Total number of printed pages–8

2 SEM PG CHM (CBCS) PC–II 203

2026

(June)

CHEMISTRY

Paper : 203

(Physical Chemistry–II)

Full Marks : 60

Time : Three hours

The figures in the margin indicate full marks for the questions.

Use separate booklets for

UNIT–I, UNIT–II** and **UNIT–III

UNIT–I

(Quantum Chemistry–II)

(Marks: 30)

1. What are radial nodes? How many radial nodes does the following unnormalized function of a hydrogen atom possess?

$$\varphi = (2-r)exp\left(-\frac{r}{2}\right)$$ 1+1=2

2. Find the degeneracy of the state of Li^{2+} ion having the electronic energy same as that of the ground state hydrogen atom. 2

3. Where is the probability density maximum for the hydrogen atom ground state ? 1

4. Answer ***any five*** of the following questions : 3×5=15

(a) Considerd any trial wave function φ, whose energy is given by $E_\varphi = \dfrac{\int \varphi^* \hat{H} \varphi d\tau}{\int \varphi^* \varphi d\tau}$.

Show that $E_\varphi \geq E_0$ (ground state energy).

(b) Find the values of mean kinetic energy and mean potential energy for a ground-state hydrogen atom.

(c) What are symmetric and antisymmetric functions ? Explain with an example.

(d) Find the point (r) at which the radial function (in a.u.)

$R_{ni} = \left(6 - \left(\dfrac{12r}{3}\right) + \dfrac{4r^2}{9}\right) e^{-r/3a_0}$ becomes zero.

(e) Determine the ground state term symbol for O_2 molecule.

(f) Show that the degeneracy of a state of hydrogen-like atoms is equal to n^2 (n is the principal quantum number).

(g) Briefly explain the time-independent perturbation method for non-degenerate systems.

(h) Write the electronic Hamiltonian and Slater determinant wave function for the ground state Helium atom.

5. State the key assumptions of the Born-Oppenheimer approximation. Using these assumptions, derive the electronic Schrödinger equation for a molecular system. 1+2=3

6. In a diatomic moleculed AB, ψ_a and ψ_β are normalized atomic orbitals. A normalized molecular orbital is given by

$$\psi = 0.50(\psi_a + \psi_\beta).$$

Determine the value of the overlap integral (S) between ψ_a and ψ_β. 2

7. Describe the Linear Combination of Atomic Orbitals (LCAO-MO) method. Apply it to the hydrogen molecule ion (H_2^+) and obtain expressions for bonding and antibonding molecular orbitals. 3

8. Derive the secular determinant for the π-electrons of ethylene using Hückel molecular orbital theory, and calculate its π-electron energies. 2

Or

Using the assumptions of Hückel molecular orbital theory, set up and solve the secular determinant for π-orbitals of the butadiene molecule in the Hückel approximation.

UNIT–II

(Surface Chemistry)

(Marks : 15)

9. Answer ***any three*** of the following : 2×3=6

   (a) Discuss the feasibility of an adsorption process with temperature.

   (b) What is meant by electrical double layer? Give a schematic explanation. ½+1½=2

   (c) Discuss how the extent of adsorption varies with pressure with help of Langmuir adsorption isotherm.

   (d) Physisorption allows multilayer formation whereas chemisorption of gasses are limited to monolayer. Explain.

   (e) What do you mean by critical micelle concentration (CMC)? Discuss *any three* Physical properties of a solution which indicate formation on Micelle. ½+1½=2

10. Answer ***any three*** of the following : 3×3=9

   (a) At $0°C$ and 1 *atm* pressure, the volume of nitrogen gas required to cover a sample of silica gel, assuming Langmuir monolayer adsorption, is found to be 130 cm^3g^{-1} of the gel. Calculate the surface area per gram of silica gel. Given that the area occupied by a nitrogen molecule is 0.162 nm^2.

(b) What is 'Inhibitor' in adsorption phenomena? Derive the rate law of Unimolecular surface reaction in the presence of Inhibitor and give an example of reaction following this mechanism. ½+2+½=3

(c) Discuss the isotherm type I, II and III diagrammatically and highlight the differences between them. 1+1+1=3

(d) What is meant by capillary condensation? Why hysteresis loop are obtained for capillary condensation? Discuss the types of hysteresis loop obtained for different capillary systems. ½+½+2=3

(e) How the charge of colloidal particles is determined using electrophoresis? Explain briefly.

UNIT–III

(Marks : 15)

11. Answer ***any three*** of the following questions : 3×3=9

(a) Derive the Sackur-Tetrode equation for an ideal monoatomic gas.

(b) Derive the expression for the chemical potential $\mu(T,P)$ of an ideal monoatomic gas and show the expression for $\mu_0(T)$. 2½+½=3

(c) Derive the Boltzmann distribution for a canonical ensemble.

(d) A system has two energy levels : a ground state with energy ε_0 and an excited state with energy ε_i. At temperature $T = 300K$, calculate the ratio of populations $\frac{n_i}{n_0}$ for the following energy differences

(i) $\varepsilon_i - \varepsilon_0 = 10^{-21} J$

(ii) $\varepsilon_i - \varepsilon_0 = 10^{-20} J$

(iii) $\varepsilon_i - \varepsilon_0 = 10^{-19} J$

Assume that the degeneracy ratio $\frac{g_i}{g_0} = 1$.

(e) Given, $S = -k_B \sum_j P_j \ln P_j$,

Prove that $E = k_B T^2 \left(\frac{\partial \ln Q}{\partial T} \right)_{V,N}$

12. Answer ***any three*** of the following questions : 2×3=6

(a) What is the ergodic hypothesis ? The hypothesis is valid for which thermodynamic system and which ensemble ? 1+1=2

(b) Derive the relationship between canonical partition function (Q) and molecular partition function (q) for independent and distinguishable particles.

(c) Experimentally it is found that for Br_2 molecule, vibrational characteristic temperature, $\theta_v = 470K$. What fraction of Br_2 molecules will be in the excited vibrational energy states at $940K$?

(d) Derive the expression for the vibrational partition function q_v of an ideal diatomic gas.
