CLASS XII: CHEMISTRY
CHAPTER 3: ELECTROCHEMISTRY
COMMON MISTAKS BY THE STUDENTS IN EXAMINATION

- **REPRESENTATION OF ELECTROCHEMICAL CELL (ANODE FOLLOWED BY SALT BRIDGE THEN CATHODE)**
- **IDENTIFICATION OF ANODE (LEFT) & CATHODE (RIGHT)**
- **IDENTIFICATION BASED ON STANDARD ELECTRODE POTENTIAL (LOWER VALUE OXIDATION OR ANODE & HIGHER VALUE REDUCTION OR CATHODE)**
- **WRITING OF HALF CELL REACTIONS (NUMERICAL BASED ON NERNST EQUATION. WRITING OF HALF CELL & OVER ALL CELL REACTION IS MENDATORY.**
- **ANSWERS OF NUMERICAL PROBLEMS MUST END WITH PROPER UNITS.**
- **QUESTIONS BASED ON CELL REACTIONS IN DIFFERENT CELLS.**
- **IDENTIFICATION OF PRODUCTS OF ELECTROLYSIS.**

BASIC CONCEPTS AND FORMULA

1. Oxidation is defined as a loss of electrons while reduction is defined as a gain of electrons.

2. In a redox reaction, both oxidation and reduction reaction takes place simultaneously.

3. In an indirect redox reaction, the device which converts chemical energy into electrical energy is known as an electrochemical cell.

4. In an electrochemical cell:

a. The half-cell in which oxidation takes place is known as oxidation half-cell b. The half cell in which reduction takes place is known as reduction half cell.

c. Oxidation takes place at anode which is negatively charged and reduction takes place at cathode which is positively charged. (In electrochemical cell)

d. Transfer of electrons takes place from anode to cathode while electric current flows in the opposite direction.

e. An electrode is made by dipping the metal plate into the electrolytic solution of its soluble salt.

f. A salt bridge is a U shaped tube containing an inert electrolyte in agar-agar and gelatin.

7. A salt bridge maintains electrical neutrality and allows the flow of electric current by completing the electrical circuit.

8.   When the concentration of all the species involved in a half cell is unity, then the electrode potential is known as standard electrode potential. It is denoted as $E^{\ominus}$.

9.   Oxidation potential is the tendency of an electrode to lose electrons or get oxidized.

10.   Reduction potential is the tendency of an electrode to gain electrons or get reduced.

11.   The electrode having a higher reduction potential has a higher tendency to gain electrons. So, it acts as a cathode.

12.   The electrode having a lower reduction potential acts as an anode and vice versa.

13.   According to convention, the Standard Hydrogen Electrode is taken as a reference electrode and it is assigned a zero potential at all temperatures.

14.   In the electrochemical series, various elements are arranged as per their standard reduction potential values.

15.   The potential difference between the 2 electrodes of a galvanic cell is called cell potential and is measured in Volts.

16.   The cell potential is the difference between the reduction potential of cathode and anode.

$E_{cell} = E_{cathode} - E_{anode}$

Cell potential is called the electromotive force of the cell (EMF) when no current is drawn through the cell.

17.   Nernst formulated a relationship between standard electrode potential $E^{\ominus}$ and electrode potential E.

$$E = E^{\circ} - \frac{2.303RT}{nF} \log \frac{1}{[M^{n+}]}$$

$$E = E^{\circ} - \frac{0.059}{n} \log \frac{1}{[M^{n+}]} \qquad \text{(At 298 K)}$$

18. Electrode potential increases with increase in the concentration of the electrolyte and decrease in temperature.

19.   Nernst equation when applied to a cell:

$$E_{cell} = E^{\circ}_{cell} - \frac{2.303RT}{nF} \log \frac{[\text{Anode ion}]}{[\text{Cathode ion}]}$$

This helps in calculating the cell potential

20. Relationship between equilibrium constant Kc and standard cell potential

$$E^{\circ}_{cell} = \frac{0.059}{n} \log K \quad \text{(At 298 K)}$$

21.   Work done by an electrochemical cell is equal to the decrease in Gibbs energy
$\Delta G° = nFE°_{cell}$

22.   Every conducting material offers some obstruction to the flow of electricity which is called resistance. It is denoted by R and is measured in ohm.

23.   The resistance of any object is directly proportional to its length I and inversely proportional to its area of cross section A.

$R = p \dfrac{l}{A}$

p is called specific resistance or resistivity. Its SI unit is ohm metre.

24.   The inverse of resistance is known as conductance,

$G = \dfrac{1}{R}$

Unit of conductance is ohm^{-1} or mho. It is also expressed in Siemens denoted by S.

25.   The inverse of resistivity is known as conductivity. It is represented by the symbol K. The SI unit of conductivity is Sm^{1}. But it is also expressed in Scm^{1}

$k = \dfrac{1}{R}\dfrac{l}{a}$

So, conductivity = Conductance x Cell constant

26. A conductivity cell consists of 2 Pt electrodes coated with Pt black. They have area of cross section A and are separated by a distance I. Resistance of such a column of solution is given by the equation:

R = p l/A = 1/K x l/A

l/A is called cell constant and is denoted by the symbol G*

27. Molar conductivity of a solution is defined as the conducting power of the ions produced by dissolving 1 mole of an electrolyte in solution.

$$\text{Molar conductivity Am} = \dfrac{K \times 1000}{M}$$

Where K = Conductivity and M is the molarity

Unit of Molar conductivity is $Scm^{2} mol^{1}$

28. Kohlrausch's Law of independent migration of ions: According to this law, molar conductivity of an electrolyte, at infinite dilution, can be expressed as the sum of individual contributions from its individual ions. If the limiting molar conductivity of the cation is denoted by $\lambda°$ and that of the anions by $\lambda°$ then the limiting molar conductivity of electrolyte

$$\Lambda_m^0 = v_+\lambda°_+ + v_-\lambda°_-$$

Where v_+ and $v-$ are the number of cations and anions per formula of electrolyte.

29. Degree of dissociation: It is ratio of molar conductivity at a specific concentration 'c' to the molar conductivity at infinite dilution, it is denoted by α.

$$a = \frac{\Lambda^c_m}{\Lambda^0_m}$$

30. $Ka = \dfrac{C a^2}{1-a}$ where K_a is acid dissociation constant, 'c' is concentration of

Electrolyte, a is degree of ionization.

31. Lead storage battery:

Anode: $Pb(s) + SO_4^{2-}$ (aq), $PbSO4(s) + 2e$

Cathode: $PbO_2(s) + SO_4^{2-}$ (aq) $+ 4 H^+(aq) + 2e^- \rightarrow PbS0_4(s) + 2H_2O$ (I)

The overall cell reaction consisting of cathode and anode reactions is:

$Pb(s) + PbO_2(s) + 2H_2SO_4(aq) \rightarrow 2PbSO_4(s) +) + 2H_2O(I)$

On recharging the battery, the reaction is reversed.

32. Fuel cells:

At anode: $2 H_2(g) + 40H^-$ (aq) $\rightarrow 4H_2O(1) + 4e$

At cathode: $O_2(g) + 2H_2O(1) + 4e^- \rightarrow 4 OH^-$ (aq)

Overall reaction:

$2 H_2(g) + O_2(g) \rightarrow 2H_2O(I)$

33. Corrosion:

Oxidation: $Fe(s) \rightarrow Fe^{2+}$ (aq) $+ 2e^-$

Reduction: O_2 (g) $+ 4H^+$ (aq) $+ 4e^- \rightarrow 2H_2O$ (I)

Atmosphere oxidation:

$2Fe^{2+}$ (aq) $+ 2H_2O$ (I) $+ \frac{1}{2}O_2$ (g) $\rightarrow Fe_2O_3$ (s) $4H^+(aq)$

34. Galvanization: It is a process of coating of zinc over iron so as to protect it from rusting.

35. Cathodic protection: Instead of coating more reactive metal or iron, the use of such metal is made as sacrificial anode.

Connecting Iron with more reactive metal with the help of a wire.

* The definition and working of electrochemical cell

Differences between electrochemical reaction and electrolysis.

Electrochemical reaction	Electrolysis.
Chemical reaction produce electricity	Electricity causes chemical reaction to take place
It is spontaneous, ΔG is -ve	It is non-spontaneous, ΔG is +ve

* LOAN concept

Alphabet rule for an electrochemical cell- According to this rule we write that term first which come first alphabetically as show below-

L.H.S.	R.H.S.
ANODE	CATHODE
OXIDATION	REDUCTION
NEGATIVE	POSITIVE
Note :Remember **LOAN** (Left, Oxidation, Anode, Negative charge)as an abbreviation for anodic properties of Electrochemical Cells	

* Purpose of using Salt bridge **Functions of Salt Bridge**
 1. Salt Bridge maintains electrical neutrality in solutions.
 2. It completes circuit internally

* Standard electrode potential and its usefulness

* Applications of electrochemical series

   i) **To compare the relative oxidizing and reducing powers**- A chemical species with higher value of E° will be stronger oxidizing agent and a chemical species with more –ve E° will be stronger reducing agent
   ii) **To compare the relative activities of metals**-A metal with more –ve E° value will be more reactive
   iii) **To calculate the E°$_{cell}$ of given cell**-
        $E°_{cell =}$ $E°_{cathode}$ - $E°_{anode}$ <u>or</u> $E°_{cell =}$ $E°_{RHS}$ - $E°_{LHS}$
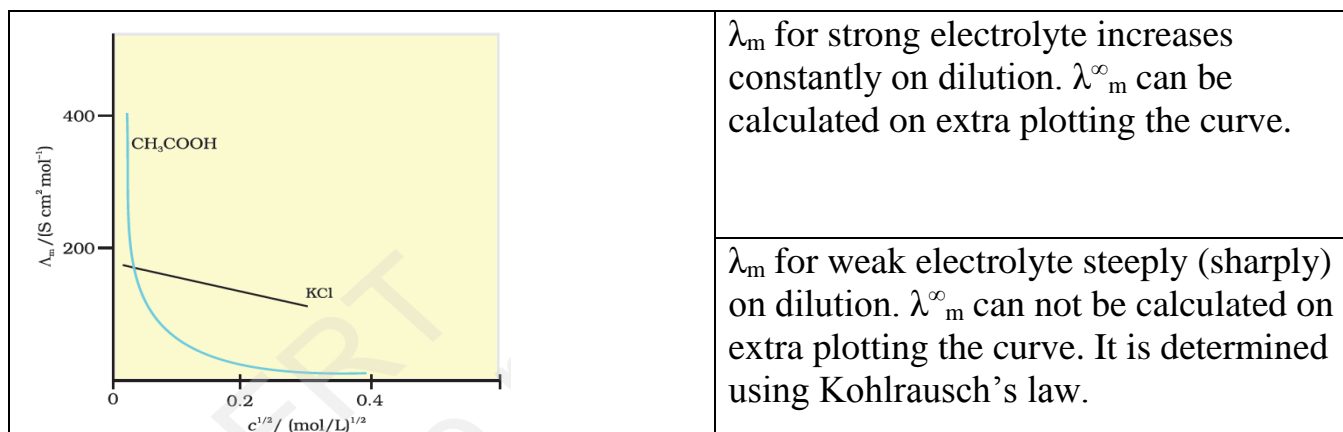   N.B. - E° for SHE is taken 0 (Zero)
    iv) To predict whether a metal will displace hydrogen from its compound or not- All the chemical species which have –ve E° value will displace hydrogen from its compounds

$M \rightarrow M^{n+} + ne^-$ **(electron lost is gained by H$^+$ ion to undergo reduction and H$_2$ is formed)**

* Usefulness of Nernst equation to calculate E_{cell} at different conc. And temp.

