Sample Paper 20 Solutions

Class XII 2023-24

Chemistry

Time: 3 Hours Max. Marks: 70

General Instructions:

1. There are 33 questions in this question paper with internal choice.
2. SECTION A consists of 16 multiple-choice questions carrying 1 mark each.
3. SECTION B consists of 5 very short answer questions carrying 2 marks each.
4. SECTION C consists of 7 short answer questions carrying 3 marks each.
5. SECTION D consists of 2 case-based questions carrying 4 marks each.
6. SECTION E consists of 3 long answer questions carrying 5 marks each.
7. All questions are compulsory.
8. Use of log tables and calculators is not allowed.

SECTION-A

Directions (Q. Nos. 1-16) : The following questions are multiple-choice questions with one correct answer. Each question carries 1 mark. There is no internal choice in this section.

1. Consider the following reaction :

$C_6H_5NO_2 \xrightarrow{Sn/HCl} X \xrightarrow{C_6H_5COCl} Y + CHl$
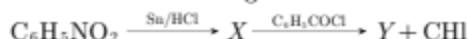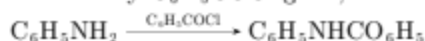
What is Y in the above reaction ?

(a) Acetanilide (b) Benzanilide

(c) Azobenzene (d) Hydrazobenzene

Ans : (b) Benzanilide

Nitrobenzene is reduced to aniline when passed through in and hydrochloric acid.

$C_6H_5NO_2 \xrightarrow{Sn/HCl} C_6H_5NH_2$

Followed by C_6H_5COCl gives,

$C_6H_5NH_2 \xrightarrow{C_6H_5COCl} C_6H_5NHCO_6H_5$

2. An industrial method of preparation of methanol is :

(a) catalytic reduction of carbon monoxide in presence of $ZnO - Cr_2O_3$

(b) by reacting methane with steam at $900°C$ with a nickel catalyst

(c) by reducing formaldehyde with lithium aluminium hydride

(d) by reacting formaldehyde with aqueous sodium hydroxide solution

Ans : (a) catalytic reduction of carbon monoxide in presence of $ZnO - Cr_2O_3$

$\underbrace{CO + H_2}_{\text{water gas}} + H_2 \xrightarrow[300°C]{Cr_2O_2 - ZnO} \underset{\text{Methanol}}{CH_3OH}$
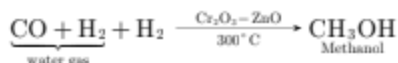
3. Which does not react with I_2 and NaOH.

(a) Ethyl Alcohol (b) Acetaldehyde

(c) Acetone (d) Propanol

Ans : (d) Propanol

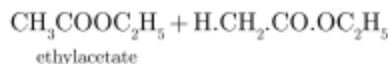$CH_3CH_2OH -$ and $CH_3CO -$ groups react with I_2 and NaOH to give haloform (Iodoform Reaction) $CH_3CH_2 - CH_2 - OH$ (propanol) Lacks this grouping therefore does not react.

4. The preparation of ethyl acetoacetate involves.

(a) Witting reaction

(b) Cannizzaro's reaction

(c) Reformatsky reaction

(d) Claisen condensation

Ans : (d) Claisen condensation

Claisen condensation : Intermolecular condensation of esters containing α-hydrogen atom in presence of strong base to form β-keto ester

$\underset{\text{ethylacetate}}{CH_3COOC_2H_5} + H.CH_2.CO.OC_2H_5$

$\xrightarrow{C_2H_5ONa} \underset{\substack{\text{Ethyl acetoacetate} \\ (\beta\text{-ketoester})}}{CH_3\overset{\overset{O}{\|}}{C}.CH_2COOC_2H_5} + C_2H_5OH$

5. An aqueous solution is 1.00 molal in KI. Which change will cause the vapour pressure of the solution to increase ?

(a) Addition of NaCl

(b) Addition of Na_2SO_4

(c) Addition of 1.00 molal KI

(d) Addition of water

Ans : (d) Addition of water

When the aqueous solution of one molal KI is diluted with water, concentration decreases, therefore the vapour pressure of the resulting solution increases.

6. Which of the following will show paramagnetism corresponding to 2 unpaired electrons ? (Atomic numbers : Ni=28, Fe=26)

(a) $[FeF_6]^{3-}$

(b) $[NiCl_4]^{2-}$

(c) $[Fe(CN)_6]^{3-}$

(d) $[Ni(CN)_4]^{2-}$

Ans : (b) $[NiCl_4]^{2-}$

As in $[NiCl_4]^{2-}$ Chloride ion being a weak ligand is not able to paired the electron in d orbital.

7. The fuel used in the cell used in Apollo mission was.

(a) H_2

(b) $H_2 - O_2$

(c) CH_4

(d) O_2

Ans : (b) $H_2 - O_2$
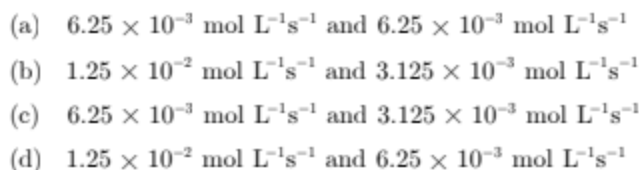
Fuel cell made of H_2-O_2 is used in Apollo-mission. It is pollution free and has highest efficiency (about 70%). It is also less in weight. Hence (b) is the correct option.

