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M.Sc. (Second Semester)

EXAMINATION, MAY-JUNE, 2022

CHEMISTRY

Paper No. CH-9

(Quantum Chemistry, Thermodynamics and Chemical Dynamics - II)

Time : Three Hours] *[Maximum Marks : 80*

Note : Attempt all sections as directed.

(Section-A)

(Objective/Multiple Choice Questions)

(1 mark each)

Note- Attempt all questions.

Choose the most appropriate answer.

1. Two matrices are defined as follows,

$$A = \begin{pmatrix} 1 & 2 \\ 1 & 2 \end{pmatrix}, B = \begin{pmatrix} 1 & 2 \\ 3 & 4 \end{pmatrix}$$

BA is given by

(A) $\begin{pmatrix} 7 & 10 \\ 7 & 10 \end{pmatrix}$

(B) $\begin{pmatrix} 10 & 7 \\ 10 & 7 \end{pmatrix}$

(C) $\begin{pmatrix} 3 & 6 \\ 7 & 14 \end{pmatrix}$

(D) $\begin{pmatrix} 14 & 7 \\ 6 & 3 \end{pmatrix}$

2. Which of the following statements is incorrect?

(A) The variation method can be used to determine the energies of the highest states corresponding to each symmetry type.

(B) The time-dependent perturbation theory provides an approximation technique of finding solution to Schrodinger equation.

(C) For systems having more than one electron it is not feasible to obtain an exact solution of the wave function.

(D) The variation method is applicable to those systems for which the wave functions can be guessed.

3. The third order determinant of following is

$$\begin{bmatrix} 1 & 2 & 3 \\ 1 & 2 & 3 \\ 3 & 2 & 1 \end{bmatrix}$$

(A) - 2

(B) 2

(C) 4

(D) 0

4. The angular momentum operator L_z in spherical coordinate is given by

(A) $i\hbar\left(\sin\phi\frac{\partial}{\partial\theta}+\cot\theta\ \cos\phi\frac{\partial}{\partial\phi}\right)$

(B) $-i\hbar\frac{\partial}{\partial\phi}$

(C) $i\hbar\left(-\cos\phi\frac{\partial}{\partial\theta}+\cot\theta\ \sin\phi\frac{\partial}{\partial\phi}\right)$

(D) $i\hbar\frac{\partial}{\partial\phi}$

5. The inverse of the matrix

$$A=\begin{bmatrix} 5 & 2 \\ 7 & 3 \end{bmatrix}$$

(A) $\begin{bmatrix} 3 & 2 \\ -7 & 5 \end{bmatrix}$

(B) $\begin{bmatrix} 3 & 2 \\ 7 & 5 \end{bmatrix}$

(C) $\begin{bmatrix} -3 & 2 \\ 7 & -5 \end{bmatrix}$

(D) $\begin{bmatrix} 3 & -2 \\ -7 & 5 \end{bmatrix}$

6. The rotational partition function of HCl at 298 K (Given that $k_bT/hc=207.224\ cm^{-1}$ and $\overline{B}=10.591\ cm^{-1}$) will be

(A) 0.0511

(B) 2194.70

(C) 19.59

(D) 5.11

7. The possible number of ways of distribution of 2 particles among 4 energy states, when particles are Bosons

   (A) 6

   (B) 10

   (C) 4

   (D) 16

8. An ensmeble which is characterized by constant V, E and N called

   (A) Microcononical ensemble

   (B) Canonical ensemble

   (C) Grand cononical ensemble

   (D) Molecular ensemble

9. Debye model of heat capacity of solids considers the vibrations of the crystal as

   (A) The vibrational motion of the atoms located at lattice points.

   (B) A giant molecule which is incompressible and inelastic medium

   (C) Vibrations of the atom in a crystal are independent and equal

   (D) A giant molecule which is homogeneous isotropic medium in which the vibrations are similar to elastic waves.

10. The Gibbs energy G(T) in terms of partition function can be expressed as

    (A) $-kT\,InQ$

    (B) $kTV\left(\frac{\partial}{\partial v}InQ\right)$

    (C) $G(0)-kTInQ+kTV\left(\frac{\partial}{\partial V}InQ\right)$

    (D) $kT\left(\frac{\partial}{\partial V}InQ\right)$

11. The potential difference between the fixed charged layer and the diffused layer having opposite charge is called

    (A) Streaming potential

    (B) Zeta Potential

    (C) Colloidal Potential

    (D) Stern Potential

12. The large and positive $(\eta \geq 0.12V)$ value of overpotential indicates

    (A) The anodic process is dominant

    (B) The cathodic process is dominant

    (C) Both anodic and cathodic process are dominant

    (D) None of the above

13. A semiconductor has ..... temperature coefficient of resistance

(A) Postive

(B) Zero

(C) Large positive

(D) Negative

14. Hydrogen electrode which is the reference electrode can be used as which of the following

(A) Anode only

(B) Cathode only

(C) Anode or Cathode

(D) Salt bridge

15. Which of the following statement is incorrect?

(A) A good electrocatalyst should show high current density at low over-potential

