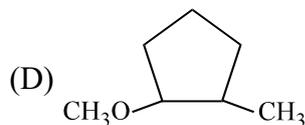
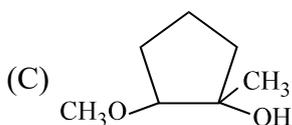
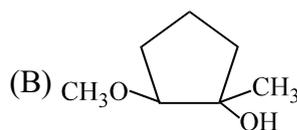
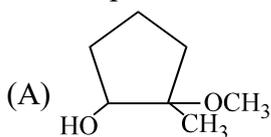


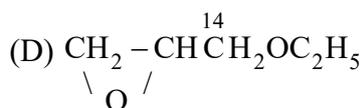
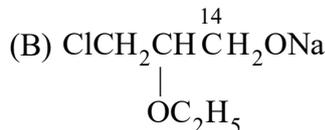
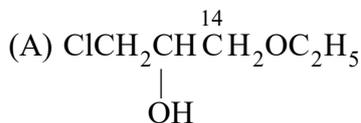
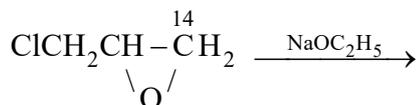
ALCOHOLS & ETHER

EXERCISE-I(A)

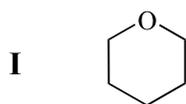
- Q.1 Which of the following reaction is called as 'Bouveault–Blanc reduction'?
- (A) Reduction of acyl halide with $\text{H}_2/\text{PdBaSO}_4$
 (B) Reduction of ester with $\text{Na}/\text{C}_2\text{H}_5\text{OH}$
 (C) Reduction of anhydride with LiAlH_4
 (D) Reduction of carbonyl compounds with Na/HgHCl
- Q.2 Glycol on treatment with PI_3 mainly gives–
- (A) Ethylene (B) Ethylene iodide (C) Ethyl iodide (D) Ethane
- Q.3 Acrolein is formed when glycerol is heated with–
- (A) Acidified KMnO_4 (B) Br_2 water (C) KHSO_4 (D) HNO_3
- Q.4 Glycerol on treatment with oxalic acid at 110°C forms–
- (A) Allyl alcohol (B) Formic acid (C) CO_2 and CO (D) Glyceric acid
- Q.5 If the starting material is 1–methyl–1,2–epoxy cyclopentane, of absolute configuration, decide which one compound correctly represent the product of its reaction with sodium methoxide in methanol.



- Q.6 When phenol is treated with PCl_5 , the yield of chlorobenzene is generally poor because of the formation of
- (A) Benzoyl chloride (B) p–chlorophenol (C) o–chlorophenol (D) Triphenyl phosphate
- Q.7 In the following reaction, final product is



Q.8 Consider the reaction of HI with the following:



Which forms di-iodide on reaction with HI (excess)?

- (A) I and II both (B) II only (C) I only (D) none

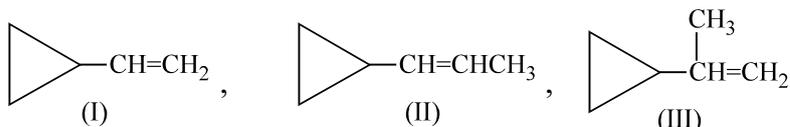
Q.9 Ethanol on reaction with acetic anhydride gives

- (A) Acetic ester (B) Formic ester
(C) Ethanoic acid (D) Acetic ester and Ethanoic acid both

Q.10 Ethanol cannot be dried by anhydrous CaCl_2 due to formation of the following solvated product

- (A) $\text{CaCl}_2 \cdot 2\text{C}_2\text{H}_5\text{OH}$ (B) $2\text{CaCl}_2 \cdot 3\text{C}_2\text{H}_5\text{OH}$ (C) $\text{CaCl}_2 \cdot 3\text{C}_2\text{H}_5\text{OH}$ (D) $\text{CaCl}_2 \cdot \text{C}_2\text{H}_5\text{OH}$

Q.11 Rate of hydration of



will be in order:

- (A) $\text{I} < \text{II} < \text{III}$ (B) $\text{I} < \text{III} < \text{II}$ (C) $\text{II} < \text{I} < \text{III}$ (D) $\text{III} < \text{II} < \text{I}$

Q.12 The reaction of $\text{CH}_3\text{OC}_2\text{H}_5$ with HI gives

- (A) CH_3I (B) $\text{C}_2\text{H}_5\text{OH}$ (C) $\text{CH}_3\text{I} + \text{C}_2\text{H}_5\text{OH}$ (D) $\text{C}_2\text{H}_5\text{I} + \text{CH}_3\text{OH}$

Q.13 The number of methoxy groups in a compound can be determined by treating it with

- (A) HI and AgNO_3 (B) Sodium carbonate (C) Sodium hydroxide (D) Acetic acid

Q.14 Most acidic alcohol out of following compounds is

- (A) $(\text{CH}_3)_3\text{C}-\text{OH}$ (B) $\text{CH}_3\text{CH}_2\text{OH}$ (C) CH_3OH (D) PhOH

Q.15 Action of HNO_2 on CH_3NH_2 gives following as major product

- (A) CH_3OH (B) $\text{CH}_3-\text{O}-\text{CH}_3$ (C) $\text{CH}_3-\text{O}-\text{N}=\text{O}$ (D) CH_3-NO_2

Q.16 A compound 'X' with molecular formula $\text{C}_3\text{H}_8\text{O}$ can be oxidised to a compound 'Y' with the molecular formula $\text{C}_3\text{H}_6\text{O}_2$, 'X' is most likely to be

- (A) Primary alcohol (B) Secondary alcohol (C) Aldehyde (D) Ketone

Q.17 Diethyl ether and air gives ether hydroperoxide. The mechanism of the reaction is

- (A) Nucleophilic substitution (B) Free radical addition
(C) Free radical substitution (D) None of the above

Q.18 Ether on carbonylation gives

- (A) Alkanoic acid (B) Alkanone (C) Alkyl alkanoate (D) Alkanal

Q.19 $\text{I}^\ominus \text{R} - \overset{\oplus}{\text{O}} - \text{R}' \longrightarrow \text{RI} + \text{R}'\text{OH}$ true about this mechanism

- (A) $\text{S}_{\text{N}}1$ in gas phase (B) $\text{S}_{\text{N}}2$ in aqueous phase
(C) both of the above (D) none

Q.20 Phenol with Hinsberg's reagent gives

- (A) Sulphone (B) Sulphanilic acid (C) Sulphonic ester (D) Sulphonol

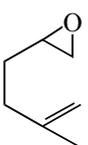
- Q.21 Select the odd structure out
 (A) $\text{CH}_3\text{-CH(OH)-CH}_2\text{-CH}_3$ (B) $\text{CH}_3\text{-CH(OH)-CH}_2\text{-CH}_2\text{-CH}_3$
 (C) $\text{CH}_3\text{-CH(OH)-CH}_3$ (D) $\text{CH}_3\text{-CH}_2\text{-CH(OH)-C}_2\text{H}_5$

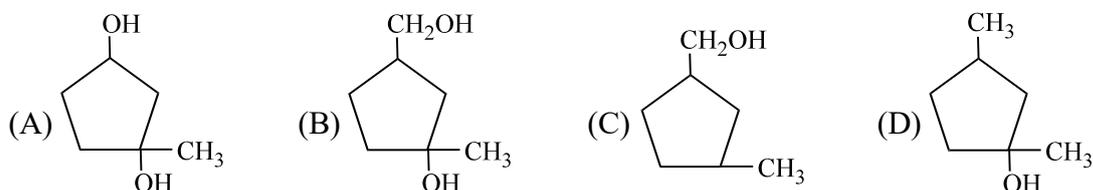
- Q.22 Glycerol $\xrightarrow{\text{KHSO}_4}$ A $\xrightarrow{\text{LiAlH}_4}$ B
 A and B are:
 (A) Acrolein, allyl alcohol (B) Glyceryl sulphate, acrylic acid
 (C) Allyl alcohol, acrolein (D) Only acrolein (B is not formed)

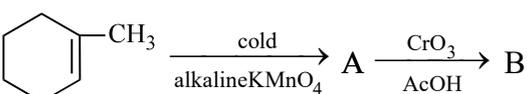
- Q.23 An ether is heated with phosphorous penta sulphide to give
 (A) Alkanthiol (B) Dialkyl sulphide (C) Hydrogen sulphide (D) Thioester

- Q.24 Phenol $\xrightarrow[\text{(ii) CO}_2/140^\circ\text{C}]{\text{(i) NaOH}}$ A $\xrightarrow[\text{CH}_3\text{COOH}, \Delta]{\text{H}^+/\text{H}_2\text{O}}$ B $\xrightarrow[\Delta]{\text{Al}_2\text{O}_3}$ C
 In this reaction, the end product C is:
 (A) salicylaldehyde (B) salicylic acid (C) phenyl acetate (D) aspirin

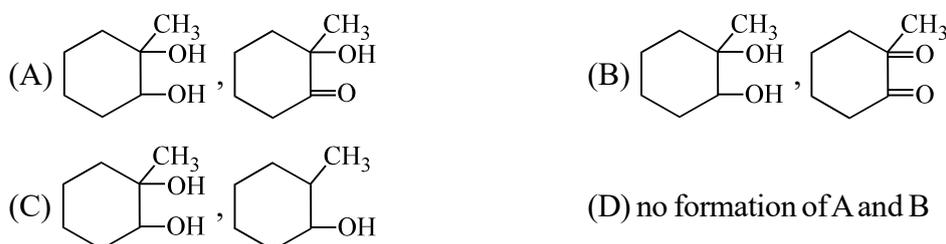
- Q.25 In the Liebermann's nitroso reaction changes in the colour of phenol occurs as:
 (A) Brown or red-greenish red-deep blue (B) red-deep blue-green
 (C) red-green-white (D) white-red-green

- Q.26  $\xrightarrow{\text{H}_3\text{O}^+}$ A. 'A' is



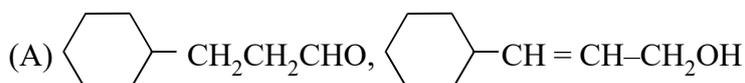
- Q.27 

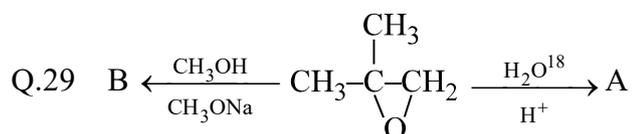
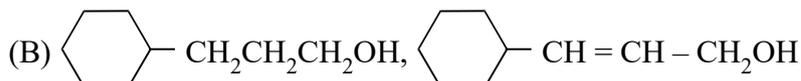
A and B are:



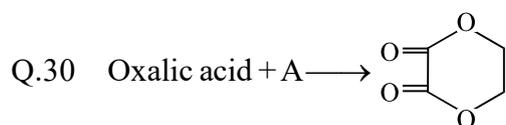
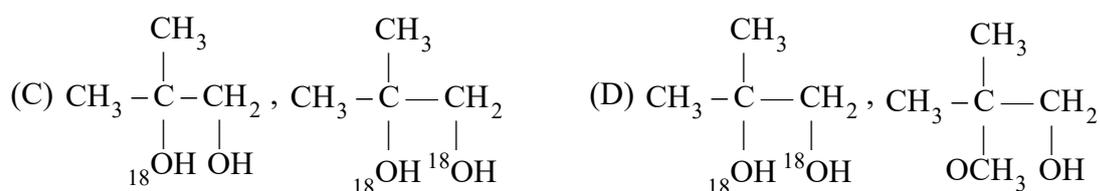
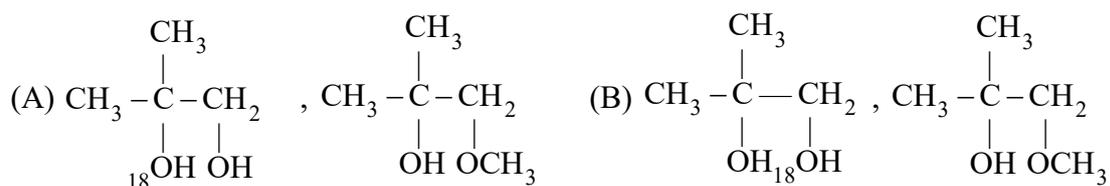
- Q.28 B $\xleftarrow{\text{NaBH}_4}$  -CH=CH-CHO $\xrightarrow{\text{H}_2/\text{Pt}}$ A

A and B are:

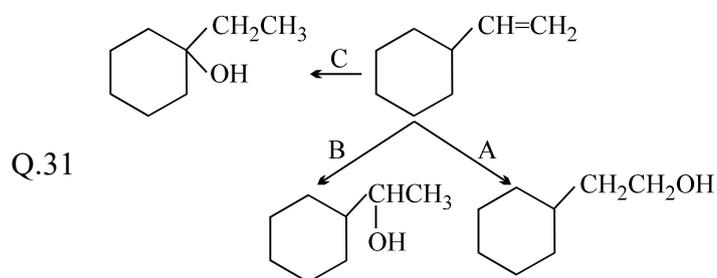
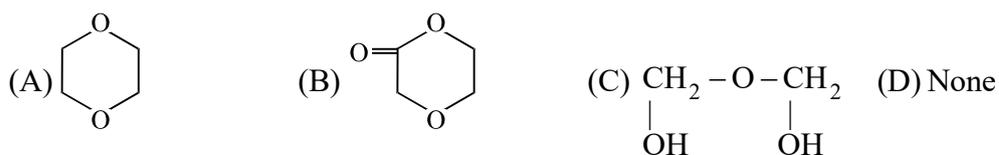




A and B are



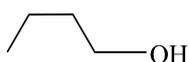
hence A $\xrightarrow{\text{conc. H}_2\text{SO}_4}$ B, B is:



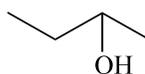
Select schemes A, B, C out of

- I** acid catalysed hydration **II** HBO **III** oxymercuration-demercuration
 (A) I in all cases (B) I, II, III (C) II, III, I (D) III, I, II

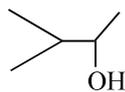
Q.32 Dehydration of the alcohols



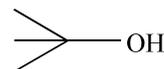
(I)



(II)



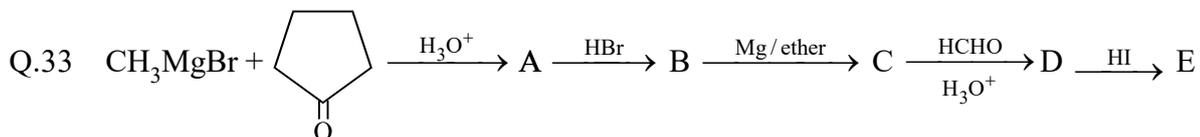
(III)



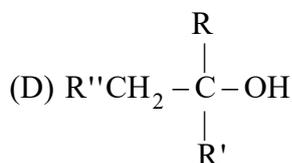
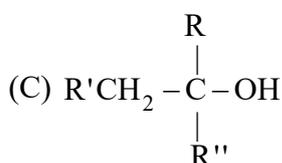
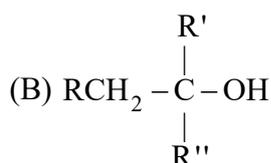
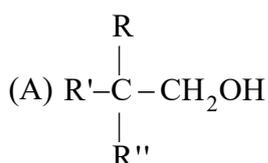
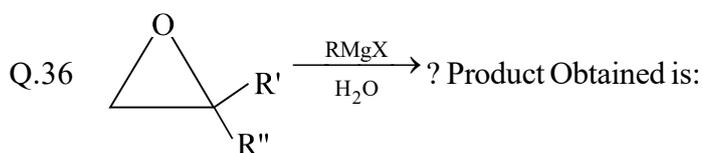
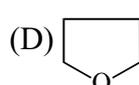
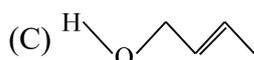
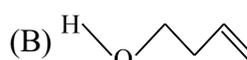
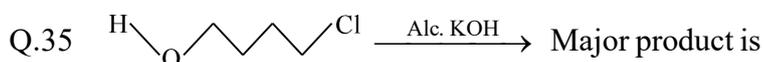
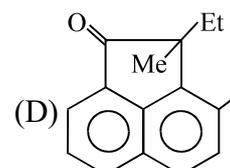
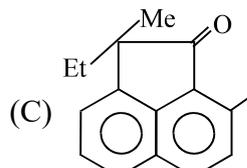
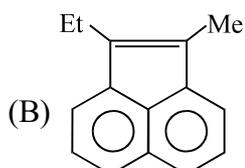
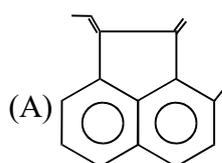
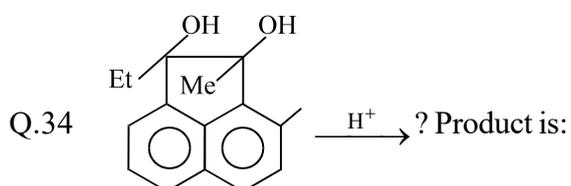
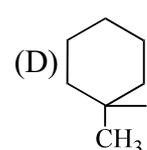
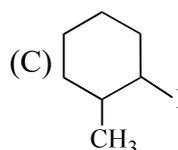
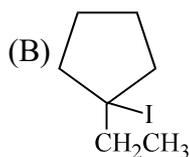
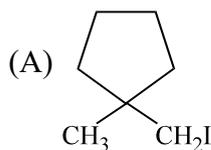
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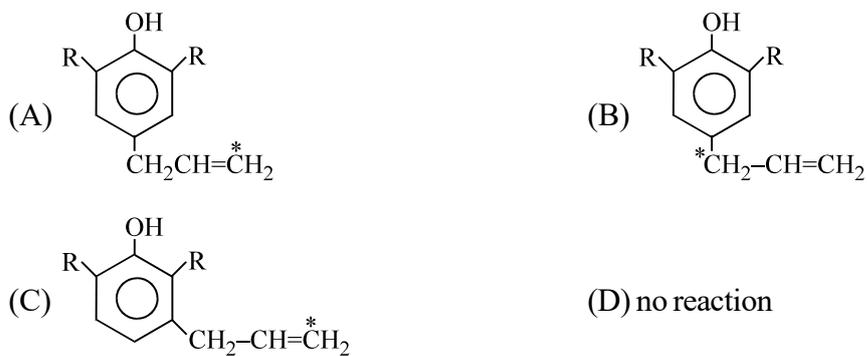
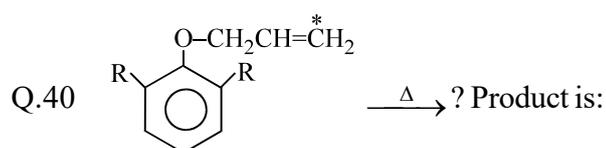
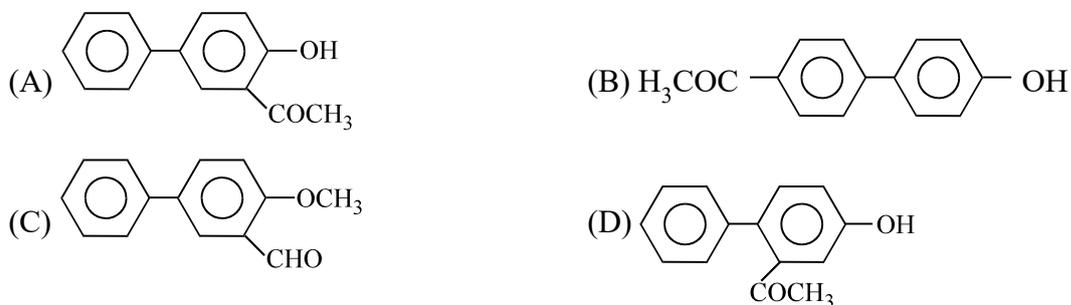
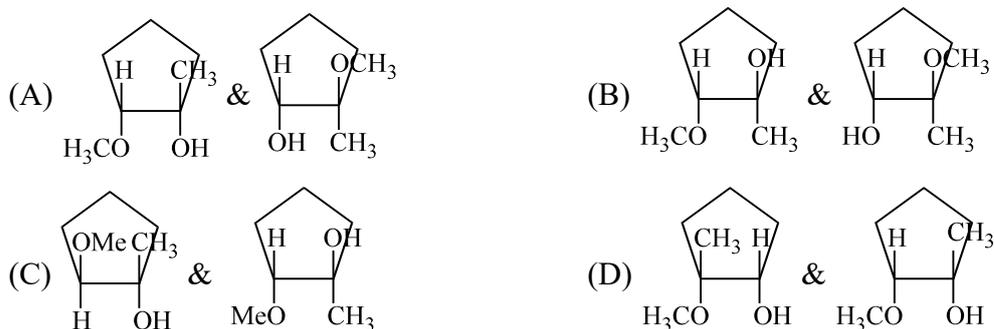
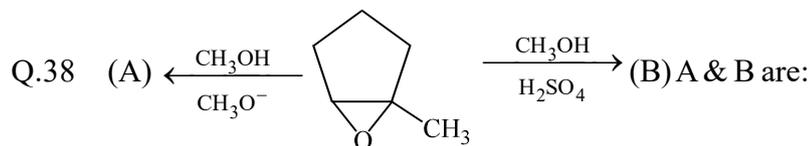
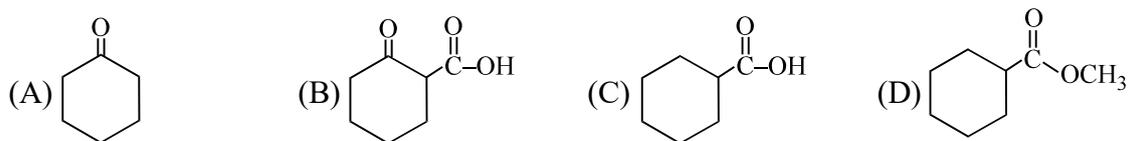
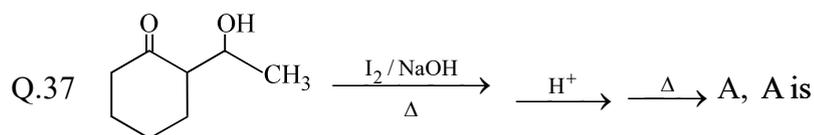
will be in order

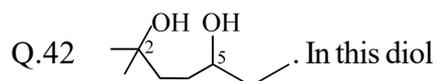
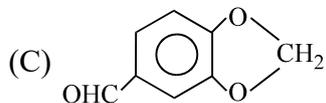
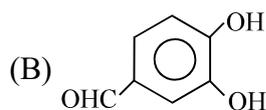
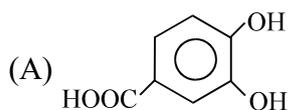
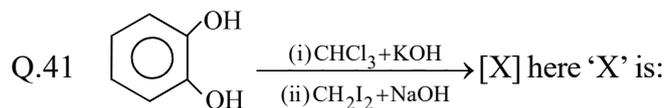
(A) IV > III > II > I (B) I > II > III > IV (C) IV > II > III > I (D) II > IV > I > III



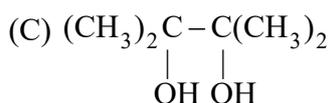
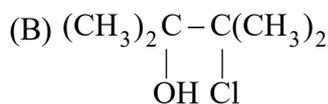
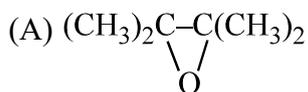
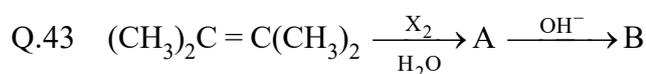
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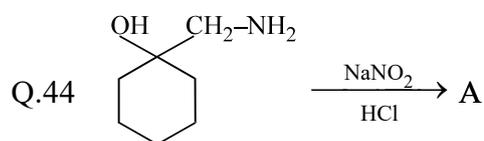




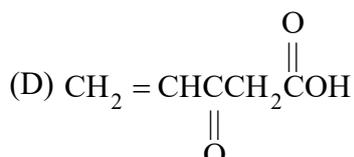
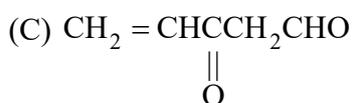
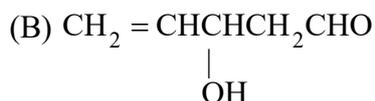
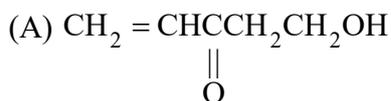
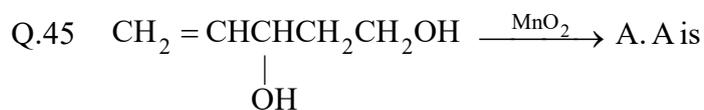
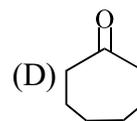
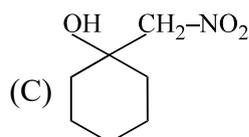
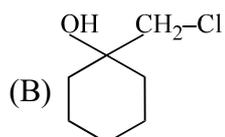
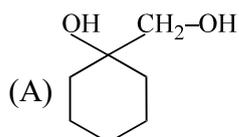
- (A) OH at C₂ is more basic than that of at C₅ (B) OH at C₂ is more acidic than at C₅.
 (C) both have same basicity (D) both have same acidic strength



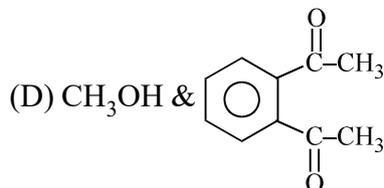
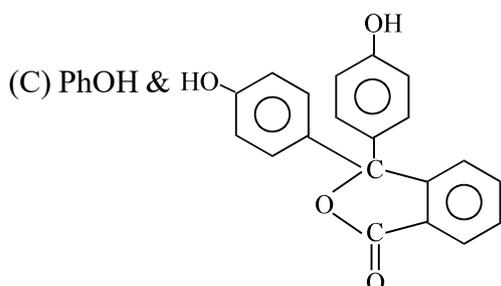
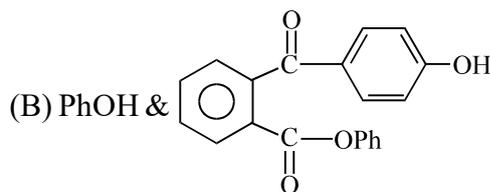
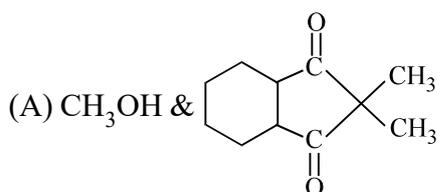
(D) None



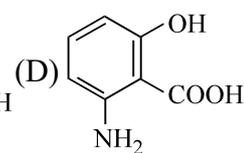
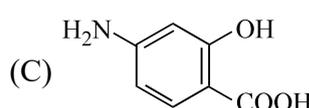
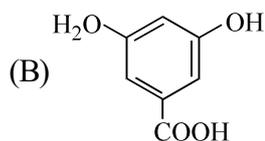
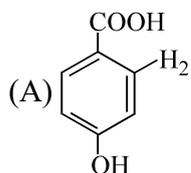
A is



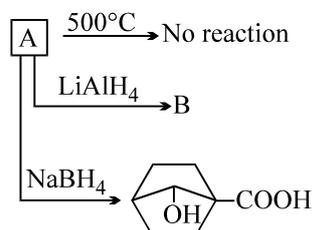
Q.46 Acetophenone $\xrightarrow{\text{HCO}_3\text{H}}$ A $\xrightarrow{\text{H}_3\text{O}^+}$ B + C $\xrightarrow[\text{H}^+]{\text{Phthalic Anhydride}}$ Indicator (D)
C & D are



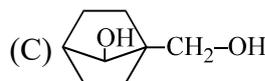
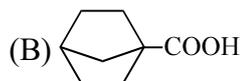
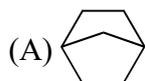
Q.47 m-Aminophenol on treatment with NaOH and CO_2 gives which of the following as major product?



Question No 48 to 50 (3 questions)



Q.48 Compound 'B' is?



Q.49 Organic compound A does not undergo decarboxylation reaction because?

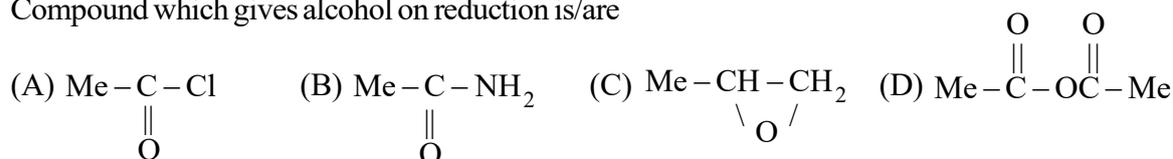
- (A) Intermediate does not follow Saytzeff's rule
(B) Intermediate does not follow Hofmann's rule
(C) Intermediate does not follow Bredt's rule
(D) Intermediate does not follow Markovnikov's rule

Q.50 Total No. of stereoisomers of B are?

- (A) 2 (B) 4 (C) 3 (D) 6

EXERCISE-I(B)

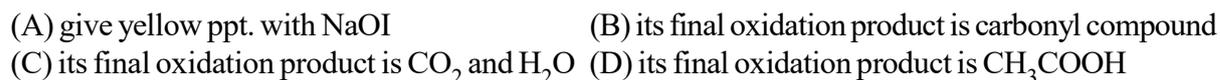
Q.1 Compound which gives alcohol on reduction is/are



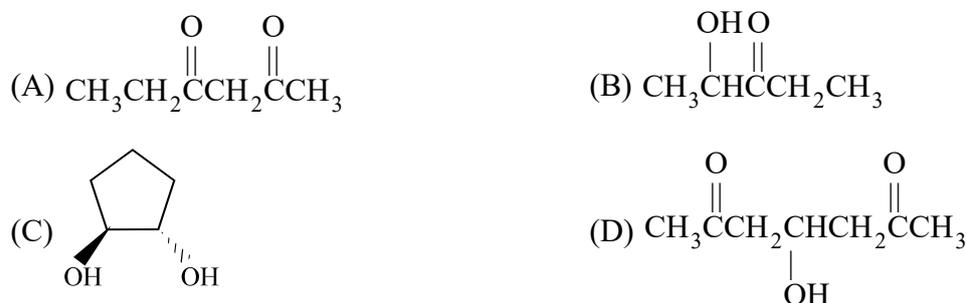
Q.2 Phenol and ethanol are distinguished by the reaction with



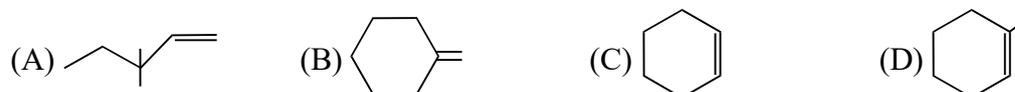
Q.3 In the reaction sequence, $\text{CaC}_2 \xrightarrow{\text{H}_2\text{O}} \text{A} \xrightarrow[\text{Hg}^{+2}]{\text{dil. H}_2\text{SO}_4} \text{B} \xrightarrow[\text{Ni}]{\text{H}_2} \text{C}$, true about the product C is



Q.4 Which can be cleaved by HIO_4 ?



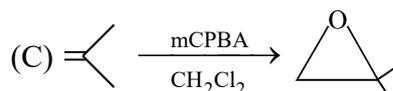
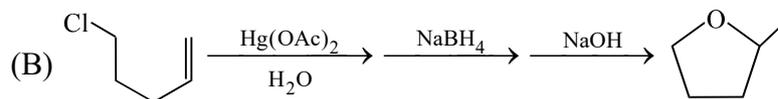
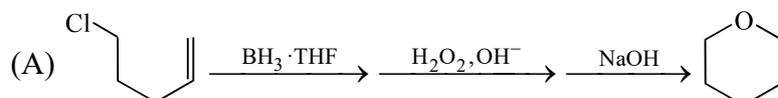
Q.5 HBO, oxymercuration-demercuration and acid catalysed hydration will not give same product in



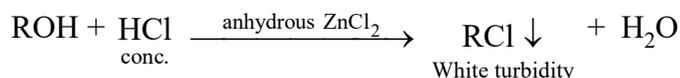
Q.6 Diethyl ether reacts with PCl_5 to form



Q.7 Select the correct synthesis products



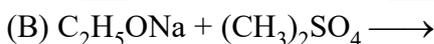
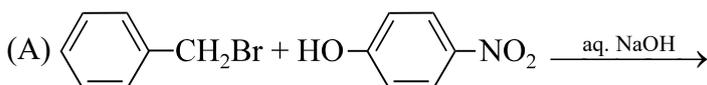
- Q.8 The molecules of ether dehydrates in the presence of—
 (A) Al_2O_3 (B) H_3PO_4 (C) $\text{H}_2\text{S}_2\text{O}_7$ (D) liq. NH_3
- Q.9 Anhydride of alcohol is
 (A) Ether (B) Aldehyde
 (C) Alkyl hydrogen sulphure (D) Alkene
- Q.10 Lucas test is used to make distinction between 1° , 2° and 3° alcohols



This shows that

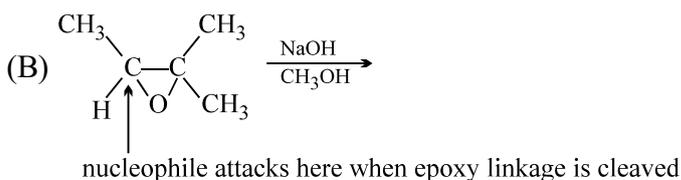
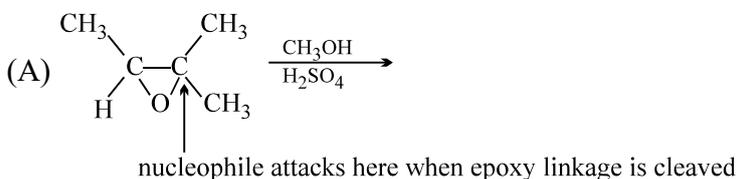
- (A) ROH behaves as a base
 (B) greater the value of pK_a (alcohol), greater the reactivity with conc. HCl and thus sooner the formation of white turbidity.
 (C) alcohol which reacts fastest with Na metal, will give turbidity at fastest rate
 (D) alcohol which gives red colour during Victor Mayor test, will give turbidity at slower rate than those giving blue or white colour during Victor Mayor test.
- Q.11 If ethanol dissolves in water, then which of the following would be done
 (A) Absorption of heat (B) Emission of heat
 (C) Increase in volume (D) Contraction in volume

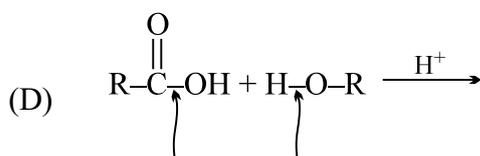
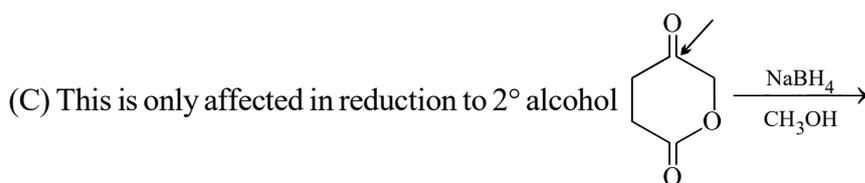
- Q.12 Which method is useful for the synthesis of ether?



- Q.13 Which of the following can react with TsCl
 (A) Glycerol (B) Oximinoacetone
 (C) Oil of wintergreen (D) dimethyl amine

- Q.14 Which is/are correct statements?



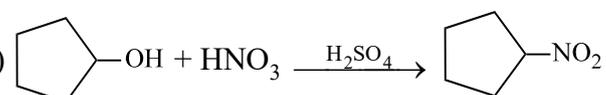
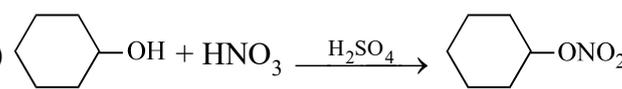
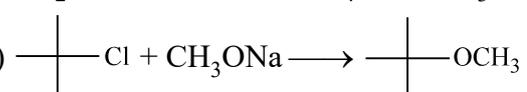


These bonds undergo cleavage in the reaction

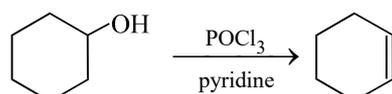
Q.15 3-methyl-3-hexanol can be prepared by

- (A) CH_3MgI and 3-hexanone, followed by hydrolysis
 (B) $\text{C}_2\text{H}_5\text{MgI}$ and 2-pentanone, followed by hydrolysis
 (C) $\text{C}_3\text{H}_7\text{MgI}$ and 2-butanone, followed by hydrolysis
 (D) $\text{C}_4\text{H}_9\text{MgI}$ and propanone, followed by hydrolysis

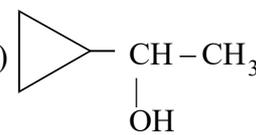
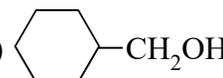
Q.16 In which cases product formed are not according to reaction?

- (A) 
 (B) 
 (C) $\text{CH}_2 = \text{CH}-\text{CHO} + \text{LiAlH}_4 \longrightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$
 (D) 

Q.17 Dehydration of alcohols take place more rapidly with POCl_3 than with H_2SO_4 . Select the correct statement(s) about the following dehydration reaction.



- (A) It does not involve carbocation.
 (B) It involves $\text{R}-\text{OPOCl}_2$ with $-\text{OPOCl}_2$ as a better leaving group.
 (C) It involves E_2 mechanism as pyridine base abstracts proton from the adjacent carbon at the same time at which $-\text{OPOCl}_2$ is leaving.
 (D) It is E_1 reaction without formation of carbocation.
- Q.18 Which of the following will get oxidised by Br_2 / KOH into carboxylic acid?

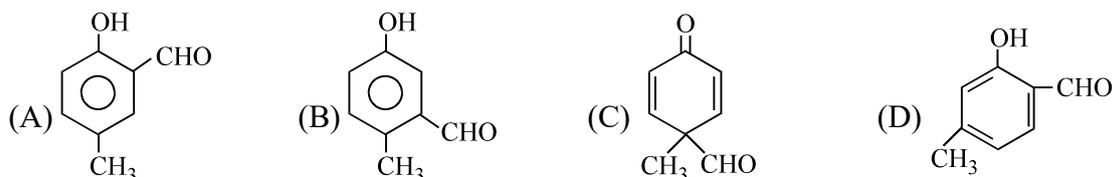
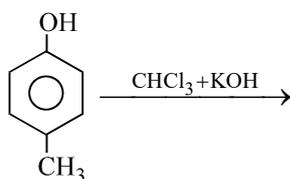
- (A) $\text{CH}_3-\text{CH}_2-\text{OH}$ (B) 
 (C)  (D) 

Q.19 In Kolbe-Schmidt reaction, o-hydroxy benzoic acid is predominantly formed. This is because

- (A) salicylate anion is a stronger base than phenoxide ion
 (B) salicylate anion is a weaker base than phenoxide ion
 (C) p-hydroxy benzoate ion is a stronger base than phenoxide ion
 (D) p-hydroxy benzoate ion is a stronger base than salicylate ion

- Q.20 Methanol can be distinguished from ethanol by
 (A) Heating with I_2 and alkali (B) Treating with schiff's reagent
 (C) Treating with CrO_3 solution in dil. H_2SO_4 (D) Treating with Lucas reagent

Q.21 Products form by following reactions are



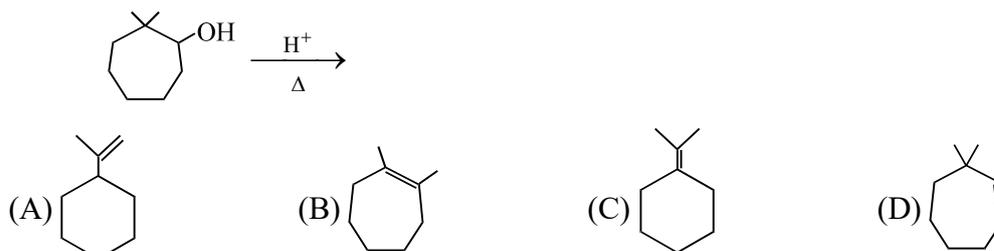
Q.22 For the reactions shown below, identify the correct statement(s) with regard to the products formed:



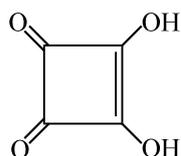
- (A) P and Q are identical
 (B) P is racemic and Q is optically active
 (C) P and Q are positional isomers
 (D) both are optically active

- Q.23 $C_2N_5NH_2 \xrightarrow[\text{reagent}]{\text{Tilden}}$ (i) $\xrightarrow{NH_3}$ (ii) $\xrightarrow[HCl]{NaNO_2}$ (iii). The product (iii) can be
 (A) Alcohol (B) Ether (C) Alkyl chloride (D) Alkyl nitrite

Q.24 Products form during dehydration of following alcohols are



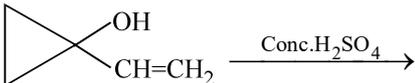
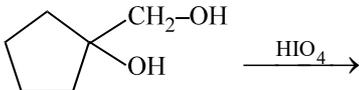
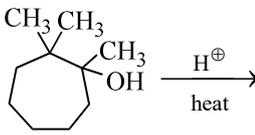
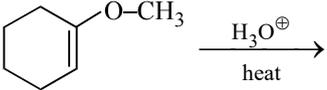
Q.25 Consider the following compound A (below)



Select the correct statement(s)

- (A) It is more acidic than CH_3OH (B) It is more acidic than CH_3COOH
 (C) It reacts very fast with Lucas reagent (D) It is a diacid base

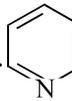
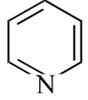
Q.26 Match the following:

- | | Reaction | | Mechanism |
|-----|---|-----|-------------------------------------|
| (A) |  | (P) | change in number of carbon in cycle |
| (B) |  | (Q) | Pinacol rearrangement |
| (C) |  | (R) | Oxidative bond cleavage |
| (D) |  | (S) | Ketone as product |

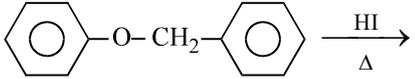
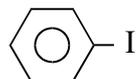
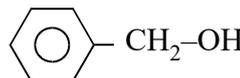
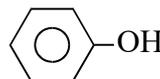
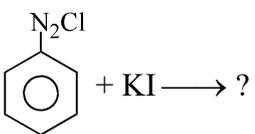
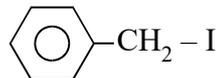
Q.27 Match the column:

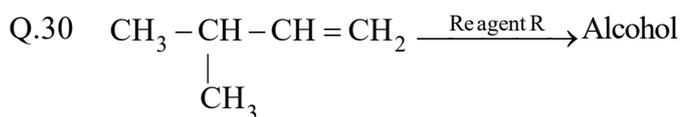
- | | Column I | | Column II |
|-----|---|-----|------------------------------|
| (A) | Identification of 1°, 2° & 3° Alcohols | (P) | Oxymercuration demercuration |
| (B) | Identification of 1°, 2° & 3° Nitro alkanes | (Q) | Cu/300° heat |
| (C) | Formation of alcohol by anti Markovnikov's addition of H ₂ O | (R) | Victor Mayer's test |
| (D) | Formation of alcohol by Markovnikov's addition | (S) | Hydroboration oxidation |
| | | (T) | Lucas test |

Q.28 Match the column:

- | | Column I | | Column II |
|-----|--|-----|----------------------|
| (A) | Oxidation of 1° alcohol in aldehyde | (P) | KMnO ₄ /Δ |
| (B) | CrO ₃ ·  · HCl | (Q) | Collin's reagent |
| (C) | CrO ₃ · 2  | (R) | Jone's reagent |
| (D) | Oxidation of alkene into acid | (S) | P.C.C |

Q.29 Match the products of following:

- | | Column I | | Column II |
|-----|--|-----|--|
| (A) |  | (P) |  |
| (B) | Violet color is obtain by the reaction of neutral FeCl ₃ with | (Q) |  |
| (C) | Reaction of benzaldehyde with LiAlH ₄ / H ₂ O gives | (R) |  |
| (D) |  + KI → ? | (S) |  |



which is true about alcohol and R?

- | | Alcohol | Reagent |
|-----|---|---|
| (A) | $\text{CH}_3 - \underset{\text{CH}_3}{\text{CH}} - \text{CH}_2 - \text{CH}_2\text{OH}$ | $\text{B}_2\text{H}_6, \text{H}_2\text{O}_2 / \text{NaOH}$ |
| (B) | $\text{CH}_3 - \underset{\text{CH}_3}{\text{CH}} - \underset{\text{OH}}{\text{CH}} - \text{CH}_3$ | $\text{PdCl}_2, \text{H}_2\text{O}, \text{O}_2 / \text{LAH}$ |
| (C) | $\text{CH}_3 - \underset{\text{CH}_3}{\overset{\text{OH}}{\text{C}}} - \text{CH}_2\text{CH}_3$ | $\text{Hg}(\text{OAc})_2, \text{H}_2\text{O} / \text{NaBH}_4$ |
| (D) | $\text{CH}_3 - \underset{\text{CH}_3}{\text{C}} - \text{CH}_2\text{CH}_3$ | $\text{dil. H}_2\text{SO}_4$ |

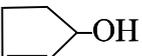
EXERCISE-II

Q.1 What reagents could you use for the following conversions

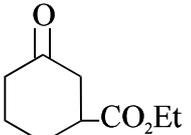
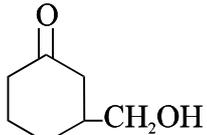
- (a) $\text{MeCO}(\text{CH}_2)_2\text{CO}_2\text{Et} \rightarrow \text{MeCHOH}(\text{CH}_2)_2\text{CO}_2\text{Et}$
 (b) $\text{HO}_2\text{C}(\text{CH}_2)_4\text{COCl} \rightarrow \text{HO}_2\text{C}(\text{CH}_2)_4\text{CH}_2\text{OH}$
 (c) $\text{O}_2\text{N}(\text{CH}_2)_2\text{CN} \rightarrow \text{O}_2\text{N}(\text{CH}_2)_2\text{CH}_2\text{NH}_2$
 (d) $\text{O}_2\text{N}(\text{CH}_2)_2\text{CH}=\text{CH}_2 \rightarrow \text{H}_2\text{N}(\text{CH}_2)_2\text{CH}=\text{CH}_2$
 (e) $\text{Me}_2\text{CHCOCl} \rightarrow \text{Me}_2\text{CHCHO}$
 (f) $\text{O}_2\text{N}(\text{CH}_2)_3\text{CHO} \rightarrow \text{O}_2\text{N}(\text{CH}_2)_3\text{CH}_2\text{OH}$
 (g) $\text{O}_2\text{N}(\text{CH}_2)_2\text{CH}=\text{CH}_2 \rightarrow \text{O}_2\text{N}(\text{CH}_2)_3\text{CH}_3$

Q.2 Following compounds undergoes reaction with MnO_2 . What are the products in each case?

- (a) $\text{CH}_3\text{CH}_2\text{CH}=\text{CHCH}_2\text{OH}$ (b) PhCH_2OH (c) $\text{PhCH}(\text{OH})\text{CH}_2\text{CH}_2\text{OH}$

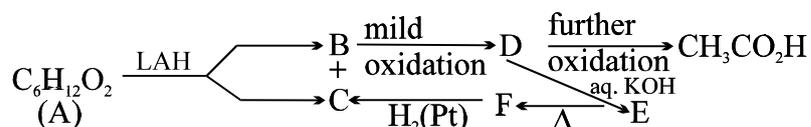
- (d) $\text{MeCH}=\text{CH}(\text{CH}_2)_3\text{OH}$ (e) 

Q.3 Carry out the following conversion

- (i)  \rightarrow 
- (ii) Acraldehyde \rightarrow Glyceraldehyde
- (iii) $\text{Br}-\text{CH}_2\text{CHO}$ \rightarrow $\text{PhCHOHCH}_2\text{CHO}$
- (iv)  \rightarrow 
- (v) $\text{CH}_2 - \text{CH}_2\text{CHO}$ \rightarrow Glyceraldehyde
 |
 Cl

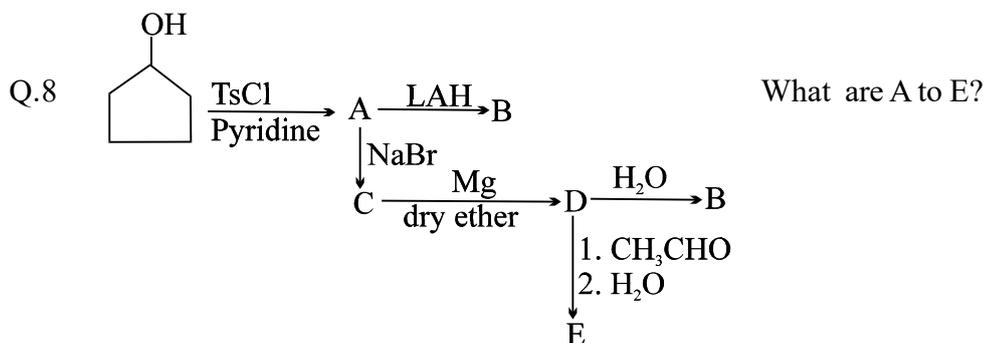
Q.4 Outline a mechanism to account for different isomer formed when $\text{Me}_2\text{C}-\text{CH}_2$ reacts with CH_3OH in acidic and in basic medium.

Q.5 Find the structures of A to F.

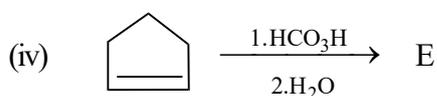
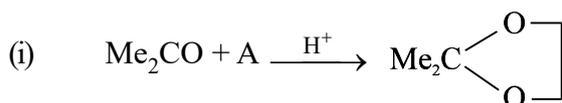


Explain product formation. How two OH groups behave differently.

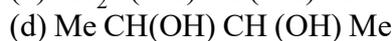
Q.7 $\text{R}_2\text{C}=\text{O} + \text{Et}_3\text{Al} \rightarrow \text{C}_2\text{H}_4 + \text{R}_2\text{CHO AlEt}_2$
Suggest a mechanism for the reaction.



Q.9 Identify A to E in the following reactions.

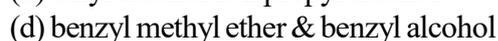
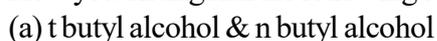


Q.10 What are the order of rates of oxidation with HIO_4 of the following diols. Explain with reasons.



Q.11 t-Butanol in presence of fenton's reagent forms 2,5 dimethyl hexane 2,5 diol as one of the product. Explain with the mechanism.

Q.12 How you distinguish the following compounds?



