2025/11

SET A

M.Sc. CHEMISTRY
THIRD SEMESTER
PHYSICAL CHEMISTRY-III
MSC – 302

[USE OMR FOR OBJECTIVE PART]

Duration: 1:30 hrs. **Full Marks: 35**

Objective

Time: 15 mins. **Marks: 10**

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

1. Which of the following distributions applies to indistinguishable particles with no restriction on the number of particles per energy state?
   a. Maxwell–Boltzmann distribution
   b. Fermi–Dirac distribution
   c. Bose–Einstein distribution
   d. Poisson distribution

2. The rotational partition function of a linear molecule at high temperature is proportional to:
   a. $T^{1/2}$
   b. $T^{3/2}$
   c. T^{2}
   d. T

3. Consider N particles at temperature T, pressure P, volume V and chemical potential μ having energy E; the parameters that are kept constant for a canonical ensemble are
   a. N, V, E
   b. N, V, T
   c. N, P, T
   d. μ, V, T

4. The single particle partition function (q) for an ideal gas in a fixed volume V depends on the thermal de-Broglie wavelength (λ) as $q \propto \lambda^{n}$, where value of n is
   a. 3
   b. -1
   c. 1
   d. -3

5. For a monatomic ideal gas, the translational contribution to molar heat capacity C_V is
   a. $\frac{1}{2}\,nR$
   b. R
   c. $\frac{3}{2}\,nR$
   d. 2nR

6. Flow system in which there is no stirring in the reactor and the flow is called
   a. Plug flow
   b. Continuous flow
   c. Stopped flow
   d. Quenched flow

7. 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

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

9. 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

10. 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

-- --- --

Descriptive

Time : 1 hr. 15 mins. **Marks : 25**

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

1. a. How the Reactions in solution are different from the reactions occurred in the gaseous phase while studying the kinetics of the reactions? Explain about Encounter and Cage effect for reactions in solution phase? **3+2=5**

   b. In how many ways can we arrange 4 particles in three energy levels of energy 0, ε, 2ε such that their total energy is 4ε ?

2. a. Assuming H_2 and HD molecules having equal bond length. What is the ratio of the rotational partition functions of these molecules at temperature above 1000 K? **3+3+2+2 =10**

   b. The molecular partition function of a system is given by $q(T) = \left(\frac{k_B T}{hc}\right)^{3/2} \left(\frac{8\pi^3 m k_B T}{h^2}\right)^{3/2}$. Calculate the heat capacity at constant volume.

c. Calculate the number of ways of distributing 20 identical objects into the boxes, with the arrangements 2, 0, 3, 5, 10.

d. What is the symmetry number (σ) for the molecules H_2 and NH_3?

3. a. Write two differences between canonical and grand canonical ensembles. 2+2+4+2 =10

b. Write Sackur–Tetrode equation for the entropy of a monatomic ideal gas.

c. Calculate the translational partition function for one molecule in a cubic volume $V = 1.00 \times 10^{-3}$ m^3 at T = 300 K. Use a diatomic molecule of mass m = 28 amu (1 amu = $1.66053906660 \times 10^{-27}$ kg).

d. A system has partition function $q(T) = aT^{3/2}$ with a constant). Using $U = kT^2(\partial \ln q/\partial T)$, show that $U = \frac{3}{2}kT$.

4. a. What are the factors which depend on diffusion of reactant while studying the rate of a chemical reaction? 1+3+3+1 +2=10

b. Derive the Double Sphere model while studying the kinetics of influence of solvent on an ionic reaction.

c. Derive the below equation for diffusion controlled reactions

$$K_D = \frac{8RT}{3\eta}$$

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

e. 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,

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

Derive the relaxation time, τ

c. Write the short notes for the following methods while studying the kinetics of fast reactions -

(i) Flow Methods (ii) Flash photolysis

d. Write about Potential Energy Surface of a reaction?

= = *** = =