[This question paper contains 8 printed pages]

Your Roll No.	:	.....
Sl. No. of Q. Paper	:	**5665 I**
Unique Paper Code	:	2172012403
Name of the Paper	:	DSC : Electrochemical Cells, Chemical Kinetics and Catalysis
Name of the Course	:	**B. Sc. (Hons.) Chemistry**
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 **(SIX)** Questions in all. **First** question is Compulsory.

(c) Use of a Scientific calculator is permitted.

(d) Graph paper will be provided.

1. Attempt any **Five** parts.

(a) What is liquid junction potential ? Why is NH_4NO_3 salt a good choice for making a salt bridge ?

(b) Construct the cell in term of cell notation using the following cell reaction :

$Fe(OH)_3(s) \rightarrow Fe^{3+}(aq) + 3OH^-(aq)$

(c) The standard redox potential of the water oxidation to dioxygen is -1.23 V.

$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$. Calculate the redox potential of the same reaction at pH = 7

(d) The acid hydrolysis of the same quantity of ester is done separately with equal normal solutions of HCl & H_2SO_4, it is given that $\frac{[H^+]_{HCl}}{[H^+]_{H_2SO_4}} = \frac{k_{HCl}}{k_{H_2SO_4}}$, explain whether the value of $k_{HCL}/k_{H_2SO_4}$ is less than, equal or greater than one.

(e) What are stationary and non-stationary chain reactions ? Discuss briefly.

(f) Ionic reactions are fast while molecular reactions are slow. Why ?

(g) Discuss, using potential energy barrier graph, the effect of catalyst on rates of the reaction.

5×3=15

2. (a) Given that :

$Fe^{3+}(aq) + 3e^- \rightarrow Fe(s)$; $E_1^0 = -0.04$ V

$Fe^{2+}(au) + 2e^- \rightarrow Fe(s)$; $E_2^0 = -0.44$V

Determine the potential of the following half-cell reaction.

$Fe^{3+}(aq) + e^- \rightarrow Fe^{2+}(aq)$

(b) What is the basic principle of potentiometric titration ? How is it applied to acid – base titration ?

(c) The standard potential of a cell "$Pt|H_2(g).|HBr(aq)|Ag$" was found to vary as $E^0(volt) = 0.01 - 1 \times 10^{-4}(T - 298) - 2 \times 10^{-6}(T - 298)^2$. Calculate the standard reaction entropy, ΔS^0 and enthalpy, ΔH^0 at 25°C.

3×5=15

3. (a) Given that the standard potential of the following half – cell reaction at 25°CK

$Cu^+(aq) + e^- \rightarrow Cu(s)$; $E_1^0 = 0.52V$

$Cu^{2+}(aq) + e^- \rightarrow Cu^+(aq)$; $E_2^0 = 0.16V$

Calculate ΔG^0 (in kJ) for the following reaction :

$2Cu^+(aq) \rightarrow Cu(s) + Cu^{2+}$

(b) A platinum electrode is immersed in a solution containing 0.1 M Fe^{2+} and 0.1 M Fe^{3+}. Its potential is found to be 0.77 V against SHE. Under standard conditions, the activity coefficient is unity. What is the potential of the electrode when the concentration of Fe^{3+} is increased to 1 M at 25°C.

(c) The cell constructed by the half cells.

$$E^0_{(Cd^{2+}|Cd)} = -0.403V \ \& \ E^0_{(I^-|AgI|Ag)} = -0.152V$$

has the potential of 0.29V at 25°C. Determine the activity of CdI_2 solution.

3×5=15

4. (a) Determine the formation of the complex, $Zn(NH_3)_4^{2+}$, Provided that

$$(a)\ Zn(s) + 4NH_3 \rightarrow Zn(NH_3)_4^{2+} + 2e^-;\ E^0 = 1.03V$$
$$(b)\ Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-;\qquad E^0 = 0.76V$$

(b) How do we use quinhydrone electrode for determination of pH of a given solution ? What are advantages and disadvantages of quinhydrone electrode ?

(c) Construct a concentration cell without transference using silver – silver chloride electrode and derive the equation for determination of cell potential of the concentration cell. 3×5=15

5. (a) The reaction

$$\nu_1 A + \nu_2 B \rightarrow \text{Products}$$

is a first order reaction with respect to A & B. Write down its differential rate law & deduce from it the Integrated rate law. What is the unit of rate constant in this case ?

(b) Suppose that in a consecutive reaction $A \xrightarrow{k_1} B \xrightarrow{k_1'} C, k_1' >> k_1$ prove that reaction with the smaller rate constant is the rate determining step. Given :

$$[C] = [A]_0 \left\{ 1 - \frac{1}{k_1' - k_1} \left(k_1' e^{-k_1 t} - k_1 e^{-k_1' t} \right) \right\}$$

(c) Write a short note on Lindemann Mechanism. 3×5=15

6. (a) Compare the rate constants as given by Arrhenius equation & the collision theory and there by show that

$$E_\alpha = E_0 + \frac{RT}{2} \quad \& \quad A = pN_A \frac{Z_{AB}}{N_A^* N_B^*} e^{1/2}$$

(b) Using the following data, obtain the differential rate expression for the following reaction & the value of rate constant

$CO + Cl_2 \rightarrow COCl_2$

Experiment No.	1	2	3	4
$[CoCl_2]_0$ / mol dm^{-3}	0.16	0.16	0.04	0.04
$[Cl_2]_0$ / mol dm^{-3}	0.16	0.04	0.16	0.04
r_0 / mol dm^{-3} s^{-1}	1.92×10^{-2}	9.6×10^{-3}	4.8×10^{-3}	2.4×10^{-3}

(c) Discuss the conditions under which the equilibrium approximation & steady state approximation is used while elucidating the mechanisms of the complex reactions. Support your answer with any general reaction in each case 3×5=15

7. (a) The following mechanism has been proposed for the decomposition of N_2O_5:

(i) $N_2O_5 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} NO_2 + NO_3$

(ii) $NO_3 + NO_2 \xrightarrow{k_2} NO + NO_2 + O_2$

(iii) $NO_3 + NO \xrightarrow{k_3} 2\,NO_2$

Show that rate law is $\frac{d[O_2]}{dt} = k[N_2O_5]$

(b) The bimolecular decomposition of Hydrogen Iodide is given by the equation

$2HI \rightarrow H_2 + I_2$

Assuming a collision diameter of 0.35×10^{-8} cm and an activation energy of 183.90 kJ mol^{-1} for the reaction, calculate (i) the collision rate, (ii) the rate of reaction and (iii) the rate constant for the above reaction at 500 K and one atmosphere pressure.

(c) Write a short note on Theory of Absolute Reaction rates. 3×5=15

8. (a) An acid, HA catalyses the substrate, S to products as follows :

$$S + H \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} SH^+ + A^{-1}$$

$$SH^+ + H_2O \xrightarrow{k_2} P + H_3O^+$$

Derive the rate law for the reaction. State when it becomes an example of "general acid catalysis" and it is *"specific hydrogen ion catalysis"*.

(b) Describe any five characteristics of catalyst.

(c) The reaction rate of enzyme – catalysed reaction changes from first – order to zero – order as the substrate concentration is increased. Discuss the reason on the basis of active sites & Explain using the graph of rate versus substrate concentration.

3×5-=15

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