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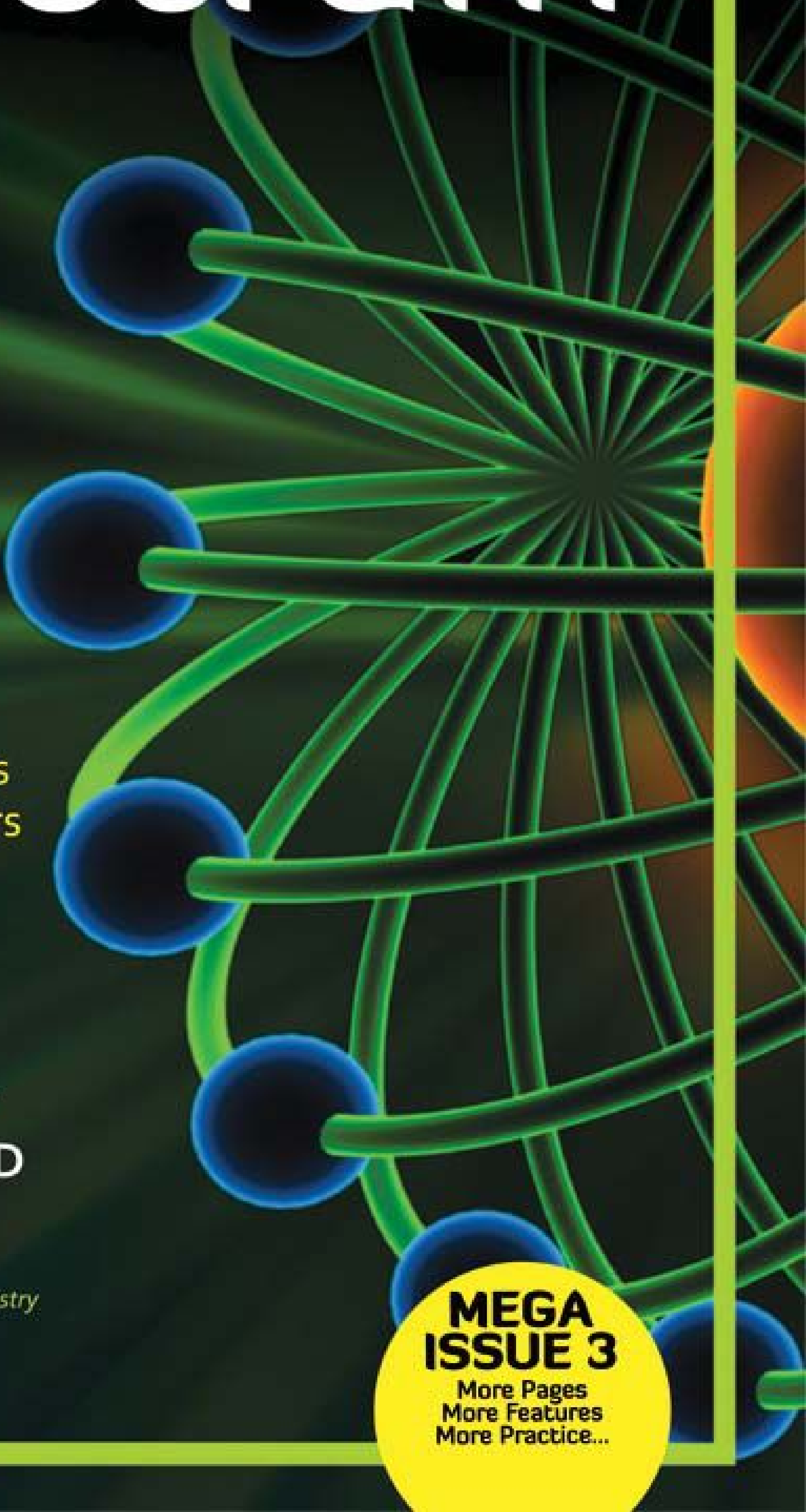
February 2017 | ₹35.00

CHEMISTRY Spectrum



TARGET 2017

Rapid
Concept Revision

Organic Chemistry : Some Basic Principles and Techniques

Hydrocarbons

FROM CLASS 11th SYLLABUS

Haloalkanes and Haloarenes

Alcohols, Phenols and Ethers

Aldehydes, Ketones and Carboxylic acids

FROM CLASS 12th SYLLABUS

TEST RiDER FOR JEE
MEDi QUEST FOR NEET
TEST DRiVE FOR BOARD

JUVENILEZ

GOLDEN OLDIES *Redox and Electrochemistry*
RAINBOW *Chemical Kinetics*
FUN ARCADE

MEGA ISSUE 3
More Pages
More Features
More Practice...

CHEMISTRY Spectrum

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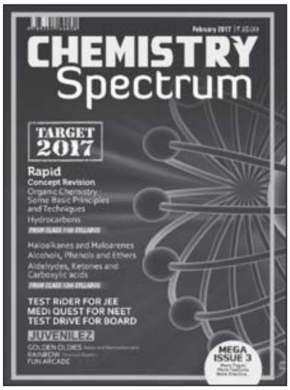
Circulation Regd. Office ARIHANT MEDIA PROMOTERS
4577/15, AGARWAL ROAD,
DARYA GANJ, NEW DELHI-2
PH. : 011-47630600

Printed and Published by Parul Jain for
Arihant Media Promoters
Printed at Arihant Publications (India) Ltd
T.P. Nagar, Meerut (U.P.)

Issue 3 Vol 3



Dear Aspirants,
The month of February is very special as it is the last formal month of preparations. Chemistry is the most dependable subject among all the three. It may be the most favourite for some and may be the scariest for others. For me Chemistry is the mysterious subject. (Chemistry – *che* + *mistry* or *mystry*). Imagine nobody has seen electron till date but many of us has written books on it. So in a way, it is a bit different and unique. That's why while going for chemistry remember!

1. There will be certain end result of any chemical reaction which limits our working arena technically.
2. The end result may change in accordance with situations, thus in turn give birth to so called **'exceptions'** in chemistry.
3. Most of the theories or rules covered in chemistry are result based and as nobody has seen interacting particles in a test tube hence, these theories or rules are considered under the **'most probable'** category.
4. In the purview of first three statements we can conclude that the aptitude of chemistry involves explorations into the subject with very limited **'kyon'** or **'why'** or 'how' like punctuations.
5. Besides the above written things language plays a very important role in tackling chemistry. A small twist in language changes the entire meaning of the question. So, nature wise a substantial control over language is required along with the aptitude to grip this subject properly.

Hope above written tips will prove helpful in targeting your goal and from the side of spectrum family I personally assure you that we will try to create more and more to help you out. Remember! One more thing

> ***"Every aspect is the world today even politics and international relation is affected by chemistry."***
>
> ***Linus Pauling***

The spectrum team will be anxiously waiting for your feed backs and comments.
Good luck

Sharma

Contents

@ CLASS XI SYLLABUS

Rapid CONCEPT REVISION

TARGET 2017

ORGANIC CHEMISTRY : SOME BASIC PRINCIPLES AND TECHNIQUES

- Due to catenation property, carbon forms a variety of compounds by making single and multiple bonds with carbon and other elements.
- These compounds of carbon are found in living beings and hence studied in a different branch of chemistry called **organic chemistry**.
- Urea is the first organic compound to be synthesised artificially by heating NH_4OCN by Friedrich Wohler.
- The organic compounds have been classified on the basis of structure (Open chain or acyclic or aliphatic and closed chain or cyclic compounds) and functional groups (double bond, triple bond, —Cl, —Br, —OH, —NH_2, etc).

Systems of Nomenclature of Organic Compounds

Trivial System

- It is the oldest system of naming organic compounds.
- In this system, the name were assigned at the wish of discoverer and had no system. These names are also called **common names**.
- Generally, they are based on the source or some property or any other reason.
- For example, acetic acid (acetum = vinegar) formic acid (first obtained from red ants formicus, etc.)

IUPAC System

In 1957, the International Union of Pure and Applied Chemistry evolved a scheme for giving systematic name to organic compounds on the basis of their structure. This is known as the **IUPAC system of nomenclature**.

Rules for Writing IUPAC Name

The following rules are followed while giving IUPAC name to an organic compound:

1. The principal chain in the organic compound is determined first which is the longest possible carbon chain in the molecule.
2. If two or more chains in a compound have same length, the chain having greatest number of branches is considered as the principal chain.

   Remember The longest chain must contain the principal functional group, secondary functional group and multiple bonds as many as possible.

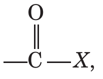
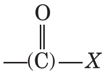
Numbering of Longest Carbon Chain

- If single branch (side chain) is present in the compound, then numbering must be done in such a manner that the side chain acquires the least possible number.
- If all the chains are of same length, then numbering must be done in accordance with lowest sum rule, i.e. the sum of numbers of side chains will be the least.
- In case of branches of different length, the numbering must be done in accordance with "lowest set of locants rule".
- If multiple bond is present alongwith the side chain, then numbering must be done such that multiple bond will get the lowest possible number.

- If any other functional group is present in the compound (other than multiple bond), then numbering must be done such that the functional group will get the lowest possible number.
- If more than one functional groups are present in the compound, then the group which comes first in the following preferential order will be considered as principal functional group and rest of the functional groups are considered as substituent groups or branch.

The decreasing order of priority of different functional groups is Radicals, anions, cations, Zwitter ionic compounds, acids, anhydrides, esters, acid halides, amides, hydrazides, imides, nitriles, aldehydes, ketones, alcohols, amines, imines, ethers, peroxides, Alkene, Alkyne, Halogens.

The prefix and suffix used for different functional groups are given in the table below:

S.No.	Class	Formula	Prefix	Suffix
1.	Acid halides	 $-\overset{O}{\overset{\parallel}{C}}-X$,  $-\overset{O}{\overset{\parallel}{(C)}}-X$ where, X = halogen	halocarbonyl	-carbonyl halide -oyl halide
2.	Alcohols, phenols	$-OH$	hydroxy-	-ol
3.	Aldehydes	$-CHO$ $-(C)HO$	formyl- —	-carbaldehyde -al
4.	Amides	$-CO-NH_2$ $-(C)O-NH_2$	carbamoyl- —	-carboxamide -amide
5.	Amines	$-NH_2$	amino-	-amine
6.	Carboxylic acids	$-COOH$ $-(C)OOH$	carboxy- —	-carboxylic acid -oic acid
7.	Ethers	$-OR$	(R)-oxy	-
8.	Esters (of carboxylic acids)	$-COOR$ $-(C)OOR$	(R)-oxycarbonyl (R)-oxycarbonyl	(R).. carboxylate (R) ... oate
9.	Imines	$=NH$ $=NR$	imino- (R)-imino	-imine
10.	Ketones	$>(C)=O$	oxo-	-one
11.	Nitriles	$-C\equiv N$ $-(C)\equiv N$	cyano- —	-carbonitrile -nitrile
12.	Sulphonic acids	$-SO_2-OH$	sulpho-	-sulphonic acid
13.	Thiols	$-SH$	Sulphanyl-	-thiol

Note In the above table, R designates any alkyl group and C-atom in ( ) means when it is included in the main chain.

Isomerism

Compounds having same molecular formula but differ in structural formula, properties and spatial arrangement are called **isomers** and the phenomenon is called **isomerism**.

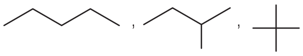
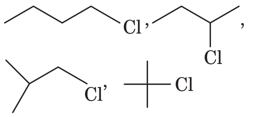
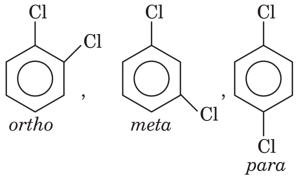
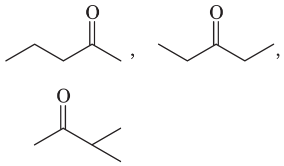
Types of Isomerism

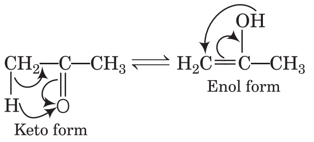
They are of following two types:

(A) Structural Isomerism

The compounds having same molecular formulae but different structural formulae are called structural isomers.

Different structural isomers are:

S. No.	Types of structural isomerism	Examples
1.	**Chain isomerism** Compounds having same chemical formulae, but different carbon skeleton are chain isomers.	C_5H_{12} 
2.	**Position isomerism** Compounds differ in the position of functional group on carbon skeleton.	• C_4H_9Cl  • $C_6H_4Cl_2$ 
3.	**Functional isomerism** Compounds having same molecular formulae but different functional groups attached are functional isomers.	• C_nH_{2n}, alkene, cycloalkane • C_nH_{2n-2}, alkadiene, alkyne, cycloalkene • $C_nH_{2n+2}O$, alcohol, ether • $C_nH_{2n}O$, aldehyde, ketone, oxirane • $C_nH_{2n}O_2$, acid, ester, hydroxy carbonyl compounds
4.	**Metamerism** Compounds having same molecular formulae but different alkyl chains on either side of the functional group are metamers.	$C_5H_{10}O$ 

5.	**Tautomerism** It is a special type of structural isomerism. Compounds differ due to wandering nature of hydrogen atom in between two polyvalent atoms are called tautomers.	

REMEMBER

- Tautomers always exist in dynamic equilibrium.
- It is a chemical phenomenon which takes place only in liquids and gaseous phase. It never takes place in solid state.
- The process of tautomerism can be catalysed by the acid as well as bases.

(B) Stereoisomerism

Compounds having same molecular and structural formulae but are different due to different arrangement of atoms/groups in three dimensional space are called **stereoisomers**.

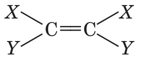
They are further divided into two types:

1. Geometrical Isomerism

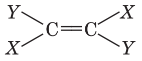
It arises due to restricted rotation of atoms or groups about the

- double bonded C-atoms in alkenes
- single bonded C-atoms in cyclic compounds.
- double bonded C and N-atoms in oximes
- double bonded N-atoms in diazo compounds.

(i) **Geometrical isomerism in alkenes** The forms in which similar groups are present on the same side of double bond are called *cis*-forms while in which similar groups are present on the different sides are called *trans*-forms. These forms show usually similar chemical but different physical properties. e.g.

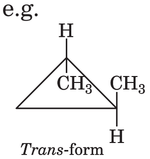


($X \neq Y$)
Cis-isomer

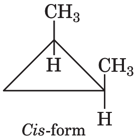


($X \neq Y$)
Trans-isomer

(ii) **Geometrical isomerism in cyclic compounds** When two identical groups are on the same side of cyclic plane, isomer is called ***cis***. If two identical groups are on opposite of cyclic plane, isomer is called ***trans***. e.g.



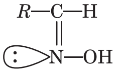
Trans-form



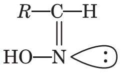
Cis-form

(iii) **Geometrical isomerism in nitrogen containing compounds** In nitrogen containing compounds, *syn* corresponds to *cis* and anti corresponds to *trans* form.

In aldoximes

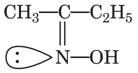


Syn-oxime

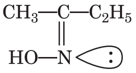


Anti-oxime

In ketoximes

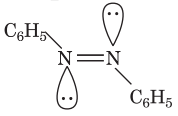


Syn-oxime
(*wrt* ethyl)

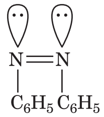


Anti-oxime
(*wrt* ethyl)

In azo compounds



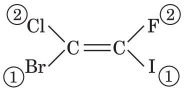
Anti-oxime



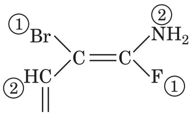
Syn-oxime

E, Z-System of Nomenclature

- *Cis* and *trans* system of geometrical isomerism doesn't work in case of alkenes having different groups on each side of double bond.
- The configuration of these compounds can be specified by using the notations *E* (from German *Entgegen*. = opposite) and *Z* (from German *Zusammen* = together).
- For determining *E* and *Z* configurations we have to assign priority to the groups attached to the doubly bonded C-atoms.
- The priority can be assigned on the basis of the atomic number of the group attached (in fact the atomic number of that atom of the group is considered which is attached directly to the atom).
- The group with higher atomic number will get the first priority.



Z-form
(Analogous to
cis-form)



E-form
(Analogous to
trans-form)

Formulae to Calculate Number of Geometrical Isomers

- In compounds with n number of π-bonds at different ends, number of geometrical isomers = 2^n.
- In compounds with n number of π-bonds at same ends.

***Case* I** When, n = even number

Number of geometrical isomers= $2^{(n-1)} + 2^{(n/2-1)}$

***Case* II** When, n = odd number

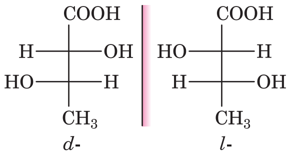
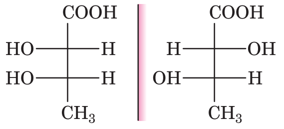
Number of geometrical isomers = $2^{(n-1)} + 2^{\left(\frac{n+1}{2}-1\right)}$

2. Optical Isomerism

Compounds with similar physical as well as chemical properties but are different only in their behaviour towards plane polarised light are called **optical isomers** and this property is called **optical isomerism**.

- The optical isomers that rotate the plane polarised light towards right are called **dextrorotatory** or *d* or (+) form and those rotate the plane polarised light towards left are called **laevorotatory** or *l* or (–) form.
- Optically active compounds must contain chiral carbon (the carbon to which 4 different groups are attached). It is not necessary that all compounds containing chiral carbon are optically active.

Optically active isomers are of two types:

	Enantiomers	**Diastereomers**
1.	These are non-superimposable mirror images of each other.	These are neither superimposable nor mirror images of each other.
2.	They have same physical and chemical properties except towards optically active reagents. The only difference is that they rotate the plane polarised light opposite to each other (*d*- and *l*-). e.g 	They have different physical and chemical properties. They are of two types such as epimers (differ in configuration about a single interstitial point) and anomers (differ in configuration about a single terminal carbon atom). e.g. 

R-S System of Nomenclature

(Absolute Configuration)

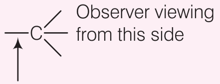
This nomenclature was proposed by Cahn, Ingold and Prelog. This follows the below given sequence rules.

(i) Atoms directly attached to the chiral carbon are arranged in decreasing atomic number.

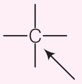
(ii) If the sequence $1 \rightarrow 2 \rightarrow 3$ traces a clockwise turn, configuration is *R*.

(iii) If the sequence $1 \rightarrow 2 \rightarrow 3$ traces an anticlockwise turn, configuration is *S*.

Now, before assigning *R*, *S*-configuration we must ensure that the lowest priority group must be directed away from observer. The positioning of the lowest priority group down and away from the observer can be assumed easily in three dimensions but difficult a bit in two dimensions, e.g.



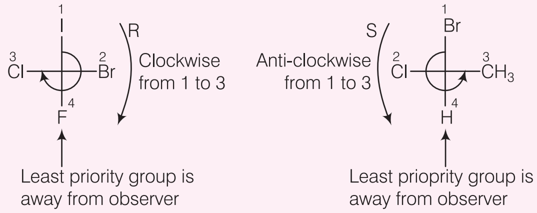
This valency is away from the observer (three-dimensional view of C-atoms)
You can easily position the group of lowest priority away from you if you see the C-atom three-dimensionally.



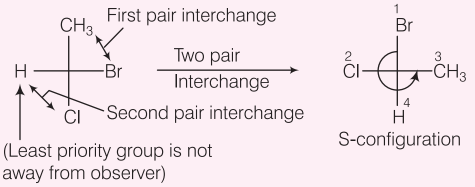
This valency is away from the observer (two-dimensional view of the C-atoms)
For positioning the group of lowest priority away from you. You have to perform pair of interchanges among the groups attached to asymmetric C-atom.

Now, we can easily assign *R*,*S*-configuration as follows.

(i) When least priority group is away from observer.



(ii) When least priority group is not away from observer, we have to follow the two pair interchange rule as stated below



Note The two pair interchange retains the original configuration.

Formulae to Calculate the Number of Optical Isomers

(i) If molecules has *n* number of asymmetric (chiral) carbon atoms and it is not divisible into two equal halves.

- Number of optically active form = $2^n = a$.
- Number of enantiomeric pairs = $a / 2$.
- Number of racemic mixtures = $a / 2$.
- Number of *meso*-forms $(m) = 0$.

(ii) If molecules are not divisible into two equal halves.

	Case I (n = even no.)	**Case II** (n = odd no.)
Number of optically active forms	$2^{n-1} = a$	$2^{n-1} - 2^{(n-1)/2} = a$
Number of enantiomeric forms	$a/2$	$a/2$
Number of racemic mixtures	$a/2$	$a/2$
Number of *meso*-forms (m)	$2^{(n/2-1)}$	$2^{(n-1)/2}$
Total number of configurational isomer	$a+m$	$a+m$

Measurement of Optical Activity

- The angle by which the plane polarised light is rotated after passing through the optically active substance is called **observed rotation** (α) and is given by

$$\alpha = [\alpha]_{\lambda}^{T} \times l \times C$$

where, l = length of polarimeter tube (in dm)

C = concentration of sample (g/mL)

$[\alpha]_{\lambda}^{T}$ = specific rotation

- As observed rotation is a variable quantity in order to standardise it, specific rotation was introduced which is constant for a particular organic sample and is given by $[\alpha]_{\lambda}^{T} = \dfrac{\alpha}{l \times C}$

Optical Purity and Enantiomeric Excess

- Optical purity deals with the composition of a mixture of enantiomers.

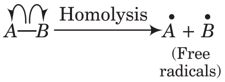
$$\text{Percentage of optical purity} = \frac{[\alpha]_{\text{sample}}}{[\alpha]_{\text{pure enantiomer}}} \times 100$$

- Enantiomeric excess (ee) is given as

$$= \frac{\text{Moles of other enantiomer}}{\text{Moles of both enantiomers}} \times 100$$

Bond Cleavage During Organic Reactions

An organic reaction begins with the cleavage of covalent bond and it is of two types:

Homolysis or symmetrical fission	Heterolysis or asymmetrical fission
Cleavage of covalent bond in such a way that each atom takes away one electron of shared pair.  	Cleavage of covalent bond in such a way that both the electrons are taken away by one of the bonded atoms. $A-B \xrightarrow{\text{Heterolysis}} A^+ + B^-$ (when, A is less electronegative than B) $A-B \xrightarrow{\text{Heterolysis}} A^- + B^+$ (when, B is less electronegative than A)

Note Energy required for heterolytic cleavage is always greater than homolytic cleavage due to electrostatic force of attraction between ions.

Reaction Intermediates

These are formed during a chemical reaction which are short lived and highly reactive.

These are of following types:

(a) Free Radicals

- These are formed during homolytic bond cleavage.
- The order of stability of free radicals is $(C_6H_5)_3\dot{C} > (C_6H_5)_2\dot{C}H > C_6H_5\dot{C}H_2 > CH_2=CH-\dot{C}H_2 > 3°\text{ radical} > 2°\text{ radical} > 1°\text{ radical} > CH_2=\dot{C}H.$
- These are sp^2-hybridised with planar structure, where an unhybridised orbital contains an odd electron.

(b) Carbocations

- These are formed during heterolytic cleavage.
- The order of stability of carbocations are

$$(C_6H_5)_3\overset{+}{C} > (C_6H_5)_2\overset{+}{C}H > (CH_3)_3\overset{+}{C} > (C_6H_5)\overset{+}{C}H_2 > 3° > 2°$$
$$CH_2=CH-\overset{+}{C}H_2 > 1° > \overset{+}{C}_6H_5 > CH_2=\overset{+}{C}H$$

- These are sp^2-hybridised with planar structure.

(c) Carbanions

- These are formed during heterolytic cleavage.
- The order of stability of carbanions are

$$(C_6H_5)_3\bar{C} > (C_6H_5)_2\bar{C}H > C_6H_5\bar{C}H_2 >$$
$$CH_2=CH-\bar{C}H_2 > \bar{C}H_3 > 1° > 2° > 3°$$

(d) Carbenes

- In carbenes, two non-bonding electrons are present along with two bond pairs.
- These are generally produced either by photolysis or pyrolysis.
- The order of stability of different carbenes is
  $:CH_2 > :CF_2 > :CCl_2 > :CBr_2$
- $:CH_2$ is the simplest carbene with sp^2-hybridisation.

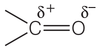
Attacking Reagents or Species

These are organic or inorganic atoms/ions/molecules that attack on the reactants during a chemical reaction.

These are of two types:

Electrophiles	Nucleophiles
(i) Electron deficient species, usually cation.	(i) Electron rich species, usually anions.
(ii) Possess an empty orbital in which they can accommodate an electron pair, thus behaves like Lewis acids.	(ii) Possess an unshared pair of electrons which they can donate easily, thus behaves as Lewis bases.
(iii) Attacks at the regions of high electron density.	(iii) Attacks at the regions of low electron density.
(iv) e.g. Cl^+, Br^+, $:CR_2$, BF_3, etc.	(iv) e.g. $\bar{O}H$, $\bar{O}R$, $H_2\ddot{\underset{..}{O}}$, etc.

Note The compound that acts both as an electrophile and nucleophile is called **ambiphiles.** e.g.



Electronic Displacement in a Covalent Bond

They are of following types:

Inductive Effect

- The induction of polarity due to the presence of polar bond in an organic compound is called inductive effect.
- It is a permanent effect and operates through σ-bond.
- It is of two types such as $-I$-effect (electron withdrawing) and $+I$-effect (electron releasing).
- The decreasing order of species showing $-I$-effect is

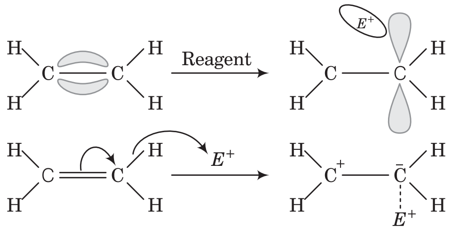
$$R_3\overset{+}{N}- > -\overset{+}{N}H_3 > -NO_2 > -CN > -SO_3H > -CHO$$
$$> -CO > -COOH > -COCl > -COOR$$
$$> -CONH_2 > -F > -Cl > -Br > -I > -OH > -OR$$
$$> -NH_2 > -C_6H_5 > -H$$

- The decreasing order of species showing $+I$-effect — O^- > — COO^- > 3°-alkyl group > 2°-alkyl group > 1°-alkyl group > — CH_3 > — H.
- The dependence of various properties on $+I$ / $-I$ group are given in the table below.

S. No.	Property	Effect of $+I$ group	Effect of $-I$ group
1.	Acidic strength	Decreases	Increases
2.	Basic strength	Increases	Decreases
3.	Stability of carbocation and free radical	Increases	Decreases
4.	Stability of carbanion	Decreases	Increases
5.	Reactivity of carbonyl compounds	Decreases	Increases

Electromeric Effect

- It is defined as polarity produced in multiple bonded compound (π-bond) as a reagent approaches the compound.



- This is a temporary effect and brought into play only in the presence of attacking reagent.
- This effect is of two types, +*E*-type and –*E*-type.
- If the electrons of the π-bond are transferred to that atom of the double bond to which the reagent gets finally attached, the effect is known as **+*E*-effect**.
- If the electrons of the double bond are transferred to an atom of the double bond other than the one to which the reagent gets finally attached, the effect is known as **–*E*-effect**.

Conjugation

It is defined as the delocalisation of electrons between alternatively placed π-bonds, lone pairs, charges (+ve or –ve) or odd electrons. It is of the following types:

(i) π-π conjugation
(ii) π-charge conjugation
(iii) π-odd electron conjugation
(iv) π-lone pair conjugation
(v) Lone pair-charge conjugation

Condition for Conjugation

The atoms/groups in conjugation with each other should be at alternate position, i.e. in the same plane and at same angle with each other.

Consequences of Conjugation

Conjugation results in delocalisation of electrons which is visible through the following observations:

(i) Improper bond length, i.e. bond length will not be as per expectations.
(ii) The compound containing conjugated system will show extra stability (with anti-aromatic compounds as exception).
(iii) The compound will have extra stability which means that its heat of formation will be greater than expected.

Note If any conjugate position has more than one π-bond or lone pair then only one π-bond or lone pair participate in conjugation.

Mesomeric Effect

- Polarity produced in a molecule due to conjugation is called mesomeric effect.
- Its intensity remains same throughout the molecule unlike to inductive effect whose intensity decreases as we move away from the cause of polarity.
- A group or atom is said to have + *M*-effect, when direction of electron displacement is away from it.

+*M*-power : $\bar{O}$ > — NH_2 > — OH > — O*R* > NHAc > — CH_3 > 1° > 2° > 3° > phenyl group.

- A group or atom is said to have – *M*-effect, if it withdraws the electrons from conjugated system.

–*M*-power : — $\overset{+}{N}H_3$ > — NO_2 > — CX_3 > — CN > — SO_3H > — CHO > — CO > — COOH > — COCl > — COO*R* > — $CONH_2$

Resonance

"When several structures may be assumed to contribute to the true structure of the molecule but no one of them can be said to represent it uniquely, the molecule is referred to as a resonance hybrid and the phenomenon is termed as resonance." Those several structures are called **canonical forms** or **resonating structures**.

In resonance,

(i) The arrangement of atoms must be identical or almost same in every formula.
(ii) The energy content of all the canonical forms must be nearly the same.
(iii) Each canonical form must have the same number of unpaired electrons.
(iv) The bond length in resonance hybrid is variable as compared to bond length in canonical forms.
(v) The resonance hybrid is always stable than any of its canonical forms.

Stability of a Canonical Form

Among the canonical forms, the most stable canonical form can be judged by the following rules:

1. Among all the canonical forms, the form without charges will be the most stable one.
2. Among the charged forms,
   (i) the structure with maximum covalent bonds is most stable one.
   (ii) the structure with maximum charge separation comes second in number.

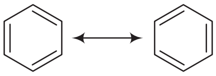
(iii) the structure with conventionally correct charges comes at third place (here, convention means the reason because of which charge arise).

RELATION BETWEEN RESONANCE AND BOND ORDER

In compounds exhibiting resonance, bond order can be given by the formula,

$$\text{Bond order} = \frac{\text{Total number of bonds between two atoms}}{\text{Total number of resonating structures}}$$

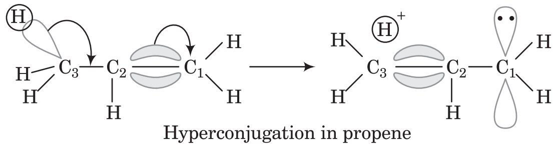
e.g. in benzene molecule with following canonical forms



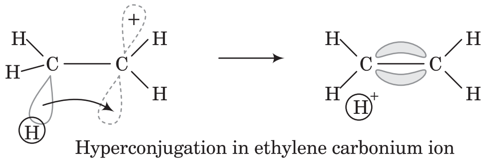
$$\text{Bond order} = \frac{2+1}{2} = 1.5$$

Hyperconjugation

- Stabilisation of alkenes by alkyl group has been attributed to delocalisation of electrons due to overlapping between a π-orbital and a σ-bond orbital of the alkyl group (C—H bond). Such an overlapping is called **hyperconjugation**.
- It is also known as no bond resonance or Baker Nathan effect.
- It is helpful in the determination of stability of alkene, free radicals and carbocations.



Hyperconjugation in propene



Hyperconjugation in ethylene carbonium ion

Note **Structure requirements for hyperconjugation**: Compound should have atleast one *sp*^{2}-carbon of either alkene, alkyl carbocation or alkyl free radical. α-carbon with respect to *sp*^{2}-carbon should have atleast one hydrogen.

Inductomeric Effect

It is a temporary effect and takes place in sigma bonded system. In the presence of attacking reagent carrying positive or negative charge transfer of sigma electrons cloud take place and polarity generates within the molecule.

Difference between electromeric and inductomeric effect Electromeric effect takes place in π-bonded system, whereas inductromeric effect takes place in sigma bonded system.

Purification of Organic Compounds

The methods which are generally employed for the purification of organic compounds are:

(i) **Filtration** It is used to separate the insoluble solid compound of the mixture from the soluble components in a given solvent.

(ii) **Crystallisation** It is based on difference in solubilities of the organic compound and the impurities in a suitable solvent.

(iii) **Sublimation** This process is used to separate sublimable compounds from non-sublimable compounds.

(iv) **Distillation** This method is used to separate volatile liquids from non-volatile impurities and the liquids having large difference in their boiling points, e.g. chloroform (boiling point = 334 K) and aniline (boiling point = 457 K) are separated by this method.

(v) **Steam Distillation** This method is used to separate compounds which are steam volatile and are immiscible with water, e.g. aniline is separated from aniline water solution by this method.

(vi) **Chromatography** This technique is used to separate and purify a mixture of compounds. It is also used to test the percentage purity of compounds.
It is of three types; **Column**, **Thin layer**, **Partition chromatography**.

Qualitative Analysis

(a) **Detection of C and H**

- These are detected by heating them with CuO followed by their reaction with $CuSO_4$ and $Ca(OH)_2$, respectively.
- H_2O vapours turn anhydrous $CuSO_4$ blue and CO_2 evolved turns lime water milky.

(b) **Detection of Other Elements : Lassaigne's Test**

- This test is used to detect the presence of elements like N,S, P, halogens, etc.
- It involves following two steps:

(i) **Preparation of Lassaigne's Extract**

- The elements present in the compound are converted from covalent to ionic form by fusing with Na metal.
- These ionic compounds are extracted by boiling them with distilled water. This extract is called **sodium fusion extract**.

(ii) **Detection of Elements Using Lassaigne's Extract**

(A) **Test for Nitrogen**

The sodium fusion extract is boiled with $FeSO_4$ and then $FeCl_3$ solution is added and resulting solution is acidified with conc. HCl. The appearance of Prussion blue colouration of ferric ferrocyanide confirm the presence of N.

(B) **Test for Sulphur**

The sodium extract gives black and purple precipitate with $(CH_3COO)_2Pb$ and $Na[Fe(CN)_5NO]$ respectively.

(C) **Test for Both N and S**

If compounds contain S and N together NaSCN is formed which gives blood red colouration of ferric sulphocyanide $Fe(SCN)_3$ with $FeCl_3$.

(D) **Test for Halogens**

The sodium fusion extract is acidified with HNO_3 followed by the addition of $AgNO_3$.

- White ppt. soluble in NH_4OH, confirms Cl.
- Dull yellow ppt. partially soluble in NH_4OH, confirms Br.
- Yellow ppt. insoluble in NH_4OH, confirms iodine.

(E) **Test for Phosphorus**

The organic compound is fused with sodium peroxide, hence phosphorus is converted into sodium phosphate. Then, it is boiled with HNO_3 followed by the addition of $(NH_4)_2MoO_4$. A yellow ppt. confirms the presence of phosphorus.

