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Reg. No. : .....

Name : .....

Second Semester M.Sc. Degree Examination, August 2017

Branch : CHEMISTRY

CH/CL/CA/CM 223 : Physical Chemistry - II  
(2013 Admission Onwards)

Time : 3 Hours

Max Marks 75

SECTION - A

(10×2=20 Marks)

Answer any two among a, b and c of each question. Each sub-question carries 2 marks.

- I.
  - a) Using M.O. theory account for the paramagnetism of  $O_2$ .
  - b) Write spectroscopic term symbols for the ground state of
    - i)  $N_2$
    - ii)  $C_2$ .
  - c) Explain the term 'ion-induced dipole' forces.
- II.
  - a) Explain 'centrifugal distortion'. How does it modify separation between lines in the microwave spectrum?
  - b) The anharmonicity constant for HCl is 0.017. How many vibrational levels are possible in the ground electronic state of HCl?
  - c) State and explain Birge-Sponer approximation.
- III.
  - a) The rate of entropy production is a minimum under steady state conditions. Why?
  - b) Explain the term 'heat of transfer'.
  - c) State and explain Glansdorf-Pregogine theorem.
- IV.
  - a) Arrange translational, rotational, vibrational and electronic partition functions in the increasing order of magnitude. Justify your answer.
  - b) The fundamental vibrational frequency of HCl is  $2990 \text{ cm}^{-1}$ . Find its characteristic temperature.
  - c) What do you mean by dilute system?

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- V. a) Calculate the thickness of the ion atmosphere for 0.01 CaCl<sub>2</sub> in water at 25°C. Dielectric constant of water is 78.5  
b) Briefly explain 'Stern' model of electrical double layer.  
c) Explain the term 'back emf'.

(5×5=25 Marks)

SECTION - B

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

- VI. a) Find the ground state energy of the particle in one-dimensional box using variation theorem. Use the trial function  $\Phi = x(a - x)$ . a is the length of the box.  
b) Find the energy of  $\pi$  molecular orbitals of benzene using HMO method.
- VII. a) What are the conditions under which linear relationship exists between forces and fluxes? Discuss the advantages of linear relationship between forces and fluxes.  
b) Rationalise any one of the electro-kinetic phenomena using irreversible thermodynamics.
- VIII. a) How would you determine C-O and C-S bond lengths of COS using microwave spectroscopy? Discuss.  
b) What is meant by Fortrat diagram? Discuss.
- IX. a) Calculate the ratio of populations for energy levels separated by 1000 cm<sup>-1</sup>. Ground state is nondegenerate and excited state is triply degenerate. T = 300 K.  
b) Calculate the absolute entropy of He at 25°C and 1 b pressure.
- X. a) The EMF of the following cell measured at 25°C is 0.3524 V. The standard electrode potential of Cl<sup>-</sup>|AgCl<sub>(s)</sub>|Ag is 0.2224 V. Calculate the mean ionic activity coefficient of 0.01 molal HCl
- $$\text{Pt} | \underset{1b}{\text{H}_2} | \underset{0.01m}{\text{HCl}} | \text{AgCl}_{(s)} | \text{Ag}.$$
- b) Derive Lippmann equation.



SECTION - C

(3×10=30 Marks)

Answer any three questions. Each question carries 10 marks.

- XI. Find the ground state energy of H atom by variation method. Use the trial function  $\Phi = e^{-\alpha r}$ .
- XII. What are the disadvantages of dispersive IR? How are they overcome in FTIR? Discuss.
- XIII. a) Draw phase diagram for a 3-component system of two salts and water. Discuss.  
b) Rationalise thermal osmosis from the concepts of irreversible thermodynamics.
- XIV. a) Briefly discuss theory of paramagnetism.  
b) Derive an equation for the vibrational contribution towards heat capacity of gases.
- XV. What are the assumptions in Debye-Hückel theory? Following the theory derive an equation for the activity coefficient of an ion in solution.
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Reg. No. : .....

Name : .....

**Second Semester M.Sc. Degree Examination, October 2018**  
**Branch : CHEMISTRY**  
**CH/CL/CA/CM 223 : Physical Chemistry - II**  
**(2016 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 **(10×2=20 Marks)**  
2 marks.

1. a) Is wave function for H atom is  $\Psi_{1s} = \frac{1}{\sqrt{\pi}} \left( \frac{1}{a_0} \right)^{3/2} e^{-r/a_0}$ . Plot  $\Psi_{1s}$  against  $r$ ?  
Explain the nature of the plot.
- b) One of the solutions of H atom is given below.  $\Psi = N \sin\theta \cos\theta \sin\phi$   
( $N$  is normalization constant). Represent the function graphically. Explain.
- c) Write first two associated Legendre polynomials.
2. a) State selection rules for microwave spectroscopy.
- b) Write the frequency for  $J = 9$  to  $J = 10$  in terms of rotational constant  $B$ .
- c) Stokes' lines are more intense than antistokes' lines in the vibrational Raman spectrum. Why?
3. a) State and explain Onsager reciprocal relation.
- b) What is 'active transport'? Explain.
- c) What is Seebeck effect?
4. a) Distinguish between microstate and macrostate.
- b) Electrons never follow Maxwell Boltzmann statistics. Why?
- c) Explain the term 'ensemble'.