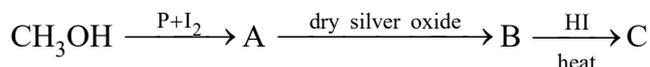
Q.13 Differentiate:

- (a) 1-Hexanol and 1-chlorohexane (b) Diethyl ether and n-butanol
 (c) Diethyl ether and n-pentane

Q.14 Explain:

- (a) No esterification takes place between ethyl alcohol and excess of sulphuric acid at 170°C.
 (b) Sodium chloride solution in water is added to decrease the solubility of organic compounds in water.

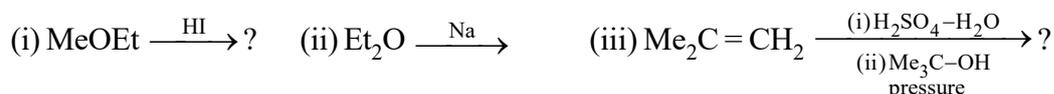
Q.15 Predict A, B & C.



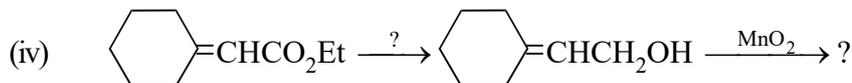
Q.16 Carry out conversion of methyl alcohol into ethyl alcohol and vice versa.

Q.17 Arrange the compounds (i) Ethanol, propane and 1-pentanol, (ii) Butane 1,2,3-pentanetriol and butyl alcohol, (iii) Pentane, 1-pentanol and 1-hexanol, on the basis of (a) in order of increasing boiling points and (b) in order of increasing solubility in water.

Q.18 Complete the following equations & comment:



Q.19 Complete the following equations:



Q.20 t-butyl alcohol reacts less rapidly with metallic sodium than the primary alcohol. Explain why?

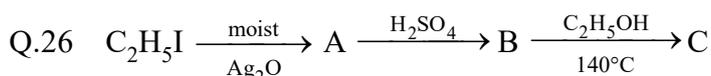
Q.21 Diethyl ether behaves as base. Why?

Q.22 What is the significance of proof spirit?

Q.23 Sodium metal can be used for drying diethyl ether but not for ethanol. Why?

Q.24 Sometimes explosion occurs during distillation of ether sample. Give the reason.

Q.25 Ethyl alcohol is denatured with methyl alcohol. Why?



Q.27 Ethyl alcohol reacts with HI but not with HCN. Explain why?

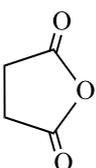
Q.28 Write the structure of the principal organic product formed in the reaction of 1-propanol with each of the following reagents:

(i) Potassium dichromate ($K_2Cr_2O_7$) in aqueous sulfuric acid, heat

(ii) Acetic acid $CH_3\overset{\overset{O}{\parallel}}{C}OH$ in the presence of dissolved hydrogen chloride.

(iii) CH_3 -- SO_2Cl in the presence of pyridine

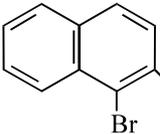
(iv) $C_6H_5\overset{\overset{O}{\parallel}}{C}O\overset{\overset{O}{\parallel}}{C}C_6H_5$ in the presence of pyridine

(v)  in the presence of pyridine

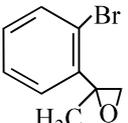
Q.29 Complete the following series of equations by writing structural formula for compounds A through I:

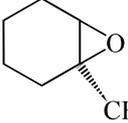
(a)  \xrightarrow{HCl} C_5H_7Cl (Compound A) $\xrightarrow[H_2O]{NaHCO_3}$ C_5H_8O (Compound B) $\xrightarrow[H_2SO_4, H_2O]{Na_2Cr_2O_7}$ C_5H_6O (Compound C)

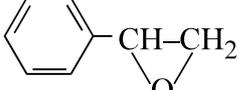
(b) $CH_2=CHCH_2CH_2\underset{\underset{OH}{|}}{CH}CH_3 \xrightarrow[pyridine]{SOCl_2} C_6H_{11}Cl$ (D) $\xrightarrow[(ii) Zn/H_2O]{(i) O_3} C_5H_9ClO$ (E) $\xrightarrow{NaBH_4} C_5H_{11}ClO$ (F)

(c)  $\xrightarrow[\text{benzoyl peroxide, heat}]{NBS}$ Compound G $\xrightarrow[\text{heat}]{H_2O, CaCO_3}$ Compound H $\xrightarrow[CH_2Cl_2]{PCC}$ Compound I

Q.30 Predict the principal organic product of each of the following reactions. Specify stereochemistry where appropriate.

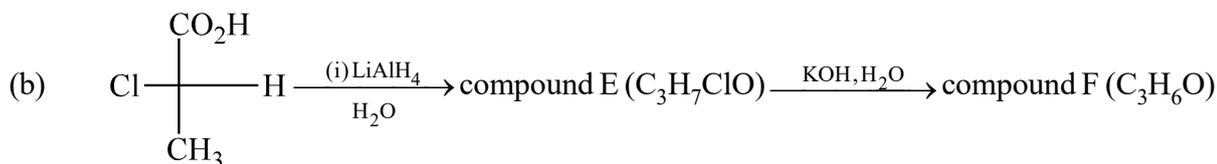
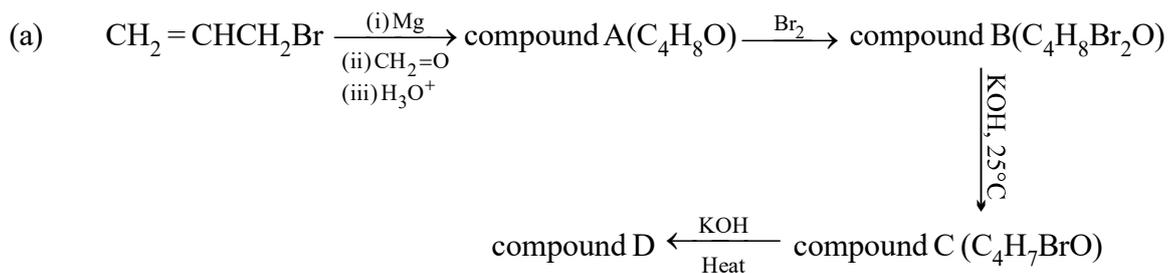
(a)  $\xrightarrow[\text{methanol}]{NH_3}$ (A)

(b)  + $CH_3ONa \xrightarrow{CH_3OH}$ (B)

(c)  $\xrightarrow[CHCl_3]{HCl}$ (C)

(d) $CH_3(CH_2)_{16}CH_2OTs + CH_3CH_2CH_2CH_2SNa \longrightarrow$ (D)

Q.31 Deduce the identity of the missing compounds in the following reaction sequences. Show stereochemistry in parts (b) through (d).

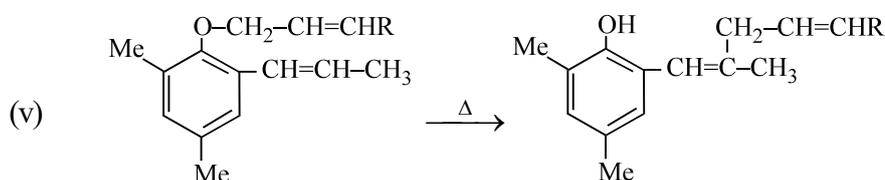
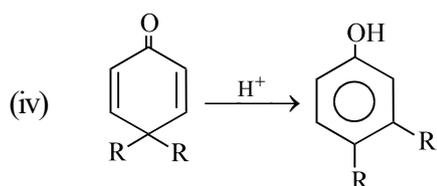
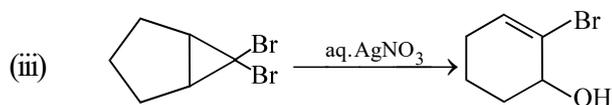
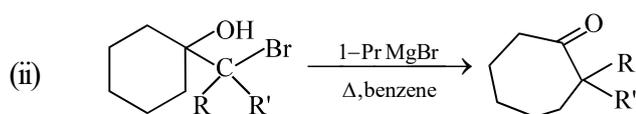
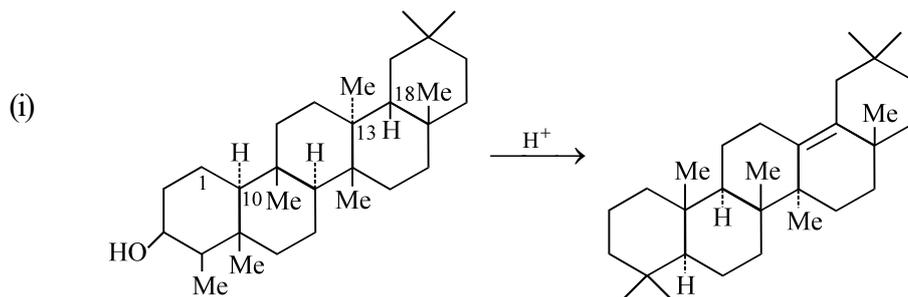


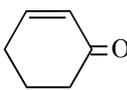
Q.32 Choose the reaction in each of the following pairs that proceeds at the faster rate. Explain your reasoning.

- Base-promoted hydrolysis of phenyl acetate or m-nitrophenyl acetate
- Base-promoted hydrolysis of m-nitrophenyl acetate or p-nitrophenyl acetate
- Reaction of ethyl bromide with phenol or with the sodium salt of phenol.
- Reaction of ethylene oxide with the sodium salt of phenol or with the sodium salt of p-nitrophenol
- Bromination of phenol or phenyl acetate.

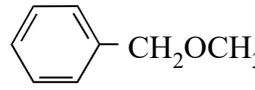
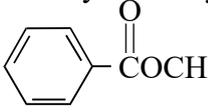
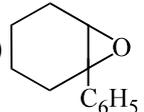
Q.33 Explain why ArOR ethers are cleaved to give RI and ArOH rather than ArI and ROH.

Q.34 Explain the mechanism of following :

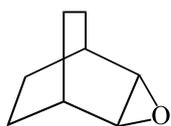


- Q.35 Outline a synthesis of each alcohol from the indicated starting materials:
 (a) Isopropyl alcohol from a hydrocarbon (b) n-butyl alcohol from acetylene
 (c) allyl alcohol from propane, and (d) t-butyl alcohol from t-butyl chloride
- Q.36 What product is expected from the reaction of  with (a) LiAlH_4 and (b) H_2/Pt
- Q.37 Give the product of the reaction of $\text{Ph}_2\text{CHCH}_2\text{OH}$ with HBr and explain its formation.
- Q.38 Give the product and write a mechanism for the acid dehydration of cyclobutylcarbinol.
- Q.39 $\text{C}_2\text{H}_5\text{OH} \xrightarrow{\text{PCl}_5} (\text{A}) \xrightarrow{\text{KCN}} (\text{B}) \xrightarrow{\text{H}_3\text{O}^+} (\text{C}) \xrightarrow{\text{NH}_3} (\text{D}) \xrightarrow{\text{heat}} (\text{E})$
- Q.40 $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH} \xrightarrow{\text{PBr}_5} (\text{A}) \xrightarrow{\text{KOH(Alc.)}} (\text{B}) \xrightarrow{\text{HBr}} (\text{C}) \xrightarrow{\text{NH}_3} (\text{D})$

EXERCISE-III

- Q.1 Compound (A) gives Lucas test within 5 minutes. 6g (A) when reacts with Na, 1120 mL of H_2 is generated at STP. (A) having one oxygen per molecule. What is the structural formula of (A)? Compound (A) when treated with PBr_3 gives (B) which when treated with benzene in presence of anhydrous AlCl_3 gives (C). What are (B) and (C)?
- Q.2 An open chain compound (A) $\text{C}_5\text{H}_8\text{O}$ is optically active. When (A) is hydrogenated in presence of Pd as catalyst, it absorbs two moles of H_2 per mole of (A) to produce compound (B) $\text{C}_5\text{H}_{12}\text{O}$ which is optically inactive. However when (A) is warmed with dilute H_2SO_4 in presence of HgSO_4 it gives compound $\text{C}(\text{C}_5\text{H}_{10}\text{O}_2)$ which is still optically active. C responds to iodoform test. What are the structures of A to C?
- Q.3 An organic compound (A) $\text{C}_{10}\text{H}_{12}\text{O}$ gives red colour when treated with ceric ammonium nitrate & also decolourises Br_2 in CCl_4 to give B ($\text{C}_{10}\text{H}_{12}\text{OBr}_2$). A can show both geometrical & optical isomerism. A on treatment with I_2 & NaOH gives iodoform & an acid (C) after acidification. Give the structures of A to C & also the stereoisomers of A.
- Q.4 $\text{A}(\text{C}_7\text{H}_{14})$ decolorises Br_2 in CCl_4 reacts with $\text{Hg}(\text{OAc})_2$, THF- NaBH_4 to form B (resolvable compound)
 $\text{A} \xrightarrow[2. \text{Zn}/\text{H}_2\text{O}]{1. \text{O}_3} \text{C} \xleftarrow{\text{KMnO}_4} \text{3 hexanol}$
 $\text{D (isomer of A)} \xrightarrow[2. \text{H}_2\text{O}_2/\text{OH}^-]{1. \text{B}_2\text{H}_6 \cdot \text{THF}} \text{E (chiral)} \xrightarrow{\text{KMnO}_4} \text{F (chiral carboxylic acid)}$
 $\text{D (isomer of A)} \xrightarrow[2. \text{Zn}/\text{H}_2\text{O}]{1. \text{O}_3} \text{G} \xleftarrow{\text{KMnO}_4/\text{alkaline}} \text{2 methyl 3 pentanol}$
 Find out A to G.
- Q.5 Suggest short, efficient reaction sequence suitable for preparing each of the following compounds from the given starting materials and any necessary organic or inorganic reagents.
- (i)  from  (ii)  from bromobenzene and cyclohexanol
- (iii) $\text{C}_6\text{H}_5\text{CH}_2\text{CH}(\text{OH})\text{CH}_3$ from bromobenzene and isopropyl alcohol

(iv) $C_6H_5CH_2CH_2CH_2OCH_2CH_3$ from benzyl alcohol and ethanol.



(v) from 1,3-cyclohexadiene and ethanol

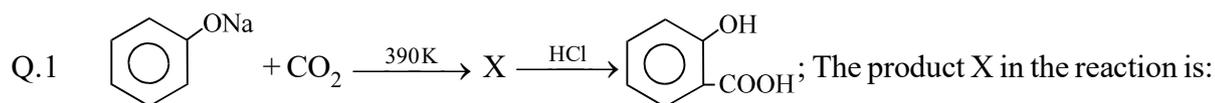
(vi) $C_6H_5CH(OH)CH_2SCH_2CH_3$ from styrene and ethanol



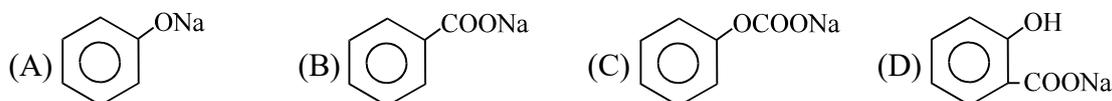
- Q.6 A compound (X) reacts with thionyl chloride to give a compound (Y). (Y) reacts with Mg to form a Grignard reagent, which is treated with acetone and the product is hydrolysed to give 2-methyl-2-butanol. What are structural formulae of (X) and (Y)?
- Q.7 The compound (D) reacts with BH_3 -Tetrahydrofuran and then alkaline H_2O_2 to give chiral (E). Oxidation of (E) with $KMnO_4$ (acidified) gives a chiral carboxylic acid (F). Ozonolysis of 'D' gives after reduction with Zn the same compound (G), which is obtained by oxidation of 2-methyl-3-pentanol with acidified $KMnO_4$. Identify (D), (E), (F) and (G).
- Q.8 An organic compound (A) contains 60.12% Carbon, 13.13% Hydrogen and has vapour density 30. On oxidation it gives (B) C_3H_6O which on further oxidation by $NaOH + I_2$ produces a salt of the acid (C) $C_2H_4O_2$. When (B) is treated with hydroxyl amine, a compound of molecular formula C_3H_7NO (D) is formed. What are (A), (B), (C) and (D)?
- Q.9 Compound (A) $C_4H_{10}O$ reacts rapidly with metallic sodium, but undergoes almost no reaction with Lucas reagent. When (A) is treated with hot concentrated sulphuric acid, a new compound (B) C_4H_8 is formed. If C_4H_8 is hydrated with sulphuric acid a new compound (C) C_4H_9OH is formed, which is almost inert to metallic sodium but reacts rapidly with Lucas reagent. What are (A), (B) and (C)?
- Q.10 A compound (X) containing C, H and O is unreactive towards sodium. It does not add bromine. It does not react with Schiff's reagent. On refluxing with an excess of HI, (X) gives only (Y). (Y) on hydrolysis gives (Z) which can be converted to (Y) by the action of $P + I_2$. Compound (Z) on oxidation gives an acid of equivalent weight 60. What are (X), (Y) and (Z)?
- Q.11 A compound (A) $C_4H_{10}O_4$ yields on acetylation (B) of formula $C_{12}H_{18}O_8$. How many hydroxyl groups are present in compound? Also write structures of (A) and (B).
- Q.12 An optically active alcohol (A) ($C_6H_{10}O$) absorbs two moles of hydrogen per mole of (A) upon catalytic hydrogenation and gives a product (B). The compound (B) is resistant to oxidation by CrO_3 and does not show any optical activity. Deduce the structures of (A) and (B).
- Q.13 An unsaturated hydrocarbon (A) on hydration gave alcohol (B). Oxidation of (B) gave a ketone (C). When the hydrocarbon (A) was submitted to ozonolysis it gave formaldehyde and acetaldehyde. What one formula would you assign to A, B and C? Give the reactions involved.
- Q.14 Compound (A) reacts with sodium to liberate H_2 forming a compound (B). When (A) is treated with $HCl + ZnCl_2$, an immediate reaction takes place liberating (C). When (A) is heated with H_2SO_4 , (D) is formed. Ozonolysis of (D) gives a three carbon ketone and another isomeric compound. What are (A), (B), (C) and (D)?

- Q.15 An organic compound (A) ($C_4H_{10}O$) reacts with HI giving a compound (B) (C_4H_9I) which on reduction gives a normal hydrocarbon having four carbon atoms. On oxidation A gives compound (C) (C_4H_8O) and then an acid (D) ($C_4H_8O_2$). Deduce the structures of, B, C and D giving reasons.
- Q.16 An organic compound (A) gives hydrogen on reacting with sodium. It also gives iodoform test and forms an aldehyde of molecular formula (B) (C_2H_4O) on oxidation. Name the compound (A) and (B).
- Q.17 An organic compound (X) on analysis gives 24.24% C, 4.04% H. Further sodium extract of 1.0 g of (X) gives 2.90 g of AgCl with acidified $AgNO_3$ solution. The compound (X) may be represented by two isomeric structures (Y) and (Z). (Y) on treatment with aqueous KOH solution gives a dihydroxy compound, while (Z) on similar treatment gives ethanal. Find out (X), (Y) and (Z).
- Q.18 Compound (X) (C_5H_8O) does not react appreciably with Lucas reagent at room temperature but gives a precipitate with ammoniacal silver nitrate. With excess of $MeMgBr$, 0.42 g of (X) gives 224 ml CH_4 at STP. Treatment of (X) with H_2 in presence of Pt catalyst followed by boiling with excess HI gives n-pentane. Suggest structure for (X) and write the equations involved.
- Q.19 An alcohol (A) when heated with concentrated H_2SO_4 gives an alkene (B). When (B) is bubbled through bromine water and the product obtained is dehydrohalogenated with excess of sodamide, a new compound (C) is obtained. The compound (C) give (D) when treated with dilute H_2SO_4 in presence of $HgSO_4$. (D) can also be obtained either by oxidising (A) with $KMnO_4$ or from acetic acid through its calcium salt. Identify (A), (B), (C) and (D).
- Q.20 Compound (A) contains only carbon and hydrogen. It decolorizes bromine in CCl_4 solution and reacts slowly with concentrated H_2SO_4 . Compound (A) reacts with HBr to form (B). (B) reacts with NaOH to form (C). (C) on oxidation gave hexanone-3. Write structures of (A), (B) and (C).
- Q.21 A hydrocarbon (A) (molecular formula C_5H_{10}) yield 2-methylbutane on catalytic hydrogenation. (A) adds HBr in accordance with Markownikoff's rule to form a compound (B), which on reaction with silver hydroxide forms an alcohol (C) $C_5H_{12}O$. Alcohol (C) on oxidation gives a ketone (D). Deduce (A) to (D) and give the reactions involved.
- Q.22 (A) $\xrightarrow[250^\circ C]{Al_2O_3}$ (B) $\xrightarrow[(ii) AgOH]{(i) HI}$ (C) $\xrightarrow[150^\circ C]{Al_2O_3}$ (B) $\xrightarrow[(ii) H_2O_2, OH^-]{(i) B_2H_6}$ (A)

In the above reactions scheme (A) and (C) are isomers. (B) has a formula of C_5H_{10} . (C) Can also be obtained from the product of the reactions of CH_3CH_2MgBr and $(CH_3)_2CO$. Give structures of (A), (B) and (C).

EXERCISE-IV (A)

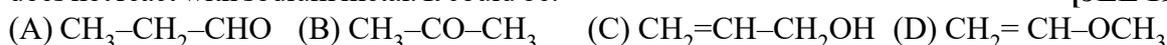
[REE 1990]



Q.2 The products of combustion of an aliphatic thiol (RSH) at 298 K are: [JEE 1992]



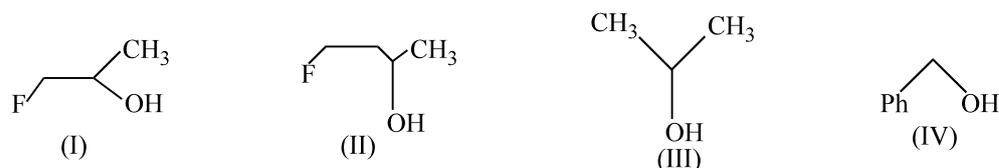
Q.3 An organic compound $\text{C}_3\text{H}_6\text{O}$ does not give a precipitate with 2,4-dinitrophenyl hydrazine reagent and does not react with sodium metal. It could be: [JEE 1993]



Q.4 The reaction products of $\text{C}_6\text{H}_5\text{OCH}_3 + \text{HI} \xrightarrow{\Delta}$ are: [JEE 1995]



Q.5 The order of reactivity of the following alcohols: [JEE 1997]



towards conc. HCl is:



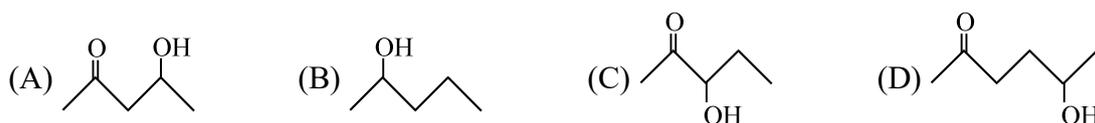
Q.6 Among the following compounds, the strongest acid is: [JEE 1998]



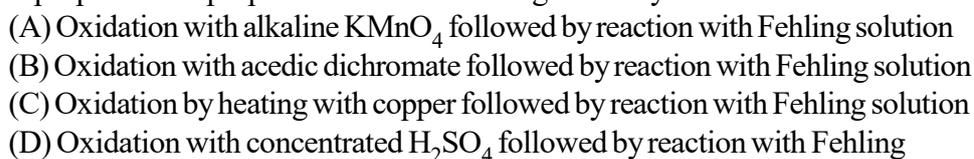
Q.7 Benzenediazonium chloride on reaction with phenol in weakly basic medium gives: [JEE 1998]

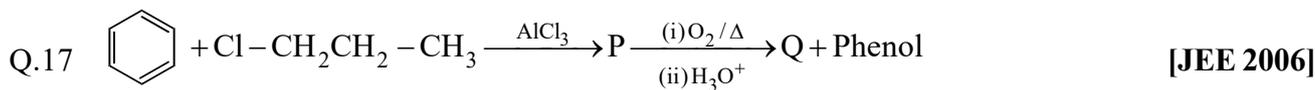


Q.8 Which one of the following will most readily be dehydrated in acidic condition: [JEE 2000]

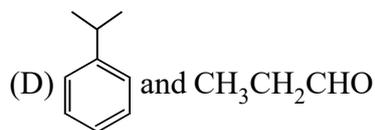
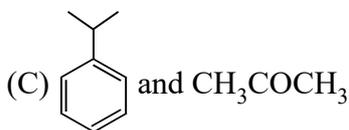
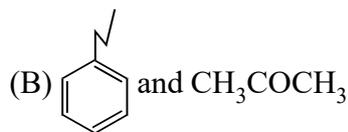
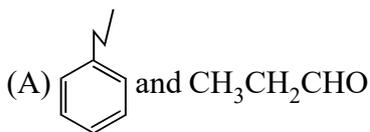


Q.9 1-propanol & 2-propanol can be best distinguished by: [JEE 2001]





The major products P and Q are



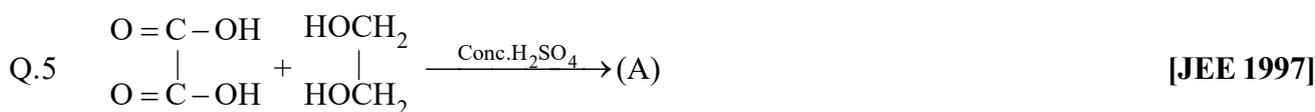
EXERCISE-IV (B)

Q.1 When t-butanol and n-butanol are separately treated with a few drops of dilute KMnO₄ in one case only, purple colour disappears and a brown precipitate is formed. Which of the two alcohols gives the above reaction and what is the brown precipitate? [JEE 1994]

Q.2 3,3-Dimethylbutan-2-ol loses a molecule of water in the presence of a concentrated sulphuric acid to give tetramethyl ethylene as a major product. Suggest a suitable mechanism. [JEE 1996]

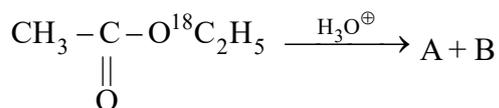
Q.3 A compound D (C₈H₁₀O) upon treatment with alkaline solution of iodine gives a yellow precipitate. The filtrate on acidification gives a white solid (E) (C₇H₆O₂). Write the structures of (D) and (E) and explain the formation of (E). [JEE 1996]

Q.4 Which of the following is the correct method for synthesising methyl-t-butyl ether and why?



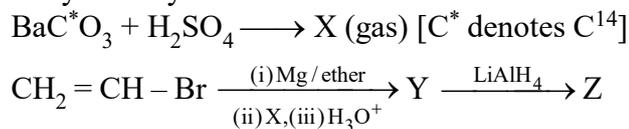
Q.6 Discuss why o-hydroxy benzaldehyde is a liquid at room temperature while p-hydroxy benzaldehyde is a high melting solid? [JEE 1999]

Q.7 Write the structures of the product A & B [JEE 2000]



Q.8 Cyclobutyl bromide on treatment with magnesium in dry ether forms an organometallic A. The organometallic reacts with ethanal to give an alcohol B after mild acidification. Prolonged treatment of alcohol B with an equivalent amount of HBr gives 1-bromo-1-methylcyclopentane (C). Write the structures of A, B and explain how C is obtained from B. [JEE 2001]

Q.9 Identify X, Y and Z in the following synthetic scheme and write their structure. Explain the formation of labelled formaldehyde (H₂C*O) as one of the products when compound Z is treated with HBr and subsequently ozonolysed. Mark the C* carbon in the entire scheme. [JEE 2001]



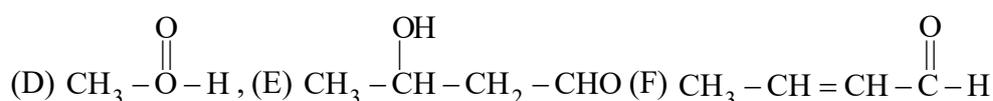
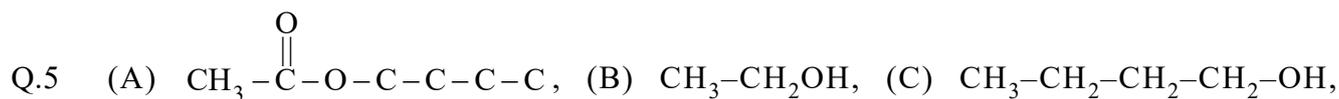
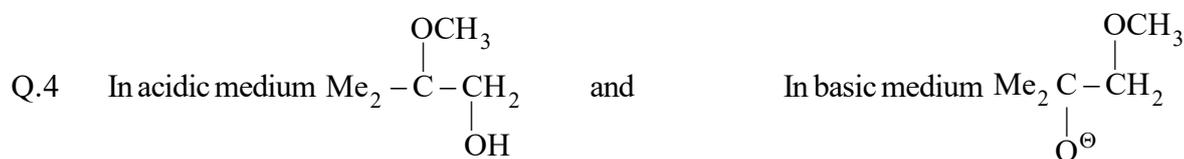
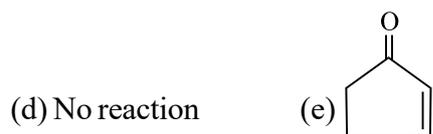
- Q.10 Mention two esters produced when a racemic mixture of 2-phenyl propanoic acid is treated with (+) 2-butanol. What is the stereochemical relationship between these esters? **[JEE 2003]**
- Q.11 An organic compound P(C₅H₁₀O) Reacts 10¹⁵ times faster than ethylene with dil.H₂SO₄ to give two products Q and R. Both Q and R give positive iodoform test. Identify P, Q and R and also give reason for very high reactivity of P. **[JEE 2004]**
- Q.12 (X) C₅H₁₃N $\xrightarrow[-N_2]{NaNO_2, HCl}$ (Y) (Tertiary alcohol + other products)
(Optically active)
Find X and Y. Is Y optically active? Write the intermediate steps. **[JEE 2005]**

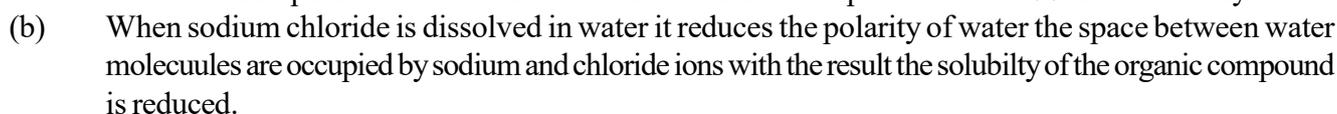
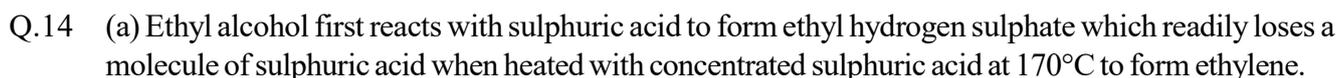
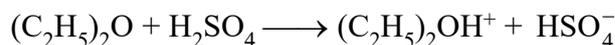
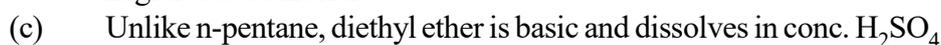
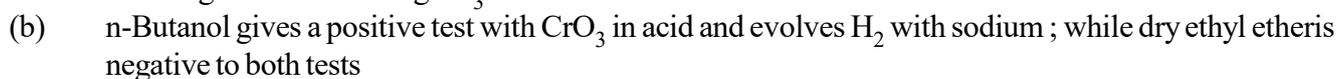
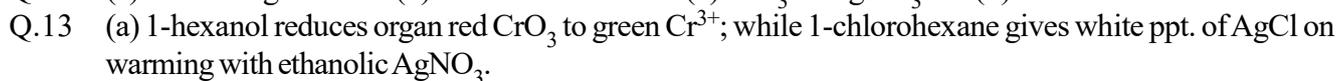
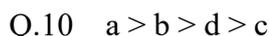
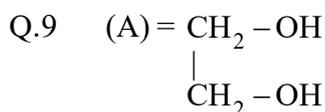
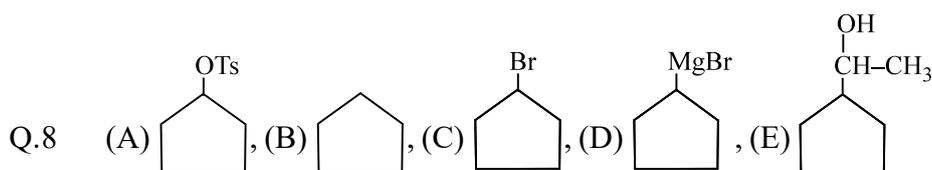
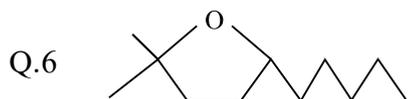
ANSWER KEY**EXERCISE-I(A)**

Q.1	B	Q.2	A	Q.3	C	Q.4	B	Q.5	B	Q.6	D	Q.7	D
Q.8	C	Q.9	D	Q.10	C	Q.11	A	Q.12	C	Q.13	A	Q.14	C
Q.15	B	Q.16	A	Q.17	B	Q.18	C	Q.19	D	Q.20	C	Q.21	D
Q.22	A	Q.23	B	Q.24	D	Q.25	A	Q.26	B	Q.27	A	Q.28	B
Q.29	A	Q.30	A	Q.31	C	Q.32	C	Q.33	D	Q.34	D	Q.35	D
Q.36	B	Q.37	A	Q.38	B	Q.39	A	Q.40	A	Q.41	C	Q.42	A
Q.43	A	Q.44	D	Q.45	A	Q.46	C	Q.47	C	Q.48	C	Q.49	C
Q.50	A												

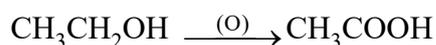
EXERCISE-I(B)

Q.1	A,C,D	Q.2	C	Q.3	A,C	Q.4	B
Q.5	A,B,D	Q.6	A,B	Q.7	A,B,C	Q.8	A,B,C
Q.9	A,D	Q.10	A,B,D	Q.11	A,C	Q.12	A,B,C
Q.13	A,B,C,D	Q.14	A,B,C,D	Q.15	A,B,C	Q.16	A,C,D
Q.17	A,B,C	Q.18	A,B	Q.19		Q.20	A
Q.21	A,C	Q.22	C,D	Q.23	A,B,C,D	Q.24	A,B,C,D
Q.25	A,B	Q.26	(A) P, Q, S; (B) R,S; (C) P; (D) S				
Q.27	(A) Q,R,T, (B) R, (C) S, (D) P			Q.28	(A) Q,R,S (B) S (C) Q (D) P		
Q.29	(A) R, S; (B) R; (C) Q; (D) P			Q.30	A,B,D		

EXERCISE-II

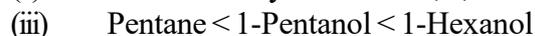
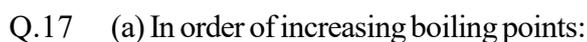


Methanol

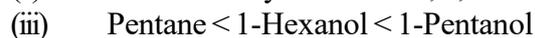
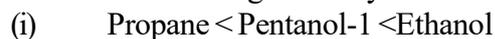


Ethylamine

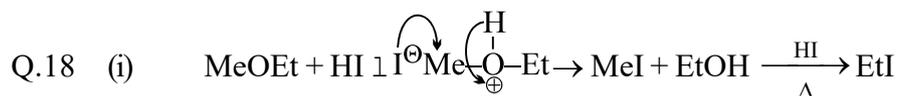
Ethanol



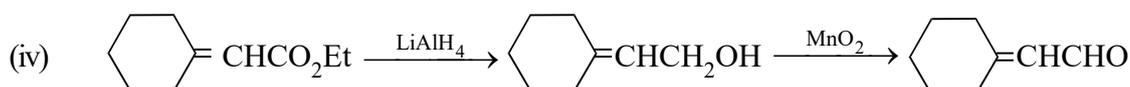
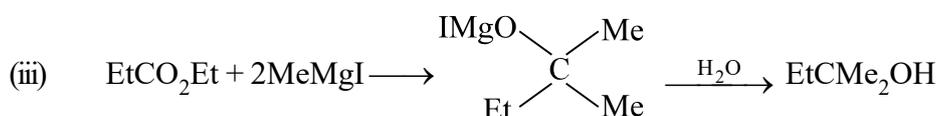
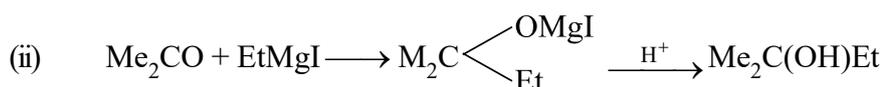
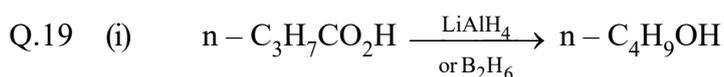
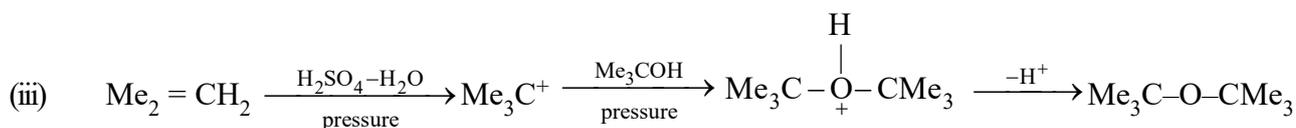
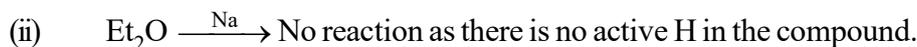
The explanation is based on molecular weight and hydrogen bonding



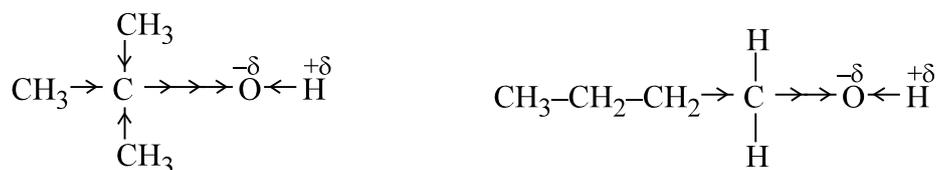
The explanation is based on hydrogen bonding



The reaction is $\text{S}_{\text{N}}2$, the smaller group forms the iodide (steric effect) & stops at the first stage in the cold. When heated, the reaction proceeds to the second stage.



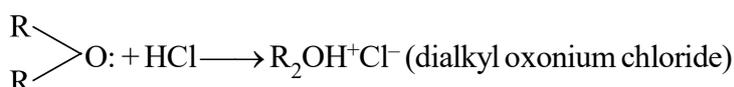
Q.20 The +I.E. of three methyl groups on central C-atom of tert-butyl alcohol makes it partially negative with the result that it pushes the electron pair of $-\text{OH}$ bond towards H-atom and thus H-atom is not replaced easily.



(less partial +ve charge)

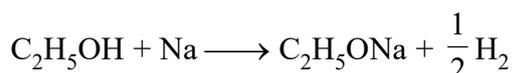
(more partial +ve charge)

Q.21 Oxygen atom in diethyl ether molecule has two lone pair of electrons available for co-ordination. Therefore ethers behave as Lewis base forming oxonium salts.



Q.22 Proof spirit is a technical term representing 57.1% by volume ethanol-water mixture for the purpose of tax levied on its production. The percentage represents the weakest possible percentage which allows the gun powder to catch fire.

Q.23 Sodium metal reacts with ethanol to form sodium ethoxide ion because of active H atom in ethanol. Ether do not have such active H and thus can be dried by sodium

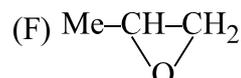
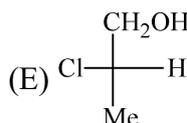
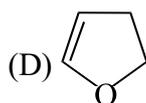
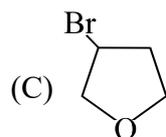
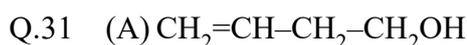
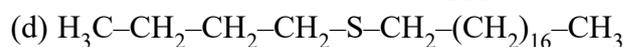
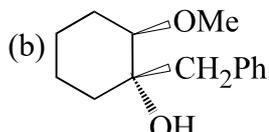
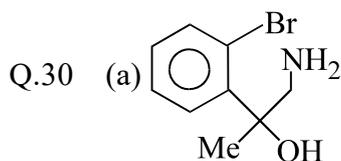
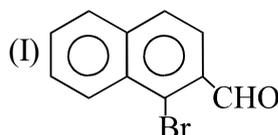
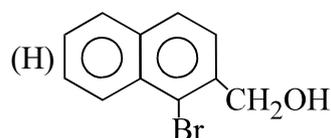
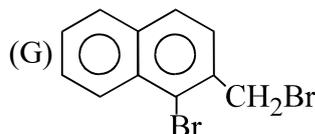
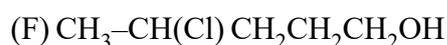
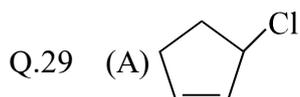
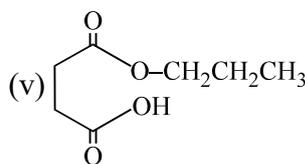


Q.24 Due to the formation of explosive peroxide by oxidation.

Q.25 Addition of methyl alcohol or naphtha or pyridine is made into ethyl alcohol to make sure that it will not be used for bevarage purposes. This process is known as denaturation of alcohol.



Q.27 Ethanol being very weak Lewis base and thus reacts with stronger acid HI

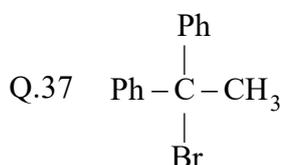
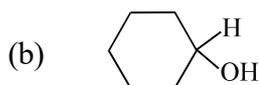
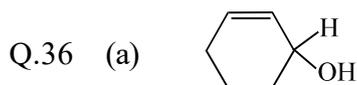


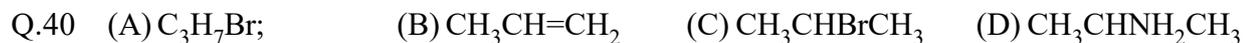
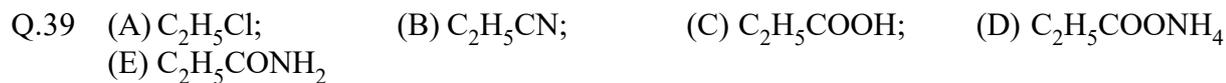
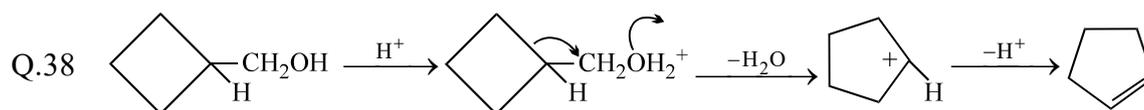
Q.32 (a) m-nitrophenyl acetate (better leaving group) (b) p-nitrophenyl acetate (better leaving group)

(c) sodium salt of phenol (better nucleophile) (d) sodium salt of phenol (better nucleophile)

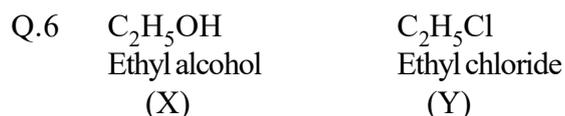
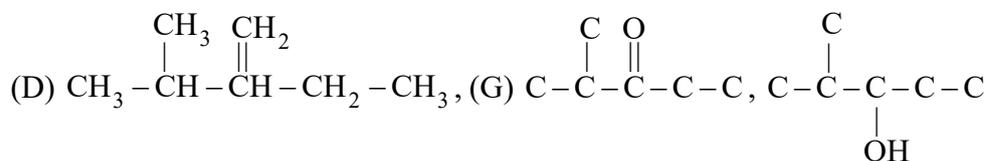
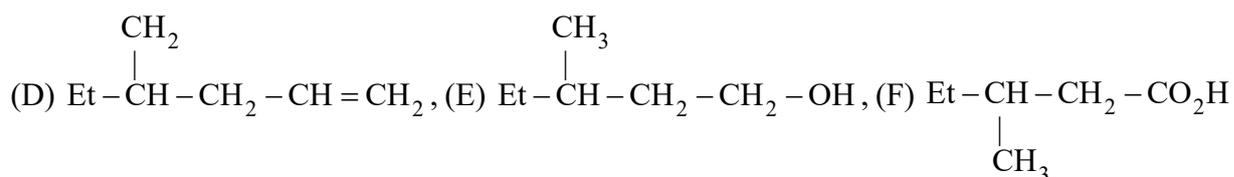
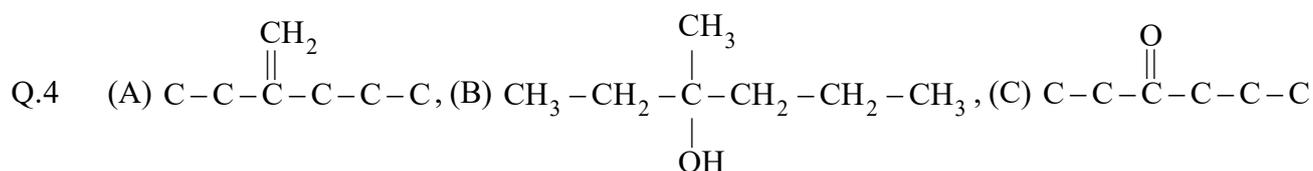
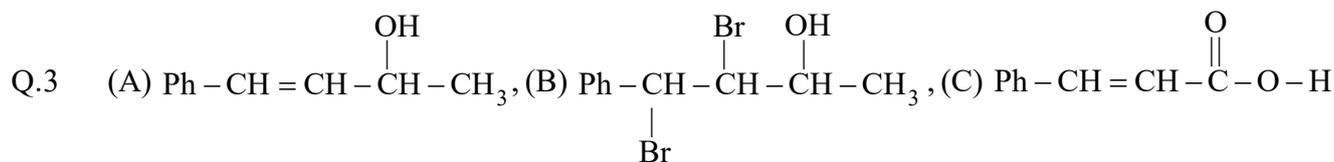
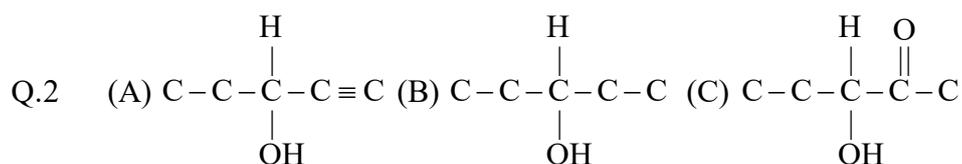
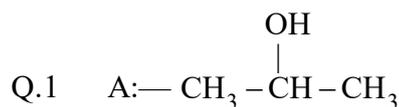
(e) Phenol (more activated aromatic ring.)