8. For the reaction :
$[N_2O_5(g) \longrightarrow 2NO_2(g) + \frac{1}{2}O_2(g)]$ the value of rate of disappearance of N_2O_5 is given as $6.25 \times 10^{-3}\,mol\,L^{-1}s^{-1}$. The rate of formation of NO_2 and O_2 is given respectively as

(a) 6.25×10^{-3} mol $L^{-1}s^{-1}$ and 6.25×10^{-3} mol $L^{-1}s^{-1}$

(b) 1.25×10^{-2} mol $L^{-1}s^{-1}$ and 3.125×10^{-3} mol $L^{-1}s^{-1}$

(c) 6.25×10^{-3} mol $L^{-1}s^{-1}$ and 3.125×10^{-3} mol $L^{-1}s^{-1}$

(d) 1.25×10^{-2} mol $L^{-1}s^{-1}$ and 6.25×10^{-3} mol $L^{-1}s^{-1}$

Ans : (b) 1.25×10^{-2} mol $L^{-1}s^{-1}$ and 3.125×10^{-3} mol $L^{-1}s^{-1}$

$[N_2O_5(g) \longrightarrow 2NO_2(g) + \frac{1}{2}O_2(g)]$
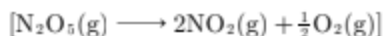
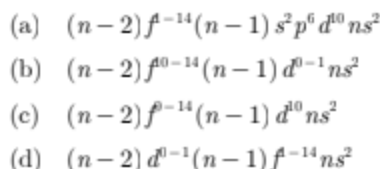$$-\frac{d}{dt}[N_2O_5] = +\frac{1}{2}\frac{d}{dt}[NO_2] = 2\frac{d}{dt}[O_2]$$
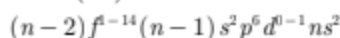
$$\frac{d}{dt}[NO_2] = 1.25 \times 10^{-2}\,mol\,L^{-1}s^{-1}$$

$$\frac{d}{dt}[O_2] = 3.125 \times 10^{-3}\,mol\,L^{-1}s^{-1}$$

9. General electronic configuration of lanthanides is :

(a) $(n-2)f^{1-14}(n-1)s^2p^6d^{10}ns^2$

(b) $(n-2)f^{0-14}(n-1)d^{0-1}ns^2$

(c) $(n-2)f^{0-14}(n-1)d^{10}ns^2$

(d) $(n-2)d^{0-1}(n-1)f^{1-14}ns^2$

Ans : (a) $(n-2)f^{1-14}(n-1)s^2p^6d^{10}ns^2$

The lanthanides are transition metals from atomic 58 (Ce) to 71 (Lu). Hence the electron configuration becomes :
$(n-2)f^{1-14}(n-1)s^2p^6d^{0-1}ns^2$

10. Kohlrausch's law states that at :

(a) finite dilution, each ion makes definite contribution to equivalent conductance of an electrolyte, whatever be the nature of the other ion of the electrolyte.

(b) infinite dilution each ion makes definite contribution to equivalent conductance of an electrolyte depending on the nature of the other ion of the electrolyte.

(c) infinite dilution, each ion makes definite contribution to conductance of an electrolyte whatever be the nature of the other ion of the electrolyte.

(d) infinite dilution, each ion makes definite contribution to equivalent conductance of an electrolyte, whatever be the nature of the other ion of the electrolyte.

Ans : (d) infinite dilution, each ion makes definite contribution to equivalent conductance of an electrolyte, whatever be the nature of the other ion of the electrolyte.

Kohlrausch's Law states that at infinite dilution, each ion migrates independently of its co-ion and contributes to the total equivalent conductance of an electrolyte a definite share which depends only on its own nature.

11. The change in optical rotation (with time) of freshly prepared solutions of sugar is known as :

(a) Specific rotation

(b) Inversion

(c) Rotatory motion

(d) Mutarotation

Ans : (d) Mutarotation

The specific rotation of a freshly prepared solution of glucose changes with time and finally attains a constant value. This phenomenon is called mutarotation.

12. When a biochemical reaction is carried out in laboratory in the absence of enzyme then rate of reaction obtained 10^{-6} times, then activation energy of reaction in the presence of enzyme is :

(a) $\frac{6}{RT}$

(b) different from E_a obtained in laboratory

(c) P is required

(d) can't say anything

Ans : (b) different from E_a obtained in laboratory

The presence of enzyme (catalyst) increases the speed of reaction by lowering the energy barrier, i.e. a new path is followed with lower activation energy.
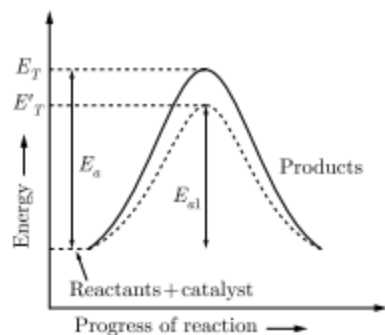
Here E_r is the threshold energy.
E_a and E_{a1} is energy of activation of reaction in absence and presence of catalyst respectively.

