

**THIRD SEMESTER M.Sc. DEGREE EXAMINATION, DECEMBER 2014**

(CUCSS)

Chemistry

CH 3C 07—PHYSICAL CHEMISTRY-II

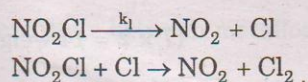
(2010 Admissions)

Time : Three Hours

Maximum : 36 Weightage

**Section A***Answer all questions.**Each question carries a weightage of 1.*

- 6 particles share a total energy of  $6\epsilon$ . The available quantum states are  $0, 1\epsilon, 2\epsilon, 3\epsilon, 4\epsilon, 5\epsilon$  and  $6\epsilon$ . What are the possible macrostates according to Fermi Dirac statistics assuming the levels to be triply degenerate.
- The ortho para ratio of hydrogen ( $H_2$ ) is  $3 : 1$ . Rationalise using statistical thermodynamics.
- Define symmetry number. Find the symmetry number of benzene.
- Rationalise Dulong-Petit's law using statistical thermodynamics.
- Define dilution factor. How is it evaluated ?
- What do you mean by communal entropy in liquids ?
- State and explain Glansdorf Pregelone equation.
- Explain the term 'local equilibrium'. How does it differ from true equilibrium ?
- Decomposition of  $NO_2Cl$  takes place according to the following mechanism. Assuming steady state for Cl atom concentration, derive the rate law :



- What is pressure jump method in relaxation spectroscopy ?
- Distinguish between collision cross-section and reaction cross-section.
- How would you distinguish XPS from AES peaks ?
- Distinguish between Arrhenius complex and Vant Hoff complex.
- Unimolecular gas phase reactions catalysed by solids follow first order kinetics at low pressures and zero order kinetics at high pressures. Justify the observation.

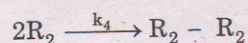
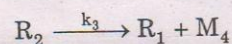
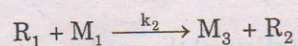
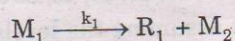
(14 × 1 = 14 weightage)

**Turn over**

### Section B

Answer any **seven** questions.  
Each question carries weightage of 2.

15. Calculate the residual entropy of  $\text{H}_2\text{O}$  assuming a tetrahedral structure with 2 sigma bonds  
2 Hydrogen bonds.
16. Show that rotations and vibrations of molecules do not contribute towards pressure.
17. Derive an equation for the vibrational contribution towards heat capacity of a gas.
18. Briefly explain Bose-Einstein condensation.
19. Discuss briefly "free volume theory" of liquids.
20. Define phenomenological coefficient. Show that direct coefficients always dominate indirect coefficients.
21. Mechanism of an organic decomposition reaction is given. Derive rate law :



$\text{R}_1$  and  $\text{R}_2$  are radicals  $\text{M}_3$  and  $\text{M}_4$  are stable products.

22. With the help of potential energy surfaces explain the term reaction coordinate.
23. Write BET adsorption isotherm in the linear form. Show that it approximates to Langmuir adsorption isotherm under limiting conditions.
24. Discuss the mechanism of surface catalysed reaction  $2\text{CO} + \text{O}_2 \rightarrow \text{CO}_2$ .

(7 × 2 = 14 weightage)

### Section C

Answer any **two** questions.  
Each question carries a weightage of 4.

25. Apply Fermi Dirac statistics for electrons in metals. Discuss.
26. Discuss briefly crossed molecular beam experiment.
27. Write a brief account of the experimental methods for studying solid surfaces.
28. With the help of suitable examples discuss the mechanism of oscillating chemical reactions.

(2 × 4 = 8 weightage)