

- (b) Construct cell having the reaction $\text{H}_2(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O}(\text{l})$. Write half-cell reactions and expression for cell potential. 5
- (c) Why does a potential develop at the boundary of two electrolyte solutions having same chemical composition but different concentrations? How can this potential be removed? 5
7. (a) Write the electrode reactions, transference reactions and cell reaction and calculate cell potential for the cell 5
 $\text{Pb}/\text{PbSO}_4(\text{s}), \text{CuSO}_4(0.2\text{mol Kg}^{-1}, \gamma_{\pm} = 0.110) ; \text{CuSO}_4(0.02\text{mol kg}^{-1}, \gamma_{\pm} = 0.32)/\text{PbSO}_4(\text{s})/\text{Pb}$ given that $t_{\text{Cu}^{2+}} = 0.37$.
- (b) Compute standard reduction potential for the reaction $\text{Cr}^{2+} + 2\text{e} \rightarrow \text{Cr}$ from the following data and derive the Nernst equation for the half cell with above reaction. 5
 $\text{Cr}^{3+} + 3\text{e} \rightarrow \text{Cr} \quad E^0 = -0.74\text{V}$
 $\text{Cr}^{3+} + \text{e} \rightarrow \text{Cr}^{2+} \quad E^0 = -0.74\text{V}$
- (c) What are reference electrodes? Give an example of reference electrode along with an expression for its reduction potential. Give one application of a reference electrode. 5
8. (a) Consider the following reaction $\text{A} \xrightarrow{k_1} \text{B} \xrightarrow{k_2} \text{C}$. If $k_1 = 40\text{s}^{-1}$ and $k_2 = 15\text{s}^{-1}$ and the reaction is carried out with pure A at initial concentration of 1 mol dm^{-3} what will be the composition of the reaction mixture after an interval of 10 mins? 5
- (b) Describe the salient features of collision theory for bimolecular reactions? 5
- (c) What are secondary cells? Explain its working using a suitable example. 5

[This question paper contains 4 printed pages]

Your Roll No. :

Sl. No. of Q. Paper : 2031

Unique Paper Code : 2172012403

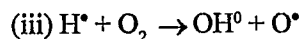
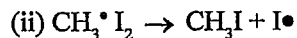
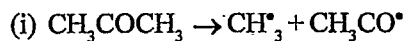
Name of the Course : DSC : B.Sc.(H.)
ChemistryName of the Paper : Electrochemical cells
Chemical Kinetics and
Catalysis

Semester : IV

Time : 3 Hours Maximum Marks : 90

Instructions for Candidates :

- (a) Write your Roll No. on the top immediately on receipt of this question paper.
- (b) Attempt any Six questions in all.
- (c) Question NO.1 is compulsory.
- (c) Use of scientific calculators is allowed.
1. Explain giving reason. Attempt any five. $3 \times 5 = 15$
- (a) Why is the polarity of electrodes reversed in galvanic and electrolytic cells?
- (b) Will Pb react with AgNO_3 if $E^0_{\text{Ag}^+/\text{Ag}} = 0.799\text{V}$ and $E^0_{\text{Pb}^{2+}/\text{Pb}} = -0.126\text{V}$
- (c) Why is there a potential jump at the equivalence point in the titration of $\text{K}_2\text{Cr}_2\text{O}_7$ with Mh 's salt?
- (d) What will be the order of the reaction $\text{A} + 2\text{B} \rightarrow \text{C}$?
- (e) Why does the rate of a reaction usually increase on increasing temperature?
- (f) Identify the following as initiation, propagation, branching or termination reaction



2. (a) The following data were obtained for dimerization of

butadiene according to the equation $\text{C}_4\text{H}_6 \rightarrow \frac{1}{2}\text{C}_8\text{H}_{12}$ 5

t/min 0 6.12 12.18 17.30 29.18

P_t/torr 632 606.6 584.2 567.3 535.4

Show that the reaction is of second order and determine the rate constant.

- (b) Describe Lindemann mechanism for unimolecular reactions. Under what conditions does the reaction becomes of second order? 5

- (c) Explain the terms enzyme selectivity and specificity giving suitable examples. 5

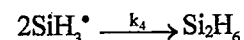
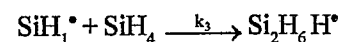
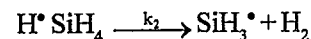
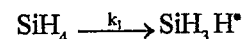
3. (a) The half life of a first order decomposition reaction is 363 min at 298K and the energy of activation is 217.6 kJmol⁻¹. Calculate the time required for 75% of the reactant to be decomposed at 650K. 5

- (b) Setup mechanism of a unimolecular surface catalyzed reaction and derive its rate law. 5

- (c) Explain the following briefly giving example of each : catalyst, promoter and Inhibitor. 5

4. (a) The enzyme catalase catalyses the reaction $2\text{H}_2\text{O}_2(\text{aq}) \rightarrow 2\text{H}_2\text{O}(\text{l}) + \text{O}_2(\text{g})$. It has a Michaelis Menten constant of $25 \times 10^{-3} \text{ mol dm}^{-3}$ and a turnover number of $4 \times 10^7 \text{ s}^{-1}$. If the total concentration of the enzyme is $1.6 \times 10^{-8} \text{ mol dm}^{-3}$ and the initial substrate concentration is $4.32 \times 10^{-6} \text{ mol dm}^{-3}$ calculate the initial rate and the maximum rate of the reaction. 5

- (b) The following mechanism has been suggested for the pyrolysis of monosilane 5



Show that

$$\frac{d[\text{H}_2]}{dt} = \frac{d[\text{Si}_2\text{H}_6]}{dt} = \left\{ k_3 \left(\frac{k_1}{k_4} \right)^{\frac{1}{2}} [\text{SiH}_4]^{\frac{1}{2}} + k_1 \right\} [\text{SiH}_4]$$

- (c) What are stationary and non-stationary chain reactions? Explain briefly. 5

5. (a) Consider the reaction $2\text{MnO}_4^- + 6\text{H}^+ + 5\text{H}_2\text{C}_2\text{O}_4 \rightarrow 2\text{Mn}^{2+} + 8\text{H}_2\text{O} + 10\text{CO}_2$. Construct the cell with this cell reaction, write electrode reactions and calculate the standard equilibrium constant given that $E^\circ_{\text{MnO}_4^-/\text{Mn}^{2+}} = 1.51\text{V}$ and

$$E^\circ_{\text{H}_2\text{C}_2\text{O}_4/\text{CO}_2} = -0.49\text{V}$$

- (b) Write activity of $(\text{NH}_4)_2\text{SO}_4$ in terms of its molality. If molality of a solution of $(\text{NH}_4)_2\text{SO}_4$ is 1.2 mol kg^{-1} and the mean activity coefficient is 0.85 calculate the activity. 5

- (c) Explain the working of a potentiometer for measurement of cell potential. Why is it essential to use potentiometer instead of a voltmeter for measuring cell potential? 5

6. (a) For the cell $\text{Pt}/\text{H}_2(\text{g}, 1\text{bar})/\text{HCl}(\text{aq})/\text{AgCl}(\text{s})/\text{Ag}$ $E^\circ = 0.222\text{V}$ and $E_{\text{cell}} = 0.332\text{V}$ at 298 K. Calculate the pH of the solution? Assume that the activities can be replaced by concentration. 5