Q.33 S_N2 attack on a carbon of a benzene ring does not occur nor does the high energy $C_6H_5^+$ form by an S_N1 reaction. Hence ArI cannot be a product even in an excess of conc. HI

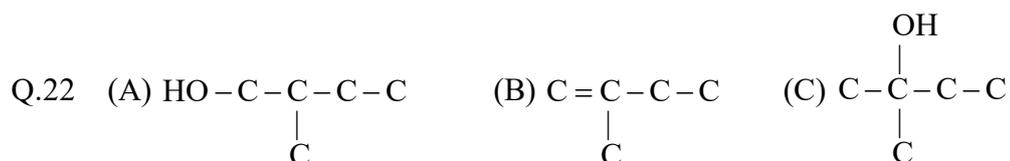
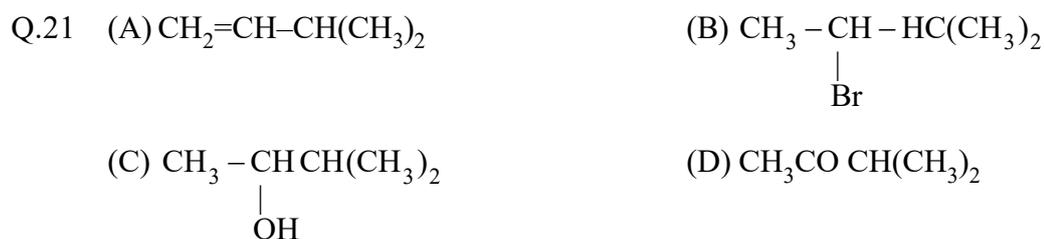
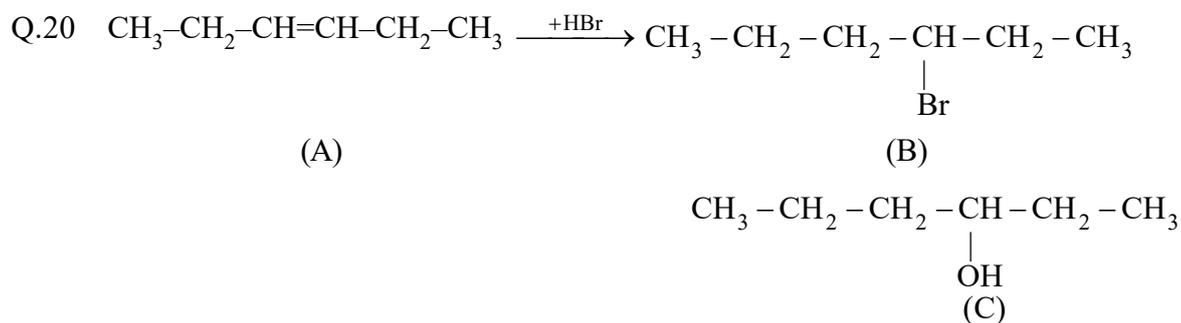
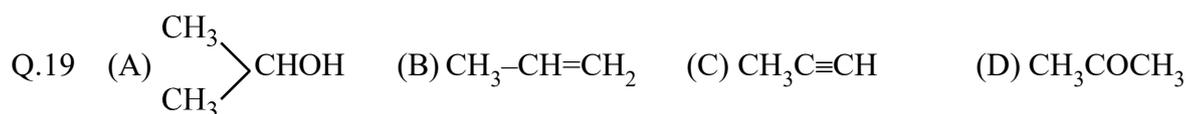
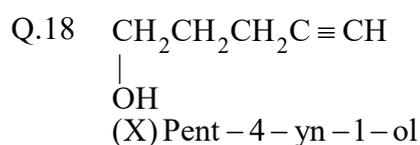
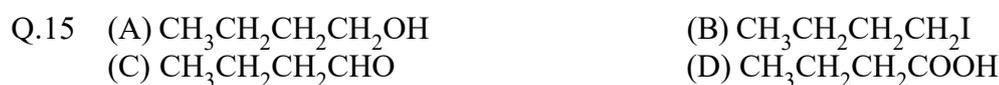
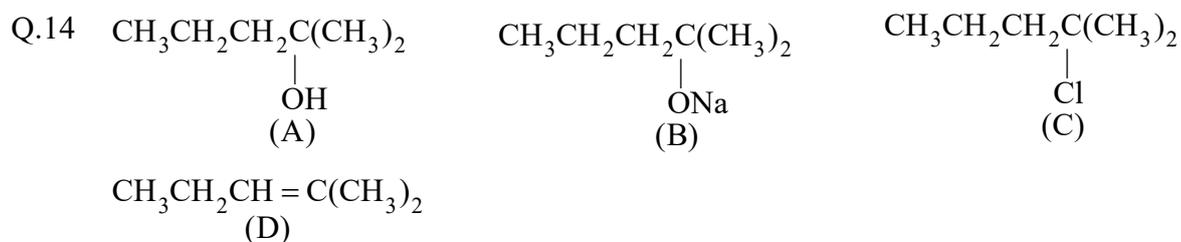




EXERCISE-III



- Q.7
$$\begin{array}{c} \text{CH}_3 - \text{CH} - \text{C} = \text{CH}_2 \\ | \quad | \\ \text{CH}_3 \quad \text{C}_2\text{H}_5 \\ \text{(D)} \end{array}$$
- $$\begin{array}{c} \text{H} \\ | \\ \text{CH}_3 - \text{CH} - \text{C} - \text{CH}_2\text{OH} \\ | \quad | \\ \text{CH}_3 \quad \text{C}_2\text{H}_5 \\ \text{(E)} \end{array}$$
- $$\begin{array}{c} \text{H} \\ | \\ \text{CH}_3 - \text{CH} - \text{C} - \text{COOH} \\ | \quad | \\ \text{CH}_3 \quad \text{C}_2\text{H}_5 \\ \text{(F)} \end{array}$$
- $$\begin{array}{c} \text{CH}_3 - \text{CH} - \text{C} = \text{O} \\ | \quad | \\ \text{CH}_3 \quad \text{C}_2\text{H}_5 \\ \text{(G)} \end{array}$$
- Q.8 $(\text{CH}_3)_2\text{CHOH};$ $\text{CH}_3\text{COCH}_3;$ $\text{CH}_3\text{COOH};$ $\text{CH}_3\text{C}(\text{CH}_3)_2\text{NOH}$
 (A) (B) (C) (D)
- Q.9 $(\text{CH}_3)_2\text{CHCH}_2\text{OH};$ $(\text{CH}_3)_2\text{C}=\text{CH}_2;$ $(\text{CH}_3)_3\text{COH}$
 (A) (B) (C)
- Q.10 $\text{C}_2\text{H}_5\text{O C}_2\text{H}_5;$ $\text{C}_2\text{H}_5\text{I};$ $\text{C}_2\text{H}_5\text{OH}$
 (X) (Y) (Z)
- Q.11 Four OH groups are present in compound A.
- $$\begin{array}{c} \text{CH}_2\text{CH} \quad \text{CH} \quad \text{CH}_2 \\ | \quad | \quad | \quad | \\ \text{OH} \quad \text{OH} \quad \text{OH} \quad \text{OH} \\ \text{(A)} \end{array}$$
- $$\begin{array}{c} \text{CH}_2\text{OCOCH}_3 \\ | \\ \text{CHOCOCH}_3 \\ | \\ \text{CHOCOCH}_3 \\ | \\ \text{CH}_2\text{OCOCH}_3 \\ \text{(B)} \end{array}$$
- Q.12
$$\begin{array}{c} \text{C}_2\text{H}_5 \\ | \\ \text{H}_3\text{C} - \text{C} - \text{C} \equiv \text{CH} \\ | \\ \text{OH} \\ \text{(A)} \end{array}$$
- $$\begin{array}{c} \text{C}_2\text{H}_5 \\ | \\ \text{CH}_3 - \text{C} - \text{CH}_2 - \text{CH}_3 \\ | \\ \text{OH} \\ \text{n(B)} \end{array}$$
- Q.13
$$\begin{array}{c} \text{CH}_3 \quad \quad \text{H} \\ \diagdown \quad \diagup \\ \text{C} = \text{C} \\ \diagup \quad \diagdown \\ \text{H} \quad \quad \text{H} \\ \text{(A)} \end{array}$$
- $$\begin{array}{c} \text{CH}_3 - \text{CH} - \text{CH}_3 \\ | \\ \text{OH} \\ \text{(B)} \end{array}$$
- $$\begin{array}{c} \text{CH}_3 - \text{C} - \text{CH}_3 \\ || \\ \text{O} \\ \text{(C)} \end{array}$$

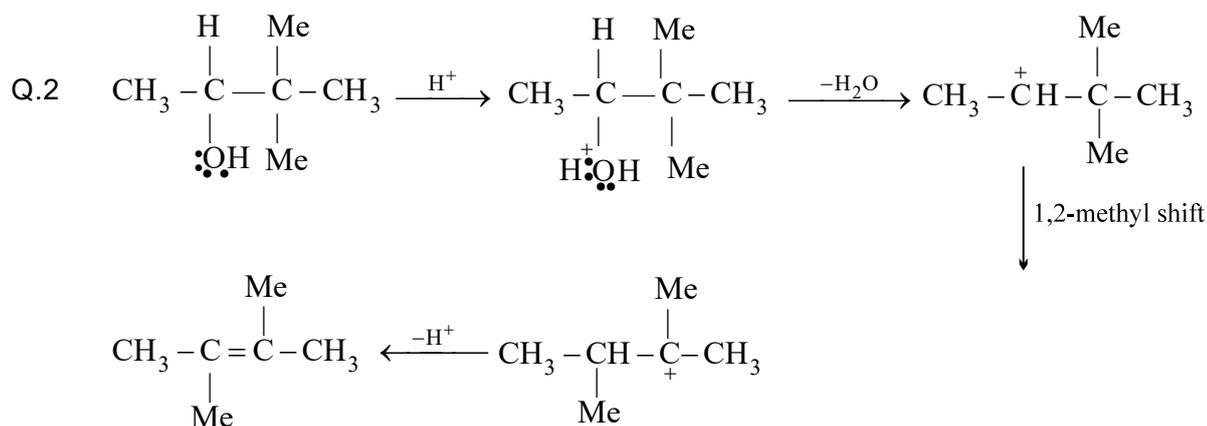
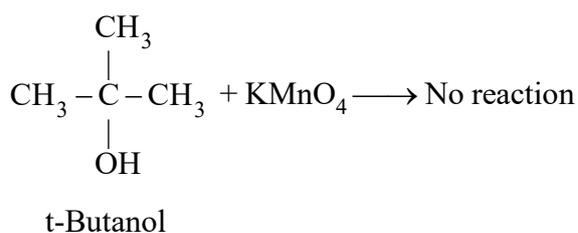
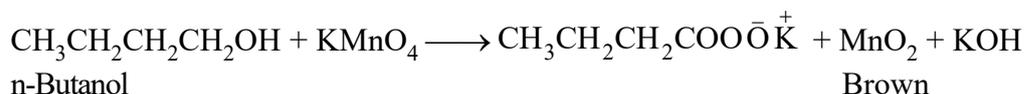


EXERCISE-IV (A)

Q.1	D	Q.2	B	Q.3	D	Q.4	A	Q.5	C
Q.6	D	Q.7	B	Q.8	A	Q.9	C	Q.10	B
Q.11	D	Q.12	B	Q.13	D	Q.14	B	Q.15	C
Q.16	A								

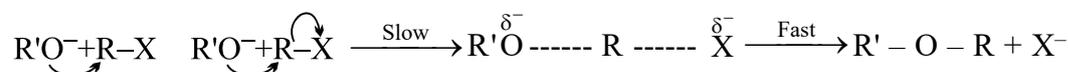
EXERCISE-IV (B)

Q.1 n-butanol is oxidised by KMnO_4 and not t-butanol as the latter does not contain H atom attached to carbinol carbon atom.

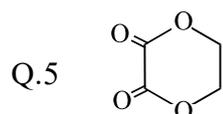


Q.3 (D) $\text{Ph} - \underset{\text{OH}}{\text{CH}} - \text{CH}_3$ (E) $\text{C}_6\text{H}_5\text{COOH}$

Q.4 The ether formation involves nucleophilic substitution of alkoxide ion for halide ion.

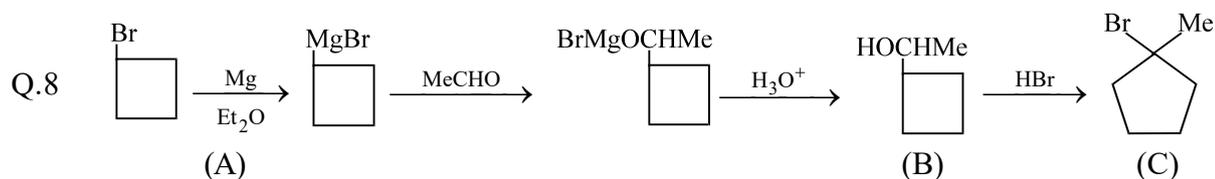


3° alkyl halide can also involve elimination of HX to give alkene in the presence of a base. So, it is better to start with 3° alkoxide and 1° alkyl halide, i.e., equation (b)

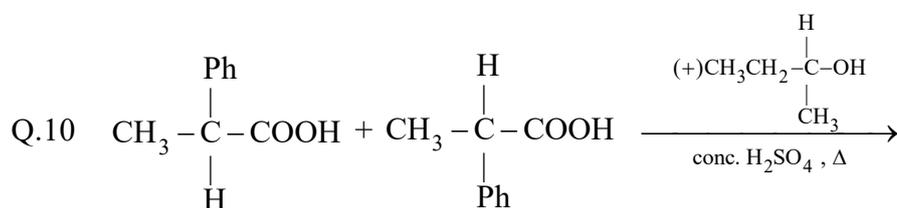
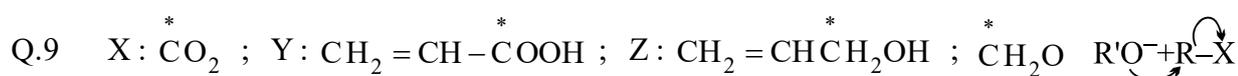
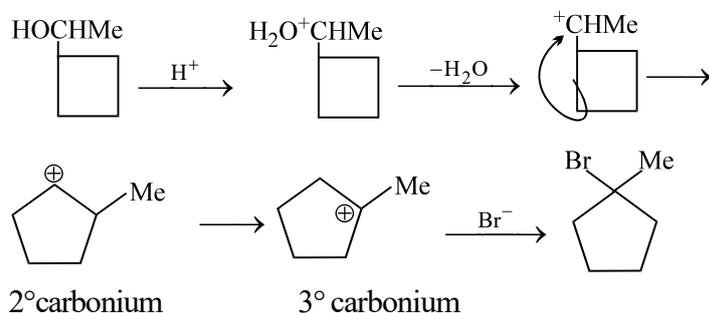


Q.6 Due to intermolecular H-Bonding

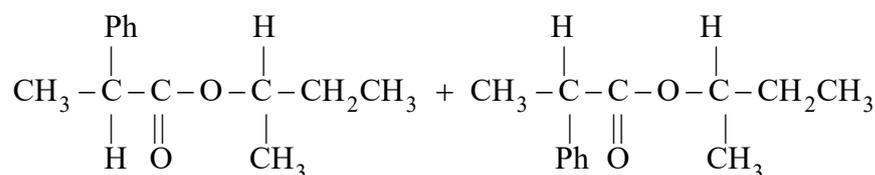
Q.7 A = $\text{CH}_3 - \underset{\text{O}}{\text{C}} - \text{OH}$, B = $\text{C}_2\text{H}_5\text{O}^{18}\text{H}$



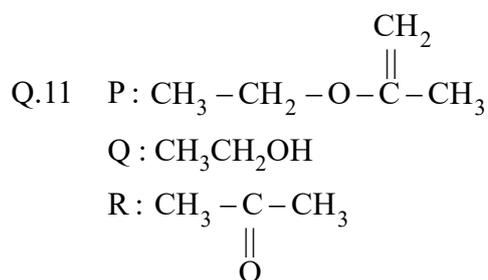
Mechanism



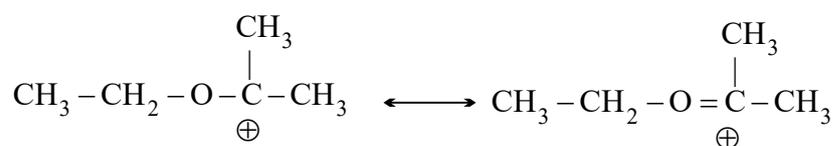
(racemic mixture)



during esterification reaction only $-\text{COOH}$ and $-\text{OH}$ participates. There is no effect on structure of configuration of carbon adjacent of these groups. So when (\pm) acid reacts with pure $(+)$ alcohol two esters are produced which are **diastereoisomers** of each other.



when ethylene reacts with dil. H_2SO_4 , $\text{CH}_3\text{CH}_2^\oplus$ is produced during rate determining step, whereas P gives resonance stabilized intermediate.



due to extra stability of intermediate the rate of reaction is very fast

THE KEY

CHEMICAL KINETICS :

It is a branch of physical chemistry deals with the "Rate of Chemical Reactions" including the effect of temperature, pressure, concentration, etc., on the rates, and the mechanism by which the reaction takes place.

RATE OF CHEMICAL REACTION is defined as the change in concentration of a reactant (or a product) in a particular time interval. Average rate of reaction, Instantaneous rate of reaction.

Units of Reaction Rate are unit of concentration divided by the unit of time (mol L⁻¹s⁻¹ or mol L⁻¹min⁻¹ or so on).

FACTORS AFFECTING REACTION RATES :

- (i) Concentration of reactants and
- (ii) Reaction temperature

Besides these, presence of catalyst and surface area (if a reactant or a catalyst is a solid) exposure to radiation also affect the reaction rates.

EXPRESSIONS OR THE RATE :

For a general reaction : $aA + bB \longrightarrow cC + dD$,

The rate of disappearance of A = $-\frac{d[A]}{dt}$; Rate of disappearance of B = $-\frac{d[B]}{dt}$;

Rate of appearance of C = $\frac{d[C]}{dt}$ & Rate of appearance of D = $\frac{d[D]}{dt}$.

The positive sign shows that concentrations of C and D increases with time and the negative sign indicating that concentrations of A and B decrease with time. Thus the rate of general reaction.

$$\text{rate} : -\frac{1}{a} \frac{d[A]}{dt} = -\frac{1}{b} \frac{d[B]}{dt} = \frac{1}{c} \frac{d[C]}{dt} = \frac{1}{d} \frac{d[D]}{dt} .$$

RATE EQUATION AND RATE CONSTANT :

An expression which relates the rate of a reaction to the concentration of the reactants is called the *Rate Equation or Rate Law*. Rate $\propto [A]^a \cdot [B]^b$ or Rate = $k [A]^a [B]^b$. The constant of proportionality, k is known as the *Rate Constant* (specific reaction rate) and may be defined as the rate at unit concentrations of the reactants. k depends on the temperature and is independent of the initial concentrations of the reactants. At a fixed temperature, k is constant characteristic of the reaction. Larger value of k indicates fast reaction and small k indicates slow reactions.

MOLECULARITY :

Molecularity of a reaction is defined as the numbers of particles (atoms, ions, groups or molecules) of reactants actually taking part in a single step chemical reaction.

Molecularity of a reaction is :

- (i) Always a whole number (not zero) and never a fraction.
- (ii) The value of molecularity of a simple or one step reaction does not exceed 3.

ORDER OF REACTION :

It is defined as the sum of the exponents (powers) of the molar concentrations of the reactants in the experimentally determined rate equations.

If rate of reaction $\propto [A]^p [B]^q [C]^r$ or Rate of reaction = $k [A]^p [B]^q [C]^r$

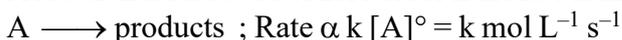
order of reaction = $p + q + r$ & the order w.r.t. A, B & C are p, q & r respectively.

For a "Reaction of nth order", the order of the reaction is n and the rate equation (or Rate law) is rate $\propto [A]^n = k [A]^n$.

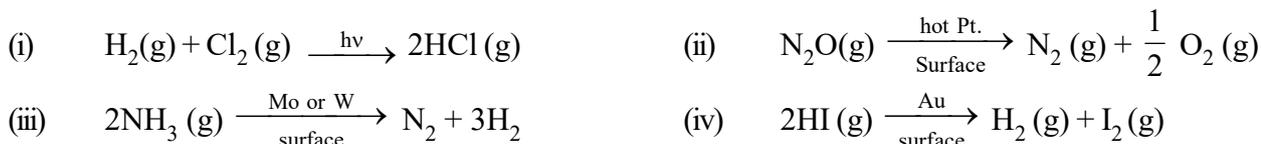
The order of a reaction is obtained from the experimentally determined rate (and not from the stoichiometric equation) and may be zero, an integer or a fraction and never exceeds 3. In a multi-step complex reaction, the order of the reaction depends on the slowest step.

ZERO ORDER REACTION :

A reaction is said to be of zero order if the rate is independent of the concentration of the reactants.



EXAMPLES :



CHARACTERISTICS OF ZERO ORDER REACTION :

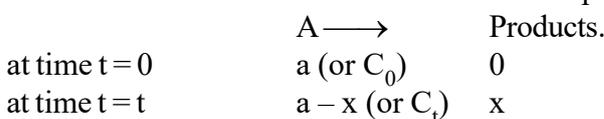
(1) Concentration of reactant decreases linearly with time. $[A]_t = [A]_0 - kt$.

(2) Units of k are, $\text{mol l}^{-1} \text{ time}^{-1}$.

(3) Time required for the completion of reaction $t = \frac{[A]_0}{k}$ & $t_{1/2} = \frac{0.5 [A]_0}{k}$

FIRST ORDER REACTION :

A reaction is said to be of first order if its rate is proportional to the concentration of one reactant only.



$$\text{Rate} \propto [A] = k_1 [A] \text{ or } \frac{dx}{dt} = k_1(a-x) \quad (1 \text{ st order differential equation})$$

$$\text{Integrated 1 st order rate equation is } k_1 = \frac{2.303}{t} \log \frac{a}{a-x}.$$

$$\text{Exponential form of 1 st order equation is } C_t = C_0 e^{-k_1 t}$$

Characteristics Of First Order Reaction :

(1) Unit of rate constant is time^{-1} .

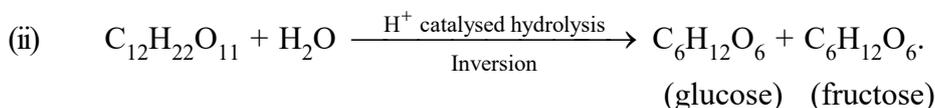
(2) Change in concentration unit will not change the numerical value of k_1 .

(3) $t_{1/2} = \frac{0.693}{k_1}$ (Half-life); Average life = $\frac{1}{k}$;

(4) $\log(a-x)$ v/s t is a straight line with slope $-\frac{k_1}{2.303}$.

EXAMPLES :

(i) Radioactive disintegration is a first order reaction.



(iii) Mineral acid catalyzed hydrolysis of esters.

(iv) Decomposition of H_2O_2 in aqueous solution.

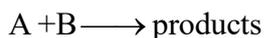
SECOND ORDER REACTION :

(i) When two molecules of the same reactant are involved or the concentrations of the both reactants are equal reactions $2A \longrightarrow \text{products}$ or $A + B \longrightarrow \text{products}$.

$$\text{Differential rate equation } \frac{dx}{dt} = k_2(a-x)^2$$

$$\text{Integrated rate equation } k_2 = \frac{1}{t} \cdot \frac{x}{a(a-x)} \text{ or } k_2 t = \frac{1}{a-x} - \frac{1}{a}.$$

(ii) When the initial concentrations of the two reactants are different;



a b

differential rate equation $\frac{dx}{dt} = k_2(a-x)(b-x)$.

Integrated rate equation $k_2 = \frac{2.303}{t(a-b)} \log_{10} \frac{b(a-x)}{a(b-x)}$

CHARACTERISTICS OF SECOND ORDER REACTION :

- (i) Unit of rate constant $L \text{ mol}^{-1} \text{ time}^{-1}$.
- (ii) Numerical value of k will depend upon unit of concentration.
- (iii) $t_{1/2} \propto a^{-1}$ (In general $t_{1/2} \propto a^{(1-n)}$; n = order of reactions).
- (iv) 2^{nd} order reaction conforms to first order when one of the reactant in excess.

EXAMPLES :

- (i) Saponification (hydrolysis of esters catalysed with alkali).
 $\text{CH}_3\text{COOC}_2\text{H}_5 + \text{NaOH} \longrightarrow \text{CH}_3\text{COONa} + \text{C}_2\text{H}_5\text{OH}$
- (ii) Hydrogenation of ethane $\text{C}_2\text{H}_4 + \text{H}_2 \xrightarrow{100^\circ\text{C}} \text{C}_2\text{H}_6$.
- (iii) $2 \text{O}_3 \longrightarrow 3 \text{O}_2$.

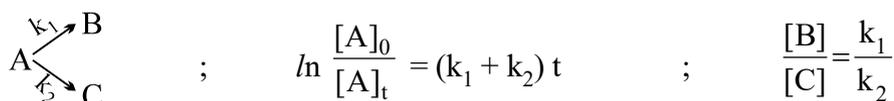
n^{th} ORDER REACTION.



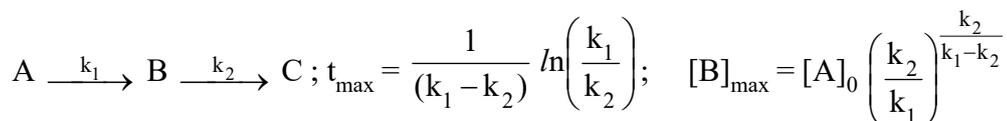
$$k_n t = \frac{1}{n-1} \left\{ \frac{1}{(a-x)^{n-1}} - \frac{1}{a^{n-1}} \right\} \quad [n \neq 1, n = \text{order}]$$

$$t_{1/2} = \frac{1}{k_n(n-1)} \left[\frac{2^{n-1} - 1}{a^{n-1}} \right]$$

SIDE OR CONCURRENT REACTION :



CONSECUTIVE REACTION :



THRESHOLD ENERGY AND ACTIVATION ENERGY :

For a reaction to take place the reacting molecules must collide together, but only those collisions, in which colliding molecules possess certain minimum energy is called threshold energy (E_T).

ACTIVATION ENERGY (E_a) :

The extra energy needed for the reactant molecules to be able to react chemically is known as Activation energy.

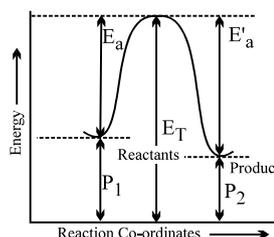
E_T = Threshold energy

E_a = Activation energy of forward reaction

E'_a = activation energy of backward reaction

P_1 = Potential energy of reactants

P_2 = Potential energy of products



INFLUENCE OF TEMPERATURE ON REACTION RATES :

TEMPERATURE COEFFICIENT :

The temperature coefficient of a chemical reaction is defined as the ratio of the reaction rates at two temperatures differing by 10°C. Its value usually lies between 2 & 3.

$$\text{Temperature coefficient} = \frac{k_{t+10}}{k_t}$$

ARRHENIUS EQUATION :

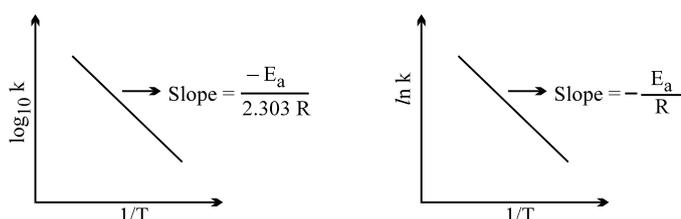
A quantitative relationship was proposed by Arrhenius $k = A \cdot e^{-E_a/RT}$ Where,

k = rate constant ; A = frequency factor (or pre-exponential factor);

R = gas constant ; T = Temperature (kelvin); E_a = Activation energy.

The Logarithmic expressions are $\log_{10} \frac{k_2}{k_1} = \frac{E_a}{2.303 R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right]$; Vant Hoff's Isochore $\frac{d}{dt} \ln k = \frac{E_a}{RT^2}$

GRAPHICAL REPRESENTATIONS ARE :



METHODS OF DETERMINATION OF ORDER OF REACTIONS :

A few methods commonly used are given below :

1. **Hit & Trial Method** : It is method of using integrated rate equations, where the experimental values of a , x & t are put into these equations. One which gives a constant value of k for different sets of a , x & t correspond to the order of the reaction.

2. **Graphical Method** :

(i) A plot of $\log(a-x)$ versus ' t ' gives a straight lines for the First order reaction.

(ii) A plot of $(a-x)^{-(n-1)}$ versus ' t ' gives a straight line any reaction of the order n (except $n = 1$).

3. **Half Life Method** : The half life of different order of reactions is given by $a_n = \left(\frac{1}{2}\right)^n a_0$.

By experimental observation of the dependence of half life on initial concentration we can determine n ,

the order of reaction. $n = 1 + \frac{\log t_2 - \log t_1}{\log a_1 - \log a_2}$.

4. **Initial rate method**. Initial rate method is used to determine the order or reaction in cases where more than one reactant is used. It involves the determination of the order of different reactants separately. A series of experiments are performed in which concentration of one particular reactant is varied whereas conc. of other reactants are kept constant. In each experiment the initial rate is determined from the plot of conc. vs. time, e.g., if conc. of A is doubled, and initial rate of reaction is also doubled, order of reaction is 1.

MECHANISM OF REACTIONS :

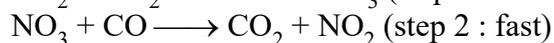
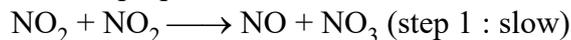
The path way which reactants are converted into the products is called the reaction mechanism. It should be clear that experimentally determined rate expression cannot be predicted from the stiochiometry of the reaction. For example for the reaction ;

$\text{NO}_2(\text{g}) + \text{CO}(\text{g}) \longrightarrow \text{CO}_2(\text{g}) + \text{NO}(\text{g})$, the rate expression is ; $\text{rate} = -\frac{d}{dt} [\text{NO}_2] = k[\text{NO}_2]^2$, i.e. the expression has no dependence of $\text{CO}(\text{g})$ concentration.

The reason is that the reaction occurs by a series of elementary steps.

The sequence of elementary processes leading to the overall stoichiometry is known as the "Mechanism of the reaction". A_n in a sequence of reactions leading to the formation of products from reactants, the slowest step is the rate determining step.

The mechanism proposed for the above reaction is a two step one.

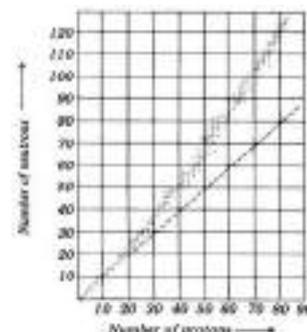


The sum of the two gives the stoichiometry & the slow step decided the rate expression.

Nuclear Chemistry

Neutron / proton ratio and stability

- ▶▶ For atomic number < 20, most stable nuclei have n: p ratio nearly 1 : 1 (except H & Ar).
- ▶▶ For n/p ratio > 1.5, nucleus is unstable. Largest stable nucleus is $^{209}_{83}\text{Bi}$ for which n/p ratio is 1.52.
- ▶▶ For atomic number > 83, there are no stable nuclei.



Magic numbers and nuclear stability

Nuclei with 2, 8, 20, 28, 50, 82 or 126 protons or neutrons are unusually stable and have a larger number of stable isotopes than neighboring nuclei in the periodic table. These numbers are called magic numbers. They are supposed to represent completely filled nuclear shells of energy levels.

- ▶▶ Nuclei with magic number of protons as well as neutrons have notably high stabilities. [eg. ^4_2He , $^{16}_8\text{O}$, $^{40}_{20}\text{Ca}$ and $^{208}_{82}\text{Pb}$]. 165 such stable nuclei are known.
- ▶▶ There exist 55 known nuclei with even number of protons and odd number of neutrons, and 50 known stable nuclei with odd number of protons and even number of neutrons. On the other hand, the number of known stable nuclei having odd numbers of both neutrons and protons is only 4.

Expected emissions from unstable nucleus

1. *n/p ratio above stability belt:* electron (β^-) or neutron.
2. *n/p ratio below stability belt:* positron (β^+) or K capture.
3. *Atomic number > 83,* various particles, including α -particles.

Radioactive decay

- ▶▶ Radioactive decay is a first order process. Hence $-\frac{dN}{dt} = \lambda N$ or $N = N_0 e^{-\lambda t}$
where N = number of radioactive nuclei at any time t ; N_0 = number of radioactive nuclei at $t=0$; λ = decay constant.

- ▶▶ **Activity** activity (a) = $-\frac{dN}{dt} = \lambda N$

S.I. units : disintegration per second (symbol s^{-1} or dps). This unit is also called *becquerel* (symbol Bq)

Other units: Curie (Ci) $1\text{Ci} = 3.7 \times 10^{10}\text{dps}$.

- ▶▶ **Half life ($t_{1/2}$)** The time taken by half the nuclei (originally present) to decay. $t_{1/2} = 0.693/\lambda$
Note : After n half-lives have passed, activity is reduced to $\frac{1}{2^n}$ of its initial value.

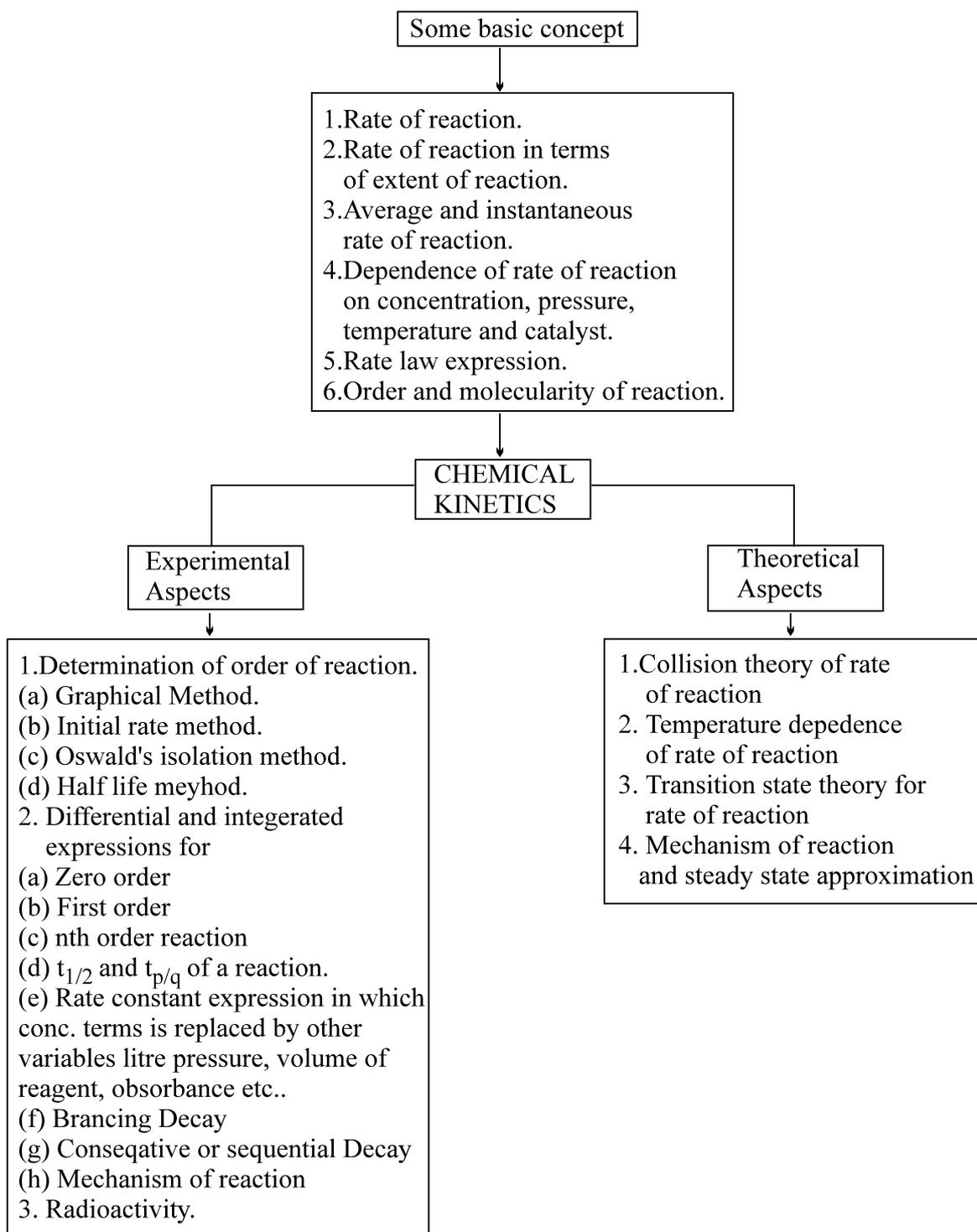
- ▶▶ **Average life (t_{av})** $t_{av} = 1/\lambda = 1.44 t_{1/2}$

Isotopes : Nuclei with same atomic number but different atomic mass number.

Isobars : Nuclei with different atomic number but same atomic mass number.

Isotones : Nuclei with same number of neutrons but different number of protons.

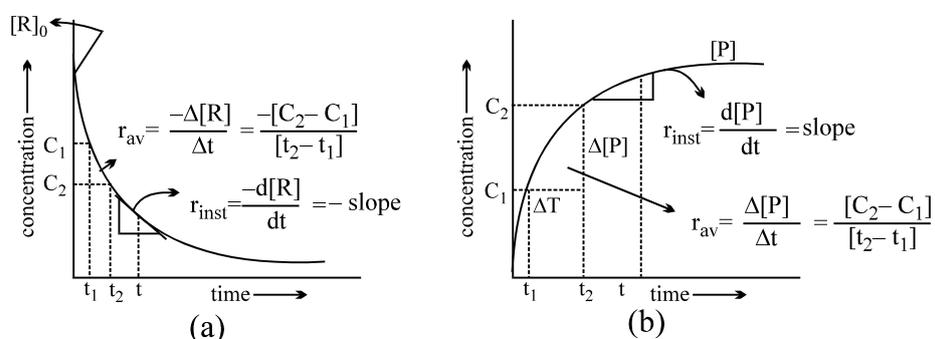
THE ATLAS



GLOSSARY

IMPORTANT TERMS AND DEFINITIONS

- Rate of reaction.** It is defined as the change in concentration of reactant (or product) in a particular time interval. Its unit is $\text{mol L}^{-1}\text{s}^{-1}$. If time is in minutes, then units are $\text{mol L}^{-1}\text{min}^{-1}$ and so on.
- Average rate.** The rate of reaction measured over a long time interval is called average rate of reaction. It is equal to $\Delta x/\Delta t$ as shown in fig.(a) and (b).



Instantaneous and average rate of reaction

- Instantaneous rate.** It is the rate of reaction when the average rate is taken over a very small interval of time. It is equal to dx/dt as shown in fig. (a) and (b).
- Rate law or rate equation.** It is the expression which relates the rate of reaction with concentration of the reactants. The constant of proportionality 'k' is known as rate constant.
- Rate constant.** When concentration of both reactants are unity, then the rate of reaction is known as rate constant. It is also called specific reaction rate.
- Molecularity.** Total number of molecules of the reactants involved in the reaction is termed as its molecularity. It is always in whole number, It is never more than three. It cannot be zero.
- Order of a reaction.** The sum of the powers of the concentration of reactants in the rate law is termed as order of the reaction. It can be in fraction. It can be zero also.
- Zero order reaction.** The rate of reaction does not change with the concentration of the reactants, i.e.,

$$\text{rate} = k[A]^0$$
- First order reaction.** The reaction in which the rate of reaction is directly proportional to the concentration of reacting substance. Rate constant of first order reaction is

$$k = \frac{2.303}{t} \log \frac{a}{a-x} \quad \text{or} \quad k = \frac{2.303}{t} \log \frac{[A_0]}{[A]}$$

where 'a' is initial concentration, (a-x) is the conc. of reactants after time 't'. The unit of 'k' is s^{-1} or min^{-1} . A plot between $\ln [A]$ vs. t is a straight line with slope equal to $-k$. [A] is concentration of reactants after time t.

- Half-life of a reaction.** The time taken for a reaction when half of the starting material has reacted is called half-life of a reaction. For first order reaction

$$t_{1/2} = \frac{0.693}{k}, \quad \text{where } k \text{ is rate constant.}$$

- Second order reaction.** The reaction in which sum of powers of concentration terms in rate law or rate equation is equal to 2, e.g.,

$$\frac{dx}{dt} = k[A]^1[B]^1$$

12. **Third order reaction.** The reaction in which sum of powers of concentration terms in rate law or rate equation is equal to 3, e.g.,

$$\frac{dx}{dt} = k[A]^x[B]^y \text{ where } x + y = 3$$

13. **Specific rate constant (k).** It is defined as equal to rate of reaction when molar concentration of reactant is unity.
14. **Activation energy.** It is extra energy which must be possessed by reactant molecules so that collision between reactant molecules is effective and leads to formation of product molecules.
15. **Initial rate.** The rate at the beginning of the reaction when the concentrations have not changed appreciably is called in initial rate of reaction.
16. **Arrhenius equation of reaction rate.** It gives the relation between rate of reaction and temperature.

$$K = Ae^{-E_a/RT}$$

where k = rate constant A = frequency factor, E_a = energy of activation

R = gas constant, T = temperature in kelvin.

$$\ln k = \ln A - E_a/RT$$

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

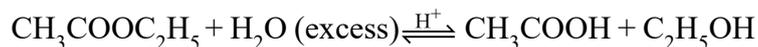
17. **Photochemical reactions.** Those reactions which take place in the presence of light are called photochemical reactions. Photosynthesis is an example of photochemical reaction.
18. **Photosensitization.** The process in which a molecule that absorbs light transfers its extra energy to another molecule which may undergo a reaction. This process is called photosensitization.
19. **Chain reaction.** The sequence of reactions, where a reactive species produces more reactive species is called chain reaction. It involves free radicals.
20. **Elementary processes.** Some reactions occur by a series of elementary steps and such simple steps are called elementary processes.
21. **Mechanism of reaction.** The sequence of elementary processes leading to the overall stoichiometry of a chemical reaction is known as mechanism of a reaction.
22. **Slow reaction.** Those reactions which take place very slowly are called slow reactions, e.g., rusting of iron and reaction of oxalic acid with acidified $KMnO_4$ at room temperature are slow reactions.
23. **Life time.** The time in which 98% of the reaction is complete is called lifetime.
24. **Threshold energy.** The minimum energy that reacting species must possess in order to undergo effective collision to form product molecules is called threshold energy.
25. **Effective collision (f).** Those collisions which lead to the formation of product molecules are called effective collisions. Rate of reaction = $f \times z$ where 'z' is collision frequency and 'f' is fraction of collisions, which are effective.
26. **Collision frequency (z).** It is defined as total number of collisions per unit volume per unit time.
27. **Activated complex.** It is defined as unstable intermediate formed between reacting molecules which is highly unstable and readily changes into product.
28. **Thermodynamic stability.** A mixture of substances may not undergo reaction although thermodynamic predict the reaction to be spontaneous. Such substances are thermodynamically unstable at ordinary temperature but may not be kinetically unstable.
29. **Kinetic stability.** The reaction occurs only when the reactant crosses energy-barrier. Once it occurs, it becomes kinetically unstable because the reaction is spontaneous. The energy evolved helps the other reactants to cross energy-barrier. Thus, reactants should be thermodynamically as well as kinetically unstable so as to change into products at a particular temperature.

30. **Rate determining step.** The slowest step in the reaction mechanism is called rate determining step.
31. **Temperature coefficient.** It is the ratio of rate constant at temperature 308 K to the rate constant at temperature 298 K.

$$\text{Temperature coefficient} = \frac{\text{Rate constant 'k' at 308 K}}{\text{Rate constant 'k' at 298 K}}$$

It lies between 2 and 3.

32. **Pseudo first order reaction.** The reaction in which one reactant is in excess so order is one is called Pseudo first order reaction, e.g., acidic hydrolysis of ester.



33. **Einstein's law of photochemical equivalence.** Each atom or molecule is activated by 1 photon (quantum of light).
34. **Chain initiation step.** The step in which neutral molecule changes into free radicals by absorbing photons is called chain initiation step.
35. **Chain propagation step.** The step in which free radical reacts with neutral molecule to form a neutral molecule and a free radical is called chain propagation step.
36. **Chain termination step.** The step in which radicals combine to form neutral molecules.
37. **Fast reactions.** Those reactions which occur instantaneously and is complete in fraction of seconds are called fast reactions, e.g., $\text{AgNO}_3(\text{aq}) + \text{HCl}(\text{aq}) \longrightarrow \text{AgCl} \downarrow + \text{HNO}_3$, takes place in 10^{-12} seconds.
38. **Thermochemical reactions.** Those reactions initiated by heat energy are called thermochemical reactions. They can occur in dark. Temperature coefficient is generally high because rate of reaction increases with increase in temperature. ΔG is –ve for such reactions.

EXERCISE-I
RATE OF REACTION AND STOICHIOMETRIC COEFFICIENT

- Q.1 In a catalytic experiment involving the Haber process, $\text{N}_2 + 3\text{H}_2 \longrightarrow 2\text{NH}_3$, the rate of reaction was measured as

$$\text{Rate} = \frac{\Delta[\text{NH}_3]}{\Delta t} = 2 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}.$$

If there were no side reactions, what was the rate of reaction expressed in terms of (a) N_2 , (b) H_2 ?

- Q.2 For the reaction $3\text{BrO}^- \rightarrow \text{BrO}_3^- + 2\text{Br}^-$ in an alkaline aqueous solution, the value of the second order (in BrO^-) rate constant at 80°C in the rate law for $-\frac{\Delta[\text{BrO}^-]}{\Delta t}$ was found to be $0.056 \text{ L mol}^{-1} \text{ s}^{-1}$.

What is the rate of constant when the rate law is written for (a) $\frac{\Delta[\text{BrO}_3^-]}{\Delta t}$, (b) $\frac{\Delta[\text{Br}^-]}{\Delta t}$?

- Q.3 Dinitropentaoxide decomposes as follows :



Given that $-\frac{d[\text{N}_2\text{O}_5]}{dt} = k_1[\text{N}_2\text{O}_5]$

$$\frac{d[\text{NO}_2]}{dt} = k_2[\text{N}_2\text{O}_5]$$

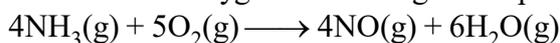
$$\frac{d[\text{O}_2]}{dt} = k_3[\text{N}_2\text{O}_5]$$

What is the relation between k_1 , k_2 and k_3 ?

- Q.4 The reaction $2\text{A} + \text{B} + \text{C} \rightarrow \text{D} + \text{E}$ is found to be first order in A second order in B and zero order in C.
(i) Give the rate law for the reaction in the form of differential equation.
(ii) What is the effect in rate of increasing concentrations of A, B, and C two times?

- Q.5 For the elementary reaction $2\text{A} + \text{B}_2 \longrightarrow 2\text{AB}$. Calculate how much the rate of reaction will change if the volume of the vessel is reduced to one third of its original volume?

- Q.6 Ammonia and oxygen reacts at higher temperatures as



In an experiment, the concentration of NO increases by $1.08 \times 10^{-2} \text{ mol litre}^{-1}$ in 3 seconds. Calculate.

- (i) rate of reaction.
(ii) rate of disappearance of ammonia
(iii) rate of formation of water

- Q.7 In the following reaction $2\text{H}_2\text{O}_2 \longrightarrow 2\text{H}_2\text{O} + \text{O}_2$
rate of formation of O_2 is 3.6 M min^{-1} .

- (a) What is rate of formation of H_2O ?
(b) What is rate of disappearance of H_2O_2 ?

- Q.8 The reaction $\text{A}(\text{g}) + 2\text{B}(\text{g}) \longrightarrow \text{C}(\text{g}) + \text{D}(\text{g})$ is an elementary process. In an experiment, the initial partial pressure of A & B are $P_A = 0.6$ and $P_B = 0.8$ atm, if $P_C = 0.2$ atm then calculate the ratio of rate of reaction relative to initial rate.

ZERO ORDER

- Q.9 In the following reaction, rate constant is $1.2 \times 10^{-2} \text{ M s}^{-1}$ $\text{A} \longrightarrow \text{B}$. What is concentration of B after 10 and 20 min., if we start with 10 M of A.

- Q.10 For the following data for the reaction $\text{A} \longrightarrow \text{products}$. Calculate the value of k.

Time (min.)	[A]
0.0	0.10 M
1.0	0.09 M
2.0	0.08 M

- Q.11 The rate constant for a zero order reaction is $2 \times 10^{-2} \text{ mol L}^{-1}\text{sec}^{-1}$, if the concentration of the reactant after 25 sec is 0.25 M, calculate the initial concentration.
- Q.12 A drop of solution (volume 0.10 ml) contains 6×10^{-6} mole of H^+ , if the rate constant of disappearance of H^+ is $1 \times 10^7 \text{ mole litre}^{-1} \text{ sec}^{-1}$. How long would it take for H^+ in drop to disappear?
- Q.13 A certain substance A is mixed with an equimolar quantity of substance B. At the end of an hour A is 75% reacted. Calculate the time when A is 10% unreacted. (Given: order of reaction is zero)

FIRST ORDER

- Q.14 A first order reaction is 75% completed in 72 min.. How long time will it take for
(i) 50% completion (ii) 87.5% completion
- Q.15 A first order reaction is 20% complete in 10 min. calculate (i) the specific rate constant, (ii) the time taken for the reactions to go to 75% completion.
- Q.16 Show that in case of unimolecular reaction, the time required for 99.9% of the reaction to take place in ten times that required for half of the reaction.
- Q.17 A first order reaction has a rate constant is $1.5 \times 10^{-3} \text{ sec}^{-1}$. How long will 5.0 g of this reactant take to reduce to 1.25 g.
- Q.18 A drug is known to be ineffective after it has decomposed 30%. The original concentration of a sample was 500 units/ml. When analyzed 20 months later, the concentration was found to be 420 units/ml. Assuming that decomposition is of I order, what will be the expiry time of the drug?
- Q.19 A viral preparation was inactivated in a chemical bath. The inactivation process was found to be first order in virus concentration. At the beginning of the experiment 2.0 % of the virus was found to be inactivated per minute. Evaluate k for inactivation process.
- Q.20 If a reaction $\text{A} \longrightarrow \text{Products}$, the concentrations of reactant A are $C_0, aC_0, a^2C_0, a^3C_0, \dots$ after time interval 0, t, 2t, 3t, where a is a constant. Given $0 < a < 1$. Show that the reaction is of first order. Also calculate the relation in k, a and t.
- Q.21 The reaction $\text{SO}_2\text{Cl}_2(\text{g}) \longrightarrow \text{SO}_2(\text{g}) + \text{Cl}_2(\text{g})$ is a first order gas reaction with $k = 2.2 \times 10^{-5} \text{ sec}^{-1}$ at 320°C . What % of SO_2Cl_2 is decomposed on heating this gas for 90 min.

ORDER OF REACTION & RATE LAW

- Q.22 At 800°C the rate of reaction

$$2 \text{ NO} + \text{H}_2 \longrightarrow \text{N}_2 + \text{H}_2\text{O}$$
 Changes with the concentration of NO and H_2 are

	[NO] in M	$[\text{H}_2]$ in M	$-\frac{1}{2} \frac{d[\text{NO}]}{dt}$ in M sec^{-1}
(i)	1.5×10^{-4}	4×10^{-3}	4.4×10^{-4}
(ii)	1.5×10^{-4}	2×10^{-3}	2.2×10^{-4}
(iii)	3.0×10^{-4}	2×10^{-3}	8.8×10^{-4}

- (a) What is the order of this reaction?
 (b) What is the rate equation for the reaction?
 (c) What is the rate when
 $[\text{H}_2] = 1.5 \times 10^{-3} \text{ M}$ and $[\text{NO}] = 1.1 \times 10^{-3} \text{ M}$?

Q.23 The data below are for the reaction of NO and Cl₂ to form NOCl at 295 K

Concentration of Cl ₂ [M]	Concentration of NO	Initial Rate (M s ⁻¹)
0.05	0.05	1 × 10 ⁻³
0.15	0.05	3 × 10 ⁻³
0.05	0.15	9 × 10 ⁻³

- (a) What is the order w.r.t NO and Cl₂ in the reaction.
 (b) Write the rate expression
 (c) Calculate the rate constant
 (d) Determine the reaction rate when concentration of Cl₂ and NO are 0.2 M & 0.4 M respectively.

Q.24 The catalytic decomposition of N₂O by gold at 900°C and at an initial pressure of 200mm is 50% complete in 53 minutes and 73% complete in 100 minutes.

- (i) What is the order of the reaction?
 (ii) Calculate the velocity constant.
 (iii) How much of N₂O will decompose in 100 min. at the same temperature but at initial pressure of 600 mm?

Q.25 The following data are for the reaction A + B → products:

Conc. A (M)	Conc. B (M)	Initial Rate (mol L ⁻¹ s ⁻¹)
0.1	0.1	4.0 × 10 ⁻⁴
0.2	0.2	1.6 × 10 ⁻³
0.5	0.1	2.0 × 10 ⁻³
0.5	0.5	1.0 × 10 ⁻²

- (i) What is the order with respect to A and B for the reaction?
 (ii) Calculate the rate constant.
 (iii) Determine the reaction rate when the concentrations of A and B are 0.2M and 0.35M, respectively.

Q.26 The pressure of a gas decomposing at the surface of a solid catalyst has been measured at different times and the results are given below

t (sec)	0	100	200	300
Pr. (Pascal)	4 × 10 ³	3.5 × 10 ³	3 × 10 ³	2.5 × 10 ³

Determine the order of reaction, its rate constant.

Q.27 The half life period of decomposition of a compound is 50 minutes. If the initial concentration is halved, the half life period is reduced to 25 minutes. What is the order of reaction?

Q.28 At 600°C, acetone (CH₃COCH₃) decomposes to ketene (CH₂ = C = O) and various hydrocarbons. Given the initial rate data in the table:

- (a) What is the order?
 (b) Write rate law
 (c) Calculate rate constant
 (d) Calculate the rate of decomposition when the acetone concentration is 1.8 × 10⁻³ M
- | Experiment | Initial [CH ₃ COCH ₃] | Rate M s ⁻¹ |
|------------|--|------------------------|
| 1. | 6.0 × 10 ⁻³ M | 5.2 × 10 ⁻⁵ |
| 2. | 9.0 × 10 ⁻³ M | 7.8 × 10 ⁻⁵ |
| 3. | 1.8 × 10 ⁻³ M | ? |

HALF LIFE

Q.29 The half life period of a first order reaction is 50 min. In what time will it go to 90% completion?

