



(Pages : 3)

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Reg. No. : 25/1/14

Name :

Third Semester M.Sc. Degree Examination, January 2016

Branch : Chemistry

CH/CL/CA 233 : PHYSICAL CHEMISTRY – III

(2013 Admission Onwards)

Time : 3 Hours

Max. Marks : 75

SECTION – A

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

1. a) Explain the term 'potential energy surface' with reference to computational methods.
b) What do you mean by split valence basis set ? Explain.
c) Distinguish between RHF and ROHF with examples.
2. a) Calculate the ratio of population of protons between alpha and beta spin states, under 100 MHz NMR experiment at 300 K.
b) How many lines do you expect in the ESR spectrum of naphthalene negative ion ? Justify your answer.
c) Explain the term 'quadrupole relaxation'.
3. a) Show that molecular partition function is the product of the partition function for the various degrees of freedom.
b) The ortho : para ratio of molecular hydrogen is 3 : 1 even though para form is quantum mechanically more stable. Why ?
c) Electronic energy does not contribute towards thermodynamic properties. Why ?

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4. a) Define surface pressure. How is it measured ?
b) What is point B method of determining surface area of a solid ?
c) Enthalpy of adsorption is a function of surface coverage. Why ?
5. a) Explain the working of $\text{el}|\text{AgCl}_{(s)}|\text{Ag}$ electrode. What are the advantages of this electrode ?
b) What is stripping voltametry ?
c) Explain the term 'sputtering' with reference to AAS.

SECTION – B

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

6. a) Briefly discuss the methods of geometry optimization in computational chemistry.
b) Write a brief account of the properties of Gaussian functions.
7. a) Explain the term 'spin-spin' relaxation. How is spin-spin relaxation time measured ?
b) Define 'g' factor of a radical. How is it measured in ESR spectroscopy ?
8. a) Evaluate translational entropy of CO_2 at 25°C .
b) Derive an equation for vibrational contribution towards heat capacity of gases.
9. a) For the dissociative chemisorption of $\text{A}_2(\text{g}) \xrightleftharpoons[K_{-1}]{K_1} 2\text{A}_{(\text{ads})}$ derive an equation for fractional surface coverage θ in terms of partial pressure of A_2 .
b) 160 ml of N_2 (corrected to 0°C and 1 atm pressure) was required to form a monolayer on a solid surface. Calculate the surface area of the solid. Cross sectional area of N_2 is 16.2 \AA^2 .
10. a) Briefly explain the principle of amperometric titration.
b) You are given a binary solution of Cu and Pb. How will you estimate the amount of Cu and Pb in the solution by electrogravimetry ? Explain.



SECTION – C

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

11. Write a brief account of the density functional method in computational chemistry.
 12. Discuss the theory and applications of Mössbauer spectroscopy.
 13. Write virial equation of state for a real molecule. Evaluate the first virial coefficient.
 14. Derive BET absorption isotherm. Discuss.
 15. Discuss briefly the theory and applications of cyclic voltametry.
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