Directions (Q. No. 13-16) : Each of the following questions consists of two statements, one is Assertion and the other is Reason. Give answer :

13. **Assertion :** The pK_a of acetic acid is lower than that of phenol.
   Reason : Phenoxide ion is more resonance stabilised.

   (a) Both Assertion and Reason are correct and Reason is a correct explanation of the Assertion.

   (b) Both Assertion and Reason are correct but Reason is not the a correct explanation of the Assertion.

   (c) Assertion is correct but Reason is incorrect.

   (d) Both the Assertion and Reason are incorrect.

   Ans : (c) Assertion is correct but Reason is incorrect.

   Low pK_a value corresponds to more acidic compound. Acetic acid ($pK_a = 4.0$) is more acidic than phenol ($pK_a = 9.0$). It is due to the fact that carboxylate ion is more stabilized due to resonance because its resonating structures are equivalent.

14. **Assertion :** The acetate ion is resonance stabilized.
   Reason : Acetate ion is more basic than the methoxide ion.

   (a) Both Assertion and Reason are correct and Reason is a correct explanation of the Assertion.

   (b) Both Assertion and Reason are correct but Reason is not the a correct explanation of the Assertion.

   (c) Assertion is correct but Reason is incorrect.

   (d) Both the Assertion and Reason are incorrect.

   Ans : (c) Assertion is correct but Reason is incorrect.

   Assertion is correct as conjugate base of a strong acid is weak. Since CH_3COOH is a stronger acid than CH_3OH,

CH_3COO is a weaker base than OCH_3^-.

15. **Assertion :** Aromatic aldehydes and formaldehyde undergo Cannizzaro reaction.
   Reason : These aldehydes which have α-H atom undergo Cannizzaro reaction.

   (a) Both Assertion and Reason are correct and Reason is a correct explanation of the Assertion.

   (b) Both Assertion and Reason are correct but Reason is not the a correct explanation of the Assertion.

   (c) Assertion is correct but Reason is incorrect.

   (d) Both the Assertion and Reason are incorrect.

   Ans : (c) Assertion is correct but Reason is incorrect.

   The aldehydes which have α-H atoms, undergo aldol condensation.

16. **Assertion :** In acidic medium, $K_2Cr_2O_7$ exists as $Cr_2O_7^{2-}$ (orange) while in basic medium it is converted to CrO_4^{2-} (yellow).
   Reason : $K_2Cr_2O_7$ is hygroscopic in nature and changes colour on reaction with water.

   (a) Both Assertion and Reason are correct and Reason is a correct explanation of the Assertion.

   (b) Both Assertion and Reason are correct but Reason is not the a correct explanation of the Assertion.

   (c) Assertion is correct but Reason is incorrect.

   (d) Both the Assertion and Reason are incorrect.

   Ans : (c) Assertion is correct but Reason is incorrect.

   $K_2Cr_2O_7$ changes colour only with change in pH of aqueous solution.

SECTION-B

Directions (Q. Nos. 17-21) : This section contains 5 questions with internal choice in one question. The following questions are very short answer type and carry 2 marks each.

17. Which out of molarity or molality will change in temperature why ?

   Ans :

   Molarity changes with rise in temperature. Volume of a solution increases with rise in temperature and this causes change in molarity because it is related as moles of solute in a given volume of solution.

18. Suggest some chemical reagents for the chemical reduction of carbonyl compounds ($\equiv$ aldehydes and ketones).

   Ans :

   1. Sodium borohydride or sodium tetrahydridoborate (III) $NaBH_4$.
   2. Lithium aluminium hydride or lithium tetrahydrido aluminate (III), $LiAlH_4$.

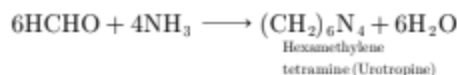**19.** Write the Nernst equation for the EMF of the cell
$Ni_{(s)} \mid Ni^{2+}_{(aq)} \parallel Ag^{2+}_{(aq)} \mid Ag$

Ans :

Given cell is $Ni_{(s)} \mid Ni^{2+}_{(aq)} \parallel Ag^{2+}_{(aq)} \mid Ag$

Nernst equation for the cell is

$$E_{cell} = E^0_{cell} + \frac{RT}{nF} \ln \frac{[Ag^+]}{[Ni]^{+2}}$$

20. Write the reaction of formaldehyde with ammonia.

Ans :

$$6HCHO + 4NH_3 \longrightarrow \underset{\substack{\text{Hexamethylene}\\\text{tetramine (Urotropine)}}}{(CH_2)_6N_4} + 6H_2O$$

Urotropine is used as a urinary antiseptic.
Nitration of hexamethylenetetramine give RDX (Research and development explosive)