* Definition of strong electrolyte, weak electrolyte, limiting molar conductivity

Molar Conductivity- It the conductance due to all the ion produced from 1 mole of an electrolyte in Vcm^3 of the solution. It is represented by λ^c_m at conc. 'C' and λ^∞_m at infinite dilution.

	λ_m for strong electrolyte increases constantly on dilution. λ^∞_m can be calculated on extra plotting the curve.
	λ_m for weak electrolyte steeply (sharply) on dilution. λ^∞_m can not be calculated on extra plotting the curve. It is determined using Kohlrausch's law.

* Usefulness of Kohlrausch law to calculate λ_m^∞ of a weak electrolyte

* Determination of products of electrolysis on the basis of their E° value, a chemical species with higher E° value will undergo reduction at cathode and formed the product, higher the negative value of reduction electrode potential more will be the reducing power

> The nature of the product obtained at cathode or anode depends upon E° value of given chemical species. The chemical species which has most –ve E° will form product at cathode and the chemical species which has least –ve/most +ve E° will form product at anode. Inert electrodes do not take part in chemical reactions

Faraday's 1st Laws	The amount of substance liberated at any electrode during electrolysis is directly proportional to the quantity of electricity passed through the electrolyte (solution or melt).
Faraday's 2nd Laws	The amounts of different substances liberated by the same quantity of electricity passing through the electrolytic solution are proportional to their chemical equivalent weights (Atomic Mass of Metal ÷ Number of electrons required to reduce the cation).

Product of Electrolysis

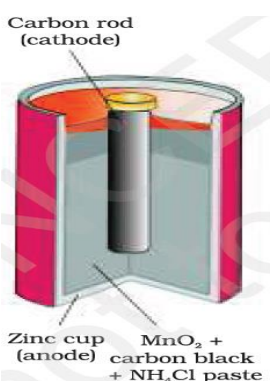NaCl (molten)   Cathode : $Na^+(l) + e^- \rightarrow Na(s)$ Anode : $Cl^- \rightarrow \frac{1}{2}Cl_2 + e^-$

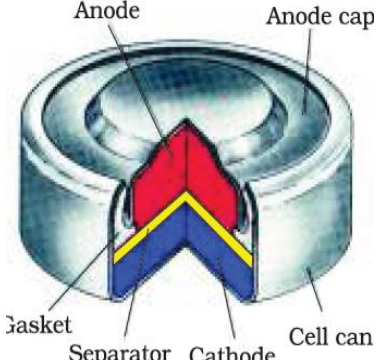|	
NaCl (aq)	Cathode : H_2O (l) + e^- → $\frac{1}{2}H_2$(g) + OH^- Anode : Cl^-→ $\frac{1}{2}Cl_2$+e^-
H_2SO_4(dil)	Cathode : H^+ + e^- → $\frac{1}{2}$ H_2 Anode: $2H_2O$(l)→ O_2(g) + $4H^+$(aq) +e^-
(H_2SO_4conc)	Cathode : H^+ + e^- → $\frac{1}{2}$ H_2 Anode: $2SO_4^{2-}$ (aq) → $S_2O_8^{2-}$ (aq) +$2e^-$
$AgNO_3$(aq)-Ag electrodes	Cathode : Ag^+(aq) + e^- → Ag(s) Anode: Ag(s) → Ag^+(aq) + e^-
$AgNO_3$(aq)- Pt electrodes	Cathode : Ag^+(aq) + e^- → Ag(s) Anode: $2H_2O$(l) → O_2(g)+$4H^+$(aq)+$4e^-$
CuCl(aq)- Pt electrodes	Cathode : Cu^+(aq) + e^- → Cu(s) Anode: $2H_2O$(l)→O_2(g)+$4H^+$(aq)+$4e^-$

* Advantages of fuel cell---long lasting, more efficient, eco friendly, give useful by products

Commercial cells-   These are of 4 types
 1) Dry cell (primary cell) – It is a Non rechargeable cell. Used in Torch, Wall clock etc.

Carbon rod (cathode) Zinc cup (anode) MnO₂ + carbon black + NH₄Cl paste	The following reaction takes place at Anode and Cathode in the Dry cell :
	Anode: Zn(s) ⟶ Zn^{2+} + $2e^-$ The above reaction takes place at anode i.e. **Zn plate**
	Cathode: MnO_2+ NH_4^++ e^-⟶ MnO(OH) + NH_3 The above reaction takes place at cathode i.e. **Carbon rod**

2) Mercury cell/Button Cell – It is used in hearing aids and watches etc.

Anode Anode cap Gasket Cell can Separator Cathode	The following reaction takes place at Anode and Cathode in the Mercury cell/Button Cell :
	Anode: Zn(Hg) + 2OH⁻ ⟶ ZnO(s) + H_2O + $2e^-$ The above reaction takes place at anode i.e. **Zn container**
	Cathode: HgO + H_2O + $2e^-$ ⟶ Hg(l) + $2OH^-$ The above reaction takes place at cathode i.e. **Carbon rod**

3) Lead storage battery – It is a Rechargeable battery. Used in automobiles and inverters, Rechargeable batteries used in house hold appliances etc.

The cell reactions when the battery is in use are given below:

Anode: $Pb(s) + SO_4^{2-}(aq) \rightarrow PbSO_4(s) + 2e^-$

Cathode: $PbO_2(s) + SO_4^{2-}(aq) + 4H^+(aq) + 2e^- \rightarrow PbSO_4(s) + 2H_2O(l)$

i.e., overall cell reaction consisting of cathode and anode reactions is:

$Pb(s) + PbO_2(s) + 2H_2SO_4(aq) \rightarrow 2PbSO_4(s) + 2H_2O(l)$

On charging the battery the reaction is reversed and $PbSO_4(s)$ on anode and cathode is converted into Pb and PbO_2, respectively.
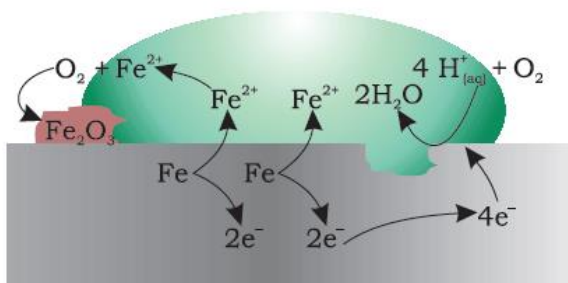
4) **Fuel cell** : This cell is based on the combustion of fuel like Hydrogen by oxygen:
   Advantages of Fuel Cells : 1. As works as long as we supply Hydrogen & oxygen gas
        2. It causes no pollution   3. Its efficiency is 70%   4. Its By product (Water) is also useful.
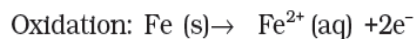

The following reaction takes place at Anode and Cathode in the fuel cell.

Cathode: $O_2(g) + 2H_2O(l) + 4e^- \longrightarrow 4OH^-(aq)$

Anode: $2H_2(g) + 4OH^-(aq) \longrightarrow 4H_2O(l) + 4e^-$

Overall reaction being:
   $2H_2(g) + O_2(g) \longrightarrow 2 H_2O(l)$

* Corrosion, eating away of metals, factors affecting the process of corrosion, corrosion because of miniature electrochemical cell

Corrosion- It is a process of eating away of metals on their surfaces, it is an unwanted process as it results in loss of mass of metals. In this process metal surface reacts with atmospheric oxygen to form a layer of oxide. It is an electrochemical reaction

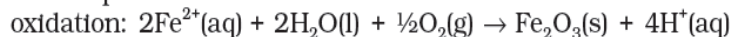The following reaction takes place during rusting :

Oxidation: $Fe\ (s) \rightarrow Fe^{2+}\ (aq) + 2e^-$ | Anodic Reaction

Reduction: $O_2\ (g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l)$ | Cathodic Reaction

Atomospheric
oxidation: $2Fe^{2+}(aq) + 2H_2O(l) + \frac{1}{2}O_2(g) \rightarrow Fe_2O_3(s) + 4H^+(aq)$ | Over all Reaction

S.No	Formula	What to calculate	Another form of the formula
1	$E^o_{cell} = E^o_{cathoe} - E^o_{anode}$	Cell potential of a cell can be calculated by this equation	$E_{cell}{}^\circ = E_R{}^\circ - E_L{}^\circ$
2	$E_{cell} = E^o_{cell} - \dfrac{0.0591}{n} \log \dfrac{1}{Mn+}$	Half Cell potential of a half cell can be calculated by this expression	
3	$E_{cell} = E^o_{cell} - \dfrac{0.0591}{n} \log \dfrac{[P]}{[R]}$	Cell potential of a cell can be calculated by this expression	
4	$E^o_{cell} = \dfrac{0.0591}{n} \log K_c$	To calculate cell potential from K_c and vice versa	$\log K_c = \dfrac{n \times E\ cell\ ^\circ}{0.0591}$
5	$\Delta G^\circ = nF\ E^o_{cell}$	To calculate cell potential from free energy change and vice versa	$E_{cell}{}^\circ = - \dfrac{\Delta G^\circ}{nF}$
6	$R = \rho \dfrac{l}{A}$		$\rho = \dfrac{R\ A}{l}$
7	$G^* = R\ \acute{K}$		$\acute{K} = G/R$
8	$\lambda_m{}^\infty = \dfrac{K \times 1000}{M}$		
9	$\lambda_m{}^\infty = \dfrac{K \times A}{l}$		

10			
	$k = \dfrac{l}{A} \times \dfrac{1}{R}$		

S.No	Formula	What to calculate	Another form of the formula
	$W = Z \times I \times t \quad Z = E/96500$	Amount of a substance produced at any electrode	
	$\dfrac{W1}{E1} = \dfrac{W2}{E2}$	Amount of a substance produced at an electrode of different cells connected in a series	
	$E^{o}_{cell} = \dfrac{0.0591}{n} \log {}_{p}H$		$E_{cell}^{\circ} = \dfrac{0.0591}{n} \log \dfrac{1}{[H+]}$
	$\alpha = \dfrac{\lambda m}{\lambda \infty \, m}$		

IMPORTANT CONCEPTS FOR SLOW LEARNERS

1.   **Limiting molar conductivity**: - conductivity at zero concentration is known as limiting molar conductivity (λ°).

2.   **Corrosion** – Gradual loss of metal from its surface in presence of air and moisture is known as corrosion.

3.   **Cathodic Protection**: - It is done for underground Pipelines, Iron connected to more reactive metal take Zn, Al, mg, with the help of a wire.

4.   **Molar conductivity**: - conductivity of an electrolytic solution between two parallel electrodes, large enough containing 1 mole of electrolytes, separated by 1 cm.

5.   **Kohlrausch Law**: - Limiting molar conductivity of an electrolyte can be represented as the sum of individual contribution of cation and onion of electrolytes. $\Lambda°m = \Lambda°(+) + \Lambda°(-)$

6.   **Electrochemical cell**: - the device which converts chemical energy into electrical energy as a result of spontaneous redox reaction.

7.   **St. Cell potential**: - The difference between st. electrode potential of cathode half cell and anode half cell is known as st. cell potential.
      E° cell = E° cathode – E° anode

8.   **Effect of concentration on molar conductivity**: - The molar conductivity of strong electrolyte slightly increases on decrease in concentration because they are fully dissociated but in weak electrolyte it increases steeply because on decreasing concentration their dissociation increases.