P.T.O.

5. a) Explain 'Wein effect'.  
b) What do you mean by electrode polarization?  
c) Write Tafel equation. Explain the terms.

## 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 a planar rotator. Find eigen functions and eigen values.  
b) What is radial distribution function? Draw radial distribution curves for 4s, 4p, 4d and 4f orbitals.
7. a) The fundamental vibrational frequency of HCl is  $2990 \text{ cm}^{-1}$ . Find the force constant.  
b) Apply particle in one dimensional box model for electronic transitions in a conjugated system. Discuss.
8. a) Draw phase diagram for a 3-component liquid-liquid system. Discuss.  
b) What are the conditions under which linear relationship exists between forces and fluxes? Explain.
9. a) Calculate the ratio of populations at  $25^\circ\text{C}$  for energy levels separated by  $1000 \text{ cm}^{-1}$ . The ground state is nondegenerate and excited state is triply degenerate.  
b) Derive Bose Einstein distribution law.
10. a) How would you calculate mean ionic activity coefficient from EMF data? Discuss.  
b) Calculate the thickness of ion atmosphere around  $\text{Cl}^-$  in 0.01 KCl in water at  $25^\circ\text{C}$ . The dielectric constant of water is 78.5.



SECTION - C

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

(3×10=30 Marks)

11. Discuss shapes of s, p, d and f atomic orbitals
  12. a) How would you evaluate C = O and C = S bond distances in COS by microwave spectroscopy? Discuss.  
b) How would you calculate dissociation constant of a diatomic molecule from electronic spectroscopy? Discuss.
  13. Discuss briefly :
    - a) Principle of minimum entropy production.
    - b) Isothermal evaporation.
  14. Apply Fermi Dirac statistics for thermionic emission. Discuss.
  15. Derive Butler-Volmer equation. Discuss.
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Reg. No. : .....

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Second Semester M.Sc. Degree Examination, July 2019

Chemistry/Polymer Chemistry

CH/CL/CM/CA/PC 223 PHYSICAL CHEMISTRY II

75

(Common for Chemistry (2016 Admission Onwards) and  
Polymer Chemistry (2018 Admission))

Time : 3 Hours

Max. Marks : 75

PART – A

Answer **any two** among (a), (b) and (c) from each question. Each sub – division carries 2 marks.

1. (a) What is spherical harmonics?  
(b) Draw the radial distribution diagram of 1s and 2p orbitals.  
(c) What are Legendre polynomials?
2. (a) How can you find the intensity of spectral lines in microwave spectra?  
(b) Define force constant.  
(c) What are group frequencies?
3. (a) Write Glansdorff-Pregogine equation.  
(b) What is meant by irreversible process?  
(c) State and explain the principle of minimum entropy production.

P.T.O.

4. (a) What are ensembles?  
(b) Define thermodynamic probability.  
(c) What is meant by super cooled liquid?
5. (a) What is Wein effect?  
(b) Define electrode potential.  
(c) Write and explain Nernst equation.

**(2 × 10 = 20 Marks)**

**PART – B**

Answer either (a) or (b) from each question. Each question carries 5 marks.

6. (a) Solve particle in a ring and its phi equation.  
(b) How can you find the potential energy of hydrogen like atoms?
7. (a) What is the difference between harmonic and anharmonic oscillator?  
(b) Explain the principle and application of laser Raman spectrum.
8. (a) Explain the influence of temperature on 3 component system.  
(b) Explain isothermal evaporation.
9. (a) Explain the theory of paramagnetism with examples.  
(b) Explain Liquid helium.
10. (a) Explain Debye-Huckel limiting law.  
(b) State and explain Butler-Volmer equation.

**(5 × 5 = 25 Marks)**





PART – C

Answer any three questions and each question carries 10 marks.

11. (a) Express the wave equation for hydrogen like atoms in polar coordinates and separate in to R, theta and phi equations.  
(b) Explain HFSCF method and Fock operator.
12. (a) Explain the principle and applications of rotational spectrum.  
(b) Explain mutual exclusion principle with an example.
13. (a) What are electrokinetic effects?  
(b) Explain the entropy production from matter flow, heat flow and current flow.
14. Discuss the relation between M-B, F-D and B-E statistics.
15. Explain the theories of over voltage.

(3 × 10 = 30 Marks)