Quantitative Analysis

The next step after the detection of elements is their estimation, i.e. to know the percentage of various elements present in organic compound.

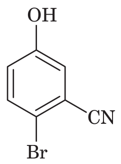
	Procedure and chemical reactions		**Formulae used**
1.	**Estimation of C and H** The organic compound is burnt in excess of air and the mass of CO_2 and H_2O formed are calculated. $C_xH_y + (x + y/4)\,O_2 \longrightarrow xCO_2 + (y/2)\,H_2O$	1.	% of C $= \dfrac{12\,m_2 \times 100}{44\,m}$ % of H $= \dfrac{2\,m_1 \times 100}{18\,m}$ where, m, m_1 and m_2 are mass of unknown organic compound, water and CO_2, respectively.
2.	**Estimation of N** (i) **Duma's method** The N containing organic compound is treated with CuO in an atmosphere of CO_2. $C_xH_yN_z + (2x + y/2)\,CuO \longrightarrow xCO_2 + \dfrac{y}{2}H_2O + \dfrac{z}{2}N_2 + \left(2x + \dfrac{y}{2}\right)Cu$ (ii) **Kjeldahl's method** Organic compound (mg) + $H_2SO_4 \longrightarrow (NH_4)_2SO_4 \xrightarrow{2NaOH} Na_2SO_4 + 2NH_3 + 2H_2O$ $2NH_3 + H_2SO_4 \longrightarrow (NH_4)_2SO_4$	2.	(i) **Duma's method** Volume of N_2 at STP(V) (in mL) $= \dfrac{p_1V_1 \times 273}{760\,T_1}$ where, p_1 and V_1 are pressure and volume of N_2 collected. $p_1 = p_{atm}$ − aqueous tension % of $N_2 = \dfrac{28\,V \times 100}{22400 \times m}$ (ii) **Kjeldahl's method** Weight of NH_3 (in g) $= \dfrac{14 \times M \times 2(V - V_1/2)}{1000}$ % of N $= \dfrac{1.4\,M \times 2(V - V_1/2)}{m}$ where, V and V_1 are volumes of $H_2SO_4(M)$ and $NaOH(M)$, respectively.
3.	**Estimation of halogens** $AgNO_3 + X^- \longrightarrow \underset{(m_1\,g)}{AgX(s)}\downarrow + NO_3^-$		Mass of halogen in Ag$X = \dfrac{\text{atomic mass of } X \times m_1}{\text{molecular mass of Ag}X}$ % of $X = \dfrac{\text{atomic mass of } X \times m_1 \times 100}{\text{molecular mass of Ag}X \times m}$
4.	**Estimation of S** S containing organic compound $(mg) \xrightarrow{[O]} H_2SO_4$ $H_2SO_4 + BaCl_2 \longrightarrow \underset{(m_1\,g)}{BaSO_4} + 2HCl$		Mass of S in $BaSO_4 = \dfrac{32 \times m_1}{233}$ g % of S $= \dfrac{32 \times m_1 \times 100}{233 \times m}$ where, m_1 = mass of $BaSO_4$
5.	**Estimation of P** P is estimated either from the mass of $(NH_4)_3PO_4 \cdot MoO_3$ $(m_1\,g)$ or from the mass of $Mg_2P_2O_7$ $(m_1\,g)$ formed.		% of P (in first case) $= \dfrac{31 \times m_1 \times 100}{1877 \times m}$ (1877 = molecular mass of $(NH_4)_3PO_4 \cdot 12\,MoO_3$) % of P (in second case) $= \dfrac{62 \times m_1 \times 100}{222 \times m}$

Note Here '*m*' represents the mass of the sample of an organic compound originally taken.

MASTER STROKES

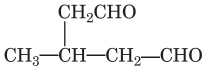
1. The IUPAC name of C_6H_5COCl is
(a) benzoyl chloride
(b) benzene chloro ketone
(c) benzene carbonyl chloride
(d) chloro phenyl ketone

2. The IUPAC name of the following compound is



(a) 4-bromo-3-cyanophenol
(b) 2-bromo-5-hydroxybenzonitrile
(c) 2-cyano-4-hydroxybromobenzene
(d) 6-bromo-3-hydroxybenzonitrile

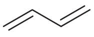
3. The IUPAC name of



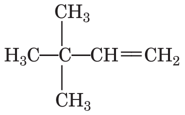
$$CH_3{-}\underset{}{\overset{CH_2CHO}{\overset{|}{C}H}}{-}CH_2{-}CHO$$ is

(a) 3-(formyl methyl) hexane 1,3-dial
(b) 3-methyl pentane 1,5-dial
(c) 3-(formyl methyl) butanal
(d) 2-(formyl methyl) butanal

4. Which of the following represent the given mode of hybridisation $sp^2 - sp^2 - sp - sp$ from left to right?
(a) $H_2C{=}CH{-}C{\equiv}CN$ *(b)* $HC{\equiv}C{-}C{\equiv}CH$
(c) $H_2C{=}C{=}C{=}CH_2$ *(d)*



5. The IUPAC name of the compound having the formula is



$$H_3C{-}\underset{CH_3}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}{-}CH{=}CH_2$$

(a) 3, 3, 3-trimethyl prop-1-ene
(b) 1, 1, 1-trimethyl prop-2-ene
(c) 3, 3-dimethyl but-1-ene
(d) 2, 2-dimethyl but-3-ene

6. In allene (C_3H_4), the type(s) of hybridisation of the carbon atoms, is(are)
(a) sp and sp^3 *(b)* sp and sp^2
(c) Only sp^3 *(d)* sp^2 and sp^3

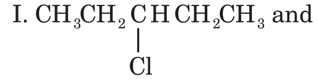
7. The IUPAC name of the compound,

$$CH_2{=}CH{-}CH(CH_3)_2 \text{ is}$$

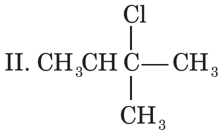
(a) 1, 1-dimethyl but-2-ene
(b) 3-methyl but-1-ene
(c) 2-vinyl propane
(d) None of the above

8. The number of sigma and pi-bonds in but-1-ene-3-yne are
(a) 5 sigma and 5 pi *(b)* 7 sigma and 3 pi
(c) 8 sigma and 2 pi *(d)* 6 sigma and 4 pi

9. Compounds with following formulae will show



$$\text{I. } CH_3CH_2\underset{Cl}{\underset{|}{C}H}CH_2CH_3 \text{ and}$$



$$\text{II. } CH_3CH\underset{CH_3}{\underset{|}{\overset{Cl}{\overset{|}{C}}}}{-}CH_3$$

(a) positional and functional isomerism
(b) chain and positional isomerism
(c) chain and functional isomerism
(d) None of the above

10. The maximum number of open chain isomers that an alkene can have with the molecular formula, C_4H_8 is
(a) 5 *(b)* 4 *(c)* 3 *(d)* 2

11. The optically active tartaric acid is named as D-(+)-tartaric acid because it has a positive
(a) optical rotation and is derived from D-glucose
(b) pH in organic solvent
(c) optical rotation and is derived from D-(+)-glyceraldehyde
(d) optical rotation when substituted by deuterium

12. How many optically active stereoisomers are possible for butan-2, 3-diol?
(a) 1 *(b)* 2 *(c)* 3 *(d)* 4

13. An isomer of ethanol is
(a) methanol *(b)* diethyl ether
(c) acetone *(d)* dimethyl ether

14. Which of the following compounds will exhibit *cis-trans* (geometrical) isomerism?
(a) but-2-ene *(b)* but-2-yne *(c)* butan-2-ol *(d)* butanal

15. Which of the following compounds will exhibit geometrical isomerism?
(a) 1-phenyl but-2-ene *(b)* 3-phenyl but-1-ene
(c) 2-phenyl but-1-ene *(d)* 1, 1-diphenyl prop-1-ene

16. The number of isomers for the compound with molecular formula $C_2BrClFI$ is
(a) 3 *(b)* 4 *(c)* 5 *(d)* 6

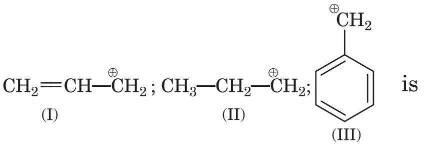
17. Which of the following compounds exhibits, stereoisomerism?
(a) 2-methylbut-1-ene *(b)* 3-methylbut-1-yne
(c) 3-methylbutanoic acid *(d)* 2-methylbutanoic acid

18. Heterolysis of $CH_3CH_2CH_3$ results in formation of
(a) $\overset{+}{C}H_3$ and $\overset{-}{C}_2H_5$ *(b)* $\dot{C}H_3$ and $\dot{C}_2H_5$
(c) $\overset{-}{C}H_3$ and $\overset{+}{C}_2H_5$ *(d)* CH_3 and C_2H_5

19. CH_3CH_2Cl undergoes homolytic fission, produces
(a) $CH_3\dot{C}H_2$ and $\dot{Cl}$ *(b)* $CH_3\overset{\oplus}{C}H_2$ and Cl^-
(c) $CH_3\overset{\oplus}{C}H_2$ and $\overset{\oplus}{Cl}$ *(d)* $CH_3\dot{C}H_2$ and Cl^-

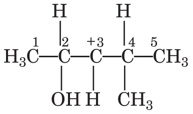
20. Among the following the strongest nucleophile is
(a) C_2H_5SH *(b)* CH_3COO^- *(c)* CH_3NH_2 *(d)* $NCCH_2^-$

21. The order of stability of the following carbocations



(a) III > II > I (b) II > III > I
(c) I > II > III (d) III > I > II

22. In the following carbocation; H/CH_3 that is most likely to migrate to the positively charged carbon is



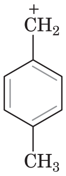
$$H_3\overset{1}{C}-\underset{OH}{\overset{H}{\overset{2}{C}}}-\underset{H}{\overset{+3}{C}}-\underset{CH_3}{\overset{H}{\overset{4}{C}}}-\overset{5}{C}H_3$$

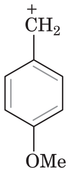
(a) CH_3 at C-4 (b) H at C-4 (c) CH_3 at C-2 (d) H at C-2

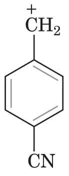
23. Which of the following statement is correct?
(a) Allyl carbonium ion ($CH_2{=}CH{-}\overset{+}{C}H_2$) is more stable than propyl carbonium ion
(b) Propyl carbonium ion is more stable than the allyl carbonium ion
(c) Both are equally stable
(d) None of the above

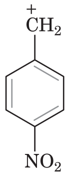
24. In which of the following reactions, carbene is not formed?
(a) CH_2N_2 + Heat$\longrightarrow$ (b) CH_2I_2 + Zn$\longrightarrow$
(c) $CH_2{=}C{=}O$ + Heat$\longrightarrow$ (d) CH_2Cl_2 + KOH$\longrightarrow$

25. Arrange the following carbocation in decreasing order of stability.


I

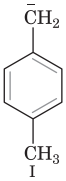

II

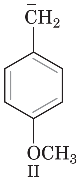

III

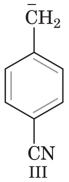

IV

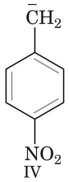
(a) I > III > II > IV (b) III > IV > II > I
(c) IV > III > II > I (d) II > I > III > IV

26. Arrange the following carbanions in decreasing order of stability.


I

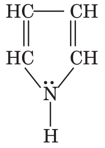

II


III


IV

(a) I > III > II > IV (b) III > IV > II > I
(c) IV > III > I > II (d) II > I > III > IV

27. The number of delocalised π-electrons in the below given compound is



(a) 8 (b) 4 (c) 2 (d) 6

28. Which of the following does not show electromeric effect?
(a) Alkenes (b) Ethers
(c) Ketones (d) Aldehyde

29. Which of the following species is paramagnetic in nature?
(a) Carbonium ion (b) Free radical
(c) Carbene (d) Nitrene

30. Which of the following orders is correct regarding the acidic nature of —COOH?
(a) Formic acid > acetic acid > propanoic acid
(b) Formic acid > acetic acid < propanoic acid
(c) Formic acid < acetic acid > propanoic acid
(d) Formic acid < acetic acid < propanoic acid

31. Which of the following order is correct regarding the acidity of carboxylic acid?
(a) $Cl_3CCOOH > Cl_2CHCOOH > ClCH_2COOH$
(b) $Cl_3CCOOH > Cl_2CHCOOH < ClCH_2COOH$
(c) $Cl_3CCOOH < Cl_2CHCOOH > ClCH_2COOH$
(d) $Cl_3CCOOH < Cl_2CHCOOH < ClCH_2COOH$

32. Which among the following statements are true with respect to electronic displacement in a covalent bond?
I. Inductive effect operates through π-bond.
II. Resonance effect operates through σ-bond.
III. Inductive effect operates through σ-bond.
IV. Resonance effect operates through π-bond.
V. Resonance and inductive effects operate through σ-bond.
(a) III and IV (b) I and II
(c) II and IV (d) I and III

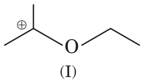
33. The correct stability order of the following resonance structure is

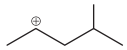
I. $H_2C{=}\overset{+}{N}{=}\overset{-}{N}$ II. $H_2\overset{+}{C}{-}N{=}\overset{-}{N}$
III. $H_2\overset{-}{C}{-}\overset{+}{N}{\equiv}N$ IV. $H_2\overset{-}{C}{-}N{=}\overset{+}{N}$

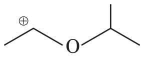
(a) I > II > IV > III (b) I > III > II > IV
(c) II > I > III > IV (d) III > I > IV > II

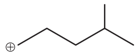
34. Hyperconjugation involves overlap of the following orbitals.
(a) σ-σ (b) σ-p (c) p-p (d) π-π

35. The correct stability order for the following species is


(I)


(II)


(III)


(IV)

(a) II > IV > I > III (b) I > II > III > IV
(c) II > I > IV > III (d) I > III > II > IV

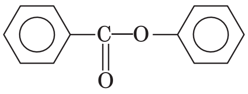
36. Which of the following belongs to –*I*-group?
(a) $—C_6H_5$ (b) $—CH_3$
(c) $—CH_2CH_3$ (d) $—C(CH_3)_3$

RAPID CONCEPT REVISION

37. Stability of which of the following intermediate is not governed by hyperconjugation
(a) carbocation
(b) carbanion
(c) carbon free radical
(d) None of the above

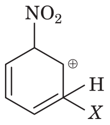
38. Which is the incorrect statement regarding resonance contributing structures?
(a) All contributing structures must have same number of valence electrons
(b) All contributing structures must have same arrangement of atoms
(c) All atoms in a contributing structures must have complete valence shells
(d) Equivalent resonance structures have same potential energies

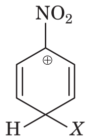
39. Which of the following is not capable of showing hyperconjugation effect?
(a) CH_3CN (b) $CH_2{=}CH{-}NH_2$
(c) $CH_2{=}CH{-}Cl$ (d) $CH_3{-}CHO$

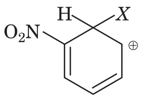
40. In , electrophilic substitution occurs at
(a) *ortho/para* at first ring (b) *meta* at first ring
(c) *ortho/para* at second ring (d) *meta* at second ring

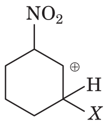
41. Polarisation of electron in acrolein may be written as
(a) $\overset{\delta-}{C}H_2{=}CH{-}\overset{\delta+}{C}H{=}O$
(b) $\overset{\delta-}{C}H_2{=}CH{-}CH{=}\overset{\delta+}{O}$
(c) $\overset{\delta-}{C}H_2{=}\overset{\delta+}{C}H{-}CH{=}O$
(d) $\overset{\delta+}{C}H_2{=}CH{-}CH{=}\overset{\delta-}{O}$

42. Which of the following carbocations is most stable?

(a) 

(b) 

(c) 

(d) 

43. The distillation technique most suited for separating glycerol from spent lye in the soap industry is [JEE Main 2016]
(a) fractional distillation
(b) steam distillation
(c) distillation under reduced pressure
(d) simple distillation

44. For the estimation of nitrogen, 1.4 g of an organic compound was digested by Kjeldahl's method and the evolved ammonia was absorbed in 60 mL of $M/10$ sulphuric acid. The unreacted acid required 20 mL of $M/10$ sodium hydroxide for complete neutralisation. The percentage of nitrogen in the compound is [JEE Main 2014]
(a) 6% (b) 10% (c) 3% (d) 5%

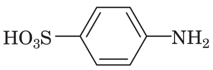
45. How will you separate a solution (miscible) of benzene and $CHCl_3$?
(a) Sublimation (b) Filtration
(c) Distillation (d) Crystallisation

46. A mixture of camphor and benzoic acid can be separated by
(a) sublimation (b) extraction with a solvent
(c) chemical method (d) fractional crystallisation

47. In Lassaigne's test, nitrogen of an organic compound is converted into
(a) NaCN (b) $NaNH_2$
(c) $NaNO_2$ (d) Na_3N

48. In Kjeldahl's method, during digestion, the nitrogen of organic compound is converted into
(a) NH_4Cl (b) NH_4NO_3
(c) $(NH_4)SO_4$ (d) NH_3

49. If nitrogen and sulphur both are present in an organic compound, which ion is formed in Lassaigne's test which confirm their presence?
(a) Na_2S and NaCN
(b) NaSCN
(c) Na_2SO_3 and NaCN
(d) Na_2S and NaCNO

50. Which of the following will not give test for nitrogen in Lassaigne's test?
(a) $C_6H_5NHNH_2$ (b) H_2NCONH_2
(c) $NH_2{-}NH_2$ (d) 

Answer

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

AMAZING REALITIES

There is about 13 billionth of a gram of gold in each litre of seawater.

HYDROCARBONS

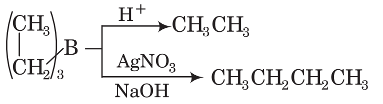
These are the organic compounds containing carbon and hydrogen. Hydrocarbons can be aliphatic (chain or cyclic) or aromatic (containing aromatic ring). Aliphatic hydrocarbons are divided into alkanes which are saturated hydrocarbons, alkenes and alkynes which are unsaturated.

Alkanes

Alkanes are the simplest organic compounds with general formula, C_nH_{2n+2}. Chemically, these are almost inert due to which they are also called **paraffins**.

Methods of Preparation

These are prepared through the following methods

Methods	Reactions involved
1. Reduction of alcohols, acids and acid derivatives	$R-CH_2OH + 2\,HI \xrightarrow[425\text{ K}]{\text{Red P}} R-CH_3 + H_2O + I_2$ $R-COOH + 6HI \xrightarrow[425\text{ K}]{\text{Red P}} R-CH_3 + 2H_2O + 3I_2$
2. Reduction of aldehydes and ketones	$>C{=}O + 6HI \xrightarrow[425\text{ K}]{\text{Red P}} >CH_2 + H_2O + 3I_2$ $>C{=}O + 4[H] \xrightarrow[\text{conc·HCl}]{\text{Zn–Hg}} >CH_2 + H_2O$ (Clemmensen's reduction) $>C{=}O + NH_2{\cdot}NH_2 \xrightarrow[-H_2O]{} >C{=}N{\cdot}NH_2 \xrightarrow[-N_2]{C_2H_5\overset{-}{O}\overset{+}{Na}} >CH_2$ (Wolff-Kishner reduction)
3. Reduction of alkyl halides	$R-X\,(1^\circ \text{ or } 2^\circ) \xrightarrow{LiAlH_4} RH$ $R-X\,(2^\circ \text{ or } 3^\circ) \xrightarrow{NaBH_4} RH$ $RI > RBr > RCl > RF$ (order of reactivity)
4. Reduction of alkenes	$3CH_2=CH_2 + BH_3 \xrightarrow[\text{DIGLYME}]{\text{THF or}} (CH_3CH_2)_3B$ $(CH_3CH_2)_3B \xrightarrow{H^+} CH_3CH_3$ $(CH_3CH_2)_3B \xrightarrow[NaOH]{AgNO_3} CH_3CH_2CH_2CH_3$
5. Hydrogenation or catalytic reduction (Raney Ni is best catalyst for this reaction)	$CH\equiv CH \xrightarrow[Ni/250^\circ C]{H_2} CH_2=CH_2 \xrightarrow[Ni/250^\circ C]{H_2} CH_3CH_3$
6. Decarboxylation	$\underset{\text{(Occurs by free radical mechanism)}}{RCOO^-Na^+} \xrightarrow[\Delta]{NaOH/CaO} \underset{\text{(1 carbon less)}}{RH} + Na_2CO_3$
7. Corey House synthesis (suitable to prepare hydrocarbons with odd number of carbon atoms)	$RBr \xrightarrow[\text{(ii) CuI}]{\text{(i) Li/ether}} LiR_2Cu \xrightarrow{R'Br}$ $R'R + RCu + LiBr$
8. Grignard reagent	$RMgX + HOH \longrightarrow RH + Mg(OH)X$ $RMgX + R'OH \longrightarrow RH + Mg(OR')X$ $RMgX + R'COOH \longrightarrow RH + Mg(OOCR')X$ $RMgX + R'C\equiv CH \longrightarrow RH + Mg(C\equiv CR')X$
9. Kolbe's electrolytic method	$2RCOO^-K^+ \xrightleftharpoons{\text{Electrolysis}} \underbrace{R-R + 2CO_2}_{\text{Anode}} + \underbrace{H_2\uparrow + KOH}_{\text{Cathode}}$
10. Wurtz reaction	$2RX + 2Na \xrightarrow{\text{Dry ether}} R-R + 2NaX$

Note CH_4 cannot be prepared by **Reaction 9** and **Reaction 10**. **Reaction 9** is not suitable for alkanes having odd number of carbon atoms, as in such case a mixture of hydrocarbons are formed which is difficult to separate.

Physical Properties

(i) The first four alkanes are colourless and odourless gases, next 13 are colourless liquids and higher ones are waxy solids.

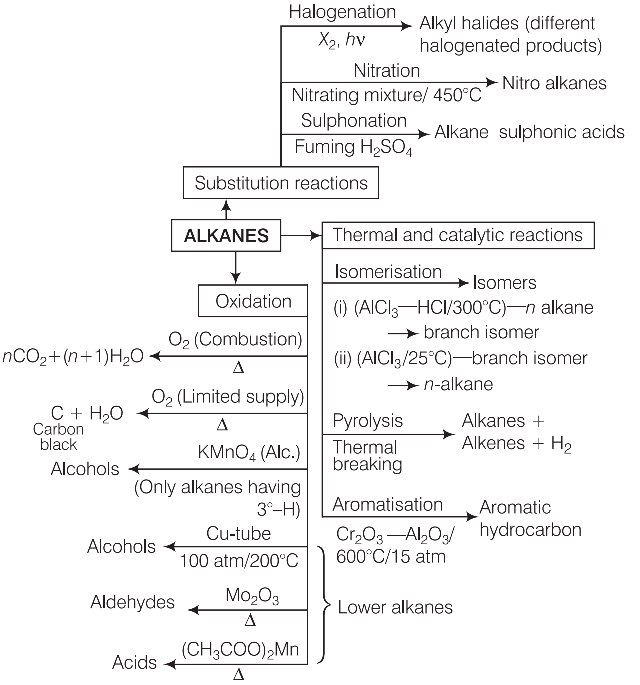
(ii) Boiling point $\propto$ number of carbon atoms $\propto \dfrac{1}{\text{Branching}}$ (for same number of C-atoms).

(iii) Dipole moment of all alkanes is zero.

(iv) Melting point of alkanes increases with increase in molecular weight but alkanes with even number of carbon atoms have higher melting point than the preceeding and succeeding members.

Chemical Properties

Alkanes show the following chemical properties



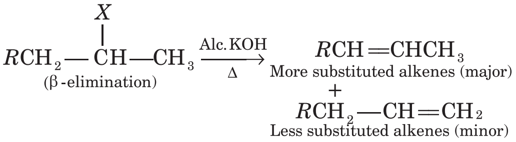
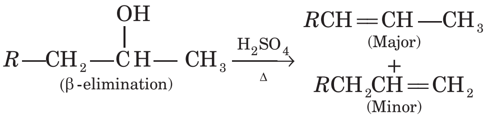
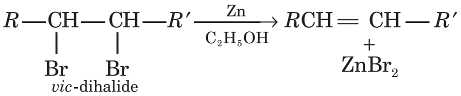
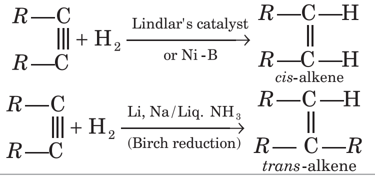
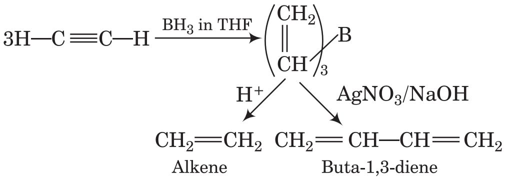
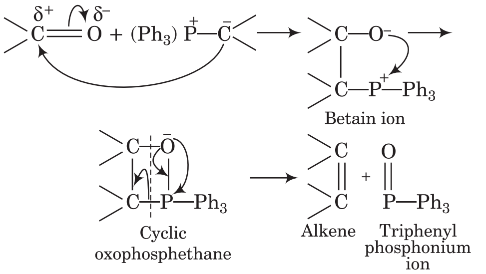
RAPID CONCEPT REVISION

Alkenes

These are unsaturated hydrocarbons containing C═C (double) bond. Their general formula is C_nH_{2n}. These are also called **olefins.**

Methods of Preparation

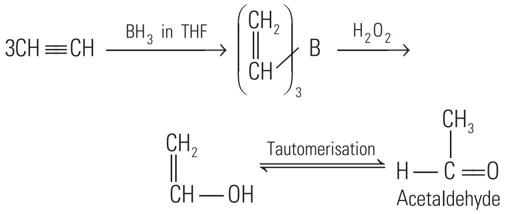
These are prepared through the following methods:

Methods	Reactions involved
1. Dehydro-halogenation	 $RCH_2-\overset{X}{\overset{\mid}{C}}H-CH_3 \xrightarrow[\Delta]{\text{Alc. KOH}} \underset{\text{More substituted alkenes (major)}}{RCH=CHCH_3} + \underset{\text{Less substituted alkenes (minor)}}{RCH_2-CH=CH_2}$ (β-elimination)
2. Dehydration	 $R-CH_2-\overset{OH}{\overset{\mid}{C}}H-CH_3 \xrightarrow[\Delta]{H_2SO_4} \underset{\text{(Major)}}{RCH=CH-CH_3} + \underset{\text{(Minor)}}{RCH_2CH=CH_2}$ (β-elimination)
3. Dehalogenation	 $R-\underset{Br}{\underset{\mid}{C}}H-\underset{Br}{\underset{\mid}{C}}H-R' \xrightarrow[C_2H_5OH]{Zn} RCH=CH-R' + ZnBr_2$ vic-dihalide
4. Hydrogenation	 $R-C\equiv C-R + H_2 \xrightarrow[\text{or Ni-B}]{\text{Lindlar's catalyst}} R-CH=CH-R$ (cis-alkene) $R-C\equiv C-R + H_2 \xrightarrow[\text{(Birch reduction)}]{Li, Na/Liq.\ NH_3} R-CH=CH-R$ (trans-alkene)
5. Hydroboration	
6. Wittig reaction	

REMEMBER

- Reactivity of alkyl halides : *R*I > *R*Br > *R*Cl and 3° > 2° > 1°.
- 3° alkyl halide/alcohol undergoes E1 elimination, 1° alkyl halide/alcohol undergoes E2 elimination and 2° alkyl halide/alcohol mostly undergoes E1 elimination (E2 when strong base is used).
- Polar protic solvents favour E2 over S_N2. Polar aprotic solvents favour S_N2 over E2.
- Saytzeff product is the major product (more substituted alkene) in most of the cases.

- The third product is also formed in hydroboration oxidation which is shown as follows:



Calculating Degree of Unsaturation

Degree of unsaturation, also called index of hydrogen deficiency is useful in drawing the structure of unsaturated hydrocarbons.

- It helps in determining the number of rings, double bond or triple bonds present in an organic compound.
- Degree of unsaturation can be calculated through the following formulae,

  Degree of unsaturation (Rings + π-bonds)

  $$= C - \frac{H}{2} - \frac{X}{2} + \frac{N}{2} + 1$$

  where, C, H, *X* and N are number of carbon, hydrogen, halogen and nitrogen atoms, respectively.
- It is important to note that, an atom with valence '*n*', contributes a total of $(n-2)$ degree of unsaturation. Hence, H, *X*, N, C and O have – 1, – 1, 1, 2 and 0 degree of unsaturation.

Physical Properties

(i) The first three alkenes are gases, next 14 are liquids and rest are solids.

(ii) All alkenes are colourless and odourless except ethene which has pleasant odour.

(iii) Boiling point ∝ number of carbon atoms

$$\propto \frac{1}{\text{Branching}} \text{ (for same number of C-atoms)}$$

(iv) *cis*-alkene has more dipole moment and boiling point than the corresponding *trans*-alkene.
However, the melting point of *trans*-alkene is more than the corresponding *cis*-alkene.

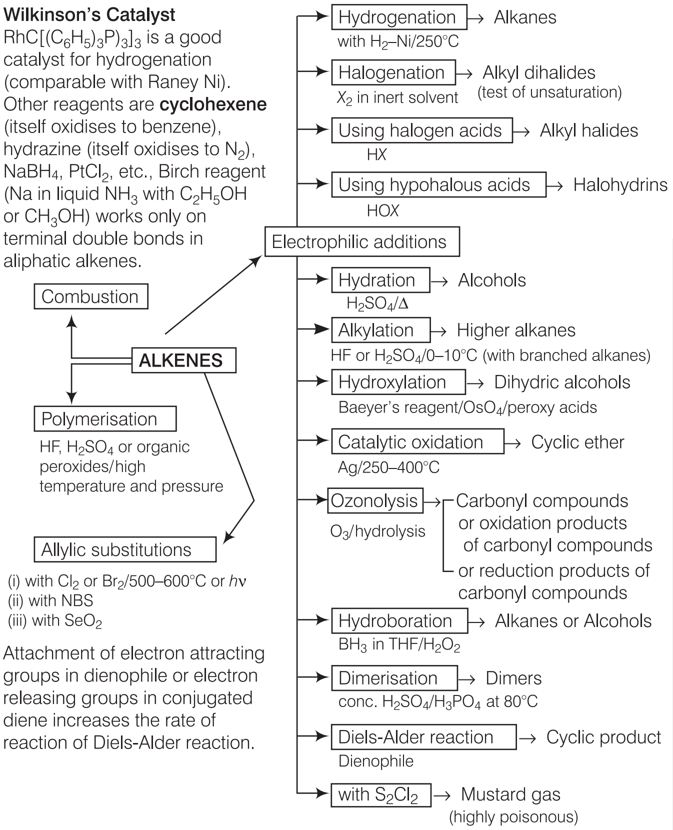
AMAZING REALITIES

If you took out all the empty space in atoms, the complete human race could fit in the volume of a sugar cube.

Chemical Properties

Alkenes show the following chemical properties:

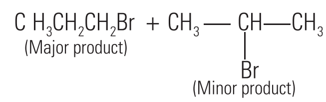
Wilkinson's Catalyst
$RhC[(C_6H_5)_3P)_3]_3$ is a good catalyst for hydrogenation (comparable with Raney Ni). Other reagents are **cyclohexene** (itself oxidises to benzene), hydrazine (itself oxidises to N_2), $NaBH_4$, $PtCl_2$, etc., Birch reagent (Na in liquid NH_3 with C_2H_5OH or CH_3OH) works only on terminal double bonds in aliphatic alkenes.



Attachment of electron attracting groups in dienophile or electron releasing groups in conjugated diene increases the rate of reaction of Diels-Alder reaction.

REMEMBER

- When HBr is added to unsymmetrical alkene in the presence of peroxide, anti-Markownikoff addition product is obtained as major product.



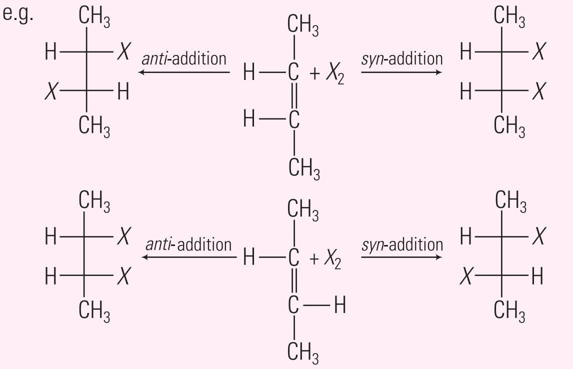
$$CH_3—CH{=}CH_2 + HBr \xrightarrow{(C_6H_5CO)_2\ O_2} \underset{\text{(Major product)}}{CH_3CH_2CH_2Br} + \underset{\text{(Minor product)}}{CH_3—\underset{\substack{|\\Br}}{CH}—CH_3}$$

- This reaction proceeds through free radical addition of HBr.

Concept Behind *syn* and *anti*-Addition

syn-addition doesn't always means that the addition of atom/group takes place on same side of double or triple bond, rather addition takes place on the available sides around double or triple bond. On the other hand in *anti*-addition, the addition of atom/group takes place opposite to the available sides around double/triple bond.

e.g.

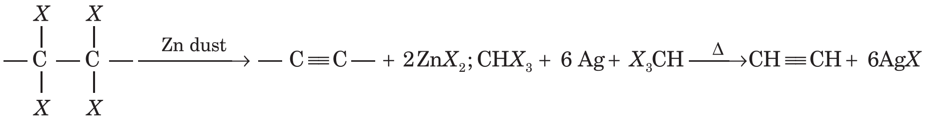
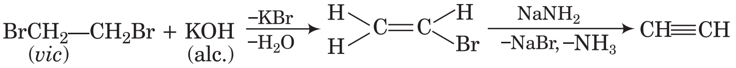


Alkynes

These are unsaturated hydrocarbons containing C≡C (triple bond) with general formula C_nH_{2n-2}.

