

[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 :

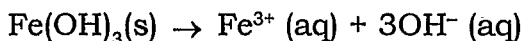
- (a) Write your Roll No. on the top immediately on receipt of this question paper.
- (b) Attempt **(SIX)** Questions in all. **First** question is Compulsory.
- (c) Use of a Scientific calculator is permitted.
- (d) Graph paper will be provided.

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 ?

P.T.O.

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



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

$2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^{+} + 4\text{e}^{-}$. 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

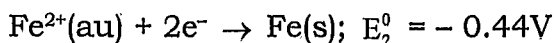
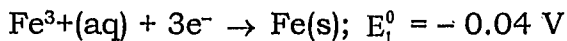
that $\frac{[\text{H}^{+}]_{\text{HCl}}}{[\text{H}^{+}]_{\text{H}_2\text{SO}_4}} = \frac{k_{\text{HCl}}}{k_{\text{H}_2\text{SO}_4}}$, explain whether the

value of $k_{\text{HCl}}/k_{\text{H}_2\text{SO}_4}$ is less than, equal or greater than one.

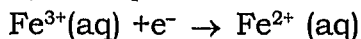
- (e) What are stationary and non-stationary chain reactions ? Discuss briefly.
- (f) Ionic reactions are fast while molecular reactions are slow. Why ?
- (g) Discuss, using potential energy barrier graph, the effect of catalyst on rates of the reaction.

5×3=15

2. (a) Given that :



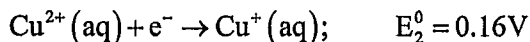
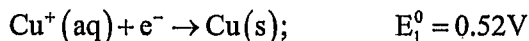
Determine the potential of the following half-cell reaction.



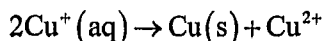
- (b) What is the basic principle of potentiometric titration ? How is it applied to acid – base titration ?
- (c) The standard potential of a cell "Pt | H₂(g) | HBr(aq) | Ag" was found to vary as $E^{\circ}(\text{volt}) = 0.01 - 1 \times 10^{-4}(T - 298) - 2 \times 10^{-6}(T - 298)^2$. Calculate the standard reaction entropy, ΔS° and enthalpy, ΔH° at 25°C.

$$3 \times 5 = 15$$

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



Calculate ΔG° (in kJ) for the following reaction :



- (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.

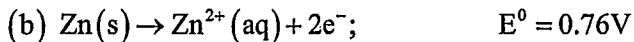
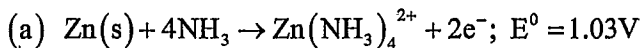
- (c) The cell constructed by the half cells.

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

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

$$3 \times 5 = 15$$

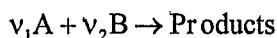
4. (a) Determine the formation of the complex, $\text{Zn}(\text{NH}_3)_4^{2+}$, Provided that



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

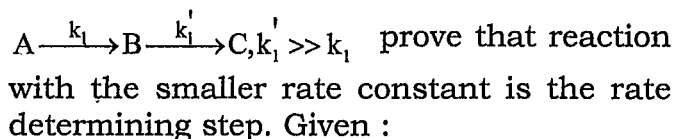
- (c) Construct a concentration cell without transference using silver – silver chloride electrode and derive the equation for determination of cell potential of the concentration cell. $3 \times 5 = 15$

5. (a) The reaction



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



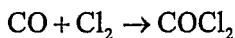
$$[C] = [A]_0 \left\{ 1 - \frac{1}{k_1' - k_1} \left(k_1' e^{-k_1 t} - k_1 e^{-k_1' t} \right) \right\}$$

- (c) Write a short note on Lindemann Mechanism. $3 \times 5 = 15$

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

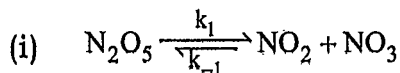
$$E_{\alpha} = E_0 + \frac{RT}{2} \quad \& \quad A = p N_A \frac{Z_{AB}}{N_A^* N_B^*} e^{1/2}$$

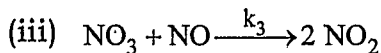
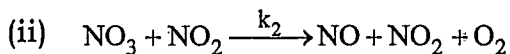
- (b) Using the following data, obtain the differential rate expression for the following reaction & the value of rate constant



Experiment No.	1	2	3	4
$[\text{CoCl}_2]_0 / \text{mol dm}^{-3}$	0.16	0.16	0.04	0.04
$[\text{Cl}_2]_0 / \text{mol dm}^{-3}$	0.16	0.04	0.16	0.04
$r_0 / \text{mol dm}^{-3} \text{ s}^{-1}$	1.92×10^{-2}	9.6×10^{-3}	4.8×10^{-3}	2.4×10^{-3}

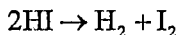
- (c) Discuss the conditions under which the equilibrium approximation & steady state approximation is used while elucidating the mechanisms of the complex reactions. Support your answer with any general reaction in each case 3×5=15
7. (a) The following mechanism has been proposed for the decomposition of N_2O_5 :





Show that rate law is $\frac{d[\text{O}_2]}{dt} = k[\text{N}_2\text{O}_5]$

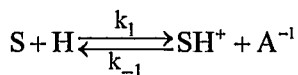
- (b) The bimolecular decomposition of Hydrogen Iodide is given by the equation

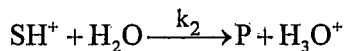


Assuming a collision diameter of 0.35×10^{-8} cm and an activation energy of $183.90 \text{ kJ mol}^{-1}$ for the reaction, calculate (i) the collision rate, (ii) the rate of reaction and (iii) the rate constant for the above reaction at 500 K and one atmosphere pressure.

- (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 :





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