9.   **Fuel Cell**- It converts fuel Energy into Electrical energy
      (i) it causes no pollution (ii) it has high efficiency.

10.   **Nernst Equation** – It is used to find cell potential of Galvanic cell
      E cell = E° cell – $\underline{0.0591}$ log $\underline{[Product]}$
 $\qquad\qquad\qquad$ n $\qquad$ [Reactant]

EXPECTED QUESTIONS

1.   Arrange the following metals in order of their increasing reducing power.
$K^+/K = - 2.93V$, $Ag^+/Ag = 0.80V$, $Hg^{2+}/Hg = 0.79$ V, $Mg^{2+}/Mg = - 2.37$ V
$Cr^{3+}/Cr = - 0.74V$.
Ans. Lower the reduction potential, easily if gets oxidized hence greater is the reducing power, therefore the increasing order of reducing power is Ag <Hg<Cr<mg<K.

2.   Define conductivity and molar conductivity.
 Ans   The conductance of a solution of 1 cm length and area of cross section equal to 1cm2 is known as conductivity. The conductivity of electrolytic solution containing 1 mole of electrolyte between 2 large electrodes at one cm apart is known as molar conductivity.

3.   What is limiting molar conductivity?
Ans. The molar conductivity of an electrolyte at zero concentration is known as Limiting molar conductivity.

4.   What is unit of molar conductivity?

Ans: - ^m = $\frac{K \times 1000}{M}$ = Scm^2/mol^{-1}

5. The conductivity of 0.20m solution of KCl at 298 K is 0.0248 Scm^{-1}. Calculate its molar conductivity.

Ans.: ^m = $\frac{K \times 1000}{M} = \frac{0.0248 \times 1000}{0.20}$ =124 Scm^2 mol^{-1}

6. How much faraday is required to produce 40gm Al from Al$_2$O$_3$?

Ans: Al^{3+} + 3e$^-$→ Al (27g)
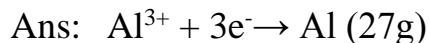
27g Al is deposited by 3f

40g Al will be deposited by = $\frac{3 \times 40}{27}$ = 4.44 F

7. Predict the products of electrolysis of AgNO$_3$ with Silver electrodes.

Ans. AgNO$_3$→Ag$^+$ + NO$_3^-$

Reaction at cathode Ag$^+$ +ē→Ag

Reaction at cathode Ag → Ag$^+$ + e$^-$
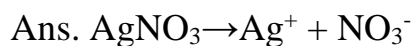
8. Predict if the reaction between the following is feasible? Fe^{3+} and Br$^-$.

Ans : Fe^{3+} + Br$^-$ →Fe2$^+$ + ½Br$_2$

E°cell = 0.77V – 1.09V = -0.32V not feasible

9. Explain Kohlrausch's law.

Ans: The Limiting molar conductivity of an electrolyte can be represented as sum of individual contribution of cation and onion of the Electrolytic

$$\Lambda°_m = V\Lambda°_+ + V\Lambda°_-$$

10. Calculate emf of the following cell

Cd/Cd^{2+} (.10 M)//H$^+$ (.20 M)/H$_2$ (0.5 atm)/Pt
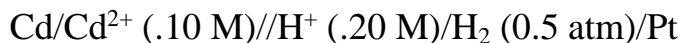
[Given E° for Cd^{2+} /Cd = -0.403 v]

Ans: Ecell = E°cell – 0.0591/n Log [Cd2+]/ [H$^+$]^2

E°cell= 0 – (–.403V) =0.403V

=0.0403 – 0.0591/2 Log (0.10) X 0.5/(0.2)^2 = 0.400V

Important questions

Q1. How much electricity in terms of Coulomb is required to reduce 1 mol of Cr$_2$O$_7^{2-}$ to Cr^{3+}.

Ans:- 2Cr$_2$O$_7^{-2}$------------→2Cr^{+3}, 2Cr^{+6}+6e---------------→2Cr^{3+}
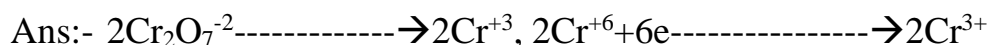
Therefore the coulomb of electricity required =6F,

=6x96500 C= 579000 C

Q2.   What is Fuel Cell?

Ans:- Fuel cell is a device which produce the energy during the combustion of fuels like

Hydrogen , Methane, Methanol.

Q3.   A solution of $CuSO_4$ is electrolysed using a current of 1.5 amperes for 10 minutes. What mass of Cu is deposited at the cathode? (Atomic mass of Cu=63.7)

Ans:- The reaction is Cu^{+2}(aq.) + 2e ------------$\rightarrow$ Cu (s)

The mass of copper deposited=$\underline{E_{Cu} \text{ X I X t}}$ = 63.7*1.5*10*60/ 2*96500C =0.297 g.

$$96500C$$

Q4.   Calculate the equilibrium constant for the reaction Cu (s) + 2Ag+ $\rightarrow$□Cu +2+2Ag(s) E^o Cu^{2+}/Cu = +0.34V, $E^o Ag^+$/Ag = + 0.80V.

Q5.   Write the Nernst equation and emf of the following cells at 298K:

Sn/Sn^{2+}(0.050M)//H^+(0.020M)/H2(g)/Pt(s) $E^o Sn^{2+}$/Sn= - 0.13V

Q6.   Calculate the standard free energy change for the following reaction at250C,Au(s) +Ca^{+2} (1 M)□$\rightarrow Au^{3+}$(1M) + Ca (s) ,The electrode values are Ca^{2+} /Ca = −2.87V,Au^{3+} / Au = +1.50V. Predict whether the reaction will be spontaneous or not at 250C.

Q7.   How do you account for conductivity of strong and weak electrolyte with concentration? Plot the graphs also.

Q8.   State Kohlrausch law . Calculate Limiting molar conductivity of NaCl, HCl and NaAc are 126.4, 425.9 &91 $SCm^2 mol^{-1}$. Calculate Limiting molar conductivity of HAc.

Ans:- According to this law, Molar conductiviy of an electrolyte, at infinite dilution can be expressed as the sum of contributions form its ividual ions. It the molar conductivity of the cation is denoted by $\Lambda^o_+$and that of the anions by Λ^o_- then the law of independent migration of ions is

Λ^o_m=$v_+ \Lambda^o_+$+ $v_- \Lambda^o_-$.

Q9. Resistance of conductivity cell filled with 0.1molL^{-1} KCl solution is 100 ohm.If the resistance of the same cell when filled with 0.02molL^{-1} KCl solution is 520 ohm. Calculate the conductivity & molar conductivity of 0.02molL^{-1} KCl solution. The conductivity of 0.1 molL^{-1} solution of KCl is 1.29Sm^{-1}.

Q10. A Copper –silver is set up.The copper ion concentration in its is 0.10M.The concentration of silver is not known.The cell potential measured 0.422V.Determine the concentration of silver ion in the cell. E^o (Ag^+/Ag) = +0.80V, E^o (Cu^{2+}/Cu)= +0.34V.

Q11. A voltaic cell is set up at 250C with the following half cells

:Al(s)/Al^{3+}(0.001M) and Ni^{2+}(0.50)/Ni(s) ,Write the equation for the cell reaction that occurs when the cell generates an electric current and determine the cell potential (givenE^o Ni^{2+}/Ni = -0.25V, E^oAl(s)/Al^{3+}=-1.66V)

Q12. Write the reaction involved in the following cells: (a) Fuel Cell (b) Lead Storage Battery.

Q13. Three electrolytic cells A,B,C containing solutions $ZnSO_4$,$AgNO_3$,and $CuSO_4$ respectively are connected in series .a Steady current of 1.5 amperes was respectively are connected in series .A steady current of 1.5 amperes was passed through them until 1.45g of silver deposited at the cathode of cell B.How long did the current flow? What mass of copper and zinc were deposited?

Q14. Conductivity of 0.00241M acetic acid is 7.896 X 10^{-6} S cm^{-1}. Calculate its molar conductivity. If Λ^0 for acetic acid is 390.5 S cm^2 mol^{-1}. What is its dissociation constant?

Q15. (a) Two half-cell reactions of an electrochemical cell are given below: MnO_{4-} + 8 H+ + 5 e- → $\square$$Mn^{2+}$ + 4 H_2O E^o =+1.51V

Sn^{2+} $\square$→$\square$$Sn^{4+}$+ 2e- Eo = +0.15V.

Construct the redox reaction from the two half-cell reaction and predict if the reaction favours formation of reactants or product shown in the reaction

(b). How much electricity in terms of Faraday is required to produce (i)20g of Ca from molten $CaCl_2$ (ii) 40g of Al from molten $AlCl_3$

HOTS QUESTION

1. A current of 5 ampere is flowing through a wire for 193 seconds. Calculate number of electrons flowing through cross section of wire for 193 seconds.
2. Calculate $\Lambda°$ m NH_4OH from the following values. $\Lambda°$ m for $Ba(OH)_2$, $BaCl_2$, NH_4Cl are 257.6, 240.6, 129.8 Scm^2 mol^{-1} respectively.
3. The EMF of following reaction is 0.28V at 25° C

   $Zn + 2H^+ \rightarrow Zn^{2+} + H_2$ (1 atm) $E°cell = .76$ V

   Calculate pH of solution at hydrogen electrode.
4. Predict the products of electrolysis of Aq H_2SO_4 sol^n with platinum electrodes
5. A solution of $CuSO_4$ is electrolyzed using a current of 1.5 amperes for 10 minutes. What mass of Cu is deposited at the cathode? (Atomic mass of Cu=63.7)
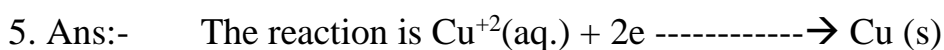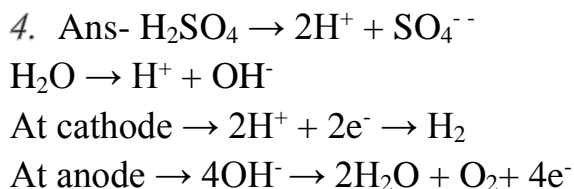
ANSWERS

1. Ans- $Q = i \times t = 5 \times 193 = 965C$

96500C is equivalent to flow of 6.022×10^{23} electrons

$\therefore$ 965C will be equivalent to flow of electrons = $6.022 \times 10^{23} \times 965 / 96500 = 6.022 \times 10^{23}$ electrons

2. Ans- $\Lambda°$ m $(NH_4OH) = \Lambda°$ $NH_4^+ + \Lambda°OH^-$

$= (\Lambda°$ $NH_4^+ + \Lambda°Cl^-) + \frac{1}{2} (\Lambda°Ba^{++} + 2\Lambda°OH^-)$

$= -1/2 (\Lambda°Ba^{++} + 2\Lambda°Cl^-)$

$= 129.8 + \frac{1}{2} \times 457.6 - \frac{1}{2} 240.6$

$= 238.3$ $Scm^2 mol^{-1}$

3. Ans- $Ecell = E°cell – 0.0591/n \times log [Zn^{2+}]/ [H^+]^2$

$= .76 - .0591/2 log [0.1]/ [H^+]^2$

$.28 = .76 - .02955 (-1 + 2pH)$

$2 pH – 1 = 16.244$

$pH = 8.62$

4. Ans- $H_2SO_4 \rightarrow 2H^+ + SO_4^{--}$

$H_2O \rightarrow H^+ + OH^-$

At cathode $\rightarrow 2H^+ + 2e^- \rightarrow H_2$

At anode $\rightarrow 4OH^- \rightarrow 2H_2O + O_2 + 4e^-$

5. Ans:-   The reaction is $Cu^{+2}(aq.) + 2e$ ------------$\rightarrow$ Cu (s)

The mass of copper deposited$= E_{Cu} \times I \times t = 63.7 \times 1.5 \times 1060 / 2 \times 96500C = 0.297$ g.