Methods of Preparation

These are prepared through the following methods:

Methods	Reactions involved
1. Hydrolysis of metal carbides	$MC_2 + 2H_2O \longrightarrow C_2H_2 + M(OH)_2\ (M = Mg, Ca, Sr, Ba); Mg_2C_3 + H_2O \longrightarrow CH_3C{\equiv}CH + Mg(OH)_2$
2. Dehalogenation	 $—\underset{X}{\overset{X}{C}}—\underset{X}{\overset{X}{C}}— \xrightarrow{\text{Zn dust}} —C{\equiv}C— + 2ZnX_2; CHX_3 + 6\,Ag + X_3CH \xrightarrow{\Delta} CH{\equiv}CH + 6AgX$
3. Dehydrohalogenation	 $\underset{(vic)}{BrCH_2—CH_2Br} + \underset{(alc.)}{KOH} \xrightarrow[-H_2O]{-KBr} \overset{H}{\underset{H}{>}}C{=}C\overset{H}{\underset{Br}{<}} \xrightarrow[-NaBr, -NH_3]{NaNH_2} CH{\equiv}CH$
4. Kolbe's electrolysis	$\begin{array}{l}CH\overset{-}{C}OO\overset{+}{K}\\ \Vert\\ CH\overset{-}{C}OO\overset{+}{K}\end{array} \xrightarrow{\text{Electrolysis}} \underbrace{CH{\equiv}CH + 2CO_2}_{\text{At anode}} + \underbrace{H_2 + KOH}_{\text{At cathode}}$
5. From sodium acetylide	$\underset{\substack{\text{Must contain}\\\text{acidic H}}}{HC{\equiv}CH} + Na \xrightarrow{\text{Liq.}NH_3} HC{\equiv}\bar{C}Na^+ \xrightarrow[-NaX]{RX} HC{\equiv}CR + Na \xrightarrow{\text{Liq.}NH_3} RC{\equiv}\bar{C}Na^+ \xrightarrow[NaX]{R'X} R'C{\equiv}CR$
6. From Grignard's reagent	$HC{\equiv}CH + RMgX \longrightarrow HC{\equiv}\overset{-}{C}\overset{+}{Mg}\overset{-}{X} \xrightarrow{RX} HC{\equiv}C—R + MgX_2$

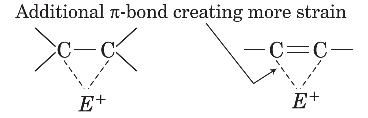
Physical Properties

(i) First three members of alkynes are colourless gases, next eight are liquids and higher alkynes are solids.
(ii) All alkynes are odourless except acetylene (garlic odour).
(iii) Melting point, boiling point and densities of alkynes are higher than the corresponding alkanes and alkenes.
(iv) Acetylene and terminal alkynes are acidic in nature.
(v) Order of acidity for different alkynes is

$$HC\equiv CH > CH_3-C\equiv CH >> CH_3-C\equiv C-CH_3$$

Chemical Properties

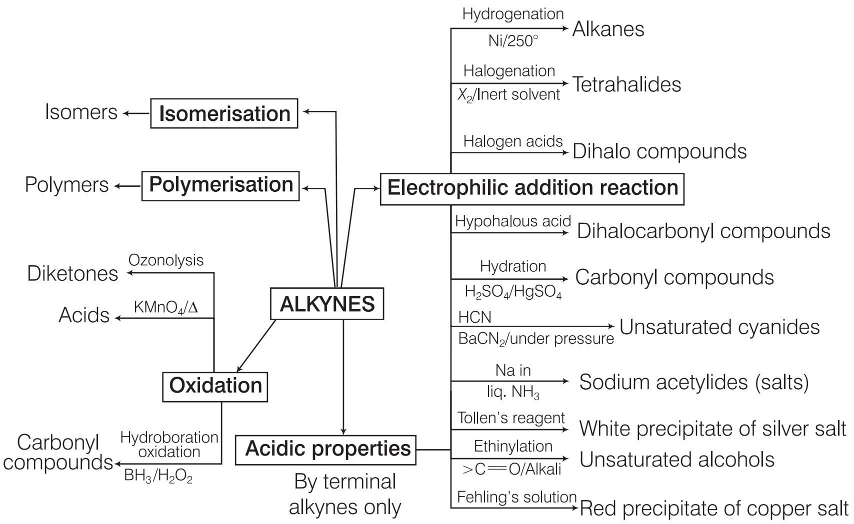
Alkynes shows electrophilic addition reaction due to availability of π-bonded electrons but they are less reactive than alkenes due to strain in cyclic intermediate as shown below:



Less strained, more stable cyclic intermediate of alkenes

More strained, less stable cyclic intermediate of alkynes

The different chemical reactions of alkynes are



Aromatic Hydrocarbons

These are cyclic compounds which are known for their unique fragrance. They can be benzenoid (containing benzene ring) or non-benzenoid (doesn't contain benzene ring).

Aromaticity

A compound can be considered as **aromatic** if it possesses the following characteristics:

- It must be cyclic and planar.
- It must have the conjugated system in it.
- It must contain $(4n+2)\pi$ electrons; where, n = integer. (Huckel's rule)

Those compounds which does not follow above rules are called **non-aromatic**.

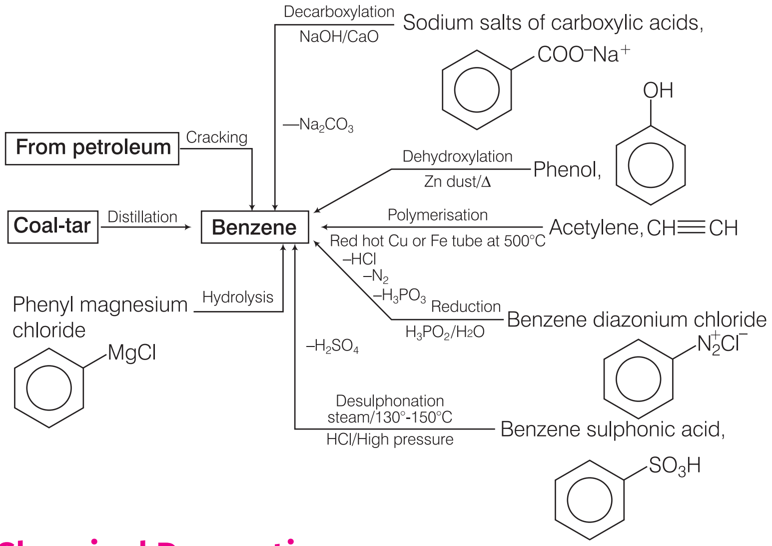
AMAZING REALITIES

Copper is the only metal that is naturally antibacterial.

Benzene

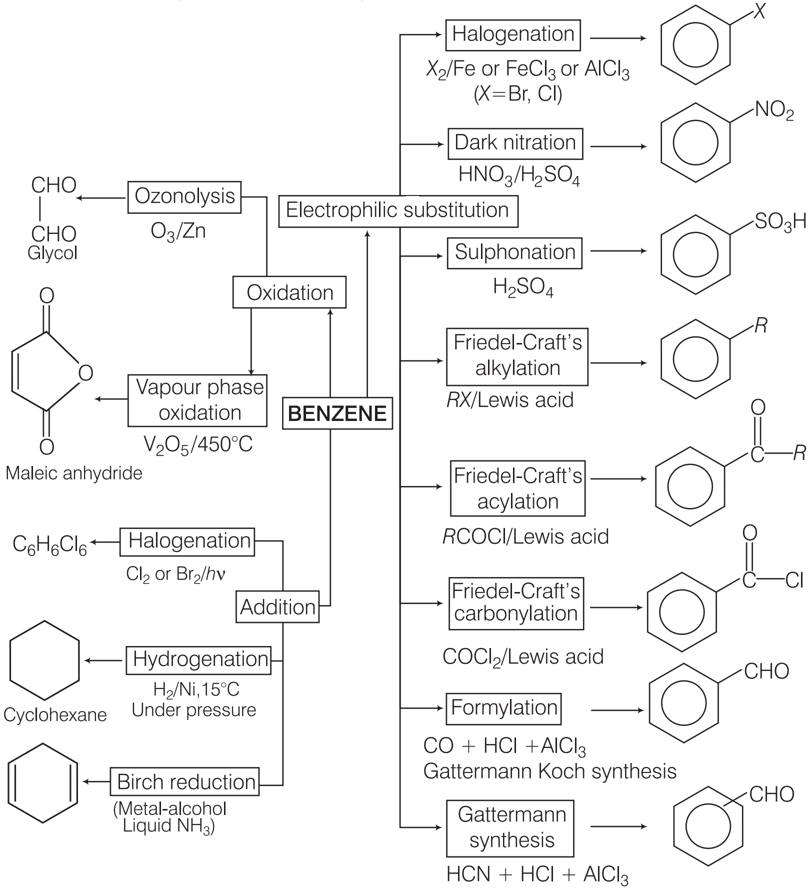
Methods of Preparation

It can be prepared through the following methods:



Chemical Properties

Benzene undergoes the following chemical reactions:



Electrophilic Substitution Reaction in Benzene

An electrophile can attack at the aromatic ring more easily than nucleophile due to high electron density on the ring.

Due to the presence of a very stable conjugated system, benzene and other aromatic compounds have a stronger tendency to undergo substitution rather than addition to leave the aromatic ring intact.

It takes place as the following three steps:

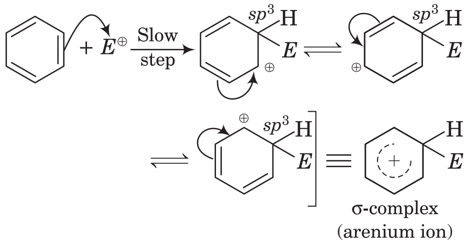
***Step* I** **Formation of Electrophile** (E^+)

The electrophile for different electrophilic substitution reactions are Cl^+ (halogenation), NO_2^+ (nitration), SO_3(sulphonation),

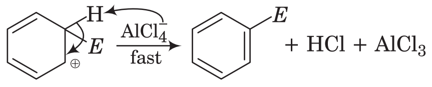
R^+ (Friedel-Craft's alkylation), $R—\overset{\overset{O}{||}}{C}{}^{\oplus}$ (Friedel-Craft's acylation), $H—\overset{\overset{O}{||}}{C}{}^{\oplus}$ (Formylation.)

***Step* II** **Formation of Carbocation Intermediate** (σ-complex)

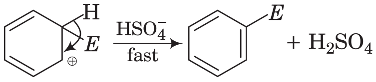
The electrophile attack the benzene ring and forms σ-complex in which one carbon becomes sp^3-hybridised.



***Step* III** **σ-complex loses a proton and gains aromaticity.**



[In case of chlorination, Friedel-Craft's reaction, Gattermann's reaction].



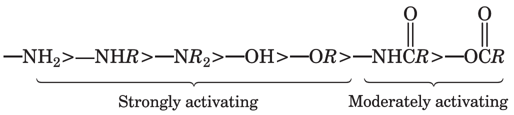
[In case of nitration and sulphonation]

Directive Influence of Functional Group

- When a functional group is attached to benzene ring and subjected to electrophilic substitution reactions, electron releasing functional groups like —OH, $—NH_2$, —*OR* etc., direct the incoming electrophile, towards *ortho* and *para*-positions and itself acts as an activating group, while an electron withdrawing functional group like $—NO_2$, —COOH, —CHO, etc., direct the incoming electrophile, towards *meta*-position.
- Although —F, —Cl, —Br and —I are weakly deactivating, they are *o*- and *p*-directing.

Order of activating power for different groups are as follows:

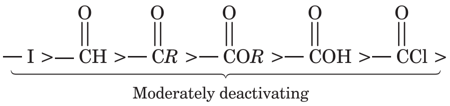
***Ortho/para*-directing**



$$\underbrace{-NH_2 > -NHR > -NR_2 > -OH > -OR}_{\text{Strongly activating}} > \underbrace{-NH\overset{O}{\overset{\|}{C}}R > -O\overset{O}{\overset{\|}{C}}R}_{\text{Moderately activating}}$$

$$\underbrace{-R > -Ar > -CH{=}CR_2}_{\text{Weakly activating}} > \underbrace{-F > -Cl > -Br}_{\text{Weakly deactivating}}$$

***Meta*-directing**

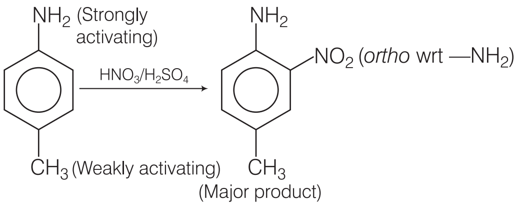


$$\underbrace{-I > -\overset{O}{\overset{\|}{C}}H > -\overset{O}{\overset{\|}{C}}R > -\overset{O}{\overset{\|}{C}}OR > -\overset{O}{\overset{\|}{C}}OH > -\overset{O}{\overset{\|}{C}}Cl >}_{\text{Moderately deactivating}}$$

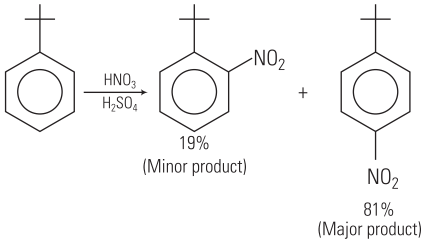
$$\underbrace{-C\equiv N > -SO_3H > -\overset{+}{N}H_3 > -\overset{+}{N}H_2R > -\overset{+}{N}HR_2 >}_{\text{Strongly deactivating}} \underbrace{-\overset{+}{N}R_3 > -\overset{+}{N}O_2}_{\text{Most deactivating}}$$

REMEMBER

- In case of benzene ring containing two functional groups, the strongest activating group has the most influence in comparison to weakly activating or deactivating groups. Hence, the electrophile is attached at *o* and *p*-position, (which one is vacant) *wrt* strongly activating group and the product obtained is the major product. e.g.

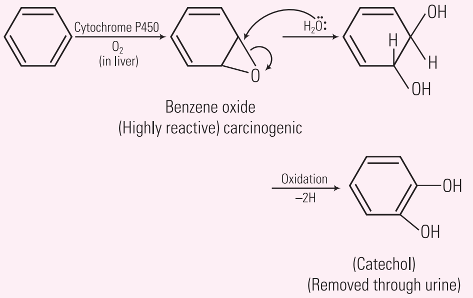


- In case of bulky activating functional groups, the formation of *o*-product is hindered by the bulky group and hence *p*-product is formed as the major product. e.g.

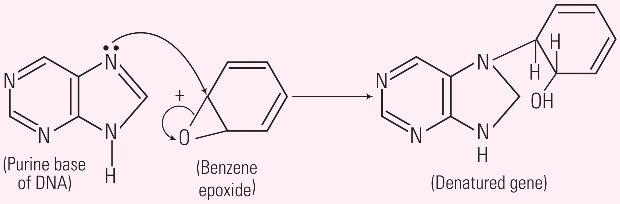


Chemical Reactions involving Carcinogenic Activity of Benzene

- Benzene is an air pollutant produced due to incomplete combustion of fossil fuel. Benzene has carcinogenic activity as it cause mutation of gene through the following chemical reaction.
- Benzene being fat soluble, is dissolved in our body fat. To remove benzene through urine it is converted into water soluble catechol by enzyme cytochrome P450 in the presence of O_2.



- Benzene oxide, being highly reactive reacts with heterogeneous base (purine, pyrimidine) of DNA and denature it causing mutation and hence cancer.



AMAZING REALITIES

The element with symbol S has traditionally been spelt 'sulphur' in the United Kingdom and most of the Commonwealth countries, while the United States used 'sulfur'. The term sulfur is now the standard name used in most contexts. In 1777, French chemist Antoine Lavoisier managed to convince the scientific community that sulfur was not a compound but in fact a basic element.

MASTER STROKES

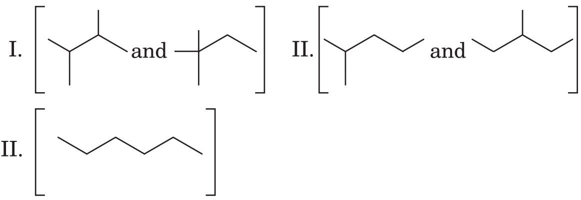
1. By Wurtz reaction a mixture of methyl iodide and ethyl iodide gives
(a) butane
(b) ethane
(c) propane
(d) a mixture of the above three

2. By which one of the following compounds both CH_4 and CH_3-CH_3 can be prepared in one step?
(a) CH_3I *(b)* CH_3OH *(c)* CH_3CH_2I *(d)* C_2H_5OH

3. The compound with highest boiling point is
(a) 2-methyl butane *(b)* *n*-pentane
(c) 2, 2-dimethyl propane *(d)* *n*-hexane

4. Marsh gas mainly contains
(a) C_2H_2 *(b)* CH_4 *(c)* H_2S *(d)* CO

5. Isomers of hexane, based on their branching, can be divided into three distinct classes as shown in the figure. [JEE Advanced 2014]



The correct order of their boiling point is
(a) I>II>III *(b)* III>II> I *(c)* II>III>I *(d)* III>I<II

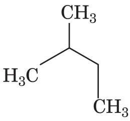
6. Which of the following compounds does not dissolve in conc. H_2SO_4 even on warming?
(a) Ethylene *(b)* Benzene *(c)* Hexane *(d)* Aniline

7. Complete oxidation of one mole of an alkane forms three moles of CO_2. The alkane is
(a) CH_4 *(b)* C_2H_6 *(c)* C_3H_8 *(d)* C_6H_{14}

8. Which of the following reactions can be used to prepare methane?
(a) Clemmensen reduction
(b) Wurtz reaction
(c) Reduction of $CH_2=CH_2$ by $LiAlH_4$
(d) Reduction of methyl iodide by using a zinc-copper couple

9. The highest boiling point is expected for
(a) *iso*-butane
(b) *n*-octane
(c) 2, 2, 3, 3-tetramethyl butane
(d) *n*-butane

10.



$\xrightarrow{Cl_2,\, h\nu}$ N, (isomeric products) $C_5H_{11}Cl$

$\xrightarrow{\text{Fractional distillation}}$ *M* (isomeric products)

What are *N* and *M*?
(a) 6, 6 *(b)* 6, 4 *(c)* 4, 4 *(d)* 3, 3

11. The C—H bond distance is longest in
(a) C_2H_2 *(b)* C_2H_4 *(c)* C_2H_6 *(d)* $C_2H_2Br_2$

12. The compound which has one isopropyl group is
(a) 2, 2, 3, 3-tetramethyl pentane
(b) 2, 2-dimethyl pentane
(c) 2, 2, 3-trimethyl pentane
(d) 2-methyl pentane

13. How many chiral compounds are possible on mono chlorination of 2-methyl butane?
(a) 2 *(b)* 4 *(c)* 6 *(d)* 8

14. The reaction of propene with HOCl (Cl_2+H_2O) proceeds through the intermediate [JEE Main 2016]
(a) $CH_3-\overset{+}{C}H-CH_2-Cl$ *(b)* $CH_3-CH(OH)-\overset{+}{C}H_2$
(c) $CH_3-CHCl-\overset{+}{C}H_2$ *(d)* $CH_3-\overset{+}{C}H-CH_2-OH$

15. An optically active hydrocarbon *X* has molecular formula C_6H_{12}. *X* on catalytic hydrogenation gives optically inactive C_6H_{14}. *X* could be
(a) 3-methylpent-1-ene *(b)* 3-methylpent-2-ene
(c) 4-methylpent-2-ene *(d)* 2-ethylbut-1-ene

16. The reagent used for catalytic hydrogenation of an alkene as well as bring about homogeneous catalysis is
(a) Raney nickel
(b) $(Ph_3P)_3RhCl$ "Wilkinson's reagent"
(c) Pd/C
(d) PtO_2

17. 3-phenylpropene on reaction with HBr gives (as a major product)
(a) $C_6H_5CH_2CH(Br)CH_3$ *(b)* $C_6H_5CH(Br)CH_2CH_3$
(c) $C_6H_5CH_2CH_2CH_2Br$ *(d)* $C_6H_5CH(Br)(CH)=CH_2$

18. Three products are obtained by the ozonolysis of penta-1, 3-diene. Out of these, if two products are formaldehyde and acetaldehyde, the name of the third one is
(a) formaldehyde *(b)* ethanal
(c) glyoxal *(d)* propanaldehyde

19. One mole of alkene *X* on ozonolysis gave one mole of acetaldehyde and one mole of acetone. The IUPAC name of *X* is
(a) 2-methylbut-2-ene *(b)* 2-methylbut-1-ene
(c) but-2-ene *(d)* but-1-ene

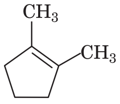
20. An alkene on ozonolysis gives formaldehyde and acetaldehyde. The alkene is
(a) ethene *(b)* propene
(c) but-1-ene *(d)* but-2-ene

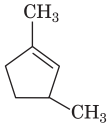
21. The reaction of propene with HOCl proceeds *via* the addition of
(a) H^+ in the first step
(b) Cl^+ in the first step
(c) OH^- in the first step
(d) Cl^+ and OH^- single step

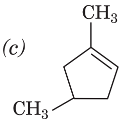
RAPID CONCEPT REVISION

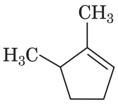
22. In the presence of peroxide, hydrogen chloride and hydrogen iodide do not give anti-Markownikoff's addition to alkenes because
(a) both are highly ionic
(b) one is oxidising and the other is reducing
(c) one of the steps is endothermic in both the cases
(d) all the steps are exothermic in both cases

23. Which compound would give 5-keto-2-methyl hexanal upon ozonolysis? [JEE Main 2015]

(a)


(b)


(c)


(d)


24. The product obtained upon the ozonolysis of pent-2-ene is
(a) CH_3CH_2CHO
(b) CH_3CHO
(c) CH_3COCH_3
(d) Both (a) and (b)

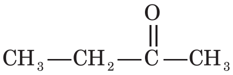
25. The treatment of ethene with cold alkaline potassium permanganate produces
(a) ethylene glycol
(b) formaldehyde
(c) formic acid
(d) carbon dioxide and water

26. $CH_3-C\equiv C-CH_3 \xrightarrow{\text{Lindlar's catalyst}} A.$

The compound *A* is
(a) *cis*-but-2-ene
(b) *trans*-but-2-ene
(c) *iso*-butene
(d) but-1-ene

27. Alkyne, C_7H_{12}, when reacted with alkaline $KMnO_4$ followed by acidification with HCl gives a mixture of $(CH_3)_2CHCOOH + CH_3CH_2COOH$. The alkyne, C_7H_{12} is
(a) hex-3-yne
(b) 2-methyl-hex-2-ene
(c) 2-methyl-hex-3-ene
(d) 3-methylhex-2-yne

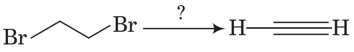
28. The product(s) obtained *via* oxymercuration ($HgSO_4 + H_2SO_4$) of 1-butyne would be

(a)

$CH_3-CH_2-\overset{\overset{O}{\|}}{C}-CH_3$

(b) $CH_3-CH_2-CH_2-CHO$
(c) $CH_3-CH_2-CHO + HCHO$
(d) $CH_3-CH_2-COOH + HCOOH$

29. Identify a reagent from the following list which can easily distinguish between but-1-yne and but-2-yne
(a) bromine, CCl_4
(b) H_2, Lindlar catalyst
(c) dilute H_2SO_4, $HgSO_4$
(d) ammoniacal $CuCl_2$ solution

30. The reagent(s) for the following conversion,



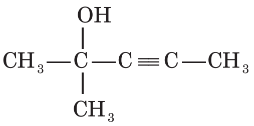
is/are
(a) alcoholic KOH
(b) alcoholic KOH followed by $NaNH_2$
(c) aqueous KOH followed by $NaNH_2$
(d) Zn/CH_3OH

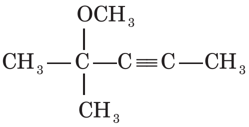
31. The synthesis of 3-octyne is achieved by adding a bromoalkane into a mixture of sodium amide and an alkyne. The bromoalkane and alkyne respectively are
(a) $BrCH_2CH_2CH_2CH_2CH_3$ and $CH_3CH_2C\equiv CH$
(b) $BrCH_2CH_2CH_3$ and $CH_3CH_2CH_2C\equiv CH$
(c) $BrCH_2CH_2CH_2CH_2CH_3$ and $CH_3C\equiv CH$
(d) $BrCH_2CH_2CH_2CH_3$ and $CH_3CH_2C\equiv CH$

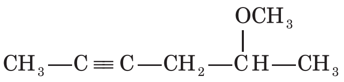
32. The major organic compound formed by the reaction of 1, 1, 1-trichloroethane with silver powder is [JEE Main 2014]
(a) acetylene
(b) ethene
(c) 2-butyne
(d) 2-butene

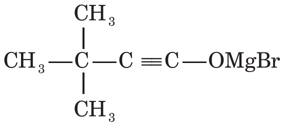
33. Identify major product of the following reaction.

$$CH_3-C\equiv C-H \xrightarrow[\text{Ether}]{CH_3MgBr} \xrightarrow{\text{Acetone}} \xrightarrow{CH_3I}$$

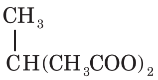
(a)

$CH_3-\overset{\overset{OH}{|}}{\underset{\underset{CH_3}{|}}{C}}-C\equiv C-CH_3$

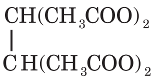
(b)

$CH_3-\overset{\overset{OCH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-C\equiv C-CH_3$

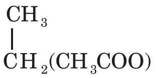
(c)

$CH_3-C\equiv C-CH_2-\overset{\overset{OCH_3}{|}}{C}H-CH_3$

(d)

$CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-C\equiv C-OMgBr$

34. $CH\equiv CH$ reacts with acetic acid in the presence of Hg^{2+} to give

(a)

$\overset{\overset{CH_3}{|}}{C}H(CH_3COO)_2$

(b)

$\overset{\overset{CH(CH_3COO)_2}{|}}{C}H(CH_3COO)_2$

(c)

$\overset{\overset{CH_3}{|}}{C}H_2(CH_3COO)$

(d) None of these

35. The product(s) obtained *via* oxymercuration ($HgSO_4 + H_2SO_4$) of but-1-yne would be
(a) $CH_3CH_2COCH_3$
(b) $CH_3CH_2CH_2CHO$
(c) $CH_3CH_2CHO + HCHO$
(d) $CH_3CH_2COOH + HCOOH$

36. When propyne is treated with aqueous H_2SO_4 in the presence of $HgSO_4$, the major product is
(a) propanal
(b) propyl hydrogen sulphate
(c) acetone
(d) propanol

37. An activating group
(a) activates only *ortho* and *para* positions
(b) deactivates *meta*-position
(c) activates *ortho* and *para*-more than *meta*
(d) deactivates *meta* more than *ortho* and *para*

38. Which one of the following *meta*-directing substituents in aromatic substitution is the most deactivating

(a) $-C\equiv N$ *(b)* $-SO_3H$
(c) $-COOH$ *(d)* $-NO_2$

39. Benzene does not undergo addition reactions easily because

(a) it has a cyclic structure
(b) double bonds in it are very strong
(c) resonance stabilised system is to be preserved
(d) it has six hydrogen atoms

40. In Friedel-Craft's alkylation besides $AlCl_3$ the other reactants are

(a) $C_6H_6 + NH_3$
(b) $C_6H_6 + CH_3COCl$
(c) $C_6H_6 + CH_3Cl$
(d) $C_6H_6 + CH_4$

41. The presence of the chlorine atom on benzene ring makes the second substituent enter at a position

(a) ortho *(b) meta*
(c) para *(d) ortho/para*

42. Which one of these is not true for benzene?

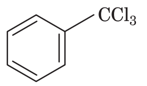
(a) It forms only one type of monosubstituted product
(b) There are three carbon-carbon single bonds and three carbon-carbon double bonds
(c) The heat of hydrogenation of benzene is less than the theoretical value
(d) The bond angle between the carbon-carbon bonds is 120°

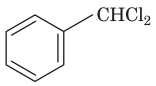
43. Which of the following statement is correct?

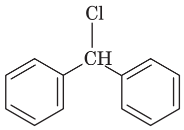
(a) Benzene has a tetrahedral geometry like an alkane
(b) Benzene is aromatic while naphthalene is not
(c) Benzene and cyclohexane are aromatic
(d) Benzene behaves more like an alkane than an alkene

44. What is the major organic product in the following reaction?

$$\underset{\text{Excess}}{C_6H_6} + CHCl_3 \xrightarrow{AlCl_3} ?$$

(a)


(b)


(c)


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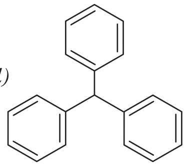
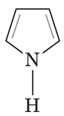


45. Which of the following is not aromatic?

(a)


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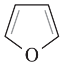

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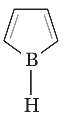

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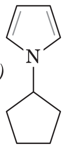
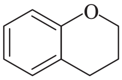


46. The example of Friedel-Crafts's alkylation reaction is

(a) $C_6H_6 + C_2H_5Cl \xrightarrow{AlCl_3} C_6H_5C_2H_5 + HCl$
(b) $C_2H_5OH + HCl \xrightarrow{ZnCl_2} C_2H_5Cl + H_2O$
(c) $C_6H_5Cl + CH_3COCl \xrightarrow{AlCl_3} C_6H_5COCH_3 + Cl_2$
(d) $C_6H_5Br + Mg \xrightarrow{Ether} C_2H_5MgBr$

47. The decreasing order of reactivity in electrophilic aromatic substitution reaction of the following compounds is

I.


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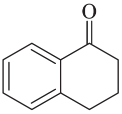
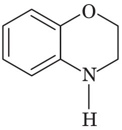
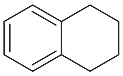
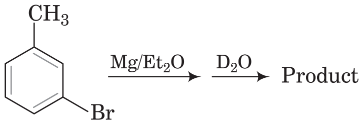


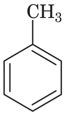
III.


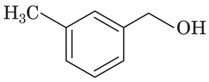
IV.


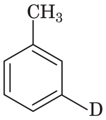
(a) IV > I > III > II *(b)* III > I > IV > II
(c) I > III > IV > II *(d)* III > II > I > IV

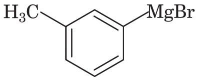
48. What could be the product of the following reaction?



(a)


(b)


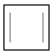
(c)


(d)


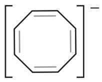
49. Benzyl chloride can be prepared from toluene by chlorination with

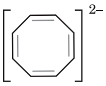
(a) SO_2Cl_2 *(b)* $SOCl_2$ *(c)* Cl_2 *(d)* NaOCl

50. Which among the following is aromatic

(a)


(b)


(c)


(d)


Answers

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

TARGET JEE 2017

TEST RIDER

Comprehensive Simulator Test Series for JEE Main & Advanced

JEE MAIN
(PAPER ONE PREP UP)

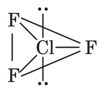
FULL TEST 3
(COMPLETE SYLLABUS)
FULLY SOLVED

Mock Questions from complete Syllabus with Complete Solutions

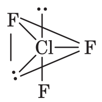
INSTRUCTIONS

- This test consists of 30 questions and each question is allotted 4 marks for correct response.
- Candidates will be awarded marks as stated above for correct response of each question. 1/4 marks will be deducted for indicating incorrect response of each question. No deduction from the total score will be made if no response is indicated for an item in the answer sheet.
- There is only one correct response for each question. Filling up more than one response in any question will be treated as wrong response and marks for wrong response will be deducted according as per instructions.

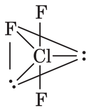
1. The central chlorine atom in ClF_3 is sp^3d-hybridised and theoretically three structures are possible.



(A)



(B)



(C)

The most probable structure is

(a) structure A
(b) structure B
(c) structure C
(d) All these three structures have same probability

2. Which of the following is more viscous?

(a) HF (b) H_2O (c) NH_3 (d) HCl

3. 50% of a gas (A) dissociates to give a gas (B) at 127°C as per the following reaction,

$$A\,(g) \xrightarrow{127^\circ\,C} 2B(g)$$

The standard free energy change for the above reaction at 1.5 atm pressure will be approximately

(a) + 9.40 kJ mol^{-1} (b) – 9.40 kJ mol^{-1}
(c) – 2.30 kJ mol^{-1} (d) + 2.30 kJ mol^{-1}

4. Which of the following statements is correct?

(a) Increase in electronegativity down the group is accompanied by decrease in non-metallic properties
(b) Electronegativity is inversely proportional to the metallic properties of elements
(c) In general, non-metals have less tendency to gain electron
(d) All of the above are incorrect

5. Electron geometry of NH_3 and SF_4 respectively are

(a) tetrahedral and pentagonal bipyramidal
(b) pyramidal and *sea-saw*
(c) tetrahedral and *sea-saw*
(d) pyramidal and pentagonal bipyramidal

6. For the reaction, $CaCO_3(s) \longrightarrow CaO(g) + CO_2(g)$,

$$\Delta H_f^\circ\ CaO(s) = -600\ kJ\ mol^{-1}$$
$$\Delta H_f^\circ\ CO_2(g) = -400\ kJ\ mol^{-1}$$
$$\Delta H_f^\circ\ CaCO_3\,(s) = -1200\ kJ\ mol^{-1}$$

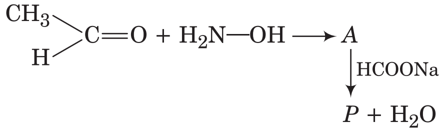
On the basis of given data, which of the following statements is correct?

(a) On increasing the temperature, reaction moves in backward direction
(b) On increasing the temperature, reaction moves in forward direction
(c) On decreasing the temperature, the reaction moves in forward direction
(d) There will be no effect of change in temperature and value of equilibrium constant remains same

7. A solution of weak 0.2 M monobasic acid (HA) having pH equal to – 2 at 27°C. The osmotic pressure of solution will be

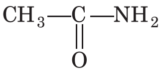
(a) 24.6 atm (b) 12.3 atm (c) 5.16 atm (d) 4.92 atm

8. In the following reaction,



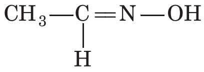
$$\begin{matrix}CH_3\\ H\end{matrix}\!\!>C{=}O + H_2N{-}OH \longrightarrow A \xrightarrow{HCOONa} P + H_2O$$

The product P is

(a) 
$CH_3—\underset{\underset{O}{\|}}{C}—NH_2$

(b) $CH_2=C=N—OH$

(c) $CH_3—C\equiv N$

(d) 
$CH_3—\underset{\underset{H}{|}}{C}=N—OH$

9. Calcium carbonate reacts with 50 mL of 0.2 M HCl as per the following reaction,

$$CaCO_3 + 2HCl(aq) \longrightarrow CaCl_2\,(aq) + CO_2(g) + H_2O(l)$$

The mass of $CaCO_3$ required to completely react with the given HCl is

(a) 1.00 g (b) 0.10 g (c) 0.50 g (d) 5.00 g

10. Which of the following statements is incorrect about the given reaction?

$$MeCHO + [Ag(NH_3)_2]^+ + \bar{O}H \longrightarrow MeCOO^- + Ag$$

(a) The equivalent weight of MeCHO is 22

(b) Three moles of $\bar{O}H$ are required in the given reaction

(c) MeCHO acts as an oxidising agent

(d) $[Ag(NH_3)_2]^+$ gets reduced

11. The energy of an electron present in first Bohr's orbit of He^+ ion is – 1312 kJ mol^{-1}, the ionisation energy for the said electron will be

(a) + 1312 kJ mol^{-1} (b) – 2624 kJ mol^{-1}

(c) + 2624 kJ mol^{-1} (d) + 5248 kJ mol^{-1}

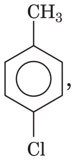
12. Volume (V) of gas is enclosed in a container, the temperature, pressure, density and number of moles of gas are respectively, tK, p atm, d gcm^{-3} and n-moles. If the container is divided into four equal parts by a partition, then the value of t, p, d and n becomes

(a) t, p and d remain same, n becomes $n/4$

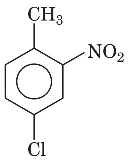
(b) t and d remain same, p becomes $4p$, n becomes $n/4$

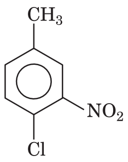
(c) t and d remain same, p becomes $2p$, n becomes $n/4$

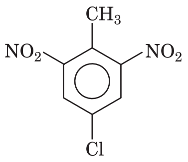
(d) All remain same

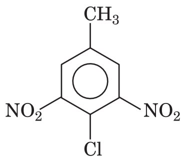
13. On nitration of 

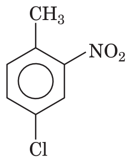
, the products formed are

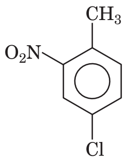
(a) 

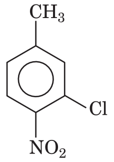
and 

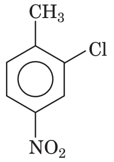
(b) 

and 

(c) 

and 

(d) 

and 

14. Entropy and enthalpy for a reaction, $R \rightarrow P$ are 15 JK^{-1} mol^{-1} and 6 kJ mol^{-1}, respectively. At what temperature the said reaction is spontaneous in nature.