(B) Electrocatalysts are usually homogeneous catalysts

(C) Platinum is considered to be the best electrocatalyst

(D) Electrocatalytic reactions are potential dependent in rate

16. According to Lindemann's theory at very low concentration or pressure the reaction will be

(A) Second order

(B) First order

(C) Zero order

(D) Inverse order

17. The relaxation time for the following fast reaction will be

$$A + B \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} C$$

(A) $\frac{1}{k_1 + k_{-1}}$

(B) $\frac{1}{k_1 + k_{-1}}(A + B)$

(C) $\frac{1}{k_1 + k_{-1}}\overline{([A]_c + [B]_c)}$

(D) $\frac{1}{k_{-1} + k_1([A]_c + [B]_c)}$

18. The stopped flow method was introduced by

(A) B. Chance

(B) R. Marcus

(C) M. Eigen

(D) G. Porter

19. The Kinetics of barrierless chemical reactions of rebinding of CO and O_2 to the iron in heme in myoglobin has been studied theoretically by

(A) B. Bagchi

(B) Forster and Hoffmann

(C) Agmon and Hopfield

(D) N. Satyamurthy

20. An example of a relaxation method of measuring fast reaction is

    (A) Continuous Flow Technique

    (B) Pressure Jump Experiment

    (C) Flash Photolysis

    (D) Stopped Flow Method

(Section- B)

(Very Short Answer Type Questions)

(2 marks each)

Note : Attempt all questions.

1. What is transpose of matrix? Write three properties.
2. What is the basic difference between the variation and perturbation methods?
3. Write the significance of partition function.
4. Write two important postulates of Einstein theory of heat capacity.
5. What is the effect of light at semiconductor solution interfaces?
6. What is interface? How this interface becomes electrified?
7. What is the principle of fast reaction technique in plug flow systems?
8. Write two demerits of Hinshelwood's treatment of unimolecular reactions.

(Section - C)

(Short Answer Type Questions)

(3 marks each)

Note : Attempt all questions.

1. Find the inverse of the matrix

$$A=\begin{bmatrix} 3 & -2 & -1 \\ -4 & 1 & -1 \\ 2 & 0 & 1 \end{bmatrix}$$

2. A 2×10^{-3} kg particle moves at a constant speed of 3.0×10^{-3} m/s around a circle of radius 4.0×10^{-3}m.

   Find the magnitude of the angular momentum of particle.

   If $L\sqrt{l(l+i)\hbar},$ where I is an integer, find the approximate value of l.

   h = 6.6256×10^{-34} Js.

3. In "Fermi-Dirac Statistics" particles possess energy even at absolute zero temperature. Justify the statement.
4. Calculate translational partition function for the H_2 molecule confined to a 1000 cm^3 vessel at 25°C.

   $m_{H_2} = 3.348 \times 10^{-27} kg$

   h = 6.626×10^{-34} Js

   $k_b = 1.38 \times 10^{-23} JK^{-1}$

5. Discuss briefly electronic and geometric factors of electrocatalysis.

6. Write the Debye heat capacity equation (No derivation). Show that at low temperatures the atomic heat capacity of an element is proportional to T^3.

7. The relaxation time for the reaction

$$A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} B + C$$ is 50 μs at 25°C

If $[A]_e = 0.1M$, and $[B]_e = [C]_c = 0.05M$, Calculate k_1 and k_{-1}

8. Define molecular reaction dynamics. Explain infrared chemiluminescence method for the following reaction

$$Cl + HI \longrightarrow I + HCl$$

Section - D

(Long Answer Type Questions)

(5 marks each)

Note:- Attempt all questions.

1. Explain angular momentum and the angular momentum operator. State the commutation relations obeyed by the components of angular momentum.

OR

Explain the variational principle. Outline the variation method used for obtaining approximate value of ground

state energy of a system.

2. Derive Bose-Einstein statistics. What is the basic difference between Bose Einstein and Maxwell-Boltzmann statistics.

OR

Define partition function and its properties. Derive vibrational partition function.

3. What is the rate of electron transfer under the influence of an electric field? Derive Butler-Volmer equation.

OR

Explain electrical double layer. Discuss Gouy-Chapman diffuse charge model of electrified interface.

4. Define unimolecular reactions with suitable examples. Derive Rice-Ramsperger-Kassel-Marcus (RRKM) Theory of unimolecular reaction.

OR

Why conventional techniques led to difficulties for fast reactions? How rate constants of following fast reaction determined by NMR method?