(b) Derive the Planck's law of black body radiation. Show that Rayleigh-Jeans law and Wein's law are special cases of the Planck's equation. (10)

UNIT V

13. (a) Write the Schordinger equation for hydrogen atom in polar coordinates. (2)

(b) State the approximations involved in Huckel Molecular Orbital theory. (2)

14. (a) Show that $[\hat{L}^2, \hat{L}_x] = 0$ (6)

Or

(b) Write briefly about the radial distribution functions of hydrogen atom. (6)

15. (a) State and explain the variation theorem. Apply variation method is calculating the ground state energy of helium atom. (10)

Or

(b) Describe the SCF method of solving the Schordinger equation for the N-electron atom. (10)

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5553/MC3   **MAY 2006**

Paper III — PHYSICAL CHEMISTRY — I

Time : Three hours   Maximum : 100 marks

Answer ALL questions.

UNIT I

1. (a) Find the entropy of mixing of 80% N_2 and 20% O_2 in air. (2)

(b) Show that an ideal gas has zero internal pressure. (2)

2. (a) How may one measure activities form partial pressure in a binary mixture? (6)

Or

(b) Derive the Gibbs-Duhem equation and indicate its applications. (6)

3. (a) Explain the concept of fugacity and activity. Describe the method of calculation of fugacity of a gas. (10)

Or

(b) Give an account of partial molar properties. Describe how partial molar volume is determined. (10)

UNIT II

4. (a) What are the limitations of quinhydrone electrode? (2)

(b) Calculate the ionic mobility value if the limiting molar conductivity of the ion is 0.5×10^{-2} $sm^2\,mol^{-1}$. (2)

5. (a) Explain any two applications of conductivity measurements. (6)

Or

(b) Examine the reasons for the deviation from Debye-Huckel Onsager equation. (6)

6. (a) (i) What are fuel cells? Discuss the working of $H_2 - O_2$ fuel cell. (6)

(ii) Calculate the equilibrium constant of the disproportionation reaction $2cu^+ \rightarrow cu^{2+} + cu$. The standard electrode potentials are :

$E^0 cu^+, cu = 0.52V$ and $E^0 cu^{2+}, cu = 0.34V$ (4)

Or

(b) Explain the term corrosion. Describe (i) the rate of corrosion and (ii) the inhibition of corrosion. (10)

UNIT III

7. (a) What is the necessity of proposing the 'Steric factor' in collision theory and 'transmission coefficient' in ARRT? (2)

(b) Bringout the difference between the continuous flow and stopped flow techniques. (2)

8. (a) Calculate the entropy of activation for bimolecular reaction in solution at 25° C, if the rate constant at this temperature is 1.2×10^{-3} l mol^{-1} sec^{-1} and the energy of activation is 30.5 k.cal mol^{-1}. (6)

Or

(b) Discuss how Hindemann theory explains the unimolecular gas phase reactions at high and low pressure regions. (6)

9. (a) Based on statistical mechanics, discuss the theory of absolute reaction rates and derive an expression for the rate constant. (10)

Or

(b) Discuss the mechanism of decomposition of acetaldehyde and derive the rate expression. (10)

UNIT IV

10. (a) What do you understand by Heisenberg's uncertainty principle? (2)

(b) Verify that the wave function $\psi(x) = e^{2x}$ is an eigen function of the operator $\dfrac{d}{dx}$. What is the corresponding eigen value? (2)

11. (a) Write a note on tunneling effect. (6)

Or

(b) State the postulates of quantum mechanics. (6)

12. (a) Set up and solve the Schordinger equation for the rigid rotator and obtain an expression for the energy and wave function. (10)

Or