(a) Any temperature above 400 K

(b) Any temperature below 400 K

(c) Only at 400 K

(d) Only at 273 K

15. Molar solubility of $Ni(OH)_2$ in 0.20 M NaOH solution will be [K_{sp} for $Ni(OH)_2 = 2.0 \times 10^{-15}$ at 25°C]

(a) 2×10^{-13} M

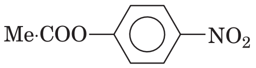
(b) 5×10^{-13} M

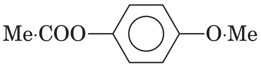
(c) 5×10^{-14} M

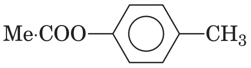
(d) 2×10^{-14} M

16. Among the following esters, the correct decreasing order for hydrolysis of ester is

I. Me·COO·Ph

II. 

III. 

IV. 

(a) I > II > III > IV (b) II > I > IV > III

(c) IV > III > II > I (d) III > IV > I > II

17. A cubic crystalline structure is composed of X, O and Y atoms. X-atoms are located at all corners of the unit cell, O-atoms are at edge centres and Y-atom at cube centre. If two O-atoms are missing from any of two edge centre per unit cell, the molecular formula of the compound will be

(a) XYO_3 (b) $X_2Y_2O_3$ (c) $X_2Y_2O_5$ (d) XYO_5

18. A mixture of benzene and toluene is kept in an open vessel. The vapour pressure of pure benzene and toluene are 958 mm and 380 mm of Hg, respectively at 90°C. The composition of benzene and toluene in the mixture at given temperature will be

(a) benzene = 66%; toluene = 34%

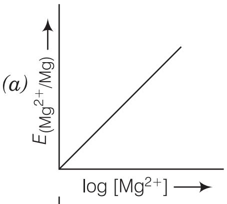
(b) benzene = 34%; toluene = 66%

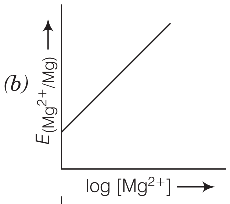
(c) benzene = 75%; toluene = 25%

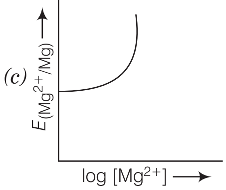
(d) benzene = 25%; toluene = 75%

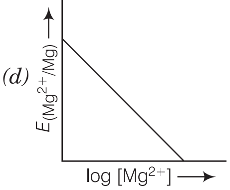
19. Electrode potential for Mg varies according to the equation, $E_{Mg^{2+}/Mg} = E^{\circ}_{Mg^{2+}/Mg} - \frac{0.059}{2} \log \frac{1}{[Mg^{2+}]}$.

The graph of $E_{Mg^{2+}/Mg}$ vs $\log [Mg^{2+}]$ is

(a)


(b)


(c)


(d)


20. Which of the following is correct about order and molecularity for an elementary reaction?

I. Order > molecularity
II. Order = molecularity
III. Order < molecularity
IV. Molecularity ≠ 0

(a) II and IV *(b)* Only I *(c)* Only III *(d)* I and IV

21. The ratio of shortest wavelength for He^+ ion to that of longest wavelength for H-atom will be

(a) 3 : 4 *(b)* 4 : 3 *(c)* 16 : 3 *(d)* 3 : 16

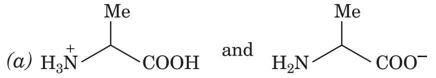
22. Which of the following is an example of auto-reduction?

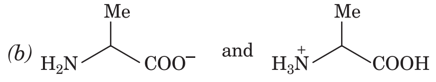
(a) $Fe_3O_4 + 4CO \longrightarrow 3Fe + 4CO_2$
(b) $Cu_2O + C \longrightarrow 2Cu + CO$
(c) $Cu^{2+}(aq) + Fe \longrightarrow Cu(s) + Fe^{2+}(aq)$
(d) $Cu_2O + \frac{1}{2}Cu_2S \longrightarrow 3Cu + \frac{1}{2}SO_2$

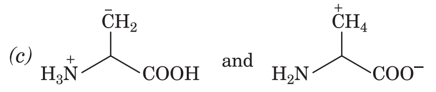
23. Mr. Bartlett got inspiration to made xenon compounds due to existence of $[O_2]^+[PtF_6]^-$ because

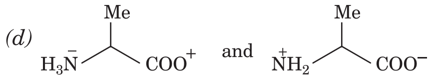
(a) O_2 and Xe have almost same ionisation enthalpy
(b) O_2 and Xe have almost same electron gain enthalpy
(c) O_2 and Xe have electropositive nature
(d) O_2 and Xe have almost same electronegativity

24. The structure of amino acid in the solution of pH = 2 and pH = 10 can represented respectively as

(a)


(b)


(c)


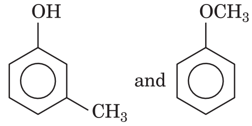
(d)


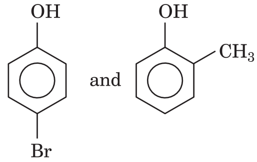
25. HCl is not used to make the solution acidic in oxidation reaction of $KMnO_4$ because

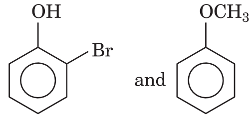
(a) $KMnO_4$ starts to act as a reducing agent
(b) $KMnO_4$ becomes a weaker oxidising agent
(c) $KMnO_4$ oxidise HCl to Cl_2, which is also an oxidising agent
(d) $KMnO_4$ and HCl both act as oxidising agent

26. An aromatic compound *A* with molecular formula, C_7H_8O gives a white precipitate of compound *B* $[C_7H_5OBr_3]$. Another compound *C* is functional isomer of compound *A*. *A* is soluble in NaOH, while *C* is insoluble in NaOH, and gives white precipitate with $Br_2 + H_2O$ having molecular formula same as *B*.

A and *C* are respectively,

(a)


(b)


(c)


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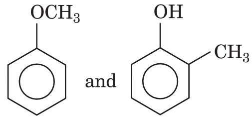
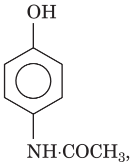


27. Which one of the following statements is not correct?

(a) In vulcanisation, the formation of sulphur bridges between different chains make rubber harder and stronger
(b) Natural rubber has the *trans*-configuration at every double bond
(c) Buna-S is a copolymer of butadiene and styrene
(d) Natural rubber is a 1, 4-polymer of isoprene

28. Th compound having structure

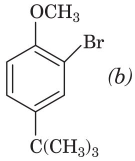


is used as

(a) antimalarial *(b)* antiseptic
(c) antipyretic *(d)* antibiotic

29. Anisole $\xrightarrow[\text{Anhy. AlCl}_3]{(CH_3)_3CCl} B \xrightarrow{Cl_2/FeCl_3} C \xrightarrow[\text{Heat}]{\text{HBr}} D$

The product *D* in the above sequence of reaction is

(a)


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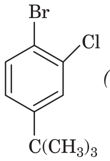
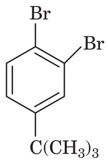


(c)


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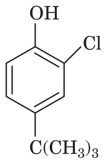


30. K_{sp}, for two hypothetical slightly soluble salts *PQ* and AB_2 are 1.6×10^{-17}. Which of the following statement regarding solubility of both the salts is true?

(a) Salt *PQ* is more soluble than AB_2
(b) Salt AB_2 is more soluble than *PQ*
(c) As K_{sp} is same, solubility of both the salts are same
(d) As K_{sp} value is positive, both the salts are 100% insoluble

Answers with Explanation

1. ***(c)*** **Key concept** The most stable structure will be the one with lowest energy or with minimum steric repulsion. The order of repulsion between different kinds of electron pairs is

$$lp\text{-}lp > lp\text{-}bp > bp\text{-}bp$$

Also, the less is separation, more is repulsion. Thus, repulsion between two electron pairs at 90° will be more than when they are at 120°.

(i) In structure A, there are 6 repulsions between lp-bp at 90°.

(ii) In structure B, there is one 90°, lp-lp repulsion and three 90°, lp-bp repulsions.

(iii) In structure C, there are four 90°, lp-bp repulsions and no 90° lp-lp repulsion. Therefore, structure (C) is most stable.

2. ***(b)*** **Key concept** Greater the intermolecular H-bonding, higher will be the viscosity.

H_2O is most viscous among the given options as each H_2O molecule will form four intermolecular H-bonds with other H_2O-molecules.

3. ***(c)*** Given reaction,

	$A(g) \xrightarrow{127^\circ C}$	$2B(g)$
Initial moles at $t = 0$	1	0
At 50% dissociation	1 – 0.5	2 × 0.5

$$\therefore \text{ Mole fraction for gas } (A) = \frac{1-0.5}{1+0.5} = \frac{0.5}{1.5}$$

$$\text{Partial pressure of gas } (A) = \frac{0.5}{1.5} \times 1.5 = 0.5 \text{ atm}$$

$$\text{and partial pressure of gas } (B) = \frac{1.0}{1.5} \times 1.5 = 1.0 \text{ atm}$$

$$\text{Thus, } K_p = \frac{P_B^2}{P_A} = \frac{(1)^2}{(0.5)} = 2$$

$$\because \quad \Delta G = -2.303\, RT \log K_p$$

$$\Delta G = -[2.303 \times 8.314 \times 400 \times \log 2]$$

$$= -[2.303 \times 8.314 \times 400 \times 0.3010]$$

$$= -2305 \text{ J mol}^{-1} = -2.305 \text{ kJ mol}^{-1}$$

$$\approx -2.30 \text{ kJ mol}^{-1}$$

4. ***(b)*** Decrease in electronegativity from top to bottom in a group is accompanied by a decrease in non-metallic properties.

Non-metals have strong tendency to gain electrons. Also, electronegativity is related to the metallic properties of elements and is inversely proportional to the metallic properties of elements.

5. ***(a)*** **Key concept** Electron geometry is the structure of the species including lone pair of electrons present in the species, while molecular geometry or simply called geometry (shape) of the molecule is the geometry due to bonded electrons.

Electron geometry of $\ddot{N}H_3$ and $:SF_4$, respectively are tetrahedral and pentagonal bipyramidal, while its molecular geometry, i.e. shape is pyramidal and *sea-saw*, respectively.

6. ***(b)*** $\Delta H_r = \sum H_f^0(\text{product}) - \sum H_f^0(\text{reactant})$

$$\Delta H_r = [(-600) + (-400)] - [-1200]$$

$$\Delta H_r = +\ 200 \text{ kJ mol}^{-1}$$

As value of $\Delta H_r = +$ ve, the reaction is endothermic in nature.

Hence, on increasing the temperature, reaction moves in forward direction.

As value of equilibrium constant depends on temperature, the value of equilibrium constant (K) also changes.

7. ***(c)*** **Thinking process** First, calculate the degree of dissociation (α), then van't Hoff factor (i) using,

$$i = 1 + (n-1)\,\alpha > 1 \text{ if } n \geq 2$$

Finally, calculate osmotic pressure (π) using, $\pi = iCRT$

For monobasic acid,

$$HA \rightleftharpoons H^+ + A^-$$

$$[H^+] = C \cdot \alpha$$

Given, $\quad pH = -2 \text{ or } [H^+] = 10^{-2}$

$$\therefore \quad \alpha = \frac{[H^+]}{C} = \frac{10^{-2}}{0.2} = 0.05$$

Thus, $\quad i = 1 - \alpha + n \cdot \alpha$

$\because \quad n = 2$ (for monobasic acid)

$\therefore \quad i = 1 - \alpha + 2\alpha = 1 + \alpha = 1 + 0.05$

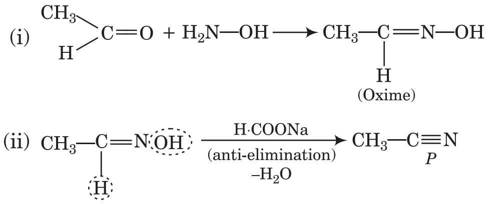
$i = 1.05$

Hence, $\quad \pi = i \times CRT$

$$= 1.05 \times 0.2 \times 0.082 \times 300$$

$$= 5.16 \text{ atm}$$

8. ***(c)*** The given reaction occurs as follows,



9. ***(c)*** As per given equation,

1 mole of $CaCO_3 \equiv$ 2 moles of HCl

$$\because \text{Molarity } (M) = \frac{\text{moles of HCl } (n)}{\text{volume of solution } (V)}$$

$$\therefore \quad n(\text{HCl}) = M \times V = \frac{0.2 \times 50}{1000}$$

$$= 0.01 \text{ mol}$$

Now, ratio of moles of $CaCO_3$ and HCl = 1 : 2

$$\text{Thus, moles of } CaCO_3 \text{ requires} = \frac{0.01}{2} = 0.005$$

We know that,

$$\text{Number of moles } (n) = \frac{\text{mass } (W)}{\text{molar mass } (M)}$$

and molar mass of $CaCO_3 = 40 + 12 + (3 \times 16) = 100$

$\therefore \ W(CaCO_3) = n \times M = 0.005 \times 100$

Mass of $CaCO_3 = 0.5$ g

10. ***(c)*** **Oxidation**

$$CH_3CHO + 3\bar{O}H \longrightarrow CH_3COO^- + 2e^- + 2H_2O$$

Reduction $[Ag(NH_3)_2]^+ + e^- \longrightarrow Ag + 2NH_3] \times 2$

Net reaction

$$CH_3CHO + 2[Ag(NH_3)_2]^+ + 3\bar{O}H \longrightarrow CH_3COO^- + 2H_2O + 2Ag + 4NH_3$$

Molecular mass (M) of $CH_3CHO = 44\ g\ mol^{-1}$

Equivalent weight (EW) $= \dfrac{M}{n\text{-factor}} = \dfrac{44}{2} = 22\ g\ mol^{-1}$

11. ***(d)*** $E_1(He) = \dfrac{-Z^2 \cdot 1312}{n^2} = \dfrac{4}{-1} \times 1312$

$= -5248\ kJ\ mol^{-1}$ [Energy for $n = 1$]

$E_\infty = 0$

$\therefore \quad \Delta E = 0 - (-5248)$

$IE = \Delta E = +5248\ kJ\ mol^{-1}$

12. ***(a)*** **Key Concept** The properties which does not depend upon the quantity of matter are intensive properties while which depend upon the quantity of matter are extensive properties.

Temperature(t), pressure(p) and density(d) remain same while number of moles(n) of gas becomes $\dfrac{n}{4}$ in each compartment.

13. ***(c)*** On nitration of a disubstituted compound containing one activating group ($-CH_3$) and one deactivating group (Cl), the third group ($-NO_2$) is introduced at *o* and *p*-positions *wrt* activating group.

If *p*-position is occupied, then the group is attached only at *o*-position *wrt* activating group.

14. ***(a)*** For a reaction to be spontaneous,

$$\Delta G = \Delta H - T \cdot \Delta S = -\text{ve}$$

At equilibrium,

$$\Delta G = 0$$

$\therefore \quad \Delta H = T\Delta S$

or $\quad T = \dfrac{\Delta H}{\Delta S} = \dfrac{6 \times 1000}{15} = \dfrac{6000}{15}$

$T = 400\ K$

As $\quad \Delta H = +\text{ve}$

Hence, the said reaction is spontaneous for any temperature above 400 K.

15. ***(c)*** $Ni(OH)_2 \rightleftharpoons Ni^{2+} + 2OH^-$

If, $S =$ Solubility in mol/L, then

$$\underset{S}{Ni(OH)_2} \rightleftharpoons \underset{S}{Ni^{2+}} + \underset{2S}{2OH^-}$$

and $\underset{0.2\ M}{NaOH} \longrightarrow \underset{0.2\ M}{Na^{2+}} + \underset{0.2\ M}{OH^-}$

Due to common ion effect,

$[OH^-] = 2S + 0.2 \approx 0.2$

[$\because$ $2S$ is very small as compared to 0.2]

$K_{sp} = 2 \times 10^{-15} = [Ni^{2+}][OH^-]^2 = [S] \cdot [0.2]^2$

$\therefore \quad S = \dfrac{K_{sp}}{(0.2)^2} = \dfrac{2 \times 10^{-15}}{0.04} = 50 \times 10^{-15}$

$S = 5 \times 10^{-14}\ M$

16. ***(b)*** **Thinking process** Stronger the deactivating group (electron withdrawing) attached with the ring, easier will be the hydrolysis of ester.

In II, electron withdrawing ($-NO_2$) group is attached hence its hydrolysis will be easiest among the given compounds. ($-OCH_3$) has more electron donating ability than ($-CH_3$) group, thus IV will easily undergo hydrolysis than III. I has neither electron withdrawing nor electron donating group. Hence, the correct order is

II > I > IV > III.

17. ***(c)*** Number of X-atoms $= 8 \times \dfrac{1}{8} = 1$

Number of O-atoms $= 12 \times \dfrac{1}{4} = 3$

Number of missing atoms $= 2 \times \dfrac{1}{4} = 0.5$

Thus, number of O-atoms $= 3 - 0.5 = 2.5$

Number of Y-atoms $= 1 \times 1 = 1$

Thus, number of atoms of X, O and Y $= X_1O_{2.5}Y_1$

Hence, simple ratio and formula of compound

$= [XO_{2.5}Y] \times 2$

or $\quad X_2O_5Y_2$ or $X_2Y_2O_5$

18. ***(a)*** Benzene and toluene form an ideal solution,

$$p_T = p_A^\circ \cdot \chi_A + p_B^\circ \cdot \chi_B \quad \text{...(i)}$$

where, χ_A and χ_B are mole fraction of benzene and toluene, respectively. p_A° and p_B° are vapour pressure of pure benzene and toluene, respectively.

p_T = total pressure = external pressure

p_T = 760 mm of Hg

p_A° = 958 mm of Hg, p_B° = 380 mm of Hg

On substituting the values in Eq. (i),

$760 = 958\chi_A + 380\chi_B$

$760 = 958(1 - \chi_B) + 380\chi_B$

$= 958 - 958\chi_B + 380\chi_B$

$760 = 958 - 578\chi_B$

$\therefore 578\chi_B = 958 - 760 = 198$

$\therefore \quad \chi_B = 0.34$

and $\quad \chi_A = 1 - 0.34 = 0.66$

Mole fraction of benzene = 0.66 or 66%.

Mole fraction of toluene = 0.34 or 34%.

19. ***(b)*** $E_{Mg^{2+}/Mg} = E^\circ_{Mg^{2+}/Mg} - \dfrac{0.059}{2} \log \dfrac{1}{[Mg^{2+}]}$

or $\quad E_{Mg^{2+}/Mg} = E^\circ_{Mg^{2+}/Mg} + \dfrac{0.059}{2} \log[Mg^{2+}] \quad$ ...(i)

On comparing Eq. (i) with $y = mx + c$

$E^\circ_{(Mg^{2+}/M)} \propto \log[Mg^{2+}]$ with positive slope

and $E^\circ_{(Mg^{2+}/M)}$ as intercept.

20. ***(a)*** For an elementary reaction, the order and molecularity are same and molecularity can never be equal to zero.

21. ***(d)*** **Thinking process** This problem can be solved by using the Rydberg formula,

$$\frac{1}{\lambda} = RZ^2\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$$

where, n_1 = lower energy level

n_2 = higher energy level

For shortest wavelength of He^+ ion,

$n_1 = 1, n_2 = \infty, Z = 2$

$\therefore \quad \left[\dfrac{1}{\lambda}\right]_{He^+} = Z^2 \cdot R\left[\dfrac{1}{n_1^2} - \dfrac{1}{n_2^2}\right]$

$= 2^2 \cdot R[1 - 0] = 4R$

For longest wavelength of H-atom,

$$n_1 = 1, n_2 = 2, Z = 1$$

$$\therefore \left[\frac{1}{\lambda}\right]_{\text{H-atom}} = 1^2 \cdot R\left[1 - \frac{1}{2^2}\right] = \frac{3}{4}R$$

$$\therefore \quad \lambda_{\text{H-atom}} = \frac{4}{3}R \qquad \ldots\text{(ii)}$$

Dividing Eq. (i) by Eq. (ii), we get

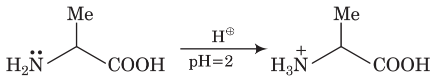
$$\frac{\lambda_{He^+}}{\lambda_{\text{H-atom}}} = \frac{1/4 \cdot R}{4/3 \cdot R} = \frac{3}{16} = 3:16$$

22. ***(d)*** Reduction of cuprous ions (Cu^+) to Cu is an example of auto-reduction

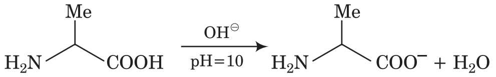
$$Cu_2O + \frac{1}{2}Cu_2S \longrightarrow 3Cu + \frac{1}{2}SO_2$$

23. ***(a)*** Both O_2 and Xe have almost same ionisation enthalpy, hence, $[O_2]^+[PtF_6]^-$ was taken as base compound to prepare compounds of xenon.

24. ***(a)*** At **pH** = **2**, i.e. in an acidic medium, amino acid exist as

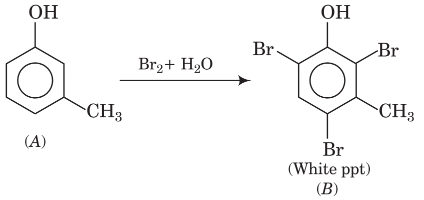


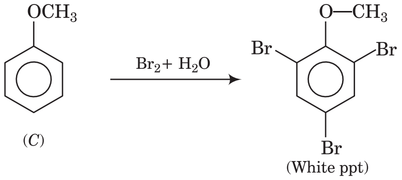
At **pH** = **10**, i.e. in a basic medium, amino acid exist as



25. ***(c)*** HCl is not used to make the solution acidic in oxidation reactions of $KMnO_4$ because $KMnO_4$ will oxidise HCl to Cl_2, which is also an oxidising agent.

26. ***(a)*** **Thinking process** —OH of ring give tri-substituted bromine compound (at *o* and *p*-position) with $Br_2 + H_2O$. (*A*) has one $—CH_3$ apart from —OH group on the ring, since 3-bromine groups are placed at *o* and *p*-positions, $—CH_3$ group must be at *m*-position *wrt* —OH group.





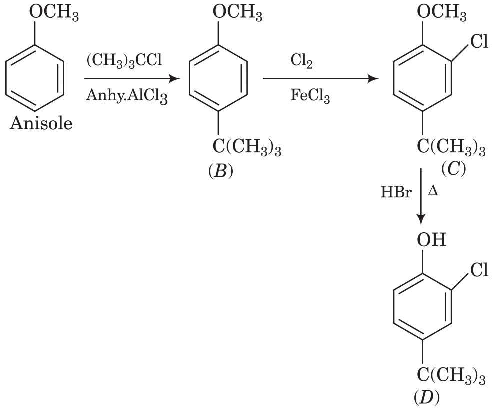
27. ***(b)*** Natural rubber is *cis*-polyisoprene and is prepared from latex which is obtained from rubber tree.

28. ***(c)***

4-acetamidophenol

It is also known as paracitamol and is widely used as antipyretic.

29. ***(d)***



30. ***(b)*** $K_{sp} = 1.6 \times 10^{-17} = 16 \times 10^{-18}$

For *PQ* type of salt

$$K_{sp} = S^2$$

$$\therefore \quad S = \sqrt{K_{sp}} = \sqrt{16 \times 10^{-18}} = 4 \times 10^{-9} \qquad \ldots\text{(i)}$$

For AB_2 type of salt

$$K_{sp} = 4S^3$$

$$\therefore \quad S = \left[\frac{16}{4} \times 10^{-18}\right]^{1/3} = [4 \times 10^{-18}]^{1/3}$$

$$= 1.6 \times 10^{-6} \qquad \ldots\text{(ii)}$$

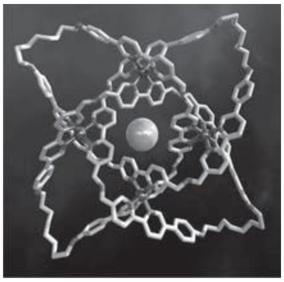
$\because$ *S* for AB_2 > *S* for *PQ* salt.

$\therefore$ Solubility of AB_2 is more than *PQ* salt.

CHEMISTRY IN action

A complex molecular knot with eight crossing points has been made

Scientists has tied the tightest molecular knot to date, comprising three molecular strands plaited together to create a circular triple helix, a loop with eight crossings.



The breakthrough knot has eight crossings in a 192-atom closed loop which is about 20 nanometres long (i.e. 20 millionths of a millimeter). The knot was tied using existing self-assembly techniques to weave the ligand strands around four octahedral iron (II) ions which fix the eight crossing points. The strands are joined up to close the loop using a transition metal catalyst, and the ions can then be removed. This latest knot is the most complex regular woven molecule ever made.

TARGET JEE 2017

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Comprehensive Simulator Test Series for JEE Main & Advanced

JEE MAIN

(PAPER TWO SCALE UP)

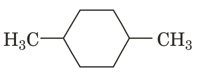
FULL TEST 4
(COMPLETE SYLLABUS)
WITH ANSWER KEY

Mock Questions from complete syllabus to enhance Your Problem Solving Skills

INSTRUCTIONS

- This test consists of 30 questions and each question is allotted 4 marks for correct response.
- Candidates will be awarded marks as stated above for correct response of each question. 1/4 marks will be deducted for indicating incorrect response of each question. No deduction from the total score will be made if no response is indicated for an item in the answer sheet.
- There is only one correct response for each question. Filling up more than one response in any question will be treated as wrong response and marks for wrong response will be deducted according as per instructions.

1. Which one of the following compounds will exhibit enantiomerism?

(a)


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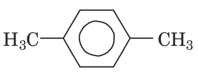
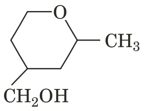


(c)


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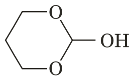
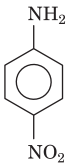
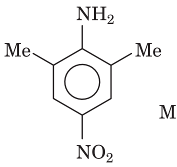


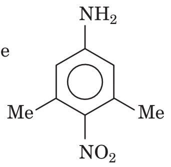
2. The decreasing order of basicity for the following compounds is



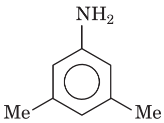
I



II



III



IV

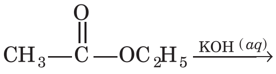
(a) I > III > II > IV
(b) I > II > III > IV
(c) IV > II > III > I
(d) IV > III > I > II

3. In which of the following sequence α,β-unsaturated aldehyde is formed?

(a) $\mathrm{HCHO} \xrightarrow{\mathrm{KOH}\,(aq)}$

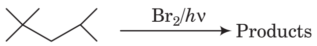
(b) $\mathrm{CH_3CHO} \xrightarrow[\text{(ii) }\Delta]{\text{(i) Dil. KOH}}$

(c) $\mathrm{CCl_3CHO} \xrightarrow{\mathrm{KOH}\,(aq)}$

(d)


$\mathrm{CH_3{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}OC_2H_5} \xrightarrow{\mathrm{KOH}\,(aq)}$

4. How many isomeric products are obtained from the reaction given below.



(a) 1 *(b)* 6 *(c)* 4 *(d)* 3

5. In an experiment, it was observed that 40 mg of diatomic volatile compound X_2 is converted to vapour phase. These vapours occupied 4.92 mL of volume at 1 atm. Atomic mass of element X is

(a) 400 g mol^{-1}
(b) 40 g mol^{-1}
(c) 200 g mol^{-1}
(d) 100 g mol^{-1}

6. What is the minimum amount of time required to measure the kinetic energy of an electron with a speed of 100 ± 1 ms^{-1}?

(a) 0.6 μs *(b)* 0.9 μs *(c)* 0.3 μs *(d)* 1.2 μs

7. Which of the following statements is correct?

(a) Plasma membrane in animal cells is a permeable membrane
(b) Animal cells could not preserve their shapes when they exist in isotonic environment having osmotic pressure equal to that of their cells
(c) If blood cells are placed in pure water, water molecules rapidly move into the cells
(d) All of the above

8. Consider the following reactions for the preparation of H_2O_2.

$$\mathrm{2NH_4HSO_4 \longrightarrow H_2 + (NH_4)_2S_2O_8}$$

$$\mathrm{(NH_4)_2S_2O_8 + 2H_2O \longrightarrow 2NH_4HSO_4 + H_2O_2}$$

How much current would have to be used in first reaction to produce enough intermediate to yield 100 g pure H_2O_2 per hour?

(Assume 50% anode current efficiency)

(a) 315.36 A *(b)* 415.36 A
(c) 31.536 A *(d)* 41.536 A

9. If 'a' is initial concentration and 'k' is rate constant, then match the following columns for different order of reactions.

Column I (Order of reaction)		Column II (Half-life)	
A.	First	p.	$0.693/k$
B.	Second	q.	$a/2k$
C.	Third	r.	$1/(ka)$
D.	Zero	s.	$3/(2ka^2)$

Codes

	A	B	C	D		A	B	C	D
(a)	p	r	s	q	*(b)*	p	q	r	s
(c)	s	r	q	p	*(d)*	s	q	r	p

10. Which of the following order is incorrect for the indicated property alongwith it?

(a) $NaCl > KCl > RbCl > CsCl$ (Melting point)
(b) $CBr_4 < SiBr_4$ (Bond length between central atom and Br)
(c) $BeF_2 < MgF_2 < CaF_2 < SrF_2 < BaF_2$ (Solubility)
(d) $CaCl_2 < MgCl_2 < MgO < NaCl$ (Ionic character)

11. The values of van der Waals' constant 'a' for O_2, N_2, NH_3 and CH_4 are 1.360, 1.390, 4.170 and 2.253 $dm^6 atm\ mol^{-2}$, respectively. The gas which can be most easily liquefied is

(a) O_2 *(b)* N_2 *(c)* NH_3 *(d)* CH_4

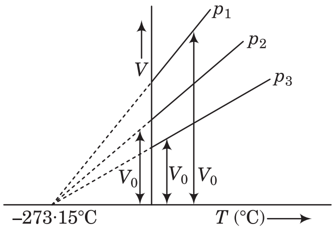
12. If the acid form of an indicator is red and that of base is blue, find out the change in $[H^+]$ required to change the indicator from 75% red to 75% blue. (K_a (acid -base indicator) $= 3 \times 10^{-5}$)

(a) 8×10^{-5} M *(b)* 9×10^{-5} M *(c)* 1×10^{-5} M *(d)* 4×10^{-5} M

13. Which of the following statements is incorrect for colloidal particles?

(a) A multimolecular colloid consists of an aggregate of small particles held by van der Waals' force
(b) A mixture of colloidal particles and true electrolytes may be separated by using dialysis or electrolysis method
(c) The colloidal particle in a solution is a three phase system
(d) The colloidal particles in solution acquire charges due to preferential adsorption of ions

14. Consider the following graph.



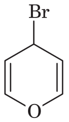
In the given graph, if slope is

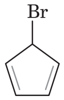
$$\left(\frac{\delta V}{\delta T}\right)_p = \frac{V_0/273.15}{1°\,C},$$

find out the relation among p_1, p_2 and p_3.

(a) $p_1 > p_2 > p_3$ *(b)* $p_1 < p_2 < p_3$
(c) $p_1 > p_2 < p_3$ *(d)* $p_1 < p_2 > p_3$

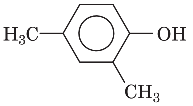
15. Which of the following statement is correct regarding the rate of hydrolysis of the compound I and II by S_N1 reaction?

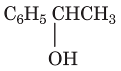

I

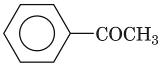

II

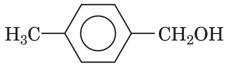
(a) I reacts faster than II
(b) II reacts faster than I
(c) Both I and II react with the same rate
(d) Neither I nor II reacts

16. An aromatic compound X with the molecular formula $C_8H_{10}O$ on reaction with iodine and dilute NaOH gives a yellow precipitate. The structure of the compound X is expected to be

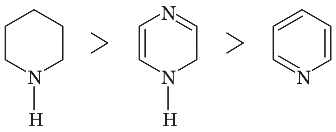
(a)


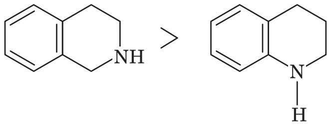
(b)

$C_6H_5CH(OH)CH_3$

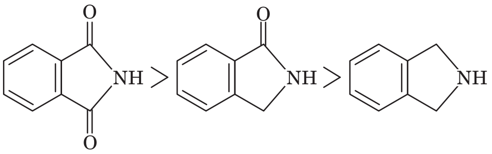
(c)


(d)


17. Consider the following comparison of basic nature of amines.

I.


II.


III.