Q.30 A first order reaction has k = 1.5 × 10⁻⁶ per second at 200°C. If the reaction is allowed to run for 10 hrs., what percentage of the initial concentration would have changed into the product? What is the half life of this reaction?

- Q.31 Show that in case of a first order reaction, the time required for 93.75% of the reaction to take place is four times that required for half of the reaction.
- Q.32 The half time of the first order decomposition of nitramide is 2.1 hour at 15°C.

$$\text{NH}_2\text{NO}_2 (\text{aq.}) \longrightarrow \text{N}_2\text{O} (\text{g}) + \text{H}_2\text{O} (\text{l})$$
 If 6.2 g of NH_2NO_2 is allowed to decompose, calculate (i) time taken for NH_2NO_2 to decompose 99%, and (ii) volume of dry N_2O produced at this point, measured at STP.
- Q.33 A flask contains a mixture of compounds A and B. Both compounds decompose by first-order kinetics. The half-lives are 54.0 min for A and 18.0 min. for B. If the concentrations of A and B are equal initially, how long will it take for the concentration of A to be four times that of B?
- Q.34 Two substances A ($t_{1/2} = 5$ mins) and B ($t_{1/2} = 15$ mins) follow first order kinetics are taken in such a way that initially $[A] = 4[B]$. Calculate the time after which the concentration of both the substance will be equal.

CONCENTRATION REPLACED BY OTHER QUANTITIES IN FIRST ORDER
INTEGRATED RATE LAW

- Q.35 In this case we have

$$\text{A} \longrightarrow \text{B} + \text{C}$$

Time	t	∞
Total pressure of A + B + C	P_2	P_3

 Find k.
- Q.36
$$\text{A} \longrightarrow \text{B} + \text{C}$$

Time	t	∞
Total pressure of (B + C)	P_2	P_3

 Find k.
- Q.37
$$\text{A} \longrightarrow \text{B} + \text{C}$$

Time	0	t
Volume of reagent	V_1	V_2

 The reagent reacts with A, B and C. Find k.
- Q.38
$$\text{A} \longrightarrow 2\text{B} + 3\text{C}$$

Time	t	∞
Volume of reagent	V_2	V_3

 Reagent reacts with all A, B and C. Find k.
- Q.39
$$\text{S} \longrightarrow \text{G} + \text{F}$$

Time	t	∞
Rotation of Glucose & Fructose	r_t	r_∞

 Find k.
- Q.40 At 27°C it was observed during a reaction of hydrogenation that the pressure of hydrogen gas decreases from 2 atmosphere to 1.1 atmosphere in 75 minutes. Calculate the rate of reaction (in M sec^{-1}) and rate of reaction in terms of pressure.
- Q.41 At 100°C the gaseous reaction $\text{A} \longrightarrow 2\text{B} + \text{C}$ was observed to be of first order. On starting with pure A it is found that at the end of 10 minutes the total pressure of system is 176 mm. Hg and after a long time 270 mm Hg. From these data find (a) initial pressure of A (b) the pressure of A at the end of 10 minutes (c) the specific rate of reaction and (d) the half life period of the reaction?
- Q.42 The reaction $\text{AsH}_3(\text{g}) \longrightarrow \text{As}(\text{s}) + \frac{3}{2} \text{H}_2(\text{g})$ was followed at constant volume at 310°C by measuring the gas pressure at intervals Show from the following figures that reaction is of first order.
- | | | | | |
|------------------------|-----|-----|-----|-----|
| Time (in hrs) | 0 | 5 | 7.5 | 10 |
| Total pressure (in mm) | 758 | 827 | 856 | 882 |

Q.43 The decomposition of N_2O_5 according to the equation $2\text{N}_2\text{O}_5(\text{g}) \longrightarrow 4\text{NO}_2(\text{g}) + \text{O}_2(\text{g})$ is a first order reaction. After 30 min. from start of decomposition in a closed vessel the total pressure developed is found to be 284.5 mm Hg. On complete decomposition, the total pressure is 584.5 mm Hg. Calculate the rate constant of the reaction.

Q.44 The thermal decomposition of dimethyl ether as measured by finding the increase in pressure of the reaction



at 500°C is as follows:

Time (sec.)	390	1195	3155	∞
Pressure increase (mm Hg)	96	250	467	619

the initial pressure of ether was 312 mm Hg. Write the rate equation for this reaction and determine the rate constant of reaction.

Q.45 From the following data show that decomposition of H_2O_2 in aqueous solution is first order.

Time (in minutes)	0	10	20
Volume (in c.c. of KMnO_4)	22.8	13.3	8.25

Q.46 A definite volume of H_2O_2 under going spontaneous decomposition required 22.8 c.c. of standard permanganate solution for titration. After 10 and 20 minutes respectively the volumes of permanganate required were 13.8 and 8.25 c.c.

- Find order of reaction. How may the result be explained?
- Calculate the time required for the decomposition to be half completed.
- Calculate the fraction of H_2O_2 decomposed after 25 minutes.

Q.47 The following data were obtained in experiment on inversion of cane sugar.

Time (minutes)	0	60	120	180	360	∞
Angle of rotation (degree)	+13.1	+11.6	+10.2	+9.0	+5.87	-3.8

Show that the reaction is of first order. After what time would you expect a zero reading in polarimeter?

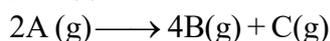
Q.48 In the hydrolysis of propyl acetate in the presence of dilute hydrochloric acid in dilute aqueous solution the following data were recorded :

Time from start in minutes	60	350
Percentage of ester decomposed	18.17	69.12

Calculate the time in which half the ester was decomposed.

Q.49 Hydrogen peroxide solution was stored in a mild steel vessel. It was found, however, that the hydrogen peroxide decomposed on the walls of the vessel (a first order reaction). An experiment with 100 ml of a solution gave 10.31 ml oxygen (corrected to N.T.P.) after 5.1 days under similar storage conditions. Find how long the peroxide can be stored before the loss of 20.00 ml oxygen occurs (per 100 ml solution) if complete decomposition of the sample to H_2O_2 gave 46.34 ml oxygen.

Q.50 The reaction given below, rate constant for disappearance of A is $7.48 \times 10^{-3} \text{ sec}^{-1}$. Calculate the time required for the total pressure in a system containing A at an initial pressure of 0.1 atm to rise to 0.145 atm and also find the total pressure after 100 sec.



PARALLEL AND SEQUENTIAL REACTION

Q.51 For a reaction $\text{x} \begin{cases} \xrightarrow{k_1} \text{y} \\ \xrightarrow{k_2} \text{z} \end{cases}$, calculate value of ratio, $\frac{[\text{x}]_t}{[\text{y}] + [\text{z}]}$ at any given instant t.

Q.52 $A \begin{cases} \xrightarrow{k_1} B \\ \xrightarrow{k_2} C \end{cases}$ $k_1 = x \text{ hr}^{-1}$; $k_1 : k_2 = 1 : 10$. Calculate $\frac{[C]}{[A]}$ after one hour from the start of the reaction. Assuming only A was present in the beginning.

Q.53 A substance undergoes first order decomposition. The decomposition follows two parallel first order reactions as $A \begin{cases} \xrightarrow{k_1} B \\ \xrightarrow{k_2} C \end{cases}$; $k_1 = 1.26 \times 10^{-4} \text{ sec}^{-1}$ and $k_2 = 3.6 \times 10^{-5} \text{ sec}^{-1}$. Calculate the % distribution of B & C.

Q.54 For a reaction $A \longrightarrow B \longrightarrow C$ $t_{1/2}$ for A & B are 4 and 2 minutes respectively. How much time would be required for the B to reach maximum concentration.

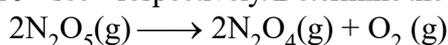
TEMPERATURE DEPENDENCE OF RATE (ACTIVATION ENERGY)

Q.55 In gaseous reactions important for understanding the upper atmosphere, H_2O and O react bimolecularly to form two OH radicals. ΔH for this reaction is 72 kJ at 500 K and $E_a = 77 \text{ kJ mol}^{-1}$, then calculate E_a for the biolecular recombination of 2OH radicals to form H_2O & O at 500 K

Q.56 The energy of activation of a first order reaction is $104.5 \text{ kJ mole}^{-1}$ and pre-exponential factor (A) is $5 \times 10^{13} \text{ sec}^{-1}$. At what temperature, will the reaction have a half life of 1 minute?

Q.57 The specific rate constant for a reaction increases by a factor of 4, if the temperature is changed from 27°C to 47°C . Find the activation energy for the reaction.

Q.58 The energy of activation and specific rate constant for a first order reaction at 25°C are 100 kJ/mole and $3.46 \times 10^{-5} \text{ sec}^{-1}$ respectively. Determine the temperature at which half life of the reaction is 2 hours.



Q.59 A first order reaction is 50% complete in 30 minutes at 27°C and in 10 minutes at 47°C . Calculate the
(a) rate constant for the reaction at 27°C & 47°C and
(b) energy of activation for the reaction.

Q.60 A catalyst lowers the activation energy for a certain reaction from 75 kJ to 25 kJ mol^{-1} . What will be the effect on the rate of reaction at 25°C , after things being equal.

Q.61 Given that the temperature coefficient for the saponification of ethyl acetate by NaOH is 1.75. Calculate activation energy for the saponification of ethyl acetate.

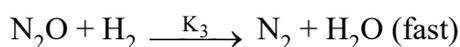
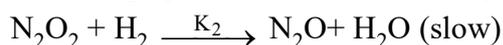
MECHANISM OF REACTION

Q.62 The reaction $2NO + Br_2 \longrightarrow 2NOBr$, is supposed to follow the following mechanism



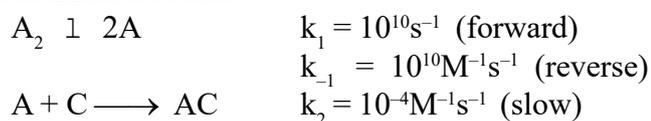
Suggest the rate of law expression.

Q.63 For the reaction $2H_2 + 2NO \longrightarrow N_2 + 2H_2O$, the following mechanism has been suggested:
 $2NO \rightleftharpoons N_2O_2$ equilibrium constant K_1 (fast)



Establish the rate law for given reaction.

Q.64 Write a stoichiometric equation for the reaction whose mechanism is detailed below. Determine the value of the equilibrium constant for the first step. Write a rate law equation for the overall reaction in terms of its initial reactants.



- Q.65 Reaction between NO and O₂ to form NO₂ is $2\text{NO} + \text{O}_2 \longrightarrow 2\text{NO}_2$ follows the following mechanism
- $$\text{NO} + \text{NO} \xrightleftharpoons[\text{K}_{-1}]{\text{K}_1} \text{N}_2\text{O}_2 \quad (\text{in rapid equilibrium})$$
- $$\text{N}_2\text{O}_2 + \text{O}_2 \xrightarrow{\text{K}_2} 2\text{NO}_2 \quad (\text{slow})$$
- Show that the rate of reaction is given by $\frac{1}{2} \left(\frac{d[\text{NO}_2]}{dt} \right) = \text{K}[\text{NO}]^2[\text{O}_2]$
- Q.66 Deduce rate law expressions for the conversion of H₂ and I₂ to HI at 400°C corresponding to each of the following mechanisms:
- (a) $\text{H}_2 + \text{I}_2 \longrightarrow 2\text{HI}$ (one step)
- (b) $\text{I}_2 \rightleftharpoons 2\text{I}$
 $2\text{I} + \text{H}_2 \longrightarrow 2\text{HI}$ (slow)
- (c) $\text{I}_2 \rightleftharpoons 2\text{I}$
 $\text{I} + \text{H}_2 \rightleftharpoons \text{IH}_2$
 $\text{IH}_2 + \text{I} \longrightarrow 2\text{HI}$ (slow)
- (d) Can the observed rate law expression rate = k[H₂][I₂] distinguish among these mechanisms?
- (e) If it is known that ultraviolet light causes the reaction of H₂ and I₂ to proceed at 200°C with the same rate law expression, which of these mechanisms becomes most improbable? Are any of these mechanisms proved?

RADIOACTIVITY

- Q.67 Classify each of the following nuclides as "beta emitter", or "positron emitter":
 ${}_{20}^{49}\text{Ca}$, ${}_{80}^{195}\text{Hg}$, ${}_{5}^8\text{B}$, ${}_{67}^{150}\text{Ho}$, ${}_{13}^{30}\text{Al}$, ${}_{36}^{94}\text{Kr}$. Note: ${}_{80}^{200}\text{Hg}$ and ${}_{67}^{165}\text{Ho}$ are stable
- Q.68 Of the three isobars ${}_{48}^{114}\text{Cd}$, ${}_{49}^{114}\text{In}$ and ${}_{50}^{114}\text{Sn}$, which is likely to be radioactive? Explain your choice.
- Q.69 Complete the following nuclear equations:
- (a) ${}_{7}^{14}\text{N} + {}_{2}^4\text{He} \rightarrow {}_{8}^{17}\text{O} + \dots$ (b) ${}_{4}^9\text{Be} + {}_{2}^4\text{He} \rightarrow {}_{6}^{12}\text{C} + \dots$ (c) ${}_{4}^9\text{Be} (p, \alpha) \dots$
- (d) ${}_{15}^{30}\text{P} \rightarrow {}_{14}^{30}\text{S} + \dots$ (e) ${}_{1}^3\text{H} \rightarrow {}_{2}^3\text{He} + \dots$ (f) ${}_{20}^{43}\text{Ca} (\alpha, \dots) \rightarrow {}_{21}^{46}\text{Sc}$
- Q.70 What symbol is needed to complete the nuclear equation ${}_{29}^{63}\text{Cu} (p, \dots) {}_{29}^{62}\text{Cu}$?
- Q.71 Complete the following equations.
- (a) ${}_{11}^{23}\text{Na} + {}_{2}^4\text{He} \rightarrow {}_{12}^{26}\text{Mg} + ?$ (b) ${}_{29}^{64}\text{Cu} \rightarrow \beta^+ + ?$
- (c) ${}_{106}^{106}\text{Ag} \rightarrow {}_{106}^{106}\text{Cd} + ?$ (d) ${}_{5}^{10}\text{B} + {}_{2}^4\text{He} \rightarrow {}_{7}^{13}\text{N} + ?$
- Q.72 How many α and β particle will be emitted when ${}_{\text{c}}^{\text{a}}\text{X}$ changes to ${}_{\text{d}}^{\text{b}}\text{Y}$?
- Q.73 What is the α -activity in disintegration per minute 1 gm sample of ${}^{226}\text{Ra}$. ($t_{1/2} = 1620$ year)
- Q.74 The half life of the nuclide Rn^{220} is 54.5 sec. What mass of radon is equivalent to 1 millicurie.
- Q.75 The activity of the radioactive sample drops to $\left(\frac{1}{64}\right)^{\text{th}}$ of its original value in 2 hr find the decay constant (λ).
- Q.76 ${}_{84}^{\text{Po}^{210}}$ decays with α to ${}_{82}^{206}\text{Pb}$ with a half life of 138.4 days. If 1.0 gm of Po^{210} is placed in a closed tube, how much helium accumulate in 69.2 days at STP.
- Q.77 The half life period of ${}_{53}^{\text{I}^{125}}$ is 60 days. What % of radioactivity would be present after 240 days.
- Q.78 At a certain instant a piece of radioactive material contains 10^{12} atoms. The half life of material is 30 days. Calculate the no. of disintegrations in one second.
- Q.79 Calculate the age of a vegetarian beverage whose tritium content is only 15% of the level in living plants. Given $t_{1/2}$ for ${}_{1}\text{H}^3 = 12.3$ years.
- Q.80 A radioactive substance decays 20% in 10 min if at start there are 5×10^{20} atoms present, after what time will the number of atoms be reduced to 10^{18} atoms?

PROFICIENCY TEST

Q.1 *Fill in the blanks with appropriate items :*

1. 1 Curie = _____ Bq.
2. ${}^{14}_6\text{C}$ decays by emission of _____.
3. Emission of a β -particle by a nuclide results in the formation _____ of the element.
4. The number of α and β -particles emitted, when the following nuclear transformation takes place are _____ and _____ respectively.
$${}^{238}_{92}\text{X} \longrightarrow {}^{206}_{82}\text{Y}$$
5. The nuclides with same difference of number of neutrons and number of protons are called _____.
6. When ${}^{30}_{15}\text{P}$ emits a positron, the daughter nuclide formed is _____.
7. A nuclide which lies above the zone of stability is likely to emit _____.
8. ${}^3_1\text{H}$ and ${}^4_2\text{He}$ are _____.
9. The half-life period of radioactive element if 87.5% of it disintegrates in 40 min is _____.
10. For collision to be effective the energy possessed by the colliding molecules should be equal to or greater than the _____.
11. In the reaction, $\text{H}_2 + \text{I}_2 \longrightarrow 2\text{HI}$, the rate of disappearance of H_2 is _____ the rate of appearance of HI.
12. For an endothermic process, the minimum value of activation energy can be _____.
13. The rate of a reaction is _____ to the collision frequency.
14. The rate constant for the zero order reaction has the dimensions _____.
15. The reactions with molecularity more than three are _____.
16. A catalyst increases the rate of the reaction by _____ activation energy of reactants.
17. If activation energy of reaction is low, it proceeds at _____ rate.
18. In a multistep reaction, the _____ step is rate determining.
19. Rate constant of a reaction, generally _____ with increase in temperature.
20. The ratio $t_{7/8} / t_{1/2}$ for a first order reaction would be equal to _____.
21. For a zero order reaction, the rate of the reaction is equal to the _____ of the reaction.
22. The value of temperature coefficient is generally between _____.
23. For a certain reaction, $x\text{M} \longrightarrow y\text{L}$, the rate of reaction increases by 4 times when the concentration of M is doubled. The rate law is _____.
24. The rate equation $r = k[\text{A}][\text{B}]^{1/2}$ suggests that order of overall reaction is _____.
25. A plot of $[\text{A}]$ vs t for a certain reaction $\text{A} \longrightarrow \text{B}$ with $r = k[\text{A}]^0$ will be a straight line with slope equal to _____.

26. $[E_{\text{activated complex}} - E_{\text{reactants}}] = \text{_____}$.
27. Among similar reactions, the endothermic reaction has _____ activation energy than exothermic reaction.
28. For a _____ order reaction the half-life ($t_{1/2}$) is independent of the initial conc. of the reactants.
29. For a first order reaction a graph of $\log [A]$ vs t has a slope equal to _____.
30. Average lifetime of a nuclei, $T_{\text{av}} = \text{_____} t_{1/2}$.

Q.2 True or False Statements :

1. Order of a reaction can be written from the balanced chemical equation.
2. For a reaction having order equal to $3/2$, the units for rate constant are sec^{-1} .
3. In a complex reaction the rate of overall reaction is governed by the slowest step.
4. $t_{1/2}$ for a first order reaction is 6.93 s, the value of rate constant for the reaction would be 10s^{-1} .
5. The ratio $t_{1/2} / t_{7/8}$ for a first order reaction is equal to $1/3$.
6. The rate of an exothermic reaction increases with the rise in temperature.
7. Molecularity of a reaction is always whole number.
8. The reactants which are thermodynamically unstable are always kinetically unstable also.
9. Order and molecularity of a single step reaction may or may not be same.
10. The activation energy of a catalysed reaction is more than the activation energy of the uncatalysed reaction.
11. For a zero order reaction $t_{3/4}$ is related to $t_{1/2}$ as $t_{3/4} = 1.5 t_{1/2}$
12. A nuclide having one proton and one neutron is represented as ${}^1_1\text{H}$.
13. A radioactive element decays by emitting one α and two β -particles. The daughter element formed is an isotope of the parent element.
14. The daughter product formed by the emission of α -particle has mass number less by 4 units than the parent nuclide.
15. ${}^{27}_{13}\text{Al}$ is a stable isotope while ${}^{29}_{13}\text{Al}$ is expected to disintegrate by β -emission.
16. Half-life period of a radioactive substance can be changed by using some suitable catalyst.
17. Emission of a β -particle by a radioactive nuclide results in decrease in N / P ratio.
18. Positron has same mass as that of an electron.
19. ${}^{14}_9\text{N}$ and ${}^{16}_8\text{O}$ are isotones.
20. The S.I. unit of activity is Curie (Ci).

EXERCISE -II

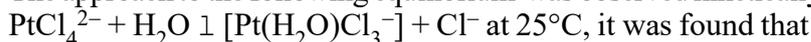
- Q.1 To investigate the decomposition of oxalic acid in concentrated H_2SO_4 at 50°C , a scientist prepared a 1/40 M solution of oxalic acid in 99.5 percent H_2SO_4 , then removed aliquots at various reaction times t , and then determined the volumes v of a potassium permanganate solution required to react with a 10 ml portion. The results are given below :

t, min	0	120	240	420	600	900	1440
v, mL	11.45	9.63	8.11	6.22	4.79	2.97	1.44

Determine the reaction order with respect to oxalic acid and evaluate the specific rate constant.

- Q.2 A solution of A is mixed with an equal volume of a solution of B containing the same number of moles, and the reaction $\text{A} + \text{B} = \text{C}$ occurs. At the end of 1h, A is 75 % reacted. How much of A will be left unreacted at the end of 2 h if the reaction is (a) first order in A and zero order in B; (b) first order in both A and B ; and (c) zero order in both A and B ?

- Q.3 The approach to the following equilibrium was observed kinetically from both directions:

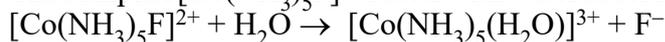


$$-\frac{\Delta}{\Delta t}[\text{PtCl}_4^{2-}] = [3.9 \times 10^{-5} \text{ sec}^{-1}][\text{PtCl}_4^{2-}] - [2.1 \times 10^{-3} \text{ L.mol}^{-1} \text{ sec}^{-1}] \times [\text{Pt}(\text{H}_2\text{O})\text{Cl}_3^-][\text{Cl}^-]$$

What is the value of equilibrium constant for the complexation of the fourth Cl^- by $\text{Pt}(\text{II})$?

- Q.4 The oxidation of certain metals is found to obey the equation $\tau^2 = \alpha t + \beta$ where τ is the thickness of the oxide film at time t , α and β are constants. What is the order of this reaction?

- Q.5 The complex $[\text{Co}(\text{NH}_3)_5\text{F}]^{2+}$ reacts with water according to the equation.



The rate of the reaction = rate const. \times [complex]^a \times $[\text{H}^+]^b$. The reaction is acid catalysed i.e. $[\text{H}^+]$ does not change during the reaction. Thus rate = $k'[\text{Complex}]^a$ where $k' = k[\text{H}^+]^b$, calculate 'a' and 'b' given the following data at 25°C .

[Complex]M	$[\text{H}^+]\text{M}$	$T_{1/2}\text{hr}$	$T_{3/4}\text{hr}$
0.1	0.01	1	2
0.2	0.02	0.5	1

- Q.6 The reaction $\text{CH}_3\text{--CH}_2\text{--NO}_2 + \text{OH}^- \longrightarrow \text{CH}_3\text{--CH--NO}_2 + \text{H}_2\text{O}$ obeys the rate law for pseudo first order kinetics in the presence of a large excess of hydroxide ion. If 1% of nitro ethane undergoes reaction in half a minute when the reactant concentration is 0.002 M, What is the pseudo first order rate constant?

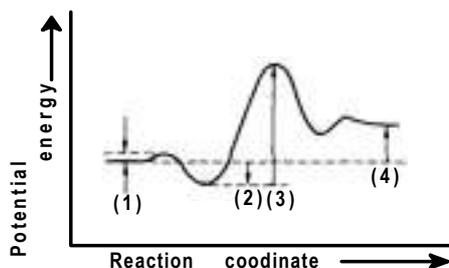
- Q.7 A flask containing a solution a solution of N_2O_5 in CCl_4 was placed in a thermostat at 40°C . The N_2O_5 began to decompose by a first-order reaction, forming NO_2 and N_2O_4 , which remained in the solution, and oxygen, which defined pressure. The measurements were started ($t = 0$) when 10.75ml gas had collected. At $t = 2400 \text{ sec.}$, 29.65ml was measured. After a very long time, ($t = \infty$)45.50ml was measured. Find the (a) rate constant, (b) half-life time for reaction at 40°C in CCl_4 solution. (c) What volume of gas should have collected after 4800 sec?

- Q.8 At room temperature (20°C) orange juice gets spoilt in about 64 hours. In a refrigerator at 3°C juice can be stored three times as long before it gets spoilt. Estimate (a) the activation energy of the reaction that causes the spoiling of juice. (b) How long should it take for juice to get spoilt at 40°C ?

- Q.9 A first order reaction, $\text{A} \rightarrow \text{B}$, requires activation energy of 70 kJ mol^{-1} . When a 20% solution of A was kept at 25°C for 20 minutes, 25% decomposition took place. What will be the percent decomposition in the same time in a 30% solution maintained at 40°C ? Assume that activation energy remains constant in this range of temperature.

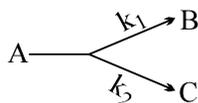
- Q.10 Two reactions (i) $\text{A} \rightarrow \text{products}$ (ii) $\text{B} \rightarrow \text{products}$, follow first order kinetics. The rate of the reaction (i) is doubled when the temperature is raised from 300 K to 310K. The half life for this reaction at 310K is 30 minutes. At the same temperature B decomposes twice as fast as A. If the energy of activation for the reaction (ii) is half that of reaction (i), calculate the rate constant of the reaction (ii) at 300K.

Q.11 Choose the correct set of identifications.



- | | | | | |
|-----|--|--|--|--|
| | (1) | (2) | (3) | (4) |
| (A) | ΔE for
$E + S \rightarrow ES$ | E_a for
$ES \rightarrow EP$ | $\Delta E_{\text{overall}}$
for $S \rightarrow P$ | E_a for
$EP \rightarrow E + P$ |
| (B) | E_a for
$E + S \rightarrow ES$ | ΔE for
$E + S \rightarrow ES$ | E_a for
$ES \rightarrow EP$ | $\Delta E_{\text{overall}}$
for $S \rightarrow P$ |
| (C) | E_a for
$ES \rightarrow EP$ | E_a for
$EP \rightarrow E + P$ | $\Delta E_{\text{overall}}$
for $S \rightarrow P$ | ΔE for
$EP \rightarrow E + P$ |
| (D) | E_a for
$E + S \rightarrow ES$ | E_a for
$ES \rightarrow EP$ | E_a for
$EP \rightarrow E + P$ | $\Delta E_{\text{overall}}$
for $S \rightarrow P$ |
| (E) | ΔE for
$E + S \rightarrow ES$ | $\Delta E_{\text{overall}}$
for $S \rightarrow P$ | ΔE for
$EP \rightarrow E + P$ | E_a for
$EP \rightarrow E + P$ |

Q.12 A certain organic compound A decomposes by two parallel first order mechanism

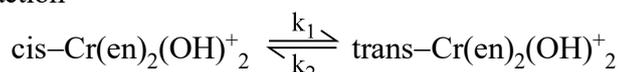


$$\text{If } k_1 : k_2 = 1 : 9 \text{ and } k_1 = 1.3 \times 10^{-5} \text{ s}^{-1}.$$

Calculate the concentration ratio of C to A, if an experiment is started with only A and allowed to run for one hour.

Q.13 Decomposition of H_2O_2 is a first order reaction. A solution of H_2O_2 labelled as 20 volumes was left open. Due to this, some H_2O_2 decomposed. To determine the new volume strength after 6 hours, 10 mL of this solution was diluted to 100 mL. 10 mL of this diluted solution was titrated against 25 mL of 0.025 M $KMnO_4$ solution under acidic conditions. Calculate the rate constant for decomposition of H_2O_2 .

Q.14 The reaction



is first order in both directions. At $25^\circ C$ the equilibrium constant is 0.16 and the rate constant k_1 is $3.3 \times 10^{-4} \text{ s}^{-1}$. In an experiment starting with the pure *cis* form, how long would it take for half the equilibrium amount of the *trans* isomer to be formed?

Q.15 A metal slowly forms an oxide film which completely protects the metal when the film thickness is 3.956 thousandths of an inch. If the film thickness is 1.281 thou. in 6 weeks, how much longer will it be before it is 2.481 thou.? The rate of film formation follows first order kinetics.

Q.16 An optically active compound A upon acid catalysed hydrolysis yield two optically active compound B and C by pseudo first order kinetics. The observed rotation of the mixture after 20 min was 5° while after completion of the reaction it was -20° . If optical rotation per mole of A, B & C are 60° , 40° & -80° . Calculate half life and average life of the reaction.

Q.17 A bacterial preparation was inactivated in a chemical bath. The inactivation process was found to be first order in bacterial concentration having rate constant $1.7 \times 10^{-2} \text{ sec}^{-1}$. Meanwhile the multiplication of bacteria ($1 \text{ bacterium} \rightarrow 2 \text{ bacteria}$) which also follows first order kinetics with rate constant $1.5 \times 10^{-3} \text{ sec}^{-1}$ also continued. Calculate the number of bacteria left after 2 minutes if the initial number of bacteria is 10^3 .

Q.18 The formation in water of *d*-potassium chromo-oxalate from its *l*-form is reversible reaction which is first order in both directions, the racemate being the equilibrium product. A polarimeter experiment at $22^\circ C$ showed that, after 506 sec, 12 mole % of the *l*-isomer was converted to the *d*-form. Find the rate constant for the forward and the reverse reactions.

Q.19 For a reversible first-order reaction $A \xrightleftharpoons[k_2]{k_1} B$

$k_1 = 10^{-2} \text{ s}^{-1}$ and $[B]_{\text{eq}}/[A]_{\text{eq}} = 4$. If $[A]_0 = 0.01 \text{ mole L}^{-1}$ and $[B]_0 = 0$, what will be the concentration of B after 30 s ?

Q.20 For the reaction $A \xrightleftharpoons[k_{-1}]{k_1} P$. Following data is produced:

Time / Hr.	0	1	2	3	4	∞	
% A	100	72.5	56.8	45.6	39.5	30	Find k_1 , k_{-1} and K_{eq} .

Q.21 For the system $A_{(g)} \rightleftharpoons B_{(g)}$, ΔH for the forward reaction is -33 kJ/mol (Note : $\Delta H = \Delta E$ in this case).

Show that equilibrium constant $K = \frac{[B]}{[A]} = 5.572 \times 10^5$ at 300 K. If the activation energies E_f & E_b are in the ratio 20 : 31, calculate E_f and E_b at this temperature. Assume that the pre-exponential factor is the same for the forward and backward reactions.

Q.22 The conversion of A into B is an autocatalytic reaction $A \rightarrow B$ where B catalyzes the reaction. The rate equation is $-dx/dt = Kxy$ where x and y are concentrations of A and B at time t. Integrate this

equation for initial concentrations x_0 and y_0 for A and B. Show that : $kt = \frac{2.303}{x_0 + y_0} \log \frac{x_0 y}{xy_0}$.

Q.23 A vessel contains dimethyl ether at a pressure of 0.4 atm. Dimethyl ether decomposes as $\text{CH}_3\text{OCH}_3(\text{g}) \rightarrow \text{CH}_4(\text{g}) + \text{CO}(\text{g}) + \text{H}_2(\text{g})$. The rate constant of decomposition is $4.78 \times 10^{-3} \text{ min}^{-1}$. Calculate the ratio of initial rate of diffusion to rate of diffusion after 4.5 hours of initiation of decomposition. Assume the composition of gas present and composition of gas diffusing to be same.

Q.24(a) The reaction A proceeds in parallel channels $A \begin{matrix} \nearrow B \\ \searrow C \end{matrix}$. Although the $A \rightarrow C$ branch is thermodynamically more favorable than the branch $A \rightarrow B$, the product B may dominate in quantity over C. Why may this be so?

(b) In the above problem, suppose the half life values for the two branches are 60 minutes and 90 minutes, what is the overall half-life value?

Q.25 For the two parallel reactions $A \xrightarrow{k_1} B$ and $A \xrightarrow{k_2} C$, show that the activation energy E' for the disappearance of A is given in terms of activation energies E_1 and E_2 for the two paths by

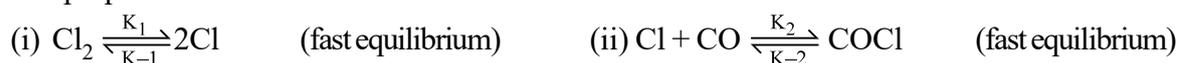
$$E' = \frac{k_1 E_1 + k_2 E_2}{k_1 + k_2}$$

Q.26 For the mechanism $A + B \xrightleftharpoons[k_2]{k_1} C \xrightarrow{k_3} D$

(a) Derive the rate law using the steady-state approximation to eliminate the concentration of C.

(b) Assuming that $k_3 \ll k_2$, express the pre-exponential factor A and E_a for the apparent second-order rate constant in terms of A_1, A_2 and A_3 and E_{a1}, E_{a2} and E_{a3} for the three steps.

Q.27 The reaction of formation of phosgene from CO and Cl_2 is $\text{CO} + \text{Cl}_2 \rightarrow \text{COCl}_2$
The proposed mechanism is

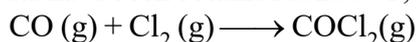


(iii) $\text{COCl} + \text{Cl}_2 \xrightarrow{k_3} \text{COCl}_2 + \text{Cl}$ (slow)

Show that the above mechanism leads to the following rate law $\frac{d[\text{COCl}_2]}{dt} = K[\text{CO}][\text{Cl}_2]^{3/2}$.

Where $K = k_3 \cdot \frac{k_2}{k_{-2}} \left(\frac{k_1}{k_{-1}} \right)^{1/2}$.

Q.28 The following kinetic data have been obtained at 250 °C, for the reaction



SET – 1

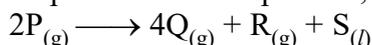
Time(sec)	Pressure of COCl ₂ (Pa)
0	0
2072	200
4140	300
10280	375
infinity	400

SET – 2

Time(sec)	Pressure of COCl ₂ (Pa)
0	0
2070	300
4140	375
infinity	400

- (i) Determine the order of reaction with respect to CO and Cl₂.
 (ii) Calculate the rate constant, when pressure in pascal and time in seconds.

Q.29 The decomposition of a compound P, at temperature T according to the equation



is the first order reaction. After 30 minutes from the start of decomposition in a closed vessel, the total pressure developed is found to be 317 mm Hg and after a long period of time the total pressure observed to be 617 mm Hg. Calculate the total pressure of the vessel after 75 minutes, if volume of liquid S is supposed to be negligible. Also calculate the time fraction $t_{7/8}$.

Given : Vapour pressure of S (l) at temperature T = 32.5 mm Hg.

Q.30 A certain reactant Bⁿ⁺ is getting converted to B⁽ⁿ⁺⁴⁾⁺ in solution. The rate constant of this reaction is measured by titrating a volume of the solution with a reducing reagent which only reacts with Bⁿ⁺ and B⁽ⁿ⁺⁴⁾⁺. In this process, it converts Bⁿ⁺ to B⁽ⁿ⁻²⁾⁺ and B⁽ⁿ⁺⁴⁾⁺ to B⁽ⁿ⁻¹⁾⁺. At $t=0$, the volume of the reagent consumed is 25 ml and at $t=10$ min, the volume used up is 32 ml. Calculate the rate constant of the conversion of Bⁿ⁺ to B⁽ⁿ⁺⁴⁾⁺ assuming it to be a first order reaction.

Q.31 The catalytic decomposition of formic acid may take place in two ways :



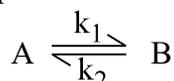
The rate constant and activation energy for reaction (a) are $2.79 \times 10^{-3} \text{ min}^{-1}$ at 236°C and 12.0 kcal mole⁻¹ respectively and for reaction (b) are $1.52 \times 10^{-4} \text{ min}^{-1}$ at 237°C and 24.5 kcal mole⁻¹ respectively. Find the temperature which will give a product made up of equimolar quantities of water vapour, carbon monoxide, hydrogen and carbon dioxide.

Q.32 The rate constant for the forward reaction $\text{A} \rightarrow \text{Product}$ is given by

$$\log k (\text{sec}^{-1}) = 14.34 - \frac{1.25 \times 10^4 \text{ K}}{T}$$

and the rate constant for the reverse reaction is $1.2 \times 10^{-4} \text{ sec}^{-1}$ at 50°C. Calculate the value of maximum rate constant possible for the backward reaction. Given : Enthalpy of the reaction = - 478 kJ/mol.

Q.33(a) The equilibrium between two isomers 'A' and 'B' can be represented as follow .



Where k_1 and k_2 are first order rate constants for forward and reverse reactions respectively. Starting with a non equilibrium mixture of conc. $[\text{A}]_0 = a$ and $[\text{B}]_0 = b$, it was found that 'x' mole of 'A' has reacted after time 't'. Give an expression for rate, $\frac{dx}{dt}$, and hence show that integrated rate expression

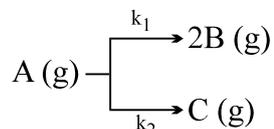
$$\text{is } \ln \left(\frac{P}{P-x} \right) = (k_1 + k_2) t \text{ where } P = \left(\frac{k_1 a - k_2 b}{k_1 + k_2} \right)$$

- (b) After 69.3 minute $x = \frac{P}{2}$. Calculate k_1 and k_2 if equilibrium constant $K = 4$.
 (Given : $\log 2 = 0.3010$)

- Q.34 The gaseous reaction : $n_1A(g) \rightarrow n_2B(g)$ is first order with respect to A. It is studied at a constant pressure, with a_0 as the initial amount of A. Show that the volume of system at the concentration of A at time 't' are given by the expressions

$$V = V_0 \left[\left(\frac{n_2}{n_1} \right) - \left(\frac{n_2}{n_1} - 1 \right) \exp(-n_1kt) \right] ; [A]_t = [A]_0 \left[\frac{\exp(-n_1kt)}{\left(\frac{n_2}{n_1} \right) - \left\{ \left(\frac{n_2}{n_1} \right) - 1 \right\} \exp(-n_1kt)} \right]$$

- Q.35 For the following first order gaseous reaction



The initial pressure in a container of capacity V litres is 1 atm. Pressure at time $t = 10$ sec is 1.4 atm and after infinite time it becomes 1.5 atmosphere. Find the rate constant k_1 and k_2 for the appropriate reactions.

RADIOACTIVITY

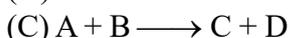
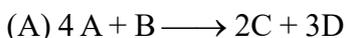
- Q.36 In a nature decay chain series starts with ${}_{90}\text{Th}^{232}$ and finally terminates at ${}_{82}\text{Pb}^{208}$. A thorium ore sample was found to contain 8×10^{-5} ml of helium at STP and 5×10^{-7} gm of Th^{232} . Find the age of ore sample assuming that source of He to be only due to decay of Th^{232} . Also assume complete retention of helium within the ore. (Half-life of $\text{Th}^{232} = 1.39 \times 10^{10}$ Y)
- Q.37 A 0.20 mL sample of a solution containing 1.0×10^{-7} Ci of ${}^3_1\text{H}$ is injected into the blood stream of a laboratory animal. After sufficient time for circulatory equilibrium to be established, 0.10 mL blood is found to have an activity of 20 dis/min. Calculate the blood volume of the animal.
- Q.38 A sample of ${}^{131}_{53}\text{I}$, as iodine ion, was administered to a patient in a carrier consisting of 0.10 mg of stable iodide ion. After 4.00 days, 67.7% of the initial radioactivity was detected in the thyroid gland of the patient. What mass of the stable iodide ion had migrated to the thyroid gland? ($t_{1/2} = 8$ days.)
- Q.39 Potassium having atomic mass=39.1u contains 93.10 atom % ${}^{39}\text{K}$, having atomic mass 38.96371 u; 0.0118 atom % ${}^{40}\text{K}$, which has mass of 40.0 u and is radioactive with $t_{1/2} = 1.3 \times 10^9$ y and 6.88 atom % ${}^{41}\text{K}$ having a mass of 40.96184 u. Calculate the specific activity of naturally occurring potassium.
- Q.40 A mixture of ${}^{239}\text{Pu}$ and ${}^{240}\text{Pu}$ has a specific activity of 6×10^9 dis/s/g. The half lives of the isotopes are 2.44×10^4 y and 6.08×10^3 y respectively. calculate the isotopic composition of this sample.
- Q.41 ${}_{92}\text{U}^{238}$ by successive radioactive decays changes to ${}_{82}\text{Pb}^{206}$. A sample of uranium ore was analyzed and found to contain 1.0g of U^{238} and 0.1g of Pb^{206} . Assuming that all the Pb^{206} had accumulated due to decay of U^{238} , find out the age of the ore. (Half life of $\text{U}^{238} = 4.5 \times 10^9$ years).
- Q.42 Fallout from nuclear explosions contains ${}^{131}\text{I}$ and ${}^{90}\text{Sr}$. Calculate the time required for the activity of each of these isotopes to fall to 1.0% of its initial value. Radioiodine and radiostrontium tend to concentrate in the thyroid and the bones, respectively, of mammals which ingest them. Which isotope is likely to produce the more serious long-term effects? Half-life of ${}^{131}\text{I} = 8$ days, ${}^{90}\text{Sr} = 19.9$ yrs.
- Q.43 ${}^{84}\text{Po}^{218}$ ($t_{1/2} = 3.05$ min) decay to ${}^{82}\text{Pb}^{214}$ ($t_{1/2} = 2.68$ min) by α -emission, while Pb^{214} is a β -emitter. In an experiment starting with 1 gm atom of Pure Po^{218} , how much time would be required for the number of nuclei of ${}^{82}\text{Pb}^{214}$ to reach maximum.
- Q.44 A sample pitch blende is found to contain 50% Uranium and 2.425% Lead. Of this Lead only 93% was Pb^{206} isotope, if the disintegration constant is $1.52 \times 10^{-10} \text{ yr}^{-1}$. How old could be the pitch blende deposit.
- Q.45 A sample of Uraninite, a Uranium containing mineral was found on analysis to contain 0.214 gm of Pb^{206} for every gram of Uranium. Assuming that the lead all resulted from the radioactive disintegration of the Uranium since the geological formation of the Uraninite and all isotopes of Uranium other than ${}^{238}\text{U}$ can be neglected. Estimate the day when the mineral was formed in the Earth's crust. [$t_{1/2}$ of ${}^{238}\text{U} = 4.5 \times 10^9$ years]

EXERCISE -III

Q.1 The rate of a reaction is expressed in different ways as follows :

$$+\frac{1}{2} \frac{d[C]}{dt} = -\frac{1}{3} \frac{d[D]}{dt} = +\frac{1}{4} \frac{d[A]}{dt} = -\frac{d[B]}{dt}$$

The reaction is:



Q.2 Units of rate constant for first and zero order reactions in terms of molarity M unit are respectively

- (A) sec^{-1} , $M \text{ sec}^{-1}$ (B) sec^{-1} , M (C) $M \text{ sec}^{-1}$, sec^{-1} (D) M, sec^{-1}

Q.3 The rate constant for the forward reaction $A(g) \rightleftharpoons 2B(g)$ is $1.5 \times 10^{-3} \text{ s}^{-1}$ at 100 K. If 10^{-5} moles of A and 100 moles of B are present in a 10 litre vessel at equilibrium then rate constant for the backward reaction at this temperature is

(A) $1.50 \times 10^4 \text{ L mol}^{-1} \text{ s}^{-1}$

(B) $1.5 \times 10^{11} \text{ L mol}^{-1} \text{ s}^{-1}$

(C) $1.5 \times 10^{10} \text{ L mol}^{-1} \text{ s}^{-1}$

(D) 1.5×10^{-11}

Q.4 Reaction $A + B \longrightarrow C + D$ follow's following rate law : $\text{rate} = k = [A]^{\frac{1}{2}} [B]^{\frac{1}{2}}$. Starting with initial conc. of one mole of A and B each, what is the time taken for amount of A of become 0.25 mole. Given $k = 2.31 \times 10^{-3} \text{ sec}^{-1}$.

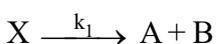
(A) 300 sec.

(B) 600 sec.

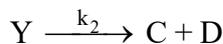
(C) 900 sec.

(D) none of these

Q.5 Consider the following first order competing reactions:



and



if 50% of the reaction of X was completed when 96% of the reaction of Y was completed, the ratio of their rate constants (k_2/k_1) is

(A) 4.06

(B) 0.215

(C) 1.1

(D) 4.65

Q.6 A first order reaction is 50% completed in 20 minutes at 27°C and in 5 min at 47°C . The energy of activation of the reaction is

(A) 43.85 kJ/mol

(B) 55.14 kJ/mol

(C) 11.97 kJ/mol

(D) 6.65 kJ/mol

Q.7 For the first order reaction $A \longrightarrow B + C$, carried out at 27°C if $3.8 \times 10^{-16}\%$ of the reactant molecules exists in the activated state, the E_a (activation energy) of the reaction is

(A) 12 kJ/mole

(B) 831.4 kJ/mole

(C) 100 kJ/mole

(D) 88.57 kJ/mole

Q.8 The reactions of higher order are rare because

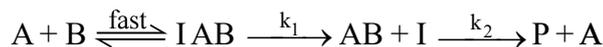
(A) many body collisions involve very high activation energy

(B) many body collisions have a very low probability

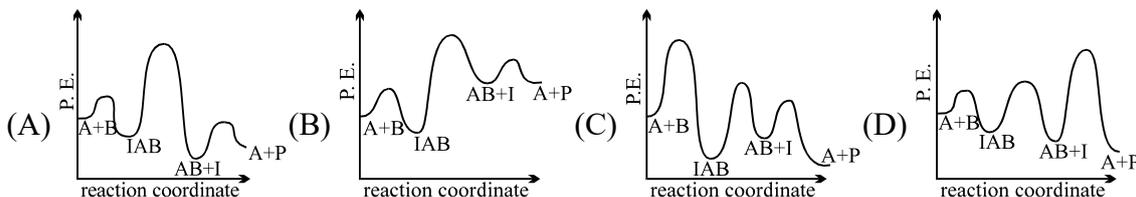
(C) many body collisions are not energetically favoured.

(D) many body collisions can take place only in the gaseous phase.

Q.9 The following mechanism has been proposed for the exothermic catalyzed complex reaction.



If k_1 is much smaller than k_2 . The most suitable qualitative plot of potential energy (P.E.) versus reaction coordinate for the above reaction.



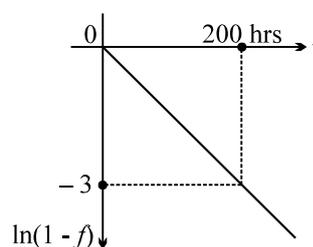
Question No. 10 to 11 (2 questions)

Oxidation of metals is generally a slow electrochemical reaction involving many steps. These steps involve electron transfer reactions. A particular type of oxidation involve overall first order kinetics with respect to fraction of unoxidised metal $(1-f)$ surface thickness relative to maximum thickness (T) of oxidised surface, when metal surface is exposed to air for considerable period of time

Rate law : $\frac{df}{dt} = k(1-f)$, where $f = x/T$,

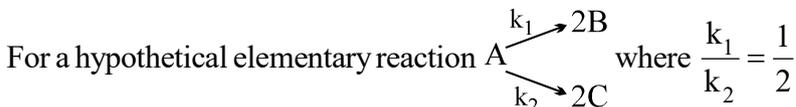
x = thickness of oxide film at time 't'
& T = thickness of oxide film at $t = \infty$

A graph of $\ln(1-f)$ vs t is shown in the adjacent figure.



- Q.10 The time taken for thickness to grow 50% of 'T' is
(A) 23.1 hrs (B) 46.2 hrs (C) 100 hrs (D) 92.4 hrs
- Q.11 The exponential variation of 'f' with t(hrs) is given by
(A) $[1 - e^{-3t/200}]$ (B) $e^{-3t/200} - 1$ (C) $e^{-3t/200}$ (D) $e^{3t/200}$

Question No. 12 to 13 (2 questions)



Initially only 2 moles of A are present.

- Q.12 The total number of moles of A, B & C at the end of 50% reaction are
(A) 2 (B) 3 (C) 5 (D) None
- Q.13 Number of moles of B are
(A) 2 (B) 1 (C) 0.666 (D) 0.333
- Q.14 Two radioactive nuclides A and B have half lives of 50 min and 10 min respectively. A fresh sample contains the nuclides of B to be eight time that of A. How much time should elapse so that the number of nuclides of A becomes double of B
(A) 30 (B) 40 (C) 50 (D) None
- Q.15 Give the correct order of initials **T** (true) or **F** (false) for following statements.
(i) On bombarding ${}_7N^{14}$ Nuclei with α -particle, the nuclei of the product formed after release of proton would be ${}_8O^{17}$.
(ii) ${}_{89}Ac^{228}$ and ${}_{90}Th^{229}$ belong respectively to Actinium and Neptunium series.
(iii) Nuclide and it's decay product after α -emission are called isodiaphers.
(iv) Half life of radium is 1580 years. Its average life will be 1097.22 years.
(A) TFTF (B) TTTF (C) FFTT (D) TFFF

EXERCISE-IV

OBJECTIVE PROBLEM

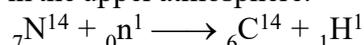
- Q.1 For a first order reaction
(A) the degree of dissociation is equal to $(1 - e^{-kt})$
(B) a plot of reciprocal concentration of the reactant vs time gives a straight line.
(C) the time taken for completeion of 75% of reaction is thrice the $t_{1/2}$ of the reaction
(D) the pre-exponential factor in the Arrhenius equation has the dimension of time, T^{-1} . [JEE 1998]
- Q.2 The rate law for the reaction
 $\text{RCl} + \text{NaOH (aq)} \longrightarrow \text{ROH} + \text{NaCl}$ is given by $\text{Rate} = k[\text{RCl}]$. The rate of the reaction will be
(A) Doubled on doubling the concentration of sodium hydroxide
(B) Halved on reducing the concentration of alkyl halide to one half
(C) Decreased on increasing the temperature of reaction
(D) Unaffected by increasing the temperature of the reaction. [JEE 1998]
- Q.3 Which of the following statement(s) is (are) correct
(A) A plot of $\log K_p$ versus $1/T$ is linear
(B) A plot of $\log [X]$ versus time is linear for a first order reaction, $X \longrightarrow P$
(C) A plot of $\log P$ versus $1/T$ is linear at constant volume.
(D) A plot of P versus $1/V$ is linear at constant temperature. [JEE 1999]
- Q.4 The rate constnat for the reaction [JEE SCR 2000]
 $2\text{N}_2\text{O}_5 \longrightarrow 4\text{NO}_2 + \text{O}_2$
is $3.0 \times 10^{-5} \text{ sec}^{-1}$. if the rate is $2.4 \times 10^{-5} \text{ mol litre}^{-1} \text{ sec}^{-1}$, then the concentration of N_2O_5 (in mol litre^{-1}) is
(A) 1.4 (B) 1.2 (C) 0.004 (D) 0.8
- Q.5 If I is the intensity of absorbed light and C is the concentration of AB for the photochemical proces
 $\text{AB} + h\nu \longrightarrow \text{AB}^*$, the rate of formation of AB^* is directly proportional to [JEE SCR 2001]
(A) C (B) I (C) I^2 (D) CI
- Q.6 Consider the chemical reaction, $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \longrightarrow 2\text{NH}_3(\text{g})$. The rate of this reaction can be expressed in term of time derivative of concentration of $\text{N}_2(\text{g})$, $\text{H}_2(\text{g})$ or $\text{NH}_3(\text{g})$. Identify the correct relationship amongst the rate expressions. [JEE SCR 2002]
(A) $\text{Rate} = -d[\text{N}_2]/dt = -1/3 d[\text{H}_2]/dt = 1/2d[\text{NH}_3]/dt$
(B) $\text{Rate} = -d[\text{N}_2]/dt = -3 d[\text{H}_2]/dt = 2d[\text{NH}_3]/dt$
(C) $\text{Rate} = d[\text{N}_2]/dt = 1/3 d[\text{H}_2]/dt = 1/2d[\text{NH}_3]/dt$
(D) $\text{Rate} = -d[\text{N}_2]/dt = -d[\text{H}_2]/dt = d[\text{NH}_3]/dt$
- Q.7 In a first order reaction the concentration of reactant decreases from 800 mol/dm^3 to 50 mol/dm^3 in $2 \times 10^4 \text{ sec}$. The rate constant of reaction in sec^{-1} is [JEE SCR 2003]
(A) 2×10^4 (B) 3.45×10^{-5} (C) 1.3486×10^{-4} (D) 2×10^{-4}
- Q.8 The reaction, $X \longrightarrow \text{Product}$ follows first order kinetics. In 40 minutes the concentration of X changes from 0.1 M to 0.025 M . Then the rate of reaction when concentration of X is 0.01 M
(A) $1.73 \times 10^{-4} \text{ M min}^{-1}$ (B) $3.47 \times 10^{-5} \text{ M min}^{-1}$
(C) $3.47 \times 10^{-4} \text{ M min}^{-1}$ (D) $1.73 \times 10^{-5} \text{ M min}^{-1}$ [JEE SCR 2004]
- Q.9 Which of the following statement is incorrect about order of reaction? [JEE 2005]
(A) Order of reaction is determined experimentally
(B) It is the sum of power of concentration terms in the rate law expression
(C) It does not necessarily depend on stoichiometric coefficients
(D) Order of the reaction can not have fractional value.

