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 in **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.

SECTION—A

1. *(a)* Write the van der Waals equation and explain the physical significance of van der Waals constants *a* and *b*. 5

(b) Why do hydrogen and helium show exceptional behaviour while discussing with van der Waals equation? 5

(c) C_{60} molecules are cubic close-packed to form the solid C_{60} unit cell. Draw the unit cell and find the number of carbon atoms present in the unit cell. 5

(d) A simple cubic crystal diffracts an X-ray beam ($\lambda = 3$ Å) at an angle of 17·5°. Identify the set of planes that cause this diffraction. Given that $a = 5$ Å. 5

(e) Explain the physical significance of chemical potential. How is it related to Gibbs free energy? 5

(f) Write the equation for Debye-Hückel limiting law for mean activity coefficient of an ion and explain the meaning of each term involved. Why is this law called 'limiting law'? 5

(g) The rate constant for the reaction

$$2HI(g) \rightarrow H_2(g) + I_2(g)$$

is $1 \cdot 33 \times 10^{-6}$ dm^3 mol^{-1} s^{-1} at 575 K and $2 \cdot 50 \times 10^{-3}$ dm^3 mol^{-1} s^{-1} at 716 K. Calculate the value of activation energy of the reaction. 5

(h) Among the electrolytes Na_2SO_4, $CaCl_2$, $Al_2(SO_4)_3$ and NH_4Cl, which one is the most effective coagulating agent for Sb_2S_3 sol? 5

(i) Calculate the standard reduction potential at 298 K for the reaction

$$Na^+(aq) + e^- \rightarrow Na(s)$$

with respect to standard hydrogen electrode. For the overall reaction

$$\Delta_r H^\circ = 240 \cdot 1 \text{ kJ mol}^{-1};\ \Delta_r S^\circ = -73 \cdot 1 \text{ J K}^{-1} \text{ mol}^{-1}$$ 5

(j) Calculate the pH of the solution containing a mixture of quinone and hydroquinone (1 : 1) in the cell, SCE | solution | H_2Q, Q, Pt. The measured EMF of the cell is 0·221 V at 298 K; $E^\circ_{SCE} = 0 \cdot 242$ V and $E^\circ_{H_2Q,\,Q} = 0 \cdot 699$ V. 5

(k) What is the degree of degeneracy of the energy level of a particle in a cubic box having energy $\frac{6h^2}{8mL^2}$? Write the wave function(s) of the particle in this energy level. 5

(l) Is the function $\psi(x) = Pe^{ikx} + Qe^{-ikx}$ an eigenfunction of $\frac{d}{dx}$ and $\frac{d^2}{dx^2}$? P, Q and k are real numbers. 5

(m) Define 'zero-point energy'. Write the equation for zero-point energy in joule and in cm^{-1}. 5

(n) Which of the following molecules is microwave active and why? Give reasons :

$$SF_6,\ CO,\ H_2,\ H_2O,\ CO_2$$ 5

(o) Consequence of which law of photochemistry predicts that a quantum yield for a photochemical process is one? Discuss the conditions under which the quantum yield (ϕ) of the reaction is—

(i) less than one;

(ii) extremely large. 5

(p) State the possible decay routes by which a photoexcited molecule can dissipate its excess energy. Explain all these possible processes with the help of a labelled diagram. 5

SECTION—B

2. Write the equation that relates van der Waals constants a and b to critical temperature and critical pressure. Using the values of T_c, P_c and V_c thus obtained in terms of a and b, find the value of critical compressibility factor (Z_c). 10

3. The parameters of a unit cell are given below :

$$\left.\begin{aligned} a &= 0\cdot 487 \text{ nm} \\ b &= 0\cdot 646 \text{ nm} \\ c &= 0\cdot 415 \text{ nm} \end{aligned}\right| \alpha = \beta = \gamma = 90^\circ$$

Identify the Bravais lattice. Calculate the interplanar distance for (2 2 2) set of planes. 10

4. At 1200 K, the equilibrium constant for the reaction $A_2 \rightarrow 2A$ is found to be $3 \cdot 3 \times 10^{-3}$. Calculate ΔG° and ΔS° for this reaction at 1200 K. Given that ΔH° for the reaction is 216·65 kJ mol^{-1}. 10

5. The Arrhenius activation energy and pre-exponential factor for the reaction

$$H(g) + Br_2(g) \rightarrow HBr(g) + Br(g)$$

are 15·5 kJ mol^{-1} and $1 \cdot 09 \times 10^{11}$ $dm^3\ mol^{-1}\ s^{-1}$ respectively. Calculate the standard enthalpy of activation ($\Delta^{\ddagger} H^\circ$) and standard entropy of activation ($\Delta^{\ddagger} S^\circ$) at 1000 K based on a standard state of 1·0 mol dm^{-3}. Assume ideal gas behaviour. 10