The correct comparisons are

(a) I and III *(b)* II and III
(c) I and II *(d)* I, II and III

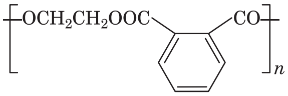
18. The secondary structure of proteins refers to

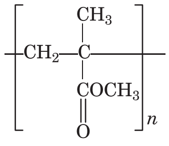
(a) regular folding patterns of continuous portions of the polypeptide chain
(b) mainly denatured proteins and structures of prosthetic group

(c) three dimensional structure, specially the bond between amino residues that are far apart from each other in polypeptide chain

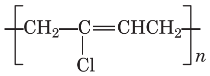
(d) linear sequence of amino acid residues in the polypeptide chain

19. Which one of the following is not correctly matched?

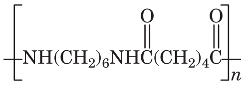
(a) Terylene 

(b) PMMA 

$$\left[-CH_2-\underset{\underset{\underset{O}{\|}}{COCH_3}}{\overset{CH_3}{C}}- \right]_n$$

(c) Neoprene 

$$\left[-CH_2-\underset{Cl}{C}=CHCH_2- \right]_n$$

(d) Nylon-6,6 

$$\left[-NH(CH_2)_6NH\overset{O}{\overset{\|}{C}}(CH_2)_4\overset{O}{\overset{\|}{C}}- \right]_n$$

20. Which one of the following statements is incorrect?

(a) Equanil is used in controlling depression and hypertension

(b) A drug which kills the organism in the body is called bacteriostatic

(c) 0.2% solution of phenol is an antiseptic while 1.0% solution is a disinfectant

(d) Mifepristone is a synthetic steroid used as 'morning after pill'

21. Which of the following statement is incorrect?

(a) The cyano complexes are far more stable than those formed by halide ions

(b) The stability constant of $[Cu(NH_3)_4]^{2+}$ is lesser than $[Cd(NH_3)_4]^{2+}$ ion

(c) $[Cr(H_2O)_6]^{3+}$ ion shows paramagnetic character

(d) $[Co(NH_3)_5NO_2]Cl_2$ complex does not show geometrical isomerism

22. An aqueous solution of titanium chloride, when subjected to magnetic measurement, shows zero magnetic moment. Assuming the octahedral complex in aqueous solution, the formulae of the complex is

(a) $[TiCl_2(H_2O)_4]$

(b) $[Ti(H_2O)_6]Cl_2$

(c) $[Ti(H_2O)_6]Cl_4$

(d) $[TiCl_3(H_2O)_3]$

23. Which of the following statement is incorrect about NO_2 and ClO_2?

(a) In both oxides, the central atom has an oxidation state of + 4

(b) On cooling, both undergo dimerisation

(c) Both are paramagnetic in nature

(d) Both have bent structure

24. In which of the following condition a chemical reaction cannot occur?

(a) ΔH and ΔS increase and $T\Delta S > \Delta H$

(b) ΔH and ΔS decrease and $\Delta H > T\Delta S$

(c) ΔH increases and ΔS decreases

(d) ΔH decreases and ΔS increases

25. Under the influence of an electric field, the particles in a sol migrate towards cathode. The coagulation of the same sol is studied using NaCl, Na_2SO_4 and Na_3PO_4 solutions. Their coagulation values will be maximum for

(a) Na_3PO_4 (b) Na_2SO_4 (c) NaCl (d) Same for all

26. In which one of the following reaction, H_2O_2 acts as a strong oxidising agent?

(a) $PbO_2 + H_2O_2 \longrightarrow PbO + H_2O + O_2$

(b) $PbS + 4H_2O_2 \longrightarrow PbSO_4 + 4H_2O$

(c) $Ag_2O + H_2O_2 \longrightarrow 2Ag + H_2O + O_2$

(d) $Cl_2 + H_2O_2 \longrightarrow 2HCl + O_2$

27. X and Y are two metals. When burnt in air, X forms only oxides while Y forms both oxide and nitride. The metals X and Y may be respectively.

(a) Na and K (b) Ca and Mg (c) Na and Mg (d) Li and Na

28. Aqueous solution of boric acid is treated with salicylic acid. Which of the following statements is correct for the product formed for the above reaction?

(a) There are two ring which are five membered

(b) No product will be formed in the above reaction

(c) Product is 4-coordinated complex and optically resolvable

(d) Product is 6-coordinated complex and optically resolvable

29. In the extraction of copper, which one of the following reaction does not occur in Bessemer's converter?

(a) $FeO + SiO_2 \longrightarrow FeSiO_3$

(b) $2Cu_2S + 5O_2 \longrightarrow 2CuSO_4 + 2CuO$

(c) $2Cu_2S + 3O_2 \longrightarrow 2Cu_2O + 2SO_2\uparrow$

(d) $2CuFeS_2 + 2O_2 \longrightarrow Cu_2S + 2FeS + 2SO_2$

30. Carbon cannot be used in the reduction of Al_2O_3 because

(a) the heat of formation of CO_2 is more than that of Al_2O_3

(b) pure carbon is not easily available

(c) the heat of formation of Al_2O_3 is too high

(d) it is a non-metal

Answers

1. (c)	**2.** (c)	**3.** (b)	**4.** (b)	**5.** (d)
6. (c)	**7.** (c)	**8.** (a)	**9.** (a)	**10.** (c)
11. (c)	**12.** (a)	**13.** (c)	**14.** (b)	**15.** (a)
16. (b)	**17.** (c)	**18.** (c)	**19.** (a)	**20.** (b)
21. (b)	**22.** (c)	**23.** (b)	**24.** (c)	**25.** (c)
26. (b)	**27.** (c)	**28.** (c)	**29.** (d)	**30.** (c)

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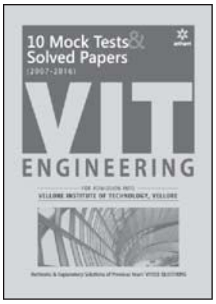
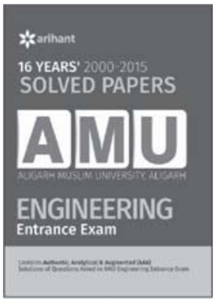


C084 ₹355

C026 ₹360

C023 ₹370



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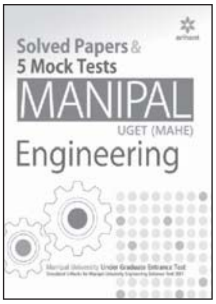

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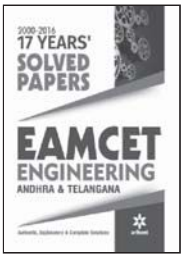

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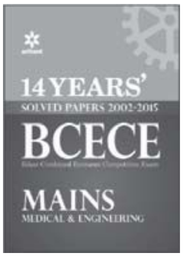
Bihar

C042 ₹320

Bihar



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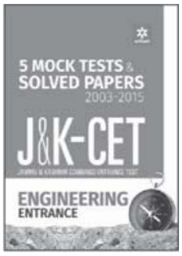

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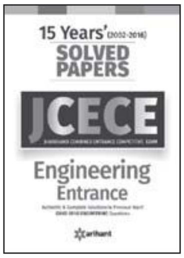

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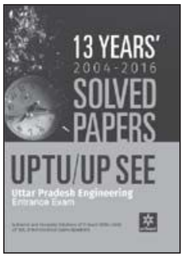

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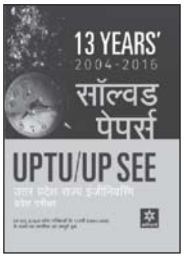

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GOLDEN OLDIES

REDOX AND ELECTROCHEMISTRY

A collection of best asked questions from JEE to revise your concepts

1. What will occur if a block of copper metal is dropped into a beaker containing a solution of 1 M $ZnSO_4$? **[JEE Main 2016]**

(a) The copper metal will dissolve and zinc metal will be deposited
(b) The copper metal will dissolve with evolution of oxygen gas
(c) The copper metal will dissolve with evolution of hydrogen gas
(d) No reaction will occur

2. For the following electrochemical cell at 298 K,

$$Pt(s)\,|\,H_2(g, 1\text{ bar})\,|\ \ ^{+}(aq, 1\quad)||\,|\,M^{4+}(aq), M^{2+}(aq)\,|\,Pt(s)$$

$$E_{cell} = 0.092\text{ V when } \frac{[M^{2+}(aq)]}{[M^{4+}(aq)]} = 10^x$$

$$\text{Given, } E^\circ_{M^{4+}/M^{2+}} = 0.151\text{ V}; 2.303\frac{RT}{F} = 0.059\text{ V}$$

The value of x is **[JEE Advanced 2016]**

(a) –2 *(b)* –1 *(c)* 1 *(d)* 2

3. Two Faraday of electricity is passed through a solution of $CuSO_4$. The mass of copper deposited at the cathode is (at. mass of Cu = 63.5 u) **[JEE Main 2015]**

(a) 0 g *(b)* 63.5 g *(c)* 2 g *(d)* 127 g

4. At 298 K, the standard reduction potentials are 1.51 V for $MnO_4^-|Mn^{2+}$, 1.36 V for $Cl_2|Cl^-$, 1.07 V for $Br_2|Br^-$ and 0.54 V for $I_2|I^-$. At pH = 3, permanganate is expected to oxidise,

$$\left(\frac{RT}{F} = 0.059\right)$$

[JEE Main 2015]

(a) Cl^-, Br^- and I^- *(b)* Br^- and I^-
(c) Cl^- and Br^- *(d)* Only I^-

5. The correct statement(s) about Cr^{2+} and Mn^{3+} is (are) [atomic number of Cr = 24 and Mn = 25] **[JEE Advanced 2015]**

(a) Cr^{2+} is a reducing agent
(b) Mn^{3+} is an oxidising agent
(c) Both Cr^{2+} and Mn^{3+} exhibit d^4 electronic configuration
(d) When Cr^{2+} is used as a reducing agent, the chromium ion attains d^5 electronic configuration

6. A variable opposite external potential (E_{ext}) is applied to the cell $Zn|Zn^{2+}(1\text{ M})||Cu^{2+}(1\text{ M})|Cu$, of potential 1.1V. When $E_{ext} < 1.1$ V and $E_{ext} > 1.1$ V respectively, electrons flow from **[JEE Main 2015]**

(a) cathode to anode in both cases
(b) cathode to anode and anode to cathode
(c) anode to cathode and cathode to anode
(d) anode to cathode in both cases

7. Resistance of 0.2 M solution of an electrolyte is 50 Ω. The specific conductance of the solution of 0.5 M solution of same electrolyte is 1.4 S m^{-1} and resistance of same solution of the same electrolyte is 280 Ω. The molar conductivity of 0.5 M solution of the electrolyte in $Sm^2\ mol^{-1}$ is **[JEE Main 2014]**

(a) 5×10^{-4} *(b)* 5×10^{-3}
(c) 5×10^{3} *(d)* 5×10^{2}

8. The equivalent conductance of NaCl at concentration C and at infinite dilution are λ_C and λ_∞, respectively. The correct relationship between λ_C and λ_∞ is given as (where, the constant B is positive) **[JEE Main 2014]**

(a) $\lambda_C = \lambda_\infty + (B)\ C$
(b) $\lambda_C = \lambda_\infty - (B)\ C$
(c) $\lambda_C = \lambda_\infty - (B)\ \sqrt{C}$
(d) $\lambda_C = \lambda_\infty + (B)\ \sqrt{C}$

9. Given below are the half-cell reactions **[JEE Main 2014]**

$$Mn^{2+} + 2e^- \longrightarrow Mn; E^\circ = -1.18\text{ V}$$

$$2\,(Mn^{3+} + e^- \longrightarrow Mn^{2+}); E^\circ = +1.51\text{ V}$$

The E° for $3Mn^{2+} \longrightarrow Mn + 2Mn^{3+}$ will be

(a) – 2.69 V; the reaction will not occur
(b) – 2.69 V; the reaction will occur
(c) – 0.33 V; the reaction will not occur
(d) – 0.33 V; the reaction will occur

10. Given, $E^\circ_{Cr^{3+}/Cr} = -0.74\text{ V}; E^\circ_{MnO_4^-/Mn^{2+}} = 1.51\text{ V}$

$$E^\circ_{Cr_2O_7^{2-}/Cr^{3+}} = 1.33\text{ V}; E^\circ_{Cl/Cl^-} = 1.36\text{ V}$$

Based on the data given above strongest oxidising agent will be **[JEE Main 2013]**

(a) Cl *(b)* Cr^{3+}
(c) Mn^{2+} *(d)* MnO_4^-

GOLDEN OLDIES

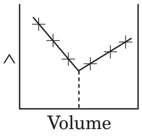
11. An aqueous solution of X is added slowly to an aqueous solution of Y as shown in Column I. The variation in conductivity of these reactions is given in Column II. Match Column I with Column II and select the correct answer using the codes given below the columns. **[JEE Advanced 2013]**

Column I	Column II
P. $\underset{X}{(C_2H_5)_3N} + \underset{Y}{CH_3COOH}$	1. Conductivity decreases and then increases
Q. $\underset{X}{KI(0.1\text{ M})} + \underset{Y}{AgNO_3(0.01\text{ M})}$	2. Conductivity decreases and then does not change much
R. $\underset{X}{CH_3COOH} + \underset{Y}{KOH}$	3. Conductivity increases and then does not change much
S. $\underset{X}{NaOH} + \underset{Y}{HI}$	4. Conductivity does not change much and then increases

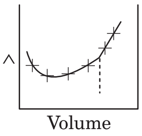
Codes

	P	Q	R	S		P	Q	R	S
(a)	3	4	2	1	(b)	4	3	2	1
(c)	2	3	4	1	(d)	1	4	3	2

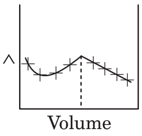
12. $AgNO_3$ (aqueous) was added to an aqueous KCl solution gradually and the conductivity of the solution was measured. The plot of conductance ($\wedge$) *versus* the volume of $AgNO_3$ is **[IIT JEE 2011]**



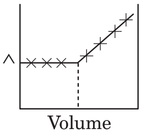
(P)



(Q)



(R)



(S)

(a) P
(b) Q
(c) R
(d) S

13. For the reduction of NO_3^- ion in an aqueous solution $E°$ is + 0.96 V. Values of $E°$ for some metal ions are given below

$V^{2+}(aq) + 2e^- \longrightarrow V; \quad E° = -1.19\text{ V}$

$Fe^{3+}(aq) + 3e^- \longrightarrow Fe; \quad E° = -0.04\text{ V}$

$Au^{3+}(aq) + 3e^- \longrightarrow Au; \quad E° = +1.40\text{ V}$

$Hg^{2+}(aq) + 2e^- \longrightarrow Hg; \quad E° = +0.86\text{ V}$

The pair(s) of metals that is/are oxidised by NO_3^- in aqueous solution is (are) **[IIT JEE 2009]**

(a) V and Hg
(b) Hg and Fe
(c) Fe and Au
(d) Fe and V

14. Electrolysis of dilute aqueous NaCl solution was carried out by passing 10 mA current. The time required to liberate 0.01 mole of H_2 gas at the cathode is ($1\text{ F} = 96500\text{ C mol}^{-1}$) **[IIT JEE 2008]**

(a) 9.65×10^4 s
(b) 19.3×10^4 s
(c) 28.95×10^4 s
(d) 38.6×10^4 s

15. $Zn \mid Zn^{2+}(a = 0.1\text{ M}) \mid\mid Fe^{2+}(a = 0.01\text{ M}) \mid Fe$

The emf of the above cell is 0.2905 V. Equilibrium constant for the cell reaction is

(a) $10^{0.32/0.059}$
(b) $10^{0.32/0.0295}$
(c) $10^{0.26/0.0295}$
(d) $10^{0.32/0.295}$

16. In the electrolytic cell, flow of electrons is from **[IIT JEE 2003]**

(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

17. A solution containing one mole per litre of each $Cu(NO_3)_2$, $AgNO_3$, $Hg_2(NO_3)_2$ and $Mg(NO_3)_2$ is being electrolysed by using inert electrodes. The values of standard electrode potentials in volts (reduction potential) are

$Ag^+/Ag = +0.80,\ Hg_2^{2+}/2Hg = +0.79$

$Cu^{2+}/Cu = +0.34,\ Mg^{2+}/Mg = -2.37$

With increasing voltage, the sequence of deposition of metals on the cathode will be **[IIT JEE 2002]**

(a) Ag, Hg, Cu, Mg
(b) Mg, Cu, Hg, Ag
(c) Ag, Hg, Cu
(d) Cu, Hg, Ag

18. 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 :

$MnO_4^-(aq) + 8H^+(aq) + 5e^- \longrightarrow Mn^{2+}(aq) + 4H_2O(l);$
$E° = 1.51\text{ V}$

$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \longrightarrow 2Cr^{3+}(aq) + 7H_2O(l);$
$E° = 1.38\text{ V}$

$Fe^{3+}(aq) + e^- \longrightarrow Fe^{2+}(aq),\ E° = 0.77\text{ V}$

$Cl_2(g) + 2e^- \longrightarrow 2Cl^-(aq),\ E° = 1.40\text{ V}$

Identify the incorrect statement regarding the quantitative estimation of aqueous $Fe(NO_3)_2$. **[IIT JEE 2002]**

(a) MnO_4^- can be used in aqueous HCl
(b) $Cr_2O_7^{2-}$ can be used in aqueous HCl
(c) MnO_4^- can be used in aqueous H_2SO_4
(d) $Cr_2O_7^{2-}$ can be used in aqueous H_2SO_4

19. The gas X at 1 atm is bubbled through a solution containing mixture of 1 M Y^- and 1 M Z^- at 25ºC. If the order of reduction potential is $Z > Y > X$, then **[IIT JEE 2000]**

(a) Y will oxidise X and not Z
(b) Y will oxidise Z and not X
(c) Y will oxidise both X and Z
(d) Y will reduce both X and Z

20. For the electrochemical cell, $(M \mid M^+) \mid\mid (X^- \mid X)$, $E°(M^+/M) = 0.44\text{ V}$ and $E°(X/X^-) = 0.33\text{ V}$. From this data one can deduce that **[IIT JEE 2000]**

(a) $M + X \longrightarrow M^+ + X^-$ is the spontaneous reaction
(b) $M^+ + X^- \longrightarrow M + X$ is the spontaneous reaction
(c) $E_{cell} = 0.77$ V
(d) $E_{cell} = -0.77$ V

Answers with Explanation

1. ***(d)*** **Key concept** A metal with lower standard reduction potential can have the ability to displace metal with higher standard reduction potential from their solutions. The reactivity of metals decreases from top to bottom in an electrochemical series, i.e. metals higher in series are more active than metals lying lower in the series.

In electrochemical series, with respect to reduction potential Cu^{2+} lies below Zn^{2+}. Hence, copper metal could not displace Zn^{2+} from $ZnSO_4$ solution.

2. ***(d)*** **Thinking process** Find out E°_{cell} using the equation,

$$E^\circ_{cell} = E^\circ_{right} - E^\circ_{left}$$

Then, apply Nernst equation,

$$E_{cell} = E^\circ_{cell} - \frac{0.059}{n}\log\frac{[M^{2+}][H^+]^2}{[M^{4+}]P_{H_2}}$$

Put $\frac{[M^{2+}][H^+]^2}{[M^{4+}]P_{H_2}} = K$ and find the value of x

Oxidation at anode

$$H_2(g) \longrightarrow 2H^+(aq) + 2e^-;\ E^\circ_{SHE} = 0.00\ V$$

Reduction at cathode

$$M^{4+}(aq) + 2e^- \longrightarrow M^{2+}(aq);\ E^\circ_{M^{4+}/M^{2+}} = 0.151\ V$$

Net $M^{4+}(aq) + H_2(g) \longrightarrow M^{2+}(aq) + 2H^+(aq)$

$$K = \frac{[M^{2+}][H^+]^2}{[M^{4+}]P_{H_2}} = \frac{[M^{2+}]}{[M^{4+}]}$$

$$E_{cell} = E^\circ_{cell} - \frac{0.059}{2}\log K$$

$$0.092 = 0.151 - \frac{0.059}{2}\log\frac{[M^{2+}]}{[M^{4+}]}$$

$$0.059 = \frac{0.059}{2}\log 10^x$$

$$\therefore \quad \log 10^x = 2$$

$$\therefore \quad x = 2$$

3. ***(b)*** **Key concept** This problem is based on Faraday's first law of electrolysis which states that when an electric current is passed through an electric solution, the amount of substance (W) deposited at the electrode is proportional to the electric charge (Q) passed through the electrolytic solution. Hence,

$$W = ZQ \quad \text{...(i)}$$

where, Z = electrochemical equivalent

$$= \frac{\text{equivalent weight of substance } (E)}{96500\ (F)}$$

Given, $Q = 2F$

Atomic mass of Cu = 63.5 u

Valency of the metal $(Z) = 2$

$$\therefore \quad W = ZQ = \frac{E}{F}\cdot 2F = 2E$$

$$= \frac{2\times 63.5}{2} = 63.5\ g$$

Short trick

We have, $CuSO_4 \longrightarrow Cu^{2+} + SO_4^{2-}$

$$\underset{1\ mol}{Cu^{2+}} + \underset{\substack{2\ mol\\ 2\ F}}{2e^-} \longrightarrow \underset{1\ mol\ =\ 63.5\ g}{Cu}$$

4. ***(b)*** **Key concept** At pH = 3, MnO_4^- will oxidise only those species which have lower reduction potential than reduction potential of MnO_4^-.

From given equation,

$$MnO_4^-/Mn^{2+} = 1.51\ V,\ Cl_2/Cl^- = 1.36\ V,$$
$$Br_2/Br^- = 1.07\ V,\quad I_2/I^- \equiv 0.54\ V$$

So, in acidic medium

$$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$$

$$n = 5,$$

From Nernst equation of electrode potential,

$$E_{cell} = 1.51 - \frac{0.0591}{5}\log\frac{[Mn^{2+}]}{[MnO_4^-][H^+]^8}$$

Taking Mn^{2+} and MnO_4^- in standard state, i.e. 1 M

$$E_{cell} = 1.51 - \frac{0.0591}{5}\times 8\log\frac{1}{[H^+]}$$

$$= 1.51 - \frac{0.0591}{5}\times 8\times 3 = 1.22632\ V$$

Hence, at this pH, MnO_4^- will oxidise only Br^- and I^- as standard reduction potential of Cl_2/Cl^- is 1.36 V is greater than that for MnO_4^-/Mn^{2+}.

5. ***(a, b, c)*** **Key concept** In a redox reaction, the atom/ion which get oxidised behaves as a reducing agent and which is reduced behaves as an oxidising agent

$$Cr^{2+} + Mn^{3+} \rightleftharpoons Cr^{3+} + Mn^{2+}$$

Since, both Cr^{2+} loses an electron to convert into Cr^{3+} (a more stable state of Cr), so it is a reducing agent whereas, Mn^{3+} gains electron from Cr^{2+} to get its stable state $^{2+}$. Hence, it is an oxidising agent

Electronic configuration of

$$Cr^{2+} = [Ar]_{18}3d^4 4s^0$$

Electronic configuration of

$$Mn^{3+} = [Ar]_{18}3d^4 4s^0$$

Therefore, Cr^{2+} and Mn^{3+} have d^4-electronic configuration.

6. ***(c)*** In Daniell cell, the anode is made up of Zn rod and dipped in solution of $ZnSO_4$ (electrolyte). Similarly, the cathode is made up of Cu rod and dipped in the solution of $CuSO_4$. The complete cell is represented as

$$Zn|Zn^{2+}(1\ M)||Cu^{2+}(1\ M)|Cu$$

When $E_{ext} < 1.10$ V, electrons flow from anode to cathode in external circuit. When $E_{ext} > 1.10$ V, electrons flows from cathode to anode in external circuit (reverse reaction).

7. ***(a)*** **Thinking process** In order to solve the problem, calculate the value of cell constant of the first solution and then use this value of cell constant to calculate the value of κ of second solution. Afterwards, finally calculate molar conductivity using value of κ and M.

For the first solution, $\kappa = 1.4\ Sm^{-1}$, $R = 50\ \Omega$, $M = 0.2$

$$\text{Specific conductance } (\kappa) = \frac{1}{R}\times\frac{l}{A}$$

$$1.4\ Sm^{-1} = \frac{1}{50\Omega}\times\frac{l}{A}$$

$$\frac{l}{A} = 50\times 1.4\ m^{-1}$$

For the second solution,

$$R = 280\,\Omega,\ \frac{l}{A} = 50 \times 1.4\ \text{m}^{-1};\ \kappa = \frac{1}{280} \times 1.4 \times 50 = \frac{1}{4}$$

Now, molar conductivity

$$\lambda_M = \frac{\kappa}{1000 \times M} = \frac{\frac{1}{4}}{1000 \times 0.5} = \frac{1}{2000} = 5 \times 10^{-4}\ \text{Sm}^2\text{mol}^{-1}$$

8. ***(c)*** According to Debye – Huckel – Onsager equation,

$$\lambda_C = \lambda_\infty - B\sqrt{C}$$

where, λ_C = limiting equivalent conductivity at concentration C

λ_∞ = limiting equivalent conductivity at infinite dilution

C = concentration

9. ***(a)*** **Key concept** Standard electrode potential E° of reaction, is an intensive (non-additive) property. Therefore, to calculate the value of E° of a reaction, first calculate ΔG° which is an extensive (additive) property. Then, calculate E° using formula,

$$\Delta G^\circ = -\,nFE^\circ_{\text{cell}}$$

If $E^\circ_{\text{cell}} = +$ ve, then reaction is spontaneous otherwise, non-spontaneous.

Given,

$$Mn^{2+} + 2e^- \longrightarrow Mn;\ E^\circ_1 = -1.18\ \text{V};\ \Delta G^\circ_1 = -2FE^\circ_1 \qquad \text{...(i)}$$

$$2(Mn^{3+} + e^- \longrightarrow Mn^{2+});\ E^\circ_2 = 1.51\text{V};\ \Delta G^\circ_2 = -2FE^\circ_2 \qquad \text{...(ii)}$$

To calculate,

$$3Mn^{2+} \longrightarrow Mn + 2Mn^{3+};\ E^\circ_3 = ?,\ \Delta G^\circ_3 = -2FE^\circ_3 \qquad \text{...(iii)}$$

On substracting Eq. (ii) from Eq. (i), we get Eq. (iii)

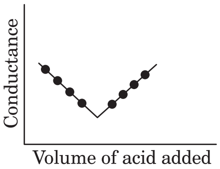
$$\therefore\ \Delta G^\circ_3 = \Delta G^\circ_1 - \Delta G^\circ_2 \Rightarrow -2FE^\circ_3 = -2FE^\circ_1 - (-2FE^\circ_2)$$

$$\therefore\ E^\circ_3 = E^\circ_1 - E^\circ_2 = -1.18 - 1.51 = -2.69\ \text{V}$$

As E° comes out to be negative so reaction will not occur.

10. ***(d)*** Higher the standard reduction potential, better is the oxidising agent. Among the given, $E^\circ_{MnO_4^-/Mn^{2+}}$ is highest, hence MnO_4^- is the strongest oxidising agent.

11. ***(a)*** The variation in conductivities in general can be seen as

In burette (Acid)	**In flask** (Base)	**Curve**
Strong (HI)	Strong (NaOH)	Conductance first decreases due to formation of H_2O and then increases due to addition of strong electrolyte 
Weak (CH_3COOH)	Strong (KOH)	Conductivity decreases due to neutralisation of conducting strong base and then remains constant due to addition of weak acid
Weak $(C_2H_5)_3N$	Weak (CH_3COOH)	Conductivity increases due to formation of ions and then remains constant due to addition of weak base
KX	$AgNO_3$	Insoluble salt AgX is formed, hence conductance remains constant. It increases due to addition of KX

12. ***(d)*** As $AgNO_3$ is added to solution, KCl will be displaced according to following reaction,

$$AgNO_3(aq) + KCl(aq) \longrightarrow AgCl(s) + KNO_3(aq)$$

For every mole of KCl displaced from solution, one mole of KNO_3 comes in solution resulting in almost constant conductivity. As the end point is reached, added $AgNO_3$ remain in solution increasing ionic concentration, hence conductivity increases.

13. ***(a,b,d)*** Metals with E° value less than 0.96 V will be able to reduce NO_3^- in aqueous solution. Therefore, metals

V ($E^\circ = -1.19$ V), Fe ($E^\circ = -\,0.04$ V), Hg ($E^\circ = +\,0.86$ V) will reduce NO_3^- but Au ($E^\circ = +\,1.40$ V) cannot reduce NO_3^- in aqueous solution.

14. ***(b)*** $2H_2O + 2e^- \longrightarrow H_2 + 2OH^-$

For 0.01 mole of H_2, 0.02 mole of electrons are consumed.

Charge required = 0.02 × 96500 C

Charge (Q) = current (i) × time (t)

$$\therefore\ \text{Time required}\ (t) = \frac{0.02 \times 96500}{10 \times 10^{-3}} = 19.3 \times 10^4\ \text{s}$$

15. ***(b)*** **Thinking process** First, calculate the value of E°_{cell} using Nernst equation,

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.059}{n}\log\frac{[M^{2+}]_{\text{oxidised}}}{[M^{2+}]_{\text{reduced}}}$$

and then substitute the value of E°_{cell} in the equation,

$$E^\circ_{\text{cell}} = \frac{0.059}{n}\log K$$

to calculate equilibrium constant (K).

The cell reaction is

$$Zn + Fe^{2+} \rightleftharpoons Zn^{2+} + Fe;\ E = 0.2905\ \text{V}$$

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.059}{2}\log\frac{[Zn^{2+}]}{[Fe^{2+}]}$$

$$E^\circ_{\text{cell}} = 0.2905 + \frac{0.059}{2}\log\frac{0.1}{0.01} = 0.32\ \text{V}$$

Also, $$E^\circ_{\text{cell}} = \frac{0.059}{n}\log K$$

$$\log K = \frac{2E^\circ}{0.059} = \frac{0.32}{0.0295}$$

$$\therefore\ K = 10^{0.32/0.0295}$$

16. ***(c)*** **Key concept** The device in which electrolysis (chemical reaction involving oxidation and reduction) is carried out by using electricity is called electrolytic cell. In other words, in which conversion of electrical energy into chemical energy is done.

In electrolytic cell, the electrons flows from cathode to anode *via* internal circuit. At anode (+ ve pole) oxidation and at cathode (– ve pole) reduction takes place.

17. ***(c)*** In aqueous solution, only those ions which are less electropositive than hydrogen ($E^\circ > 0$) would be deposited. Therefore, in the present case, only Ag, Hg and Cu would be deposited on passing electricity through aqueous solution of these ions, Mg will not deposited.

To be Continued at Page 38

RAINBOW

CHEMICAL KINETICS

Stepwise Learning and Practice through Selective Problems

1 Decomposition of H_2O_2 follows a first order reaction. In 50 min, the concentration of H_2O_2 decreases from 0.5 M to 0.125 M in one such decomposition. When the concentration of H_2O_2 reaches 0.05 M, the rate of formation of O_2 will be [JEE Main 2016]

(a) 6.93×10^{-4} mol min^{-1} *(b)* 2.66 L min^{-1} at STP
(c) 1.34×10^{-2} mol min^{-1} *(d)* 6.93×10^{-2} mol min^{-1}

(a) **Step 1** *Write the expression for rate constant (k) of first order reaction.*

$$k = \frac{2.303}{t} \log \frac{a}{a - x} \qquad \ldots\text{(i)}$$

where, 'a' is initial concentration and $(a - x)$ is the concentration after time 't'.

Step 2 *Substitute the values of* $a = 0.5$ M, $a - x = 0.125$ M *and* $t = 50$ min *in the above Eq. (i)*

$$k = \frac{2.303}{50\,\text{min}} \log \frac{0.5\text{ M}}{0.125\text{ M}} = 0.0277\text{ min}^{-1}$$

Step 3 *Write the expression for rate of reaction,* $2H_2O_2 \longrightarrow 2H_2O + O_2$, *in terms of rate of disappearance of reactants and rate of appearance of products.*

As per reaction,

$$2H_2O_2 \longrightarrow 2H_2O + O_2$$

$$-\frac{1}{2}\frac{d[H_2O_2]}{dt} = +\frac{1}{2}\frac{d[H_2O]}{dt} = +\frac{d[O_2]}{dt}$$

Rate of reaction, $\dfrac{-d[H_2O_2]}{dt} = k[H_2O_2]$

$$\therefore \qquad \frac{d[O_2]}{dt} = -\frac{1}{2}\frac{d[H_2O_2]}{dt} = \frac{1}{2}k[H_2O_2] \qquad \ldots\text{(ii)}$$

Step 4 *Now, to calculate rate of formation of* O_2 *when concentration of* H_2O_2 *reaches* 0.05 M, *substitute the value of k and* $[H_2O_2]$ *in Eq. (ii)*

$$\frac{d[O_2]}{dt} = \frac{1}{2} \times 0.0277 \times 0.05$$
$$= 6.93 \times 10^{-4}\text{ mol min}^{-1}$$

TRY THESE

1. For an elementary reaction, $2A + B \longrightarrow 3C$, the rate of appearance of C at time t is 1.3×10^{-4} mol L^{-1}s^{-1}. The rate of reaction at this time is

(a) 2×10^{-3} mol L^{-1}s^{-1} *(b)* 2×10^{-6} mol L^{-1}s^{-1}
(c) 4×10^{-5} mol L^{-1}s^{-1} *(d)* 3×10^{-2} mol L^{-1}s^{-1}

2. For the reaction, $N_2 + 3H_2 \rightleftharpoons 2NH_3$, the rate of change of concentration for hydrogen is -0.3×10^{-4} Ms^{-1}. The rate of change of concentration of ammonia is

(a) -0.2×10^{-4} *(b)* 0.2×10^{-4} *(c)* 0.1×10^{-4} *(d)* 0.3×10^{-4}

3. In the reaction, $2A + B \longrightarrow A_2B$, if the concentration of A is doubled and of B is halved, then the rate of the reaction will

(a) increases by two times *(b)* decreases by two times
(c) increases by four times *(d)* remains the same

1. (c) **2.** (b) **3.** (a)

2 For a reaction between A and B, the initial rate of reaction is measured for various initial concentrations of A and B. The data provided are

S.No.	[*A*]	[*B*]	Initial reaction rate
1.	0.20 M	0.30 M	5×10^{-5}
2.	0.20 M	0.10 M	5×10^{-5}
3.	0.40 M	0.05 M	1×10^{-4}

The overall order of reaction is

(a) one *(b)* two
(c) two and half *(d)* three

(a) **Step 1** *Write the rate law equation, considering the order of reaction w.r.t. A is n and w.r.t. B is m.*

$$\text{Rate} = k[A]^n[B]^m$$

Step 2 *Substitute the values of* $[A]$, $[B]$ *and rate at different conditions given as* (1), (2) *and* (3).

