyle temperature (T_B).   *10*

(b)   Show that the average position of a particle confined to the 3-dimensional box of length (a, b, c) is $(\frac{a}{2}, \frac{b}{2}, \frac{c}{2})$.   *10*

Q12. The dissociation vapour pressure of NH_4Cl (s) at 427°C is 608 kPa but at 459°C it has risen to 1115 kPa. Calculate (i) equilibrium constant, (ii) the standard reaction free energy, (iii) the standard enthalpy, and (iv) the standard entropy of dissociation, all at 427°C. Assume that the vapours behave as a perfect gas and that $\Delta H°$ and $\Delta S°$ are independent of temperature in the range given.   *20*

Q13. (a)   For the reaction : $A + B \rightarrow P$;

derive the expression of rate constant (k) where reaction is first order with respect to each A and B and initial concentrations of A and B are 'a' and 'b' respectively.   *10*

(b)   Calculate the rate constant of above reaction, when 'a' = 0·075 mol L^{-1}; 'b' = 0·050 mol L^{-1} and concentration of B = 0·020 mol L^{-1} after 1 h.   *10*

Q14. (a)   For the following galvanic cell :

Zn (s) | $ZnCl_2$ (aq) | AgCl (s) | Ag (s)

(i)   Write down electrode reactions and cell reaction.

(ii)   Is it a cell with transference ? Give reason in support of your answer.

(iii) Find the E^o of cell and equilibrium constant (K^o) of cell reaction at 25°C.

Given : $E^o_{Zn^{++}/Zn} = -0·76$ V and $E^o_{AgCl/Ag,\ Cl^-} = +0·22$ V at 25°C.   *10*

(b)   The emf of the cell :

Ag | AgI | (0·05 M KI) || 0·05 M $AgNO_3$ | Ag

is 0·788 V. Calculate the concentration solubility product (K_{sp}) of AgI.   *10*

Q15. (a) Define rotational constant of a molecule. How will its value change with the equilibrium bond length and reduced mass ? *5*

(b) Bending vibration of linear carbon dioxide molecule is IR active but Raman inactive though both electric dipole moment and electrical polarisability changes with vibration. Explain with reason. *5*

(c) Dimerisation of anthracene (A) in benzene happens by absorption of electromagnetic radiation. The concentration of its dimer at equilibrium, $[A_2]_{eq}$ is independent of initial monomer concentration, $[A]_o$ at higher concentration region. Explain with reason. *10*