RDX or cyclonite
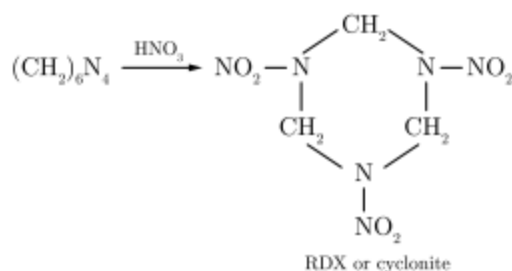
or

How will you convert ?
1. $CH_3COOH \longrightarrow CH_3 - CH_3$
2. $CH_3COOH \longrightarrow CH_3 - CH_2 - OH$
3. $C_6H_5COOH - C_6H_4 - Br - COOH$

Ans :

1. $CH_3COOH + 6HI \xrightarrow{\text{Red P}} CH_3 - CH_3 + 2H_2O + 3I_2$

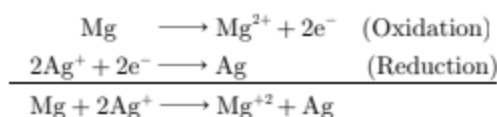2. $CH_3COOH \xrightarrow{\text{LiAlH}_4} CH_3CH_2OH + H_2O$

3.

m-bromobenzoic acid
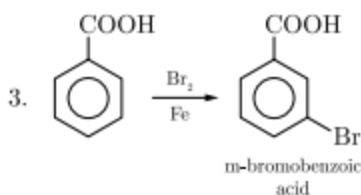
21. Write the cell reaction for which $E_{cell} = E^0_{cell} - \frac{RT}{2F} \ln \frac{[Mg^{2+}]}{[Ag^+]^2}$

Ans :

Given, $E_{cell} = E^0_{cell} - \frac{RT}{2F} \ln \frac{[Mg^{2+}]}{[Ag^+]^2}$

The cell reaction is $Mg_{(s)}/Mg^{2+}_{(aq)} \parallel Ag^+_{(aq)} \mid Ag_{(s)}$

$$\begin{aligned} Mg &\longrightarrow Mg^{2+} + 2e^- \quad \text{(Oxidation)}\\ 2Ag^+ + 2e^- &\longrightarrow Ag \quad\quad\quad\quad \text{(Reduction)}\\ \hline Mg + 2Ag^+ &\longrightarrow Mg^{+2} + Ag \end{aligned}$$

SECTION-C

Directions (Q. Nos. 22-28) : This section contains 7 questions with internal choice in one question. The following questions are short answer type and carry 3 marks each.

22. Complete the following reactions :
1. $CH_3 - O - C_2H_5 + HI \xrightarrow{373\,K}$
2. $C_6H_5ONa + CH_3Br \xrightarrow{\Delta}$
3. $CH_3 - O - CH_2CH_3 + HBr \xrightarrow{373\,K}$

Ans :

1. $CH_3 - O - C_2H_5 + HI \xrightarrow{373\,K} CH_3I + CH_3CH_2 - OH$

2. $C_6H_5ONa + CH_3Br \xrightarrow{\Delta} C_6H_5OCH_3 + NaBr$

3. $CH_3 - O - CH_2CH_3 + HBr$
$\xrightarrow{373\,K} CH_3Br + CH_3CH_2 - OH$

23. How is standard Gibbs energy of a reaction is related to its equilibrium constant ?

Ans :

If standard emf of a cell is E°_{cell} and nF is the amount of charge passed, then standard gibbs energy of the reaction,

$$\Delta_r G^\circ = - nF E^\circ_{cell}$$

Further, we know

$$E^\circ_{cell} = \frac{RT}{nF} \ln K_C$$

Hence, $\Delta_r G^\circ = - nF \times \dfrac{RT}{nF} \ln K_C$

$$= - RT \ln K_C$$
$$= - 2.303\, RT \log K_C$$

24. What is a racemic mixture ? Give one example.

Ans :

A 50 : 50 mixture of two enantiomers of any optically active compound is called a racemic mixture. It is optically inactive. Since rotation caused by the molecules of one enantiomer is exactly cancelled by equal and opposite rotation caused by the same molecules of the other enantiomers. For example an equimolar mixture of (+)-2-bromobutane and (−)-2-bromobutane.

25. Discuss the following terms :

(a) Coordination Number.

(b) Effective Atomic Number.

Ans :

(a) **Coordination Number :** The total number ligands to which the metal is bounded through a Co-ordinate bond in the given complex is known as Co-ordination Number. e.g.

$[Co(NH_3)_6]^{3+}$ has co-ordination number $= 6$

$[Ni(CO)_4]$ has co-ordination number $= 4$
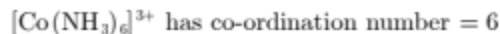
(b) **Effective Atomic Number (EAN) :** It is the difference between the atomic number (Z) of a metal and its oxidation-number plus twice of the co-ordination number of that metal.