For (1), $5 \times 10^{-5} = [0.20]^n[0.30]^m$ … (i)
For (2), $5 \times 10^{-5} = [0.20]^n[0.10]^m$ …(ii)
For (3), $1 \times 10^{-4} = [0.40]^n[0.05]^m$
or, $10 \times 10^{-5} = [0.40]^n[0.05]^m$ … (iii)

Step 3 *Divide Eq. (i) by (ii) and (ii) by (iii) and calculate m and n, respectively.*

For Eqs. (i) and (ii),

$$\frac{5 \times 10^{-5}}{5 \times 10^{-5}} = \left[\frac{0.20}{0.20}\right]^n \left[\frac{0.30}{0.10}\right]^m, \; 1 = (3)^m \Rightarrow (3)^0 = (3)^m$$

$$\Rightarrow \qquad m = 0$$

From Eqs. (ii) and (iii)

$$\frac{5 \times 10^{-5}}{10 \times 10^{-5}} = \left[\frac{0.20}{0.40}\right]^n \left[\frac{0.10}{0.05}\right]^m, \; \frac{1}{2} = \left(\frac{1}{2}\right)^n \left(\frac{0.10}{0.05}\right)^0$$

$$\frac{1}{2} = \left(\frac{1}{2}\right)^n \Rightarrow \left(\frac{1}{2}\right)^1 = \left(\frac{1}{2}\right)^n \Rightarrow n = 1$$

$\therefore$ Overall order of the reaction $= n + m$

$$1 + 0 = 1$$

TRY THESE

1. For the chemical change, $A \rightarrow B$ it is found that the rate of reaction doubles when the concentration is increased by 4 times. The order of the reaction is

(a) one *(b)* two *(c)* half *(d)* None of these

2. For the reaction, $A + B \rightarrow C$,

S.No.	[*A*]	[*B*]	$-\dfrac{d[A]}{dt}$
1.	1M	1M	0.25 M min^{-1}
2.	2M	1M	0.50 M min^{-1}
3.	1M	2M	0.25 M min^{-1}

The order of reaction w.r.t. A is

(a) 2 *(b)* 0 *(c)* 3 *(d)* 1

1. (c) **2.** (d)

③ At 380°C, the half-life period for the first order decomposition of H_2O_2 is 360 min. The energy of activation of the reaction is 200 kJ/mol. The time required for 75% decomposition at 450°C is

(a) 1.421×10^3 s	*(b)* 1.612×10^4 s
(c) 1.223×10^3 s	*(d)* 1.812×10^4 s

⊙ **(c)** **Step 1** *Write the equation for half life period of a first order reaction.*

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

Step 2 *Substitute the value of $t_{1/2}$ equal to 360 min to calculate k_1 at 380°C*

$$k_1 = \frac{0.693}{360} = 1.925 \times 10^{-3} \text{min}^{-1}$$

Step 3 *Write the Arrhenius equation in terms of rate constants, k_1 and k_2 at two different temperatures, T_1 (380°C) and T_2 (450°C).*

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

Step 4 *Substitute the value of* $T_1 = (380 + 273)\text{ K} = 653\text{ K}$, $T_2 = (450 + 273)\text{ K} = 723\text{ K}$, $E_a = 200 \times 10^3$ J / mol, $R = 8.314 \text{ JK}^{-1}\text{ mol}^{-1}$ *and* $k_1 = 1.925 \times 10^{-3} \text{ min}^{-1}$ *to calculate k_2*

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

$$= \frac{200 \times 10^3}{2.303 \times 8.314}\left[\frac{1}{653} - \frac{1}{723}\right] = 1.548$$

$$\frac{k_2}{k_1} = \text{antilog}\,(1.548) = 35.32$$

$$k_2 = 35.32 \times k_1 = 35.32 \times 1.925 \times 10^{-3} = 0.068$$

Step 5 *Write the equation of time required for 75% decomposition of H_2O_2 and substitute the values to calculate t_2.*

$$t_2 = \frac{2.303}{k_2}\log\frac{[a]}{[a-x]}$$

$$= \frac{2.303}{0.068}\log\frac{100}{100-75}$$

$$= \frac{2.303 \times 2 \times 0.3010}{0.068}$$

$$= 20.39 \text{ min} \times 60 \text{ s/min}$$

$$= 1223.3 \text{ s} = 1.223 \times 10^3 \text{ s}$$

TRY THESE

1. The activation energy of a reaction is 9 kcal/mol. The increase in the rate constant when its temperature is raised from 295 K to 300 K is approximately.

(a) 10%	*(b)* 50%	*(c)* 100%	*(d)* 28%

2. The rate constant, the activation energy and the Arrhenius parameter of a chemical reaction at 25°C are $3 \times 10^{-4}\text{ s}^{-1}$, $104.4 \text{ kJ mol}^{-1}$ and $6 \times 10^{14}\text{ s}^{-1}$, respectively. The value of the rate constant at $T \rightarrow \infty$ is

(a) $2 \times 10^{18}\text{ s}^{-1}$	*(b)* $6 \times 10^{14}\text{ s}^{-1}$
(c) $3.6 \times 10^{30}\text{ s}^{-1}$	*(d)* Infinity

⊙ **1.** (d) **2.** (b)

④ The half-time of a first order decomposition of nitramide is 2.1 h at 15°C.

$$NH_2NO_2(aq) \longrightarrow NO_2(g) + H_2O(l)$$

If 6.2 g of nitramide is allowed to decompose, then time taken for it to decompose 99% will be

(a) 2.1 h	*(b)* 12 h
(c) 13.96 h	*(d)* 33 h

⊙ **(c)** **Step 1** *Write the relation between rate constant (k) and half-life period ($t_{1/2}$) for first order reaction.*

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

Step 2 *Substitute the value of $t_{1/2}$ equal to 2.1 h to calculate k.*

$$k = \frac{0.693}{2.1} = 0.33 \text{h}^{-1}$$

Step 3 *Write the expression for first order reaction in terms of initial concentration a and concentration (a − x) after time t.*

$$k = \frac{2.303}{t}\log\frac{a}{a-x}$$

Step 4 *Substitute all the given values to calculate time (t) taken for nitramide to decompose 99%.*

$$t = \frac{2.303}{k}\log\frac{100}{100-99}$$

$$= \frac{2.303}{0.33}\log 100$$

$$= \frac{2.303}{0.33} \times 2$$

$$= 13.96 \text{ h}$$

TRY THESE

1. A reaction has a rate constant of $0.5 \text{ mol}^{-1}\text{dm}^3\text{min}^{-1}$. If initial concentration of the reactant is 0.2 mol dm^{-3}, half-life of the reaction is

(a) 1.4 min	*(b)* 10 min
(c) 15 min	*(d)* 20 min

2. The half-life period for a first order reaction is 693 s. The rate constant of this reaction would be

(a) 0.1 s^{-1}	*(b)* 0.01 s^{-1}
(c) 0.001 s^{-1}	*(d)* 0.0001 s^{-1}

3. The value of rate constant for a first order reaction is $2.303 \times 10^{-2}\text{ s}^{-1}$. What will be the time required to reduce the concentration to $\frac{1}{10}$th of its initial concentration?

(a) 100 s	*(b)* 10 s
(c) 2303 s	*(d)* 23.03 s

⊙ **1.** (b) **2.** (c) **3.** (a)

AMAZING REALITIES

Osmium is the densest known stable element on Earth.

⑤ A reaction proceeds by first order. 75% of this reaction was completed in 32 min. The time required for 50% completion is

(a) 8 min *(b)* 16 min
(c) 20 min *(d)* 24 min

⊙ **(b)** **Step 1** *Write the expression for rate constant of first order reaction,*

$$k = \frac{2.303}{t}\log_{10}\frac{a}{a-x} \quad \ldots(i)$$

where, a = initial concentration
x = change in concentration during time 't'

Step 2 *Calculate the value of rate constant using above equation (i) when 75% of the reaction was completed in 32 min.*

$$k = \frac{2.303}{32}\log_{10}\frac{100}{100-75}$$
$$= \frac{2.303}{32}\log_{10}4$$
$$k = 0.0433\ \text{min}^{-1}$$

Step 3 *Finally, calculate the time required for the completion of 50% of reaction by substituting all the values in Eq. (i) including $k = 0.0433\ \text{min}^{-1}$*

$$t = \frac{2.303}{0.0433}\log_{10}\frac{100}{100-50}$$
$$= \frac{2.303}{0.0433}\log_{10}2 = 16\,\text{min}$$

TRY THESE

1. A first order reaction is 20% complete in 10 min. Calculate the time required for 75% completion of the reaction.

(a) 0.233 min *(b)* 62.18 min
(c) 112.12 min *(d)* 36.18 min

2. The rate constant for the first order reaction is 60 s^{-1}. How much time will it take to reduce the concentration of the reactant to $\frac{1}{16}$th?

(a) 4.6×10^{-2} s *(b)* 4.6×10^{4} s
(c) 4.6×10^{2} s *(d)* 4.6×10^{-4} s

⊙ **1.** (b) **2.** (a)

⑥ For a first order reaction, $A \to P$, the temperature (T) dependent rate constant (k) was found to follow the equation,

$$\log k = -\frac{2000}{T} + 6.0$$

the pre-exponential factor A and the activation energy E_a, respectively, are **[IIT JEE 2009]**

(a) $1.0 \times 10^{6}\ s^{-1}$ and 9.2 kJ mol^{-1}
(b) 6.0 s^{-1} and 16.6 kJ mol^{-1}
(c) $1.0 \times 10^{6}\ s^{-1}$ and 16.6 kJ mol^{-1}
(d) $1.0 \times 10^{6}\ s^{-1}$ and 38.3 kJ mol^{-1}

⊙ **(d)** **Step 1** *Write the logarithmic form of Arrhenius equation,*

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

Step 2 *Compare the above equation with given equation,*

$$\log k = 6 - \frac{2000}{T}$$

On comparing, we get

$$\log A = 6 \quad \ldots(i)$$

and $$\frac{E_a}{2.303\,R} = 2000 \quad \ldots(ii)$$

Step 3 *Solve the Eqs. (i) and (ii) obtained in Step 2 to calculate pre-exponential factor (A) and the activation energy (E_a), respectively.*

$$A = 10^{6}$$

and $$E_a = 2000 \times 2.303 \times 8.314$$
$$= 38.3\ \text{kJ mol}^{-1}$$

TRY THESE

1. A first order reaction is 50% complete in 30 min at 27°C and in 10 min at 47°C. The energy of activation of the reaction is

(a) 52.8 kJ *(b)* 23.6 kJ *(c)* 29.5 kJ *(d)* 43.8 kJ

2. The rate constant of a reaction increases by 5% when its temperature is raised from 27°C to 28°C. The activation energy of the reaction is

(a) 36.6 kJ/mol *(b)* 16.6 kJ/mol
(c) 46.6 kJ/mol *(d)* 26.6 kJ/mol

⊙ **1.** (d) **2.** (a)

Continued from Page 35

Also, higher the value of $E°$, easier will be their reduction, therefore, the sequence in which ions will be deposited on increasing voltage across the electrodes is Ag, Hg, Cu.

18. ***(a)*** MnO_4^- cannot be used for oxidation of Fe^{2+} in HCl because the following reaction is spontaneous.

$$MnO_4^- + Cl^- \longrightarrow Mn^{2+} + Cl_2;\ E° = 1.51 - 1.40 = 0.11\ V$$

In all other cases, the redox process between oxidising agent and medium (HCl or H_2SO_4) are non-spontaneous, hence would not interfere oxidation of Fe^{2+}.

19. ***(a)*** **Key concept** The substance which have lower reduction potential are stronger reducing agent, i.e. reduce the other substances. However, the substances which have higher reduction potential are stronger oxidising agent.

Given, the decreasing order of $E°$ values for some metal ions,

$$Z > Y > X$$

∴ Y will oxidise X but not Z.

20. ***(b)*** For the given cell,

$M \mid M^+ \parallel X^- \mid X$, the cell reaction is derived as follows :

RHS : Reduction : $X + e^- \longrightarrow X^-$ ...(i)
LHS : Oxidation : $M \longrightarrow M^+ + e^-$ ...(ii)

Add Eqs. (i) and (ii)

$$M + X \longrightarrow M^+ + X^-$$

The cell potential = – 0.11 V

Since, E_{cell} = –ve, the cell reaction derived above is non-spontaneous. In fact, the reverse reaction will occur, spontaneously.

BRAIN TEASERS

To boost up your rank in JEE Main and Advanced

1. Which of the following phenols is most soluble in aqueous sodium bicarbonate? [NSEC 2013]

(a) 2, 4-dihydroxyacetophenone
(b) *p*-cyanophenol
(c) 3, 4-dicyanophenol
(d) 2, 4, 6-tricyanophenol

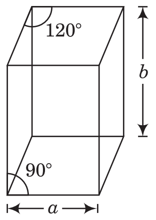
2. Ti^{3+}, V^{3+}, Fe^{3+} and Co^{3+} afford a large number of tetrahedral complex but, Cr^{3+} never does this, the correct reason is

(a) Cr^{3+} forces high crystal field splitting with a varieties of ligands
(b) crystal field stabilisation energy in octahedral as well as in tetrahedral Cr^{3+} system plays the deciding role
(c) the ionic radius of Cr^{3+} is the largest among the other M^{3+} ions mentioned
(d) electronegativity of Cr^{3+} is the largest among other trivalent 3*d*-metals and so Cr prefers to be linked with as many ligands as its ionic radius allows

3. 500 mL of 1 M $H_2C_2O_4$ and 100 mL of 2 M H_2SO_4 are mixed with 40 g of NaOH and a solution was obtained. 30 mL of the above solution are titrated against a standard solution of $Na_2CO_3 \cdot 10H_2O$ containing 14.3 g of the compound in 100 mL of the solution. The volume of sodium carbonate required for the complete neutralisation of 30 mL of the solution is

(a) 20 mL *(b)* 40 mL *(c)* 50 mL *(d)* 30 mL

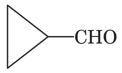
4. X_2Y molecules (molar mass $= 259.8 \text{ g mol}^{-1}$) crystallises in a hexagonal lattice as shown in given figure. The lattice constant were $a = 5$ Å and $b = 8$ Å. If density of crystal is 5 g cm^{-3}, then how many molecules are contained in the given unit cell. (Given that, $N_A = 6 \times 10^{23}$).

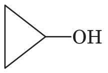


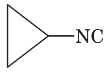
(a) 8 *(b)* 6
(c) 4 *(d)* 2

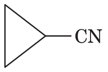
5. Identify the final product of the following reaction.

$$\text{Cyclopropane carboxylic acid} \xrightarrow[\Delta]{NH_3} (A) \xrightarrow[\Delta]{KOH/Br_2} (B) \xrightarrow{CHCl_3/KOH} (C)$$

(a)


(b)


(c)


(d)


6. In order to know the composition of an unknown mixture of NaCl and NaI, 8 g of the mixture was dissolved in 2 L of water and the solution was treated with $AgNO_3$. If 60 mL of the solution required 12 mL of 0.25 N $AgNO_3$ for complete precipitation. The percentage composition of the mixture is

(a) NaCl = 56% and NaI = 44%
(b) NaCl = 44% and NaI = 56%
(c) NaCl = 52% and NaI = 48%
(d) NaCl = 48% and NaI = 52%

7. The complexation of Fe^{2+} with the chelating agent dipyridyl has been studied kinetically in both forward and reverse directions.

$$Fe^{2+} + 3\,\text{dipy} \rightleftharpoons [Fe(\text{dipy})_3]^{2+}$$

$$\text{Rate (forward)} = (1.4 \times 10^{13})\,[Fe^{2+}]\,[\text{dipy}]^{3+}$$

$$\text{Rate (reverse)} = (1.22 \times 10^{-4})\,[Fe(\text{dipy})_3]^{2+}$$

The stability constant for the complex is

(a) 2.12×10^{15} *(b)* 1.19×10^{17}
(c) 4.61×10^{16} *(d)* 3.24×10^{15}

8. A solution was prepared by dissolving 18 g of glucose in 15 g of water. The resulting solution was found to have a boiling point of 100.34°C. The molar mass of glucose is [Glucose is a molecular solid, i.e. present as individual molecules in a solution].

(a) 0.70 mol *(b)* 0.10 mol *(c)* 1.0 mol *(d)* 0.3 mol

BRAIN TEASERS

9. An intimate mixture of ferric oxide (Fe_2O_3) and aluminium (Al) is used as solid rocket fuel. Heat of formation and densities are as follows

$\Delta H_f(Al_2O_3) = 399$ kcal mol^{-1},

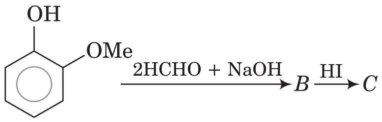
$\Delta H_f(Fe_2O_3) = 199$ kcal mol^{-1},

Density of $Fe_2O_3 = 5.2$ g/cc, density of Al = 2.7 g/cc.

The fuel value per cc of the mixture is

(a) 4.21 kcal/cc
(b) 3.94 kcal/cc
(c) 5.28 kcal/cc
(d) 3.21 kcal/cc

10. In the reaction of



The number of decarboxylated products possible if *C* undergoes strong heating is

(a) 1
(b) 2
(c) 3
(d) 0

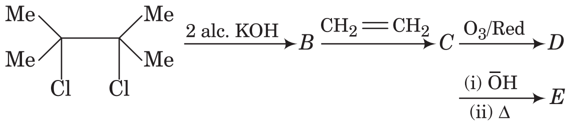
11. An electron diffraction experiment was performed with a beam of electrons accelerated by a potential difference of 10 keV. The wavelength of the electron beam is

(a) 0.234 Å *(b)* 0.641 Å *(c)* 0.123 Å *(d)* 0.412 Å

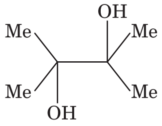
12. A red coloured oxide *X* on treatment with conc. HNO_3 gives a compound *Y*. *Y* with HCl produces a chloride *Z* which is insoluble in cold water but soluble in hot water. *Z* can also be formed by treating *X* with conc. HCl. Compound *X*, *Y* and *Z* are respectively.

(a) $Pb_3O_4, PbO_2, PbCl_2$
(b) $Fe_3O_4, FeO, FeCl_2$
(c) $Fe_3O_4, Fe_2O_3, FeCl_3$
(d) $Mn_3O_4, MnO_2, MnCl_2$

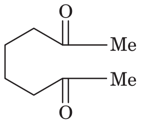
13. For the given reaction, which of the following option is correct?



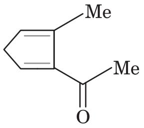
(a) Compound *B* is



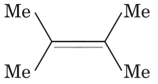
(b) Compound *D* is



(c) Compound *E* is



(d) Compound *B* is



14. K_{sp} of AgCN is 4×10^{-16} at 25°C, while K_a for HCN is 4×10^{-10}. The molar solubility of AgCN in a 0.01 M HNO_3 solution is

(a) 1×10^{-6} M
(b) 2×10^{-2} M
(c) 2×10^{-4} M
(d) 1×10^{-2} M

15. Calculate the mass of KCN required to extract gold from 100 kg of a rock sample having 2.2% gold on *w*/*w* basis. **[INChO 2014]**

(a) 1.59 kg *(b)* 1.62 kg *(c)* 1.45 kg *(d)* 1.33 kg

Answers

1. (d)	**2.** (b)	**3.** (a)	**4.** (d)	**5.** (c)
6. (a)	**7.** (b)	**8.** (b)	**9.** (b)	**10.** (d)
11. (c)	**12.** (a)	**13.** (b)	**14.** (a)	**15.** (c)

CHEMISTRY IN action

Nanotechnology enables new insights into chemical reactions

Eighty percent of all products of the chemical industry are manufactured with catalytic processes. Catalysis is also indispensable in energy conversion and treatment of exhaust gases. It is important for these processes to run as quickly and efficiently as possible. This in turn protects the environment while also saving time and conserving resources. Industry is always testing new substances and arrangements that could lead to new and better catalytic processes. Researchers have now developed a method for improving the precision of such experiments, which may speed up the search for optimal solutions.

The researchers built a model system that enables them to study catalysis in the minutest detail. For the model experiment the team used iron oxide, which was converted to iron through the addition of hydrogen and with assistance from the catalyst platinum. The platinum splits the molecular hydrogen (H_2) into elemental hydrogen (H), which can more easily react with iron oxide. The size of the iron oxide particles was only 60 nanometres and the platinum particles were even smaller at 30 nanometres, i.e. about two-thousandths of the diameter of a human hair.

The researchers positioned these particles in pairs on a grid-like model at 15 different distances from each other. In the first grid segment the platinum particle lay precisely on top of the iron oxide particle, and in the 15th segment, the particles lay 45 nanometres apart. In a 16th segment, the iron oxide was completely alone. This was helpful in sorting reactivity patterns which in turn makes it possible to selectively optimize the efficiency of catalytic processes.

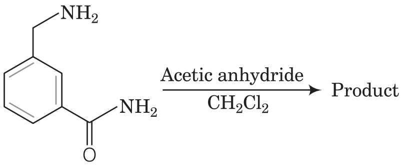
Saleha Pervez

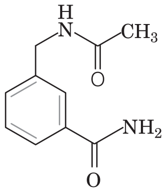
JEE ADVANCED DRILL

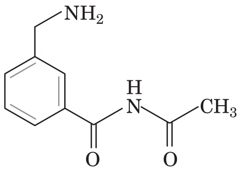
A collection of 30 innovative problems on JEE Advanced pattern from complete syllabus.

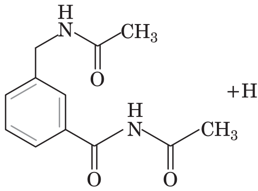
Single Answer Correct Type

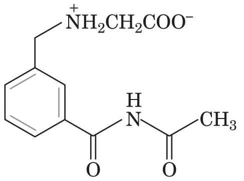
1. In the reaction shown below, the major product formed is [JEE Advanced 2013]



(a)

+ CH_3COOH

(b)

+ CH_3COOH

(c)

$+H_2O$

(d)


2. In an insulated container, 1 mol of a liquid with molar volume 100 mL is kept at 1 bar. When the volume of liquid decreases by 1 mL, the liquid is steeply taken to 100 bar. The ΔH for the process is

(a) 8400 bar mL
(b) 9900 bar mL
(c) 9240 bar mL
(d) 7430 bar mL

3. Given, $Pb^{2+}/Pb = -0.126$ V; $Zn^{2+}/Zn = -0.763$ V.

The emf of the following cell;

$$Zn/Zn^{2+}\ (0.1\ M)\ ||\ Pb^{2+}(1\ M)/Pb \text{ is}$$

(a) – 0.637 *(b)* + 0.66
(c) > 0.637 *(d)* + 0.889

4. Which of the following statement is correct regarding the characteristics of sodium peroxide?

(a) It liberates O_2 with cold water
(b) It turns into white colour on exposure to moist air
(c) It reduces chromic compounds to chromate
(d) All of the above

5. Consider the following sequence of reactions,

$$CH_3COOH \xrightarrow{LiAlH_4} A \xrightarrow{PCl_5} B \xrightarrow{\text{Alc. KOH}} C$$

The product C is

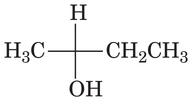
(a) acetaldehyde *(b)* acetylene
(c) ethylene *(d)* acetyl chloride

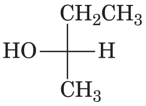
One or More than One Answer Correct Type

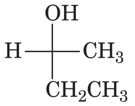
6. Select the correct statement.

(a) $SbCl_3$ is hydrolysed to orange coloured SbOCl soluble in dil. HCl
(b) $BiCl_3$ is hydrolysed to white coloured BiOCl soluble in dil. HCl
(c) NCl_5 and PCl_5 are stable compounds
(d) PCl_5 can change to PCl_6^- and PCl_4^+ with no change in hybridisation of P

7. Consider the following compounds and choose the correct statement.

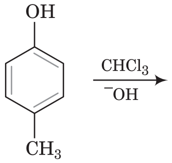

(I)

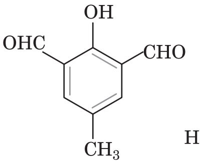

(II)

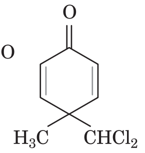

(III)

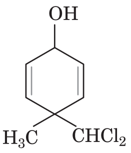
(a) Structure I and II are identical
(b) All are identical
(c) Structure I and III are identical
(d) Structure I and III are different

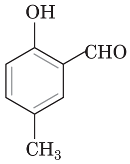
8. In the following reaction, the product(s) formed is/are [JEE Advanced 2013]




(P)


(Q)


(R)

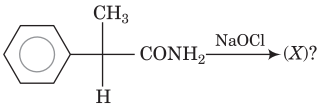

(S)

(a) P (major) (b) Q (minor) (c) R (minor) (d) S (major)

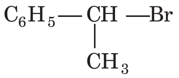
9. The correct statement(s) regarding, (i) HClO, (ii) $HClO_2$ (iii) $HClO_3$ and (iv) $HClO_4$ is (are) [JEE Advanced 2015]

(a) the number of Cl═O bonds in (ii) and (iii) together is two
(b) the number of lone pairs of electrons on Cl in (ii) and (iii) together is three
(c) the hybridisation of Cl in (iv) is sp^3
(d) amongst (i) to (iv), the strongest acid is (i)

10. Which of the following statement(s) is/are true about the major product (X) in the reaction,



(a) X is a cyclic amide
(b) X has an asymmetric centre
(c) X is a primary amine
(d) X can also be obtained by treatment of NH_3 with


$$C_6H_5—\underset{\displaystyle CH_3}{\underset{|}{CH}}—Br$$

11. A gas described by van der Waals' equation
(a) behaves similar to an ideal gas in the limit of large molar volumes
(b) behaves similar to an ideal gas in the limit of large pressures
(c) is characterised by van der Waals' coefficients that are dependent on the identity of the gas but are independent of the temperature
(d) has the pressure that is lower than the pressure exerted by the same gas behaving ideally

12. The number of lone pair on iodine and number of d-orbitals used in hybridisation by iodine are different in

(a) ICl_2^- (b) ICl_2^+ (c) IF_7 (d) ICl_4^-

13. Which of the following statement(s) is/are true about the separate solution of 0.500 M $C_2H_5OH\,(aq)$, 0.100 M $Mg_3(PO_4)_2\,(aq)$, 0.250 M KBr (aq) and 0.125M $Na_3PO_4(aq)$ at 25°C [Assuming all salts to be strong electrolytes]?

(a) 0.100 M $Mg_3(PO_4)_2\,(aq)$ has the highest osmotic pressure
(b) 0.125 M $Na_3PO_4\,(aq)$ has the highest osmotic pressure
(c) 0.500 M $C_2H_5OH\,(aq)$ has the lowest osmotic pressure
(d) They all have the same osmotic pressure

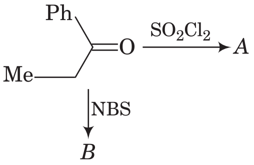
Single Integer Type

14. MX_2 dissociates into M^{2+} and X^- ions in an aqueous solution, with a degree of dissociation (α) of 0.5. The ratio of the observed depression of freezing point of the aqueous solution to the value of the depression freezing point in the absence of ionic dissociation is [JEE Advanced 2014]

15. The diffusion coefficient of an ideal gas is proportional to its mean free path and mean speed. The absolute temperature of an ideal gas is increased 4 times and its pressure is increased 2 times. As a result, the diffusion coefficient of this gas increase x times. The value of x is .... [JEE Advanced 2016]

16. Cyclobutene when refluxed in presence of potassium metal, evolve hydrogen gas and an aromatic system is formed. How many π-electrons are involved in the above formed aromatic system?

17. Consider the following reaction,



Sum of the active hydrogen atoms present in A and B is ... .

18. When the following aldohexose exists in its D-configuration, the total number of stereoisomers in its pyranose form is ... .

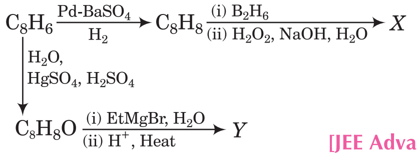
$$CHO—CH_2—CHOH—CHOH—CHOH—CH_2OH$$

19. A mixture of formic acid and oxalic acid is heated with conc. H_2SO_4. The gas produced is collected and on its treatment with KOH solution, the volume of the gas decreased by 1/6th. If the molar ratio of the two acids in the original mixture is $x : y$, the vlaue of x is ....

20. When a trisubstituted asymmetric benzene gets converted into tetrasubstituted compound, then how many derivatives can be obtained?

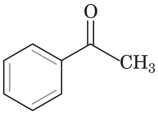
21. The total number of reagents among acidified $K_2Cr_2O_7$, alkaline $KMnO_4$, $CuSO_4$, H_2O_2, Cl_2, O_3, $FeCl_3$, HNO_3 and $Na_2S_2O_3$ that can oxidise aqueous iodide to iodine is … .

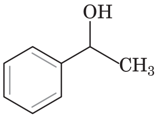
Comprehension I

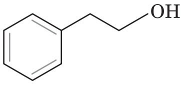


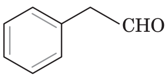
[JEE Advanced 2015]

22. Compound X is

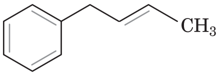
(a) 

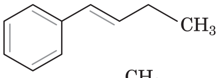
(b) 

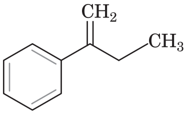
(c) 

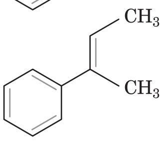
(d) 

23. The major compound Y is

(a) 

(b) 

(c) 

(d) 

Comprehension II

In a unit cell, atoms A are present at all corners of lattice, B atoms are present at alternate faces and all edge centres. Atoms C are present at face centres left from B and at each body diagonal at a distance of $\frac{1}{4}$ th of the body diagonal from corner.

24. A tetrad axis is passed from the given unit cell and all the atoms touching the axis are removed. The possible formula of the compound left is

(a) AB_3C_6 and AB_4C_5
(b) $A_3B_6C_7$ and $A_3B_6C_5$
(c) $A_4B_5C_8$ and $A_4B_5C_7$
(d) AB_2C and ABC_2

25. Total fraction of voids occupied is

(a) 0.58 (b) 0.25 (c) 0.48 (d) 0.86

Comprehension III

Three compounds A, B and C have empirical formula $CrCl_3 \cdot 6H_2O$. When 1 g of compound A was kept in a container with dehydrating agent, it lost water content and attained a constant weight of 0.865 g. When 1 g of B was kept in that vessel, it attained a constant weight of 0.932 g. Compound C showed no loss in water content.

26. Compound A is

(a) $[Cr(H_2O)_4Cl_2]Cl \cdot 2H_2O$
(b) $[Cr(H_2O)Cl]Cl_2$
(c) $[Cr(H_2O)_3Cl_3]\,H_2O$
(d) $[Cr(H_2O)_4Cl(H_2O)]Cl$

27. Mass of AgCl obtained in C is

(a) 16.14 g (b) 1.614 g (c) 0.807 g (d) 3.228 g

Matrix Match Type

28. Match the thermodynamic processes given under Column I with the expressions given under Column II. [JEE Advanced 2015]

Column I	Column II
A. Freezing of water at 273 K and 1 atm.	p. $q = 0$
B. Expansion of 1 mole of an ideal gas into a vacuum under isolated conditions.	q. $w = 0$
C. Mixing of equal volumes of two ideal gases at constant temperature and pressure in an isolated container.	r. $\Delta S_{sys} < 0$
D. Reversible heating of $H_2(g)$ at 1 atm from 300 K to 600 K, followed by reversible cooling to 300 K at 1 atm.	s. $\Delta U = 0$
	t. $\Delta G = 0$

Codes

	A	B	C	D		A	B	C	D
(a)	r,t	p,q,s	p,q,s	p,q,s,t	(b)	p,t	q,s	r,s	s,t
(c)	t,s	r,q,t	p,s	p,q	(d)	s,q	q,s	p,t,s	t,r

29. Match the compounds/ions in Column I with their properties/reaction in Column II.

Column I	Column II
A. C_6H_5CHO	p. gives precipitate with 2, 4−dinitrophenyl hydrazine
B. $CH_3C{\equiv}CH$	q. gives precipitate with $AgNO_3$
C. CN^-	r. is a nucleophile
D. I^-	s. is involved in cyanohydrin formation

Codes

	A	B	C	D
(a)	p, s	q	s	r
(b)	p, q, s	q, r	q, s	q, r
(c)	p, r	q	s	p
(d)	p, q	q, r	p, s	q

30. Match the following Column I with Column II.

Column I	Column II
A. Conversion of proteins into amino acids	p. Shape selective catalysis
B. Conversion of alcohols into gasoline	q. Enzymatic catalysis
C. Polymerisation of ethylene	r. *Ziegler-Natta* catalyst
D. Manufacture of margarine	s. Heterogeneous catalysis

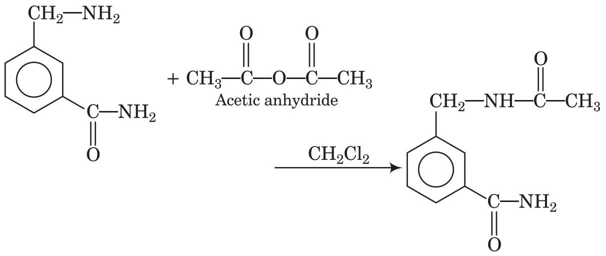
Codes

	A	B	C	D		A	B	C	D
(a)	q	q, s	r, s	s	(b)	p	q, s	r, s	q
(c)	q	p,s	r,s	s	(d)	p	r, s	q, s	s

Answers with Explanation

1. ***(a)*** **Thinking process** This problem includes concept of acetylation reaction and regioselectivity of chemical reaction.

Regioselectivity means which group will react selectively in the presence of two or more than two functional groups. Here, among two functional groups $—NH_2$ and $—CONH_2$, $—NH_2$ is more nucleophilic, hence $—NH_2$ group will undergo reaction faster than $—CONH_2$.



$—CH_2—NH_2$ is more nucleophilic than $—\underset{\underset{O}{\|}}{C}—NH_2$.

