# M.Sc. CHEMISTRY
## THIRD SEMESTER
## PHYSICAL CHEMISTRY-III
### MSC – 302
[USE OMR FOR OBJECTIVE PART]

SET B

Duration: 1:30 hrs.

Full Marks: 35

## [ Objective ]

Time: 15 mins.

Marks: 10

### *Choose the correct answer from the following:*          1×10=10

1. The relation between the rate constant and size of the molecule for diffusion controlled reaction is
   a. Rate constant is directly proportional to size of the molecule
   b. Rate constant is inversely proportional to size of the molecule
   c. Rate constant is half of the radii of the molecule
   d. No relation

2. The isotope effect is said to be inverse isotope effect if
   a. $K_H/K_D = 1$
   b. $K_H/K_D < 1$
   c. $K_H/K_D > 1$
   d. None of the above

3. The reaction for the deuterated reactant proceeds faster, the common isotope effects values are -
   a. 0.8 to 0.9
   b. 1.0 to 1.2
   c. 0.2 to 0.6
   d. 1.4 to 1.6

4. Molecular reaction dynamics provides insights into
   a. Reaction mechanisms
   b. Energy transfer in reactions
   c. Product distributions
   d. All of the above

5. For a system, the specific heat capacity ($C_v$) for an Einstein model at high temperature is equal to
   a. $1/t$
   b. R
   c. 3R
   d. 2T

6. The symmetrical wave functions of Bosons do not obey---------
   a. Aufbau principle
   b. Pauli's Exclusion principle
   c. Hund's rule of maximum multiplicity
   d. Heisenberg's uncertainty principle

7. In Fermi Dirac statistics the spin of fermion is considered as
   a. 1/2, 1/2
   b. 1/2, 3/2
   c. -1/2, 3/2
   d. -3/2, 3/2

8. For an ideal gas, the molecular partition function (q) in the canonical ensemble that is proportional to the system volume (V)
   a. Vibrational partition function
   b. Rotational partition function
   c. Translational partition function
   d. Electronic partition function

9. The order for characteristic rotational temperature for $H_2$ and $D_2$ is
   a. $H_2 > D_2$
   b. $D_2 > H_2$
   c. $H_2 = D_2$
   d. $D_2 = - H_2$

10. Very powerful flash having energy of the order of $10^5$ J is used to excite the molecules and to dissociate into free radicals. The process is called
    a. Pulse Methods
    b. Flash photolysis
    c. Pulse radiolysis
    d. None of the above

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## ( **Descriptive** )

Time : 1 hr. 15 mins.                                           Marks: 25

*[ Answer question no.1 & any two (2) from the rest ]*

1.  a.  Assuming $hv = k_B T$, prove $q_{vib} = 1/(1-e^{-1})$ for a harmonic       3+2=5
        oscillator with energy levels $E = nhv$ where $n = 1,2,3,....$ etc.

    b.  Write the importance to study the isotope effects in terms of
        kinetic study of a reaction?

2.  a.  Explain four basic differences between Fermi-Dirac and              2+3+3+2
        Maxwell Boltzman statistics.                                        =10

    b.  According to Einstein model, considering average energy,
        $\hat{E} = 3Nhv/(e^{hv/kT}-1)$ and $C_v = (d\hat{E}/dT)_v$ , prove
        $C_v = 3R(hv/RT)^2 . [e^{hv/kT}/(e^{hv/kT}-1)^2$.

    c.  If U is the internal energy then prove $U = NKT^2(\partial lnq/\partial T)_v$ for
        establishing its relation to partition function (q).

    d.  If $\Theta_r$ denotes the characteristics rotational temperature, find
        the magnitude of $[(\Theta_r)_{N2}(\Theta_r)_{O2}/(\Theta_r)^2_{NO}]$.

3.  a.  Write equations for distinguishable and indistinguishable           2+3+3+2
        system in terms of partition function (q) and internal energy       =10
        (U).

    b.  Find the translational partition function ($q_{trans}$) of a hydrogen
        molecule confined in a 100 ml flask at 298K. (Given
        molecular wt. of hydrogen = 2.016 g/mol).

    c.  Write the equation for rotational partition function ($q_r$) if:
        (i) $T < \Theta_r$ and (ii) $T > \Theta_r$

    d.  Find the indistinguishability factor (σ) for $H_2O$ molecule
        with schematic representation.

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4. a. What is the role of solvents while studying the kinetics of a Chemical reaction?      1+1+3+1 +2+2

   b. What are the factors which depend on diffusion of reactant while studying the rate of a chemical reaction?

   c. Derive the equation for diffusion controlled reactions

   $$k_D = (8RT \,/\, 3\eta)$$

   d. Write the advantages of isotope effects over traditional kinetics studies.

   e. How zero point energy is related to isotope effects of reaction rates?

   f. Estimate the diffusion controlled rate constant for the combination of molecules A and B in water at 25 °C. The coefficient of viscosity of water at this temperature is 1cP.

5. a. What is a fast reaction? What are the techniques used to study the kinetics of fast reactions?      2+3+4+1 =10

   b. For the chemical reaction,

   $$A \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} B + C$$
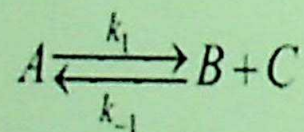
   Derive the relaxation time, $\tau$

   c. Write the short notes for for Fast Reactions
      (i) Flow Methods (ii) Flash photolysis

   d. Write about Potential Energy Surface of a reaction?

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