Roll No. ....

E–517

M. Sc. (Second Semester)
EXAMINATION, May-June, 2021
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   1 each

(Objective/Multiple Choice Questions)

Note : Attempt all questions.

Choose the correct answer :

1. If $A = \begin{pmatrix} 0 & 1 \\ 2 & 3 \end{pmatrix}$ and $B = \begin{pmatrix} 1 & -1 \\ 5 & 2 \end{pmatrix}$, which of the following is false ?

    (a) $3A - 4B = \begin{pmatrix} -4 & 7 \\ -14 & 1 \end{pmatrix}$

    (b) $A^2 = \begin{pmatrix} 0 & 1 \\ 4 & 9 \end{pmatrix}$

    (c) $A + B = \begin{pmatrix} 1 & 0 \\ 7 & 5 \end{pmatrix}$

    (d) $AB = \begin{pmatrix} 5 & 2 \\ 17 & 4 \end{pmatrix}$

2. If $\psi_n^{(0)}$ is the wave function of unperturbed non-degenerate level with energy $E_n^{(0)}$ and perturbed wave function is ψ_n; the Schrödinger equation will be :

    (a) $\hat{H} = \hat{H}_0 + \lambda \hat{H}_1$

    (b) $\hat{H} = \psi_n^{(0)} = E_n^0 \psi_n^0 + \lambda$

    (c) $\hat{H} \psi_n = E_n \psi_n + \lambda$

    (d) $\hat{H}\psi_n = \left(\hat{H}^0 + \lambda\hat{H}' \right)\psi_n = E_n \psi_n$

3. For the inverse of a matrix A, it is necessary that A must be :

    (a)   Non-singular

    (b)   Singular

    (c)   Diagonal

    (d)   None of the above

P. T. O.

4. Which of the following statements is correct ?

   (a) Angular momentum is extremely important in the quantum mechanics of atomic structure.

   (b) In classical mechanics, the angular momentum L of a particle is defined as the vector product of its position vector and the linear momentum.

   (c) Many properties of angular momentum operators can be derived from their commutation relations.

   (d) All of the above statements are correct.

5. The determinant of the following is ....

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

   (a) 10

   (b) 2

   (c) – 2

   (d) 4

6. Five distinguishable particles are distributed in three non-degenerate levels with energies 0, E and 2E. The most probable distributions for total energy 3E corresponds to what combination of options given below ?

   (a) $N_3 = 1$, $N_2 = 1$, $N_1 = 3$

   (b) $N_3 = 2$, $N_2 = 2$, $N_1 = 1$

   (c) $N_3 = 3$, $N_2 = 2$, $N_1 = 1$

   (d) $N_3 = 2$, $N_2 = 3$, $N_1 = 1$

7. In a grand canonical ensemble, a system A fixed volume is contact with a large resorvoir B. Then :

   (a) A cannot exchange energy with B

   (b) A can exchange energy with B

   (c) A cannot exchange anything with B

   (d) None of the above

8. The translational partition function for A_r confined to a volume of 1 L at 300 K, having thermal wavelength of 1.60×10^{11} m, is closet to ....

   (a) 0.244×10^{29}

   (b) 2.4×10^{29}

   (c) 244×10^{29}

   (d) 24.4×10^{29}

9. Statistical thermodynamic relation between the partition function Q and internal energy, E is :

   (a) $kT \ln Q$

   (b) $- RT \ln \left(\dfrac{Q}{N} \right)$

   (c) $RT^2 \ln Q$

   (d) $RT^2 \left(\dfrac{\partial \ln Q}{\partial T} \right)_v$

10. The specific heats of non-metallic solids at very low temperatures obey :

   (a) $C°_{p,m} = aT^3 - bT$

   (b) $C°_{p,m} = aT^3 + bT$

   (c) $C°_{p,m} = aT^3$

   (d) $C°_{p,m} = \dfrac{aT^3}{3}$

11. For studying fast chemical reactions using relaxation spectrometry .... awarded Nobel Prize in 1967.
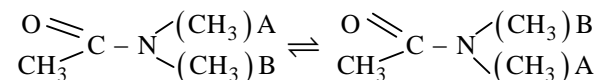
   (a)   Prof. Manfred Eigen

   (b)   Prof. George Porter

   (c)   Prof. R. G. W. Norrish

   (d)   Prof. R. Marcus

12. For the studying molecular reaction dynamics of the reactions, $HI + Cl \rightarrow HCl + I$, which method is suitable ?