2. ***(b)*** At 1 bar pressure,

Volume of 1 mol of liquid $(V_1) = 100$ mL

At 100 bar pressure,

Volume of 1 mol of liquid $(V_2) = 99$ mL

Since, the process is steeply changed from 1 bar to 100 bar, it is irreversible process.

$$\therefore \quad w = -p(V_2 - V_1) = -100 \times (99 - 100) = 100 \text{ bar mL}$$

$$\Delta U = q + w$$

$$\Delta U = w \quad (\because q = 0, \text{ adiabatic nature due to insulation}).$$

$$\Delta U = 100 \text{ bar mL}$$

$$\begin{aligned}\Delta H &= \Delta U + p\Delta V = \Delta U + (p_2V_2 - p_1V_1)\\ &= 100 + (100 \times 99 - 1 \times 100)\\ &= 9900 \text{ bar mL}\end{aligned}$$

3. ***(b)***

$$\begin{aligned}E^\circ_{\text{cell}} &= E^\circ_{\text{Pb}^{2+}/\text{Pb}} - E^\circ_{\text{Zn}^{2+}/\text{Zn}}\\ &= -0.126 - (-0.763) = +0.637 \text{ V}\\ E_{\text{cell}} &= E^\circ_{\text{cell}} - \frac{0.0591}{n}\log\frac{[\text{Zn}^{2+}]}{[\text{Pb}^{2+}]}\\ &= 0.637 - \frac{0.0591}{2}\log 0.1\\ &= 0.637 + 0.02955 = 0.667 \text{ V}\end{aligned}$$

4. ***(b)*** (a) Sodium peroxide liberates O_2 with hot water.

$$2Na_2O_2 + 2H_2O(\text{warm}) \longrightarrow 4NaOH + O_2$$

(b) Sodium peroxide is a yellow coloured substance but turns white on exposure to moist air due to the formation of NaOH and Na_2CO_3.

$$Na_2O_2 + 2H_2O \longrightarrow 2NaOH + H_2O_2$$

$$2NaOH + CO_2 \longrightarrow Na_2CO_3 + H_2O$$

(c) Sodium peroxide is a powerful oxidising agent and it oxidises chromic compounds (Cr^{3+}) to chromate (Cr^{6+}).

$$5Na_2O_2 + \overset{+3}{Cr_2}(SO_4)_3 \longrightarrow 3Na_2SO_4 + 2Na_2\overset{+6}{Cr}O_4 + O_2$$

5. ***(c)*** **Thinking process** This problem is based on successive reduction, chlorination and elimination reaction. To solve such problem, use the function of the given reagents.

(i) $LiAlH_4$ causes reduction

(ii) PCl_5 causes chlorination

(iii) Alc. KOH causes elimination reaction

$$\begin{tikzcd} CH_3COOH \arrow[r, "LiAlH_4"] & \underset{(A)}{CH_3CH_2OH} \arrow[r, "PCl_5"] & \underset{(B)}{CH_3CH_2Cl} \arrow[d, "-HCl"', "Alc.KOH"] \\ & & \underset{\text{Ethylene}}{\underset{(C)}{CH_2{=}CH_2}} \end{tikzcd}$$

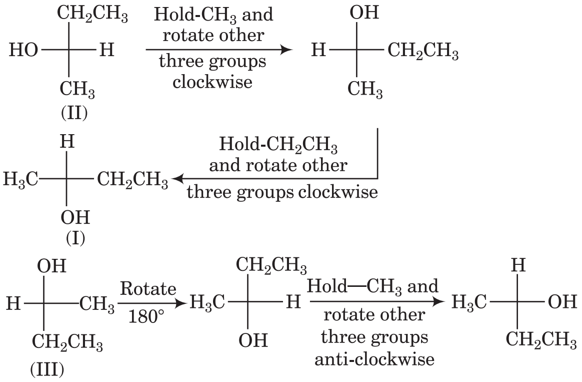
6. ***(a, b)*** $SbCl_3$ is a salt which is hydrolysed to form oxychloride.

$$SbCl_3 + H_2O \longrightarrow \underset{\text{Orange coloured}}{SbOCl} + 2HCl$$

Also, $BiCl_3$ is hydrolysed to form BiOCl, a white coloured oxychloride.

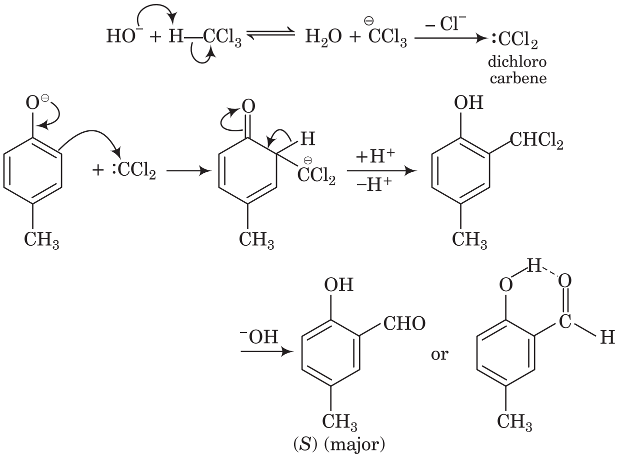
$$BiCl_3 + H_2O \longrightarrow \underset{\text{White coloured}}{BiOCl} + 2HCl$$

7. ***(a, d)***

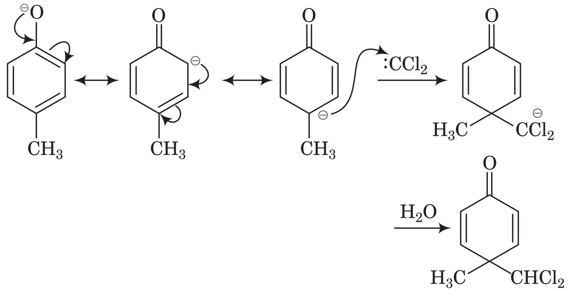


Since, the configuration of II and I are same i.e S while that of III is R. Hence, I and II are identical.

8. ***(b, d)*** **Key concept** Phenolic compounds in alkaline solution react with chloroform $(CHCl_3)$ at a temperature lower than that of $CHCl_3$ to form *ortho*-isomer as the major product (due to greater stability resulting from intramolecular hydrogen bonding).

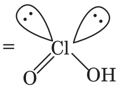


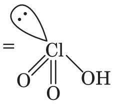
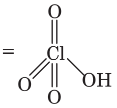
(S) is major product as it is stable due to intramolecular H-bonding.



Q (minor)

9. ***(b, c)*** At first, we draw the structure of the given compounds as,

(i) HClO = :Cl—O—H (ii) $HClO_2$ =


(iii) $HClO_3$ =

(iv) $HClO_4$ =


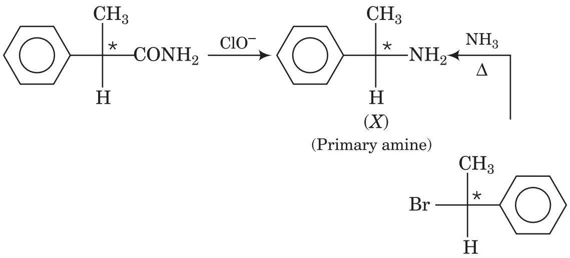
Number of Cl=O bonds in (ii) and (iii) together are three.

Number of lone pairs on Cl in (ii) and (iii) together = 2 + 1 = 3. The hybridisation of Cl in (iv) is sp^3.

Among (i) to (iv), the (iv), i.e. $HClO_4$ is the strongest acid having highest oxidation state of Cl among all given compounds.

$HClO_4$ = oxidation state of Cl = + 7.

10. ***(b, c, d)***



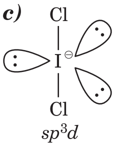
11. ***(a, c)*** Option (a) is correct because in the limit of large volume, both intermolecular force and molecular volume becomes negligible in comparison to volume of gas.

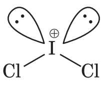
Option (b) is incorrect because in the limit of large pressure, $Z > 1$.

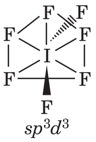
Option (c) is correct, for a van der Waals' gas, van der Waals' constant a and b are characteristics of a gas, independent of temperature.

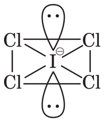
Option (d) is incorrect because Z can be either less or greater than unity, hence real pressure can be less or greater than ideal pressure.

12. ***(a, b, c)***


sp^3d


sp^3


sp^3d^3


sp^3d^2

13. ***(a, c)*** **Thinking process** This problem includes concept of colligative properties and van't Hoff factor. Calculate the effective molarity of each solution.

Effective molarity = van't Hoff factor × molarity

(i) For 0.5 M C_2H_5OH (aq)

Effective molarity = 0.5 (i = 1)

(ii) For 0.25 M KBr (aq)

Effective molarity = 0.5 M (i = 2)

(iii) For 0.1 M $Mg_3(PO_4)_2$ (aq)

Effective molarity = 0.5 M (i = 5)

(iv) For 0.125 M Na_3PO_4 (aq)

Effective molarity = 0.5 M (i = 4)

Molarity is same hence, their all colligative properties are also same.

Note This question is solved by assuming that the examiner has taken $Mg_3(PO_4)_2$ to be completely soluble. However, in real it is insoluble (sparingly soluble).

14. ***(2)*** $MX_2 \longrightarrow M^{2+} + 2X^-$

van't Hoff factor for any salt can be calculated by using equation, $i = 1 + \alpha(n-1)$

where, n = number of constituent ions

$$\therefore \; i(MX_2) = 1 + \alpha(3-1) = 1 + 2\alpha$$

$$\frac{(\Delta T_f)_{\text{observed}}}{(\Delta T_f)_{\text{theoretical}}} = i = 1 + 2\alpha$$

$$i = 1 + 2 \times 0.5 = 2$$

15. ***(4)*** **Key concept** Diffusion coefficient (DC) ∝ λ (mean free path)

$$\text{DC} \propto U_{\text{mean}}$$

Thus, $$(\text{DC}) \propto \lambda\, U_{\text{mean}} \quad \text{...(i)}$$

But, $$\lambda = \frac{RT}{\sqrt{2}\, N_0 \sigma p}$$

$$\lambda = \frac{T}{p} \quad \text{...(ii)}$$

and $$U_{\text{mean}} = \sqrt{\frac{8RT}{\pi M}}$$

$$U_{\text{mean}} \propto \sqrt{T} \quad \text{...(iii)}$$

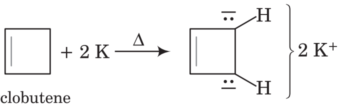
Using (i), (ii) and (iii) we get,

$$\therefore \quad \text{DC} \propto \frac{(T)^{3/2}}{p}$$

$$\frac{(\text{DC})_2}{(\text{DC})_1} = \left(\frac{p_1}{p_2}\right)\left(\frac{T_2}{T_1}\right)^{3/2} = \left(\frac{p_1}{2p_1}\right)\left(\frac{4T_1}{T_1}\right)^{3/2}$$

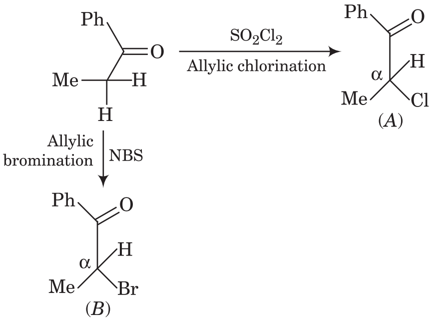
$$= \left(\frac{1}{2}\right)(8) = 4$$

16. ***(6)***



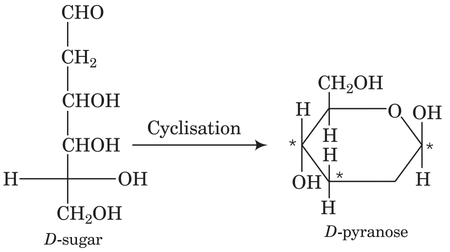
Aromatic dianion
(It has 6 delocalised
π-electrons)

17. ***(2)*** Halogenation occurs at the α-position of the carbonyl group (C = O) *via* free radical mechanism.



Hence, sum of active hydrogen in A and B is $1 + 1 = 2$.

18. ***(8)*** The D-form of given sugar is



Configurations at the three chiral carbons (starred) can be changed maintaining D-configuration. Hence, the total number of stereoisomers of D-pyranose $= 2^3 = 8$

19. ***(4)*** Let the no. of moles of formic acid is x and that of oxalic acid is y. Then,

$$\underset{x\text{ mole}}{HCOOH} \xrightarrow[H_2SO_4]{\text{conc.}} H_2O(l) + \underset{x\text{ mole}}{CO(g)}$$

$$\underset{y\text{ mole}}{\begin{matrix}COOH\\ |\\ COOH\end{matrix}} \xrightarrow[H_2SO_4]{\text{conc.}} \underset{y\text{ mole}}{CO(g)} + \underset{y\text{ mole}}{CO_2(g)} + H_2O(l)$$

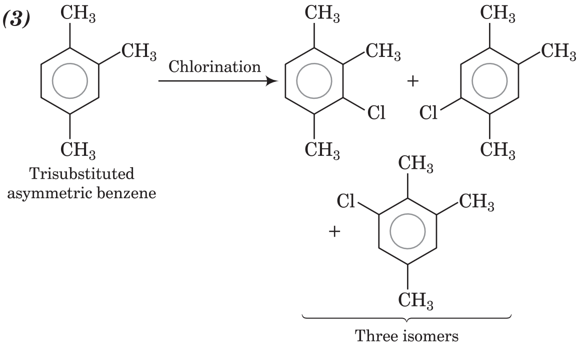
Total no. of moles of gaseous product $= x + 2y$

As only CO_2 is absorbed by KOH, therefore fraction of

$$CO_2 = \frac{y}{x+2y} = \frac{1}{6}$$

$$\text{or,}\quad 6y = x + 2y \quad \text{or,}\quad 4y = x \quad \text{or}\quad \frac{x}{y} = \frac{4}{1}$$

20. ***(3)***



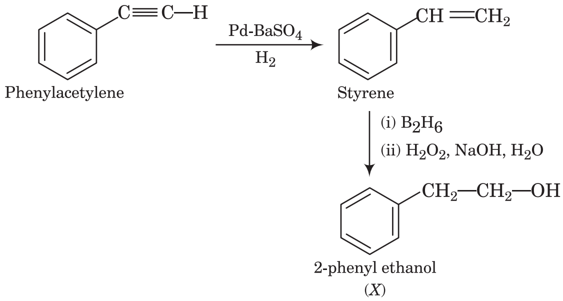
21. ***(7)*** Acidified $K_2Cr_2O_7$, $CuSO_4$, H_2O_2, Cl_2, O_3, $FeCl_3$ and HNO_3 oxidise *aq*. iodide to iodine. Alkaline $KMnO_4$ oxidise *aq*. iodide to IO_3^-.

$Na_2S_2O_3$ is a strong reducing agent which on reaction with I_2 produces I^-.

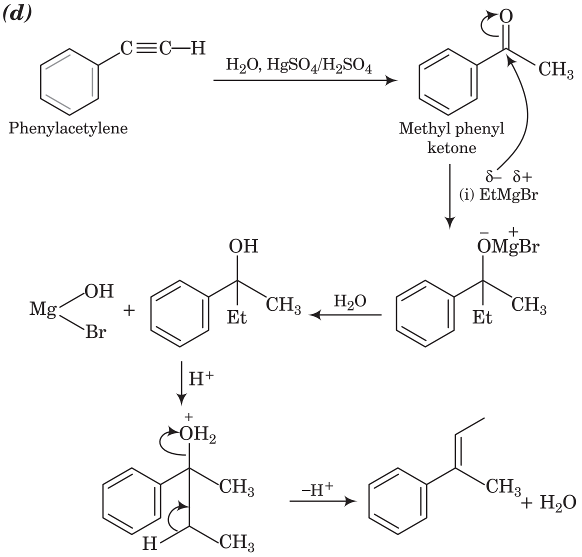
$$2Na_2S_2O_3 + I_2 \longrightarrow 2NaI + Na_2S_4O_6$$

Therefore, no reaction takes place between $Na_2S_2O_3$ and iodide ion.

22. ***(c)*** **Key concept** Lindlar's catalyst reduces triple bond of phenyl acetylene to double bond to form styrene which further reacts with diborane in the presence of H_2O_2 and forms 2-phenyl ethanol.



23. ***(d)***



24. ***(a)*** Number of A atoms per unit cell $= 8 \times \frac{1}{8} = 1$

Number of B atoms per unit cell $= 2 \times \frac{1}{2} + 12 \times \frac{1}{4} = 4$

Number of C atoms per unit cell$= 4 \times \frac{1}{2} + 1 \times 4 = 6$

Hence, the formula of compound is AB_4C_6

But in the given question two cases arises,

***Case* I** If the tetrad axis passes through the face-centres where B 'lies', then,

Number of B-atoms $= 4 - \left[\frac{1}{2} \times 2\right] = 3$

The formula of the compound left is AB_3C_6.

***Case* II** If the tetrad axis passes through the face-centres where 'C' lies, then

Number of C-atoms $= 6 - \left[\frac{1}{2} \times 2\right] = 5$

$\therefore$ Formula of the compound is AB_4C_5

25. ***(a)*** There are 8-effective tetrahedral voids out of which four are occupied (one at each body diagonal) and 4-effective octahedral voids such that one is not filled (body-centred). So, out of 12 (8 tetrahedral voids + 4 octahedral voids), only 7 are filled (4 tetrahedral voids + 3 octahedral voids).

$\therefore$ Fraction of voids occupied $= \dfrac{7}{12} = 0.58$

26. ***(a)*** Molecular weight of $CrCl_3 \cdot 6H_2O = 266.5$ g

1 g of A gives $(1 - 0.865)$ g $= 0.135$ g of H_2O

$\therefore$ 266.5g of A will give $= 0.135 \times 266.5$ g

$= 35.977$ g $= 36$ g H_2O

36 g of H_2O means 2 molecules of water, i.e. two H_2O molecules are present outside the coordination sphere.

$\therefore \quad A = [Cr(H_2O)_4Cl_2]Cl \cdot 2H_2O$

Similarly, $B = [Cr(H_2O)_5Cl]Cl_2 \cdot H_2O$, $C = [Cr(H_2O)_6]Cl_3$

27. ***(b)*** Molecular weight of AgCl = 143.5 g

$$A = [Cr(H_2O)_4Cl_2]Cl \cdot 2H_2O + AgNO_3 \longrightarrow AgCl + [Cr(H_2O)_4Cl_2]^+$$

1 mole $A = [Cr(H_2O)_4Cl_2]Cl \cdot 2H_2O$ gives 1 mole of AgCl

$\because$ 266.5 g of A gives = 143.5 g AgCl

$\therefore$ 1 g of A will give $= \dfrac{143.5}{266.5} = 0.538$ g AgCl

Similarly, mass of AgCl formed in $B = 1.076$ g

and mass of AgCl formed in $C = 1.614$ g

28. ***(a)*** A. $H_2O(l) \longrightarrow H_2O(s)$ at 273 K and 1 atm.

$\Delta H = -\text{ve} = q$

$\Delta S_{sys} < 0$, $\Delta G = 0$

$w \neq 0$ (as water expands on heating)

$\Delta U \neq 0$

B. Free expansion of ideal gas, $q = 0$, $w = 0$

$\Delta U = 0$, $\Delta S_{sys} > 0$, $\Delta G < 0$

C. Mixing of equal volume of ideal gases at constant pressure and temperature in an isolated container,

$q = 0$, $w = 0$, $\Delta U = 0$

$\Delta S_{sys} > 0$

$\Delta G < 0$

D. $H_2(g)$ 300 K $\xrightarrow[\text{heating, 1 atm}]{\text{Reversible}}$ 600 K $\xrightarrow[\text{cooling, 1 atm}]{\text{Reversible}}$ 300 K

29. ***(b)***

A. C_6H_5CHO	Gives phenylhydrazone with 2, 4-dinitrophenyl hydrazine, gives precipitate with $AgNO_3$, Tollen's test, forms cyanohydrin.
B. $CH_3C{\equiv}CH$	Gives precipitate ($CH_3{-}C{\equiv}CAg$) with $AgNO_3$, a nucleophile, undergo electrophilic attack
C. CN^-	Forms AgCN with $AgNO_3$, a nucleophile involved in cyanohydrin formation.
D. I^-	Gives AgI precipitate with $AgNO_3$, a nucleophile involved in cyanohydrin formation.

30. ***(c)*** Conversion of proteins into amino acids is an enzymatic catalysis.

Conversion of alcohols into gasoline is a shape selective catalysis. It is also an example of heterogeneous catalysis. *Ziegler-Natta* catalyst is used in the polymerisation of ethylene which is an example of heterogeneous catalysis. Manufacture of margarine is an example of heterogeneous catalysis.

CONCEPT MAP
your Revision Tool

SURFACE CHEMISTRY

- It is the branch of physical chemistry which deals with the nature of surfaces and also with physical and chemical processes which takes place on the surfaces.
- This branch deals with three different kinds of phenomenon, i.e. adsorption, catalysis and colloidal system.

❶ ADSORPTION

- The accumulation/adhesion of atoms/ions/molecules of gas, liquid or solid (adsorbate) at the surface rather than the whole mass of a substance (adsorbent) is called **adsorption**.
- It proceeds with a negative value of ΔH (exothermic), ΔS (decreases in entropy) and ΔG (spontaneous).

Distinction between Adsorption and Absorption

	Adsorption	Absorption
(i)	It implies concentrated at the surface only.	It implies penetration into the body of the solid.
(ii)	It is a rapid process and equilibrium is maintained in a short time.	In this, the equilibrium is reached slowly.

Note Both adsorption and absorption often takes place side by side and it is difficult to distinguish between these two processes.
Mc Bain introduced the general term sorption, which includes both the processes.

Ⓐ TYPES OF ADSORPTION

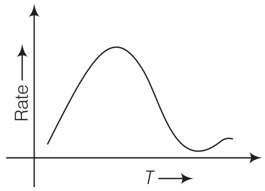
It is of two types:

ⓐ Physisorption

- The absorbate and adsorbent are held together by weak van der Waals' forces of attraction.
- It is reversible and not specific in nature.
- Rate of physisorption is directly proportional to ease of liquefaction of adsorbate. Also, it increases with increase in surface area of absorbent.
- Rate of physisorption increases with increase in pressure upto a certain extent and decreases with increase in temperature.

ⓑ Chemisorption

- The adsorbate and adsorbent are held together by chemical bond.
- It is irreversible and highly specific in nature.
- It increases with increase in surface area of adsorbent.
- Rate of chemisorption increases with increase in temperature till the activation energy is achieved.



Ⓑ APPLICATIONS OF ADSORPTION

- Adsorbents like silica and aluminium gels are used to remove moisture to control humidity.
- Noble gases are separated by adsorbing them on coconut charcoal at different temperatures due to different degree of adsorption of noble gases.
- Coloured impurities are removed from a solution by adsorbing them with the help of animal charcoal.
- Froth floatation process for the concentration of sulphide ores is based on adsorption.
- In the creation of completely vacuum space, etc.

❸ CATALYSIS

A substance that alters the rate of a reaction without being consumed in the reaction is called catalyst and phenomenon is known as **catalysis**.

Ⓐ TYPES OF CATALYSIS

ⓐ **Homogeneous Catalysis** Both reactants and the catalyst are in same phase

e.g. $2SO_2(g) + O_2(g) \longrightarrow 2SO_3(g)$ [catalyst-$NO(g)$]

ⓑ **Heterogeneous Catalysis** The reactants and the catalyst are in different phase

e.g. $N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$ [catalyst-$Fe(s)$]

ⓒ **Positive Catalysis** When a catalyst increases the rate of reaction

e.g. $2H_2 + O_2 \longrightarrow 2H_2O$ [catalyst-$Pt(s)$]

ⓓ **Negative Catalysis** When a catalyst decreases the rate of reaction.

e.g. $2Na_2SO_3(s) + O_2(g) \longrightarrow 2Na_2SO_4(s)$
[catalyst-alcohol]

ⓔ **Auto Catalysis** The phenomenon in which a chemical reaction is catalysed by one of the product of the reaction.

e.g. $CH_3COOC_2H_5 + H_2O \longrightarrow CH_3COOH + C_2H_5OH$
[Auto Catalyst-CH_3COOH]

Ⓑ ADSORPTION THEORY OF HETEROGENEOUS CATALYSIS

It is based on theory of intermediate complex formation and involves the following continuous steps:

***Step* I** Reactant molecules are diffused to the surface of the catalyst.

***Step* II** Reactant molecules are adsorbed at the surface of catalyst.

***Step* III** Chemical reaction is occurred at the surface of catalyst through the formation of intermediate.

***Step* IV** Products formed are desorbed making the surface available for new reaction.

Ⓒ SHAPE SELECTIVE CATALYSIS (ZEOLITES)

- The catalytic reaction depends upon the size of reactants, products and pore sizes of catalysts.
  e.g. Zeolites (microporous aluminosilicates in which some Si-atoms are replaced by Al-atoms). ZSM-5, a zeolite directly converts alcohol to gasoline.

Ⓓ ENZYME CATALYSIS

- Enzymes are biochemical catalysts and catalyse a specific chemical reaction in plants and animals.
- An enzyme is a protein molecule and form colloidal solution in water.
- Enzymes are highly efficient, highly specific, highly active under optimum temperature range (298-310 K), highly active under optimum pH (5-7).
- Enzyme activity is increased in presence of activators and co-enzymes and decreases in presence of inhibitors or poisons.
- Enzyme catalysis reaction proceeds through the formation of enzyme substrate complex according to lock and key mechanism, in which the substrate acts as the closed lock and enzyme acts as the key.

$$\underset{\text{Enzyme}}{E} + \underset{\text{Substrate}}{S} \rightleftharpoons \underset{\substack{\text{(Concept of its}\\ \text{existence was proposed by}\\ \text{Charles A. Wurtz in 1880)}}}{E-S \text{ complex}}$$

$$\rightleftharpoons E-P \text{ complex} \rightleftharpoons E + P$$

❷ ADSORPTION ISOTHERMS

At constant temperature, the variation of the amount of gas adsorbed by the solid absorbent with pressure, can be expressed by means of a curve. This curve is called **adsorption isotherm** at a particular temperature.

The two such types of curve are

Ⓐ FREUNDLICH ADSORPTION ISOTHERM

- It gives the variation of rate of adsorption with pressure.

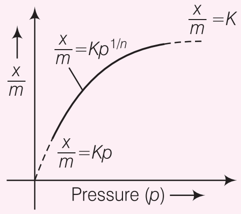
$$\frac{x}{m} = Kp^{\frac{1}{n}} \; (n > 1)$$

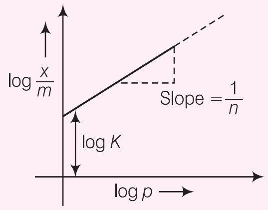
or

$$\log \frac{x}{m} = \log K + \frac{1}{n} \log p$$

where, x = amount of adsorbate,
m = amount of adsorbent,
p = pressure

K and n are constants which depend upon the nature of gas and adsorbent at a given temperature.





❹ COLLOIDS

- These are heterogeneous system in which insoluble microscopic particles are suspended and dispersed (dispersed phase) throughout another substance (dispersion medium).

LIMITATIONS

- This concept is purely empirical.
- It is not applicable at high pressure.
- It does not consider the role of surface area of adsorbent in the process of adsorption.
- It is applicable only for physical adsorption as it considers multimolecular layer of adsorption.
- It is unable to explain, constant adsorption at higher pressures.

Ⓑ LANGMUIR ADSORPTION ISOTHERM

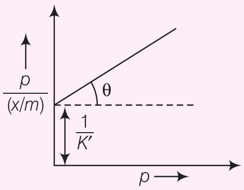
- Langmuir derived an adsorption isotherm on theoretical considerations based on kinetic theory of gases.
- According to Langmuir, the degree of adsorption is directly proportional to θ, i.e. the fraction of surface area covered.

$$\frac{x}{m} \propto \theta = K\theta; \ \frac{x}{m} = \frac{K'p}{1 + Kp}$$

where, K and K' are constants.

- It can also be written as

$$\frac{p}{x/m} = \frac{1}{K'} + \left(\frac{K}{K'}\right)p$$



SUCCESS

- It explains physisorption as well as chemisorption.
- It gives better results than Freundlich isotherm.

LIMITATION

It does not hold good at high pressures.

The size of colloids range from 10^{-9} to 10^{-6} m.

Ⓐ CLASSIFICATION OF COLLOIDS

Based on the nature of interaction between the dispersed phase and the dispersion medium.

ⓐ Lyophilic Colloids

- These are liquid loving colloids and are formed directly by mixing substances like gelatin, starch, etc.
- These are more stable and cannot be easily coagulated.

ⓑ Lyophobic Colloids

- These are liquid hating colloids and are usually formed by metals, metal sulphides, etc.
- These are prepared by special methods like chemical methods, Bredig's arc method, etc.
- These are also called irreversible sols because once they are precipitated, it is difficult to convert them back to colloidal solution.

Based on types of particles of dispersed phase

ⓐ **Multimolecular Colloids** A large number of atoms/molecules/ions aggregate together to form colloids, e.g. gold sol, sulphur sol.

ⓑ **Macromolecular Colloids**
Macromolecules like protein, starch, enzyme, etc., form colloidal solution.

ⓒ **Associated Colloids** (micelles) These colloids behave as strong electrolyte at low concentration but behave as colloids at high concentration due to association of particles called **micelles.**

Note Micelles are formed only at a particular temperature called **kraft temperature** (T_K) and concentration called **Critical Micelle Concentration** (CMC), e.g. cleansing action of soap.

Ⓑ PREPARATION OF COLLOIDS

ⓐ **Chemical methods** In these methods chemical reactions are carried out and products formed associated leading to the formation of colloidal solution.
e.g. $As_2O + 3H_2S \longrightarrow As_2S_3(sol) + 3H_2O$

ⓑ **Bredig's arc method** Colloidal solution of metals like Au, Ag, Pt etc., are prepared by this method. Metal electrodes are dipped in dispersion medium and high voltage is provided. Metal atoms are vaporised due to intense heat, which are then condensed to form colloidal solution.

ⓒ **Peptisation** Precipitates are converted back to colloidal solution by shaking it in dispersion medium with the help of a small amount of electrolyte.

Note **Gold number** It is defined as the minimum weight of protective colloid in milligrams which must be added to 10 mL of a substance (red gold sol) so that no coagulation of the gold sol takes place when 1 mL of 10% sodium chloride solution is rapidly added to it.

Ⓒ PROPERTIES OF COLLOIDAL SOLUTION

ⓐ **Tyndall Effect** Colloidal solutions show Tyndall effect due to scattering of light by colloidal particles in all directions in space.

- Tyndall effect is observed only under the following conditions
  (i) The diameter of the colloids should not be much smaller than the wavelength of light used.
  (ii) The refractive indices of the dispersed phase and the dispersion medium should differ greatly in magnitude.

ⓑ **Colour** The colour of colloidal solution depends on wavelength of light scattered by dispersed particles, size and nature of colloidal particles and direction of observation.

ⓒ **Brownian Movement** Colloidal particles show a continuous *zig-zag* motion which is independent of nature of particles but small sized particles show faster movement.

ⓓ **Charge on Colloidal Particles** Each colloidal particle of a solution are either positively or negatively charged, the reason for this charge is best explained by preferential adsorption of ions from solution.

- **Positively Charged Sols** Sols of haemoglobin, hydrated metallic oxides like $Al_2O_3 . xH_2O$, $CrO_3 \cdot xH_2O$, $Fe_2O_3 \cdot xH_2O$ etc., basic dye like methylene blue, oxides like TiO_2 etc.
- **Negatively Charged Sols** Sols of starch gum, gelatin, clay, charcoal, acid dyes like eosin, congo red sols etc. Metals like Cu, Ag, Au etc., metallic sulphides like As_2S_3, Sb_2S_3, CdS etc.

❺ CLEANSING ACTION OF SOAP

- The hydrophobic part (hydrocarbon) of soap is attached to dirt particles while the hydrophilic part is projected towards water forming micelles.
- The micelle alongwith dirt particle is pulled away towards water due to emulsification and washed away.

ⓐ **Theory of Preferential Adsorption of Ions** When two or more ions are present in the dispersion medium, the colloidal particles prefer to adsorb the ion common among them. e.g.

$$\underset{\text{(Positively charged)}}{FeCl_3 + H_2O \text{ (hot)} \longrightarrow Fe_2O_3 \cdot xH_2O / \ Fe^{3+}}$$

$$\underset{\text{(Negatively charged)}}{FeCl_3 + NaOH \longrightarrow Fe_2O_3 \cdot xH_2O / OH^-}$$

ⓑ **Helmholtz Electrical Double Layer** The charged colloidal particles layer after preferential adsorption, further attracts oppositely charged ions from dispersion medium forming a second layer called Helmholtz electrical double layer. e.g.

$$\underset{\text{(Layer - 1, fixed layer)}}{[AgI]\,I^-} \quad \underset{\text{(Layer - 2, diffused layer)}}{K^+}$$

- The potential difference between the fixed layer and diffused layer is called electrokinetic potential or zeta potential.

❻ COAGULATION (PRECIPITATION) OF COLLOIDAL PARTICLES

Ⓐ COAGULATION OF LYOPHOBIC SOLS

- These are coagulated by electrophoresis, mixing two oppositively charged sols, boiling or persistent dialysis etc.
- A positively charged ion causes the precipitation of a negatively charged sol and *vice-versa*.
- **Hardy-Schulze Rule** According to this rule, higher the charge on the flocculating ion added for coagulation, higher is the coagulating power of the ion.
- For the coagulation of a positively charged sol, the coagulation power of different negatively charged ions is $[Fe(CN)_6]^{4-} > PO_4^{3-} > SO_4^{2-} > NO_3^-$.
- For the coagulation of a negatively charged sol, the coagulation power of different positively charged ion is $Al^{3+} > Ba^{2+} > Na^+$.

Ⓑ COAGULATION OF LYOPHILIC SOLS

- These sols having high solvation energy and charge are more stable than lyophobic sols.
- These are coagulated by adding an electrolyte and a suitable solvent like alcohol, acetone etc.

❼ EMULSIONS (LIQUID-LIQUID COLLOIDAL SYSTEM)

When two immiscible or partially miscible liquids are mixed and shaken together, one liquid is dispersed over another forming a colloidal system called **emulsions**.

Ⓐ TYPES OF EMULSION

These are of two types

ⓐ **Oil Dispersed in Water** (O/W) **Type** In this type, water acts as a dispersion medium, e.g. milk.

ⓑ **Water Dispersed in Oil** (W/O) **Type** In this type, oil acts as a dispersion medium, e.g. butter, cream, etc.

Ⓑ EMULSIFYING AGENTS

- Oil in water type of emulsion is unstable due to their lyophobic nature and hence required an emulsifying agent for their stabilisation.
- e.g. proteins, gums, long chain alcohols, heavy metal salts, fatty acids, soaps, etc.

❽ APPLICATIONS OF COLLOIDS

Colloids have many important applications such as

- Electrical precipitation of pollutants present in smoke.
- Purification of drinking water by coagulating suspended particles.
- Colloidal medicines are more effective due to the large surface area of colloids in dispersion medium.
- Cleansing action of soaps and detergents due to micelle formation.
- Photographic film is an emulsion of light sensitive AgBr in gelatin.