$$96500C$$

Electrochemistry

Q 1.What do you mean by kohlrauch's law: from the following molar conductivities at infinite dilution

Δm^∞ Ba(OH)$_2$ =457.6 Ω^{-1} cm^2 mol^{-1}

Δm^∞ Ba Cl$_2$ = 240.6 Ω^{-1} cm^2 mol^{-1}

Δm^∞ NH$_4$Cl= 129.8 Ω^{-1} cm^2 mol^{-1}

Calculate Δm^∞ for NH$_4$OH

Ans. 238.3 Ω^{-1}cm^2 mol^{-1}

Q2. Calculate the equilibrium constant for the reaction

Zn + Cd^{2+} $\longleftrightarrow$ Zn^{2+} +Cd

If E^0 Cd^{++}/Cd =-.403 v
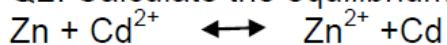
E^0 Zn^{++}/Zn= -0.763 v

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Ans.1.52*10^{12}

Q3. Predict the products of electrolyzing of the following

(a) a dil. Solution of h^{2}So^4 with Pt. electrode

(b). An aqueous solution of AgNO3 with silver electrode

2. Equilibrium constant is related to E^θ cell but not to Ecell. Explain.
3. Why sodium metal is not obtained at cathode when aq NaCl is electrolysed with Pt electrodes but obtained when molten NaCl is electrolysed ? 2
4. Zn rod weighing 25 g was kept in 100 mL of 1M copper sulphate solution. After certain time interval, the molarity of Cu^{2+} was found to be 0.8 M. What is the molarity of SO_4^{-2} in the resulting solution and what should be the mass of Zn rod after
cleaning and drying ?
5. Which will have greater molar conductivity and why? Sol A. 1mol KCl dissolved in 200cc of the solution or Sol B. 1 mol KCl dissolved in 500cc of the solution.

3/ 5 mark questions:-
1. What do you mean by (i) negative standard electrode potential and
(ii) positive standard electrode potential ?
2. Which cell is generally used in hearing aids?Name the material of the anode, cathode and the electrolyte. Write the reactions involved.
3. Iron does not rust even if Zinc coating is broken in agalvanised iron pipe but rusting occurs much faster if tin coating over iron is broken.Explain.
4. ' Corrosion is an electrochemical phenomenan', explain.

5. Calculate the pH of following cell: Pt, H_2/ H_2SO_4, if its electrode potential is0.03V.
6 . A cell contains two hydrogen electrodes. The negative electrode is in contact witha solution of 10^{-5} M H+ ions. The emf of the cell is 0.118 V at 298 K. Calculate theconcentration of the H+ ions at the positive electrode.

7. Crude copper containing Fe and Ag as contaminations was subjected to electro refining by using a current of 175 A for 6.434 min. The mass of anode was found to decrease by 22.260 g, while that of cathode was increased by 22.011 g. Estimate the % of copper, iron and silver in crude copper.

8 Zinc electrode is constituted at 298 K by placing Zn rod in 0.1 M aq solution of zinc sulphate which is 95 % dissociated at this concentration. What will be the electrode potential of the electrode given that $E^\theta Zn2+/Zn$= - 0.76 V. 3

9. At what pH will hydrogen electrode at 298 K show an electrode potential of -0.118 V, when Hydrogen gas is bubbled at 1 atm pressure ? 3

10 Electrolysis of the solution of MnSO4 in aq sulphuric acid is a method for the preparation of MnO2 as per the chemical reaction
Mn2+ + 2H2O → MnO2 + 2H+ + H2
Passing a current of 27 A for 24 Hrs gives 1 kg of MnO2. What is the current efficiency ? What are the reactions occurring at anode and cathode ?

VALUE BASED QUESTIONS

Q.1   People are advised to limit the use of fossil fuels resulting in Green House Effect leading to a rise in the temperature of earth. Hydrogen provides an ideal alternative and its combustion in fuel cells.

a. Write electrode reaction in H_2-O_2 fuel cell.

b. How is greenhouse effect reduced by the use of fuel cells?

c. Write the values associated with preference of using fuel cells to fossil fuel.

Q.2   In Apollo Space programs, hydrogen-oxygen fuel cell was used.

(a) Explain why, fuel cell is preferred in space programme.?

(b) Mention the values associated with the decision of using fuel cell?

Q.3   Ira a student of science went with her grandfather to buy a battery for their inverter and camera. They found two types of batteries, one a lead storage battery and other a Nickel-Cadmium storage battery. Later was more expensive but lighter in weight. Ira insisted to purchase costlier Nickels-Cadmium battery.

(a)   In your opinion, why Ira insisted for Nickel-Cadmium battery? Give reasons

(b)   Write the values associated with above decision?

Q.4   Shyam's father wants to buy a new car. In the market various options are available. Shyam persuades his father to buy a hybrid car which can run both on electricity as well as on petrel.

a.   Mention the values associated with this decision.

b.   Name the battery used for running the car.

c.   Write the reactions taking place at the anode and cathode of battery.

Q.5   Reema the student of class XII Science suggested her father to place a pouch of silica gel in the opening of iron pipes when he was preparing a shed for parking his car?

a.   How does Reema apply the knowledge of chemistry?

b.   What value was associated with this decision?

c.   How she shows the concern to society?

Ans.

1. a. Cathode: O_2 (g) + $2H_2O$ (I) + $4e^-$ → $4OH^-$(aq)

        Anode: $2H_2$ (g) + $4OH^-$(aq) → $4H_2O$ (I) + $4e^-$

   b. no any pollutant is being formed as product of cell reaction.

   c. Environmental conservation

2. a. No any pollutant is formed only water is formed which is used for drinking purpose.

    b. Environmental conservation

3. a. Pollution free, No poisoning of lead as in lead storage battery.

b Environmental conservation, Concern for workers associated with lead storage battery repairment.

4. a Environmental conservation, Energy Conservation

b. Lead Storage Battery

c. Anode: $Pb(s) + SO_4^{2-} (aq) \rightarrow PbSO_4(s) + 2e^-$

Cathode: $PbO_2(s) + SO_4^{2-}(aq) + 4H^+ (aq) + 2e^- \rightarrow PbSO_4 (s) + 2H_2O (I)$

5. I. Silica gel is a good adsorbent therefore prevent from rusting.

ii. Knowledge is useful when it is put in practice.

iii. She shows her concern to the environment.

CHEMICAL KINETICS

## COMMON MISTAKES BY THE STUDENTS IN EXAMINATION

- **UNITS OF RATE CONSTANTS FOR DIFFERENT ORDER OF REACTIONS**
- **STEPS INVOLVED IN SOLVING NUMERICALS (WRITING FORMULA, PUTTING VALUES etc.)**
- **STUDY OF GRAPHS.**
- **USE OF LOGARITHM (ln VALUE)**
- **DEFINATIONS FOLLOWED BY SUITABLE EXAMPLES.**
- **NUMERICALS TO END WITH PROPER UNITS.**

(IMPORTANT CONCEPTS)

Chemical kinetics. (Greek word 'kinesis' means movement). It is the branch of chemistry which deals with the study of the rates of reaction, factors affecting rates of reaction and mechanism of chemical reactions.

Rate of reaction. It is the change in concentration of the reactants or products in unit time. It is expressed in $molL^{-1}s^{-1}$ units.

Average rate. Consider a hypothetical reaction, assuming that the volume of the system remains constant.

$$R \rightarrow P$$
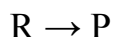
If $[R]_1$ and $[P]_1$ are the concentrations of R and P respectively at time t_1 and $[R]_2$ and $[P]_2$ are their concentrations at time t_2, then

$$\Delta t = t_2 - t_1$$
$$\Delta[R] = [R]_2 - [R]_1$$
$$\Delta[P] = [P]_2 - [P]_1$$

The square brackets in the above expression are used to express the molar concentration.

Rate of reaction r = Rate of disappearance of R = Decrease in concentration of R/ Time taken

$$r = -\frac{\Delta[R]}{\Delta t}$$

Rate of reaction = Rate of appearance of P = Increase in concentration of P/ Time taken

$$r = \frac{\Delta[P]}{\Delta t}$$

Since, $\Delta[R]$ is a negative quantity it is multiplied by -1 to make the rate of the reaction a positive quantity. Average rate depends upon the change in concentration of reactants or products and the time taken for the change to occur.
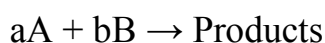
Instantaneous rate. It is defined as the rate of change in concentration of any of the reactant or product at a particular instant of time.

$$\lim_{\Delta t \to 0} \left[\frac{\Delta x}{\Delta t}\right] = \frac{dx}{dt}$$

Factors on which the rate of reaction depends.

1. Concentration of reactants and products.
2. Temperature.
3. Nature of reactants.
4. Presence of catalyst.

Rate law. It is the mathematical expression in which the reaction rate is given in terms of molar concentration of product of reactants with each concentration term raised to the power, which may or may not be same as the stoichiometric coefficient of the reacting species in a balanced chemical equation.

aA + bB → Products

Rate α $[A]^a. [B]^b$

Rate = $k[A]^a. [B]^b$

Where k is the proportionality constant

Rate constant. It is defined as the rate of reaction when the molar concentration of the reactants is taken to be unity.

Order of reaction. Order is defined as the sum of the powers of the concentration of the reactants in the rate equation or rate law. Order of the reaction is experimentally determined and is not written from the balanced chemical equation. Order of reaction can be a whole number, zero or fractional.

Molecularity of reaction. The number of reacting species which must collide simultaneously in a step leading to a chemical reaction is known as molecularity of a reaction.

Pseudo first order reaction. The reactions which are not truly of first order but become reactions of first order under certain conditions are called pseudo first order reactions. For example, hydrolysis of ester.

$CH_3COOC_2H_5$ + HOH $\xrightarrow{H+}$ CH_3COOH + C_2H_5OH
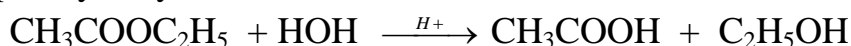
Rate = k'$[CH_3COOC_2H_5]$ $[H_2O]$

Since water is in excess and $[H_2O]$ is constant, so

Rate = k$[CH_3COOC_2H_5]$, where k = k'$[H_2O]$

Integrated rate law method to find the order of reaction. This is the most common method for studying the kinetics of a chemical reaction. The values of $[A]_o$, $[A]$ and t are determined and substituted in the kinetic equations of various orders. The equation which the most constant value for the specific reaction rate constant (k) for different time intervals

is one corresponding to the order of reaction. The integrated rate equations for various orders are:

$$k = \frac{1}{t}\{[A]o - [A]\} \qquad \text{for zero order reaction}$$

$$k = \frac{2.303}{t} \log [A]o/[A] \qquad \text{for first order reaction}$$

$$k = \frac{1}{t} x/a(a - x) \qquad \text{for first order reaction}$$

Common example of first order reactions

    1. Radioactive decay

    2. Rate of growth of population if there is no change in the birth rate or death rate.

    3. Rate of growth of bacterial culture until the nutrients is exhausted.

Half-life. The time during which the concentration of a reactant is reduced to one half of its initial concentration is half-life of the reaction. For first order reaction the half-life, $t_{1/2}$ is independent of the initial concentration and is given as,

$$t_{1/2} = \frac{0.693}{k} \quad \text{Here } k = \text{rate constant}$$

Activated complex. Activated complex is the highest energy unstable intermediate state between the reactants and products and get decomposed immediately to give the products. In this bonds of reactants are not fully broken while the bonds of the products are not fully formed.