Mathematically :

$$EAN = [(Z - Oxidation\ number)$$
$$+ (2 \times Co - ordination\ Number)]$$

e.g., $K_4[Fe(CN)_6]$ has EAN No.

$$= [(26 - 2) + (2 \times 6)] = 36\ (\approx Kr)$$

26. Which would undergo S_N1 reaction faster in the following pair and why ?

$$CH_3-CH_2-Br \text{ and } H_3C-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle Br}{|}}{C}}-CH_3$$
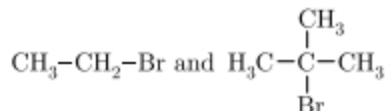
Ans :

$3°$ carbocation $> 2°$ carbocation $> 1°$ carbocation $> CH_3^+$. Therefore, the reactivity of alkyl halides towards S_N1 rations decreases in the same order.

Among the given compounds bromoethane is primary alkyl halide which forms a $1°$ carbocation intermediate in the S_N1 reaction. The other compound is 2-chloro 2-methylpropane which is a tertiary alkyl halide which forms a tertiary carbocation intermediate in the S_N1 reaction.

Hence, 2-bromo-2-methylpropane undergoes an S_N1 reaction faster than bromoethane.

27. How substituents effect the acidity of carboxylic acids ?

Ans :

Electron withdrawing groups (EWG) increase the acidity of carboxylic acid by stabilising the condjugate base through delocalisation of the negative charge. Electron donating groups (EDG) decrease the acidity by destabilising the conjugate base.
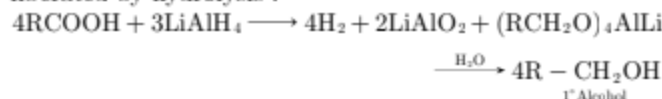

The effect of the following groups in increasing acidity order is

$ph < I < Br < Cl < F < CN < NO_2 < CF_3$
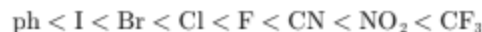
28. How can one reduce carboxylic acid to alcohol?

Ans :

The acids can be reduced to alcohols by using a strong reducing agent, Lithium aluminium hydride $(LiAlH_4)$. The intial product is an alkoxide from which the alcohol is liberated by hydrolysis :

$$4RCOOH + 3LiAlH_4 \longrightarrow 4H_2 + 2LiAlO_2 + (RCH_2O)_4AlLi$$
$$\xrightarrow{H_2O} 4R-CH_2OH$$
$$1°Alcohol$$

i.e., $R-COOH \xrightarrow[(ii)H_2O]{*(i)LiAlH_4} R-CH_2OH$

NOTE : Along the arrow, the numbers in front of the reagents indicate that the second reagent is added only when the reaction with first is complete.

The alcohol is obtained in excellent yield. However, $LiAlH_4$ being an expensive reagent, is used in industry only for the reduction of small amounts of valuable raw materials, as in the synthesis of certain drugs and hormones.

or

How carboxylic acids are commercially converted into alcohols ?

Ans :

Commercially, carboxylic acids are converted into alcohols by a two-step process : esterification, and reduction of the ester.

Esters can be reduced in two ways :

1. By catalytic hydrogenation using molecular hydrogen.

2. By chemical reduction.

$$RCOOH \xrightarrow[Esterification]{R'OH+H^+} RCOOR'$$
$$Ester$$
$$\xrightarrow[Reduction]{(H_2/Ni)} RCH_2OH + R'OH$$
$$1°alcohol$$

In either case, the ester is cleaved to yield (in addition to the alcohol or phenol form which it was derived) a primary alcohol corresponding to the acid portion of the ester.

SECTION-D

Directions (Q. Nos. 29-30) : The following questions are case-based questions. Each question has an internal choice and carries 4 marks each. Read the passage carefully and answer the questions that follow.

29. A reaction is said to be unimolecular if, on the microscopic level, rearrangement of the structure of a single molecule produces the appropriate product molecules. An example of a unimolecular process is conversion of cis-2-butene to trans-2-butene (in the absence of any catalyst).
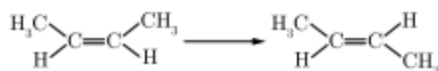
All that is required for this reaction to occur is a twist or rotation around the double bond interchanging the methyl group with the hydrogen atom on the right-hand side. Only one cis-2-butene molecule need to be involved as a reactant in this process. Rotating part of a molecule about a double bond is not easy, because it involves a distortion of the electron clouds forming the double bond. A considerable increase in energy is required to twist one end of cis-2-butene around the other. This is shown in figure.
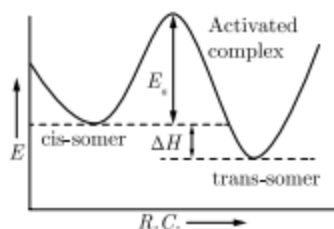
The minimum quantity of energy required to surmount an energy barrier during a chemical reaction is called the activation energy, E_a and the molecular species at the top of the barrier is called the activated complex or transition state.