RADIOACTIVITY

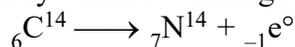
- Q.10 Loss of a β^- particle is equivalent to [JEE 1998]
(A) Increase of one proton only (B) Decrease of one neutron only
(C) Both (A) and (B) (D) None of these.
- Q.11 Decrease in atomic number is observed during [JEE 1998]
(A) α -emission (B) β^- -emission (C) Positron emission (D) Electron capture.
- Q.12 The number of neutrons accompanying the formation of ${}_{54}\text{X}^{139}$ and ${}_{38}\text{Sr}^{94}$ from the absorption of slow neutron by ${}_{92}\text{U}^{235}$ followed by nuclear fission is [JEE 1999]
(A) 0 (B) 2 (C) 1 (D) 3

Question No. 13 to 15 (3 questions)

Carbon 14 is used to determine the age of organic material. The procedure is based on the formation of ${}^{14}\text{C}$ by neutron capture in the upper atmosphere.



${}^{14}\text{C}$ is absorbed by living organisms during photosynthesis. The ${}^{14}\text{C}$ content is constant in living organism once the plant or animal dies, the uptake of carbon dioxide by it ceases and the level of ${}^{14}\text{C}$ in the dead being falls due to the decay which C^{14} undergoes.



The half life period of ${}^{14}\text{C}$ is 5770 years. The decay constant (λ) can be calculated by using the following

formula $\lambda = \frac{0.693}{t_{1/2}}$

The comparison of the β^- activity of the dead matter with that of carbon still in circulation enables measurement of the period of the isolation of the material from the living cycle. The method however, ceases to be accurate over periods longer than 30,000 years. The proportion of ${}^{14}\text{C}$ to ${}^{12}\text{C}$ in living matter is $1 : 10^{12}$ [JEE 2006]

- Q.13 Which of the following option is correct?
(A) In living organisms, circulation of ${}^{14}\text{C}$ from atmosphere is high so the carbon content is constant in organism
(B) Carbon dating can be used to find out the age of earth crust and rocks
(C) Radioactive absorption due to cosmic radiation is equal to the rate of radioactive decay, hence the carbon content remains constant in living organism
(D) Carbon dating cannot be used to determine concentration of ${}^{14}\text{C}$ in dead beings.
- Q.14 What should be the age of fossil for meaningful determination of its age?
(A) 6 years (B) 6000 years
(C) 60000 years (D) it can be used to calculate any age
- Q.15 A nuclear explosion has taken place leading to increase in concentration of C^{14} in nearby areas. C^{14} concentration is C_1 in nearby areas and C_2 in areas far away. If the age of the fossil is determined to be t_1 and t_2 at the places respectively, then
- (A) The age of the fossil will increase at the place where explosion has taken place and $t_1 - t_2 = \frac{1}{\lambda} \ln \frac{C_1}{C_2}$
(B) The age of the fossil will decrease at the place where explosion has taken place and $t_1 - t_2 = \frac{1}{\lambda} \ln \frac{C_1}{C_2}$
(C) The age of fossil will be determined to be the same
(D) $\frac{t_1}{t_2} = \frac{C_1}{C_2}$

SUBJECTIVE PROBLEM

- Q.1(a) In the Arrhenius equation $k = A \exp(-E/RT)$, A may be termed as the rate constant at _____ .
[JEE 1997]
- (b) The rate constant for the first order decomposition of a certain reaction is described by the equation
- $$\ln k (\text{s}^{-1}) = 14.34 - \frac{1.25 \times 10^4 \text{ K}}{T}$$
- (i) What is the energy of activation for this reaction?
(ii) The rate constant at 500 K.
(iii) At what temperature will its half life period be 256 minutes? [JEE 1997]
- (c) The time required for 10% completion of a first order reaction at 298 K is equal to that required for its 25% completion at 308 K. If the pre exponential factor for the reaction is $3.56 \times 10^9 \text{ s}^{-1}$, calculate the rate constant at 318 K and also the energy of activation. [JEE 1997]
- (d) The rate constant for an isomerisation reaction $A \rightarrow B$ is $4.5 \times 10^{-3} \text{ min}^{-1}$. If the initial concentration of A is 1 M. Calculate the rate of the reaction after 1 h. [JEE 1999]
- Q.2 A hydrogenation reaction is carried out at 500 K. If the same reaction is carried out in the presence of a catalyst at the same rate, the temperature required is 400 K. Calculate the activation energy of the reaction if the catalyst lowers the activation barrier by 20 kJ mol^{-1} . [JEE 2000]
- Q.3 The rate of a first order reaction is $0.04 \text{ mole litre}^{-1} \text{ s}^{-1}$ at 10 minutes and $0.03 \text{ mol litre}^{-1} \text{ s}^{-1}$ at 20 minutes after initiation. Find the half life of the reaction. [JEE 2001]

Q.4 $2X(g) \longrightarrow 3Y(g) + 2Z(g)$

Time (in Min)	0	100	200
Partial pressure of X (in mm of Hg)	800	400	200

Assuming ideal gas condition. Calculate

- (a) Order of reaction (b) Rate constant
(c) Time taken for 75% completion of reaction (d) Total pressure when $P_x = 700 \text{ mm}$. [JEE 2005]

RADIOACTIVITY

- Q.5 ^{64}Cu (half-life = 12.8 hr) decays by β^- emission (38%), β^+ emission (19%) and electron capture (43%). Write the decay product and calculate partial half-lives for each of the decay processes. [JEE'2002]
- Q.6 Fill in the blanks
- (a) $^{235}_{92}\text{U} + {}^1_0\text{n} \longrightarrow {}^{137}_{52}\text{A} + {}^{97}_{40}\text{B} + \text{_____}$.
- (b) $^{82}_{34}\text{Se} \longrightarrow 2 {}^0_{-1}\text{e} + \text{_____}$. [JEE 2005]

ANSWER KEY

EXERCISE-I

RATE OF REACTION AND STOICHIOMETRIC COEFFICIENT

- Q.1 (a) $1 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$, (b) $3 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$
Q.2 (a) $0.019 \text{ mol L}^{-1} \text{ s}^{-1}$, (b) $0.037 \text{ mol L}^{-1} \text{ s}^{-1}$
Q.3 $2k_1 = k_2 = 4k_3$ Q.4 (i) $\frac{dx}{dt} = k[A][B]^2$, (ii) rate increases by 8 times
Q.5 rate increase by 27 times
Q.6 (i) $r = \frac{1}{4} \frac{d[\text{NO}]}{dt} = 9 \times 10^{-4} \text{ mol litre}^{-1} \text{ sec}^{-1}$, (ii) $36 \times 10^{-4} \text{ mol litre}^{-1} \text{ sec}^{-1}$, (iii) $54 \times 10^{-4} \text{ mol litre}^{-1} \text{ sec}^{-1}$
Q.7 (i) $7.2 \text{ mol litre}^{-1} \text{ min}^{-1}$, (ii) $7.2 \text{ mol litre}^{-1} \text{ min}^{-1}$ Q.8 1/6

ZERO ORDER

- Q.9 (i) 7.2 M, (ii) Think Q.10 $K = 0.01 \text{ M min}^{-1}$
Q.11 0.75 M Q.12 $6 \times 10^{-9} \text{ sec}$ Q.13 1.2 hr

FIRST ORDER

- Q.14 (i) 36 min., (ii) 108 min. Q.15 (i) 0.0223 min^{-1} , (ii) 62.17 min Q.17 924.362 sec
Q.18 expiry time = 41 months Q.19 $3.3 \times 10^{-4} \text{ s}^{-1}$ Q.20 $k = \frac{2.303}{t} \log \frac{1}{a}$ Q.21 11.2%

ORDER OF REACTION & RATE LAW

- Q.22 (a) Third order, (b) $r = k[\text{NO}]^2[\text{H}_2]$, (c) $8.85 \times 10^{-3} \text{ M sec}^{-1}$.
Q.23 (a) order w.r.t NO = 2 and w.r.t Cl₂ = 1, (b) $r = K[\text{NO}]^2[\text{Cl}_2]$, (c) $K = 8 \text{ L}^2 \text{ mol}^{-2} \text{ s}^{-1}$,
(d) rate = $0.256 \text{ mole L}^{-1} \text{ s}^{-1}$
Q.24 (i) first order (ii) $k = 1.308 \times 10^{-2} \text{ min}^{-1}$ (iii) 73%
Q.25 (i) rate = $[A][B]$; (ii) $k = 4 \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$; (iii) rate = $2.8 \times 10^{-3} \text{ M} \cdot \text{s}^{-1}$
Q.26 (i) Zero order, (ii) $K = 5 \text{ Pa/s}$
Q.27 Zero order Q.28 (a) $n = 1$, (b) $\frac{dx}{dt} = k[\text{CH}_3\text{COCH}_3]$, (c) $8.67 \times 10^{-3} \text{ s}^{-1}$, (d) $1.56 \times 10^{-5} \text{ M s}^{-1}$

HALF LIFE

- Q.29 166.6 min Q.30 $4.62 \times 10^5 \text{ sec}$ Q.32 (i) $t = 13.96 \text{ hrs}$, (ii) 2.2176 litre
Q.33 54 min Q.34 15 min

CONCENTRATION REPLACED BY OTHER QUANTITIES IN FIRST ORDER

INTEGRATED RATE LAW

- Q.35 $k = \frac{1}{t} \ln \frac{P_3}{2(P_3 - P_2)}$ Q.36 $k = \frac{1}{t} \ln \frac{P_3}{(P_3 - P_2)}$
Q.37 $k = \frac{1}{t} \ln \frac{V_1}{(2V_1 - V_2)}$ Q.38 $k = \frac{1}{t} \ln \frac{4V_3}{5(V_3 - V_2)}$ Q.39 $k = \frac{1}{t} \ln \frac{r_\infty}{(r_\infty - r_t)}$
Q.40 $8.12 \times 10^{-6} \text{ Ms}^{-1}$, $0.012 \text{ atm min}^{-1}$

- Q.41 (a) 90 mm, (b) 47 mm, (c) 6.49×10^{-2} per minutes, (d) 10.677 min.
 Q.42 First order Q.43 $k_1 = 2.605 \times 10^{-3} \text{ min}^{-1}$
 Q.44 (i) $r = K[(\text{CH}_3)_2\text{O}]$, $0.000428 \text{ sec}^{-1}$ Q.45 First order
 Q.46 (a) first order, (b) 13.75 minutes, (c) 0.716
 Q.47 966 min Q.48 206.9 min Q.49 11.45 days
 Q.50 0.180 atm, 47.69 sec

PARALLEL AND SEQUENTIAL REACTION

- Q.51 $\frac{1}{e^{(K_1+K_2)t}-1}$ Q.52 $\frac{[C]}{[A]} = \frac{10}{11}(e^{11x}-1)$ Q.53 72.7, 22.3 Q.54 $t=4 \text{ min}$

TEMPERATURE DEPENDENCE OF RATE (ACTIVATION ENERGY)

- Q.55 5 kJ mol^{-1} Q.56 349.1 k Q.57 $55.33 \text{ kJ mole}^{-1}$ Q.58 306 k
 Q.59 (a) $2.31 \times 10^{-12} \text{ min}^{-1}$, $6.93 \times 10^{-2} \text{ min}^{-1}$, (b) $43.85 \text{ kJ mole}^{-1}$
 Q.60 rate of reaction increases 5.81×10^8 times
 Q.61 $10.757 \text{ k cal mol}^{-1}$

MECHANISM OF REACTION

- Q.62 $r = K' [\text{NO}]^2 [\text{Br}_2]$ Q.63 $r = K [\text{NO}]^2 [\text{H}_2]$, where $K = k_2 \times K_1$
 Q.64 $k_{\text{eq}} = 1$, rate = $k_2 (\text{C}) (\text{A}_2)^{1/2}$ Q.66 (d) No, (e) mechanism (a) is incorrect

RADIOACTIVITY

- Q.67 beta emitter : ^{49}Ca , ^{30}Al , ^{94}Kr , positron emitter : ^{195}Hg , ^8B , ^{150}Ho
 Q.68 $^{114}_{49}\text{In}$, odd number of nucleons Q.69 (a) ^1_1H , (b) ^1_0n , (c) ^6_3Li , (d) $^0_{+1}\text{e}$, (e) $^0_{-1}\text{e}$, (f) p (proton)
 Q.70 d, deuteron Q.71 (a) ^1_1H (b) $^{64}_{28}\text{Ni}$ (c) $^0_{-1}\beta$ (d) ^1_0n
 Q.72 $\alpha = \frac{a-b}{4}$; $\beta = d + \frac{(a-b)}{2} - c$ Q.73 $2.16 \times 10^{12} \text{ events / min}$
 Q.74 $1.06 \times 10^{-15} \text{ kg}$ Q.75 $\lambda = 5.77 \times 10^{-4} \text{ sec}^{-1}$ Q.76 32 ml
 Q.77 6.25 % Q.78 $2.674 \times 10^5 \text{ dps}$ Q.79 33.67 years Q.80 4.65 hour

PROFICIENCY TEST

- Q.1**
- | | | | | | | | |
|-----|-----------------------|-----|----------------------------------|-----|--------------------|-----|------------------------|
| 1. | 3.7×10^{10} | 2. | β -rays | 3. | isobar | 4. | 8, 6 |
| 5. | isodiaphers | 6. | $^{30}_{14}\text{Si}$ | 7. | β -particles | 8. | isotones |
| 9. | 10 min. | 10. | threshold energy | 11. | half | 12. | equal to ΔH |
| 13. | directly proportional | 14. | $\text{mol L}^{-1}\text{s}^{-1}$ | 15. | rare | | |
| 16. | lowering | 17. | faster | 18. | slowest | 19. | increases |
| 20. | 3 | 21. | rate constant | 22. | 2 and 3 | 23. | rate = $k[\text{M}]^2$ |
| 24. | $\frac{1}{2}$ | 25. | -k | 26. | Activation energy | | |
| 27. | higher | 28. | first | 29. | $-\frac{k}{2.303}$ | 30. | 1.44 |
- Q.2**
- | | | | | | | | |
|-----|-------|-----|-------|-----|-------|-----|-------|
| 1. | False | 2. | False | 3. | True | 4. | False |
| 5. | True | 6. | True | 7. | True | 8. | False |
| 9. | False | 10. | False | 11. | True | 12. | False |
| 13. | True | 14. | True | 15. | True | 16. | False |
| 17. | True | 18. | True | 19. | False | 20. | False |

EXERCISE-II

- Q.1 First order, $k = 0.00144, 0.00144, 0.00145, 0.00145, 0.00150, 0.00140$, average 0.00145 min^{-1}
Q.2 (a) 6.25 ; (b) 14.3 ; (c) 0% Q.3 53.84 Q.4 $(d\tau/dt) = \alpha / 2\tau, -1$ order
Q.5 $a = b = 1$ Q.6 $2 \times 10^{-2} \text{ min}^{-1}$
Q.7 (a) $3.27 \cdot 10^{-4} \text{ sec}^{-1}$; (b) 2120 sec; (c) 38.27 (measured : 55.00ml)
Q.8 (a) $43.46 \text{ kJ mol}^{-1}$, (b) 20.47 hour Q.9 % decomposition = 67.21%
Q.10 $k = 0.0327 \text{ min}^{-1}$ Q.11 B Q.12 0.537 Q.13 $k = 0.022 \text{ hr}^{-1}$
Q.14 4.83 mins Q.15 15.13 week Q.16 20 min, 28.66 min
Q.17 156 Q.18 $K_f = K_b = 0.00027 \text{ sec}^{-1}$ Q.19 0.0025 m
Q.20 $k = 9.74 \times 10^{-5} \text{ sec}^{-1}, k_{-1} = 4.18 \times 10^{-5} \text{ sec}^{-1}$ Q.21 $E_f = 6 \times 10^4 \text{ J}; E_b = 9.3 \times 10^4 \text{ J}$
Q.23 0.26 : 1 Q.24 (b) $t_{1/2} = 36 \text{ min}$
Q.26 (a) $\frac{d(D)}{dt} = \frac{k_1 k_3 (A)(B)}{k_2 + k_3}$; (b) $E_a = E_{a1} + E_{a3} - E_{a2}$. $A = \frac{A_1 A_3}{A_2}$
Q.28 Set – I : $3.5 \times 10^{-4} \text{ S}^{-1}$; Set – II : $6.7 \times 10^{-4} \text{ S}^{-1}$
Q.29 $P_t = 379.55 \text{ mm Hg}, t_{7/8} = 399.96 \text{ min}$ Q.30 0.0207 min^{-1}
Q.31 $399^\circ \text{C}; R = 1.987 \text{ Kcal. mol}^{-1} \text{ K}^{-1}$ Q.33 $k_2 = 2 \times 10^{-3} \text{ sec}^{-1}, k_1 = 8 \times 10^{-3} \text{ sec}^{-1}$
Q.35 0.805

RADIOACTIVITY

- Q.36 $t = 4.89 \times 10^9$ years Q.37 $V = 1.1 \text{ L}$ Q.38 0.0958 mg
Q.39 Specific activity = $30.69 \text{ dis. g}^{-1} \text{ s}^{-1}$ Q.40 $^{239}\text{Pu} = 45.1\%, ^{240}\text{Pu} = 54.9\%$
Q.41 $t = 7.1 \times 10^8$ years Q.42 53.1 days, 132 yrs, ^{90}Sr is likely to be serious, the iodine will soon be gone
Q.43 4.125 min Q.44 3.3×10^8 years Q.45 1.4×10^9 yrs

EXERCISE-III

- Q.1 B Q.2 A Q.3 D Q.4 B Q.5 D Q.6 B Q.7 C
Q.8 B Q.9 A Q.10 B Q.11 A Q.12 B Q.13 C Q.14 C
Q.15 A

EXERCISE-IV

OBJECTIVE PROBLEM

- Q.1 A, D Q.2 B Q.3 A, B, D Q.4 D Q.5 B
Q.6 A Q.7 C Q.8 C Q.9 D

RADIOACTIVITY

- Q.10 C Q.11 C, D Q.12 D Q.13 C Q.14 B
Q.15 A

SUBJECTIVE PROBLEM

- Q.1 (a) infinite temperature ; (b) (i) $2.50 \times 10^4 \text{ cal mol}^{-1}$, (ii) $2.35 \times 10^{-5} \text{ sec}^{-1}$, (iii) 513 ;
(c) $K_{318} = 9.2 \times 10^{-4} \text{ sec}^{-1}$, $E_a = 18.33 \text{ K cal mol}^{-1}$; (d) $A = 5.40 \times 10^{10} \text{ sec}^{-1}, E_a = 2.199 \times 10^4 \text{ J mol}^{-1}$
Q.2 100 kJ mol^{-1} Q.3 $t_{1/2} = 24.14 \text{ min}$ Q.4 (a) 1, (b) $6.93 \times 10^{-3} \text{ min}^{-1}$, (c) 200, (d) 950 mm

RADIOACTIVITY

- Q.5 $^{64}_{30}\text{Zn}, ^{64}_{28}\text{Ni}, (t_{1/2})_1 = 33.68 \text{ hr}, (t_{1/2})_2 = 67.36 \text{ hr}, (t_{1/2})_3 = 29.76 \text{ hr}$ Q.6 (a) 2^1_0n , (b) $^{82}_{36}\text{Kr}$

KEY CONCEPTS

ELECTROCHEMICAL CELLS

An electrochemical cell consists of two electrodes (metallic conductors) in contact with an electrolyte (an ionic conductor).

An electrode and its electrolyte comprise an **Electrode Compartment**.

Electrochemical Cells can be classified as:

- (i) **Electrolytic Cells** in which a non-spontaneous reaction is driven by an external source of current.
- (ii) **Galvanic Cells** which produce electricity as a result of a spontaneous cell reaction

Note: In a **galvanic cell**, cathode is positive with respect to anode.

In a **electrolytic cell**, anode is made positive with respect to cathode.

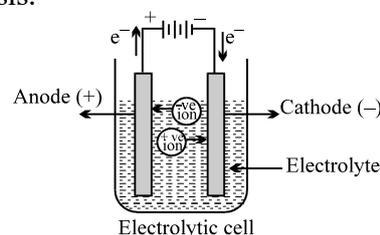
ELECTROLYSIS

The decomposition of electrolyte solution by passage of electric current, resulting into deposition of metals or liberation of gases at electrodes is known as electrolysis.

ELECTROLYTIC CELL

This cell converts electrical energy into chemical energy.

The entire assembly except that of the external battery is known as the electrolytic cell

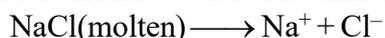


ELECTRODES

The metal strip at which positive current enters is called **anode**; anode is positively charged in electrolytic cell. On the other hand, the electrode at which current leaves is called **cathode**. Cathodes are negatively charged.

Anode	Positive	Loss of electron or oxidation takes place	Positive current enters
Cathode	Negative	Gain of electron or reduction takes place	Current leaves

ELECTROLYSIS OF MOLTEN SODIUM CHLORIDE

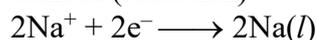


Reactions at

anode (oxidation) :



cathode (reduction)



There are two types of electrodes used in the electrolytic cell, namely attackable and non-attackable. The attackable electrodes participate in the electrode reaction. They are made up of reactive metals like Zn, Cu, Ag etc. In such electrodes, atom of the metal gets oxidised into the corresponding cation, which is passed into the solution. Thus, such anodes get dissolved and their mass decreases. On the other hand, non-attackable electrodes do not participate in the electrode reaction as they are made up of unreactive elements like Pt, graphite etc. Such electrodes do not dissolve and their mass remains the same.

FARADAY'S LAWS OF ELECTROLYSIS:

(i) *First law of electrolysis :*

Amount of substance deposited or liberated at an electrode is directly proportional to amount of charge passed (utilized) through the solution.

$$w \propto Q$$

W = weight liberated, Q = charge in coulomb

$$w = ZQ$$

Z = electrochemical equivalent

when Q = 1 coulomb, then w = Z

Thus, weight deposited by 1 coulomb charge is called electrochemical equivalent.

Let 1 ampere current is passed till 't' seconds .

Then, $Q = It$ $\therefore w = ZIt$

1 Faraday = 96500 coulomb = Charge of one mole electrons

One faraday is the charge required to liberate or deposit one gm equivalent of a substance at corresponding electrode.

Let 'E' is equivalent weight then 'E' gm will be liberated by 96500 coulomb.

\therefore 1 Coulomb will liberate $\frac{E}{96500}$ gm ; By definition, $Z = \frac{E}{96500}$

$$\therefore W = \frac{ItE}{96500}$$

When a gas is evolved at an electrode, then above formula changes as,

$$V = \frac{ItV_e}{96500}$$

where V = volume of liberated gas, V_e = equivalent volume of gas.

Equivalent volume may be defined as:

The volume of gas liberated by 96500 coulomb at STP.

(ii) *Second law of electrolysis :*

When same amount of charge is passed through different electrolyte solutions connected in series then weight of substances deposited or dissolved at anode or cathode are in ratio of their equivalent weights. i.e.

$$w_1/w_2 = E_1/E_2$$

QUALITATIVE ASPECTS OF ELECTROLYSIS

In the electrolysis process we have discussed above, we have taken molten salt as electrolyte, which contains only one cation and anion. Now, if the electrolyte taken contains more than one cation and anion (for example, aqueous solution of the ionic electrolyte), then the cation and anion that will get discharged depends on the ability of cation to get reduced and the ability of anion to get oxidised.

The ability of an ion to get oxidised or reduced depends upon the size, mass, positive charge, negative charge etc. Thus, it is not possible to predict qualitatively that which ion would be discharged first, as one factor might enhance the ability to discharge while the other factor may hamper it. This can only be predicted on the basis of quantitative value assigned based on the cumulative effect of all the factors responsible for an ion's ability to discharge. The value is referred as standard potential, which is determined by keeping the concentration of ion as 1 M, pressure of gas at 1 atm, and the measurement done at 25°C. For a cation, the standard reduction potential (SRP) values are compared. The cation having higher standard reduction potential value is discharged in preference to cation with lower SRP value provided the ions are at 1 M concentration. For an anion, the standard oxidation potential (SOP) values are compared and anion having higher SOP is preferentially discharged, if the concentration is 1 M for each of the ion. The SRP values at 25°C for some of the reduction half reactions are given in the table below.

S.NO.	Reduction half cell reaction	E° in volts at 25°C
1.	$F_2 + 2e^- \longrightarrow 2F^-$	+ 2.65
2.	$S_2O_8^{2-} + 2e^- \longrightarrow 2SO_4^{2-}$	+ 2.01
3.	$Co^{3+} + e^- \longrightarrow Co^{2+}$	+ 1.82
4.	$PbO_2 + 4H^+ + SO_4^{2-} + 2e^- \longrightarrow PbSO_4 + 2H_2O$	+ 1.65
5.	$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$	+ 1.52
6.	$Au^{3+} + 3e^- \longrightarrow Au$	+ 1.50
7.	$Cl_2 + 2e^- \longrightarrow 2Cl^-$	+ 1.36
8.	$Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O$	+ 1.33
9.	$O_2 + 4H^+ + 4e^- \longrightarrow 2H_2O$	+ 1.229
10.	$Br_2 + 2e^- \longrightarrow 2Br^-$	+ 1.07
11.	$NO_3^- + 4H^+ + 3e^- \longrightarrow NO + 2H_2O$	+ 0.96
12.	$2Hg^{2+} + 2e^- \longrightarrow Hg_2^{2+}$	+ 0.92
13.	$Cu^{2+} + I^- + e^- \longrightarrow CuI$	+ 0.86
14.	$Ag^+ + e^- \longrightarrow Ag$	+ 0.799
15.	$Hg_2^{2+} + 2e^- \longrightarrow 2 Hg$	+ 0.79
16.	$Fe^{3+} + e^- \longrightarrow Fe^{2+}$	+ 0.77
17.	$I_2 + 2e^- \longrightarrow 2I^-$	+ 0.535
18.	$Cu^+ + e^- \longrightarrow Cu$	+ 0.53
19.	$Cu^{2+} + 2e^- \longrightarrow Cu$	+ 0.34
20.	$Hg_2Cl_2 + 2e^- \longrightarrow 2Hg + 2Cl^-$	+ 0.27
21.	$AgCl + e^- \longrightarrow Ag + Cl^-$	+ 0.222
22.	$Cu^{2+} + e^- \longrightarrow Cu^+$	+ 0.15
23.	$Sn^{4+} + 2e^- \longrightarrow Sn^{2+}$	+ 0.13
24.	$2H^+ + 2e^- \longrightarrow H_2$	0.00
25.	$Fe^{3+} + 3e^- \longrightarrow Fe$	- 0.036
26.	$Pb^{2+} + 2e^- \longrightarrow Pb$	- 0.126
27.	$Sn^{2+} + 2e^- \longrightarrow Sn$	- 0.14
28.	$AgI + e^- \longrightarrow Ag + I^-$	- 0.151
29.	$Ni^{2+} + 2e^- \longrightarrow Ni$	- 0.25
30.	$Co^{2+} + 2e^- \longrightarrow Co$	- 0.28
31.	$Cd^{2+} + 2e^- \longrightarrow Cd$	- 0.403
32.	$Cr^{3+} + e^- \longrightarrow Cr^{2+}$	- 0.41
33.	$Fe^{2+} + 2e^- \longrightarrow Fe$	- 0.44
34.	$Cr^{3+} + 3e^- \longrightarrow Cr$	- 0.74
35.	$Zn^{2+} + 2e^- \longrightarrow Zn$	- 0.762
36.	$2H_2O + 2e^- \longrightarrow H_2 + 2OH^-$	- 0.828
37.	$Mn^{2+} + 2e^- \longrightarrow Mn$	- 1.18
38.	$Al^{3+} + 3e^- \longrightarrow Al$	- 1.66
39.	$H_2 + 2e^- \longrightarrow 2H^-$	- 2.25
40.	$Mg^{2+} + 2e^- \longrightarrow Mg$	- 2.37
41.	$Na^+ + e^- \longrightarrow Na$	- 2.71
42.	$Ca^{2+} + e^- \longrightarrow Ca$	- 2.87
43.	$Ba^{2+} + 2e^- \longrightarrow Ba$	- 2.90
44.	$Cs^+ + e^- \longrightarrow Cs$	- 2.92
45.	$K^+ + e^- \longrightarrow K$	- 2.93
46.	$Li^+ + e^- \longrightarrow Li$	- 3.03

When solution of an electrolyte contains more than one type of cations and anions at concentrations different than 1 M, the discharge of an ion does not depend solely on standard potentials but also depends on the concentration of ion in the solution. This value is referred as potential, called as reduction potential for cation and oxidation potential for anion. The relation between reduction potential and standard reduction potential is given by Nernst equation, as

$$E_{RP} = E_{RP}^{\circ} - \frac{RT}{nF} \ln \frac{[\text{concentration of product}]}{[\text{concentration of reactant}]}$$

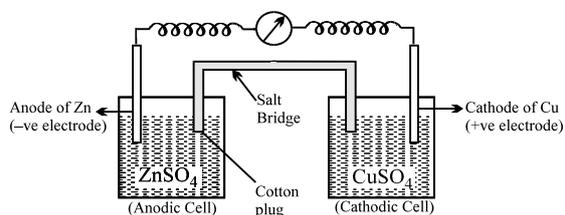
where E_{RP} = Reduction potential of cation and E_{RP}° = Standard reduction potential of cation.

Thus, it is possible that a cation (A^+) with lower standard reduction potential getting discharged in preference to cation (B^+) having higher standard reduction potential because their concentration might be such that the reduction potential of A^+ is higher than that of B^+ .

When two metal ions in the solution have identical values of their reduction potentials, the simultaneous deposition of both the metals will occur in the form of an alloy.

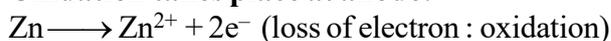
GALVANIC CELL

This cell converts chemical energy into electrical energy.

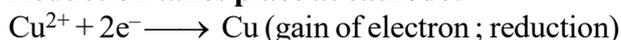


Galvanic cell is made up of two half cells i.e., anodic and cathodic. The cell reaction is of redox kind. Oxidation takes place at anode and reduction at cathode. It is also known as *voltaic cell*. It may be represented as shown in Fig. Zinc rod immersed in $ZnSO_4$ behaves as anode and copper rod immersed in $CuSO_4$ behaves as cathode.

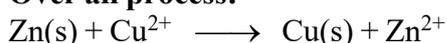
Oxidation takes place at anode:



Reduction takes place at cathode:



Over all process:



In galvanic cell like Daniell cell; electrons flow from anode (zinc rod) to the cathode (copper rod) through external circuit; zinc dissolves as Zn^{2+} ; Cu^{2+} ion in the cathode cell picks up two electron and become deposited at cathode.

SALT BRIDGE

Two electrolyte solutions in galvanic cells are separated using salt bridge as represented in the Fig. salt bridge is a device to minimize or eliminate the liquid junction potential. Saturated solution of salt like KCl, KNO_3 , NH_4Cl and NH_4NO_3 etc. in agar-agar gel is used in salt bridge. Salt bridge contains high concentration of ions viz. K^+ and NO_3^- at the junction with electrolyte solution. Thus, salt bridge carries whole of the current across the boundary; moreover the K^+ and NO_3^- ions have same speed. Hence, salt bridge with uniform and same mobility of cations and anions minimize the liquid junction potential & completes the electrical circuit & permits the ions to migrate.

Representation of a cell (IUPAC conventions): Let us illustrate the convention taking the example of Daniel cell.

- (i) Anodic half cell is written on left and cathodic half cell on right hand side.

$$\text{Zn(s)} \mid \text{ZnSO}_4(\text{sol}) \parallel \text{CuSO}_4(\text{sol}) \mid \text{Cu(s)}$$
- (ii) Two half cells are separated by double vertical lines: Double vertical lines indicate salt bridge or any type of porous partition.
- (iii) EMF (electromotive force) may be written on the right hand side of the cell.
- (iv) Single vertical lines indicate the phase separation between electrode and electrolyte solution.

$$\text{Zn} \mid \text{Zn}^{2+} \parallel \text{Cu}^{2+} \mid \text{Cu}$$

 (Illustration of Phase boundary)
- (v) Inert electrodes are represented in the bracket

$$\text{Zn} \mid \text{ZnSO}_4 \parallel \text{H}^+ \mid \text{H}_2, \text{Pt}$$

CONCEPT OF ELECTROMOTIVE FORCE (EMF) OF A CELL

Electron flows from anode to cathode in external circuit due to a pushing effect called or electromotive force (e.m.f.). E.m.f. is some times called as *cell potential*. Unit of e.m.f. of cell is volt.

EMF of cell may be calculated as :

$$E_{\text{cell}} = \text{reduction potential of cathode} - \text{Reduction potential of anode}$$

Similarly, standard e.m.f. of the cell (E°) may be calculated as

$$E^\circ_{\text{cell}} = \text{Standard reduction potential of cathode} - \text{Standard reduction potential of anode}$$

SIGN CONVENTION OF EMF

EMF of cell should be positive other wise it will not be feasible in the given direction .

$$\text{Zn} \mid \text{ZnSO}_4 \parallel \text{CuSO}_4 \mid \text{Cu} \quad E = +1.10 \text{ volt (Feasible)}$$

$$\text{Cu} \mid \text{CuSO}_4 \parallel \text{ZnSO}_4 \mid \text{Zn} \quad E = -1.10 \text{ volt (Not Feasible)}$$

NERNST EQUATION

Walter Nernst derived a relation between cell potential and concentration or Reaction quotient.

$$\Delta G = \Delta G^\circ + RT \ln Q \quad \dots(1)$$

where ΔG and ΔG° are free energy and standard free energy change; 'Q' is reaction quotient.

Let n, Faraday charge is taken out from a cell of e.m.f. (E) then electrical work done by the cell may be calculated as,

$$\text{Work done} = \text{Charge} \times \text{Potential} = nFE$$

From thermodynamics we know that decrease in Gibbs free energy of a system is a measure of reversible or maximum obtainable work by the system if there is no work due to volume expansion

$$\therefore -\Delta G = nFE \quad \text{and} \quad -\Delta G^\circ = nFE^\circ$$

Thus from Eq. (i), we get $-nFE = -nFE^\circ + RT \ln Q$

$$\text{At } 25^\circ\text{C, above equation may be written as } E = E^\circ - \frac{0.0591}{n} \log Q$$

Where 'n' represents number of moles of electrons involved in process.

E, E° are e.m.f. and standard e.m.f. of the cell respectively.

In general, for a redox cell reaction involving the transference of n electrons

$aA + bB \longrightarrow cC + dD$, the EMF can be calculated as:

$$E_{\text{Cell}} = E^\circ_{\text{Cell}} - \frac{0.0591}{n} \log \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

Prediction and feasibility of spontaneity of a cell reaction.

Work done by the cell = nFE ;

It is equivalent to decrease in free energy $\Delta G = -nFE$

Under standard state $\Delta G^0 = -nFE^0$ (i)

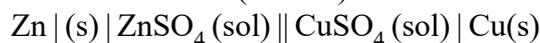
- (i) From thermodynamics we know, $\Delta G = \text{negative}$ for spontaneous process. Thus from eq.(i) it is clear that the EMF should be +ve for a cell process to be feasible or spontaneous.
- (ii) When $\Delta G = \text{positive}$, $E = \text{negative}$ and the cell process will be non spontaneous.
- (iii) When $G = 0$, $E = 0$ and the cell will attain the equilibrium.

Reactions	ΔG	E
Spontaneous	(-)	(+)
Non- spontaneous	(+)	(-)
Equilibrium	0	0

Standard free energy change of a cell may be calculated by electrode potential data.

Substituting the value of E^0 (i.e., standard reduction potential of cathode- standard reduction potential of anode) in eq. (i) we may get ΔG^0 .

Let us see whether the cell (Daniell) is feasible or not: i.e. whether Zinc will displace copper or not.



$$E_{\text{Zn}^{2+}/\text{Zn}}^0 = -0.76 \text{ volt} ; E_{\text{Cu}^{2+}/\text{Cu}}^0 = +0.34 \text{ volt}$$

$$E_{\text{cell}}^0 = E_{\text{Cu}^{2+}/\text{Cu}}^0 - E_{\text{Zn}^{2+}/\text{Zn}}^0$$

$$= 0.34 - (-0.76) = +1.10 \text{ volt}$$

Since $E^0 = +ve$, hence the cell will be feasible and zinc will displace copper from its salt solution. In the other words zinc will reduce copper.

THERMODYNAMIC TREATMENT OF NERNST EQUATION

Determination of equilibrium constant : We know, that

$$E = E^0 - \frac{0.0591}{n} \log Q \quad \dots(i)$$

At equilibrium, the cell potential is zero because cell reactions are balanced, i.e. $E = 0$

\therefore From Eq. (i), we have

$$0 = E^0 - \frac{0.0591}{n} \log K_{\text{eq}} \quad \text{or} \quad K_{\text{eq}} = \text{anti log} \left[\frac{nE^0}{0.0591} \right]$$

Heat of Reaction inside the cell: Let n Faraday charge flows out of a cell of e.m.f. E , then

$$-\Delta G = nFE \quad (i)$$

Gibbs Helmholtz equation (from thermodynamics) may be given as,

$$\Delta G = \Delta H + T \left[\frac{\partial \Delta G}{\partial T} \right]_p \quad (ii)$$

From Eqs. (i) and (ii), we have

$$-nFE = \Delta H + T \left[\frac{\partial (-nFE)}{\partial T} \right]_p = \Delta H - nFT \left[\frac{\partial E}{\partial T} \right]_p$$

$$\therefore \Delta H = -nFE + nFT \left[\frac{\partial E}{\partial T} \right]_p$$

Entropy change inside the cell : We know that $G = H - TS$ or $\Delta G = \Delta H - T\Delta S$... (i)
 where ΔG = Free energy change ; ΔH = Enthalpy change and ΔS = entropy change.
 According to Gibbs Helmholtz equation,

$$\Delta G = \Delta H + T \left[\frac{\partial \Delta G}{\partial T} \right]_p \quad \dots \text{(ii)}$$

From Eqs. (i) and (ii), we have

$$-T\Delta S = T \left[\frac{\partial \Delta G}{\partial T} \right]_p \quad \text{or} \quad \Delta S = - \left[\frac{\partial \Delta G}{\partial T} \right]_p$$

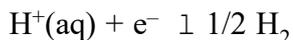
$$\text{or} \quad \Delta S = nF \left[\frac{\partial E}{\partial T} \right]_p$$

where $\left[\frac{\partial E}{\partial T} \right]_p$ is called temperature coefficient of cell e.m.f.

DIFFERENT TYPES OF HALF-CELLS AND THEIR REDUCTION POTENTIAL

(1) Gas-Ion Half Cell:

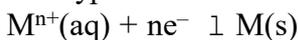
In such a half cell, an inert collector of electrons, platinum or graphite is in contact with gas and a solution containing a specified ion. One of the most important gas-ion half cell is the hydrogen-gas-hydrogen ion half cell. In this half cell, purified H_2 gas at a constant pressure is passed over a platinum electrode which is in contact with an acid solution.



$$E_{H^+ / H_2} = E^0_{H^+ / H_2} - \frac{0.0591}{1} \log \frac{(pH_2)^{1/2}}{[H^+]}$$

(2) Metal-Metal Ion Half Cell:

This type of cell consist of a metal M in contact with a solution containing M^{n+} ions.

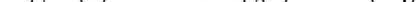


$$E_{M^{n+} / M} = E^0_{M^{n+} / M} - \frac{0.0591}{n} \log \frac{1}{[M^{n+}]}$$

(3) Metal-Insoluble Salt - Anion Half Cell:

In this half cell, a metal coated with its insoluble salt is in contact with a solution containing the anion of the insoluble salt. eg. Silver-Silver Chloride Half Cell:

This half cell is represented as $Cl^- / AgCl / Ag$. The equilibrium reaction that occurs at the electrode is

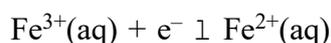


$$E_{Cl^- / AgCl / Ag} = E^0_{Cl^- / AgCl / Ag} - \frac{0.0591}{1} \log [Cl^-]$$

potential of such cells depends upon the concentration of anions. Such cells can be used as **Reference Electrode**.

(4) Oxidation-reduction Half Cell:

This type of half cell is made by using an inert metal collector, usually platinum, immersed in a solution which contains two ions of the same element in different states of oxidation. eg. $Fe^{2+} - Fe^{3+}$ half cell.



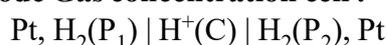
$$E_{\text{Fe}^{3+}/\text{Fe}^{2+}} = E_{\text{Fe}^{3+}/\text{Fe}^{2+}}^0 - \frac{0.0591}{1} \log \frac{[\text{Fe}^{2+}]}{[\text{Fe}^{3+}]}$$

CONCENTRATION CELL

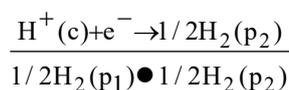
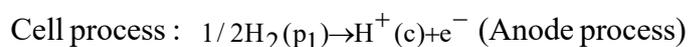
The cells in which electrical current is produced due to transport of a substance from higher to lower concentration. Concentration gradient may arise either in electrode material or in electrolyte. Thus there are two types of concentration cell.

- (i) Electrode concentration cell
- (ii) Electrolyte concentration cell

Electrode Gas concentration cell :



Here, hydrogen gas is bubbled at two different partial pressures at electrode dipped in the solution of same electrolyte.

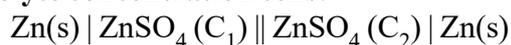


$$\therefore E = -\frac{2.303RT}{F} \log \left[\frac{\text{p}_2}{\text{p}_1} \right]^{1/2}$$

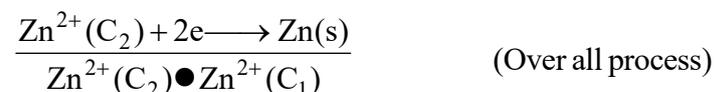
$$\text{or } E = \left[\frac{2.303RT}{2F} \right] \log \left[\frac{\text{p}_2}{\text{p}_1} \right], \text{ At } 25^\circ\text{C}, E = \frac{0.059}{2F} \log \left[\frac{\text{p}_1}{\text{p}_2} \right]$$

For spontaneity of such cell reaction, $\text{p}_1 > \text{p}_2$

Electrolyte concentration cells:



In such cells, concentration gradient arise in electrolyte solutions. Cell process may be given as,



\therefore From Nernst equation, we have

$$E = 0 - \frac{2.303RT}{2F} \log \left[\frac{\text{C}_1}{\text{C}_2} \right] \quad \text{or} \quad E = \frac{2.303RT}{2F} \log \left[\frac{\text{C}_2}{\text{C}_1} \right]$$

For spontaneity of such cell reaction, $\text{C}_2 > \text{C}_1$

CONDUCTANCE

Introduction:

Both metallic and electrolytic conductors obey Ohm's law
i.e. $V = IR$

where V = Potential difference in volt; I = Current in ampere ; R = resistance in Ohm

We know, resistance is directly proportional to length of conductor and inversely proportional to cross sectional area of the conductor.

$$R \propto \frac{l}{A} \quad \text{or} \quad R = \rho \frac{l}{A} \quad (\rho = \text{Specific resistance})$$

Specific resistance is the resistance of a conductor having lengths of 1 cm and cross sectional area of 1 cm².

Unit of R is ohm and unit of specific resistance is ohm cm

Reciprocal of resistance is called as *conductance* and reciprocal of specific resistance is called as *specific conductance*.

$$\frac{1}{R} = \frac{1}{\rho} \frac{A}{l} \quad \text{or} \quad C = K \frac{A}{l}$$

where C = conductance ohm⁻¹ ; K = specific conductance ohm⁻¹cm⁻¹.

Mho and siemens are other units of conductance

$$K = \frac{l}{A} C$$

Specific conductance = Cell constant x Conductance

SPECIFIC CONDUCTANCE IS CONDUCTANCE OF 1 CM³ OF AN ELECTROLYTE SOLUTION.

In case of electrolytic solution, the specific conductance is defined as the conductance of a solution of definite concentration enclosed in a cell having two electrodes of unit area separated by 1 cm apart.

1. Equivalent Conductance

Equivalent conductance is the conductance of an electrolyte solution containing 1 gm equivalent of electrolyte. It is denoted by \wedge .

$$\wedge = K \times V$$

$$(\wedge = \text{ohm}^{-1} \text{cm}^{-1} \times \text{cm}^3 = \text{ohm}^{-1} \text{cm}^2)$$

Usually concentration of electrolyte solution is expressed as C gm equivalent per litre.

$$\text{Thus, } V = \frac{1000}{C}$$

$$\{\text{Volume having 1 gm equivalent electrolyte in the solution}\} \text{ Thus, } \wedge = K \times \frac{1000}{C}$$

2. Molar Conductance

Molar conductance may be defined as conductance of an electrolyte solution having 1 gm mole electrolyte in a litre. It is denoted by \wedge_m .

$$\wedge_m = K \times V$$

Usually concentration of electrolyte solution is expressed as 'M' gm mole electrolyte per litre.

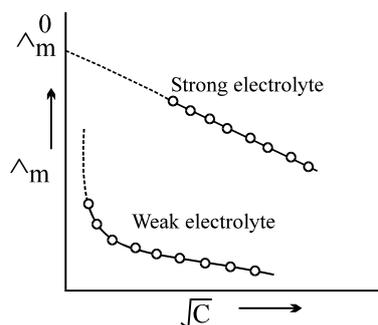
$$\text{Thus, } V = \frac{1000}{M}$$

$$\text{Hence, } \wedge_m = K \times \frac{1000}{M}$$

$$\text{Relation between } \wedge \text{ and } \wedge_m : \quad \wedge_m = n \times \wedge$$

DETERMINATION OF Λ_m^0 OR Λ^0

A plot of Λ_m vs \sqrt{C} as found experimentally is as shown below graphically.



The Λ_m vs \sqrt{C} plot of strong electrolyte being linear it can be extrapolated to zero concentration.

Thus, Λ_m values of the solution of the test electrolyte are determined at various concentrations the concentrations should be as low as good.

Λ_m values are then plotted against \sqrt{C} when a straight line is obtained. This is the extrapolated to zero concentration. The point where the straight line intersects Λ_m axis is Λ_m^0 of the strong electrolyte.

However, the plot in the case weak electrolyte being non linear, shooting up suddenly at some low concentration and assuming the shape of a straight line parallel to Λ_m axis. Hence extrapolation in this case is not possible. Thus, Λ_0 of a weak electrolyte cannot be determined experimentally. It can, however, be done with the help of Kohlrausch's law to be discussed later.

Kohlrausch's Law of Independent Migration of Ions

Kohlrausch determined Λ_0 values of pairs of some strong electrolytes containing same cation say KF and KCl, NaF and NaCl etc., and found that the difference in Λ_0 values in each case remains the same:

$$\Lambda_m^0(\text{KCl}) - \Lambda_m^0(\text{KF}) = \Lambda_m^0(\text{NaCl}) - \Lambda_m^0(\text{NaF})$$

He also determined Λ_0 values of pairs of strong electrolytes containing same anion say KF and NaF, KCl and NaCl etc. and found that the difference in Λ_0 values in each case remains the same.

$$\Lambda_m^0(\text{KF}) - \Lambda_m^0(\text{NaF}) = \Lambda_m^0(\text{KCl}) - \Lambda_m^0(\text{NaCl})$$

This experimental data led him to formulate the following law called Kohlrausch's law of independent migration of ions.

At infinite dilution when dissociation is complete, every ion makes some definite contribution towards molar conductance of the electrolyte irrespective of the nature of the other ion which with it is associated and that the molar conductance at infinite dilution for any electrolyte is given by the sum of the contribution of the two ions. Thus,

$$\Lambda_m^0 = \lambda_+^0 + \lambda_-^0$$

Where λ_+^0 is the contribution of the cation and λ_-^0 is the contribution of the anion towards the molar conductance at infinite dilution. These contributions are called molar ionic conductances at infinite dilution.

Thus, λ_+^0 is the molar ionic conductance of cation and λ_-^0 is the molar ionic conductance of anion, at infinite dilution. The above equation is, however, correct only for binary electrolyte like NaCl, MgSO_4 etc.

