

(8 Pages)

Reg. No. : .....

Code No. : 5804

Sub. Code : WCHM 22

M.Sc. (CBCS) DEGREE EXAMINATION, APRIL 2024.

Second Semester

Chemistry — Core

PHYSICAL CHEMISTRY — I

(For those who joined in July 2023 onwards)

Time : Three hours

Maximum : 75 marks

PART A — (15 × 1 = 15 marks)

Answer ALL questions.

Choose the correct answer :

1. Partial molar volume of a component in a mixture is given by

(a)  $V_i = \left( \frac{\partial V}{\partial n_i} \right)_{T, P, n_1, n_2, \dots}$

(b)  $V_i = \left( \frac{\partial V}{\partial P} \right)_{T, n_1, n_2, \dots}$

(c)  $V_i = \left( \frac{\partial V}{\partial T} \right)_{P, n_1, n_2, \dots}$

(d)  $V_i = \frac{\partial V}{\partial T}, \frac{\partial T}{\partial P}$

2. The activity coefficient of a components in a ideal solution is

- (a) Always equal to 1
- (b) Always greater than 1
- (c) Always less than 1
- (d) Dependent on temperature and Pressure

3. Fugacity becomes equal to pressure in the limit of

- (a) Low pressure
- (b) High Pressure
- (c) Infinite temperature
- (d) Zero temperature

4. The ensemble in statistical thermodynamics which possess fixed number of particles, Volume and Temperature is

- (a) Micro canonical ensemble
- (b) Canonical ensemble
- (c) Grand canonical ensemble
- (d) Isothermal - Isobaric ensemble

5. Which of the following is referred to as Bosons and obeys Bose - Einstein statistics?

- (a) system with large number of particles
- (b) photons
- (c) electrons
- (d) nuclei of atoms

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6. At extremely low temperatures, \_\_\_\_\_ Partition function contributes the least to the overall partition function of a molecule.
- (a) Vibrational (b) Rotational  
(c) Translational (d) Electronic
7. In the irreversible Thermodynamics, the entropy production is always
- (a) 0 (b) negative  
(c) positive (d) constant
8. Flux in irreversible thermodynamics refers to
- (a) state function  
(b) energy conservation  
(c) internal energy change  
(d) rate of flow of quantity
9. Which is an example of thermo mechanical effect?
- (a) Ideal gas expansion  
(b) Joule Thompson effect  
(c) Reversible heat transfer  
(d) Isochoric process
10. In a reaction, which involves a non-electrolyte as one of the reactants, the value of  $Z_A Z_B$  will be
- (a) Positive (b) Negative  
(c) Zero (d) None of the above

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11. According to Lindemann and Christiansen hypothesis, what is the relationship between the rate constant of a reaction and temperature?
- (a) Rate constant is independent of Temperature  
(b) Rate constant increases with increasing temperature  
(c) Rate constant decreases with increasing temperature  
(d) Rate constant remains constant over a wide range of temperature
12. The assumption made while deriving the Michaelis-Menten equation is
- (a) The enzyme - substrate complex is reversible  
(b) The reaction follows I order kinetics  
(c) The concentration of enzyme - substrate complex is constant  
(d) The enzyme concentration is much lower than the substrate concentration
13. "Chain length" in polymerization refers to
- (a) The length of monomer molecule  
(b) Average number of monomer units in a polymer chain  
(c) Rate of Polymerisation reaction  
(d) The size of the polymer

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[P.T.O.]





14. The radiation source used in pulse radiolysis experiment is

- (a) X-rays (b) UV light  
(c)  $\gamma$ -rays (d) neutrons

15. Two reactions simultaneously compete for the same reactant to form different products. Such reactions are called

- (a) Reversible reactions  
(b) Parallel reactions  
(c) Consecutive reactions  
(d) None of the above

PART B — ( $5 \times 4 = 20$  marks)

Answer ALL questions, choosing either (a) or (b).

Each answer should not exceed 250 words.

16. (a) How will you determine the mean activity coefficient of an electrolyte using E.M.F method?

Or

(b) Explain the variation of fugacity with temperature.

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17. (a) Write a note on macrostates and microstates in statistical thermodynamics with illustration.

Or

(b) Calculate the translational Partition function for a mole of ideal gas  $O_2$  of mass  $5.31 \times 10^{-27}$  kg at 1 atm. pressure at 298 K ( $h = 6.626 \times 10^{-34}$  J.s;  $k = 1.381 \times 10^{-23}$  J/K ;  $R = 8.3141$  J ;  $R = 8.314$  JK $^{-1}$  mol $^{-1}$ . 1 atm =  $1.031 \times 10^5$  Nm $^{-2}$ )

18. (a) Write a note on electrokinetic effect.

Or

(b) Give the application of irreversible thermodynamics to biological systems.

19. (a) Derive Eyring equation.

Or

(b) Explain the effect of pH on the rate of acid - base catalysed reaction.

20. (a) What are chain reactions? Explain the characteristics of chain reactions.

Or

(b) Derive the rate law for the following reaction :



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PART C — ( $5 \times 8 = 40$  marks)

Answer ALL questions, choosing either (a) or (b).

Each answer should not exceed 600 words.

21. (a) (i) Derive Gibbs-Duhem equation for binary system.  
(ii) How does Chemical potential changes with the temperature?

Or

- (b) (i) How is partial molar property determined by using method of intercepts?  
(ii) Explain the graphical method for the determination of fugacity.

22. (a) Derive Bose – Einstein statistics.

Or

- (b) Derive the following thermodynamic property in terms of partition function :  
(i) Enthalpy  
(ii) Entropy

23. (a) Write about Onsager reciprocal relation and explain its validity.

Or

- (b) Explain about the entropy production in Chemical reactions.

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24. (a) Derive the rate equation of a bimolecular reaction considering the collisions between the reactant molecules.

Or

- (b) Derive Michaelis Menten equation and explain the variation of substrate concentration on the rate of Enzyme catalysed reactions.

25. (a) Derive the rate equation of Cationic polymerization.

Or

- (b) Explain the following methods to determine the rate of fast reactions :  
(i) Pulse Radiolysis  
(ii) Flash Photolysis.

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