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Reg. No. : .....

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 ?

P.T.O.

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 el|$AgCl_{(s)}$|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 Mark**

6. a) Briefly discuss the methods of geometry optimization in computational chemistry.
   b) Write a brief account of the properties of Guassian 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 $A_2(g) \underset{K_{-1}}{\overset{K_1}{\rightleftharpoons}} 2A_{(ads)}$ 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 $\mathring{A}^2$.

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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B – 4319

Reg. No. : .....

Name : .....

Third Semester M.Sc. Degree Examination, January 2017

Branch : Chemistry

CL/CA/CH 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 following terms :
   I) Stationary point
   II) Saddle point with reference to computational methods.
   b) Distinguish between polarized and differed basis set with examples.
   c) Write Z-matrix for NH_3.

2. a) Distinguish between scalar coupling and dipolar coupling.
   b) State and explain Kramer's rules.
   c) Distinguish between ENDOR and ELDOR.

3. a) Arrange translational, rotational and vibrational partition function in the increasing order of magnitude. Justify your answer.
   b) What is Langevin's partition function ?
   c) Rotational motion does not contribute towards pressure of a gas. Justify the statement.

4. a) Spontaneous adsorption is always exothermic. Justify the statement.
   b) Write Harkin's Jura isotherm. Explain the terms.
   c) Write Langmuir adsorption isotherm in the linear form. What is the significance of the slope and intercept ?

P.T.O.

5. a) Explain the working of a Calomel electrode.
   b) How would you detect the end point in a titration by potentiometric method ? Explain.
   c) Explain the working of an atomizer in AAS.

SECTION – B

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

6. a) Explain the principle and applications of X-ray photoelectron spectroscopy.
   b) How is Doppler effect made use of in Mössbauer spectroscopy ? Explain.

7. a) What are the properties of slater type of orbitals ? Discuss.
   b) What are the assumptions in Restricted Hartree Fock method ? Discuss.

8. a) How do you evaluate the equilibrium constant of a reaction from molecular data ? Discuss.
   b) How would you evaluate rotational partition function of molecular H_2 ? Discuss.

9. a) Derive Gibbs adsorption isotherm. How is it verified ? Discuss.
   b) Briefly explain microscopic methods of surface analysis.

10. a) Explain the working of glass electrode.
    b) 0.800 amperes of current is passed through an aqueous solution of $CuSO_4$ for 20 minutes. Calculate the amount of Cu deposited at the cathode.

SECTION – C

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

11. Write a brief account of ab initio methods in computational chemistry.

12. Discuss the theory and instrumentation in pulsed NMR.

13. Briefly discuss Debye's theory of heat capacity of solids.

14. Derive BET adsorption isotherm. Show that it approximates to Langmuir adsorption isotherm under limiting conditions. What is the limiting condition ?

15. Discuss the principle and instrumentation in AAS.

Reg. No. : .....

(Pages : 2)

D – 3832

Name : .....

Third Semester M.Sc. Degree Examination, January 2018
Branch : CHEMISTRY
CH/CL/CA/CM 233 – Physical Chemistry – III
(2016 Admission)

Time : 3 Hours

Max. Marks : 75

SECTION – A

Answer **any two** from **a**, **b** or **c** of **each** question. **Each** sub-question carries **2** marks.

I. a) NO^+ is more stable than NO. Why ?

b) Write Hamiltonian for Helium.

c) Write spectroscopic term symbol for ground state of O_2.

II. a) Explain with example 'double zeta basis set'.

b) State and explain Hohenberg-Kohn theorems.

c) Write Z-matrix for H_2O.

III. a) Explain the term gyromagnetic ratio.

b) Solid state NMR spectra are generally broad. Why ?

c) How many lines are expected in the ESR spectrum of naphthalene negative ion ? Justify your answer.

IV. a) Arrange translational, rotational, vibrational and electronic partition function in the increasing order of magnitude. Justify your answer.

b) Find symmetry number for CH_4.

c) What is Langevin function ? Explain its significance.

V. a) 800 mA of current is passed through an aqueous solution of $CuSO_4$ for 20 minutes. Find the amount of Cu deposited at Cathode.

b) What is anodic stripping voltammetry ?

c) Explain the term 'nebulization'.

(10×2=20 Marks)

P.T.O.