Application of Kohlrausch's law :

(1) Determination of Λ_m^0 of a weak electrolyte:

In order to calculate Λ_m^0 of a weak electrolyte say CH_3COOH , we determine experimentally Λ_m^0 values of the following three strong electrolytes:

- (a) A strong electrolyte containing same cation as in the test electrolyte, say HCl
- (b) A strong electrolyte containing same anion as in the test electrolyte, say CH_3COONa
- (c) A strong electrolyte containing same anion of (a) and cation of (b) i.e. NaCl.

Λ_m^0 of CH_3COOH is then given as:

$$\Lambda_m^0 (\text{CH}_3\text{COOH}) = \Lambda_m^0 (\text{HCl}) + \Lambda_m^0 (\text{CH}_3\text{COONa}) - \Lambda_m^0 (\text{NaCl})$$

Proof:

$$\Lambda_m^0 (\text{HCl}) = \lambda_{\text{H}^+}^0 + \lambda_{\text{Cl}^-}^0 \quad \dots\dots\dots\text{(i)}$$

$$\Lambda_m^0 (\text{CH}_3\text{COONa}) = \lambda_{\text{CH}_3\text{COO}^-}^0 + \lambda_{\text{Na}^+}^0 \quad \dots\dots\dots\text{(ii)}$$

$$\Lambda_m^0 (\text{NaCl}) = \lambda_{\text{Na}^+}^0 + \lambda_{\text{Cl}^-}^0 \quad \dots\dots\dots\text{(iii)}$$

Adding equation (i) and equation (ii) and subtracting (iii) from them:

$$\Lambda_m^0 (\text{HCl}) + \Lambda_m^0 (\text{CH}_3\text{COONa}) - \Lambda_m^0 (\text{NaCl}) = \lambda_{\text{H}^+}^0 + \lambda_{\text{CH}_3\text{COO}^-}^0 = \Lambda_m^0 (\text{CH}_3\text{COOH})$$

(2) Determination of degree of dissociation (α):

$$\alpha = \frac{\text{No. of molecules ionised}}{\text{total number of molecules dissolved}} = \frac{\Lambda_m}{\Lambda_m^0}$$

(3) Determination of solubility of sparingly soluble salt

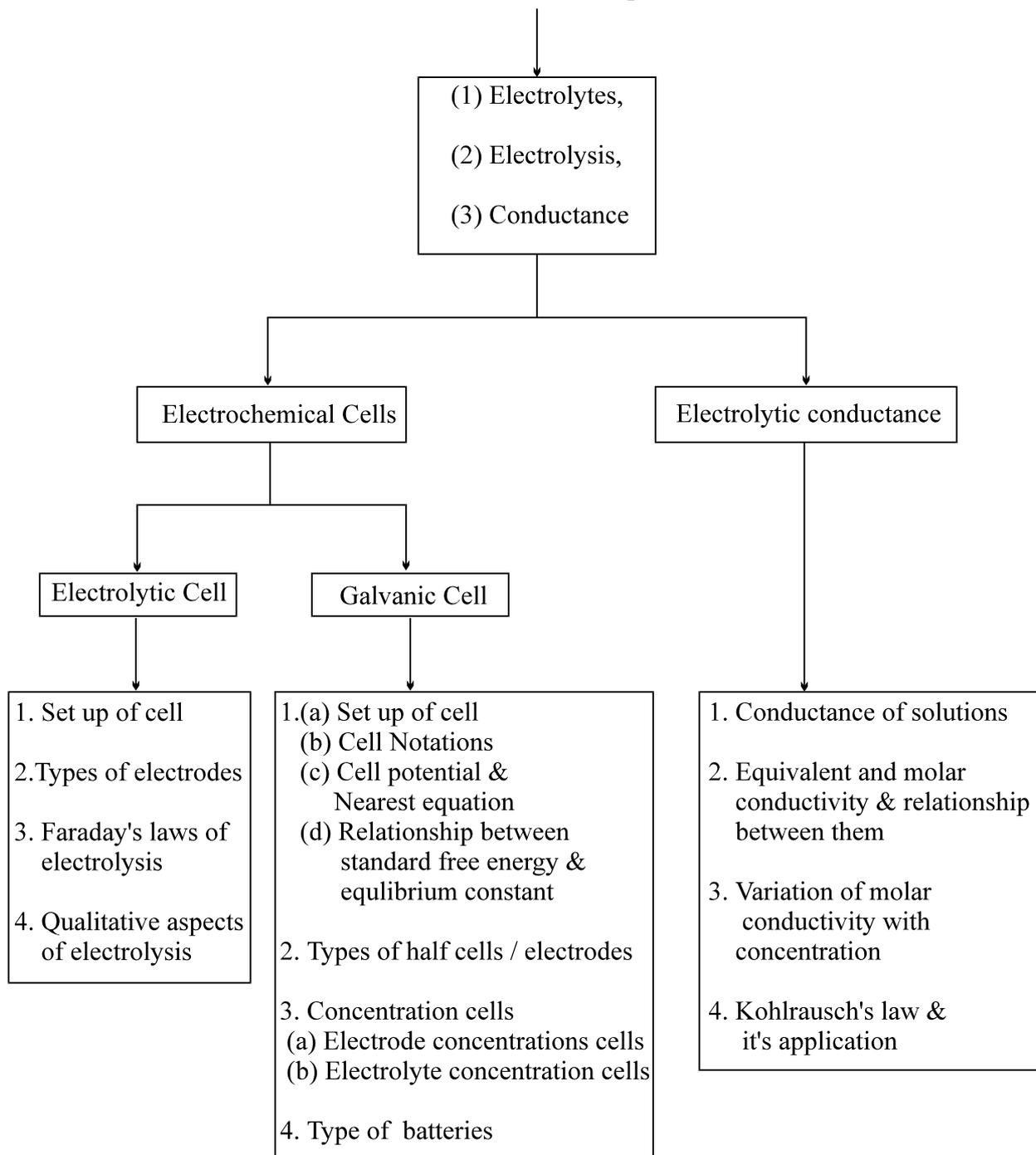
The specific conductivity of a saturated solution of the test electrolyte (sparingly soluble) made in conductivity water is determined by the method as described above. From this the specific conductivity of conductivity water is deducted. The molar conductance of the saturated solution is taken to be equal to Λ_m^0 as the saturated solution of a sparingly soluble salt is extremely dilute. Hence from equation (4).

$$\Lambda_m^0 = \frac{1000\kappa}{C},$$

where C is the molarity of solution and hence the solubility.

ATLAS

Some Basic Concept



EXERCISE I

ELECTROLYTIC CELL :

- Q.1 Calculate the no. of electrons lost or gained during electrolysis of
(a) 3.55 gm of Cl^- ions (b) 1 gm Cu^{2+} ions (c) 2.7 gm of Al^{3+} ions
- Q.2 How many faradays of electricity are involved in each of the case
(a) 0.25 mole Al^{3+} is converted to Al.
(b) 27.6 gm of SO_3 is converted to SO_3^{2-}
(c) The Cu^{2+} in 1100 ml of 0.5 M Cu^{2+} is converted to Cu.
- Q.3 0.5 mole of electron is passed through two electrolytic cells in series. One contains silver ions, and the other zinc ions. Assume that only cathode reaction in each cell is the reduction of the ion to the metal. How many gm of each metals will be deposited.
- Q.4 The electrosynthesis of MnO_2 is carried out from a solution of MnSO_4 in H_2SO_4 (aq). If a current of 25.5 ampere is used with a current efficiency of 85%, how long would it take to produce 1 kg of MnO_2 ?
- Q.5 A constant current of 30 A is passed through an aqueous solution of NaCl for a time of 1.0 hr. How many grams of NaOH are produced? What is volume of Cl_2 gas at S.T.P. produced?
- Q.6 If 0.224 litre of H_2 gas is formed at the cathode, how much O_2 gas is formed at the anode under identical conditions?
- Q.7 If 0.224 litre of H_2 gas is formed at the cathode of one cell at S.T.P., how much of Mg is formed at the cathode of the other electrolytic cell.
- Q.8 Assume 96500 C as one unit of electricity. If cost of electricity of producing x gm Al is Rs x, what is the cost of electricity of producing x gm Mg?
- Q.9 Chromium metal can be plated out from an acidic solution containing CrO_3 according to following equation:
 $\text{CrO}_3(\text{aq}) + 6\text{H}^+(\text{aq}) + 6\text{e}^- \rightarrow \text{Cr}(\text{s}) + 3\text{H}_2\text{O}$
Calculate :
(i) How many grams of chromium will be plated out by 24000 coulombs and
(ii) How long will it take to plate out 1.5 gm of chromium by using 12.5 ampere current
- Q.10 Calculate the quantity of electricity that would be required to reduce 12.3 g of nitrobenzene to aniline, if the current efficiency for the process is 50 percent. If the potential drop across the cell is 3.0 volts, how much energy will be consumed?
- Q.11 How long a current of 2A has to be passed through a solution of AgNO_3 to coat a metal surface of 80cm^2 with $5\mu\text{m}$ thick layer? Density of silver = 10.8g/cm^3 .
- Q.12 3A current was passed through an aqueous solution of an unknown salt of Pd for 1Hr. 2.977g of Pd^{+n} was deposited at cathode. Find n.
- Q.13 50mL of 0.1M CuSO_4 solution is electrolyzed with a current of 0.965 A for a period of 200 sec. The reactions at electrodes are:
Cathode : $\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu}(\text{s})$ Anode : $2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+ + 4\text{e}^-$.
Assuming no change in volume during electrolysis, calculate the molar concentration of Cu^{2+} , H^+ and SO_4^{2-} at the end of electrolysis.
- Q.14 A metal is known to form fluoride MF_2 . When 10A of electricity is passed through a molten salt for 330 sec., 1.95g of metal is deposited. Find the atomic weight of M. What will be the quantity of electricity required to deposit the same mass of Cu from CuSO_4 ?
-

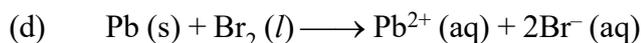
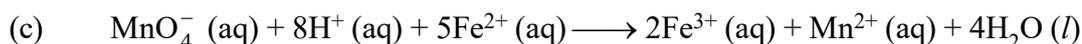
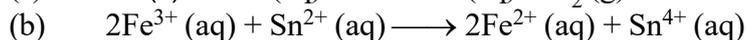
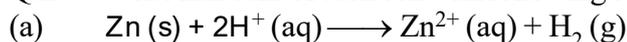
- Q.15 10g fairly concentrated solution of CuSO_4 is electrolyzed using 0.01F of electricity. Calculate:
 (a) The weight of resulting solution (b) Equivalents of acid or alkali in the solution.
- Q.16 An electric current is passed through electrolytic cells in series one containing $\text{Ag}(\text{NO}_3)(\text{aq.})$ and other $\text{H}_2\text{SO}_4(\text{aq.})$. What volume of O_2 measured at 25°C and 750mm Hg pressure would be liberated from H_2SO_4 if
 (a) one mole of Ag^+ is deposited from AgNO_3 solution
 (b) 8×10^{22} ions of Ag^+ are deposited from AgNO_3 solution.
- Q.17 Cadmium amalgam is prepared by electrolysis of a solution of CdCl_2 using a mercury cathode. How long should a current of 5A be passed in order to prepare 12% Cd–Hg amalgam on a cathode of 2gm Hg (Cd=112.4)
- Q.18 After electrolysis of NaCl solution with inert electrodes for a certain period of time. 600 mL of the solution was left. Which was found to be 1N in NaOH. During the same time, 31.75 g of Cu was deposited in the copper voltameter in series with the electrolytic cell. Calculate the percentage yield of NaOH obtained.
- Q.19 Three electrolytic cells A, B, C containing solution of ZnSO_4 , AgNO_3 and CuSO_4 , respectively are connected in series. A steady current of 2 ampere was passed through them until 1.08 g of silver deposited at the cathode of cell B. How long did the current flow? What mass of copper and of zinc were deposited?
- Q.20 Copper sulphate solution (250 mL) was electrolysed using a platinum anode and a copper cathode. A constant current of 2 mA was passed for 16 minutes. It was found that after electrolysis the concentration of the solution was reduced to 50% of its original value. Calculate the concentration of copper sulphate in the original solution.
- Q.21 A solution of $\text{Ni}(\text{NO}_3)_2$ is electrolysed between platinum electrodes using a current of 5 ampere for 20 mintue. What mass of Ni is deposited at the cathode?
- Q.22 A current of 3.7A is passed for 6hrs. between Ni electrodes in 0.5L of 2M solution of $\text{Ni}(\text{NO}_3)_2$. What will be the molarity of solution at the end of electrolysis?

GALVANIC CELL :

Representation of Cell diagrams, complete and half cell reactions :

- Q.23 Make complete cell diagrams of the following cell reactions :
- (a) $\text{Cd}^{2+}(\text{aq}) + \text{Zn}(\text{s}) \longrightarrow \text{Zn}^{2+}(\text{aq}) + \text{Cd}(\text{s})$
 (b) $2\text{Ag}^+(\text{aq}) + \text{H}_2(\text{g}) \longrightarrow 2\text{H}^+(\text{aq}) + 2\text{Ag}(\text{s})$
 (c) $\text{Hg}_2\text{Cl}_2(\text{s}) + \text{Cu}(\text{s}) \longrightarrow \text{Cu}^{2+}(\text{aq}) + 2\text{Cl}^-(\text{aq}) + 2\text{Hg}(\text{l})$
 (d) $\text{Cr}_2\text{O}_7^{2-}(\text{aq.}) + 14\text{H}^+(\text{aq}) + 6\text{Fe}^{2+}(\text{aq}) \longrightarrow 6\text{Fe}^{3+}(\text{aq}) + 2\text{Cr}^{3+}(\text{aq}) + 7\text{H}_2\text{O}(\text{l})$
- Q.24 Write cell reaction of the following cells :
- (a) $\text{Ag} | \text{Ag}^+(\text{aq}) || \text{Cu}^{2+}(\text{aq}) | \text{Cu}$
 (b) $\text{Pt} | \text{Fe}^{2+}, \text{Fe}^{3+} || \text{MnO}_4^-, \text{Mn}^{2+}, \text{H}^+ | \text{Pt}$
 (c) $\text{Pt}, \text{Cl}_2 | \text{Cl}^-(\text{aq}) || \text{Ag}^+(\text{aq}) | \text{Ag}$
 (d) $\text{Pt}, \text{H}_2 | \text{H}^+(\text{aq}) || \text{Cd}^{2+}(\text{aq}) | \text{Cd}$
-

Q.25 Write half cells of each cell with following cell reactions :

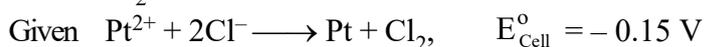
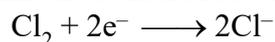


Electrode potential and standard electrode potential :

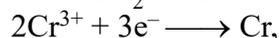
Q.26 For the cell reaction $2\text{Ce}^{4+} + \text{Co} \longrightarrow 2\text{Ce}^{3+} + \text{Co}^{2+}$

E_{cell}° is 1.89 V. If $E_{\text{Co}^{2+}|\text{Co}}^{\circ}$ is -0.28 V, what is the value of $E_{\text{Ce}^{4+}|\text{Ce}^{3+}}^{\circ}$?

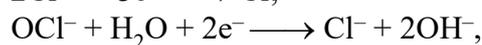
Q.27 Determine the standard reduction potential for the half reaction :



Q.28 What is E_{Cell}° if



$$E^{\circ} = -0.74$$
 V



$$E^{\circ} = 0.94$$
 V

ΔG° , E_{Cell}° and K_{eq} :

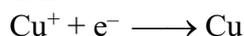
Q.29 Is 1.0 M H^+ solution under H_2SO_4 at 1.0 atm capable of oxidising silver metal in the presence of 1.0 M Ag^+ ion?

$$E_{\text{Ag}^+|\text{Ag}}^{\circ} = 0.80$$
 V, $E_{\text{H}^+|\text{H}_2(\text{Pt})}^{\circ} = 0.0$ V

Q.30 If for the half cell reactions $\text{Cu}^{2+} + \text{e}^- \longrightarrow \text{Cu}^+$ $E^{\circ} = 0.15$ V



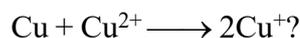
Calculate E° of the half cell reaction



also predict whether Cu^+ undergoes disproportionation or not.

Q.31 If $E_{\text{Fe}^{2+}|\text{Fe}}^{\circ} = -0.44$ V, $E_{\text{Fe}^{3+}|\text{Fe}^{2+}}^{\circ} = 0.77$ V. Calculate $E_{\text{Fe}^{3+}|\text{Fe}}^{\circ}$.

Q.32 If $E_{\text{Cu}^+|\text{Cu}}^{\circ} = 0.52$ V, $E_{\text{Cu}^{2+}|\text{Cu}}^{\circ} = 0.34$ V, what is E_{Cell}° of the cell reaction



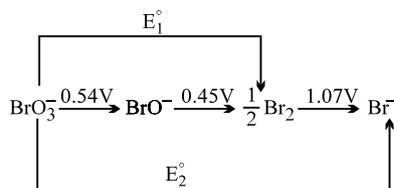
is cell reaction spontaneous?

Q.33 Calculate the EMF of a Daniel cell when the concentration of ZnSO_4 and CuSO_4 are 0.001 M and 0.1M respectively. The standard potential of the cell is 1.1V.

Q.34 Calculate the equilibrium constant for the reaction $\text{Fe} + \text{CuSO}_4 \rightleftharpoons \text{FeSO}_4 + \text{Cu}$ at 25°C .

Given $E^{\circ}(\text{Fe}/\text{Fe}^{2+}) = 0.44$ V, $E^{\circ}(\text{Cu}/\text{Cu}^{2+}) = -0.337$ V.

- Q.35 For a cell $\text{Mg(s)} | \text{Mg}^{2+}(\text{aq}) || \text{Ag}^+(\text{aq}) | \text{Ag}$, Calculate the equilibrium constant at 25°C . Also find the maximum work that can be obtained by operating the cell.
 $E^0(\text{Mg}^{2+}/\text{Mg}) = -2.37\text{V}$, $E^0(\text{Ag}^+/\text{Ag}) = 0.8\text{V}$.
- Q.36 The standard reduction potential at 25°C for the reduction of water
 $2\text{H}_2\text{O} + 2\text{e}^- \rightleftharpoons \text{H}_2 + 2\text{OH}^-$ is -0.8277 volt . Calculate the equilibrium constant for the reaction
 $2\text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{OH}^-$ at 25°C .
- Q.37 At 25°C the value of K for the equilibrium $\text{Fe}^{3+} + \text{Ag} \rightleftharpoons \text{Fe}^{2+} + \text{Ag}^+$ is 0.531 mol/litre . The standard electrode potential for $\text{Ag}^+ + \text{e}^- \rightleftharpoons \text{Ag}$ is 0.799V . What is the standard potential for $\text{Fe}^{3+} + \text{e}^- \rightleftharpoons \text{Fe}^{2+}$?
- Q.38 The EMF of the cell $\text{M} | \text{M}^{n+} (0.02\text{M}) || \text{H}^+ (1\text{M}) | \text{H}_2(\text{g}) (1\text{ atm}), \text{Pt}$ at 25°C is 0.81V . Calculate the valency of the metal if the standard oxidation of the metal is 0.76V .
- Q.39 Equinormal Solutions of two weak acids, HA ($\text{pK}_a = 3$) and HB ($\text{pK}_a = 5$) are each placed in contact with equal pressure of hydrogen electrode at 25°C . When a cell is constructed by interconnecting them through a salt bridge, find the emf of the cell.
- Q.40 In two vessels each containing 500ml water, 0.5m mol of aniline ($K_b = 10^{-9}$) and 25mmol of HCl are added separately. Two hydrogen electrodes are constructed using these solutions. Calculate the emf of cell made by connecting them appropriately.
- Q.41 Calculate E^0 and E for the cell $\text{Sn} | \text{Sn}^{2+} (1\text{M}) || \text{Pb}^{2+} | \text{Pb} (10^{-3}\text{M})$, $E^0(\text{Sn}^{2+} | \text{Sn}) = -0.14\text{V}$, $E^0(\text{Pb}^{2+} | \text{Pb}) = -0.13\text{V}$. Is cell representation is correct?
- Q.42 At what concentration of Cu^{2+} in a solution of CuSO_4 will the electrode potential be zero at 25°C ?
 Given : $E^0(\text{Cu} | \text{Cu}^{2+}) = -0.34\text{V}$.
- Q.43 A zinc electrode is placed in a 0.1M solution at 25°C . Assuming that the salt is 20% dissociated at this dilutions calculate the electrode potential. $E^0(\text{Zn}^{2+} | \text{Zn}) = -0.76\text{V}$.
- Q.44 From the standard potentials shown in the following diagram, calculate the potentials E_1° and E_2° .



- Q.45 For the reaction, $4\text{Al(s)} + 3\text{O}_2(\text{g}) + 6\text{H}_2\text{O} + 4\text{OH}^- \rightleftharpoons 4[\text{Al}(\text{OH})_4^-]$; $E_{\text{cell}}^\circ = 2.73\text{V}$. If $\Delta G_f^\circ(\text{OH}^-) = -157\text{ kJ mol}^{-1}$ and $\Delta G_f^\circ(\text{H}_2\text{O}) = -237.2\text{ kJ mol}^{-1}$, determine $\Delta G_f^\circ[\text{Al}(\text{OH})_4^-]$.
-

Concentration cells :

- Q.46 Calculate the EMF of the following cell
 $\text{Zn} | \text{Zn}^{2+} (0.01\text{M}) || \text{Zn}^{2+} (0.1 \text{ M}) | \text{Zn}$
at 298 K.
- Q.47 Calculate the EMF of the cell,
 $\text{Zn} - \text{Hg}(c_1\text{M}) | \text{Zn}^{2+} (\text{aq}) | \text{Hg} - \text{Zn}(c_2\text{M})$
at 25°C, if the concentrations of the zinc amalgam are: $c_1 = 10\text{g per } 100\text{g}$ of mercury and $c_2 = 1\text{g per } 100\text{g}$ of mercury.
- Q.48 Calculate pH using the following cell :
 $\text{Pt} (\text{H}_2) | \text{H}^+ (x \text{ M}) || \text{H}^+ (1 \text{ M}) | \text{Pt} (\text{H}_2)$ if $E_{\text{cell}} = 0.2364 \text{ V}$.
1 atm 1 atm
- Q.49 Calculate the EMF of following cells at 25°C.
(i) $\text{Fe} | \text{Fe}^{2+} (a_1 = 0.3) || \text{Sn}^{2+} (a_2 = 0.1) | \text{Sn}$ $E^0 (\text{Fe}^{2+}/\text{Fe}) = -0.44 \text{ V}$
(ii) $\text{Pt}, \text{H}_2 (2\text{atm}) | \text{HCl} | \text{H}_2 (10 \text{ atm}), \text{Pt}$. $E^0 (\text{Sn}^{2+}/\text{Sn}) = -0.14 \text{ V}$
- Q.50 EMF of the cell $\text{Zn} | \text{ZnSO}_4 (a_1=0.2) || \text{ZnSO}_4(a_2) | \text{Zn}$ is -0.0088V at 25°C. Calculate the value of a_2 .

CONDUCTANCE

Conductivities and cell constant:

- Q.51 The resistance of a conductivity cell filled with 0.01N solution of NaCl is 210 ohm at 18°C. Calculate the equivalent conductivity of the solution. The cell constant of the conductivity cell is 0.88 cm^{-1} .
- Q.52 The molar conductivity of 0.1 M CH_3COOH solution is $4.6 \text{ S cm}^2 \text{ mole}^{-1}$. What is the specific conductivity and resistivity of the solution ?
- Q.53 The conductivity of pure water in a conductivity cell with electrodes of cross sectional area 4 cm^2 and 2 cm apart is $8 \times 10^{-7} \text{ S cm}^{-1}$.
(i) What is resistance of conductivity cell ?
(ii) What current would flow through the cell under an applied potential difference of 1 volt?
- Q.54 Resistivity of 0.1M KCl solution is 213 ohm cm in a conductivity cell. Calculate the cell constant if its resistance is 330 ohm.
- Q.55 Resistance of a 0.1M KCl solution in a conductance cell is 300 ohm and specific conductance of 0.1M KCl is $1.29 \times 10^{-2} \text{ ohm}^{-1} \text{ cm}^{-1}$. The resistance of 0.1M NaCl solution in the same cell is 380 ohm. Calculate the equivalent conductance of the 0.1M NaCl solution.
- Q.56 For 0.01N KCl, the resistivity 709.22 mho cm. Calculate the conductivity and equivalent conductance.
- Q.57 A solution containing 2.08 g of anhydrous barium chloride is 400 CC of water has a specific conductivity $0.0058 \text{ ohm}^{-1} \text{ cm}^{-1}$. What are molar and equivalent conductivities of this solution.
-

Application of Kohlrausch's law:

- Q.58 Equivalent conductance of 0.01 N Na_2SO_4 solution is $112.4 \text{ ohm}^{-1} \text{ cm}^2 \text{ eq}^{-1}$. The equivalent conductance at infinite dilution is $129.9 \text{ ohm}^{-1} \text{ cm}^2$. What is the degree of dissociation in 0.01 N Na_2SO_4 solution?
- Q.59 Specific conductance of a saturated solution of AgBr is $8.486 \times 10^{-7} \text{ ohm}^{-1} \text{ cm}^{-1}$ at 25°C . Specific conductance of pure water at 25°C is $0.75 \times 10^{-6} \text{ ohm}^{-1} \text{ cm}^{-2}$. Λ_m^∞ for KBr, AgNO_3 and KNO_3 are 137.4, 133, 131 ($\text{S cm}^2 \text{ mol}^{-1}$) respectively. Calculate the solubility of AgBr in gm/litre.
- Q.60 Saturated solution of AgCl at 25°C has specific conductance of $1.12 \times 10^{-6} \text{ ohm}^{-1} \text{ cm}^{-1}$. The $\lambda_\infty \text{Ag}^+$ and $\lambda_\infty \text{Cl}^-$ are 54.3 and $65.5 \text{ ohm}^{-1} \text{ cm}^2 / \text{equi.}$ respectively. Calculate the solubility product of AgCl at 25°C .
- Q.61 Hydrofluoric acid is weak acid. At 25°C , the molar conductivity of 0.002M HF is $176.2 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1}$. If its $\Lambda_m^\infty = 405.2 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1}$, calculate its degree of dissociation and equilibrium constant at the given concentration.
- Q.62 The value of Λ_m^∞ for HCl, NaCl and $\text{CH}_3\text{CO}_2\text{Na}$ are 426.1, 126.5 and $91 \text{ S cm}^2 \text{ mol}^{-1}$ respectively. Calculate the value of Λ_m^∞ for acetic acid. If the equivalent conductivity of the given acetic acid is 48.15 at 25°C , calculate its degree of dissociation.
- Q.63 Calculate the specific conductance of a 0.1 M aqueous solution of NaCl at room temperature, given that the mobilities of Na^+ and Cl^- ions at this temperature are 4.26×10^{-8} and $6.80 \times 10^{-8} \text{ m}^2 \text{ v}^{-1} \text{ s}^{-1}$, respectively.
- Q.64 For the strong electrolytes NaOH, NaCl and BaCl_2 the molar ionic conductivities at infinite dilution are 248.1×10^{-4} , 126.5×10^{-4} and $280.0 \times 10^{-4} \text{ mho cm}^2 \text{ mol}^{-1}$ respectively. Calculate the molar conductivity of Ba(OH)_2 at infinite dilution.
- Q.65 At 25°C , $\lambda_\infty(\text{H}^+) = 3.4982 \times 10^{-2} \text{ S m}^2 \text{ mol}^{-1}$ and $\lambda_\infty(\text{OH}^-) = 1.98 \times 10^{-2} \text{ S m}^2 \text{ mol}^{-1}$. Given: Sp. conductance = $5.1 \times 10^{-6} \text{ S m}^{-1}$ for H_2O , determine pH and K_w .
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PROFICIENCY TEST

1. In highly alkaline medium, the anodic process during the electrolytic process is
$$4\text{OH}^- \longrightarrow \text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^-.$$
 2. Compounds of active metals (Zn, Na, Mg) are reducible by H_2 whereas those of noble metals (Cu, Ag, Au) are not reducible.
 3. The mass of a substance deposited on the cathode or anode during electrolysis is given by $w = \frac{EIt}{F}$.
 4. Faraday's second law of electrolysis is related to the equivalent, mass of the electrolyte.
 5. Equivalent conductance at infinite dilution of salt AB is equal to the sum of equivalent conductances of ions, A^+ and B^- at infinite dilution.
 6. The standard reduction potential of $\text{Cl}^-|\text{AgCl}|\text{Ag}$ half-cell is related to that of $\text{Ag}^+|\text{Ag}$ half-cell through the expression $E_{\text{Ag}^+|\text{Ag}}^\circ = E_{\text{Cl}^-|\text{AgCl}|\text{Ag}}^\circ + \frac{RT}{F} \ln K_{\text{SP}}(\text{AgCl})$.
 7. The cell potential is given by $E_{\text{cell}} = E_{\text{RP}(\text{cathode})} - E_{\text{RP}(\text{anode})}$.
 8. A half-cell reaction is $\text{A}^{(x+n)} + n\text{e}^- \longrightarrow \text{A}^{x+}$. It is possible to determine the value of n from the measurements of cell potential.
 9. In a galvanic cell, the half-cell with higher reduction potential acts as a reducing agent.
 10. In an electrode concentration cell, the cell reaction $\text{Zn}(c_1) \longrightarrow \text{Zn}(c_2)$ will be spontaneous if $c_1 > c_2$.
 11. The absolute value of electrode potential cannot be determined.
 12. All chemical reactions used in galvanic cells are redox reactions.
 13. The amount of the product formed by the passage of 1 coulomb of electricity through electrolyte is called electrochemical equivalent of the substance.
 14. The redox reaction involved in galvanic cell is a non-spontaneous process.
 15. In galvanic cell, the cathode is a -ve terminal of the cell.
 16. The specific conductance of a 0.1 N KCl solution at 23°C is $0.012 \text{ ohm}^{-1} \text{ cm}^{-1}$. The resistance of the cell containing the solution at the same temperature was found to be 55 ohms. The cell constant is _____.
 17. Dilute sulphuric acid on electrolysis liberates _____ at the anode.
 18. The electrical conductivity of a solution of acetic acid will _____ if a solution of sodium hydroxide is added.
 19. A cation having a _____ reduction potential is preferentially reduced at the cathode.
-

20. When an aqueous solution of sodium sulphate is electrolysed, the gases liberated at the anode & cathode are _____ and _____, respectively.
21. A cell in which two electrodes of the same metal are dipped in solutions of metal ion of different concentrations is called _____.
22. The half-cell involving the reaction,

$$\text{Cr}_2\text{O}_7^{2-}(\text{aq.}) + 14\text{H}^+(\text{aq.}) + 6\text{e}^- \longrightarrow 2\text{Cr}^{3+}(\text{aq.}) + 7\text{H}_2\text{O}$$
 is represented as _____.
23. During discharge of lead storage battery, the overall reaction is _____.
24. In the calomel half-cell, the reduction reaction is _____.
25. Temperature coefficient and change in enthalpy are related by the expression _____.
26. In salt bridge, the electrolyte used should be _____.
27. In electrochemical cell, the electrical neutrality in two half cells is maintained by _____.
28. The E° value for $\text{H}_2 \longrightarrow 2\text{H}^+ + 2\text{e}^-$ is _____.
29. E°_{cell} of $E^\circ_{\text{oxi.}}$ (anode) + _____.
30. Coulomb refers to _____ of electricity while ampere refers to _____ at which it flows.
31. The cathodic reactions always involve _____.
32. During electrolysis of aqueous solution of CuSO_4 using Pt electrodes the product at anode is _____.
33. The quantity of electricity required for complete reduction of 0.5 mole MnO_4^- to Mn^{2+} is _____ C.
34. During electrolysis process _____ energy is converted into _____.
35. $\wedge_{\text{eq}} \times \text{normality} = \text{_____}$.
-

EXERCISE II

- Q.1 Same quantity of electricity is being used to liberate iodine (at anode) and a metal x (at cathode). The mass of x deposited is 0.617g and the iodine is completely reduced by 46.3 cc of 0.124M sodium thiosulphate. Find the equivalent mass of x.
- Q.2 The standard reduction potential values, $E^0(\text{Bi}^{3+}|\text{Bi})$ and $E^0(\text{Cu}^{2+}|\text{Cu})$ are 0.226V and 0.344V respectively. A mixture of salts of bismuth and copper at unit concentration each is electrolysed at 25°C. to what value can $[\text{Cu}^{2+}]$ be brought down before bismuth starts to deposit, in electrolysis.
- Q.3 In a fuel cell, H_2 & O_2 react to produce electricity. In the process, H_2 gas is oxidized at the anode & O_2 at the cathode. If 67.2 litre of H_2 at STP react in 15 minutes, what is the average current produced? If the entire current is used for electrode deposition of Cu from Cu (II) solution, how many grams of Cu will be deposited?
Anode : $\text{H}_2 + 2\text{OH}^- \longrightarrow 2\text{H}_2\text{O} + 2\text{e}^-$ Cathode : $\text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^- \longrightarrow 4\text{OH}^-$
- Q.4 One of the methods of preparation of per disulphuric acid, $\text{H}_2\text{S}_2\text{O}_8$, involve electrolytic oxidation of H_2SO_4 at anode ($2\text{H}_2\text{SO}_4 \rightarrow \text{H}_2\text{S}_2\text{O}_8 + 2\text{H}^+ + 2\text{e}^-$) with oxygen and hydrogen as by-products. In such an electrolysis, 9.722 L of H_2 and 2.35 L of O_2 were generated at STP. What is the weight of $\text{H}_2\text{S}_2\text{O}_8$ formed?
- Q.5 During the discharge of a lead storage battery the density of sulphuric acid fell from 1.294 to 1.139 $\text{g}\cdot\text{ml}^{-1}$. H_2SO_4 of density 1.294 $\text{g}\cdot\text{mL}^{-1}$ is 39% and that of density 1.39 $\text{g}\cdot\text{mL}^{-1}$ is 20% by weight. The battery holds 3.5L of acid and the volume practically remains constant during the discharge. Calculate the number of ampere hours for which the battery must have been used. The discharging reactions are:
 $\text{Pb} + \text{SO}_4^{2-} \rightarrow \text{PbSO}_4 + 2\text{e}^-$ (anode)
 $\text{PbO}_2 + 4\text{H}^+ + \text{SO}_4^{2-} + 2\text{e}^- \rightarrow \text{PbSO}_4 + 2\text{H}_2\text{O}$ (cathode)
- Q.6 The emf of the cells obtained by combining Zn and Cu electrode of a Daniel cell with N calomel electrode in two different arrangements are 1.083V and 0.018V respectively at 25°C. If the standard reduction potential of N calomel electrode is 0.28V and that of Zn is -0.76 V, find the emf of Daniel cell.
- Q.7 Given the standard reduction potentials $\text{TI}^+ + \text{e}^- \rightarrow \text{TI}$, $E^0 = -0.34\text{V}$ and $\text{TI}^{3+} + 2\text{e}^- \rightarrow \text{TI}^+$, $E^0 = 1.25\text{V}$. Examine the spontaneity of the reaction, $3\text{TI}^+ \rightarrow 2\text{TI} + \text{TI}^{3+}$. Also find E^0 for this disproportionation.
- Q.8 The emf of the cell $\text{Ag}|\text{AgI}|\text{KI}(0.05\text{M})||\text{AgNO}_3(0.05\text{M})|\text{Ag}$ is 0.788V. Calculate the solubility product of AgI.
- Q.9 The cell $\text{Pt}, \text{H}_2(1\text{ atm})|\text{H}^+(\text{pH}=x)||\text{Normal calomel Electrode}$ has an EMF of 0.67V at 25°C. Calculate the pH of the solution. The oxidation potential of the calomel electrode on hydrogen scale is -0.28 V.
- Q.10 Estimate the cell potential of a Daniel cell having 1 M Zn^{++} & originally having 1 M Cu^{++} after sufficient NH_3 has been added to the cathode compartment to make NH_3 concentration 2 M.
 K_f for $[\text{Cu}(\text{NH}_3)_4]^{2+} = 1 \times 10^{12}$, E^0 for the reaction,
 $\text{Zn} + \text{Cu}^{2+} \longrightarrow \text{Zn}^{2+} + \text{Cu}$ is 1.1 V.
- Q.11 Consider the cell $\text{Ag}|\text{AgBr}(\text{s})|\text{Br}^-||\text{AgCl}(\text{s}), \text{Ag}|\text{Cl}^-$ at 25°C. The solubility product constants of AgBr & AgCl are respectively 5×10^{-13} & 1×10^{-10} . For what ratio of the concentrations of Br^- & Cl^- ions would the emf of the cell be zero?
- Q.12 The $\text{p}K_{\text{sp}}$ of AgI is 16.07. If the E^0 value for $\text{Ag}^+|\text{Ag}$ is 0.7991 V. Find the E^0 for the half cell reaction $\text{AgI}(\text{s}) + \text{e}^- \longrightarrow \text{Ag} + \text{I}^-$.
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- Q.13 Voltage of the cell $\text{Pt}, \text{H}_2(1 \text{ atm})|\text{HOCN}(1.3 \times 10^{-3} \text{ M})||\text{Ag}^+(0.8 \text{ M})|\text{Ag(s)}$ is 0.982 V . Calculate the K_a for HOCN . Neglect $[\text{H}^+]$ because of oxidation of $\text{H}_2(\text{g})$.
 $\text{Ag}^+ + \text{e} \longrightarrow \text{Ag(s)} = 0.8 \text{ V}$.
- Q.14 The normal oxidation potential of Zn referred to SHE is 0.76V and that of Cu is -0.34V at 25°C . When excess of Zn is added to CuSO_4 , Zn displaces Cu^{2+} till equilibrium is reached. What is the ratio of Zn^{2+} to Cu^{2+} ions at equilibrium?
- Q.15 Calculate the potential of an indicator electrode versus the standard hydrogen electrode, which originally contained 0.1M MnO_4^- and 0.8M H^+ and which was treated with 90% of the Fe^{2+} necessary to reduce all the MnO_4^- to Mn^{2+} .
 $\text{MnO}_4^- + 8\text{H}^+ + 5\text{e} \rightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O}, E^0 = 1.51\text{V}$
- Q.16 K_d for complete dissociation of $[\text{Ag}(\text{NH}_3)_2]^+$ into Ag^+ and 2NH_3 is 6×10^{-8} . Calculate E^0 for the following half reaction; $\text{Ag}(\text{NH}_3)_2^+ + \text{e}^- \rightarrow \text{Ag} + 2\text{NH}_3$
 $\text{Ag}^+ + \text{e}^- \rightarrow \text{Ag}, E^0 = 0.799 \text{ V}$
- Q.17 The overall formation constant for the reaction of 6 mol of CN^- with cobalt (II) is 1×10^{19} . The standard reduction potential for the reaction $[\text{Co}(\text{CN})_6]^{3-} + \text{e}^- \rightarrow \text{Co}(\text{CN})_6^{4-}$ is -0.83 V . Calculate the formation constant of $[\text{Co}(\text{CN})_6]^{3-}$
 Given $\text{Co}^{3+} + \text{e}^- \rightarrow \text{Co}^{2+}; E^0 = 1.82 \text{ V}$
- Q.18 Calculate the emf of the cell
 $\text{Pt}, \text{H}_2(1.0 \text{ atm}) | \text{CH}_3\text{COOH}(0.1\text{M}) || \text{NH}_3(\text{aq}, 0.01\text{M}) | \text{H}_2(1.0 \text{ atm}),$
 $\text{Pt } K_a(\text{CH}_3\text{COOH}) = 1.8 \times 10^{-5}, K_b(\text{NH}_3) = 1.8 \times 10^{-5}.$
- Q.19 A current of 3 amp was passed for 2 hour through a solution of CuSO_4 , 3 g of Cu^{2+} ions were deposited as Cu at cathode. Calculate percentage current efficiency of the process.
- Q.20 The Edison storage cell is represented as $\text{Fe(s)} | \text{FeO(s)} | \text{KOH(aq)} | \text{Ni}_2\text{O}_3(\text{s}) | \text{Ni(s)}$ The half-cell reaction are
 $\text{Ni}_2\text{O}_3(\text{s}) + \text{H}_2\text{O(l)} + 2\text{e}^- \rightleftharpoons 2\text{NiO(s)} + 2\text{OH}^-, E^0 = + 0.40\text{V}$
 $\text{FeO(s)} + \text{H}_2\text{O(l)} + 2\text{e}^- \rightleftharpoons \text{Fe(s)} + 2\text{OH}^-, E^0 = - 0.87\text{V}$
- (i) What is the cell reaction?
 (ii) What is the cell e.m.f.? How does it depend on the concentration of KOH?
 (iii) What is the maximum amount of electrical energy that can be obtained from one mole of Ni_2O_3 ?
- Q.21 For the galvanic cell : $\text{Ag}|\text{AgCl(s)}|\text{KCl}(0.2\text{M})||\text{KBr}(0.001 \text{ M})|\text{AgBr(s)}|\text{Ag},$
 Calculate the EMF generated and assign correct polarity to each electrode for a spontaneous process after taking into account the cell reaction at 25°C .
 $[\text{K}_{\text{sp}}(\text{AgCl}) = 2.8 \times 10^{-10}; \text{K}_{\text{sp}}(\text{AgBr}) = 3.3 \times 10^{-13}]$
- Q.22 An aqueous solution of NaCl on electrolysis gives $\text{H}_{2(\text{g})}$, $\text{Cl}_{2(\text{g})}$ and NaOH according to the reaction:
 $2\text{Cl}^-_{(\text{aq})} + 2\text{H}_2\text{O} \rightleftharpoons 2\text{OH}^-_{(\text{aq})} + \text{H}_{2(\text{g})} + \text{Cl}_{2(\text{g})}$
 A direct current of 25 amperes with a current efficiency of 62% is passed through 20 liters of NaCl solution (20% by weight). Write down the reactions taking place at the anode and the cathode. How long will it take to produce 1Kg of Cl_2 ? What will be the molarity of the solution with respect to hydroxide ion? (Assume no loss due to evaporation).
- Q.23 An acidic solution of Cu^{2+} salt containing 0.4 g of Cu^{2+} is electrolyzed until all the copper is deposited. The electrolysis is continued for seven more minutes with the volume of solution kept at 100 ml and the current at 1.2 amp. Calculate the volume of gases evolved at NTP during the entire electrolysis.
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- Q.24 In the refining of silver by electrolytic method what will be the weight of 100 gm Ag anode if 5 ampere current is passed for 2 hours? Purity of silver is 95% by weight.
- Q.25 Hydrogen peroxide can be prepared by successive reactions:
 $2\text{NH}_4\text{HSO}_4 \rightarrow \text{H}_2 + (\text{NH}_4)_2\text{S}_2\text{O}_8$
 $(\text{NH}_4)_2\text{S}_2\text{O}_8 + 2\text{H}_2\text{O} \rightarrow 2\text{NH}_4\text{HSO}_4 + \text{H}_2\text{O}_2$
 The first reaction is an electrolytic reaction the second is steam distillation. What amount of current would have to be used in first reaction to produce enough intermediate to yield 100 gm pure H_2O_2 per hour? Assume 50% anode current efficiency.
- Q.26 Dal lake has water 8.2×10^{12} litre approximately. A power reactor produces electricity at the rate of 1.5×10^6 coulomb per second at an appropriate voltage. How many years would it take to electrolyse the lake?
- Q.27 The standard reduction potential for $\text{Cu}^{2+} / \text{Cu}$ is 0.34 V. Calculate the reduction potential at $\text{pH} = 14$ for the above couple. K_{sp} of $\text{Cu}(\text{OH})_2$ is 1×10^{-19} .
- Q.28 Calculate E° for the following reactions at 298 K,
 $\text{Ag}(\text{NH}_3)_2^+ + e^- \rightleftharpoons \text{Ag} + 2\text{NH}_3$
 $\text{Ag}(\text{CN})_2^- + e^- \rightleftharpoons \text{Ag} + 2\text{CN}^-$
 Given: $E^\circ_{\text{Ag}^+/\text{Ag}} = 0.7991 \text{ V}$, $K_{\text{Ins}}[\text{Ag}(\text{NH}_3)_2^+] = 6.02 \times 10^{-8}$ and $K_{\text{Ins}}[\text{Ag}(\text{CN})_2^-] = 1.995 \times 10^{-19}$
- Q.29 Determine the degree of hydrolysis and hydrolysis constant of aniline hydrochloride in M/32 solution of salt at 298 K from the following cell data at 298 K.
 $\text{Pt} | \text{H}_2 (1 \text{ atm}) | \text{H}^+(1\text{M}) || \text{M}/32 \text{ C}_6\text{H}_5\text{NH}_3\text{Cl} | \text{H}_2 (1 \text{ atm}) | \text{Pt}$; $E_{\text{cell}} = -0.188 \text{ V}$.
- Q.30 The emf of the cell, $\text{Pt} | \text{H}_2 (1 \text{ atm}), | \text{H}^+ (0.1 \text{ M}, 30 \text{ ml}) || \text{Ag}^+ (0.8 \text{ M}) | \text{Ag}$ is 0.9 V. Calculate the emf when 40 ml of 0.05 M NaOH is added.
- Q.31 Given, $E^\circ = -0.268 \text{ V}$ for the $\text{Cl}^- | \text{PbCl}_2 | \text{Pb}$ couple and -0.126 V for the $\text{Pb}^{2+} | \text{Pb}$ couple, determine K_{sp} for PbCl_2 at 25°C ?
- Q.32 The equivalent conductance of 0.10 N solution of MgCl_2 is $97.1 \text{ mho cm}^2 \text{ eq}^{-1}$ at 25°C . a cell with electrode that are 1.5 cm^2 in surface area and 0.5 cm apart is filled with 0.1 N MgCl_2 solution. How much current will flow when potential difference between the electrodes is 5 volt.
- Q.33 A dilute aqueous solution of KCl was placed between two electrodes 10 cm apart, across which a potential of 6 volt was applied. How far would the K^+ ion move in 2 hours at 25°C ? Ionic conductance of K^+ ion at infinite dilution at 25°C is $73.52 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1}$?
- Q.34 When a solution of specific conductance $1.342 \text{ ohm}^{-1} \text{ metre}^{-1}$ was placed in a conductivity cell with parallel electrodes, the resistance was found to be 170.5 ohm. Area of electrodes is $1.86 \times 10^{-4} \text{ m}^2$. Calculate separation of electrodes.
- Q.35 The specific conductance at 25°C of a saturated solution of SrSO_4 is $1.482 \times 10^{-4} \text{ ohm}^{-1} \text{ cm}^{-1}$ while that of water used is $1.5 \times 10^{-6} \text{ mho cm}^{-1}$. Determine at 25°C the solubility in gm per litre of SrSO_4 in water. Molar ionic conductance of Sr^{2+} and SO_4^{2-} ions at infinite dilution are 59.46 and $79.8 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1}$ respectively. [Sr = 87.6 , S = 32 , O = 16]
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- Q.36 A lead storage cell is discharged which causes the H_2SO_4 electrolyte to change from a concentration of 34.6 % by weight (density 1.261 g ml^{-1} at 25°C) to 27 % by weight. The original volume of electrolyte is one litre. Calculate the total charge released at anode of the battery. Note that the water is produced by the cell reaction as H_2SO_4 is used up. Over all reaction is
- $$\text{Pb(s)} + \text{PbO}_2\text{(s)} + 2\text{H}_2\text{SO}_4\text{(l)} \longrightarrow 2\text{PbSO}_4\text{(s)} + 2\text{H}_2\text{O(l)}$$
- Q.37 Assume that impure copper contains only iron, silver and a gold as impurities. After passage of 140 A, for 482.5s of the mass of the anode decreased by 22.260g and the cathode increased in mass by 22.011 g. Estimate the % iron and % copper originally present.
- Q.38 100ml $\text{CuSO}_4\text{(aq)}$ was electrolyzed using inert electrodes by passing 0.965 A till the pH of the resulting solution was 1. The solution after electrolysis was neutralized, treated with excess KI and titrated with 0.04M $\text{Na}_2\text{S}_2\text{O}_3$. Volume of $\text{Na}_2\text{S}_2\text{O}_3$ required was 35 ml. Assuming no volume change during electrolysis, calculate:
(a) duration of electrolysis if current efficiency is 80% (b) initial concentration (M) of CuSO_4 .
- Q.39 Calculate the equilibrium constant for the reaction:

$$3\text{Sn(s)} + 2\text{Cr}_2\text{O}_7^{2-} + 28\text{H}^+ \longrightarrow 3\text{Sn}^{4+} + 4\text{Cr}^{3+} + 14\text{H}_2\text{O}$$

$$E^0 \text{ for Sn/Sn}^{2+} = 0.136 \text{ V} \quad E^0 \text{ for Sn}^{2+}/\text{Sn}^{4+} = -0.154 \text{ V}$$

$$E^0 \text{ for Cr}_2\text{O}_7^{2-}/\text{Cr}^{3+} = 1.33 \text{ V}$$
- Q.40 Calculate the equilibrium concentrations of all ions in an ideal solution prepared by mixing 25.00 mL of 0.100M Ti^+ with 25.00mL of 0.200M Co^{3+} .

