

**M. SC. (CHEMISTRY)/
M. SC. (ANALYTICAL CHEMISTRY)
(MSCCHEM/MSCANCHEM)
Term-End Examination
December, 2025**

MCH-013 : GENERAL PHYSICAL CHEMISTRY

Time : 2 Hours

Maximum Marks : 50

*Note : Question No. 1 is compulsory. Attempt any **four** questions from question nos. 2 to 7.*

Use the following values wherever required :

$$k_B = 1.38 \times 10^{-23} \text{ JK}^{-1}; h = 6.626 \times 10^{-34} \text{ Js};$$

$$N_A = 6.022 \times 10^{23} \text{ mol}^{-1},$$

$$R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1};$$

$$1 \text{ cm}^{-1} = 1.98 \times 10^{-23} \text{ J}$$

1. Attempt any *five* questions from the following : 5×2=10

- (i) Define molecular partition function.
- (ii) What are the characteristics of the unimolecular reactions ?
- (iii) Outline the advantage of the stopped flow method over continuous flow method in studying fast reactions.
- (iv) Write any *two* limitations of the Debye-Hückel's law. In which type of solution does this law hold good ?
- (v) At high pressure the thermal conductivity of gases is independent of pressure. Explain.
- (vi) What is the difference between diffraction phenomenon and diffraction pattern ?

- (vii) Define the flux in the context of transport phenomenon and outline its significance.
2. (a) Draw a schematic diagram of potential energy profiles of catalyzed and uncatalyzed reactions. 2
- (b) Four moles of an ideal gas undergo isothermal expansion from 10 m^3 to 100 m^3 at 300 K . Calculate the change in Gibbs' energy for the process. 2
- (c) Write the steps involved in the Lindemann-Christiansen's theory of unimolecular reaction. Also give the rate equations of each step. 3
- (d) Show that for an ideal gas in a mixture, the partial molar volume is equal to RT/P . 3

3. (a) In what way is electrical transport different from the other type of transport phenomenon ? 2
- (b) Calculate the Miller indices of crystal planes which cut through the crystal axes respectively at (i) $(6a, 3b, 3c)$ and (ii) $(1, 1, 1)$. 2
- (c) At room temperature, which among N_2 and H_2 will have a higher translational partition function ? Justify your answer. 2
- (d) The relaxation time for a given fast reaction $A \rightleftharpoons B$ is found to be $5 \mu s$ from the temperature jump method and the

equilibrium constant is 1.0×10^{-3} .

Calculate the rate constants for the forward and the reverse reactions. 4

4. (a) Define mean free path. How does it depend on the (i) pressure and (ii) size of the molecule ? 1+1+1

(b) Using Stirling approximation, calculate the % error introduced in computing the value of $6 !$ [Use $\ln 2 = 0.69$ and $\ln 3 = 1.1$]. 3

(c) Calculate mean ionic activity coefficient, a_{\pm} of NaCl at a molarity of 0.01 in aqueous solution at 25°C . [Use $\text{antilog}(-0.0509) = 0.9$] 4

5. (a) In Michaelis-Menten mechanism of an enzyme substrate system, the reaction rate changes from first order to the zero order. Give the physical reason for this.

3

- (b) Define Fick's second law of diffusion. Outline its significance in terms of curvature of the concentration gradient.

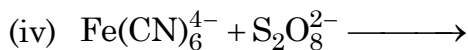
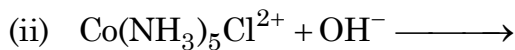
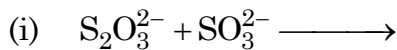
1+2

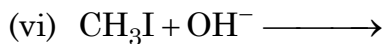
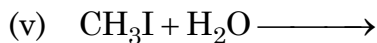
- (c) Derive rate equation for the kinetics of a unimolecular catalytic reaction involving a single species adsorbed on the surface of the catalyst. Comment on the order of the reaction at (i) low and (ii) high concentration of the reactant. 4

6. (a) Draw a schematic diagram of the tetrahedral and octahedral void in a cubic close packed structure. 2

(b) The parameters of an orthorhombic unit cell are $a = 50$ pm, $b = 100$ pm, $c = 150$ pm. Determine the spacing between the (1, 2, 3) planes. 3

(c) Predict the nature (slope) of Bronsted-Bierrum plot for any *five* of the following : $1 \times 5 = 5$





7. (a) What is the Debye length in Debye-Hückel's theory? 2

(b) Based on given values, predict whether the following processes will be spontaneous or non-spontaneous at 300 K : 2

(i) $\Delta U = 70 \text{ kJ mol}^{-1}$ and

$$\Delta S = 80 \text{ JK}^{-1} \text{ mol}^{-1}$$

Or

(ii) $\Delta H = 10 \text{ kJ mol}^{-1}$ and

$$\Delta S = -25 \text{ JK}^{-1} \text{ mol}^{-1}$$

- (c) How many possible ways are there for distributing five indistinguishable particles among five energy levels with energies of $0E$, $1E$, $2E$, $3E$, $4E$, $5E$, where the total energy of the system equals to $5E$? Calculate the probability of each configuration. 1+4+1

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