

M.Sc.(Chemistry) (C.B.C.S. Pattern) Sem-I  
**PSCCHT03 - CHE-103 : Physical Chemistry Paper-III**

P. Pages : 2

Time : Three Hours



GUG/W/19/11185

Max. Marks : 80

- Notes : 1. All questions are compulsory and carry equal marks.  
2. Use of log table and calculators is permitted.

1. a) What are the cartesian components of the angular momentum operators? **8**  
Show that  $[L_x L_y] = i \hbar L_z$

b) Set up and solve the Schrodinger wave equation for the hydrogen atom. **8**

**OR**

c) Show that  $\sin x$  and  $\cos nx$  are not the eigen functions of the operator  $\frac{d}{dx}$  where as  $e^{iax}$  is. Where  $n$  and  $a$  are number only. Determine eigenvalue where appropriate. **4**

d) Consider a particle of mass  $m$  in a cubic box with length  $a$ . What is the degeneracy of the eigen state with energy  $\frac{11h^2}{8m^2}$  and  $\frac{14h^2}{8ma^2}$ ? **4**

e) What are the conditions for acceptability of wave functions? **4**

f) Write equation of quantised rotational energy of rigid diatomic rotator. Draw and explain its rotational energy. **4**

2. a) What is the Pfaff differential expression? Derive condition of exactness of Pfaff differential equation writing  $V$  as a function of  $T$  and  $P$ . Show that for an ideal gas  $dV$  is an exact differential. **8**

b) Explain the third law of thermodynamics. For a substance the heat capacity  $C_p$  in  $\text{JK}^{-1}\text{mol}^{-1}$  is given by the following equation. **8**

$$C_p(s) = 16.73 \times 10^{-5} T^3 (0\text{K} < T < 50\text{K})$$

$$C_p(s) = 20.92 (50 < T < 150\text{K})$$

$$C_p(l) = 25.10 (150 < T < 400\text{K})$$

The melting point of the substance is  $150\text{K}$  and  $\Delta H_f = 1252.2 \text{ J mol}^{-1}$ . Calculate the absolute entropy of a substance in the liquid state at  $300\text{K}$ .

**OR**

c) Introduce the concept of fugacity in the case of real gas and describe its experimental determination. **4**

d) Using Maxwell relations show that  $C_p - C_U = R$ . **4**

e) Justify the chemical potential of a component in a system is the measure of the escaping tendency of that component. **4**

f) Derive Gibb's Duhem equation for binary system taking partial molar volume as an example. **4**

3. a) How are three component system studied with the help of the phase rule? Discuss briefly the system  $\text{CH}_3\text{COOH} - \text{CHCl}_3 - \text{H}_2\text{O}$ . 8
- b) Draw and discuss the phase diagram for ferric chloride – water system. What changes are observed if a solution of Ferric chloride is subjected to isothermal evaporation at  $50^\circ\text{C}$ ? 8

**OR**

- c) Draw and discuss the phase diagram of carbon system. 4
- d) Discuss lambda line observed in the liquid Helium system. 4
- e) Discuss the phase diagram of systems exhibiting formation of three pairs of partially miscible liquids. 4
- f) State phase rule and explain the significance of the terms involved. 4
4. a) Describe the Lindemann Hinshelwood theory of unimolecular reaction. 8
- b) Discuss the kinetics of the Anthracene reactions. 8

**OR**

- c) Discuss the effect of pH and temperature on enzyme catalysis. 4
- d) According to activated complex theory the rate constant of a reaction is given by  $k = K^* \cdot RT / Nh$   
formulate the rate constant in terms of  $DG^*$ ,  $DS^*$ ,  $DH^*$  4
- e) Discuss the mechanism of photosensitization using suitable examples? 4
- f) Derive Michaelis Menten equation. 4
5. a) Write quantum mechanical operator for. 2
- i) Total energy (H)
- ii) X – component of momentum ( $P_x$ )
- b) Explain the term. 2
- i) Hamiltonian operator.
- ii) Hermitian operator.
- c) Write Gibbs – Duhem – Margules equation. 2
- d) What are the conditions for exactness? 2
- e) Calculate the number of degree of freedom. 2
- i)  $\text{N}_{2(g)} + \text{O}_{2(g)} \rightleftharpoons 2\text{NO}_{(g)}$
- ii)  $\text{CaCO}_{3(s)} \rightleftharpoons \text{CaO}_{(s)} + \text{CO}_{2(g)}$
- f) State Clausius Clapeyron equation for phase equilibrium. 2
- g) Explain the term quantum yield. 2
- h) What are two types of catalysis? Explain with examples. 2

\*\*\*\*\*