   (a)   Flash phtolysis

   (b)   NMR method

   (c)   Infrared chemiluminescence method
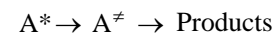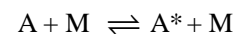
   (d)   Crossed molecular beam method

P. T. O.

13. One sharp NMR peak is observed for the following exchange reaction :

$$O=\underset{CH_3}{C}-N\begin{smallmatrix}(CH_3)A\\(CH_3)B\end{smallmatrix} \rightleftharpoons O=\underset{CH_3}{C}-N\begin{smallmatrix}(CH_3)B\\(CH_3)A\end{smallmatrix}$$

It indicates :

   (a)   No change

   (b)   Fast exchange

   (c)   Coalescence

   (d)   Slow exchange

14. One unimolecular reaction is considered best in terms of the following scheme :

$$A + M \rightleftharpoons A^* + M$$

$$A^* \rightarrow A^{\neq} \rightarrow Products$$

The name of this unimolecular theory is :

   (a)   Hinshelwood's theory

   (b)   Lindemann-Christiansen theory

   (c)   Slater's theory

   (d)   Rice-Ramsperger-Kassel theory

15. k^1 is the first order rate constant for the following unimolecular reactions :

$$A + M \xrightarrow[k_{-1}]{k_1} A^* + M$$

$$A^* \xrightarrow{k_2} P$$
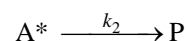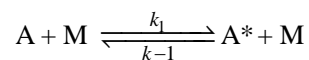
The slope and intercept of the plot of $1/k^1$ vs. $1/[M]$ are 4×10^6 and 8×10^{11} respectively. The value of k_{-1} / k_2 will be :

(a)　2×10^5

(b)　0.5×10^5

(c)　32×10^{17}

(d)　2×10^{-5}

16. Standard Tafel extrapolation assumes that the contribution of the following to the measured current is negligible :

(a)　Cathodic reaction

(b)　Anodic reaction

(c)　Double layer capacitance and solution resistance

(d)　None of the above

17. Correct statement about Helmholtz electrical double layer is :

(I)　It is a combination of two layers of opposite charges around the colloidal sol.

(II)　It is a combination of two layers of similar charges around the colloidal sol.

(III)　In it 1st layer of ions is diffused while 2nd layer of ions is fixed.

(IV)　The potential difference between the fixed layer and the diffuse layer is called Zeta potential.

(a)　II and III

(b)　I and IV

(c)　III and IV

(d)　II and IV

18. Fermi Energy level for intrinsic semiconductors lies :

(a)　Close to conduction band

(b)　Close to valence band

(c)　Outside the conduction band

(d)　In the middle of the forbidden gap

19. For a semiconductor-based light sources, it should be a/an :

(a)　Direct band gap semiconductor

(b)　Indirect band gap semiconductor

(c)　Either direct band gap or indirect band gap

(d)　The semiconductor cannot be used a light source

20. Why is standard hydrogen electrode called as the primary reference electrode ?

    (a)   It has a constant output potential.

    (b)   It has a known output potential.

    (c)   Its output potential is zero volts.

    (d)   Its output potential is independent of the composition of the solution.

Section—B 2 each

(Very Short Answer Type Questions)

Note : Attempt all questions.

1. Find the inverse of the matrix :

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

2. Define angular momentum operator.

3. What is micro canonical ensemble ?

4. Write three applications of Fermi-Dirac statistics.

5. Write one limitation of Gouy-Chapmon theory of electrical double layer.

6. What is the effect of light at semiconductor solution interfaces ?

7. Write the principle of pressure jump technique of fast reaction.

8. Write *five* examples of unimolecular reactions.

P. T. O.

Section—C 3 each

(Short Answer Type Questions)

Note : Attempt all questions.

1. Determine the value of x for which the matrix :

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

   is singular.

2. Discuss the advantage of variation method over perturbation method.

3. In CO, the first excited vibrational level is 25 kJ mol^{-1} above the ground level. Calculate the proportion of the population in 1st excited and ground vibrational level at 25°C. (R = 8.314 J).

4. How is entropy determined using partition function ?

5. Write one theory of electrocatalysis. What factors influencing electrocatalysis ?

6. What do you understand by structure of electrified interface ?

7. For the fast reaction $H + O\bar{H} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} H_2O$ the relaxation time has been measured is 36 μs at 25° C. Calculate k_1 and k_{-1} ($k_w = 1 \times 10^{-14}$).

8. Using Lindemann's unimolecular theory prove that as the pressure is lowered the first order kinetics changes to second order.

Section—D 5 each

(Long Answer Type Questions)

Note : Attempt all questions.

1. What are the various methods for obtaining approximate solutions to wave equation ? Discuss the perturbation methods and application of first-order perturbation theory to Helium atom.

Or

What is the importance of angular momentum in quantum mechanics ? Devise ladder operators for angular momentum.

2. Derive Bose-Einstein statistics. How Planck's equation for the distribution of energy is black body radiation is deduced from Bose-Einstein statistics ?

Or

Define specific heat of solid. Describe Debye's theory of specific heat of solid state and explain Debye's T^3 law.

3. Define overpotential and exchange current density. How variation of current density with over potential is studied ?

P. T. O.

Or

Explain electrical double layer. Discuss Stern model of electrical double layer.

4. What are the limitations of Hinshelwood theory ? Discuss Rice-Ramsperger-Kassel (RRK) theory of unimolecular reaction.

Or

How are fast reactions determined ? Describe NMR and flow method for the determination of fast reactions.