(6 pages)

Reg. No. : .....

Code No. : 6409 **Sub. Code : ZCHM 33**

M.Sc. (CBCS) DEGREE EXAMINATION, NOVEMBER 2022.

Third Semester

Chemistry — Core

GROUP THEORY AND CHEMICAL THERMODYNAMICS

(For those who joined in July 2021 onwards)

Time : Three hours Maximum : 75 marks

PART A — (10 × 1 = 10 marks)

Answer ALL questions.

Choose the correct answer :

1. Which of the following does not contain a C_3 axis?

   (a) $POCl_3$ (b) $[NH_4]^+$

   (c) $[H_3O]^+$ (d) ClF_3

2. Which molecule or ion has D_{3h} symmetry?

   (a) $[H_3O]^+$ (b) $CHCl_3$

   (c) $[CO_3]^{2-}$ (d) NF_3

3. Which of the following gives the correct description of the stretching modes of SO_3, and how many absorptions do these vibrational modes give rise to in the IR spectrum of SO_3?

   (a) Symmetric stretch, asymmetric stretch (doubly degenerate); one absorption

   (b) Symmetric stretch; asymmetric stretch (doubly degenerate); two absorptions

   (c) Symmetric stretch; asymmetric stretch; two absorptions

   (d) Symmetric stretch; asymmetric stretch; one absorption

4. The symmetric stretching mode for PCl_3 is of A_1 symmetry. In the C_{3v} character table, there are z and $(x^2 + y^2, z^2)$ entries in the A1 row. this tells you that the symmetric stretching mode is ———

   (a) IR active and Raman inactive

   (b) IR active and Raman active

   (c) IR inactive and Raman active

   (d) IR inactive and Raman inactive

5. Helmholtz free energy (A) is defined as

   (a) A = H - TS (b) A = E - TS

   (c) A = H + TS (d) None of these

6. For a spontaneous process, free energy

(a) Is zero

(b) Increase

(c) Decreases whereas the entropy increases

(d) And entropy both decrease

7. The Maxwell-Boltzmann law is given by the expression ————

(a) $1/e^{(EkT)}$ (b) $1/e^{(1+EkT)}$

(c) $1/e^{(\alpha+EkT)}$ (d) $1/e^{(\alpha+nEkT)}$

8. Maxwell-Boltzmann statistics cannot be applied to ————

(a) Atoms (b) Molecules

(c) Photons (d) Lattice

9. Which of the following is correct for the net entropy change in an irreversible process?

(a) It is positive (b) It is negative

(c) It is zero (d) All of the above

10. Unfolding of regular secondary protein structure causes ————

(a) Large decrease in the entropy of the protein

(b) Little increase in the entropy of protein

(c) No change in the entropy of the protein

(d) Large increase in the entropy of the protein

PART B — (5 × 5 = 25 marks)

Answer ALL questions, choosing either (a) or (b).
Each answer should not exceed 250 words.

11. (a) Construct a multiplication table for C_{3v} point group.

Or

(b) Write briefly about classes of symmetry operations.

12. (a) Explain briefly about symmetry selection rule for Raman and infrared spectra.

Or

(b) Write a note on determination of hybridization of atomic orbitals in methane.

13. (a) Write briefly about partial molar quantities and their determination.

Or

(b) Write a note on excess thermodynamic functions.

14. (a) Write briefly about partition functions.

Or

(b) Write briefly about negative Kelvin temperature.

15. (a) Write briefly about the Phenomenological laws and their applications in chemistry.

Or

(b) Write briefly about application of irreversible thermodynamics to biological system.

PART C — (5 × 8 = 40 marks)

Answer ALL questions, choosing either (a) or (b)
Each answer should not exceed 600 words.

16. (a) Give a detailed account on constructing character table for C_{4v} using the great orthogonality theorem.

Or

(b) Give a detailed account on the great orthogonality theorem.

17. (a) Give a detailed account on determination of hybridization of atomic orbitals in non-linear molecule methane and PF_5.

Or

(b) Write a note on electronic spectra of ethylene and formaldehyde.

18. (a) Discuss the significance of free energy concepts.

Or

(b) Write a note on chemical potential and derive Gibbs - Duhem equation.

19. (a) Give the derivation of Maxwell - Boltzman statistics.

Or

(b) Give the derivation of Maxwell - Boltzmann statistics.

20. (a) Discuss onsager reciprocal relations and application of irreversible thermodynamics to biological system.

Or

(b) Discuss the entropy changes due to coupling of chemical reaction.

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