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MCH–013

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*

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

Use the following values whenever it requires :

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

$N_A = 6.022 \times 10^{23} mol^{-1}$, $R = 8.314\ JK^{-1}$ mol^{-1}; $1\ cm^{-1} = 1.98 \times 10^{-23} J$.

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 η 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, γ_1 of 0.001 M aqueous solution of a Na_2SO_4 at 25°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 $A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} B$ is found to be 5 μs from temperature jump method. If the equilibrium constant is 1.4×10^{-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 J/K and 54 kJ/mol, respectively. Calculate the following : 4

(i) Whether this process is spontaneous at 57°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 $n_A = 7.5 n_B$. If the partial molar volume of B is decreased by $0.05\ m^3/mol$, 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 nm are diffracted by the atom of a crystal, given that the inter-planar distance is 0.4 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 cm^{-1} at 27°C.

Or

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

(d) For Mechaelis-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 :

$$N_2O(g) + 3H_2(g) \rightarrow N_2H_4(g) + H_2O(l)$$

Given that : 5

	N_2O	H_2	N_2H_4	H_2O
$\Delta H°_f$ (kJ/mol)	80	0	50	– 240
S°(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 : 5

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

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