SECTION – B

Answer **either A** or **B** of **each** question. **Each** question carries **5** marks.

VI. A) Apply HMO method to find energy of π molecular orbitals of allyl cation. Find the delocalization energy.

B) Find the ground state energy of H atom by variation method. Use the trial function $\Phi = e^{-\alpha r}$. α is the variational parameter r is the distance from the nucleus.

VII. A) What are the drawbacks of molecular mechanics in computational chemistry ? Discuss.

B) What do you mean by STO ? Discuss.

VIII. A) What are the mechanisms of spin spin interaction in NMR ? Discuss.

B) Briefly explain 2 dimensional NMR experiment.

IX. A) How would you calculate equilibrium constant of a reaction from molecular data ? Discuss.

B) Derive Sackur Tetrode equation.

X. A) Explain the working of a glass electrode.

B) Briefly discuss the principle of amperometric titration. **(5x5=25 Marks)**

SECTION – C

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

XI. Apply HMO method for π bonding in butadiene and find the energy of π molecular orbitals. What is the delocalization energy ? Derive mathematical expression for any one of the π molecular orbitals.

XII. Write a brief account of the ab initio methods of computational chemistry.

XIII. Discuss theory and applications of Mössbauer spectroscopy.

XIV. Define partition function. Derive equation for (a) translational partition function for a delocalized system. (b) rotational partition function for diatomic molecule.

XV. Discuss instrumentation of AAS. **(3x10=30 Marks)**

(Pages : 3) **D – 3931**

Reg. No. : .....

Name : .....

Third Semester M.Sc. Degree Examination, January 2018
Branch : CHEMISTRY
CH/CL/CA 233 : Physical Chemistry – III
(2013 Admission)

Time : 3 Hours Max. Marks : 75

SECTION – A

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

1. a) What is stationary points and different kinds of stationary points used by chemists ?

   b) Construct the Z matrix for CO_2.

   c) Define Slater Type orbitals.

2. a) Define coupling constant and chemical shift in NMR spectroscopy.

   b) Draw e.s.r. spectrum of methyl radical.

   c) Explain the principle of Mossbauer spectroscopy.

3. a) Write down the expression for vibrational partition function and explain.

   b) Explain Dulong and Petits law.

   c) Explain virial coefficients of real gas.

4. a) Explain the principle of Auger electron spectroscopy.

   b) Explain the principle of BET surface area analysis.

   c) Mention about different thermal methods used for the characterization of the catalyst.

P.T.O.

5. Write short note on :
   a) Define half wave potential. What is its significance ?
   b) How do you detect end point in conductometric titration ?
   c) What is coulometric titrations ? **(2×10=20 Marks)**

SECTION – B

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

6. a) What is meant by geometry optimisation ? Explain.
   b) Define polarised and diffused basic sets.

7. a) Explain the position and hyperfine structure of E.S.R. absorptions.
   b) Explain the principle of ELDOR spectroscopy.

8. a) Explain Debye and Einstein theory of heat capacity of solids.
   b) Derive an expression for the equilibrium constant of a chemical reaction in terms of partition functions.

9. a) Explain the principle and application of scanning Electron Microscope.
   b) Write short note on enzyme catalysis and mechanism.

10. a) Discuss the working principle and schematic representation of atomic absorption spectroscopy.
    b) Explain principle of potentiometric titrations. **(5×5=25 Marks)**

SECTION – C

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

11. Outline the similarities and differences between MM, ab intio and SE methods.

12. Explain the principle and working of :
    a) Nuclear Quadrupole Resonance spectroscopy.
    b) Mossbauer spectroscopy.

13. a) Derive the formula for the entropy, energy and Helmoltz free energy of a planar rotor.

    b) Derive and explain Sackur Tetrode equation.

14. Explain the principle and applications of :

    a) Photoelectron spectroscopy.

    b) Low energy electron diffraction.

15. Explain and discuss the working principle of :

    a) Electrogravimetry.

    b) Polarography.

    c) Cyclic voltammetry. **(10×3=30 Marks)**

Reg. No. : .....

Name : .....

Third Semester M.Sc. Degree Examination, January 2020

Chemistry/Polymer Chemistry

CH/CL/CM/CA/PC 233 : PHYSICAL CHEMISTRY – III

(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** of each question. Each sub question carries **2** marks.

1. (A) State variation theorem.