In the sample of gaseous cis-2-butene at room temperature, only a tiny fraction of molecules have enough energy to surmount the activation energy barrier. Not only do few molecules have enough energy to overcome the activation energy barrier, but fewer still have that energy concentrated so that it can cause the atomic movements needed for the reaction to occur. For a uni-molecular process, the reaction rate must always be directly proportional to the concentration of the reacting species. For a general uni-molecular process, $A \rightarrow$ products, the rate equation is, Rate $= k[A]$, where $[A] =$ concentration of A.

Read the above passage and answer the following questions:

(a) With the help of diagram, explain the physical significance of energy of activation (E_a) in chemical reactions.

(b) Can molecularity of a reaction be zero ?

(c) Over a given period of time only a very small fraction of cis-2-butene molecule will be converted to trans-2-bttene. Give reason.

or

(d) How is the rate of reaction affected if the concentration of cis-2-butene is doubled ?

Ans :

(a) The energy required to form activated complex is called activation energy. It is the difference between the threshold energy and the average energy possessed by the reacting molecules.

(b) No, the molecularity can never be zero or a fractional number as it shows the number of reactants taking part in a reaction which can never be zero.

(c) In case of cis-2-butene, a very small fraction of molecules have enough energy to overcome the activation energy

barrier and very few of the high energy molecules have their energy distributed so that most of it is causing a twist around the double bond to form trans-2-butene. For this reason, over a given period of time, only a very small fraction of the cis-2-butene molecules will be converted to trans-2-butene.

or

(d) $\text{Rate}_1 = k[cis - 2 - \text{butane}]$

If $[cis - 2 - \text{butane}]$ is doubled

$\text{Rate}_2 = k \times 2[cis - 2 - \text{butane}] = 2 \text{Rate}_1$

i.e., rate will also be doubled.

30. The simple aryl halides generally are resistant to attack by nucleophiles in either S_N1 or S_N2 reactions. However, this low reactivity can be changed dramatically by changes in the reaction conditions and the structure of the aryl halide. In fact, nuclephilic displacement becomes quite rapid.(i) when the aryl halide is activated by substitution with strongly electron attracting groups such as NO_2 and (ii) when very strongly basic nucleophilic reagents are used. The generally accepted mechanism of nucleophilic aromatic substitution of aryl halides carrying activating groups involve two steps. The first step involves attack of the nucleophile Y at the carbon bearing halogen substitutent to form an intermediate carbanion. The aromatic system is destroyed on forming the anion and the carbon at the reaction site changes from planar (sp^2 bonds) to tetrahedral (sp^3 bonds).
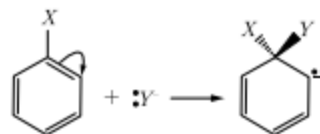
In the second step, loss of an anion, X^- or Y^-, regenerated an aromatic system and if X^- is lost, the overall reaction is nucleophilic displacement of X by Y
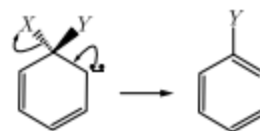
When strongly electron attracting groups are located on the ring at the ortho-parapositions, the intermediate anion is stabilised by the delocalization of the electrons from the ring carbons to more favourable locations on the substituent groups.
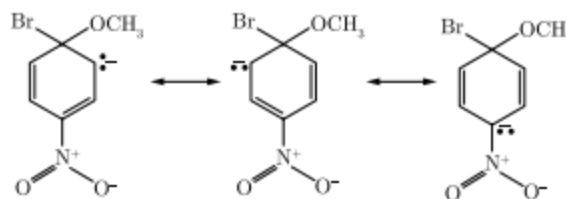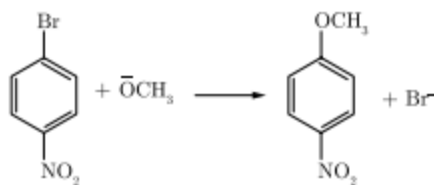
Read the above passage carefully and answer the following questions :

(a) Chlorobenzene is extremely less reactive towards a nucleophilic substitution reaction. Give two reasons for the same.

(b) Write the product formed when p-nitrochlorobenzene is heated with aqueous NaOH at 443 K followed by acidification.

(c) Why NO_2, group shows its effect only at ortho and para-positions and not at meta-position?

or

(d) Aryl halides are extremely less reactive towards nucleophilic substitution. Predict and explain the order of reactivity of the following compounds towards nucleophilic substitution :
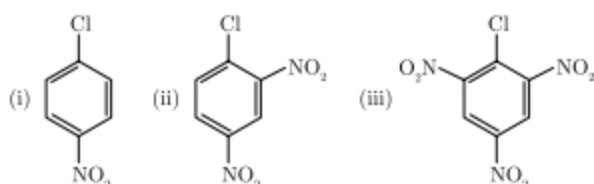
Ans :

(a) Haloarenes are much less reactive than haloalkanes towards nucleophilic substitution reactions due to the following reasons.

