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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 × 10^{-23} JK^{-1}; h = 6·626 × 10^{-34} Js; N_A = 6·022 × 10^{23} mol^{-1}; R = 8·314 JK^{-1} mol^{-1}; 1 cm^{-1} = 1·98 × 10^{-23} J.

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

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

(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. 2

(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 m^3 at 25°C. 3

[$k_B = 1{\cdot}38 \times 10^{-23}$ JK^{-1}; $h = 6{\cdot}626 \times 10^{-34}$ 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 H_2 = 2 g/mol. 2

[Given R = 8.314 JK^{-1} 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 propabilities 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 cm^3/mol and 15.5 cm^3/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 $k_2 >> k_{-1}$. 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 JK^{-1} 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

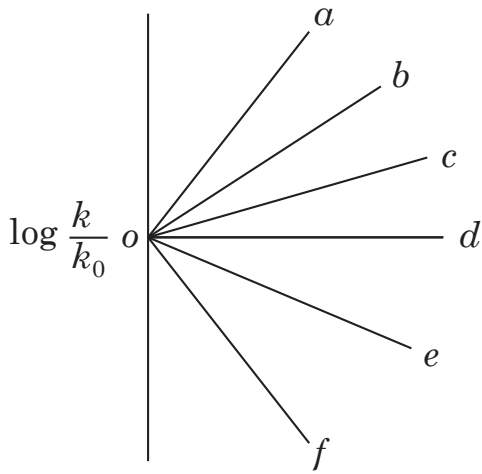
(c) The Gibbs energy changes for a process at 25°C and 35°C are – 85·1 kJ and – 80·2 kJ, respectively. Calculate the change in enthalpy for the process at 30°C. 4

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

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

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



(i) $CH_3COOC_2H_5 + OH^- \longrightarrow$

(ii) $S_2O_3^{2-} + I^- \longrightarrow$

(iii) $Fe^{2+} + [Co(C_2H_4)_3]^{3-} \longrightarrow$

(iv) $H^+ + Br^- + H_2O \longrightarrow$

(v) $Fe(CN)_6^{4-} + S_2O_8^{2-} \longrightarrow$

(vi) $[Co(NH_3)_5\ Br]^{2+} + Hg^{2+} \longrightarrow$

(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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