No. of Printed Pages : 9

MCH–013

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 :

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

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

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

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

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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 μs 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 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 : 1×5=5

(i) $S_2O_3^{2-} + SO_3^{2-} \longrightarrow$

(ii) $Co(NH_3)_5Cl^{2+} + OH^- \longrightarrow$

(iii) $CH_2ClCOO^- + OH^- \longrightarrow$

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

(v) $CH_3I + H_2O \longrightarrow$

(vi) $CH_3I + OH^- \longrightarrow$

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

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

Or

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

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

(c) How many possible ways are there for distributing five indistinguishable particles among fives 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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