$$E^0 (\text{Ti}^+/\text{Ti}^{3+}) = -1.25 \text{ V} ; E^0 (\text{Co}^{3+}/\text{Co}^{2+}) = 1.84 \text{ V}$$
- Q.41 Calculate the voltage, E, of the cell at 25°C

$$\text{Mn(s)} | \text{Mn(OH)}_2\text{(s)} | \text{Mn}^{2+}(\text{x M}), \text{OH}^-(1.00 \times 10^{-4}\text{M}) || \text{Cu}^{2+}(0.675\text{M}) | \text{Cu(s)}$$
 given that $K_{\text{sp}} = 1.9 \times 10^{-13}$ for $\text{Mn(OH)}_2\text{(s)}$ $E^0 (\text{Mn}^{2+}/\text{Mn}) = -1.18 \text{ V}$
- Q.42 Calculate the voltage, E, of the cell

$$\text{Ag(s)} | \text{AgIO}_3\text{(s)} | \text{Ag}^+(\text{x M}), \text{HIO}_3 (0.300\text{M}) || \text{Zn}^{2+}(0.175\text{M}) | \text{Zn(s)}$$
 if $K_{\text{sp}} = 3.02 \times 10^{-8}$ for $\text{AgIO}_3\text{(s)}$ and $K_{\text{a}} = 0.162$ for HIO_3 .
- Q.43 The voltage of the cell

$$\text{Pb(s)} | \text{PbSO}_4\text{(s)} | \text{NaHSO}_4(0.600\text{M}) || \text{Pb}^{2+}(2.50 \times 10^{-5}\text{M}) | \text{Pb(s)}$$
 is $E = +0.061 \text{ V}$. Calculate $K_2 = [\text{H}^+] [\text{SO}_4^{2-}] / [\text{HSO}_4^-]$, the dissociation constant for HSO_4^- .
 Given : $\text{Pb(s)} + \text{SO}_4^{2-}(\text{aq}) \rightleftharpoons \text{PbSO}_4\text{(s)} + 2\text{e}^-$ ($E^0 = 0.356$) $E^0(\text{Pb}^{2+}/\text{Pb}) = -0.126 \text{ V}$
- Q.44 The voltage of the cell

$$\text{Zn(s)} | \text{Zn(CN)}_4^{2-}(0.450\text{M}), \text{CN}^-(2.65 \times 10^{-3}\text{M}) || \text{Zn}^{2+}(3.84 \times 10^{-4}\text{M}) | \text{Zn(s)}$$
 is $E = +0.099 \text{ V}$. Calculate the constant K_{f} for $\text{Zn}^{2+} + 4\text{CN}^- \rightleftharpoons \text{Zn(CN)}_4^{2-}$, the only $\text{Zn}^{2+} + \text{CN}^-$ complexation reaction of importance.
- Q.45 An external current source giving a current of 5.0 A was joined with Daniel cell and removed after 10 hrs. Before passing the current the LHE and RHE contained 1L each of 1M Zn^{2+} and Cu^{2+} respectively. Find the EMF supplied by the Daniel cell after removal of the external current source. E^0 of Zn^{2+}/Zn and Cu^{2+}/Cu at 25°C is -0.76 and $+0.34\text{V}$ respectively.
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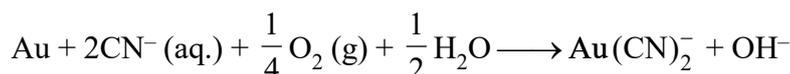
- Q.46 Determine at 298 for cell
 $\text{Pt} | \text{Q}, \text{QH}_2, \text{H}^+ || 1\text{M KCl} | \text{Hg}_2\text{Cl}_2(\text{s}) | \text{Hg}(\text{l}) | \text{Pt}$
- (a) it's emf when $\text{pH} = 5.0$
 (b) the pH when $E_{\text{cell}} = 0$
 (c) the positive electrode when $\text{pH} = 7.5$
 given $E^0_{\text{RP(RHS)}} = 0.28, E^0_{\text{RP(LHS)}} = 0.699$
- Q.47 At 25°C , $\Delta H_f(\text{H}_2\text{O}, \text{l}) = -56700 \text{ cal/mol}$ and energy of ionization of $\text{H}_2\text{O}(\text{l}) = 19050 \text{ cal/mol}$. What will be the reversible EMF at 25°C of the cell,
 $\text{Pt} | \text{H}_2(\text{g}) (1 \text{ atm}) | \text{H}^+ || \text{OH}^- | \text{O}_2(\text{g}) (1 \text{ atm}) | \text{Pt}$, if at 26°C the emf increases by 0.001158 V .
- Q.48 Calculate the cell potential of a cell having reaction: $\text{Ag}_2\text{S} + 2\text{e}^- \rightleftharpoons 2\text{Ag} + \text{S}^{2-}$ in a solution buffered at $\text{pH} = 3$ and which is also saturated with $0.1 \text{ M H}_2\text{S}$.
 For H_2S : $K_1 = 10^{-8}$ and $K_2 = 1.1 \times 10^{-13}$, $K_{\text{sp}}(\text{Ag}_2\text{S}) = 2 \times 10^{-49}$, $E^{\circ}_{\text{Ag}^+/\text{Ag}} = 0.8$.
- Q.49 Calculate the solubility and solubility product of $\text{Co}_2[\text{Fe}(\text{CN})_6]$ in water at 25°C from the following data:
 Conductivity of a saturated solution of $\text{Co}_2[\text{Fe}(\text{CN})_6]$ is $2.06 \times 10^{-6} \Omega^{-1} \text{ cm}^{-1}$ and that of water used $4.1 \times 10^{-7} \Omega^{-1} \text{ cm}^{-1}$. The ionic molar conductivities of Co^{2+} and $\text{Fe}(\text{CN})_6^{4-}$ are $86.0 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ and $444.0 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$.
- Q.50 A sample of water from a large swimming pool has a resistance of 9200Ω at 25°C when placed in a certain conductance cell. When filled with 0.02 M KCl solution, the cell has a resistance of 85Ω at 25°C . 500 gm of NaCl were dissolved in the pool, which was thoroughly stirred. A sample of this solution gave a resistance of 7600Ω . Calculate the volume of water in the pool.
 Given : Molar conductance of NaCl at that concentration is $126.5 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ and molar conductivity of KCl at 0.02 M is $138 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$.
-

EXERCISE III

- Q.1 One gm metal M^{+2} was discharged by the passage of 1.81×10^{22} electrons. What is the atomic weight of metal?
(A) 33.35 (B) 133.4 (C) 66.7 (D) 55
- Q.2 One mole of electron passes through each of the solution of $AgNO_3$, $CuSO_4$ and $AlCl_3$ when Ag, Cu and Al are deposited at cathode. The molar ratio of Ag, Cu and Al deposited are
(A) 1 : 1 : 1 (B) 6 : 3 : 2 (C) 6 : 3 : 1 (D) 1 : 3 : 6
- Q.3 Salts of A (atomic weight = 7), B (atomic weight = 27) and C (atomic weight = 48) were electrolysed under identical conditions using the same quantity of electricity. It was found that when 2.1 g of A was deposited, the weights of B and C deposited were 2.7 and 7.2 g. The valencies of A, B and C respectively are
(A) 3, 1 and 2 (B) 1, 3 and 2 (C) 3, 1 and 3 (D) 2, 3 and 2
- Q.4 The density of Cu is 8.94 g cm^{-3} . The quantity of electricity needed to plate an area $10 \text{ cm} \times 10 \text{ cm}$ to a thickness of 10^{-2} cm using $CuSO_4$ solution would be
(A) 13586 C (B) 27172 C (C) 40758 C (D) 20348 C
- Q.5 During electrolysis of an aqueous solution of sodium sulphate, 2.4 L of oxygen at STP was liberated at anode. The volume of hydrogen at STP, liberated at cathode would be
(A) 1.2 L (B) 2.4 L (C) 2.6 L (D) 4.8 L
- Q.6 During electrolysis of an aqueous solution of $CuSO_4$ using copper electrodes, if 2.5 g of Cu is deposited at cathode, then at anode
(A) 890 ml of Cl_2 at STP is liberated (B) 445 ml of O_2 at STP is liberated
(C) 2.5 g of copper is deposited (D) a decrease of 2.5 g of mass takes place
- Q.7 An aqueous solution containing one mole per litre each of $Cu(NO_3)_2$, $AgNO_3$, $Hg_2(NO_3)_2$, $Mg(NO_3)_2$ is being electrolysed by using inert electrodes. The value of standard potentials are
 $E^\circ_{Ag^+|Ag} = 0.80V$, $E^\circ_{Hg_2^{2+}|Hg} = 0.79V$, $E^\circ_{Cu^{2+}|Cu} = 0.34V$ and $E^\circ_{Mg^{2+}|Mg} = -2.3V$
With increasing voltage, the sequence of deposition of metals on the cathode will be
(A) Ag, Hg, Cu, Mg (B) Mg, Cu, Hg, Ag (C) Ag, Hg, Cu (D) Cu, Hg, Ag
- Q.8 The charge required for the oxidation of one mole Mn_3O_4 into MnO_4^{2-} in presence of alkaline medium is
(A) $5 \times 96500 \text{ C}$ (B) 96500 C (C) $10 \times 96500 \text{ C}$ (D) $2 \times 96500 \text{ C}$
- Q.9 The cost at 5 paise / KWH of operating an electric motor for 8 hours which takes 15 amp at 110 V is
(A) Rs. 66 (B) 66 paise (C) 37 paise (D) Rs. 6.60
- Q.10 A solution of sodium sulphate in water is electrolysed using inert electrodes. The products at the cathode and anode are respectively.
(A) H_2 , O_2 (B) O_2 , H_2 (C) O_2 , Na (D) none
-

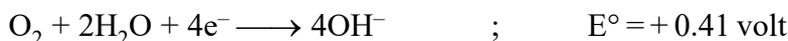
- Q.11 When an aqueous solution of lithium chloride is electrolysed using graphite electrodes
 (A) Cl_2 is liberated at the anode.
 (B) Li is deposited at the cathode
 (C) as the current flows, pH of the solution around the cathode remains constant
 (D) as the current flows, pH of the solution around the cathode decreases.
- Q.12 If the pressure of H_2 gas is increased from 1 atm to 100 atm keeping H^+ concentration constant at 1 M, the change in reduction potential of hydrogen half cell at 25°C will be
 (A) 0.059 V (B) 0.59 V (C) 0.0295 V (D) 0.118 V
- Q.13 The equilibrium constant for the reaction
 $\text{Sr(s)} + \text{Mg}^{+2}(\text{aq}) \rightleftharpoons \text{Sr}^{+2}(\text{aq}) + \text{Mg(s)}$ is 2.69×10^{12} at 25°C
 The E° for a cell made up of the Sr/Sr^{+2} and Mg^{+2}/Mg half cells
 (A) 0.3667 V (B) 0.7346 V (C) 0.1836 V (D) 0.1349 V
- Q.14 A silver wire dipped in 0.1 M HCl solution saturated with AgCl develops a potential of -0.25 V. If $E^\circ_{\text{Ag}/\text{Ag}^+} = -0.799$ V, the K_{sp} of AgCl in pure water will be
 (A) 2.95×10^{-11} (B) 5.1×10^{-11} (C) 3.95×10^{-11} (D) 1.95×10^{-11}

- Q.15 Consider the reaction of extraction of gold from its ore



Use the following data to calculate ΔG° for the reaction

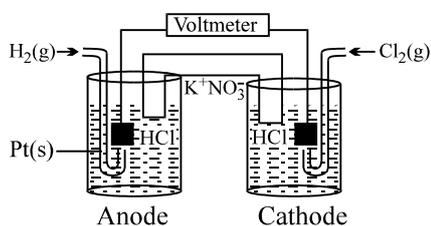
$$K_f \{ \text{Au}(\text{CN})_2^- \} = X$$



(A) $-RT \ln X + 1.29 F$ (B) $-RT \ln X - 2.11 F$

(C) $-RT \ln \frac{1}{X} + 2.11 F$ (D) $-RT \ln X - 1.29 F$

- Q.16 Consider the following Galvanic cell.



By what value the cell voltage change when concentration of ions in anodic and cathodic compartments both increased by factor of 10 at 298 K

(A) +0.0591 (B) -0.0591 (C) -0.1182 (D) 0

- Q.17 For the cell



The measured potential at 25°C is

(A) -0.1 V (B) -0.5 (C) -0.041 (D) none

Q.18 For the fuel cell reaction $2\text{H}_2(\text{g}) + \text{O}_2(\text{g}) \longrightarrow 2\text{H}_2\text{O}(\text{l})$; $\Delta_f H_{298}^\circ(\text{H}_2\text{O}, \text{l}) = -285.5 \text{ kJ/mol}$

What is ΔS_{298}° for the given fuel cell reaction?

Given: $\text{O}_2(\text{g}) + 4\text{H}^+(\text{aq}) + 4\text{e}^- \longrightarrow 2\text{H}_2\text{O}(\text{l})$ $E^\circ = 1.23 \text{ V}$

(A) -0.322 J/K (B) -0.635 kJ/K (C) 3.51 kJ/K (D) -0.322 kJ/K

Q.19 If $E_{\text{Au}^+/\text{Au}}^\circ$ is 1.69 V & $E_{\text{Au}^{3+}/\text{Au}}^\circ$ is 1.40 V , then $E_{\text{Au}^{3+}/\text{Au}^+}^\circ$ will be

(A) 0.19 V (B) 2.945 V (C) 1.255 V (D) none

Question No. 20 to 21 (2 questions)

Copper reduces NO_3^- into NO and NO_2 depending upon conc. of HNO_3 in solution. Assuming

$[\text{Cu}^{2+}] = 0.1 \text{ M}$, and $P_{\text{NO}} = P_{\text{NO}_2} = 10^{-3} \text{ atm}$ and using given data answer the following questions:

$E_{\text{Cu}^{2+}/\text{Cu}}^\circ = +0.34 \text{ volt}$; $E_{\text{NO}_3^-/\text{NO}}^\circ = +0.96 \text{ volt}$

$E_{\text{NO}_3^-/\text{NO}_2}^\circ = +0.79 \text{ volt}$; at 298 K $\frac{RT}{F} (2.303) = 0.06 \text{ volt}$

Q.20 E_{Cell} for reduction of $\text{NO}_3^- \longrightarrow \text{NO}$ by $\text{Cu}(\text{s})$, when $[\text{HNO}_3] = 1 \text{ M}$ is [At $T = 298$]

(A) ~ 0.61 (B) ~ 0.71 (C) ~ 0.51 (D) ~ 0.81

Q.21 At what HNO_3 concentration thermodynamic tendency for reduction of NO_3^- into NO and NO_2 by copper is same?

(A) $10^{1.23} \text{ M}$ (B) $10^{0.56} \text{ M}$ (C) $10^{0.66} \text{ M}$ (D) $10^{0.12} \text{ M}$

Q.22 The resistance of 0.5 M solution of an electrolyte in a cell was found to be 50Ω . If the electrodes in the cell are 2.2 cm apart and have an area of 4.4 cm^2 then the molar conductivity (in $\text{S m}^2 \text{ mol}^{-1}$) of the solution is

(A) 0.2 (B) 0.02 (C) 0.002 (D) None of these

Q.23 Equivalent conductance of 0.1 M HA (weak acid) solution is $10 \text{ Scm}^2 \text{ equivalent}^{-1}$ and that at infinite dilution is $200 \text{ Scm}^2 \text{ equivalent}^{-1}$ Hence pH of HA solution is

(A) 1.3 (B) 1.7 (C) 2.3 (D) 3.7

Q.24 If x is specific resistance of the electrolyte solution and y is the molarity of the solution, then \wedge_m is given by

(A) $\frac{1000x}{y}$ (B) $1000 \frac{y}{x}$ (C) $\frac{1000}{xy}$ (D) $\frac{xy}{1000}$

Q.25 The dissociation constant of n-butyric acid is 1.6×10^{-5} and the molar conductivity at infinite dilution is $380 \times 10^{-4} \text{ Sm}^2 \text{ mol}^{-1}$. The specific conductance of the 0.01 M acid solution is

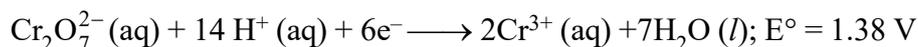
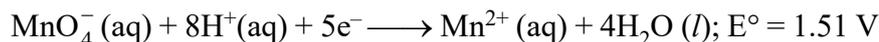
(A) $1.52 \times 10^{-5} \text{ Sm}^{-1}$ (B) $1.52 \times 10^{-2} \text{ Sm}^{-1}$
(C) $1.52 \times 10^{-3} \text{ Sm}^{-1}$ (D) None

EXERCISE IV

OBJECTIVE

- Q.1 The standard reduction potentials of Cu^{2+}/Cu and $\text{Cu}^{2+}/\text{Cu}^+$ are 0.337 and 0.153 V respectively. The standard electrode potential of Cu^+/Cu half cell is
(A) 0.184 V (B) 0.827 V (C) 0.521 V (D) 0.490 V [JEE 1997]
- Q.2 A standard hydrogen electrode has zero electrode potential because
(A) hydrogen is easier to oxidise
(B) this electrode potential is assumed to be zero
(C) hydrogen atom has only one electron
(D) hydrogen is the lightest element. [JEE 1997]
- Q.3 The standard reduction potential values of the three metallic cations X, Y, Z are 0.52, -3.03 , and -1.18 V respectively. The order of reducing power of the corresponding metals is
(A) $Y > Z > X$ (B) $X > Y > Z$ (C) $Z > Y > X$ (D) $Z > X > Y$ [JEE 1998]
- Q.4 A gas X at 1 atm is bubbled through a solution containing a mixture of 1 M Y and 1 M Z at 25°C . If the reduction potential of $Z > Y > X$, then
(A) Y will oxidise X and not Z (B) Y will oxidise Z and X
(C) Y will oxidise both X and Z (D) Y will reduce both X and Z. [JEE 1999]
- Q.5 For the electrochemical cell, $\text{M} | \text{M}^+ || \text{X}^- | \text{X}$, $E^\circ(\text{M}^+/\text{M}) = 0.44$ V and $E^\circ(\text{X}/\text{X}^-) = 0.33$ V. From this data, one can deduce that
(A) $\text{M} + \text{X} \longrightarrow \text{M}^+ + \text{X}^-$ is the spontaneous reaction
(B) $\text{M}^+ + \text{X}^- \longrightarrow \text{M} + \text{X}$ is the spontaneous reaction
(C) $E_{\text{cell}} = 0.77$ V
(D) $E_{\text{cell}} = -0.77$ V [JEE 2000]
- Q.6 The reaction,
$$3\text{ClO}^-(\text{aq}) \longrightarrow \text{ClO}_3^-(\text{aq}) + 2\text{Cl}^-(\text{aq})$$
is an example of
(A) Oxidation reaction (B) Reduction reaction
(C) Disproportionation reaction (D) Decomposition reaction [JEE 2001]
- Q.7 The correct order of equivalent conductance at infinite dilution of LiCl, NaCl and KCl is
(A) $\text{LiCl} > \text{NaCl} > \text{KCl}$ (B) $\text{KCl} > \text{NaCl} > \text{LiCl}$
(C) $\text{NaCl} > \text{KCl} > \text{LiCl}$ (D) $\text{LiCl} > \text{KCl} > \text{NaCl}$ [JEE 2001]
- Q.8 Saturated solution of KNO_3 is used to make salt bridge because
(A) velocity of K^+ is greater than that of NO_3^-
(B) velocity of NO_3^- is greater than that of K^+
(C) velocities of both K^+ and NO_3^- are nearly the same
(D) KNO_3 is highly soluble in water [JEE 2001]
-

- Q.9 Standard electrode potential data are useful for understanding the suitability of an oxidant in a redox titration. Some half cell reactions and their standard potentials are given below:



Identify the only incorrect statement regarding quantitative estimation of aqueous $\text{Fe}(\text{NO}_3)_2$

(A) MnO_4^- can be used in aqueous HCl

(B) $\text{Cr}_2\text{O}_7^{2-}$ can be used in aqueous HCl

(C) MnO_4^- can be used in aqueous H_2SO_4

(D) $\text{Cr}_2\text{O}_7^{2-}$ can be used in aqueous H_2SO_4 [JEE 2002]

- Q.10 In the electrolytic cell, flow of electrons is from:

(A) Cathode to anode in solution (B) Cathode to anode through external supply

(C) Cathode to anode through internal supply (D) Anode to cathode through internal supply.

[JEE 2003]

- Q.11 $\text{Zn} | \text{Zn}^{2+} (a = 0.1\text{M}) || \text{Fe}^{2+} (a = 0.01\text{M}) | \text{Fe}$. The emf of the above cell is 0.2905 V. Equilibrium constant for the cell reaction is

(A) $10^{0.32/0.0591}$

(B) $10^{0.32/0.0295}$

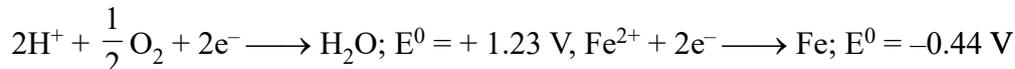
(C) $10^{0.26/0.0295}$

(D) $e^{0.32/0.295}$

[JEE 2004]

- Q.12 The half cell reactions for rusting of iron are:

[JEE 2005]



ΔG^0 (in kJ) for the reaction is:

(A) -76

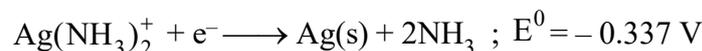
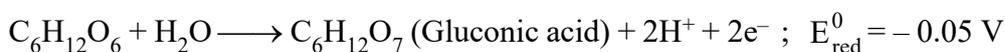
(B) -322

(C) -122

(D) -176

Question No. 13 to 15 (3 questions)

Tollen's reagent is used for the detection of aldehyde when a solution of AgNO_3 is added to glucose with NH_4OH then gluconic acid is formed



[Use $2.303 \times \frac{RT}{F} = 0.0592$ and $\frac{F}{RT} = 38.92$ at 298 K]

[JEE 2006]

- Q.13 $2\text{Ag}^+ + \text{C}_6\text{H}_{12}\text{O}_6 + \text{H}_2\text{O} \longrightarrow 2\text{Ag}(\text{s}) + \text{C}_6\text{H}_{12}\text{O}_7 + 2\text{H}^+$
Find $\ln K$ of this reaction

(A) 66.13

(B) 58.38

(C) 28.30

(D) 46.29

- Q.14 When ammonia is added to the solution, pH is raised to 11. Which half-cell reaction is affected by pH and by how much?
- (A) E_{oxd} will increase by a factor of 0.65 from E_{oxd}^0
- (B) E_{oxd} will decrease by a factor of 0.65 from E_{oxd}^0
- (C) E_{red} will increase by a factor of 0.65 from E_{red}^0
- (D) E_{red} will decrease by a factor of 0.65 from E_{red}^0
- Q.15 Ammonia is always added in this reaction. Which of the following must be incorrect?
- (A) NH_3 combines with Ag^+ to form a complex.
- (B) $\text{Ag}(\text{NH}_3)_2^+$ is a weaker oxidising reagent than Ag^+ .
- (C) In absence of NH_3 silver salt of gluconic acid is formed.
- (D) NH_3 has affected the standard reduction potential of glucose/gluconic acid electrode.

SUBJECTIVE

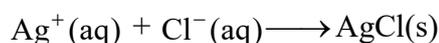
- Q.16 Electrolysis of a solution of MnSO_4 in aqueous sulphuric acid is a method for the preparation of MnO_2 as per the reaction, $\text{Mn}^{2+}_{\text{aq}} + 2\text{H}_2\text{O} \rightarrow \text{MnO}_2(\text{s}) + 2\text{H}^+_{\text{aq}} + \text{H}_2(\text{g})$
Passing a current of 27A for 24 hours gives one kg of MnO_2 . What is the value of current efficiency? Write the reaction taking place at the cathode and at the anode. **[JEE 1997]**
- Q.17 How many grams of silver could be plated out on a serving tray by electrolysis of a solution containing silver in +1 oxidation state for a period of 8.0 hours at a current of 8.46 Amperes? What is the area of the tray if the thickness of the silver plating is 0.00254 cm? Density of silver is 10.5 g/cm³. **[JEE 1997]**
- Q.18 Calculate the equilibrium constant for the reaction
 $\text{Fe}^{2+} + \text{Ce}^{4+} \rightleftharpoons \text{Fe}^{3+} + \text{Ce}^{3+}$, [given : $E^0_{\text{Ce}^{4+}/\text{Ce}^{3+}} = 1.44\text{V}$; $E^0_{\text{Fe}^{3+}/\text{Fe}^{2+}} = 0.68\text{V}$] **[JEE 1997]**
- Q.19 Calculate the equilibrium constant for the reaction, $2\text{Fe}^{3+} + 3\text{I}^- \rightleftharpoons 2\text{Fe}^{2+} + \text{I}_3^-$. The standard reduction potentials in acidic conditions are 0.77 and 0.54 V respectively for $\text{Fe}^{3+}/\text{Fe}^{2+}$ and I_3^-/I^- couples. **[JEE 1998]**
- Q.20 Find the solubility product of a saturated solution of Ag_2CrO_4 in water at 298 K if the emf of the cell $\text{Ag}|\text{Ag}^+(\text{satd. Ag}_2\text{CrO}_4 \text{ soln.}) || \text{Ag}^+(0.1 \text{ M})|\text{Ag}$ is 0.164 V at 298K. **[JEE 1998]**
- Q.21 Copper sulphate solution (250 mL) was electrolysed using a platinum anode and a copper cathode. A constant current of 2 mA was passed for 16 min. It was found that after electrolysis, the absorbance of the solution was reduced to 50% of its original value. Calculate the concentration of copper sulphate in the solution to begin with. **[JEE 2000]**
- Q.22 The following electrochemical cell has been set up
 $\text{Pt}_{(\text{I})} | \text{Fe}^{3+}, \text{Fe}^{2+} (a=1) || \text{Ce}^{4+}, \text{Ce}^{3+} (a=1) | \text{Pt}_{(\text{II})}$
 $E^0_{\text{Fe}^{3+}/\text{Fe}^{2+}} = 0.77 \text{ V}$ and $E^0_{\text{Ce}^{4+}/\text{Ce}^{3+}} = 1.61 \text{ V}$
If an ammeter is connected between the two platinum electrodes, predict the direction of flow of current. Will the current increase or decrease with time? **[JEE 2000]**

- Q.23 The standard potential of the following cell is 0.23 V at 15° C & 0.21 V at 35° C
 $\text{Pt} | \text{H}_2(\text{g}) | \text{HCl}(\text{aq}) | \text{AgCl}(\text{s}) | \text{Ag}(\text{s})$
- (i) Write the cell reaction.
(ii) Calculate $\Delta H^\circ, \Delta S^\circ$ for the cell reaction by assuming that these quantities remain unchanged in the range 15° C to 35° C.
(iii) Calculate the solubility of AgCl in water at 25° C. Given standard reduction potential of the Ag^+/Ag couple is 0.80 V at 25° C. **[JEE 2001]**

- Q.24 Two students use same stock solution of ZnSO_4 and a solution of CuSO_4 . The e.m.f of one cell is 0.3 V higher than the other. The conc. of CuSO_4 in the cell with higher e.m.f value is 0.5 M. Find out the conc. of CuSO_4 in the other cell $\left(\frac{2.303 RT}{F} = 0.06\right)$. **[JEE 2003]**

- Q.25 Find the equilibrium constant at 298 K for the reaction,
 $\text{Cu}^{2+}(\text{aq}) + \text{In}^{2+}(\text{aq}) \rightleftharpoons \text{Cu}^+(\text{aq}) + \text{In}^{3+}(\text{aq})$
Given that $E^\circ_{\text{Cu}^{2+}|\text{Cu}^+} = 0.15\text{V}$, $E^\circ_{\text{In}^{3+}|\text{In}^{2+}} = -0.42\text{V}$, $E^\circ_{\text{In}^{2+}|\text{In}^+} = -0.40\text{V}$ **[JEE 2004]**

- Q.26(a) Calculate ΔG_f° of the following reaction

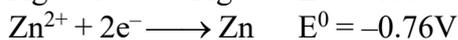


Given: $\Delta G_f^\circ(\text{AgCl}) = -109 \text{ kJ/mole}$, $\Delta G_f^\circ(\text{Cl}^-) = -129 \text{ kJ/mole}$, $\Delta G_f^\circ(\text{Ag}^+) = 77 \text{ kJ/mole}$

Represent the above reaction in form of a cell

Calculate E° of the cell. Find $\log_{10} K_{\text{sp}}$ of AgCl

- (b) $6.593 \times 10^{-2} \text{ g}$ of metallic Zn ($\text{amu} = 65.39$) was added to 100 ml of saturated solution of AgCl.
Calculate $\log_{10} \left[\frac{[\text{Zn}^{2+}]}{[\text{Ag}^+]^2} \right]$, given that



Also find how many moles of Ag will be formed? **[JEE 2005]**

- Q.27 We have taken a saturated solution of AgBr. K_{sp} of AgBr is 12×10^{-14} . If 10^{-7} mole of AgNO_3 are added to 1 litre of this solution find conductivity (specific conductance) of this solution in terms of $10^{-7} \text{ S m}^{-1} \text{ mol}^{-1}$.

Given: $\lambda^\circ_{(\text{Ag}^+)} = 6 \times 10^{-3} \text{ S m}^2 \text{ mol}^{-1}$; $\lambda^\circ_{(\text{Br}^-)} = 8 \times 10^{-3} \text{ S m}^2 \text{ mol}^{-1}$; $\lambda^\circ_{(\text{NO}_3^-)} = 7 \times 10^{-3} \text{ S m}^2 \text{ mol}^{-1}$

[JEE 2006]

ANSWER KEY
EXERCISE I

- Q.1 (a) 6.02×10^{22} electrons lost, (b) 1.89×10^{22} electrons gained, (c) (b) 1.80×10^{23} electrons gained
 Q.2 (a) 0.75 F, (b) 0.69 F, (c) 1.1 F
 Q.3 (i) 54 gm, (ii) 16.35 gm
 Q.4 1.023×10^5 sec
 Q.5 1.12 mol, 12.535 litre
 Q.6 0.112 litre
 Q.7 0.24 gms
 Q.8 Rs. 0.75x
 Q.9 (i) 2.1554 gm ; (ii) 1336. 15 sec
 Q.10 115800C, 347.4 kJ
 Q.11 $t = 193$ sec
 Q.12 $n = 4$
 Q.13 $\text{Cu}^{2+} = 0.08\text{M}$, $\text{H}^+ = 0.04\text{M}$, $\text{SO}_4^{2-} = 0.1\text{M}$
 Q.14 $A = 114$, $Q = 5926.8\text{C}$
 Q.15 Final weight = 9.6g, 0.01Eq of acid
 Q.16 (a) $V(\text{O}_2) = 6.2\text{L}$, (b) $V(\text{O}_2) = 0.824\text{L}$
 Q.17 $t = 93.65$ sec.
 Q.18 60 %
 Q.19 (i) 482.5 sec (ii) 0.3175 gm (iii) 0.327 gm
 Q.20 $7.958 \times 10^{-5}\text{M}$
 Q.21 1.825 g
 Q.22 2M
 Q.23 (a) $\text{Zn} | \text{Zn}^{2+} || \text{Cd}^{2+} | \text{Cd}$, (b) $\text{Pt}, \text{H}_2 | \text{H}^+ || \text{Ag}^+ | \text{Ag}$, (c) $\text{Cu} | \text{Cu}^{2+} || \text{Cl}^- | \text{Hg}_2\text{Cl}_2 | \text{Hg}$
 (d) $\text{Pt} | \text{Fe}^{2+}, \text{Fe}^{3+} || \text{Cr}_2\text{O}_7^{2-}, \text{Cr}^{3+} | \text{Pt}$
 Q.24 (a) $2\text{Ag} + \text{Cu}^{2+} \longrightarrow 2\text{Ag}^+ + \text{Cu}$, (b) $\text{MnO}_4^- + 5\text{Fe}^{2+} + 8\text{H}^+ \longrightarrow \text{Mn}^{2+} + 5\text{Fe}^{3+} + 4\text{H}_2\text{O}$
 (c) $2\text{Cl}^- + 2\text{Ag}^+ \longrightarrow 2\text{Ag} + \text{Cl}_2$, (d) $\text{H}_2 + \text{Cd}^{2+} \longrightarrow \text{Cd} + 2\text{H}^+$
 Q.25 Anode Cathode
 (a) $\text{Zn} | \text{Zn}^{2+}$ $\text{H}^+, \text{H}_2 | \text{Pt}$
 (b) $\text{Pt} | \text{Sn}^{2+}, \text{Sn}^{4+}$ $\text{Fe}^{3+}, \text{Fe}^{2+} | \text{Pt}$
 (c) $\text{Pt} | \text{Fe}^{2+}, \text{Fe}^{3+}$ $\text{MnO}_4^-, \text{Mn}^{2+} | \text{Pt}$
 (d) $\text{Pb} | \text{Pb}^{2+}$ $\text{Br}_2, \text{Br}^- | \text{Pt}$
 Q.26 1.61 V
 Q.27 1.35 V
 Q.28 1.68 V
 Q.29 -0.80 V, NO
 Q.30 0.53 V, disproportionation
 Q.31 -0.0367 V
 Q.32 $E_{\text{cell}}^{\circ} = -0.36$ V, not spontaneous
 Q.33 $E = 1.159$ V
 Q.34 $K_c = 1.96 \times 10^{26}$
 Q.35 $K_c = 1.864 \times 10^{107}$, $\Delta G^{\circ} = -611.8$ kJ
 Q.36 $K_w \approx 10^{-14}$
 Q.37 $E^{\circ} = 0.7826$ V
 Q.38 $n = 2$
 Q.39 $E = 0.059$
 Q.40 $E = 0.395$ V
 Q.41 $E_{\text{cell}}^{\circ} = +0.01\text{V}$, $E_{\text{cell}} = -0.0785\text{V}$, correct representation is $\text{Pb} | \text{Pb}^{2+} (10^{-3}\text{M}) || \text{Sn}^{2+} (1\text{M}) | \text{Sn}$
 Q.42 $[\text{Cu}^{2+}] = 2.97 \times 10^{-12}\text{M}$ for $E = 0$
 Q.43 $E = -0.81\text{eV}$
 Q.44 0.52 V, 0.61 V
 Q.45 -1.30×10^3 kJ mol⁻¹
 Q.46 0.0295 V
 Q.47 0.0295 V
 Q.48 pH = 4
 Q.49 (i) $E = 0.286\text{V}$; (ii) $E = -0.0206\text{V}$
 Q.50 $a_2 = 0.1006$ M
 Q.51 419 S cm² equivalent⁻¹
 Q.52 0.00046 S cm⁻¹; 2174 ohm cm
 Q.53 (i) 6.25×10^5 ohm, (ii) 1.6×10^{-6} amp
 Q.54 1.549 cm⁻¹
 Q.55 101.8 ohm⁻¹ cm² / gm equivalent
 Q.56 0.0141 mho g equiv⁻¹ m², 0.141 mho m⁻¹
 Q.57 (i) 232 Mho cm² mol⁻¹, (ii) 116 Mho cm² equivalent⁻¹
 Q.58 0.865
 Q.59 1.33×10^{-4} gm/litre
 Q.60 8.74×10^{-11} mole² /litre²
 Q.61 $\alpha = 0.435$, $k = 6.7 \times 10^{-4}$
 Q.62 (i) 390.6 S cm² mol⁻¹ (ii) 12.32%
 Q.63 1.067 S m⁻¹
 Q.64 523.2×10^{-4} mho cm² mol⁻¹
 Q.65 (i) 6.98 (ii) 1.08×10^{-14}

PROFICIENCY TEST

1. T 2. F 3. T 4. T 5. T
6. F 7. T 8. T 9. F 10. T
11. T 12. T 13. T 14. F 15. F
16. 0.66 cm^{-1} 17. O_2 18. increase 19. higher
20. O_2 & H_2 21. Electrolyte concentration cell
22. $\text{Cr}_2\text{O}_7^{2-}(\text{aq.}), \text{Cr}^{3+}(\text{aq.}), \text{H}^+ | \text{Pt}$
23. $\text{Pb}(\text{s}) + \text{PbO}_2(\text{s}) + 2\text{H}_2\text{SO}_4 \rightarrow 2\text{PbSO}_4(\text{s}) + 2\text{H}_2\text{O}(\text{l})$
24. $\text{Hg}_2\text{Cl}_2(\text{s}) + 2\text{e}^- \rightarrow 2\text{Hg}(\text{l}) + 2\text{Cl}^-(\text{aq.})$
25. $\Delta H = nF \left[T \left(\frac{dE}{dT} \right) - E \right]$ 26. inert, i.e., should not interfere with net cell reaction
27. Salt bridge or porous partition 28. zero 29. E°_{red} cathode
30. Amount, rate 31. reduction process 32. Oxygen
33. $2.5 \times 96500 \text{ C}$

EXERCISE II

- Q.1 Eq. wt. = 107.3 Q.2 $[\text{Cu}^{2+}] = 10^{-4} \text{ M}$ Q.3 643.33amp, 190.5g
Q.4 43.456g Q.5 265 Amp. hr. Q.6 $E = 1.1 \text{ V}$
Q.7 $E^\circ = -1.59 \text{ V}$, non-spontaneous Q.8 $K_{\text{sp}} = 1.1 \times 10^{-16}$
Q.9 $\text{pH} = 6.61$ Q.10 $E^0 = 0.71 \text{ V}$ Q.11 $[\text{Br}^-] : [\text{Cl}^-] = 1 : 200$
Q.12 $E^0 = -0.1511 \text{ V}$ Q.13 $K_a = 6.74 \times 10^{-4}$ Q.14 $[\text{Zn}^{2+}]/[\text{Cu}^{2+}] = 1.941 \times 10^{37}$
Q.15 1.39V Q.16 0.373V Q.17 $K_f = 8.227 \times 10^{63}$
Q.18 -0.46 V Q.19 42.2 % Q.20 (ii). 1.27 V, (iii) 245.1 kJ
Q.21 -0.037 V Q.22 A48.71 hour, $[\text{OH}^-] = 1.41 \text{ M}$
Q.23 $V(\text{O}_2) = 99.68 \text{ mL}$, $V(\text{H}_2) = 58.46 \text{ mL}$, Total vol. = 158.1 mL
Q.24 57.5894 gm Q.25 315.36 A Q.26 1.9 million year
Q.27 $E^0 = -0.22 \text{ V}$
Q.28 0.372 V, -0.307 V Q.29 $h = 2.12 \times 10^{-2}$, $K_h = 1.43 \times 10^{-5} \text{ M}$
Q.30 0.95 V Q.31 $1.536 \times 10^{-5} \text{ M}^3$ Q.32 0.1456 ampere
Q.33 3.29 cm Q.34 $4.25 \times 10^{-2} \text{ metre}$ Q.35 0.1934 gm/litre
Q.36 $1.21 \times 10^5 \text{ coulomb}$ Q.37 $\text{Cu} = 98.88\%$, $\text{Fe} = 0.85\%$ Q.38 1250 s, 0.064 M
Q.39 $K = 10^{268}$ Q.40 $\text{Ti}^+ = 10^{-8}$; $\text{Co}^{3+} = 2 \times 10^{-8}$ Q.41 1.66V
Q.42 -1.188 V Q.43 10^{-2} Q.44 5.24×10^{16}
Q.45 1.143V Q.46 (a) -0.124 V , (b) 7.1, (c) calomel electrode
Q.47 0.4414 V Q.48 -0.167 V Q.49 $K_{\text{sp}} = 7.682 \times 10^{-17}$
Q.50 $2 \times 10^5 \text{ dm}^3$

EXERCISE III

- Q.1 C Q.2 B Q.3 B Q.4 B Q.5 D Q.6 D Q.7 C
Q.8 C Q.9 B Q.10 A Q.11 A Q.12 A Q.13 A Q.14 B
Q.15 A Q.16 C Q.17 C Q.18 D Q.19 C Q.20 B Q.21 C
Q.22 C Q.23 C Q.24 C Q.25 B
-

EXERCISE IV

OBJECTIVE

Q.1	C	Q.2	B	Q.3	A	Q.4	A	Q.5	B
Q.6	C	Q.7	B	Q.8	C	Q.9	A	Q.10	C
Q.11	B	Q.12	B	Q.13	B	Q.14	A	Q.15	D

SUBJECTIVE

Q.16 $\eta = 94.8\%$; Cathode : $2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$, Anode : $\text{Mn}^{2+} \rightarrow \text{Mn}^{4+} + 2\text{e}^-$

Q.17 $W_{\text{Ag}} = 272.2\text{g}$, area = $1.02 \times 10^4 \text{ cm}^2$ Q.18 $K_c = 7.6 \times 10^{12}$ Q.19 $K_c = 6.26 \times 10^7$

Q.20 $K_{\text{sp}} = 2.287 \times 10^{-12} \text{ M}^{-3}$ Q.21 $7.95 \times 10^{-5} \text{ M}$

Q.22 decrease with time

Q.23 $\Delta H^0 = -49987 \text{ J mol}^{-1}$, $\Delta S^0 = -96.5 \text{ J mol}^{-1} \text{ K}^{-1}$, $s = 1.47 \times 10^{-5} \text{ M}$

Q.24 0.05 M Q.25 $K_c = 10^{10}$

Q.26 (a) $E^0 = 0.59 \text{ V}$, $\log_{10} K_{\text{sp}} = -10$
(b) $52.8, 10^{-6} \text{ moles}$

Q.27 55 S m^{-1}

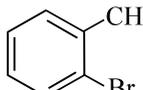
HALOGEN DERIVATIVES

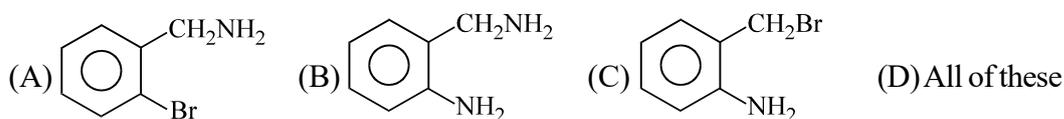
EXERCISE-I (A)

(Choose the correct option. Only one is correct)

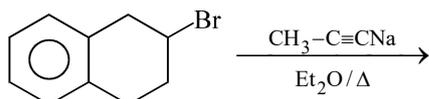
Q.1 Which one of the following compounds will be most reactive for S_N1 reactions:



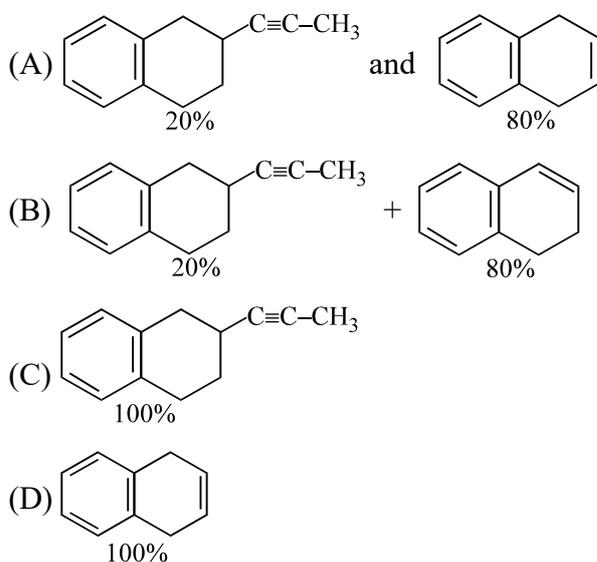
Q.2 The major product in the given reaction:  + $NH_3 \longrightarrow$



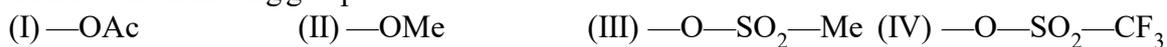
Q.3 In the given reaction:



the products are:



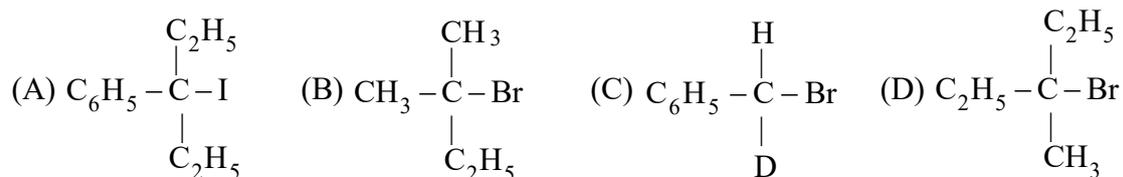
Q.4 Consider the following groups:



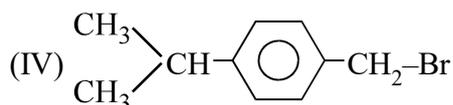
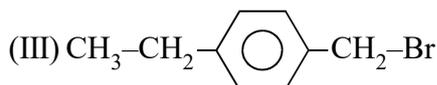
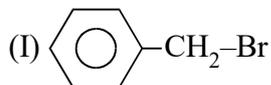
The order of leaving power is:



Q.5 Which one of the following compounds will give enantiomeric pair on treatment with HOH?

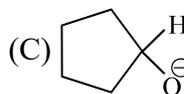


Q.6 Arrange the following compounds in order of decreasing rate of hydrolysis for $\text{S}_{\text{N}}1$ reaction:

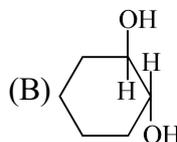
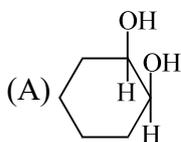
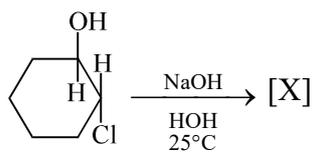


(A) II > III > IV > I (B) IV > III > II > I (C) III > IV > II > I (D) I > II > III > I

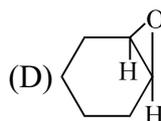
Q.7 Which of the following nucleophile will show minimum reactivity towards $\text{S}_{\text{N}}2$ reaction:



Q.8 In the given reaction



(C) Mixture of (A) and (B)

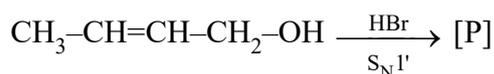


Q.9 Rate of $\text{S}_{\text{N}}2$ reactions depends on:

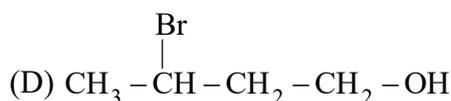
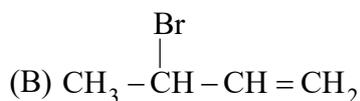
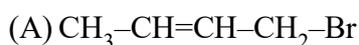
(A) The nucleophile
(C) The leaving group

(B) The carbon skeleton
(D) All of these

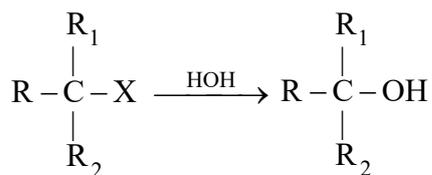
Q.10 Consider the given reaction:



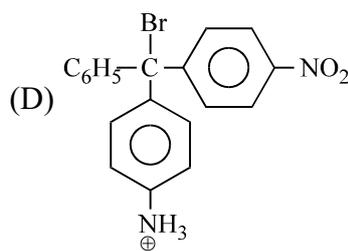
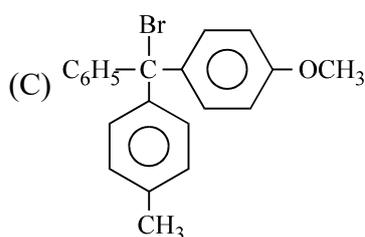
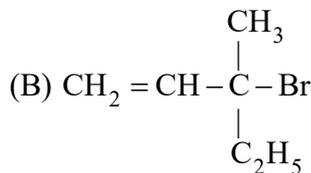
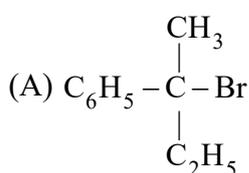
In the given reaction the product [P] is :



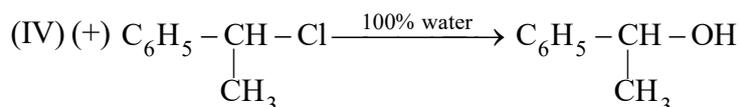
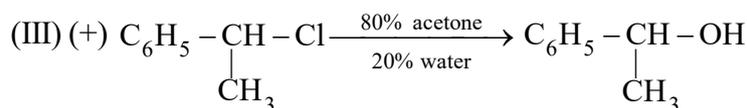
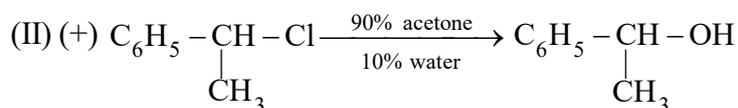
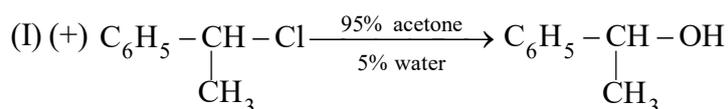
Q.11 For the given reaction



Which substrate will give maximum racemisation?



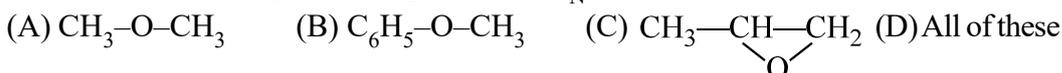
Q.12 Consider the following four reactions:



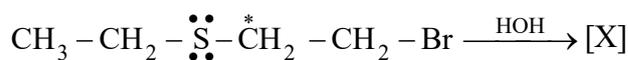
Arrange these reactions in decreasing order of greater proportion of inverted product and select correct answer from the codes given below:

(A) I > II > III > IV (B) II > I > III > IV (C) III > II > I > IV (D) IV > III > II > I

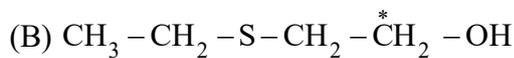
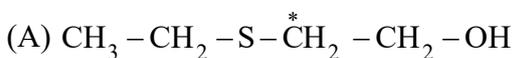
Q.13 Which of the following ester will give always S_N2 mechanism in acidic as well as basic conditions?



