(b) Construct cell having the reaction $H_2(g) + ½ O_2(g) \rightarrow H_2O(I)$. 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

Pb/PbSO4(s), $CuSO_4$(0.2mol Kg^{-1}, $\gamma\mp = 0.110$) : $CuSO_4$(0.02mol kg^{-1}, $\gamma\mp = 0.32$)/$PbSO_4$(s)/Pb given that $t_{cu^{2+}} = 0.37$.

(b) Compute standard reduction potential for the reaction $Cr^{2+} + 2e \rightarrow Cr$ from the following data and derive the Nernst equation for the half cell with above reaction. 5

$Cr^{3+} + 3e \rightarrow Cr \quad E^0 = -0.74V$

$Cr^{3+} + e \rightarrow Cr^{2+} \quad E^0 = -0.74V$

(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 $A \xrightarrow{k_1} B \xrightarrow{k_2} C$. If $k_1 = 40s^{-1}$ and $k_2 = 15s^{-1}$ and the reaction is carried out with pure A at initial concentration of 1 $moldm^{-3}$ 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.) Chemistry**

Name 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.** 3×5=15

(a) Why is the polarity of electrodes reversed in galvanic and electrolytic cells ?

(b) Will Pb react with $AgNO_3$ if $E^0_{Ag+/Ag} = 0.799V$ and $E^0_{Pb2+/Pb} = -0.126V$

(c) Why is there a potential jump at the equivalence point in the titration of $K_2Cr_2O_7$ with Mh's salt ?

(d) What will be the order of the reaction $A + 2B \rightarrow C$?

(e) Why does the rate of a reaction usually increase on increasing temperature ?

(f) Identify the following as initiation, propagation, branching or termination reaction

P.T.O.

(i) $CH_3COCH_3 \rightarrow CH^{\bullet}_3 + CH_3CO^{\bullet}$

(ii) $CH_3^{\bullet} I_2 \rightarrow CH_3I + I\bullet$

(iii) $H^{\bullet} + O_2 \rightarrow OH^0 + O^{\bullet}$

2. (a) The following data were obtained for dimerization of butadiene according to the equation $C_4H_6 \rightarrow \frac{1}{2}C_8H_{12}$ 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 $2H_2O_2(aq) \rightarrow 2H_2O(I)+O_2(g)$ It has a Michaelis Menten constant of 25×10^{-3} moldm^{-3} and a turnover number of $4 \times 10^7 s^{-1}$. If the total concentration of the enzyme is 1.6×10^{-8} moldm^{-3} and the initial substrate concentration is 4.32×10^{-6} moldm^{-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

$SiH_4 \xrightarrow{k_1} SiH_3H^{\bullet}$

$H^{\bullet} SiH_4 \xrightarrow{k_2} SiH_3^{\bullet} + H_2$

$SiH_1^{\bullet} + SiH_4 \xrightarrow{k_3} Si_2H_6H^{\bullet}$

$2SiH_3^{\bullet} \xrightarrow{k_4} Si_2H_6$

Show that

$$\frac{d[H_2]}{dt} = \frac{d[Si_2H_6]}{dt} = \left\{k_3\left(\frac{k_1}{k_4}\right)^{\frac{1}{2}}[SiH_4]^{\frac{1}{2}} + k_1\right\}[SiH_4]$$

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

5. (a) Consider the reaction $2MnO_4^- + 6H^+ + 5H_2C_2O_4 \rightarrow 2Mn^{2+} + 8H_2O + 10CO_2$. Construct the cell with this cell reaction, write electrode reactions and calculate the standard equilibrium constant given that $E^0_{MnO_4^-/Mn^{2+}} = 1.51V$ and $E^0_{H_2C_2O_4/CO_2} = -0.49V$

(b) Write activity of $(NH_4)_2SO_4$ in terms of its molality. If molality of a solution of $(NH_4)_2SO_4$ 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 pt/H_2(g.1bar)/HCl(aq)/AgCl(s)/Ag $E^0 = 0.222V$ and $E_{cell} = 0.332V$ at 298 K. Calculate the pH of the solution ? Assume that the activities can be replaced by concentration. 5