

**M. SC. (CHEMISTRY)/M. SC. IN  
ANALYTICAL CHEMISTRY  
(MSCCHEM AND MSCANCHEM)**

**Term-End Examination**

**June, 2025**

**MCH-013 : GENERAL PHYSICAL CHEMISTRY**

*Time : 2 Hours*

*Maximum Marks : 50*

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

Use the following values whenever it requires :

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

$$N_A = 6.022 \times 10^{23} \text{ mol}^{-1}, R = 8.314 \text{ JK}^{-1}$$

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

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

- (i) Outline the advantages of the stopped flow method over continuous flow methods.
- (ii) Write any *two* limitations of the Debye-Hückel's law. In which type of solution this law holds good ?
- (iii) What is the mechanism of enzyme action which involves the binding of the substrates ?
- (iv) Write any *two* limitations of Lindemann's theory of unimolecular reaction.
- (v) What are amorphous materials ? Give any *two* examples.
- (vi) What is the difference between isobaric and isochoric processes ?

- (vii) Write Stirling's approximation and outline its limitations.
- (viii) Define the flux in transport phenomenon and outline its significance.
2. (a) Write the expression for drift speed in terms of viscosity  $\eta$  and name the terms involved. 2
- (b) Can a catalyst alter the equilibrium constant for a reaction ? Justify your answer. 2
- (c) Calculate the mean activity coefficient,  $\gamma_1$  of 0.001 M aqueous solution of a  $\text{Na}_2\text{SO}_4$  at  $25^\circ\text{C}$ . 3
- (d) Using Stirling's approximation, calculate the % error introduced in computing the value of  $6!$  [Use  $\ln 2 = 0.7$  and  $\ln 3 = 1.1$ ]. 3

3. (a) Define Fick's second law of diffusion and outline its significance in terms of curvature of the concentration gradient. 3
- (b) The relaxation time for a given fast equilibrium reaction  $A \xrightleftharpoons[k_{-1}]{k_1} B$  is found to be  $5 \mu\text{s}$  from temperature jump method. If the equilibrium constant is  $1.4 \times 10^{-3}$ , calculate the rate constant for forward and reverse reactions. 3
- (c) For an isothermal and isobaric process the change in entropy and enthalpy are found to be  $175 \text{ J/K}$  and  $54 \text{ kJ/mol}$ , respectively. Calculate the following : 4
- (i) Whether this process is spontaneous at  $57^\circ\text{C}$  ?

- (ii) At which temperature the system will attain equilibrium, assuming that the enthalpy and entropy changes are not affected by the change in the temperature ?
4. (a) In a binary mixture of an ideal gas in which  $n_A = 7.5n_B$ . If the partial molar volume of B is decreased by  $0.05 \text{ m}^3/\text{mol}$ , what would be the change in partial molar value of A ? 2
- (b) Write the mathematical expression of most probable molecular speed,  $u_{mp}$  and name the terms involved. 2
- (c) Calculate the angle (in  $\sin^{-1} \theta$ ) at which the second order reflection will occur when X-rays of wavelength  $0.16 \text{ nm}$  are diffracted by the atom of a crystal, given that the inter-planar distance is  $0.4 \text{ nm}$ . 2

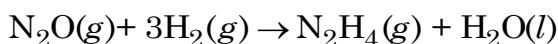
- (d) Derive the relationship between the term activation energy in Arrhenius equation and the critical barrier energy proposed in collision theory. 4
5. (a) Write the rate determining step under high pressure condition for Lindemann unimolecular reaction. 2
- (b) Why the pressure-jump method is better for studying the gaseous system ? Give reasons. 2
- (c) Calculate the relative population of two energy levels separated by  $1000\text{ cm}^{-1}$  at  $27^\circ\text{C}$ .

*Or*

Calculate the rotational partition function at 500 K for a diatomic molecule having moment of inertia of  $2.70 \times 10^{-43}\text{ kgm}^2$ . 3

- (d) For Michaelis-Menten mechanism for enzyme substrate system, the reaction rate changes from first order to the zero order. Give the physical reason for this. 3
6. (a) Write the physical significance of turnover number in Michaelis-Menten mechanism. 2
- (b) Draw a labelled schematic diagram showing the potential energy profiles of catalyzed and uncatalyzed reactions. 2
- (c) What are the basic assumptions of the Debye-Hückel's theory ? Why do we use water as an electrolyte in this model ? 3
- (d) At room temperature, sodium crystallizes in a body centered cubic cell with  $a = 0.4$  nm. Calculate the density of sodium. [Given : Molar mass of sodium = 23.0 g/mol.] 3

7. (a) Calculate the standard Gibbs energy change for the following reaction at 300 K :



Given that :

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	$\text{N}_2\text{O}$	$\text{H}_2$	$\text{N}_2\text{H}_4$	$\text{H}_2\text{O}$
$\Delta H^\circ_f (\text{kJ/mol})$	80	0	50	– 240
$S^\circ (\text{J/K})$	220	130	120	190

- (b) Derive the translational partition function for a particle of mass  $m$  confined into a one-dimensional box of length  $l$ , where the energy of the particle is given as :

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$$\epsilon_{n, \text{trans}} = \frac{n^2 h^2}{8ml^2}$$

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