



Reg. No. :

Name :

First Semester M.Sc. Degree Examination, January 2017

Branch : CHEMISTRY

CH/CL/CA/CM 213 : Physical Chemistry – I

(2013 Admission Onwards)

Time : 3 Hours

Max. Marks : 75

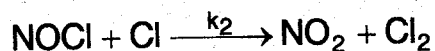
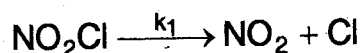
SECTION – A

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

1. a) Explain Compton effect. What is its significance towards origin of quantum mechanics.
b) Write \hat{L}_z in (I) Cartesian coordinates (II) Spherical polar coordinates.
c) Write time dependent Schrödinger wave equations. What are the conditions under which time independent Schrödinger wave equation is made use of ?
2. a) List the symmetry operations possible on (I) Td (II) D_{2h}.
b) With the help of examples distinguish between inverse operation and conjugate operation.
c) Show that E, C_{2z}, $\sigma_v(xz)$ and $\sigma_v(yz)$ form a mathematical group under multiplication.
3. a) Show that $\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$.
b) Define chemical potential in terms of (I) internal energy (II) Helmholtz free energy.
c) Free energy functions are better criteria than entropy in predicting spontaneity of reactions. Justify the statement.



4. a) Find the steady state concentration of Cl from the following mechanism.



- b) Distinguish between collision cross section and reaction cross section.
c) Define entropy of activation. Explain its physical significance.
5. a) Calculate the most probable velocity of CO_2 at 0°C .
b) How does mean free path depend on
(I) Collision diameter
(II) Temperature?
Justify your answer.
c) What do you mean by internal pressure of a liquid? Explain.

SECTION - B

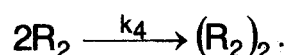
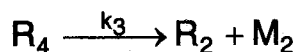
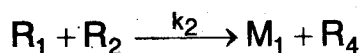
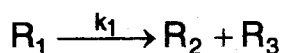
Answer either 'a' or 'b' of **each** question. **Each** question carries 5 marks :

(5×5=25 Marks)

6. a) Discuss briefly postulates of quantum mechanics.
b) Briefly discuss 'Self Consistent Field' method of solving many electron atoms.
7. a) Ethylene belongs to D_{2h} point group. The symmetry operations are E , $C_{2(z)}$, $C_{2(y)}$, $C_{2(x)}$, σ_{xy} , σ_{xz} , σ_{yz} and i . Taking the positional coordinates of all the atoms of ethylene generate a reducible representation. (Write only the character of the matrices).
b) Use great Orthogonality theorem to derive C_{2h} character table.
8. a) Define partial molal quantity. Show that partial molal quantities are intensive variables.
b) Define excess thermodynamic property. Explain its significance in the properties of binary solutions.



9. a) The general mechanism for organic decomposition reaction is given below



M_1 and M_2 are stable products. Derive the rate law by finding $\frac{dM_2}{dt}$.

- b) Derive an equation to show primary salt effect.
10. a) Derive an equation for the distribution of molecular velocities for a 2-dimensional gas.
- b) How would you determine vapor pressure of volatile solid ? Discuss.

SECTION - C

Answer **any three** questions. **Each** question carries **10** marks. **(3×10=30 Marks)**

11. Apply Schrodinger wave equation for one dimensional simple harmonic oscillator. Find eigen functions and eigen values.
12. Find hybridized orbitals of Xe in XeF_4 . Use D_{4h} character table.
13. a) What is the need for third law of thermodynamics ? Discuss.
- b) Derive Duhem Margulis equation. Discuss its applications.
14. Write mechanism for photochemical reaction between H_2 and Cl_2 . Derive the rate law.