    Energy of Activated complex = Energy of reactants + Activation Energy

Threshold energy. The minimum amount of energy which the reactant molecules must possess in order that collision between them may be effective is known as threshold energy.

Activation energy. The minimum extra amount of energy required by the reactants to form the activated complex is known as activation energy.

Threshold energy = Energy of reactants + Activation energy

Lower the activation energy, faster is the reaction.

Collision frequency.   The number of collisions between the reacting molecules taking place per second per unit volume is known as collision frequency (Z).

Effective Collisions. The collisions in which the molecules collide with sufficient kinetic energy (threshold energy) and proper orientation so as to result in chemical reaction are called effective collisions.

Arrhenius Equation. Arrhenius derived a mathematical expression to give a quantitative relationship between rate constant and temperature. The expression is

$$k = Ae^{-Ea/RT} \qquad \text{, where} \qquad A = \text{frequency factor}$$

$$E_a = \text{activation energy}$$

$$R = \text{universal gas constant}$$

$$T = \text{absolute temperature}$$

The term $e^{-Ea/RT}$ is called Boltzmann factor gives the fraction of molecules having energy equal to or greater than E_a.

Arrhenius equation can also be written as

$$log\frac{k_2}{k_1} = \frac{Ea}{2.303}[\frac{T_2-T_1}{T_1T_2}]$$

Thus knowing the values of rate constants k_1 and k_2 at two different temperatures T_1 and T_2, the value of E_a can be calculated. Alternatively, knowing the rate constant at any one temperature, its value at another temperature can be calculated provided the value of activation energy is known.

CHEMICAL KINETICS   M.M. = 05

1. Definition of -

a) **Chemical kinetics-**The branch of chemistry which deals with the study of reaction rates and their mechanisms is called kinetics.

b) **Rate of a reaction-**Change in molar concentration of reactant/product per unit time is Called rate of reaction rate

Change of molar concentration divide by time taken i.e. Rate $= \frac{\Delta[R]}{\Delta t}$

c) **Average rate of reaction-**Rate of change of concentration of any one of reactant or Product at an interval of time is called average rate of reaction

d)**Instantaneous rate of reaction-**Rate of change of concentration of any one of reactant or

Product at an instant of time is called instantaneous rate of reaction

e) **Rate law- I**t is the mathematical expression which tells us about the concentration terms which affect the rate of a reaction. It is determined experimentally

f) **Specific reaction rate -**The rate of reaction when conc. of all the reactant is taken unity.

g) **Order of a reaction-** The sum of powers raised to the each concentration term in the rate

law expression is known as order of the reaction.

Reaction	Order	Units of rate constant
Zero order reaction	0	$\dfrac{\text{mol L}^{-1}}{\text{s}} \times \dfrac{1}{\left(\text{mol L}^{-1}\right)^0} = \text{mol L}^{-1}\text{s}^{-1}$
First order reaction	1	$\dfrac{\text{mol L}^{-1}}{\text{s}} \times \dfrac{1}{\left(\text{mol L}^{-1}\right)^1} = \text{s}^{-1}$
Second order reaction	2	$\dfrac{\text{mol L}^{-1}}{\text{s}} \times \dfrac{1}{\left(\text{mol L}^{-1}\right)^2} = \text{mol}^{-1}\text{L s}^{-1}$

h)**Activation energy** – The excess of energy which must be supplied to the reactant
Molecules to undergo chemical reaction. It is the energy required to form unstable
Intermediate called activation complex.
Lower the value of **activation energy** faster will be rate of a reaction.
i) **Threshold energy-The** amount of energy reactant molecules must possess to form
products.
J) Transition state-The reaction intermediate which is having highest energy state, prior to
Product formation
k) Effective collision – The collisions out of total collisions among the reacting species
Which result in the formation of product is called effective collision?
2. Differences between –
Molecularity& Order of reaction-

Molecularity	Order of reaction
the number of reacting molecules taking part in an elementary reaction.	The sum of powers raised to the each concentration term in the rate law expression is known as order of the reaction.
It is determined theoretically	It is determined experimentally
It normally has higher value	It normally has lower value
Its value can't be zero or fractional	It is always a whole number

Rate of a reaction & Rate constant-

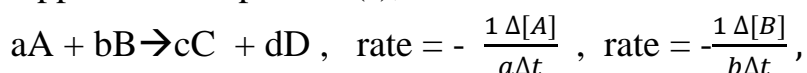| Rate of reaction	Rate constant
Change in molar concentration of reactant/product per unit time is called rate of reaction rate	Rate constant is equal to the rate of a reaction when conc. of reactant is taken unity.
It varies for same reaction and depend on	It is constant for a reaction at a

conc. of reactant	temperature. It is independent of conc. of reactant
Its unit is always mol L^{-1} sce^{-1}	For different order reaction its unit vary

Elementary & complex reaction-

Elementary reaction	Complex Reaction
The reaction taking place in one step is called elementary reaction.	The reaction taking place in more than one step is called elementary reaction.

3. Reason for difference in rates- Different reactions has different **activation energy**

4. Expressions for rate of a reaction, rate of disappearance of reactant(s), rate of Appearance of product(s), Unit of rate of reaction-

$aA + bB \rightarrow cC + dD$, rate $= -\dfrac{1}{a}\dfrac{\Delta[A]}{\Delta t}$, rate $= -\dfrac{1}{b}\dfrac{\Delta[B]}{\Delta t}$,

rate $= \dfrac{1}{c}\dfrac{\Delta[C]}{\Delta t}$, rate $= \dfrac{1}{d}\dfrac{\Delta[D]}{\Delta t}$

Unit of rate of a reaction is mol L^{-1} sce^{-1}

5. Show that rate of a reaction can be expressed in terms of each reactant and product-

Rate of disappearance of reactant = rate of reaction × stoichiometric coefficient of thereactant

Rate of appearance of product = rate of reaction × stoichiometric coefficient of theproduct

6. Factors affecting rate of a reaction-

Name of factors	Their effect
Concentration of reactant	Increases with increasing conc.
Temperature	Increases with increasing temperature
Nature of reactant	reactions involved ionic compounds are faster than covalent compounds
Catalyst	Increases the rate of reaction
Physical state of reactant	Powdered reactant give faster reaction than a solid lump, reactions are faster in solution than solid state

7. Different ways to determine order of a reaction from-

i) Rate law- The sum of powers of all the conc. terms is equal to the order of the reaction. It
May be zero or even fractional.

ii) Unit of K- For zero order reaction unit of K is mol L^{-1} sec^{-1}, **for 1st** order reaction unit of K
is sec^{-1}, **for 2nd** order reaction unit of K is mol^{-1} L sec^{-1}

iii) Initial rate method- A chemical reaction is carried out with different initial conc. of each

reactant and rate of reaction is determined in each case. The rate law is written in each Case. Rate laws are divided suitably to get the value of powers raised to each conc. terms in rate law.

iv) Integrated equation- In this method integrated rate equations for zero, first & second order reaction are used for given data. If the value of K comes to be constant, putting different time& concentration, using a particular expression so the reaction follow thatorder.

v) Half life period- Knowing the time required for the completion of 50% of the reaction we
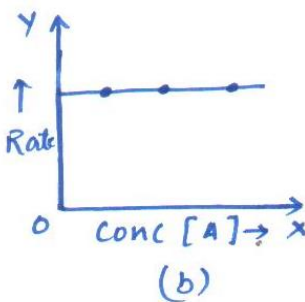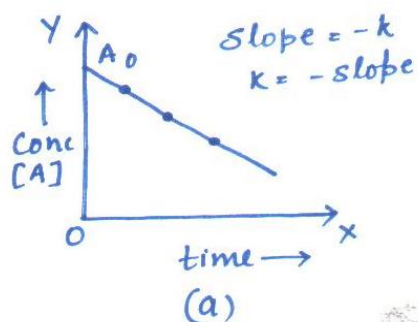can identify the order of the reaction.$t_{1/2}$ **for** zero order reaction is directly proportional to the initial conc. of the reactant**, $t_{1/2}$ for 1st** order reaction is independent of initial conc. of the reactant**.**

vi) From reaction mechanism- For a complex reaction different steps are written. (Or from
given reaction mechanism). The slowest step is identified; the order of over all reaction is equal to the no. of conc. terms involved in the slowest step
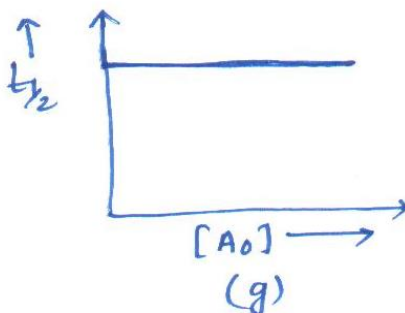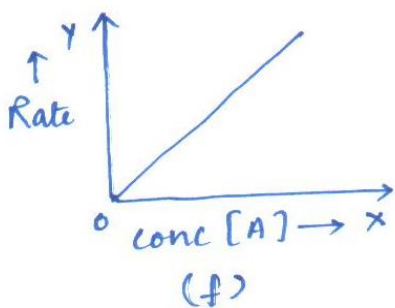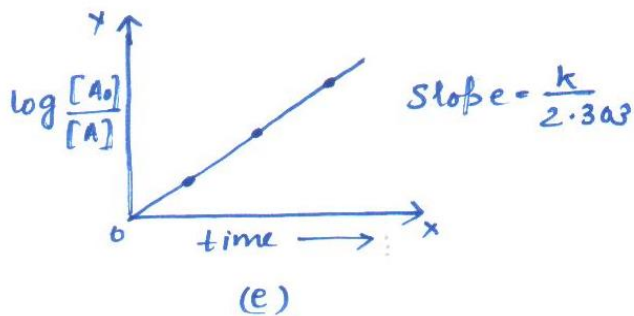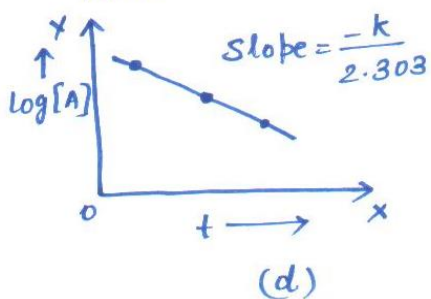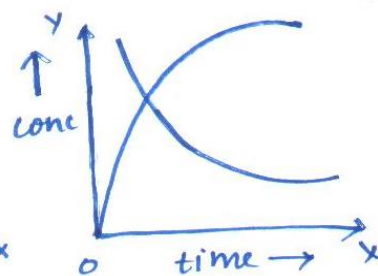
vii) Graph-

Graph of chemical kinetics

Zero order

$$Slope = -k$$
$$k = -slope$$

Y — A_0 — Conc $[A]$ — time → X

(a)

Y — Rate — Conc $[A]$ → X

(b)

$$slope = \frac{1}{2k}$$

Y — $t_{1/2}$ — A_0 → X

(c)

First order

$$Slope = \frac{-k}{2.303}$$

Y — $\log[A]$ — t → X

(d)

$$Slope = \frac{k}{2.303}$$

Y — $\log\frac{[A_0]}{[A]}$ — time → X

(e)

Y — Rate — conc $[A]$ → X

(f)