   (B) Draw the MO diagram of HF.

   (C) Calculate the bond order of O_2, F_2 and CO.

2. (A) Explain the terms in 6 – 31 ++ G*.

   (B) Differentiate between RHF, ROHF and URHF.

   (C) Write any two drawbacks of MM method.

3. (A) Define nuclear resonance.

   (B) What are the requirements of Mossbauer spectroscopic analysis?

   (C) State the principle of NQR spectroscopy.

4. (A) What are the limitations of Einstein's theory of heat capacity of solids?

(B) Explain Dulong and Petit's law.

(C) Explain the significance of principle of equipartition of energy.

5. (A) Explain Calomel electrode.

(B) What is the principle behind coulometry?

(C) What are the applications of AAS?

(2 × 10 = 20 Marks)

PART – B

Answer either **A** or **B** of each question. Each question carries **5** marks.

6. (A) Apply variation theorem for particle in ID box and calculate the ground state energy.

(B) Apply HMO method to benzene and explain the bonding.

7. (A) Write the Z-matrix of CH_3CHO and NH_3.

(B) Explain Hohenberg-Kohn theorem of DFT calculations.

8. (A) Explain briefly the instrumentation of NMR spectroscopy.

(B) Explain Kramer's degeneracy.

9. (A) Derive statistically the relation between probability and entropy.

(B) Derive the expressions for molecular partition functions.

10. (A) How can you find the pH of a solution by using glass electrode?

(B) Explain the principle of polarography.

(5 × 5 = 25 Marks)

PART – C

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

11. Explain quantum mechanical treatment of sp^3 hybridization for alkanes.

12. What are basis sets and explain different types of basis sets.

13. How can you differentiate (i) low spin and high spin complexes and (ii) oxy and deoxy hemoglobin by Mossbauer spectroscopy?

14. Express the thermodynamic properties in terms of partition functions.

15. How can you estimate the mass of copper from copper sulphate solution by using electrogravimetry?

(3 × 10 = 30 Marks)

(Pages : 3) K – 4911

Reg. No. : .....

Name : .....

Third Semester M.Sc. Degree Examination, February 2021

Chemistry/Polymer Chemistry

CH/CL/CA/CM/PC 233 : PHYSICAL CHEMISTRY III

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

Time : 3 Hours Max. Marks : 75

SECTION – A

Answer **any two** among **A**, **B** and **C** of each questions. Each sub question carries **2** marks.

1. (A) State perturbation theorem.

   (B) Draw the MO diagram of LiH.

   (C) Write the term symbol of outermost electron in sodium.

2. (A) Explain the terms in cc-p VTDZ.

   (B) Differentiate between MM and SE methods.

   (C) Write any two drawbacks of ab-initio method.

3. (A) What is the principle of ESR spectroscopy?

   (B) How many peaks are observed in the Mossbauer spectrum of $[Fe(H_2O)_6]^{2+}$?

   (C) What are ENDOR and ELDOR?

P.T.O.

4. (A) Explain Debye theory of heat capacity of solids.

(B) Explain law of mass action.

(C) Define Kopp's law.

5. (A) Explain Ag-AgCl electrode.

(B) What is the principle behind voltametry?

(C) What are the applications of amperometry?

(10 × 2 = 20 Marks)

SECTION – B

Answer **either A or B** of each question. Each question carries **5** marks.

6. (A) Explain the MO theory of H_2^+.

(B) Apply HMO method to allyl system and explain the bonding.

7. (A) Write the differences between STOs and GTOs.

(B) Explain Huckel and extended Huckel model.

8. (A) Explain fine and hyperfine structures in ESR with an example.

(B) Explain Doppler effect and chemical shift.

9. (A) Derive the expression for the total partition function.

(B) Explain quantum theory of heat capacity of solids.

10. (A) How can you determine the concentration of a given alkali by potentiometric titrations?

(B) Explain the instrumentation of AAS.

(5 × 5 = 25 Marks)

SECTION – C

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

11. Explain quantum mechanical treatment of sp^2 hybridization for alkenes.

12. What are ab-initio and DFT methods?

13. How can you explain (a) spin crossover process and (b) iron complexes by Mossbauer spectroscopy.

14. Explain Einstein theory of heat capacity of solids.

15. Differentiate between cyclic and stripping voltametry.

(3 × 10 = 30 Marks)