(i) **Resonance effect :** In haloarenes the electron pairs on halogen atom are in conjugation with π-electrons of the ring and the following resonating structures are possible.
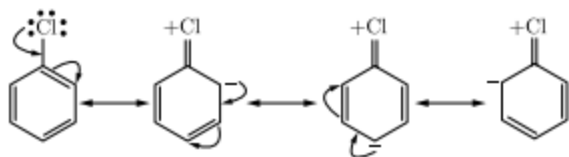
C-Cl bond acquires a partial double bond character due to resonance. As a result, the bond cleavage in haloarene is difficult than haloalkane and therefore, are less reactive towards nucleophilic substitution reaction.

(ii) In halorenes, halogen is attached to sp^2-hybridised

carbon while in haloalkanes, halogen is attached to sp^3-hvbridised carbon.

(b)

(c) The presence of nitro group at ortho and para positions withdraws the electron density from the benzene ring and thus facilitates the attack of the nucleophile on aryl halide. The carbanion thus formed is stabilised by resonance. The negative charge appeared at ortho- and parc-positions with respect to the halogen substituent is stabilised by $-NO_2$, group while in case of meta-nitrobenzene none of the resonating structures bear the negative on carbon atom bearing the $-NO_2$, group. Therefore, the presence of $-NO_2$, group at meta position does not stabilise the negative charge and hence no effect on reactivity of $-NO_2$, group at meta position.

or

(d) III > II > I. Presence of an electron withdrawing group (like $-NO_2$) at ortho and para positions increases the reactivity of haloarenes towards nucleophilic substitution.
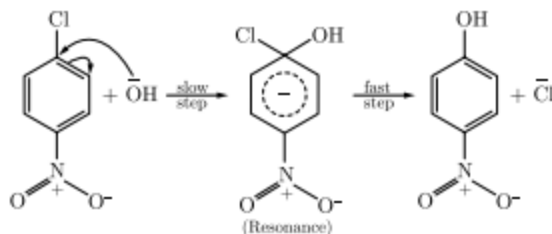
SECTION-E

Directions (Q. Nos. 31-33) : The following questions are long answer type and carry 5 marks each. Two questions have an internal choice.

31. Derive the Arrhenius equation.

Ans :

Quantitatively the effect of temperature on the rate of a reaction and hence on the rate constant K was proposed by Arrhenius (1889). The equation, called Arrhenius equation.

$$K = Ae^{-Ea/RT} \qquad ...(1)$$

Where A is constant known as frequency fact 1 or (It gives the frequency of binary collisions of the reacting molecules

per second per litre) E_a is the energy of activation, R is gas constant and R is the absolute temperature. The two quantities A and E_a are collectively called Arrhenius parameters.

Taking logarithm equation (1),

$$\ln K = \ln A + \ln e^{-Ea/RT}$$

$$\ln K = \ln A - \frac{E_a}{RT} \ln e$$

$$\ln K = \ln A - \frac{E_a}{RT} \qquad [\text{Hence}, \ln e = 1] ...(2)$$

If K_1 and K_2 are the values of rate constant at temperature T_1 and T_2 then,

$$\ln K_1 = \ln A - \frac{E_a}{RT_1} \qquad\qquad ...(3)$$

$$\ln K_2 = \ln A - \frac{E_a}{RT_2} \qquad\qquad ...(4)$$

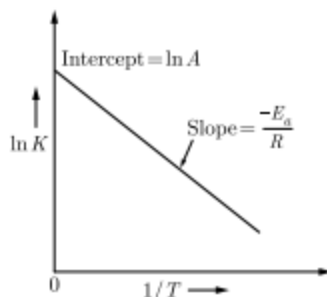Subtracting equation (4) from equation (3), we get

$$\ln K_2 - \ln K_1 = -\frac{E_a}{RT_2} - \left(-\frac{E_a}{RT_1}\right)$$

$$\ln K_2 - \ln K_1 = \frac{E_a}{RT_1} - \frac{E_a}{RT_2}$$

$$\ln \frac{K_2}{K_1} = \frac{E_a}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

Converting to common logarithm

$$\log \frac{K_2}{K_1} = \frac{E_a}{3.303\,R}\left[\frac{T_2 - T_1}{T_1 T_2}\right]$$

or

Briefly explain the effect of adding catalyst on the rate of reaction.

Ans :

Catalyst : A catalyst is a substance which increase the rate of a reaction without itself undergoing any permanent chemical change. For example MnO_2 catalyses the following reaction to increase its rate considerably

$$2KClO_3 \xrightarrow{MnO_2} 2KCl + 3O_2$$

The action of the catalyst is explained by intermediate complex theory. According to this theory, a catalyst participates in a chemical reaction by forming temporary bonds with the reactants resulting in an intermediate complex. This has a transitory existence and decomposes to yield products and the catalyst.
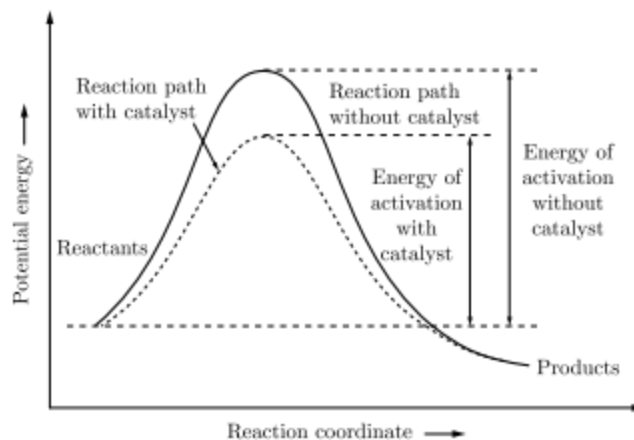

