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MCH-013

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

Term-End Examination

December, 2024

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 :

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

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

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

1. Attempt any *five* questions from the following :

$$5 \times 2 = 10$$

- (i) Write the expression of chemical potential
and give its physical significance.

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- (ii) Outline any *two* limitations of the Collision theory.
 - (iii) Define magnetic susceptibility. What is its sign for (a) diamagnetic, and (b) paramagnetic substances ?
 - (iv) List the properties of the solvents that influence the kinetics of reactions.
 - (v) How do the pH and temperature affect the enzyme activity for a reaction ?
 - (vi) What is the mean free path of a gas molecule ? How does it depend on pressure and size of the molecule ?
 - (vii) What are the homogeneous and heterogeneous catalysis ? Explain with the help of examples.
 - (viii) What are true and potential electrolytes ?
2. (a) Write the expressions for the rate of adsorption and desorption when the adsorption of the reactant molecule is accompanied by its dissociation on the surface.

(b) Give the expression for thermal conductivity and identify the terms involved it. 2

(c) Calculate the translational partition function for benzene (molar mass = 78.0 g/mol) in a volume of 1 m³ at 25°C. 3

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

(d) In an accelerated flow experiment the spectrophotometric concentration determinations are made at a fixed point located at 2 cm from the mixing chamber along the observation tube. If the initial flow rate of 2.0 ms⁻¹, is accelerated progressively to 5.0 and 10.0 ms⁻¹, calculate the corresponding reaction times. 3

3. (a) State the Curie-Weiss' law and give its mathematical expression. 2

(b) For hydrogen gas, calculate the most probable velocity at 0°C. Consider the molar mass of H₂ = 2 g/mol. 2

$$[\text{Given } R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}]$$

- (c) Consider a solution containing glucose and hemoglobin, which one of these will have a higher diffusion coefficient ? Justify your answer. 2
- (d) Calculate the number of microstates and their probabilities for each configuration of distributing 3 distinguishable particles among 3 energy levels with energies of $0\epsilon_0$, $1\epsilon_0$, $2\epsilon_0$ and $3\epsilon_0$, such that total energy of the system equals to $3\epsilon_0$. 4
4. (a) 2.0 moles of pure ethanol is added to 2.0 moles of pure water. If the partial molar volumes of ethanol and water for $\chi_A = \chi_B = 0.5$ are $50.5 \text{ cm}^3/\text{mol}$ and $15.5 \text{ cm}^3/\text{mol}$, respectively, calculate the total volume of the solution. 3
- (b) Draw a schematic Lineweaver-Burk plot for non-competitive enzyme inhibition at three concentrations A, B and C that are in the order $[A] > [C] > [B]$. How can we calculate $R_{\max}$ from this plot ? 3

- (c) A solution contains 29.0 g of NaCl and 3.99 g of AlCl_3 in 500 g of water. Calculate the ionic strength of this solution. 4

[Molar mass of NaCl = 58 g/mol;
Molar mass of AlCl_3 = 133 g/mol]

5. (a) List the different methods of experimental determination of activity coefficients. Which of these is most convenient ? 2

- (b) For an enzyme-substrate system, obeying the simple Michaelis-Menten mechanism, the rate of product formation when the substrate concentration is very high has a limiting value 0.03 mol dm^{-3} . At a substrate concentration of 0.300 mg dm^{-3} , the rate is half this value. Calculate k_1/k_{-1} assuming that $k_2 \gg k_{-1}$. 4

- (c) Calculate the activation energy of a reaction whose rate constant is tripled by 10 K rise in temperature from 300 K. 4

[Given $R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}$ and $\ln 3 = 1.1$]

6. (a) Write the steps involved in the Hinshelwood's theory of unimolecular reactions. 2

(b) Calculate the Miller indices of crystal planes which cut through the crystal axes respectively at (i) $(2a, 3b, 5c)$ and (ii) $(-2a, 4b, -3c)$. 2+2

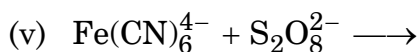
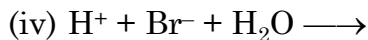
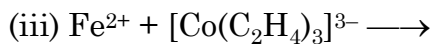
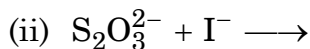
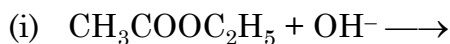
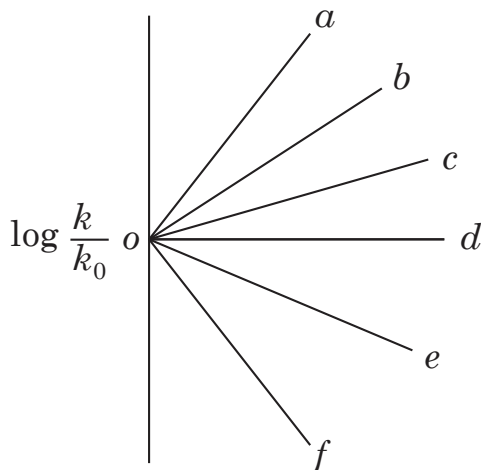
(c) The Gibbs energy changes for a process at 25°C and 35°C are -85.1 kJ and -80.2 kJ , respectively. Calculate the change in enthalpy for the process at 30°C . 4

7. (a) What is the significance of the Maxwell relations. Derive the following expressions for Maxwell relation by using suitable Gibbs equation : 1+2+2

$$(i) \quad \left(\frac{\partial S}{\partial V} \right)_T = \left(\frac{\partial P}{\partial T} \right)_V \quad \text{or} \quad \left(\frac{\partial V}{\partial T} \right)_P = - \left(\frac{\partial S}{\partial P} \right)_T$$

$$(ii) \quad \left(\frac{\partial T}{\partial V} \right)_S = - \left(\frac{\partial P}{\partial S} \right)_V \quad \text{or} \quad \left(\frac{\partial V}{\partial S} \right)_P = - \left(\frac{\partial T}{\partial P} \right)_S$$

- (b) Consider the following schematic Bronsted-Bjerrum plots for different ionic reactions given below :



(A) Match the plots with the corresponding ionic reaction : 3

(i) a

(ii) b

(iii) c

(iv) d

(v) e

(vi) f

(B) From the plot, answer the following questions : 2

(i) Which reaction would have the most negative slope ?

(ii) For which reaction(s), the rate constant is independent of ionic strength ?

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