



Reg. No. : .....

Name : .....

**Third Semester M.Sc. Degree Examination, February 2019**  
**Branch : Chemistry**  
**CH/CL /CA /CM 233 : PHYSICAL CHEMISTRY – III**  
**(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 **2** marks.

- I. a) Write Hamiltonian for  
i)  $H_2^+$                   ii)  $H_2$
- b) State and explain Born-Oppenheimer approximation.
- c) The energy of  $\pi$  molecular orbitals of benzene are  $\alpha + 2\beta$ ,  $\alpha + \beta$ ,  $\alpha + \beta$ ,  $\alpha - \beta$ ,  $\alpha - \beta$  and  $\alpha - 2\beta$ . Find the delocalization energy.
- II. a) Distinguish between local and global minima.
- b) Write Z-matrix for  $CH_3CHO$ .
- c) What do you mean by CNDO approach ?
- III. a) How many lines do you expect in the ESR spectrum of  $NH_3$  radical ? Justify your answer.
- b) Distinguish between ENDOR and ELDOR.
- c) How would you distinguish between XPS and AES lines in the spectrum ?
- IV. a) Show that molecular partition function is the product of the partition function for the various degrees of freedom.
- b) Calculate  $C_v$  for  $NH_3$  using equipartition principle.
- c) State and explain Kopp's law.





- V. a) An aqueous solution of  $\text{CuSO}_4$  is electrolysed between 2 Pt electrodes. Predict products at anode and cathode. Justify your answer.
- b) A cell is formed by combining a normal calomel electrode and a hydrogen electrode. The EMF of the cell is 0.35 V. Calculate the pH of the solution. Potential of normal calomel electrode is 0.2802 V.  $T = 25^\circ\text{C}$ .
- c) What is Coulometric titration ? **(10×2=20 Marks)**

## SECTION – B

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

- VI. A) State and prove variation theorem.  
B) Find the ground state energy of He by first order Perturbation method.
- VII. A) What are the general features of a Gaussian input file ?  
B) Discuss basic principles of DFT.
- VIII. A) How would you determine spin-spin relaxation time ( $T_2$ ) ? Discuss.  
B) Briefly discuss Doppler effect.
- IX. A) Calculate rotational partition function of CO at  $25^\circ\text{C}$ . Bond length is 1.13 Å.  
B) Calculate  $\bar{\epsilon}_v$  for diamond at 1000 K. Characteristic temperature is 1870 K.
- X. A) Explain the working of a hollow cathode lamp.  
B) How would you detect end point in potentiometric titration ? Discuss.  
**(5×5=25 Marks)**

## SECTION – C

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

- XI. Discuss VB method of bonding as applied to  $\text{H}_2$ .
- XII. Briefly discuss SCF method of solving many electron atoms.
- XIII. Discuss briefly 2D NMR experiment.
- XIV. Discuss briefly Debye's theory of heat capacity of solids.
- XV. Briefly discuss cyclic voltametry as an analytical technique. **(3×10=30 Marks)**