Figure : Effect of Catalyst on Activation Energy.

$$\underset{\text{Reactants}}{A+B} + \underset{\text{Catalyst}}{C} \longrightarrow \underset{\underset{\text{Intermediate}}{\underset{\text{complex}}{C}}}{A\cdots B} \longrightarrow \underset{\text{Products}}{A-B} + \underset{\underset{\text{(Regenerated)}}{\text{Catalyst}}}{C}$$

The catalyst provides an alternate pathway of reaction mechanism by reducing the activation energy between reactants and products and hence lowering the potential energy.

32. (a) In the titration of $FeSO_4$ with $KMnO_4$ in the acidic medium, why is dil. H_2SO_4 used instead of dil. HCl ?

(b) Give reason :
1. Among transition metals, the highest oxidation states is exhibited on oxo-anions of a metal.
2. Ce^+ is used as an oxidising agent in volumetric analysis.
3. Transition metals form a number of interstitial compounds.
4. Zn^{2+} salts are white while Cu^{2+} salts are blue.

Ans :

(a) Dil H_2SO_4 is an oxidising agent and oxidises $FeSO_4$ to $Fe_2(SO_4)_3$.
On the other hand, dil. HCl is a reducing agent and liberates chlorine on reacting with $KMnO_4$ solution.
Thus, a part of the oxygen produced from $KMnO_4$ is used up by HCl.

(b)
1. In these oxoanions the oxygen atoms are directly bonded to the transition metal atom/ion.
Since oxygen is highly electronegative, therefore, the oxoanions bring out the highest oxidation state of the
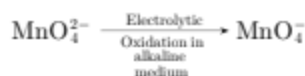
metal.

2. Ce^{4+} has the tendency to attain +3 oxidation state in volumetric analysis.

3. This is due to the presence of voids of appropriate size in their crystal lattices.

4. Zn^{2+} ions has all its orbitals completely filled whereas in Cu^{2+} ions there is one half filled $3d$-orbital. It therefore has a tendency to form coloured salts whereas Zn^{2+} has no such tendency.

or

(a) A blackish brown coloured solid 'A' when fused with alkali metal hydroxides in presence of air produces a dark green coloured compound 'B' which an electrolytic oxidation in alkaline medium gives a dark purple coloured compound 'C'. Identify A, B and C and write the reactions involved.

(b) What happens when an acidic solution of the green compound (B) is allowed to stand for sometime ? Give the equation involved. What is this type of reaction called ?

Ans :

(a)
$$A = MnO_2$$
$$B = K_2MnO_4$$
$$C = KMnO_4$$
$$2MnO_2 + 4KOH + O_2 \longrightarrow 2K_2MnO_4 + 2H_2O$$

$$MnO_4^{2-} \xrightarrow[\substack{\text{Oxidation in} \\ \text{alkaline} \\ \text{medium}}]{\text{Electrolytic}} MnO_4^-$$

(b) In acidic medium, K_2MnO_4 changes to give purple coloured solution along with a black precipitate.

$$\underset{\substack{\text{Green} \\ \text{compound}}}{3MnO_4^{2-}} + \xrightarrow{4H^+} \underset{\text{Purple}}{2MnO_4^-} + \underset{\text{Black}}{MnO_2} + 2H_2O$$

It is called disproportionation reaction.

33. Amino acids may be acidic, alkaline or neutral. How does this happen ?

Ans :

Amino acids are classified as acidic, basic or neutral depending upon the relative number of amino and carboxyl groups in their molecule.
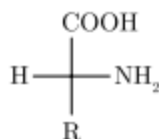
(i) **Neutral Amino Acids :** Neutral amino acids own equal number of amino and carboxyl groups.

Examples :

Glycine $(R \equiv -H)$,

Alanine $(R \equiv -CH_3)$

Valine $(R \equiv (H_3C)_2CH-)$

(ii) **Basic Amino Acids :** Basic amino acids own more number of amino than carboxyl groups.

Examples :

Lysine $\quad (R \equiv H_2N-(CH_2)_4-)$

Glutamine $\quad (R \equiv H_2N-\overset{\overset{O}{\|}}{C}-CH_2CH_2-)$

Asparagine $\quad (R \equiv H_2N-\overset{\overset{O}{\|}}{C}-CH_2-)$

(iii) **Acidic Amino Acids :** Acidic amino acids own more number of carboxyl groups as compared to amino groups.

Examples :

Glutamic acid $(R \equiv -CH_2CH_2COOH)$

Aspartic acid $(R \equiv -CH_2COOH)$

□□□□□□□