$t_{1/2}$ — $[A_0]$ →

(g)
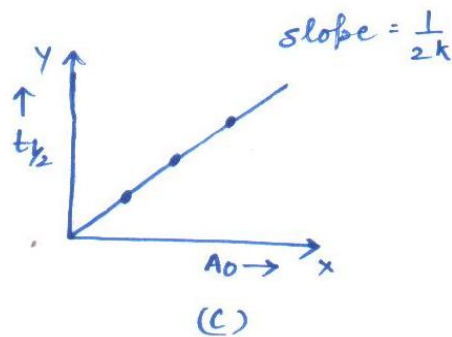
Temperature dependence

$$Slope = \frac{-E_a}{2.303\,R}$$

Y — $\log k$ — $1/T$ → X

(h)

Rate of reaction

Y — Con — time → X

Y — conc — time → X

Effect of catalyst

E_A

→ without catalyst

→ with catalyst

→ reaction progress
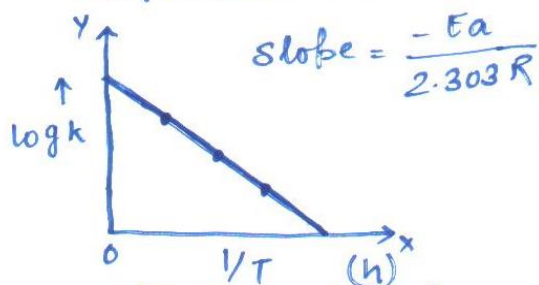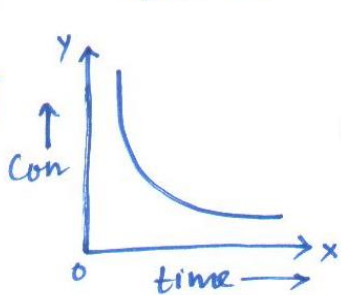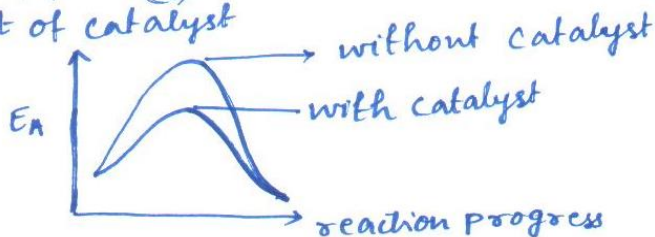
8. Unit of K for zero, first and second order reaction- **For zero** order reaction unit of K is mol L^{-1} sec^{-1}, **for 1st** order reaction unit of K is sec^{-1}, **for 2nd** order reaction unit of K is mol^{-1} L sec^{-1}

10. Useful formulae-

Formulae	Usefulness
$K = \dfrac{[A^\circ]\,[A]}{t}$	To calculate rate constant for zero order reaction
$t_{1/2} = \dfrac{[A^\circ]}{2K}$	Determination of $t_{1/2}$ from K and vice versa
$K = \dfrac{2.303}{t} \log \dfrac{[A^\circ]\,]}{[A]}$	To calculate rate constant for first order reaction from initial conc. and conc. at time '**t**'
$t_{1/2} = \dfrac{0.693}{K}$	Determination of $t_{1/2}$ from K and vice versa
$K = \dfrac{2.303}{t} \log \dfrac{P^\circ}{2P - Pt}$	To calculate rate constant for first order reaction for gases from initial pressure of gas and partial pressure of gas at time '**t**'
$t_{1/2} \propto \dfrac{1}{[A]n-1}$ (n-1 is raised as power to [A])	To determine $t_{1/2}$ for nth order reaction
$t = \dfrac{2.303}{K} \log\ n$	To calculate time required for reduction of initial conc. of a reactant to nth fraction
$[A] = \dfrac{[A^\circ]}{2n}$ (n is raised as power to the number 2)	To calculate conc. of reactant after 'n' half lives
$\text{Log}\ \dfrac{K2}{K1} = \dfrac{Ea}{2.303R}\left[\dfrac{T2-T1}{T1\,T2}\right]$	To calculate K$_1$ **or** K$_2$ **or E$_a$ at** different temperatures
$\text{Log K} = \dfrac{-Ea}{2.303R} + \log A$	To calculate K from E$_a$ and pre exponential factor A
$\text{Log A} = \log K + \dfrac{Ea}{2.303R}$	To calculate A from E$_a$ and K for a reaction
$\log x = \dfrac{-Ea}{2.303RT}$, next step is	To calculate fraction of molecules (x) which is having threshold energy in a reaction.

$x = $ antilog of $\dfrac{-Ea}{2.303RT}$ (value of $\dfrac{-Ea}{2.303RT}$ is calculated and antilog is taken)	

IMPORTANT CONCEPTS FOR SLOW LEARNERS

1. **Rate of reaction**: it is defined as the change in concentration of a reactant or product in unit time
2. **Factors affecting rate of reaction**: a) nature of reactant b) concentration of reactants c) temperature d) catalyst e) surface area of reactant
3. **Rate law**: the rate expression in terms of concentration of reactants with each concentration terms raised to some power which may or may not be equal to stochiometric coefficient
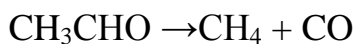
$$aA + bB \rightarrow \text{Product}$$
$$\text{Rate} = k\,[A]^{P}\,[B]^{Q}$$
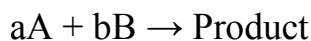
4. **Order of reaction**: it is sum of power of concentration of reactants in the rate law expression.
5. **Unit of rate constant**: rate $= k[A]x$
   $k = $ rate/$[con]^{x}$
   Where $x = 0,1,2,3$
6. **Pseudo first order reaction**: a reaction which is not truly of first order but under certain condition becomes reaction of first order .
   Exp $C_{12}H_{22}O_{11} + H_2O \xrightarrow{H+} C_6H_{12}O_6 + C_6H_{12}O_6$
   Rate $= k[C_{12}H_{22}O_{11}]^{1}$
7. **Half life period**: time in which concentration of reactants is reduced to half of its initial concentration
   $T_{1/2} = .693/k$ half life expression for first order
8. **Activation energy**: amount of energy required to form activated complex is called activation energy
9. **Effect of temperature**: the rate of reaction increases with the increase in temperature, rate becomes double on every ten degree rise in temperature
10. **Calculation of activation energy**: $Ea = 2.303R[T_1T_2/T_2\text{-}T_1] \log k_2/k_1$

SURE SHOT QUESTIONS WITH ANSWERS

1. The gas phase decomposition of acetaldehyde
$CH_3CHO \rightarrow CH_4 + CO$
Follow the rate law.
What are the units of its rate constant?
Ans- $Atm^{-1/2}sec^{-1}$

2. State the order with respect to each reactant and overall reaction.
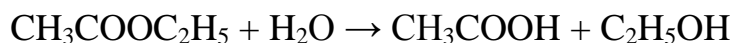$H_2O + 3I^- + 2H^+ \rightarrow 2H_2O + I_3^-$
Rate= $k [H_2O_2]^1[I]^1$
Ans- order of reaction = 1+1= 2

3. Give one example of pseudo first order reaction
Ans- Hydrolysis of an ester
$CH_3COOC_2H_5 + H_2O \rightarrow CH_3COOH + C_2H_5OH$

4. The conversation of molecules X to Y follows the second order of kinetics. If concentration of X is increased 3 times, how will it affect the rate of formation of Y.
Ans- rate = $k [A]^2$
$= k [3A]^2$
$= k [9A]^2$
The rate of formation will become nine times.

5. The rate law for reaction is
Rate = $k [A][B]^{3/2}$
Can the reaction be an elementary process? Explain
Ans- no, an elementary process would have a rate law with orders equal to its molecular ties and therefore must be in integral form.

6. The rate of a particular reaction quadruples when the temperature changes from 293K to 313K. Calculate activation energy.
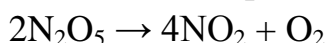Ans- $k_2/k_1 = 4$,
$T_1 = 293$ K $T_2 = 313K$
LOG $[K2/K1] = Ea[T_2-T_1]/ 19.15$
Thus on calculating and substituting values we get
$Ea = 52.86$ KJ mol^{-1}

7. If the decomposition of nitrogen oxide as
$2N_2O_5 \rightarrow 4NO_2 + O_2$
Follow first order kinetic.

(i)   Calculate the rate constant for a 0.05 M solution if the instantaneous rate is 1.5
        x 10^{-6} mol/l/s ?

Ans- rate= $K[N_2O_5]$

    $K = rate/[N_2O_5]$

    $K = 1.5 \times 10^{-6}/0.05$

    $K = 3.0 \times 10^{-5}$

(ii)   What concentration of N_2O_6 would give a rate of 2.45 x 105 mol L-1 s-1

Rate $= 2.45 \times 10^{-5}$ mol L^{-1} s^{-1}

$[N_2O_5] = Rate/K = 2.45 \times 10^{-5}/3.0 \times 10^{-5}$

        $= .82$ M

8. Write the difference between order & molecularity of reaction
Ans-

ORDER	MOLECULARITY
It is the sum of the powers of concentration terms in the rate law expression	It is the number of reacting species undergoing simultaneously collision in a reaction
It is determined experimentally	It is a theoretical concept
Order of reaction need not to be whole number	It is whole number only
Order of reaction can be zero	It can't be zero or fractional

9. The rate constant for first order reaction is 60/s. how much time will it take to
    reduce the concentration of the reaction to 1/10 of its initial value.

Ans- t= 2.303/k log $[R_o]/[R]$

    t= 2.303/1/10 log $[R_o]/[R]$

    t= 2.303/60 log 10

    t $= 2.303/60 = 3.38 \times 10^{-2}$ s $^{-1}$

10. The rate of most reaction double when their temperature is raised from 298 K to
    308 K. calculates the activation energy of such a reaction.

Ans- log k_2/k_1 = Ea /2.303 R x T_2-T_1/T_1T_2

    Ea = 2.303 x 8.314 x 298 x 308 x .3010/ 1000

    Ea = 52.89 KJ/mol

11. Define threshold energy and activation energy. How they are related?

Ans- **Threshold energy**: it is the minimum amount of energy which the reactant
molecules must possess for the effective collision in forming the products.

Activation energy: it is the excess energy required by the reactants to undergo chemical reaction.

Activation energy = threshold energy – average kinetic energy of molecules

Important questions

Q1.   Define Pseudo order reaction?

Ans:- Reaction showing higher order but actually follow lower order is known as Pseudo order

Q2.   The decomposition reaction of ammonia gas on platinum surface has a rate constant $= 2.3 \times 10^{-5}$L mol^{-1}s^{-1}. What is the order of the reaction?

Q3   Mention the factors that affect the rate of a chemical reaction.
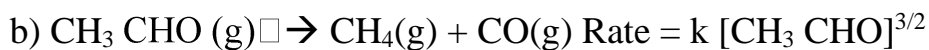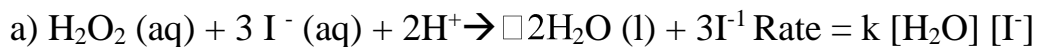
Ans. (i) Nature of reactants

 (ii) Concentration of reactants

(iii) Surface area of reactants

 (iv) Temperature

(v) Presence of catalyst

Q4   From the rate expression for the following reactions determine their order of reaction and dimensions of the rate constants.

a) H_2O_2 (aq) + 3 I $^-$ (aq) + 2H$^+$→$\square$2H$_2$O (l) + 3I^{-1} Rate $= k$ [H$_2$O] [I$^-$]

b) CH_3 CHO (g)$\square$→ CH$_4$(g) + CO(g) Rate $= k$ [CH$_3$ CHO]$^{3/2}$

Q5..   A reaction is first order in A and second order in B.

i) Write differential rate equation.

ii) How is the rate affected when concentration of B is tripled?

iii) How is the rate affected when the concentration of both A and B is doubled?