Q.14 In the given reaction:



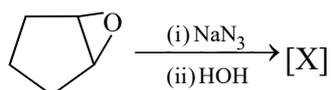
[X] will be:



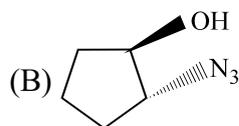
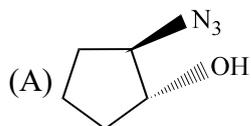
(C) 1 : 1 mixture of (A) and (B)

(D) 2 : 1 mixture of (A) and (B)

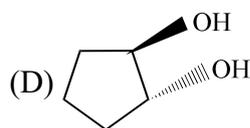
Q.15 In the given reaction:



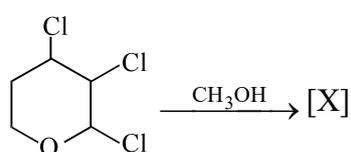
[X] will be:



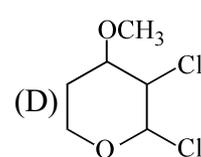
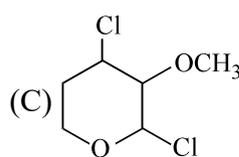
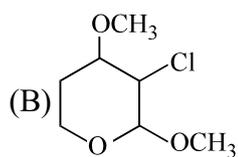
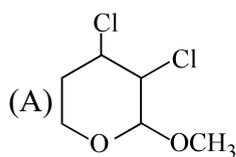
(C) Mixture of (A) and (B)



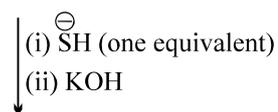
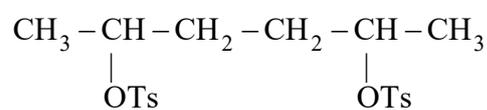
Q.16 In the given reaction:



(excess)

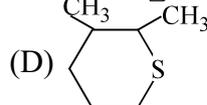
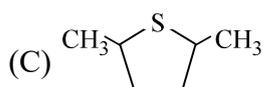
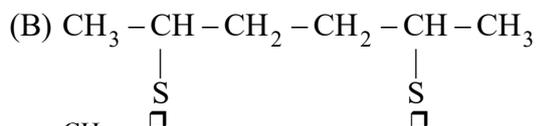
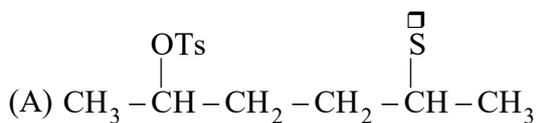


Q.17 In the given reaction

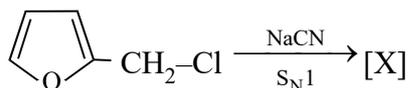


[X]

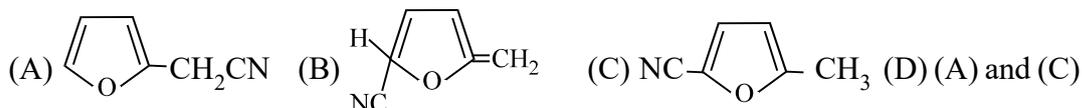
[X] will be:



Q.18 In the given reaction:



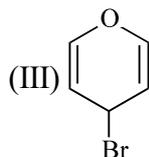
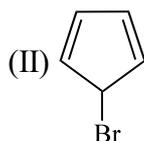
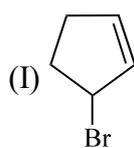
[X] will be:



Q.19 The given compound CH₃-O-CH₂-Br gives which one of the following reactions:

- (A) Only S_N1 (B) Only S_N2
(C) S_N1 as well as S_N2 (D) E1

Q.20 Among the bromides I–III given below, the order of reactivity in S_N1 reaction is:



- (A) III > I > II (B) III > II > I (C) II > III > I (D) II > I > III

Q.21 Which one is liquid at room temperature:

- (A) CH₃Cl (B) C₂H₅Cl (C) CH₃Br (D) C₂H₅Br

Q.22 The correct order of melting and boiling points of the primary (1°), secondary (2°) and tertiary (3°) alkyl halides is:

- (A) P > S > T (B) T > S > P (C) S > T > P (D) T > P > S

Q.23 CCl₄ + KOH (excess) → end product of the reaction is:

- (A) K₂CO₃ (B) CO₂ (C) C(OH)₄ (D) HCOOK

Q.24 The yield of alkyl bromide obtained as a result of heating the dry silver salt of carboxylic acid with bromine if CCl₄ is:

- (A) 1° > 3° > 2° bromides (B) 1° > 2° > 3° bromides
(C) 3° > 2° > 1° bromides (D) 3° > 1° > 2° bromides

Q.25 Which of the following statements is invalid:

- (A) The more stable the carbocation the faster it is formed
(B) Propyl cation changes to more stable isopropyl carbocation by 1,2 shift of a hydrogen
(C) Isopropyl chloride reacts with sodium ethoxide to form 1-ethoxypropane
(D) Propyl halides reacts with sodium ethoxide to form 1-ethoxypropane

Q.26 Nitrochloroform is prepared by the action of chloroform and:

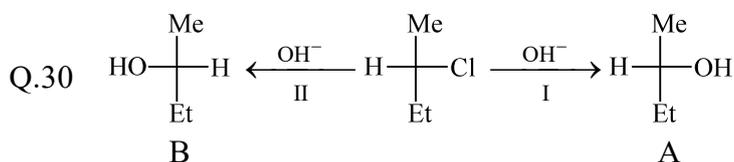
- (A) Hot aqueous solution of KNO₃ (B) Hot aqueous solution of NaNO₂
(C) Hot concentrated nitric acid (D) Hot dilute HCl + aq. NaNO₂ solution

Q.27 Which of the following compounds is most rapidly hydrolysed by S_N1 mechanism.

- (A) C₆H₅Cl (B) Cl-CH₂-CH=CH₂
(C) (C₆H₅)₃CCl (D) C₆H₅CH₂Cl

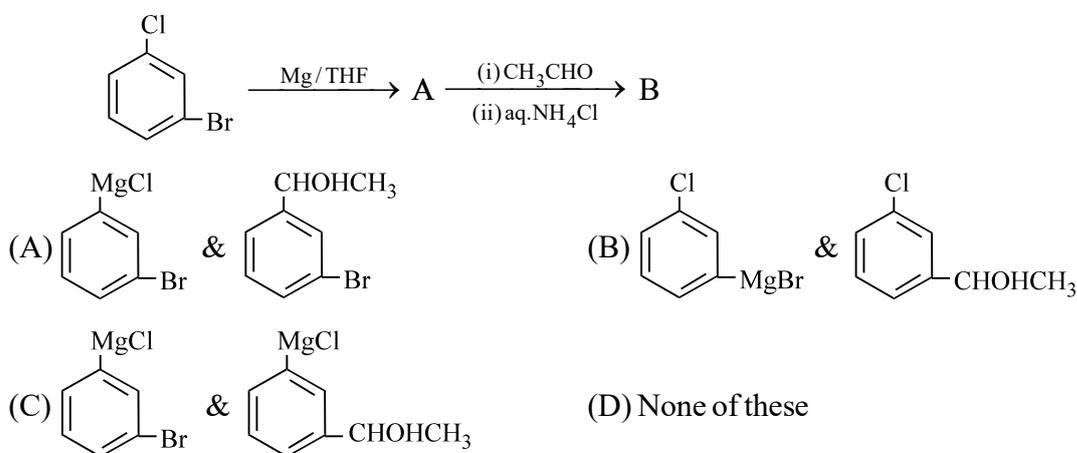
- Q.28 Which is incorrect about Hunsdicker reaction?
 (A) Only Cl_2 can give alkyl halide
 (B) I_2 will give ester when treated with RCOOAg
 (C) The reaction proceeds through free radical
 (D) F_2 cannot give alkyl halide

- Q.29 Major product for the reaction  is:

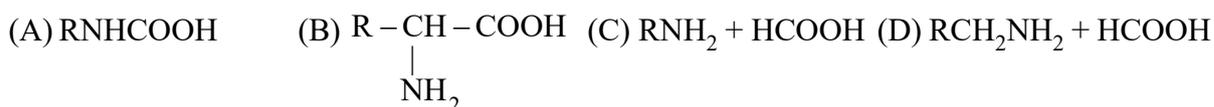


Steps I and II are

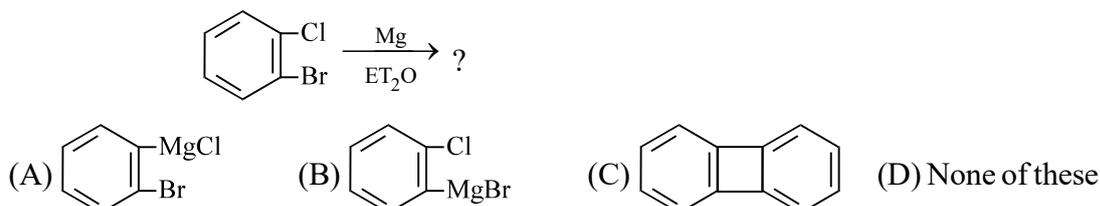
- (A) I can't be $\text{S}_{\text{N}}1$ (B) II can't be $\text{S}_{\text{N}}1$ (C) I $\text{S}_{\text{N}}1$ & II $\text{S}_{\text{N}}2$ (D) I $\text{S}_{\text{N}}2$ & II $\text{S}_{\text{N}}1$
- Q.31 What are A & B in the following reaction?

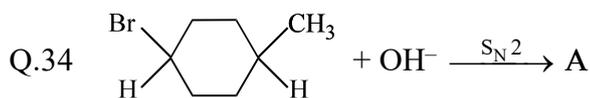


- Q.32 The hydrolysis of alkyl isocyanides ($\text{R}-\text{CH}_2-\text{N} \equiv \text{C}$) gives

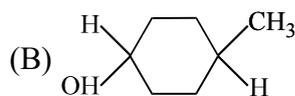
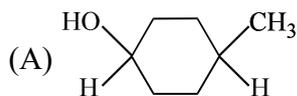


- Q.33 What is product of the following reaction?





A is:



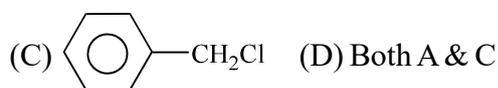
(C) Both

(D) None

- Q.35 Racemic mixture is obtained due to halogenation of:
 (A) n-pentane (B) Isopentane (C) neopentane (D) Both A & B

- Q.36 For $\text{CH}_3\text{Br} + \text{OH}^- \longrightarrow \text{CH}_3\text{OH} + \text{Br}^-$
 the rate of reaction is given by the expression:
 (A) rate = $k[\text{CH}_3\text{Br}]$ (B) rate = $k[\text{OH}^-]$
 (C) rate = $k[\text{CH}_3\text{Br}][\text{OH}^-]$ (D) rate = $k[\text{CH}_3\text{Br}]^0[\text{OH}^-]^0$

- Q.37 Which will give white ppt. with AgNO_3 ?



- Q.38 The reaction of SOCl_2 on alkanols to form alkyl chlorides gives good yields because
 (A) Alkyl chlorides are immiscible with SOCl_2
 (B) The other products of the reaction are gaseous and escape out
 (C) Alcohol and SOCl_2 are soluble in water
 (D) The reaction does not occur via intermediate formation of an alkyl chloro sulphite

- Q.39 True about alkyl halides is / are:
 (A) Tertiary alkyl halides undergo S_N2 substitutions
 (B) Alkyl iodides on exposure to sunlight gradually darken
 (C) Alkyl chlorides do not give beilstein test
 (D) A nucleophilic substitution is most difficult in alkyl iodides

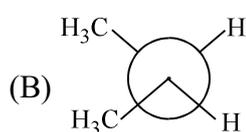
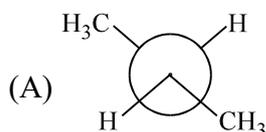
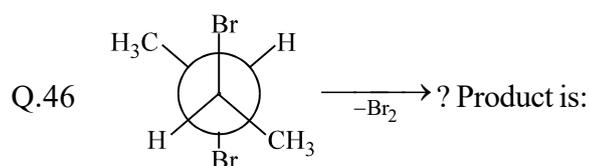
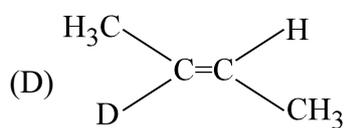
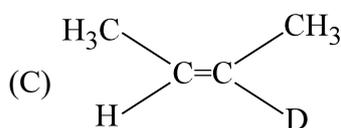
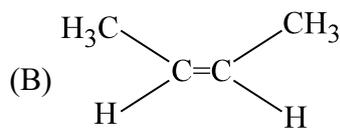
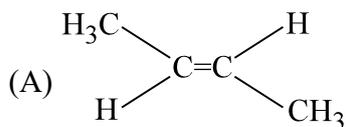
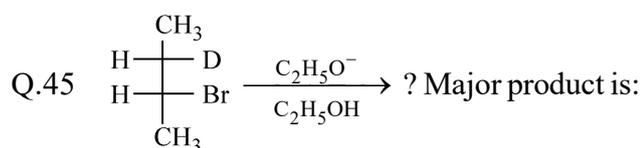
- Q.40 The product formed when glycerol reacts with PCl_5 is—
 (A) 1,2,3-trichloropropane (B) Glycero monochlorohydrin
 (C) Glycero dichlorohydrin (D) All of these

- Q.41 On heating glycerol with excess amount of HI , the product formed is—
 (A) Allyl iodide (B) Isopropyl iodide (C) Propylene (D) 1,2,3-tri-iodopropane

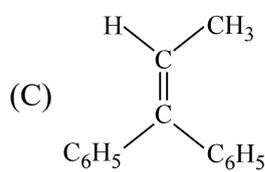
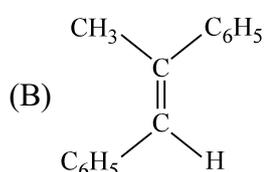
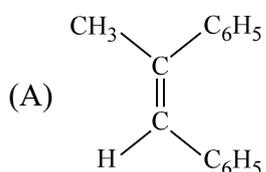
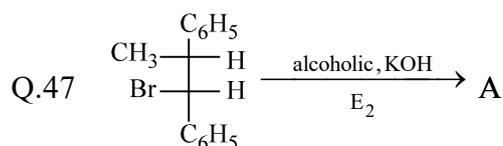
- Q.42 Non-occurrence of the following reaction
 $\text{Br}^- + \text{CH}_3\text{OH} \longrightarrow \text{BrCH}_3 + \text{OH}^-$, is due to
 (A) Attacking nucleophile is stronger one (B) Leaving group is a strong base
 (C) Alcohols are not good substrate (D) Hydroxide ions are weak bases

- Q.43 When ethyl bromide is treated with moist Ag_2O , main product is:
 (A) Ethyl ether (B) Ethanol (C) Ethoxy ethane (D) All of the above

- Q.44 When ethyl bromide is treated with dry Ag_2O , main product is:
 (A) Ethyl ether (B) Ethanol (C) Ethoxy ethane (D) All of the above

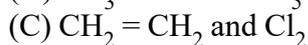


(C) both (A) & (B) (D) none of these



(D) None is correct

Q.48 A gem dichloride is formed in the reaction except:



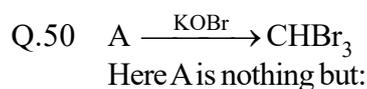
Q.49 Which of the following statement is wrong:

(A) All carbonyl compounds of the general structure $\text{CH}_3 - \overset{\text{O}}{\parallel}{\text{C}} - \text{R}$ give a positive iodoform test

(B) All secondary alcohols give iodoform reaction

(C) Alkanols of the structure $\text{CH}_3\text{CH}(\text{OH}) - \text{R}$ (where $\text{R} = \text{H}$, alkyl or aryl) give iodoform reaction.

(D) The only aldehyde giving iodoform reaction is acetaldehyde.

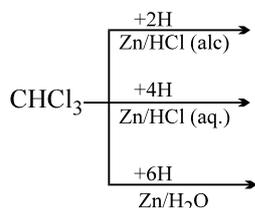


(A) Isopropyl alcohol (B) Methanol

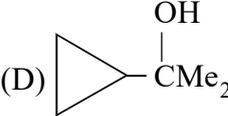
(C) Ethanoic acid

(D) n-Butyl alcohol

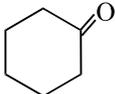
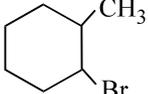
- Q.51 The appropriate naming for the second step in the haloform reaction is:
 (A) Halogenation (B) Dehydrohalogenation
 (C) Reduction (D) Dehydrogenation
- Q.52 Which product is obtained when bleaching powder is distilled with acetone:
 (A) CCl_4 (B) CHCl_3 (C) CH_2Cl_2 (D) CH_3Cl
- Q.53 What will be the reduction product of following reactions:



- (A) CH_2Cl_2 , CH_3Cl , CH_4 (B) CH_4 , CH_3Cl , CH_2Cl_2
 (C) CH_3Cl , CH_2Cl_2 , CH_4 (D) CH_3Cl , CH_4 , CH_2Cl_2
- Q.54 $\text{Me}_2\text{C}=\text{CH}-\text{CH}_2-\text{CH}_2-\text{Cl} \xrightarrow[\text{CaCO}_3]{\text{H}_2\text{O}} (\text{X})$
 Major product of above reaction is

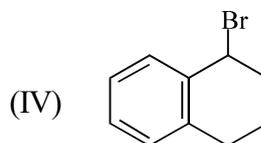
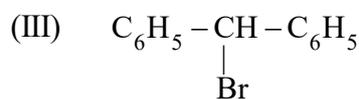
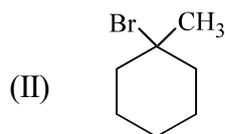
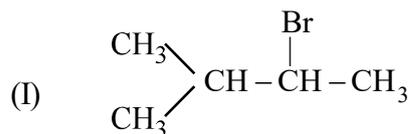
- (A) $\text{Me}-\overset{\text{OH}}{\underset{\text{Me}}{\text{C}}}-\text{CH}_2-\text{CH}_2-\text{CH}_2$ (B) $\text{Me}_2\text{C}=\text{CH}-\text{CH}_2-\text{CH}_2-\text{OH}$
 (C) $\text{Me}_2\text{C}=\text{CH}-\underset{\text{OH}}{\text{CH}}-\text{CH}_2-\text{OH}$ (D) 

- Q.55 Addition of bromine on propene in the presence of brine yields a mixture of:
 (A) $\text{CH}_3\text{CHClCH}_2\text{Br}$ and $\text{CH}_3\text{CHBrCH}_2\text{Cl}$ (B) $\text{CH}_3\text{CHClCH}_2\text{Br}$ and $\text{CH}_3\text{CHBrCH}_2\text{Br}$
 (C) $\text{CH}_3\text{CHClCH}_2\text{Cl}$ and $\text{CH}_3\text{CHBrCH}_2\text{Br}$ (D) $\text{CH}_2\text{CHClCH}_2\text{Cl}$ and $\text{CH}_3\text{CHBrCH}_2\text{Cl}$

- Q.56  is converted into  by:

- (A) (i) CH_3-MgI , H_3O^+ (ii) H_2SO_4 , Δ , (iii) HBr , R_2O_2
 (B) (i) CH_3-MgI , H_3O^+ (ii) H_2SO_4 , Δ , (iii) HBr
 (C) (i) CH_3-MgI , H_3O^+ (ii) HBr
 (D) (i) HBr , R_2O_2 (ii) CH_3-MgI , H_3O^+
- Q.57 The reactivity of 2-bromo-2-methylbutane (I), 1-bromopentane (II) and 2-bromopentane (III) towards $\text{S}_{\text{N}}2$ displacement is such that:
 (A) $\text{I} > \text{II} > \text{III}$ (B) $\text{I} > \text{III} > \text{II}$ (C) $\text{II} > \text{III} > \text{I}$ (D) $\text{II} > \text{I} > \text{III}$

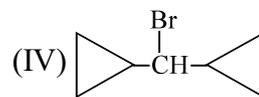
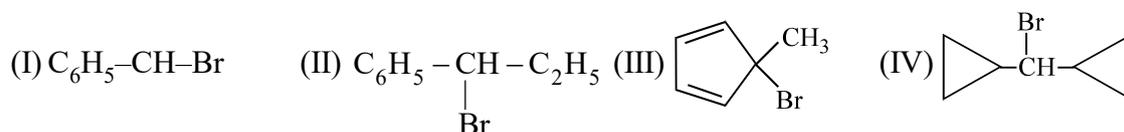
Q.58 Consider the S_N1 solvolysis of the following halides in aqueous formic acid:



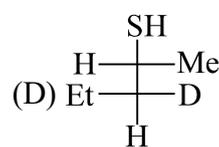
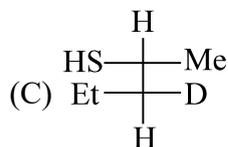
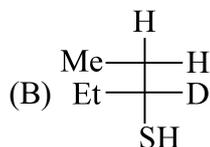
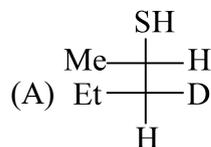
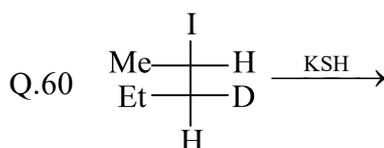
Which one of the following is correct sequence of the halides given above in the decreasing order of their reactivity?

- (A) III > IV > II > I (B) II > IV > I > III (C) I > II > III > IV (D) III > I > II > IV

Q.59 Arrange the following compounds in decreasing order of their reactivity for hydrolysis reaction



- (A) I > II > III > IV (B) IV > II > I > III (C) III > IV > II > I (D) IV > III > II > I

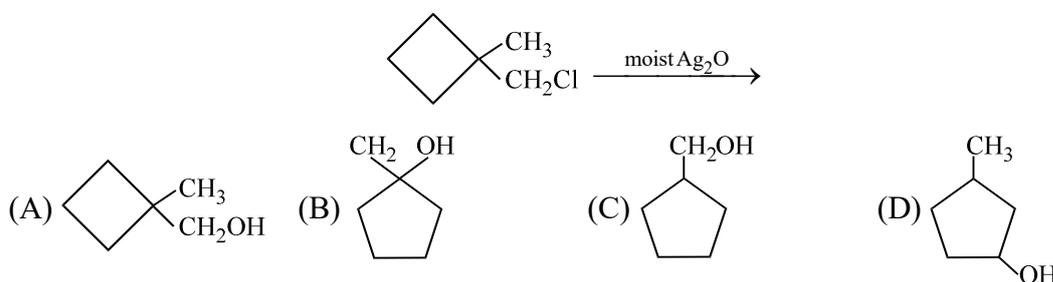


EXERCISE-I (B)

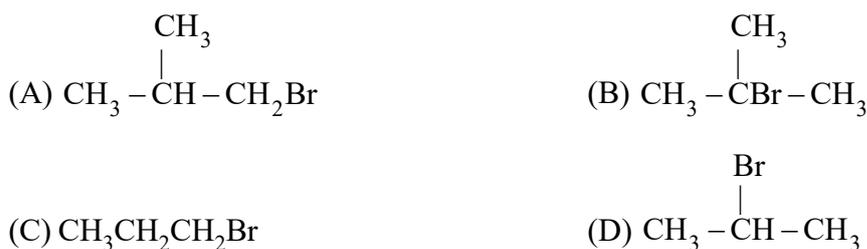
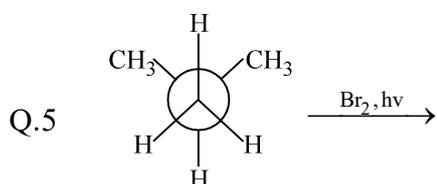
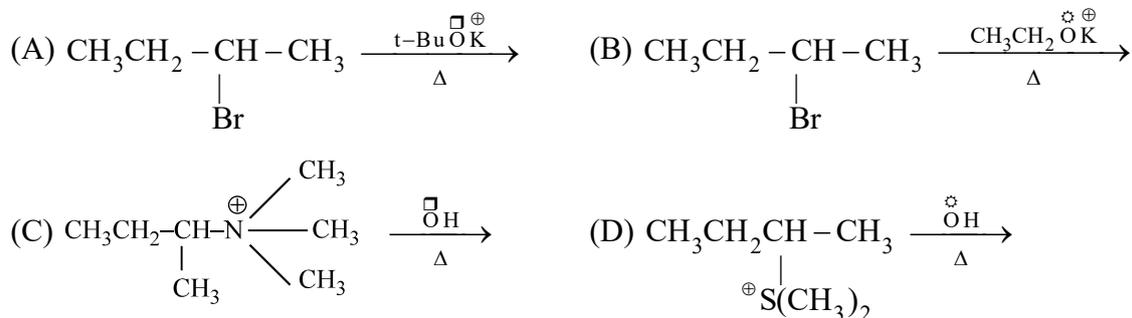
(Choose the correct option. One or more than one are correct)

- Q.1 Consider the following statements?
- (A) $\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-I}$ will react more readily than $(\text{CH}_3)_2\text{CHI}$ for $\text{S}_{\text{N}}2$ reactions.
- (B) $\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-Cl}$ will react more readily than $\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-Br}$ for $\text{S}_{\text{N}}2$ reaction.
- (C) $\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-Br}$ will react more readily than $(\text{CH}_3)_3\text{C-CH}_2\text{-Br}$ for $\text{S}_{\text{N}}2$ reactions
- (D) $\text{CH}_3\text{-O-C}_6\text{H}_5\text{-Br}$ will react more readily than $\text{NO}_2\text{-C}_6\text{H}_5\text{-CH}_2\text{Br}$ for $\text{S}_{\text{N}}2$ reaction
- Q.2 A solution of (R)-2-iodobutane, $[\alpha] = -15.9^\circ$ in acetone is treated with radioactive iodine, until 1.0% of iodobutane contain radioactive iodine, the specific rotation of recovered iodobutane is found to be -15.58° , which statement is correct about above information.
- (A) It has optical purity 96% (B) % of R in solution is 99%
- (C) Racemic mixture is 2% (D) Final solution is dextrorotatory

- Q.3 Which are possible products in following



- Q.4 In which product formation takes place according to Hoffmann's rule



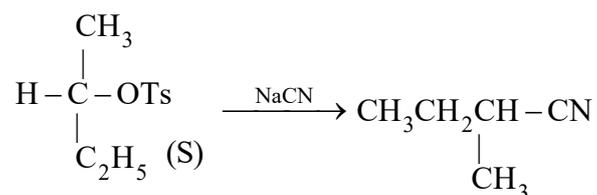
Q.6 Select the correct statements from following

- (A) $\text{CH}_3\text{CH}_2\text{CH}_2\text{I}$ will react more readily than $(\text{CH}_3)_2\text{CHI}$ for $\text{S}_{\text{N}}2$
 (B) $\text{CH}_3\text{CH}_2\text{CH}_2\text{Cl}$ will react more readily than $\text{CH}_3\text{CH}_2\text{CH}_2\text{Br}$ for $\text{S}_{\text{N}}2$
 (C) $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Br}$ will react more readily than $(\text{CH}_3)_2\text{CH}-\text{CH}_2\text{Br}$ for $\text{S}_{\text{N}}2$
 (D) $\text{CH}_3-\text{O}-\text{C}_6\text{H}_4-\text{CH}_2\text{Br}$ will react more readily than $\text{NO}_2-\text{C}_6\text{H}_4-\text{CH}_2\text{Br}$ for $\text{S}_{\text{N}}2$

Q.7 Which of the following will react with AcOAg

- (A) $\text{R}-\text{NH}_2$ (B) $\text{R}-\text{OTs}$ (C) $\text{R}-\text{N}_3$ (D) $\text{R}-\text{Br}$

Q.8 Consider the given reaction

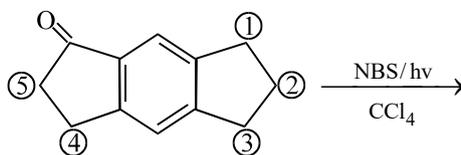


which of following statements are correct for above reaction.

- (A) Product formation takes place due to the breaking of $\text{O}-\text{Ts}$
 (B) The reaction is $\text{S}_{\text{N}}2$
 (C) The reaction is $\text{S}_{\text{N}}1$
 (D) Configuration of product is (R)
- Q.9 Benzoyl chloride is less reactive than acetyl chloride for nucleophilic acyl substitution reaction because

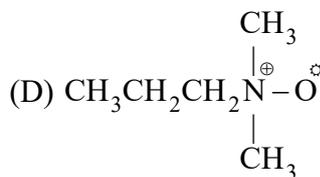
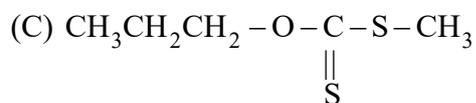
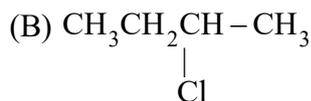
- (A) $\text{C}=\text{O}$ group of benzoyl chloride is in conjugation with benzene ring. This makes benzoyl chloride more stable than acylchloride.
 (B) CH_3- group of acetyl chloride make $\text{C}-\text{Cl}$ bond stronger due to the +I effect.
 (C) C_6H_5- group of benzoyl chloride make $\text{C}-\text{Cl}$ bond weaker due to +R effect.
 (D) Carbonyl carbon in benzoyl chloride is less electron deficient than acetyl chloride

Q.10 Bromination can take place at

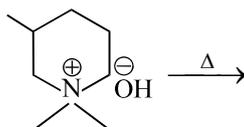


- (A) 1 (B) 5 (C) 3 (D) 4

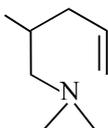
Q.11 Which of following will give syn-elimination



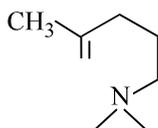
Q.12 Which of following are correct for given reaction



(A) Major product of reaction is



(B) Major product is



(C) The reaction is thermal elimination reaction

(D) The reaction is E_2 reaction

Q.13 Haloform reaction is given by

(A) All 2° alcohol

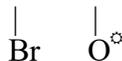
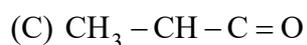
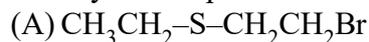
(B) All methyl ketones

(C) All the compounds having $\text{CH}_3\text{-C(=O)-}$ group

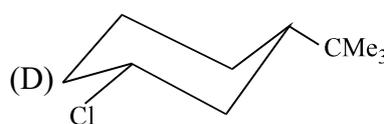
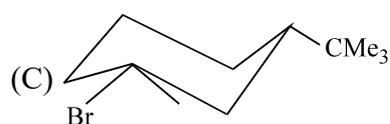
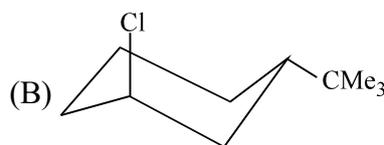
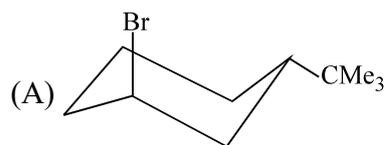
(D) Chloral



Q.14 Identify the compounds that will undergo NGP reaction

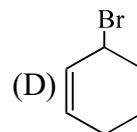
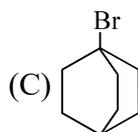
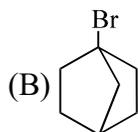
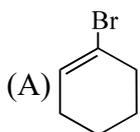


Q.15 Which alkyl halide undergo E_2 elimination

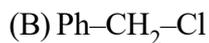
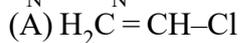


Q.16 3-Phenyl-3-pentanol can be prepared from grignard reagent & other component which can be
 (A) 3-pentanone (B) Ethylbenzoate (C) Ethyl phenyl ketone (D) Propanoyl chloride

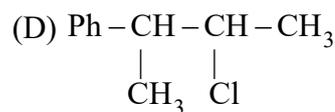
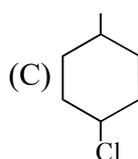
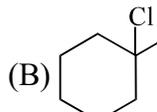
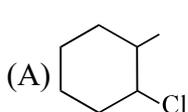
Q.17 Rate of S_N2 will be negligible in



Q.18 S_N1 & S_N2 is not favourable in



Q.19 S_N1 & S_N2 product are same in (excluding stereoisomer)



Q.20 Rate of S_N2 depends on

(A) Conc of Nucleophile

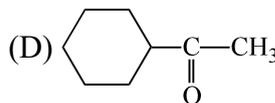
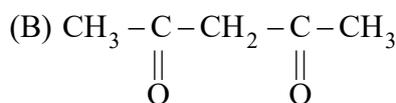
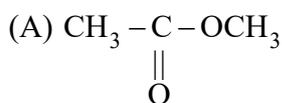
(B) Conc of substrate

(C) Nature of leaving group

(D) Nature of solvent

Q.21 $G \xrightarrow{NaOI}$ yellow solid

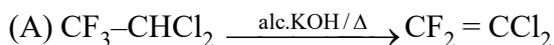
G can be



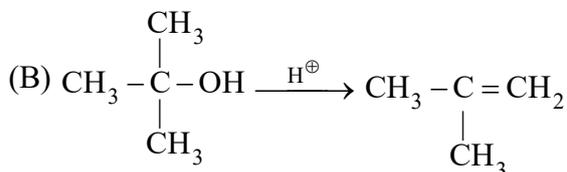
Q.22 Match the List I (reaction) with List II (reaction intermediate) and select the correct answer using the codes given below the Lists.

List I

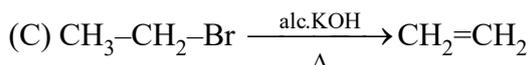
List II



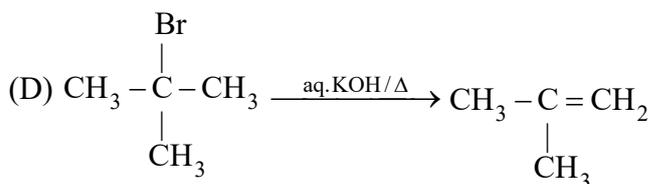
(1) Transition state



(2) Carbocation



(3) Carbanion



(4) Free radical

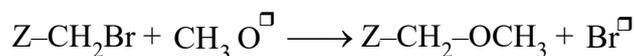
Q.23 Match the List I with List II and select the correct answer using the codes given below the Lists.

- | List I | List II |
|--------------------------------------|--|
| (A) E1CB | (1) 3° Amine oxide |
| (B) Saytzeff alkene as major product | (2) Xanthate |
| (C) E2 | (3) $\text{CH}_3 - \text{CH}_2 - \overset{\text{Cl}}{\underset{ }{\text{CH}}} - \text{CH}_3$ |
| (D) Ei | (4) $\text{C}_6\text{H}_5 - \text{CH}_2 - \overset{\text{F}}{\underset{ }{\text{CH}}} - \text{CH}_3$ |

Q.24 Match List I with List II and select the correct answer from the codes given below:

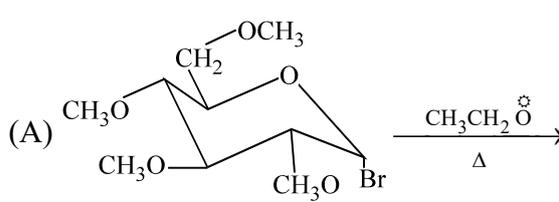
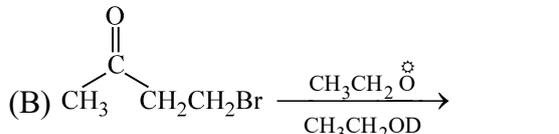
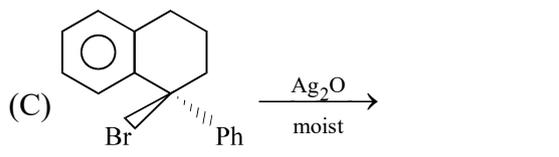
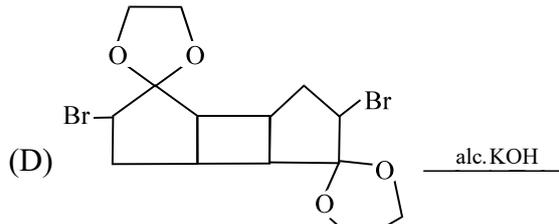
- | List I | List II |
|---|---|
| (A) $\text{CH}_3 - \text{O} - \text{SO}_2\text{CH}_3 + \text{C}_2\text{H}_5\text{O}^\ominus$ | (1) $\text{CH}_3 - \text{CH}_2 - \text{PH}_2$ |
| (B) $\text{CH}_3 - \text{CH}_2 - \text{I} + \text{PH}_3$ | (2) $\text{CH}_3 - \text{O} - \text{C}_2\text{H}_5$ |
| (C) $\text{HC} \equiv \overset{\ominus}{\text{C}}\text{Na} + \text{CH}_3 - \text{CH}_2 - \text{Br}$ | (3) $\text{CH}_3 - \text{O} - \text{CH}_3$ |
| (D) $\text{CH}_3 - \text{Cl} + \text{CH}_3 - \overset{\ominus}{\text{O}}$ | (4) $\text{CH} \equiv \text{C} - \text{CH}_2 - \text{CH}_3$ |

Q.25 Match List-I with List-II for given $\text{S}_{\text{N}}2$ reaction & select the correct answer from the codes given below



- | List-I | List-II |
|--|---------|
| (A) H ⁻ | (P) 0.1 |
| (B) CH ₃ ⁻ | (Q) 3 |
| (C) C ₂ H ₅ ⁻ | (R) 1 |
| (D) $\begin{array}{l} \text{CH}_3 \\ \diagdown \\ \text{CH} - \\ \diagup \\ \text{CH}_3 \end{array}$ | (S) 100 |

Q.26 Match the following

- | List-I | List-II |
|---|----------|
| (A)  | (P) E1 |
| (B)  | (Q) E2 |
| (C)  | (R) E1cb |
| (D)  | (S) Ei |

EXERCISE-II

- Q.1 Explain the following giving proper reasoning :
- (i) Treatment of 1,1-dimethyl oxirane with sodium methoxide in methanol gives primarily one product. Also identify the product giving its IUPAC name
 - (ii) Optically active 2-iodo butane on treatment with NaI*/Acetone gives a product which do not show optical activity.
 - (iii) In the solvent DMSO the order of reactivity of halide ions with methyl bromide is $F^- > Cl^- > Br^- > I^-$ opposite to that observed in methanol solution.
 - (a) $(n - C_3H_7)_3N + CH_3I \rightarrow (n - C_3H_7)_3NCH_3^+ I^-$
Relative rate : in hexane, 1 ; in chloroform, 13000
 - (b) $Br^- + CH_3OTs \rightarrow CH_3Br + TsO^-$
Relative rates : in methanol, 1; in HMPT, 10^5 .
 - (iv) Although ethers are weakly polar, are used as solvent of choice for Grignard reagents.
 - (v) Treatment of either $CH_3-\underset{\text{O}}{\underset{\diagup \diagdown}{\text{C}}}-CH_2Br$ or $CH_3-\underset{\text{Br}}{\text{C}}-\underset{\text{O}}{\underset{\diagup \diagdown}{\text{C}}}-CH_2$ with aqueous HO^- gives the

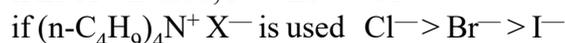
same product. Also write down mechanism involved, & IUPAC name of product.

- Q.2 On reaction between an alkyl halide and KOH in a mixture of water and ethanol, compare the two mechanisms SN_1 and SN_2 :
- (a) relative rates of CH_3X , C_2H_5X , iso- C_3H_7X & tert- C_4H_9X
 - (b) relative rates for RCl, RBr and RI
 - (c) effect on rate of a rise in temperature
 - (d) effect on rate of increasing water content of the solvent.
 - (e) effect on rate increasing alcohol content of the solvent.

- Q.3 In the following reaction is carried out in the weakly ionizing solvent, acetone $(CH_3)_2C=O$. (Bs is brosyl, p-bromo benzene sulfonyl)

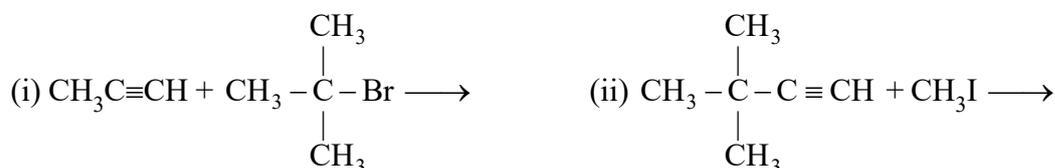


The order of reactivity of halide ions depends on the salt used on their source :

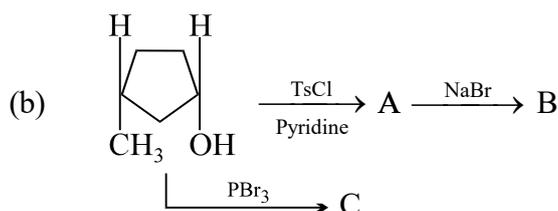


How do you account for this contrast in behavior ?

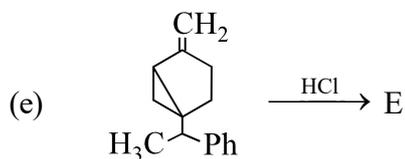
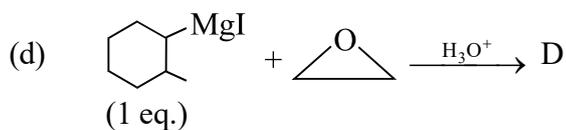
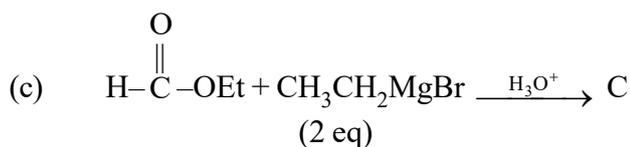
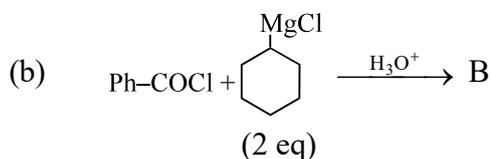
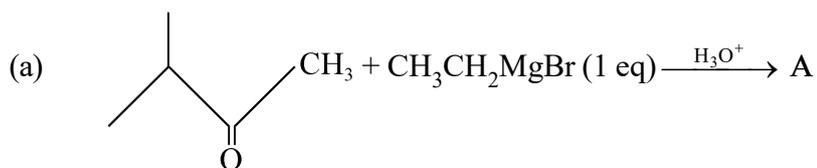
- Q.4 Which of the following is the correct method for synthesizing 4,4-dimethyl-pent-2-yne, using sodamide in liquid NH_3 ? Given reasons.



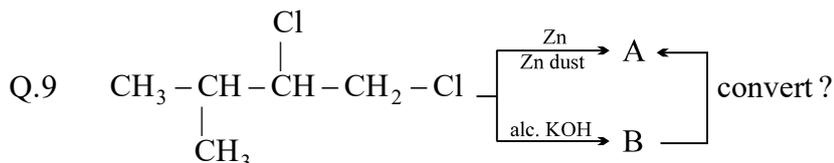
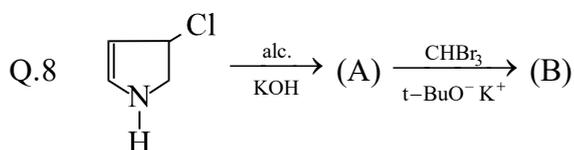
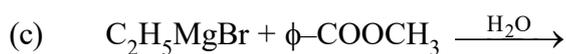
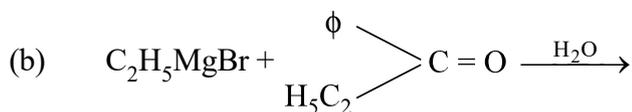
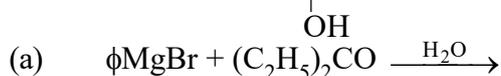
- Q.5 Give the products and find all unknowns.



Q.6 Find out the unknown alphabets.



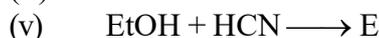
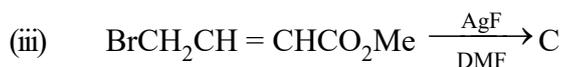
Q.7 To prepare $\phi-\overset{\text{C}_2\text{H}_5}{\underset{\text{OH}}{\text{C}}}-\text{C}_2\text{H}_5$ by RMgX which is the incorrect pair



Q.10 What is/are the limitation in the formation of Grignard reagent by $\text{RX} + \text{Mg} \xrightarrow{\text{dry ether}}$

- R should not contain any acidic group
- R should not contain any electronegative group
- Alkyl halide should not be vicinal dihalide
- Alkyl halide can't be Tertiary.

Q.11 Write major product of the the following reactions:



Q.12 $\text{CH}_3\text{-CH}_2\text{I}$ reacts more rapidly with strong base in comparison to $\text{CD}_3\text{CH}_2\text{I}$

Q.13 2-chloro-3-methylbutane on treatment with alcoholic potash gives 2-methylbutene-2 as major product.

Q.14 Iodoform gives precipitate with AgNO_3 on heating while CHCl_3 does not.

Q.15 Hydrogen atom of chloroform is definitely acidic, but that of methane is not.

Q.16 A small amount of alcohol is added to chloroform bottles.

Q.17 Iodine reacts with alcohols to give alkyl iodine only in presence of phosphorous.

Q.18 KCN reacts with R-I to give alkyl cyanide, while AgCN results in isocyanide as major product.

Q.19 Dry gaseous hydro halogen acid and not their aqueous solutions are used to prepare alkyl halides from alkenes.

Q.20 RCl is hydrolysed to ROH slowly but reaction fastens on addition of KI .

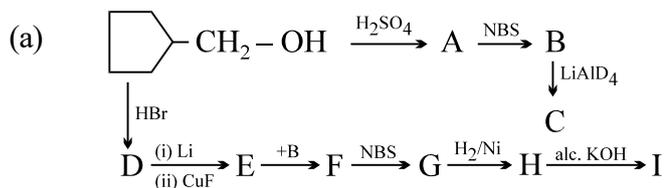
Q.21 The mechanism of decomposition of $\text{Me}_3\text{S}^+\text{OH}^-$ is $\text{S}_{\text{N}}2$ whereas of $\text{Me}_3\text{S}^+\text{I}^-$ is $\text{S}_{\text{N}}1$.

Q.22 Alkaline hydrolysis of benzyl chloride in 50% aqueous acetone proceeds by both $\text{S}_{\text{N}}2$ and $\text{S}_{\text{N}}1$ mechanism, when water is used as solvent, mechanism was now mainly $\text{S}_{\text{N}}1$.

Q.23 Anhydrous AlCl_3 is used as a catalyst in Friedel-Crafts alkylation.

Q.24 Arrange following compounds according to their reactivity with alcoholic silver nitrate. t-Butyl chloride, sec butyl chloride and CCl_4 .

Q.25



EXERCISE-III

- Q.1 A primary alkyl halide (X) C_4H_9Br reacted with alcoholic KOH to give (Y). (Y) reacts with HBr to give (Z) an isomer of (X). On reacting with alkali metal such as sodium/dry ether gives (S) C_8H_{18} which was different from the compound produced when n-butylbromide was treated with Na. What (X), (Y), (Z) and (S).
- Q.2 On electrolysis an aqueous ethanoic solution of sodium chloride gives sweet smelling liquid (X). (X) gives isocyanide test and condenses with acetone to form hypnotic (Y). What are (X) and (Y)?
- Q.3 The alkyl halide C_4H_9Br (A) reacts with alcoholic KOH and gives an alkene (B), which reacts with bromine to give dibromide (C). (C) is transformed with KOH & sodamide to gas (D) which forms a precipitate when passed through an ammoniacal silver nitrate solution. Give the structure formulae of the compounds (A), (B), (C) and (D) and explain reactions involved.
- Q.4 An unsaturated hydrocarbon (A) C_6H_{10} readily gives (B) on treatment with $NaNH_2$ in liquid NH_3 . When (B) is allowed to react with 1-chloropropane, a compound (C) is obtained. On partial hydrogenation in the presence of Lindlar catalyst, (C) gives (D), C_9H_{18} . On ozonolysis (D) gives 2, 2-dimethylpropanal and 1-butanal. Give structures of (A), (B), (C) and (D) with proper reasoning.
- Q.5 One mole of each bromoderivative (A) and NH_3 react to give one mole of an organic compound (B). (B) reacts with CH_3I to give (C). Both (B) and (C) react with HNO_2 to give compounds (D) and (E), respectively. (D) on oxidation and subsequent decarboxylation gives 2-methoxy-2-methylpropane. Give structures of (A) to (E) with proper reasoning.
- Q.6 A chloro derivative (A) on treatment with zinc-copper couple gives a hydrocarbon with five carbon atoms. When 'A' is dissolved in ether and treated with sodium, 2,2,5,5-tetramethylhexane is obtained. What is the original compound 'A'?
- Q.7 A primary alkyl halide (A) C_4H_9Br reacted with alcoholic KOH to give (B). (B) reacts with HBr to give (C) an isomer of (A). (A) on reacting with sodium gives (D) C_8H_{18} which was different from the compound produced when n-butylbromide was treated with Na. What are (A), (B), (C) and (D).
- Q.8 One mole of a hydrocarbon (A) reacts with 1 mole of bromine giving a dibromo compound $C_5H_{10}Br_2$. (A) on treatment with cold dilute alkaline $KMnO_4$ solution forms a compound $C_5H_{12}O_2$. On ozonolysis (A) gives equimolar quantities of propanone and ethanal. Deduce structure of (A).
- Q.9 A hydrocarbon (A) was found to contain 85.7% carbon and 14.3% H. This compound consumes 1 molar equivalent of hydrogen to give a saturated hydrocarbon. 1 g of (A) just decolourised 38.05 g of 5% solution by weight of Br_2 in CCl_4 . Compound (A) on oxidation with conc. $KMnO_4$ gave a compound (C), C_4H_8O and (B) acetic acid. Compound (C) can easily be prepared by the action of acidic aqueous mercuric sulphate on 2-butyne. Deduce (A), (B) and (C).
- Q.10 When a hydrocarbon (A) is treated with excess of hydrogen chloride, a dihalogen derivative (B) is obtained. The compound (B) is treated separately with aqueous and alcoholic KOH to give compounds (C) and (A) respectively both having three carbon atoms. Compound (C) does not reduce Tollen's reagent and compound (A) give white precipitate with ammoniacal silver nitrate. Assign structures to compounds (A) to (C).

- Q.11 An organic compound (A) $C_7H_{15}Cl$ on treatment with alcoholic caustic potash gives a hydrocarbon (B) C_7H_{14} . (B) on treatment with ozone and subsequent hydrolysis gives acetone and butyraldehyde. What are (A) and (B). Explain reactions.
- Q.12 A dihalogen derivative (A) of a hydrocarbon having two carbon atoms react with alcoholic potash and forms another hydrocarbon which gives a red precipitate with ammonical cuprous chloride. Compound (A) gives an aldehyde when treated with KOH (aq). What is (A)?
- Q.13 A white precipitate was formed slowly when $AgNO_3$ was added to a compound (A) with molecular formula $C_6H_{13}Cl$. Compound (A) on treatment with hot alcoholic KOH gave a mixture of two isomeric alkenes (B) and (C) having formula C_6H_{12} . The mixture of (B) and (C) on ozonolysis furnished four compounds (i) CH_3CHO , (ii) C_2H_5CHO , (iii) CH_3COCH_3 , (iv) $(CH_3)_2CH.CHO$
What are (A), (B) and (C).
- Q.14 0.369 g of a bromo derivative of a hydrocarbon (A) when vaporized occupied 67.2 mL at NTP. (A) on reaction with aqueous NaOH gives (B). (B) when passed over alumina at $250^\circ C$ gives a neutral compound (C) while at $350^\circ C$ it gives a hydrocarbon (D). (D) when heated with HBr gives an isomer of (A). When (D) is treated with dil. H_2SO_4 , (E) is obtained. Identify (A) to (E) and explain the reactions.
- Q.15 An organic compound (X) on analysis gives 24.24% C, 4.04% H. Further sodium extract of 1.0 g of (X) gives 2.90 g of AgCl with acidified $AgNO_3$ solution. The compound (X) may be represent by two isomeric structures (Y) and (Z). (Y) on treatment with aqueous KOH solution gives a dihydroxy compound, while (Z) on similar treatment gives ethanal. Find out (X), (Y) and (Z).
- Q.16 A chloro compound (A) showed the following properties :
- Decolourized bromine in CCl_4
 - Absorbed hydrogen catalytically.
 - Gave a precipitate with ammonical cuprous chloride
 - When vaporised 1.49 g of (A) gave 448 mL of vapours at STP.
- Identify (A) and write down the equations of reactions.