



10271

**Reg. No. :** .....

**Name :** .....

**First Semester M.Sc. Degree Examination, February 2016**

**Branch : CHEMISTRY**

**CH/CL/CA/CM 213 : Physical Chemistry – I**  
**(2013 Admission Onwards)**

Time : 3 Hours

**Max. Marks : 75**

## SECTION – A

Answer **any two** among **a), b) and c)** of **each** question. **Each** sub-question carries **2 marks**. **(10×2=20 Marks)**

1. a) 18 wave function for H atom is given as  $\frac{1}{\sqrt{\pi}} \left( \frac{1}{a_0} \right)^{3/2} e^{-(r/a_0)}$  ( $a_0$  is Bohr radius). Plot the function against r. Where do you find maximum electron density ? Comment on the observation.

b) Write recursion formula. Explain its significance.

c) Write Slater determinantal wave function for lithium atom.
2. a) Which of the following point groups possess inversion centre ? Why ?

|               |              |
|---------------|--------------|
| i) $D_{3d}$   | ii) $D_{3h}$ |
| iii) $D_{4h}$ | iv) $C_{4v}$ |

b) List the symmetry operations possible on a  $C_{4v}$  molecule. Classify them into different classes of operations.

c) Show that the symmetry operation E,  $C_{2z}$ ,  $\sigma_{xy}$  and i form a mathematical group under multiplication.
3. a) Show that  $\left( \frac{\partial u}{\partial v} \right)_T = \frac{a}{v^2}$  for a Van der Waals gas. a is the Van der Waals constant.

b) What do you mean by regular solutions ? Explain.

c) Define residual entropy. Write two examples showing residual entropy.

**P.T.O.**



4. a) Unimolecular gas phase reactions follow first order kinetics at high pressures and second order kinetics at low pressures. Account for the observation.  
 b) Account for the first and second explosion limits of  $\text{H}_2 - \text{O}_2$  reaction.  
 c)  $\text{H}_2 - \text{I}_2$  reaction follows molecular mechanism but  $\text{H}_2 - \text{Br}_2$  and  $\text{H}_2 - \text{Cl}_2$  reactions follow radical mechanism. Why?
5. a) Calculate most probable velocity of  $\text{O}_2$  at  $0^\circ\text{C}$ .  
 b) Viscosity of gases increases with temperature, but viscosity of liquids decreases with temperature. Why?  
 c) Explain Oscillator theory of liquid state.

### SECTION – B

Answer either **a)** or **b)** of **each** question. **Each** question carries **5** marks. **(5×5=25 Marks)**

6. a) Apply Schrödinger wave equation for particle in a ring problem. Find eigen functions and eigen values.  
 b) Briefly explain 'Self Consistent Field' method of solving many electron atoms.
7. a) Cis butadiene belongs to  $\text{C}_{2v}$  point group. Taking the positional co-ordinates of all the atoms in the molecule generate a reducible representation. (Write only the characters of the matrices.)  
 b) State Great Orthogonality theorem. What are the consequences of the theorem? Discuss.
8. a) Show that solvent obeys Raoult's law in the limit of solute obeying Henry's law.  
 b) How would you determine partial molal enthalpy? Discuss.
9. a) When a sample of pure water was heated by a pulse of microwave radiation the equilibrium in the water dissociation reaction is shifted. Relaxation time for the return to the new equilibrium was 36 microseconds at  $25^\circ\text{C}$ . Calculate  $k_1$  and  $k_{-1}$  in the reaction  $\text{H}^+ + \text{OH}^- \xrightleftharpoons[k_{-1}]{k_1} \text{H}_2\text{O}$ . Ion product of water at  $25^\circ\text{C}$  is  $10^{-14}$ .  
 b) The pre exponential factor for a first order reaction is  $5 \times 10^{13} \text{ s}^{-1}$ . Calculate entropy of activation at 300K.
10. a) Briefly discuss one of the theories of liquid crystals.  
 b) Derive an equation for the average value of the component of velocity in one direction.



## SECTION – C

Answer **any three** questions. **Each** question carries **10** marks.

**(3×10=30 Marks)**

11. Apply Schrödinger wave equation for H-atom. Transform into spherical polar coordinates. Separate the variables. Solve  $\theta$  (theta) equation.
12. Find hybridized orbitals of C in  $\text{CH}_4$  use  $T_d$  character table.

| $T_d$ | E | $8C_3$ | $3C_2$ | $6S_4$ | $6\sigma_d$ |                   |                   |
|-------|---|--------|--------|--------|-------------|-------------------|-------------------|
| $A_1$ | 1 | 1      | 1      | 1      | 1           |                   | $x^2 + y^2 + z^2$ |
| $A_2$ | 1 | 1      | 1      | -1     | -1          |                   |                   |
| E     | 2 | -1     | 2      | 0      | 0           |                   | $x^2 - y^2$       |
| $T_1$ | 3 | 0      | -1     | 1      | -1          | $(R_x, R_y, R_z)$ |                   |
| $T_2$ | 3 | 0      | -1     | -1     | 1           | $(x, y, z)$       | $(xy, xz, yz)$    |

13. a) What is the need for second law of thermodynamics ? Discuss.
- b) Calculate the activity coefficient of acetone in acetone-ether mixture from the following data. (Assume the vapor to be ideal.)

| Mole Fraction<br>of Acetone | Partial Pressure<br>of Acetone |
|-----------------------------|--------------------------------|
| 0.2                         | 90                             |
| 0.4                         | 148                            |
| 0.6                         | 190                            |
| 0.8                         | 235                            |
| 1.0                         | 283                            |

14. Briefly discuss absolute rate theory of reaction rates.
15. Rationalise (a) thermal conductivity, (b) diffusion using kinetic theory of gases.