(i)   Rate = K[A] [B]2
(ii)   Rate1 = K[A] [B]2

Rate = 9K [A][B]2 = Rate X 9

(iii) Rate2 = K[2A][2B]2

Rate2 = 2X 2 X2 X K [A][B]2 = 8 x Rate

Q6. The decomposition of NH_3 on platinum surface is zero order reaction.

What are the rates of production of N_2 and H_2 if k = 2.5 x 10^{-4} mol L^{-1} S^{-1}?

Ans. 2NH3 ⇌ N2 (g) +H2(g)

Rate of reaction = $-\frac{1}{2}\frac{\Delta[NH3]}{\Delta t} = \frac{\Delta[N2]}{\Delta t} = \frac{\Delta[H2]}{\Delta t}$

For Zero order reaction, Rate of reaction = K = 2.5 X 10-4 mol L-1 S-1

$\frac{\Delta[N2]}{\Delta t}$ = 2.5 x 10^{-4} mol L^{-1} S^{-1}

$\frac{\Delta[H2]}{\Delta t}$ = 3 X2.5 x 10^{-4} mol L^{-1} S^{-1}

=7.5 X 10-4 mol L^{-1} S^{-1}

Q7   . Derive the Integrated rate equation for first order reaction. Also find half life period and plot the graph associated to it.

Q8. For a first order reaction, show that time required for 99% completion is twice the time required for the completion of 90% of reaction.

Q9. A first order reaction has a rate constant 0.0051min^{-1} .If we begin with 0.10 M concentration of the reactant, what concentration of the reactant will   be left after 3 hours.

K = 0.0051min-1   [R]o = 0.10 M t = 3h = 3 X 60 min

$t = \frac{2.303}{K} \log \frac{[R]o}{[R]}$

$3 X 60 = \frac{2.303}{0.0051} \log \frac{[0.10]}{[R]}$

$$\text{Log } \left[\frac{0.1}{R}\right] = \frac{180X\ 0.0051}{2.303} = 0.03986$$

$$\left[\frac{0.1}{R}\right] = \text{antilog } 0.3986$$

$$\frac{0.1}{[R]} = 2.503$$

$$[R] = \frac{0.1}{2.503}\ 0.0399\ M$$

Q10. The half-life for radioactive decay of ^{14}C is 5730 years. An archaeological

Artifact containing wood had only 80% of the ^{14}C found in a living tree.

Estimate the age of the sample

$$\text{Given } t_{1/2} \ = 5730\ yr \quad [R] = 100 \quad [R] = 80 \quad K = \frac{0.693}{t1/2} = \frac{0.693}{5730}$$

$$t = \frac{2.303}{K}\ \log\frac{[R]o}{[R]}$$

$$t = \frac{2.3.03\ X\ 5730}{0.693}\ \log\frac{100}{80}$$

$$= \frac{2.3.03\ X\ 5730}{0.693}\ X\ 0.0969$$

=1845.18 yr

Q11. What is the effect of temperature on the rate constant of a reaction? How

Can this temperature effect on rate constant be represented quantitatively?

Ans. Most of the chemical reaction are accelerated by increase in temperature. It has been found that for a chemical reaction with the rise in temperature by 10^0 , the rate of reaction is nearly doubled.

$$\text{Temperatue coefficient} = \frac{Rate\ constant9T+10)K}{Rate\ constant\ at\ T\ K}$$

Q12. The rate of a reaction quadruples when the temperature changes from 293K to 313 K. Calculate the energy of activation of the reaction assuming that it does not change with temperature.

T1 = 293K T2 = 313K K2/K1 = 4

$$\log\frac{K2}{K1} = \frac{Ea}{2.303R}\ [\frac{T2-T1}{T1T2}]$$

$$\log 4 = \frac{Ea}{2.303X\,8.314}\left[\frac{313-293}{313\ X\ 293}\right]$$

$$0.6021 = \frac{Ea}{191.47}\left[\frac{20}{91704}\right.$$

$$Ea = \frac{0.6021\ X\ 19.147\ X\ 91709}{20}$$

$$= 52862.94\ \text{jmol}^{-1}$$

Q13. A first order reaction takes 40 min for 30% decomposition. Calculate t1/2..

Ans. $K = \frac{2.303}{t}\log\frac{[R]o}{[R]}$

$t_{1/2} = \frac{0.963}{K}$

$t = 40$ min

30% decomposition means

$[R]o = 100M\ [R] = 70M$

$. K = \frac{2.303}{t}\log\frac{[R]o}{[R]}$

$. K = \frac{2.303}{t}\log\frac{[100]}{[70]}$

$K = \frac{2.303}{40}\log 1.428$

$K = \frac{2.303\ X\ 0.1548}{40}$

$= 0.0089\ \text{min}^{-1}$

$t_{1/2} = \frac{0.693}{0.0089} = 77.865$ min

Q14 (a) Distinguish between order of reaction &Molecularity.

(b) For a decomposition reaction the values of rate constant k at two different temperatures are given below:k1 =2.15 x 10⁻⁸ L mol⁻¹s⁻¹ at 650K, k2 =2.39 x 10⁻⁷ L mol⁻¹s⁻¹ at 700K Calculate the value of Activation Energy for this reaction.

Q15. (i) Write short notes on the following:

(a) Activation energy of a reaction (b) Elementary step in a reaction (c)Rate of a reaction

(ii) The following result has been obtained during the kinetic studies of the

reaction $2A + B \rightarrow C+D$

Experiment	[A] mol L-1	[B] mol L-1	Intial rate mol $L^{-1}min^{-1}$
I	0.1	0.1	$6.0x10^{-3}$
II	0.3	0.2	$7.2X10^{-2}$
III	0.3	0.4	$2.88X10^{-1}$
IV	0.4	0.1	$2.40X10^{-2}$

Determine the rate law and rate constant for the reaction.

Let rate law in terms of rate of formation of D be $\frac{d[[D]}{dt}=\frac{dx}{dt}= K[A]^a [B]^b$

(i) $6.0X10\text{-}3 =k (0.1)^a (0.1)^b$
(ii) $7.2X10\text{-}3 =K(0.3)^a(0.2)^b$
(iii) $2.88X10\text{-}3=K(0.3)^a(0.4)^b$
(iv) $2.40X10\text{-}3=K(0.4)^a(0.1)^b$

Divide Eq. (iv) by (i)

$4=(4)a$ $a=1$

Divide eq. (iii) by (ii)

$4 = (2)b$

$2^2=2$

Order w.r.t. A $= 1$

Order w.r.t. $= 2$

Rate law $= \frac{d[D]}{dt} = K\,[A]\,[B]^2$

$6.0 \times 10^{-3}M\ min^{-1} = K\,(0.1M)\,(0.1M)^2$

$K = 6M^{-2}\,min^{-1}$

HIGHER ORDER THINKING SKILLS (HOTS) QUESTIONS

1. For the reaction, $2N_2O_5 \rightarrow 4NO_2 + O_2$, the rate of reaction can be expressed in three ways:

$$-\frac{d[N_2O_5]}{dt} = k[N_2O_5] \qquad ; \ +\frac{d[NO_2]}{dt} = k'[N_2O_5] \text{ and} \qquad +\frac{d[O_2]}{dt} = k''[N_2O_5]$$

Establish a relation between k and k' and between k and k''.

2. Rate constant for a first order reaction is $5.78 \times 10^{-5}s^{-1}$. What percentage of initial reactant will react in 10 hours?

3. For a first order reaction $A \rightarrow B$, the rate constant k is 5 min^{-1}. In another first order reaction $C \rightarrow D$, only 10% of C decomposes in the time that takes 50 % of A to decompose in the first order reaction. What is the rate constant for the second reaction?

4. In the Arrhenius equation, for a certain reaction the value of A and E_a are 4×10^{13} sec^{-1} and 98.6 kJmol^{-1} respectively. If the reaction is of first order, at what temperature will its half-life be 10 minutes?

5. Answer the following questions on the basis of the curve for the first order reaction $R \rightarrow P$.
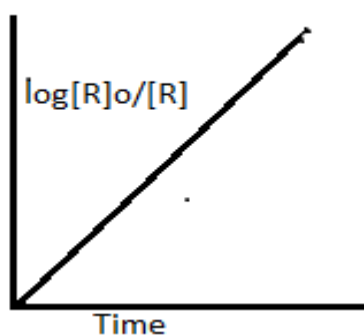
(i) What is the relation between slope of this line and rate constant?

(ii) Calculate the rate constant of the above reaction if the slope is $2 \times 10^{-4}\,s^{-1}$.

6. Give reasons for the following:

(i) On the basis of the heat of combustion values, graphite is more stable than diamond. However, diamond does not change into graphite for the years together.

(ii) Explosives release a lot of energy on heating or when hit, yet they can be stored confidently for long time.

7. A substance with initial concentration A, follows zero order kinetics. In how much time the reaction will go to completion? Derive mathematically.

8. The rate constant for an isomerism reaction, A → B is 4.5×10^{-3} min^{-1}. If the initial concentration of A is 1 M, calculate the rate of reaction after one hour.

9. At constant temperature and volume, X decomposes as

   2X (g) → 3Y (g) + 2Z (g)

   P_x is the partial pressure of X

Experiment	Time in minutes	P_x in mm Hg
1	0	800
2	100	400
3	200	200

   (i) What is the order of reaction with respect to X?

   (ii) Find the time for 75% completion of the reaction.

   (iii) Find the total pressure when pressure of X is 700 mm Hg.

10. The rate constants of a reaction at 700K and 760K are 0.011M^{-1}s^{-1} and 0.105M^{-1}s^{-1} respectively. Calculate the value of Arrhenius parameter.

Answers to the HOTS questions.

1. The rate of the reaction:

   $2N_2O_5 \rightarrow 4NO_2 + O_2$ is given by

   $-\dfrac{d[N_2O_5]}{dt} = k[N_2O_5] = \dfrac{1}{2}\dfrac{d[NO_2]}{2dt} = k[N_2O_5] = 2\dfrac{d[O_2]}{dt}$

   But the rate of the reaction, $\dfrac{dx}{dt} = k[x]$

   $-\dfrac{d[N_2O_5]}{dt} = k[N_2O_5]$ and $\dfrac{1}{2}\dfrac{d[NO_2]}{2dt} = k[N_2O_5]$

   Or $\dfrac{d[NO_2]}{dt} = 2k[N_2O_5]$

   But $\dfrac{d[NO_2]}{dt} = k'[N_2O_5]$ (given)

   Hence $k' = 2k$

   Also $2\dfrac{d[O_2]}{dt} = k[N_2O_5]$

   But $\dfrac{d[O_2]}{dt} = k''[N_2O_5]$ (given)

   Hence $k'' = \dfrac{1}{2}k$

2. t = 10 hours = $10 \times 60 \times 60 = 36000$s, x/a = ?

   The first order equation

$$k = \frac{2.303}{t} \log \frac{a}{a-x} \quad \text{or} \quad \log \frac{a}{a-x} = \frac{k}{2.303/t} \quad \text{or} \quad \log \frac{a}{a-x} = \frac{kt}{2.303}$$

$$\log \frac{a}{a-x} = \frac{0.0000578*36000}{2.303}$$

$$\log \frac{a}{a-x} = 0.9031$$

$$\frac{a}{a-x} = antilog\, 0.9031 = 8$$

$a = 8(a\text{-}x) \quad$ or $\quad a = 8a - 8x$

$8x = 8a - a \;$ or $\quad 8x = 7a$

$x/a = 7/8 \quad$ or $\quad x/a = 0.875$

or $x/a = 87.5\%$.