6. *(a)* Calculate the potential of the following cell :

$$Pt(H_2, 0 \cdot 1\ atm) | HCl\ (1\ M) | Pt(H_2, 1\ atm)$$ 5

(b) Match the following :

Reversible electrode		*Example*
(i) Metal-metal ion	1.	$Pt \| I_2(s) \| I^-(aq)$
(ii) Redox	2.	$Pt \| H_2(g) \| H^+(aq)$
(iii) Metal-insoluble	3.	$Pt \| MnO_4^-, Mn^{2+}(aq)$
(iv) Gas	4.	$Ag \| AgCl(s) \| Cl^-(aq)$
(v) Non-metal	5.	$Hg_2^{2+} \| Hg$

5

7. *(a)* Normalize the wave function $\phi_m(\phi) = A e^{-im\phi}$; ϕ varies from 0 to 2π. 5

(b) Identify the allowed/forbidden wave functions. Explain why :

(i) $\frac{1}{10x}$ in the interval $0 \le x \le \infty$

(ii) e^{-kx} in the interval $-\infty \le x \le \infty$

(iii) xe^{-kx} in the interval $0 > x < \infty$ 5

8. The rotational absorption of $^{14}N^{16}O$ is observed at 50121·15 Hz and that of $^{15}N^{16}O$ at 48375·05 Hz. Calculate the atomic weight of ^{15}N. [Mass of $^{14}N = 14 \cdot 007$; mass of $^{16}O = 15 \cdot 9994$] 10

9. Justify or criticize the following statements :

(a) Half-life method is one of the best methods for determination of order of reaction.

(b) For the ionic reaction

$$S_2O_8^{2-} + I^- \rightarrow I_2 + 2SO_4^{2-}$$

the reaction rate constant decreases with increase in ionic strength.

(c) Adsorption is accompanied with increase in entropy.

(d) Atomic species exhibit resonance fluorescence if they absorb light radiation.

(e) Phosphorescence is a delayed transition while fluorescence is spontaneous. 2×5=10

10. (a) Explain the process of photosensitization with at least two examples. How does it differ from catalysis? 5

(b) The photodecomposition of hydrogen iodide vapour was carried out with a light source having wavelength of 2100 Å. Absorption of each calorie of light gave $1 \cdot 44 \times 10^{-5}$ g of hydrogen. What will be its quantum yield? 5

SECTION—C

11. (a) An electron confined in a one-dimensional box undergoes the longest wavelength transition at 400 nm. What is the length of the box in nm? 10

(b) Pure silicon crystallizes in face-centred cubic diamond structure with four adjacent Si atoms at the corners of a regular tetrahedron. Calculate the unit cell length of silicon in Å. The density of pure silicon is 2·33 g/cm^3 and the molar mass of silicon is 28·09 g/mol. 10

12. (a) Derive Gibbs-Duhem equation in the form $S\,dT - V\,dP + \Sigma\, n_i\, d\mu_i = 0$. 15

(b) Calculate the ionic strength of 1 molal solution of $La_2(SO_4)_3$. 5

13. *(a)* For the consecutive first-order reaction

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C$$

$[A] = [A]_0$, $[B] = 0$ and $[C] = 0$ at time $t = 0$. Derive the expressions of $[A]$, $[B]$ and $[C]$ as a function of time. Provide a general graphical representation of variation in concentration of $[A]$, $[B]$ and $[C]$ with respect to time. 15

(b) For the above reaction, if the rate constant k_1 is $5 \cdot 0 \times 10^6$ s^{-1} and k_2 is $3 \cdot 0 \times 10^6$ s^{-1}, determine the time at which $[B]$ is at a maximum. 5

14. *(a)* The standard electrode potentials for the two half-reactions are given below :

$$Fe^{3+} + e^- \rightleftharpoons Fe^{2+}; \quad E^\circ = 0 \cdot 771 \text{ V}$$

$$Sn^{4+} + 2e^- \rightleftharpoons Sn^{2+}; \quad E^\circ = 0 \cdot 154 \text{ V}$$

Explain if the following reactions are possible or not :

(i) Reaction between Fe^{2+} and Sn^{4+}

(ii) Reaction between Fe^{2+} and Sn^{2+}

(iii) Reaction between Fe^{3+} and Sn^{2+}

(iv) Reaction between Sn^{4+} and Fe^{2+} 10

(b) Among the above, identify the spontaneous reaction, if any, and write down the overall cell reaction. Calculate its E°_{cell} and the equilibrium constant of the overall cell reaction at 298 K. 10

15. *(a)* Assuming that the force constant (k) of HCl and DCl are same being equal to 483 N m^{-1}, calculate the fundamental vibrational frequency ($\bar{\nu}$) of DCl, if that of HCl is 2890 cm^{-1}. (H = 1, D = 2, Cl = 35 · 5) 10

(b) State and explain the 'rule of mutual exclusion'. Why in H_2O molecule, all the vibrations are IR and Raman active while in CO_2, only some vibrations are IR and some Raman active? 10

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