3. For the reaction $\quad$ A → B

$x = 50\%a \quad$ or $\quad x = 0.5a, \quad k = 5min^{-1}$

$$t_{50\%} = \frac{2.303}{k} \log \frac{a}{a-x}$$

Putting the values and solving

$$t_{50\%} = \frac{2.303}{5} 0.3010$$

For the reaction $\quad$ C → D

$k = ?, x = 10a \quad$ or $\quad x = 0.1a$

$$t_{10\%} = \frac{2.303}{k} \log \frac{a}{a-0.1a}$$

$$t_{10\%} = \frac{2.303}{k} \log \frac{a}{0.9a}$$

$$t_{10\%} = \frac{2.303}{k} \log \frac{10}{9}$$

$$t_{10\%} = \frac{2.303}{k} 0.0458$$

Now according to the question $t_{50\%} = t_{10\%}$

$$\frac{2.303}{5} 0.3010 = \frac{2.303}{k} 0.0458$$

$$\frac{0.3010}{5} = \frac{0.0458}{k}$$

$$k = \frac{0.0458 \times 5}{0.03010} \quad = \quad 0.76min^{-1}$$

4. $A = 4 \times 10^{13} s^{-1} \qquad E_a = 98.6\ kJmol^{-1} = 98600\ Jmol^{-1}$

$T = ? \qquad\qquad t_{1/2} = 10\ min = 10 \times 60 = 600\ s$

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{600}$$

$K = 0.001155\ s^{-1}$

Arrhenius equation is

$$k = Ae^{-Ea/RT} \qquad or \qquad \frac{k}{A} = e^{-Ea/RT}$$

Taking log on both sides

$$2.303 \, log \frac{k}{A} = -\frac{Ea}{2.303RT}$$

$$log \frac{0.001155}{4 \times 10^{13}} = -\frac{98600}{2.303 \times 8.314 \times T}$$

$$T = \frac{98600}{19.147 \times 16.54} = 311.34K$$

5. (i) This plot is for the first order reaction.

For a first order reaction

$$log \frac{[R]_o}{[R]} = \frac{kt}{2.303}$$

When a graph is plotted between $log \frac{[R]_o}{[R]}$ versus t, the slope $= \frac{k}{2.303}$

(ii) $k = slope \times 2.303 = 2 \times 10^{-4} \times 3.303 = 4.606 \times 10^{-4}$

6. (i) Diamond does not change into graphite for years together. This is because the activation energy for the conversion between these two forms of carbon is very high and is not available under normal conditions.

(ii) Explosives can be stored at room temperature for a long time. This is because there are no effective collisions of the explosive materials. On heating or when hit, the energy of the constituents of the explosive material increases and necessary activation energy is attained, collisions of the particles becomes effective and the reaction takes place resulting in the release of huge amount of energy.

7. For a zero order reaction, $\frac{-d[A]}{dt} = k[A]^0$

Or $\frac{-d[A]}{dt} = k$ or $d[A] = -kdt$

On integration

Or $[A] = -kt + I$, ... (i) Where 'I' is the constant of integration

At $t = 0 \, s$, $[A] = [A]_o$

∴ $[A]_o = -k \times 0 + I$

Or $I = [A]_o$

Substituting in equation (i)

$[A] = -kt + [A]_o$

Or $[A]_o - [A] = kt$

At completion, $[A] = 0$

$[A]_o = kt$

Or $t = \frac{[A]_o}{k}$

8.   To calculate the concentration after one hour,

$$k = \frac{2.303}{t} log \frac{[A]_o}{[A]}$$

$$4.5 \times 10^{-3} = \frac{2.303}{60min} log \frac{1}{[A]}$$

$$\log[A] = -0.1172 = \bar{1}.8828$$

$\therefore \quad [A] antilog\ (\bar{1}.8828) = 0.7635\ molL^{-1}$

To find the rate after one hour

Rate after one hour   *1h* $= k[A]$

$= 4.5\times10^{-3} \times0.7635\ molL^{-1}min^{-1}$

$=3.44\times10^{-3}\ molL^{-1}min^{-1}$

9. (i) As the pressure of X is changing with time, it cannot be a zero order reaction. let us now check it for first order.

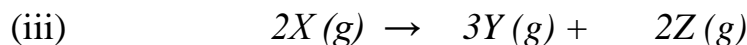At   *t = 100 minute*   *s* $k = \dfrac{2.303}{100} log \dfrac{Po}{Pt} = \dfrac{2.303}{100} log \dfrac{800}{400}$

$k = 6.932\times10^{-3} min^{-1}$

At   *t = 200 minutes* $k = \dfrac{2.303}{200} log \dfrac{Po}{Pt} = \dfrac{2.303}{200} log \dfrac{800}{200}$

$k = 6.932\times10^{-3} min^{-1}$

As k comes out to be constant, hence it is a reaction of first order.

(ii) $t_{75\%} = \dfrac{2.303}{k} log \dfrac{100}{100-75}$

$t_{75\%} = \dfrac{2.303}{6.932\times10^{-3}} log4 = 200\ minutes$

(iii)   *2X (g)* $\rightarrow$ *3Y (g)* +   *2Z (g)*

Initial   *800mmHg*   *0*   *0*

At time t   *800-2p*   *3p*   *2p*

When pressure of X is 700 mmHg,

800 – 2p = 700   *or*   *p = 50 mmHg*

Total pressure P $=$ *(800-2p) + 3p + 2p*

                $=$ *800 + 3p* $=$ *800 + 3 ×50*

                $=$ *950 mmHg*

10.   Arrhenius parameters are E_a and A

Step I. To calculate E_a

$T_1 = 700K$; $k_1 = 0.011M^{-1}s^{-1}$

$T_2 = 760\ K$; $k_2 = 0.105\ M^{-1}s^{-1}$

$log \dfrac{k_2}{k_1} = \dfrac{Ea}{2.303R} \left[\dfrac{T_2-T_1}{T_1T_2}\right]$

$log \dfrac{0.105}{0.011} = \dfrac{Ea\times\left[\dfrac{760-700}{700\times760}\right]}{2.303\times8.314}$ *upon solving*

$E_a = 166.351kJmol^{-1}$

Step II. To calculate frequency factor

Arrhenius equation

$$k = Ae^{-Ea/RT}$$

Taking log on both sides

$$2.303 \log k = 2.303 \log A - \frac{-Ea}{RT}$$

$$\log k = \log A - \frac{-Ea}{2.303RT}$$

$$\log A = 0.011 + \frac{166351}{2.303 \times 8.314 \times 700} \qquad \textit{Upon solving}$$

$A = 2.8 \times 10^{10}$ collisions / second

VALUE BASED QUESTIONS WITH ANSWERS

CHEMICAL KINETICS

1. One day in the class, Rohit learnt that conversion of diamond to graphite is energetically favoured. He felt very concerned about it. If it was likely to happen, then it will cause a lot of financial loss to those people who have diamonds because their diamonds will be ultimately converted to graphite which will be of no value. He discussed it with the teacher. His teacher told him that it was unlikely to happen, though it was thermodynamically favourable.

   a. In your opinion why it is not possible for a diamond to get converted into graphite through process is energetically favourable?

   b. How do you relate these observations to values of daily life?

   Answer. a. Although the conversion of diamond into graphite is energetically favourable yet it is unlikely to occur due to occurrence of very large activation energy barrier for this process to occur.

   b. In day to day life, we find that sometimes it seems that is chaos, gloominess, dishonesty and crookedness everywhere but there are incidents which provide us moral courage to overcome to these negative forces and help us for positive thinking, happiness and wellbeing. We strive with greater efforts to create an atmosphere of honesty, responsibility, support, commitment, perseverance and achieve new heights of success.

2. A catalyst is a substance which increases the rate of a reaction without undergoing any change in itself. A small amount of the catalyst is sufficient to bring large change in the rate of a reaction. It takes part in the reaction but is regenerated at the end of the reaction.

a.   How does a catalyst increases the rate of a reaction?

b.   In society how do catalytic elements play their role in strengthening or weakening the social value?

Answer. a. A catalyst increases the rate of a reaction by lowering the potential energy barrier and providing a alternate path which requires less activation energy.

b.   In our society we find certain people to act as catalysts in certain incidents. Sometimes we find that person who has negative thinking and does not like peaceful atmosphere, add fuel to the fire whenever there is a clash between two groups of people. He provokes indirectly one group of people against the other. At the same time there are people who like peace and harmony in the society. Even if there is a little problem in the people in society, they try to sub side the issues by their understanding and goodwill.

3. Coal does not burn by itself in air but once initiated by flame, it continues to burn. In our surroundings we can observe many processes in day to day life of such type. It is blissful to existence of life on earth otherwise there would have been a great harm to civilization as fuels would have burnt by themselves and explosives could not be stored safely.

   a.   What reason do you assign for non-occurrence of such processes at room temperature?

   b.   How do you find values linked with such processes?

   Answer. a. The reason for non-occurrence of such processes is the existence of activation energy barrier. The occurrence of such process requires a very high activation energy which is not available at room temperature.

   b.   Our society is facing a lot of problems which are major hurdles in our progress. People have innovative ideas to solve such problems. Lack of proper atmosphere, infrastructure and orientation hinders their ideas. When they get proper channel and platform they exploit their ideas to get rid of evils facing our society. Once the process starts, other people come forward with innovative ideas and this is how progress begins which achieves greater heights resulting in upliftment of society.

CHEMICAL KINETICS
[MIND MAPS AND CONCEPT MAPS]

REACTANT (R)→ PRODUCT (P)

Rate $= -\dfrac{\Delta[R]}{\Delta t}$

Instantaneous rate $= -\dfrac{d[R]}{dt}$

Units- $molL^{-1}s^{-1}$

aA + bB→ Products

Rate law :- Rate of reaction $= k[A]^p[B]^q$

Where p and q may or may not be equal to a and b respectively. The value of p and q can be find experimentally.

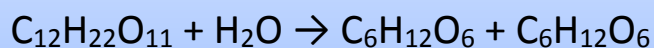K is rate constant and expression is called as rate law expression.

Order of reaction (n) = p + q

Units of $k = \dfrac{Rate}{[R[^n}$ where n is order of reaction

Order	Units of K
0	$molL^{-1}s^{-1}$
1	s^{-1}
2	$Lmol^{-1}s^{-1}$
3	$L^2mol^{-2}s^{-1}$

Pseudo-first order reaction: The reactions which appears to be of higher order but actually of first order.

For example: Hydrolysis of sucrose

$C_{12}H_{22}O_{11} + H_2O \rightarrow C_6H_{12}O_6 + C_6H_{12}O_6$

SOME IMPORTANT FORMULAE

Integrated rate equation for first order: $k = \dfrac{2.303}{t} \log \dfrac{[R_o]}{[R]}$

Half-life of first order reaction: $t_{1/2} = \dfrac{0.693}{k}$

Integrated rate equation for zero order: $k = \dfrac{[R]_o - [R]}{t}$

Half-life of zero order reaction: $t_{1/2} = \dfrac{[R]_o}{2k}$

The minimum amount of energy required to form activated complex is called activation energy, E_a.

Activation Energy = Threshold energy – Average energy

Formula to calculate Activation energy $\quad E_a = 2.303R \left[\dfrac{T_1 T_2}{T_2 - T_1}\right] \log \dfrac{k_2}{k_1}$