Rapid CONCEPT REVISION

TARGET 2017

HALOALKANES AND HALOARENES

Organic compounds formed by the replacement of one or more hydrogen atoms from aliphatic and aromatic hydrocarbons by an equal number of halogen atoms are called **haloalkanes** (aliphatic halogen derivatives) and **haloarenes** (aromatic halogen derivatives), respectively.

Monohalogen Derivatives

Methods of Preparation

Monohalogen derivatives are prepared by the following methods:

S. No.	Methods	Reactions involved
1.	Halogenation of alkanes	$RH + X_2 \xrightarrow[\text{sunlight or } 400°\text{C}]{h\nu \text{ or}} RX + HX$ [where, X = Cl, Br, I]
2.	Addition of halogen acids to alkenes	$RCH{=}CH_2 + HBr \longrightarrow RCHBrCH_3$
3.	Substitution of —OH group of alcohol by (i) PX_3 (ii) PX_5 (iii) conc. HCl + anhy · $ZnCl_2$ (iv) HX (v) $SOCl_2$	$3ROH + PX_3 \longrightarrow 3RX + H_3PO_3$ $ROH + PX_5 \longrightarrow RX + POX_3 + HX$ $ROH + \text{dry } HCl \xrightarrow{\text{Anh. } ZnCl_2} RCl + H_2O$ $ROH + HX \longrightarrow RX + H_2O$ $ROH + SOCl_2 \xrightarrow{\text{Pyridine}} RCl + HCl + SO_2$
4.	Borodine-Hunsdiecker reaction	$CH_3COOAg + Br_2 \xrightarrow{CCl_4} CH_3Br + AgBr + CO_2$
5.	Finkelstein reaction	Alkyl chloride or bromide $\xrightarrow{\text{NaI/acetone}}$ Alkyl iodide + Na chloride or bromide
6.	Swarts reaction	Alkyl chloride or bromide $\xrightarrow[\text{like } Hg_2F_2]{\text{Inorganic fluorides}}$ Alkyl fluoride + Hg chloride or bromide $2CH_3Cl + Hg_2F_2 \longrightarrow 2CH_3F + Hg_2Cl_2$ $CH_3Br + AgF \longrightarrow CH_3F + AgBr$

Note All of the above methods give chlorides and bromides in good yield but fluorides or iodides in poor yield. The reactivity of alcohol towards HX is allyl, benzyl, > 3° > 2° > 1° and the reactivity of halogen acids is HI > HBr > HCl > HF.

Physical Properties

(i) CH_3Cl, CH_3Br, CH_3F and C_2H_5Cl are gases at room temperature, rest of alkyl halides upto C_{18} are colourless liquids and beyond it, these are colourless solids.

(ii) Haloalkanes have polar nature but insoluble in polar solvents like water while soluble in organic solvents like ether, benzene, etc.

(iii) Fluoro and chloro compounds are lighter whereas bromo and iodo derivatives are heavier than water.

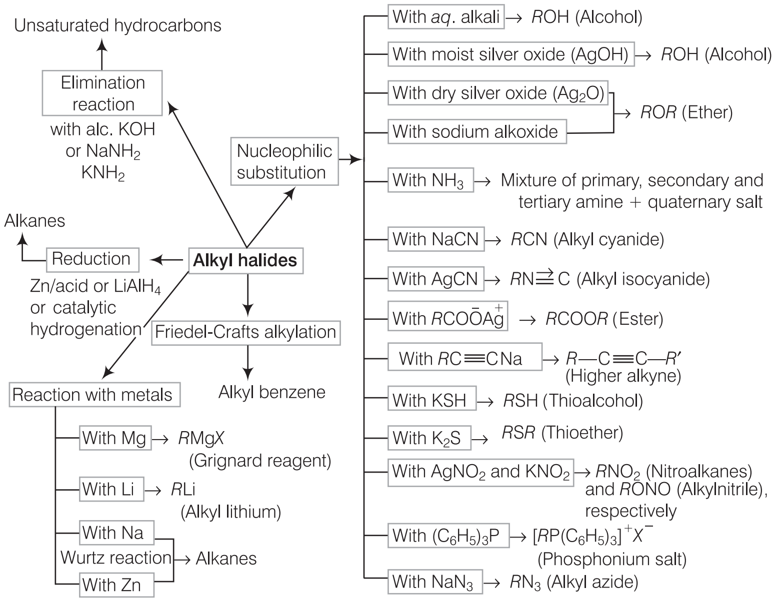
(iv) The density of alkyl halides decreases as the size of alkyl group increases.

(v) Boiling point of alkyl halides are higher than the corresponding hydrocarbons.

$$\text{Boiling point} \propto \text{number of} -CH_2- \text{groups} \propto \frac{1}{\text{Branching}}$$

Chemical Properties

Alkyl halides shows the following chemical properties:



REMEMBER

- Alkyl halides react with NaCN to give alkyl cyanide ($R-C\equiv N$), whereas it reacts with AgCN to give alkyl isocyanide ($R-N\overset{\rightarrow}{=}C$). This is due to the electrovalent nature of NaCN and covalent nature of AgCN.
- The order of reactivity of different alkyl halides towards Grignard reagent is $RI > RBr > RCl$.

Substitution Reaction in Alkyl Halides

- Due to the presence of electron withdrawing group, the alkyl group acquires partial positive charge. Hence, it undergoes nucleophilic substitution reaction giving different products with different reagents.
- The nucleophilic substitution reaction either follows unimolecular mechanism (S_N1) or bimolecular mechanism (S_N2) depending upon the nature of alkyl group, solvent, leaving group, etc.

Differences Between S_N2 and S_N1 Reactions

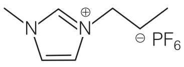
S_N2	S_N1
One step mechanism and follows second order kinetics. Rate = $k[RX][Nu]$	Two step mechanism and follows first order kinetics. Rate = $k[RX]$
Chiral centre undergo inversion of configuration.	Chiral centre undergo racemisation forming a racemic mixture.
Reactivity of alkyl halides is $CH_3X > RCH_2X > R_2CHX >> R_3CX$	Reactivity of alkyl halides is $R_3CX > R_2CHX >> RCH_2X > CH_3X$
No rearrangement of carbocation occurs.	Rearrangement of carbocation occurs forming the most stable product.
Favoured by polar aprotic solvents.	Favoured by polar protic solvents.
Stronger nucleophile favours this mechanism and the order of reactivity of alkyl halides is $RI > RBr > RCl > RF$	Any type of nucleophile favours this mechanism and the order of reactivity of alkyl halides is $RI > RBr > RCl > RF$

Designer Solvents

Volatile organic compounds like dichloromethane are used as an organic solvent during chemical reaction. However, due to their role in the depletion of ozone layer, they have been replaced by ionic liquids.

Ionic liquids are salts that are liquids at room temperature and their use offers several advantages over traditional organic solvents. e.g. ionic liquids are non-volatile and so do not escape into the atmosphere; they dissolve a wide range of polar organic compounds; they are stable to heating to relatively high temperature and are non-flammable. Ionic liquids are also called designer solvents because different combinations of cations and anions produce ionic liquids with different physical and chemical properties.

An important class of ionic liquids are bmim which contain a 1-butyl-3-methylimidiazolium cation and an anion such as PF_6^-.

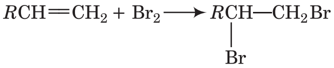
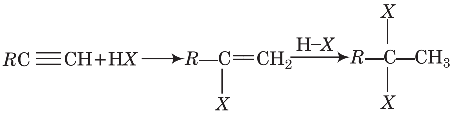
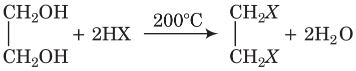
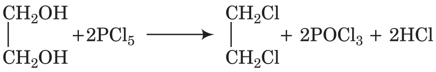


[bmim] $[PF_6]$

Dihalogen Derivatives

Methods of Preparation

These are prepared by the following methods:

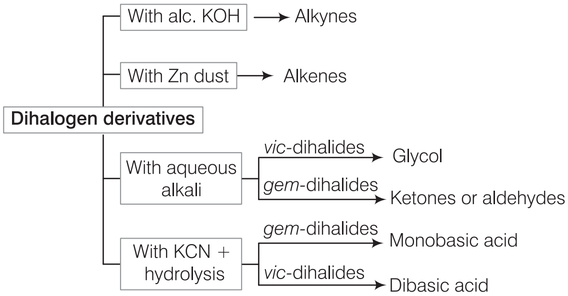
Methods	Reactions involved
1. **Addition reactions** (i) Br_2 to alkenes	 $RCH{=}CH_2 + Br_2 \longrightarrow R\underset{\underset{Br}{\vert}}{CH}-CH_2Br$ *vic*-dihalide
(ii) Halogen acids to alkynes	 $RC\equiv CH + HX \longrightarrow R-\underset{\underset{X}{\vert}}{C}{=}CH_2 \xrightarrow{H-X} R-\overset{\overset{X}{\vert}}{\underset{\underset{X}{\vert}}{C}}-CH_3$ *gem*-dihalide
2. **Substitution reactions** (i) With HX	 $\begin{array}{l}CH_2OH\\ \vert\\ CH_2OH\end{array} + 2HX \xrightarrow{200^\circ C} \begin{array}{l}CH_2X\\ \vert\\ CH_2X\end{array} + 2H_2O$
(ii) With PCl_5	 $\begin{array}{l}CH_2OH\\ \vert\\ CH_2OH\end{array} + 2PCl_5 \longrightarrow \begin{array}{l}CH_2Cl\\ \vert\\ CH_2Cl\end{array} + 2POCl_3 + 2HCl$

Physical Properties

These are colourless, volatile and mildly sweet smelling liquids.

Chemical Properties

Dihalogen derivatives shows the following chemical properties.



Reactions Used to Distinguish Between *vicinal* and *geminal* Dihalides

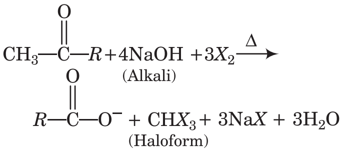
- *gem*-dihalides that give aldehyde on hydrolysis, would be terminal dihalides.
- *gem*-dihalides that give ketone on hydrolysis would be non-terminal dihalides.
- When any dihalide on reaction with KCN, followed by hydrolysis yields an anhydride, it will be a *vic*-dihalide.
- When any dihalide on reaction with KCN, followed by hydrolysis and heat gives a monobasic acid, it will be *gem*-dihalide.

Trihalogen Derivatives

These compounds are commonly called haloform (chloroform, iodoform, etc.).

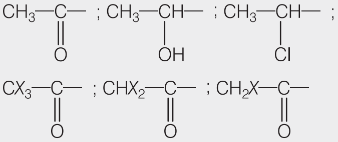
Methods of Preparation

These are prepared by the following methods:

S.No.	Methods	Reactions involved
1.	Haloform reaction	 $CH_3-\overset{\overset{O}{\Vert}}{C}-R + \underset{(Alkali)}{4NaOH} + 3X_2 \xrightarrow{\Delta} R-\overset{\overset{O}{\Vert}}{C}-O^- + \underset{(Haloform)}{CHX_3} + 3NaX + 3H_2O$
2.	Reaction of bleaching powder with ethyl alcohol or acetone	$CaOCl_2 + H_2O \longrightarrow Ca(OH)_2 + Cl_2$ $CH_3COCH_3 + 3Cl_2 \longrightarrow CCl_3COCH_3 + 3HCl$ $CCl_3COCH_3 + Ca(OH)_2 \xrightarrow{Hydrolysis} \underset{Chloroform}{2CHCl_3} + (CH_3COO)_2Ca$
3.	Halogenation of alkanes	$CH_4 + Cl_2 \xrightarrow{h\nu} CH_3Cl \xrightarrow{Cl_2/h\nu} CH_2Cl_2 \xrightarrow[h\nu]{Cl_2} \underset{(Chloroform)}{CHCl_3}$
4.	Reaction of ethanol or acetone with aq. Na_2CO_3 and KI	$CH_3CH_2OH + 4I_2 + 3Na_2CO_3 \longrightarrow CHI_3 + HCO\bar{O}Na^+ + 5NaI + 2H_2O + 3CO_2$

Haloform Reaction

- Compounds containing any one of the following groups give haloform reaction.

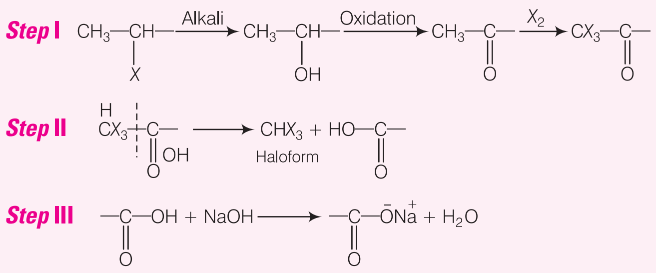


$$CH_3-\underset{\underset{O}{\Vert}}{C}- \;;\; CH_3-\underset{\underset{OH}{|}}{CH}- \;;\; CH_3-\underset{\underset{Cl}{|}}{CH}- \;;$$

$$CX_3-\underset{\underset{O}{\Vert}}{C}- \;;\; CHX_2-\underset{\underset{O}{\Vert}}{C}- \;;\; CH_2X-\underset{\underset{O}{\Vert}}{C}-$$

- Although, $CH_3-\underset{\underset{O}{\Vert}}{C}-CH_2-\underset{\underset{O}{\Vert}}{C}-OC_2H_5$ contain CH_3CO- group, but it doesn't give haloform reaction. This is due to the presence of active methylene ($-CH_2-$) group which prevents the conversion of $CH_3-\underset{\underset{O}{\Vert}}{C}-$ to, $CX_3-\underset{\underset{O}{\Vert}}{C}-$ which is the most necessary condition for an organic compound to give haloform reaction.

Mechanism of Haloform Reaction



Physical Properties

(i) $CHCl_3$ and $CHBr_3$ are sickly smelling liquid, whereas CHI_3 is a yellow coloured solid that forms hexagonal plates.

(ii) Their boiling point increases with increases in molecular weight.

(iii) $CHCl_3$ and $CHBr_3$ are sparingly soluble in water but more soluble in organic solvents, CHI_3 is insoluble in H_2O but soluble in ether and ethanol.

Chemical Properties

- Due to the presence of 3 halogen atoms, these are highly polar organic compound and hence, C—H bond can be easily broken in the presence of any base producing dihalocarbenes. e.g.

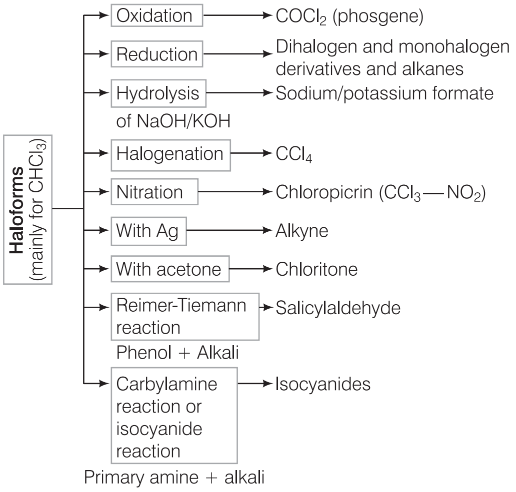
$$CHCl_3 + \bar{O}H \rightleftharpoons :\bar{C}Cl_3 + H_2O$$

$$:\bar{C}Cl_3 \longrightarrow \underset{\text{Dichlorocarbene}}{:CCl_2} + Cl^-$$

- Dichlorocarbene acts as a very good nucleophile.
- The reactivity order of different haloforms is

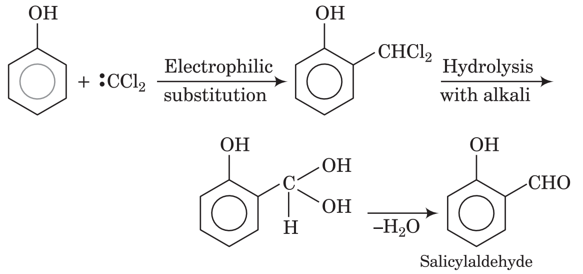
$$CHI_3 > CHBr_3 > CHCl_3 > CHF_3$$

- Haloforms shows the following chemical properties:



Reimer-Tiemann Reaction

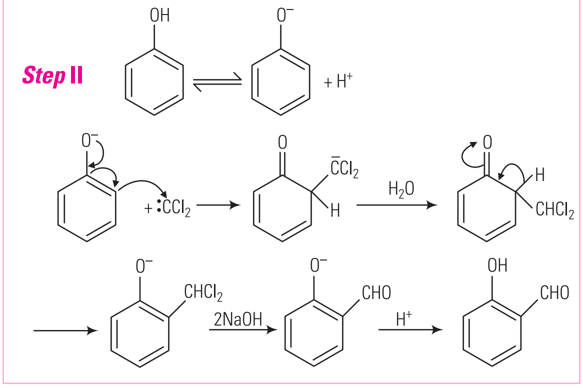
Dichlorocarbene ($:CCl_2$) is the attacking electrophile in this reaction which attacks itself to benzene ring through electrophilic substitution.



Mechanism of Reimer Tiemann Reaction

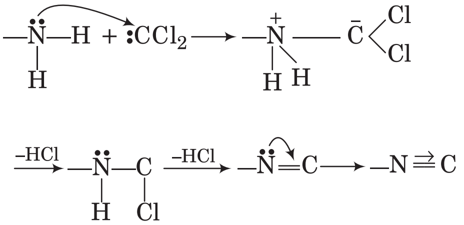
Step I $CHCl_3 + \bar{O}H \rightleftharpoons :\bar{C}Cl_3 + H_2O$

$$:\bar{C}Cl_3 \longrightarrow :CCl_2 + Cl^-$$



Carbylamine Reaction

The attacking reagent in this reaction is also $:CCl_2$ which attacks by the lone pair of nitrogen of amino group as:



The complete reaction is as follows :

$$CHCl_3 + 3KOH + RNH_2 \xrightarrow{\Delta} \underset{\substack{\text{Isocyanide or}\\ \text{carbylamine}}}{RNC} + 3KCl + 3H_2O$$

Chloroform and its Effect

Chloroform is so sensitive to oxygen that it auto-oxidises in the presence of sunlight with air only and result in the formation of phosgene (carbonyl chloride) gas.

The reaction looks like

$$CHCl_3 + \frac{1}{2}O_2 \longrightarrow COCl_2 + HCl$$

The phosgene gas formed is extremely poisonous.

To retard this oxidation, we use 1% C_2H_5OH which converts poisonous phosgene to non-poisonous ethyl carbonate.

$$COCl_2 + 2C_2H_5OH \longrightarrow \underset{\text{Ethyl carbonate}}{(C_2H_5O)_2CO} + 2HCl$$

Effects noticed in humans exposed to chloroform *via* anaesthesia include change in respiratory rate, cardiac effects, gastro intenstinal effects such as nausea, vomiting and effects on the liver and kidney. Chloroform is not currently used as a surgical anaesthetic.

Polyhalogen Derivatives

Carbon Tetrachloride (CCl_4)

CCl_4 is a colourless, non-inflammable and poisonous liquid with a characteristic odour.

Methods of Preparation

It is prepared by the chlorination of methane, chloroform, carbondisulphide or propane under different reaction conditions.

$$CH_4 + \underset{\text{(Excess)}}{4Cl_2} \xrightarrow{400^\circ C} CCl_4 + 4HCl$$

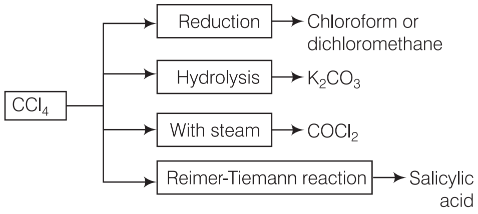
$$CHCl_3 + Cl_2 \xrightarrow{h\nu} CCl_4 + HCl$$

$$CS_2 + 3Cl_2 \xrightarrow[SbCl_3]{AlCl_3 \text{ or}} CCl_4 + \underset{\text{Sulphur monochloride}}{S_2Cl_2}$$

$$C_3H_8 + 9Cl_2 \xrightarrow[\text{pressure}]{\Delta} CCl_4 + \underset{\text{Hexachloro ethane}}{C_2Cl_6} + 8HCl$$

Chemical Properties

CCl_4 undergo the following chemical reactions:



Note CCl_4 also shows Reimer-Tiemann reaction in which phenol is converted into salicylic acid and follows the same mechanism as in case of chloroform.

The Environmental Impact of Freons

Freons are chlorofluorocarbon (CFC), a polyhalogen derivative and produced as a volatile derivatives of methane and ethane.

At room temperature, the chlorofluorocarbons are either gases or low boiling point liquids. They are essentially insoluble in water and inert towards most other substances. These properties make them ideal propellants in aerosol cans but, unfortunately, their inertness allows these compounds to persist in the environment.

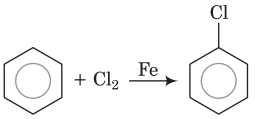
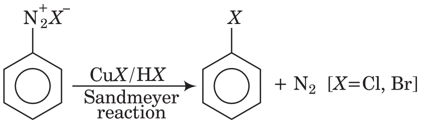
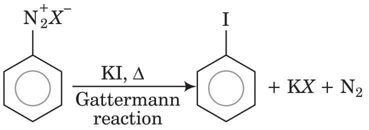
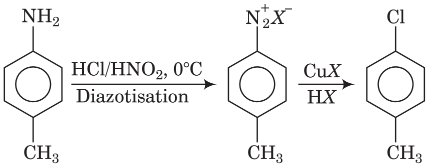
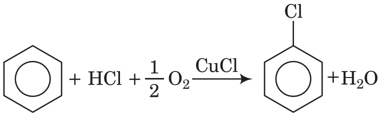
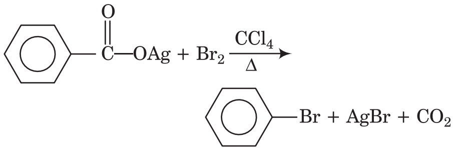
When released into the air, CFCs escape to the lower atmosphere, slowly they find their way to the stratosphere, where they absorb ultraviolet radiation from the sun and then decompose. As they do so, they set up a chemical reaction that leads to the destruction of the stratospheric ozone layer, which shields earth against short wavelength ultraviolet radiation from the sun. An increase in short-wavelength ultraviolet radiation promotes the destruction of certain crops and even to increase the incidence of skin cancer in light skinned individuals.

Haloarenes

These are compounds having halogen atom directly attached to the aromatic ring.

Methods of Preparation

They can be prepared through the following reactions:

S. No.	Methods	Reaction involved
1.	Halogenation of benzene and homologues	
2.	Decomposition of diazonium salts	 
3.	From aromatic amino and nitro compounds	
4.	Raschig process	
5.	Borodine Hunsdiecker reaction	

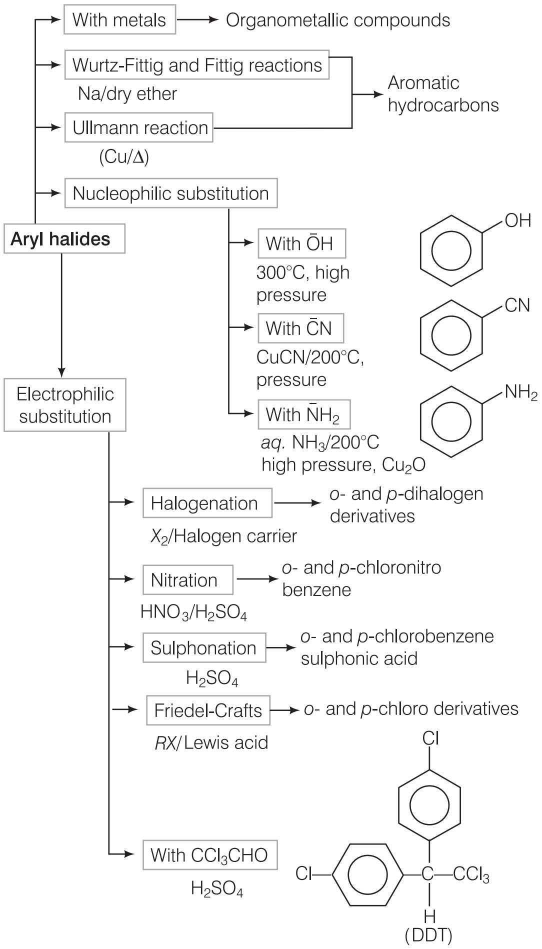
Physical Properties

Aryl halides or haloarenes are heavier than water, though polar but immiscible with water (due to incapability of forming H-bonds).

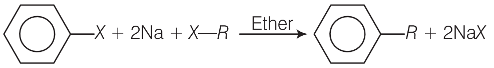
Chemical Properties

The C—*X* bond in haloarenes have double bond character due to conjugation between lone pair of halogen and benzene ring. Due to the presence of such double bond character, haloarenes show nucleophilic substitution with difficulty.

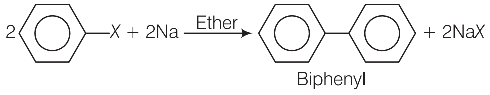
Aryl halides give the following reactions:



Wurtz-Fittig reaction



Fittig reaction



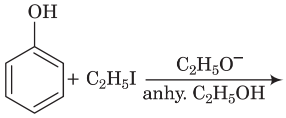
MASTER STROKES

1. Identify the correct statement about alkyl halide.
(*a*) These are associated with each other by H-bonds
(*b*) These dissolve in water quickly
(*c*) These dissolve easily in organic solvent
(*d*) These do not contain any polar bonds in their molecules

2. Which of the following statement is incorrect with respect to S_N1 and S_N2 mechanism for alkyl halide?
(*a*) A strong nucleophile is an aprotic solvent increases the rate or favours S_N2 reaction
(*b*) Competing reaction for S_N2 is rearrangement
(*c*) S_N1 reactions can be catalysed by some Lewis acids
(*d*) A weak nucleophile and aprotic solvent increases the rate of S_N1 reaction

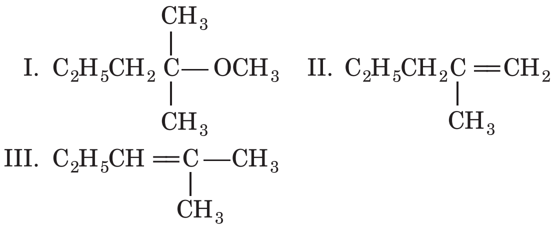
3. A *geminal* dichloride is formed in all of the following reactions except
(*a*) CH_3CHO and PCl_5 (*b*) CH_3COCH_3 and PCl_5
(*c*) $CH_2=CH_2$ and Cl_2 (*d*) $CH_2=CHCl$ and HCl

4. The product of following reaction is



(*a*) $C_6H_5OC_2H_5$ (*b*) $C_2H_5OC_2H_5$
(*c*) $C_6H_5OC_6H_5$ (*d*) C_6H_5I

5. 2-chloro-2-methylpentane on reaction with sodium methoxide in methanol yields



$$\text{I. } C_2H_5CH_2\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}—OCH_3 \quad \text{II. } C_2H_5CH_2\underset{\displaystyle CH_3}{C}=CH_2$$

$$\text{III. } C_2H_5CH=\underset{\displaystyle CH_3}{C}—CH_3$$

(*a*) I and II (*b*) Only III
(*c*) I and II (*d*) All of these

6. In order to get ethanethiol from bromoethane, the reagent used is
(*a*) sodium bisulphide (*b*) sodium sulphide
(*c*) potassium thiocyanate (*d*) potassium sulphide

7. An S_N2 reaction at an asymmetric carbon of a compound always gives
(*a*) an enantiomer of the substrate
(*b*) a product with opposite optical rotation
(*c*) a mixture of diastereomers
(*d*) a single stereoisomer

8. The reaction condition leading to the best yield of C_2H_5Cl is
(*a*) $C_2H_6(\text{excess}) + Cl_2 \xrightarrow{\text{UV light}}$ (*b*) $C_2H_6 + Cl_2(\text{excess}) \xrightarrow[\text{room temp.}]{\text{dark}}$
(*c*) $C_2H_6 + Cl_2(\text{excess}) \xrightarrow{\text{UV light}}$ (*d*) $C_2H_6 + Cl_2 \xrightarrow{\text{UV light}}$

RAPID CONCEPT REVISION

9. The synthesis of alkyl fluorides is best accomplished by [JEE Main 2015]
(*a*) free radical fluorination (*b*) Sandmeyer's reaction
(*c*) Finkelstein reaction (*d*) Swarts reaction

10. A mixture of 1-chloropropane and 2-chloropropane when treated with alcoholic KOH, gives
(*a*) *iso*-propylene
(*b*) 2-propene
(*c*) 1-propene
(*d*) a mixture of 1-propene and 2-propene

11. The bad smelling substance formed by the reaction of chloroform with methylamine and alcoholic KOH will be
(*a*) methylamine (*b*) methyl alcohol
(*c*) methyl cyanide (*d*) methyl isocyanide

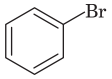
12. Identify *A* and *B* (both are different reagents) in the following reaction

$$C_2H_5Cl \xrightarrow{A} C_2H_5OH \xleftarrow{B} C_2H_5Cl$$

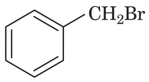
(*a*) A = aqueous KOH; B = AgOH
(*b*) A = alcoholic KOH/Δ; B = aqueous NaOH
(*c*) A = aqueous NaOH; B = $AgNO_2$
(*d*) A = $AgNO_2$; B = KNO_2

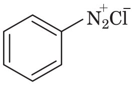
13. $X \xrightarrow[HNO_3]{AgNO_3}$ yellow or white ppt.

Which of the following cannot be X?

(*a*)


(*b*) $(CH_3)_2CHCl$

(*c*)


(*d*)


14. Tertiary alkyl halides are practically inert to substitution by S_N2 mechanism because of
(*a*) steric hindrance (*b*) inductive effect
(*c*) instability (*d*) insolubility

15. Select the reagent that will yield the greater amount of substitution on reaction with 1-bromobutane.
(*a*) $CH_3CH_2\overset{-}{O}\overset{+}{K}$ in dimethyl sulphoxide (DMSO)
(*b*) $(CH_3)C\overset{-}{O}\overset{+}{K}$ in dimethyl sulphoxide (DMSO)
(*c*) Both (a) and (b) will give comparable amount of substitution
(*d*) Neither (a) nor (b) will give any appreciate amount of substitution

16. When chlorine reacts with ethyl alcohol, it forms
(*a*) chloroform (*b*) chloral
(*c*) ethyl chloride (*d*) carbon tetrachloride

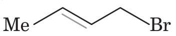
17. Which of the following alkyl halides can produce only a single alkene product when treated with sodium methoxide?
(*a*) 2-chloro-2-methyl pentane (*b*) 3-chloro-3-ethyl pentane
(*c*) 3-chloro-2-methyl pentane (*d*) 2-chloro-4-methyl pentane

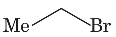
18. In the reaction, $R—X \xrightarrow{\text{alc. KCN}} A \xrightarrow{\text{dil. HCl}} B$, the product B is
(*a*) alkyl chloride (*b*) aldehyde
(*c*) carboxylic acid (*d*) ketone

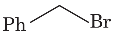
19. When *neo*-pentyl bromide is subjected to Wurtz reaction, the product formed is
(*a*) 2, 2, 4, 4-tetramethylhexane
(*b*) 2, 2, 4, 4-tetramethylpentane
(*c*) 2, 2, 5, 5-tetramethylhexane
(*d*) 2, 2, 3, 3-tetramethylhexane

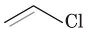
20. A solution of (+)-1-chloro-phenylethane in toluene racemises slowly in the presence of a small amount of $SbCl_5$ due to the formation of
(*a*) carbanion (*b*) carbene (*c*) free radical (*d*) carbocation

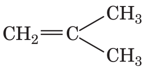
21. Which one of the following compounds gives S_N1 and S_N2 mechanisms?

(*a*)


(*b*)


(*c*)


(*d*)


22. The treatment of tertiary butyl chloride with 80% aqueous ethanol at 140°C gives
(*a*) $(CH_3)_3C—OH$ (*b*) $(CH_3)_3C—OCH_2CH_3$
(*c*)


$CH_2{=}C(CH_3)_2$

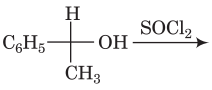
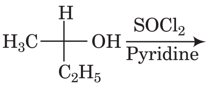
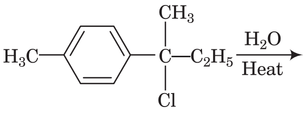
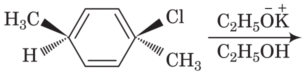
(*d*) All of these

23. The Friedel-Crafts reaction of *n*-propylbromide with benzene in the presence of anhydrous $AlCl_3$ gives
(*a*) *n*-propyl benzene (*b*) isopropyl benzene
(*c*) 1, 4-dipropyl benzene (*d*) 1, 2-dipropyl benzene

24. The ease of dehydrohalogenation with alcoholic KOH in case of chloroethane (I), 2-chloropropane (II) and 2-chloro-2-methylpropane (III) is of the order
(*a*) III > II > I (*b*) I > II > III (*c*) II > I > III (*d*) I > III > II

25. Which of the following statements are correct?
(*a*) The addition of HBr to propene gives 2-bromopropane
(*b*) The addition of HBr to propene gives 1-bromopropane
(*c*) The addition of HCl to vinyl chloride gives 1, 2-dichloroethane
(*d*) The addition of HCl to vinyl chloride gives ethylene chloride

26. Match the reactions from Column I and their corresponding properties from Column II and mark the correct option from codes given below.

Column I	**Column II**
i. 	p. Complete retention of configuration
ii. 	q. Racemic mixture is formed
iii. 	r. S_N2
iv. 	s. S_N1

Codes

	i	ii	iii	iv		i	ii	iii	iv
(a)	p,s	r	q	q	*(b)*	p	q	r	s
(c)	s	q	p	r	*(d)*	r	s	p	q

27. An organic compound which produces a bluish green coloured flame on heating in the presence of copper is

(a) chlorobenzene *(b)* benzaldehyde
(c) aniline *(d)* benzoic acid

28. The raw materials for the commercial manufacture of DDT are

(a) chlorobenzene and chloroform
(b) chlorobenzene and chloromethane
(c) chlorobenzene and chloral
(d) chlorobenzene and iodoform

29. Chlorobenzene reacts with Mg in dry ether to give a compound *A*, which further reacts with ethanol to give

(a) phenol *(b)* benzene
(c) ethylbenzene *(d)* phenyl ether

30. Chlorobenzene gives aniline with

(a) NH_3 / Cu_2O *(b)* NH_3 / H_2SO_4
(c) $NaNH_2$ *(d)* None of these

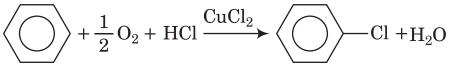
31. Chloropicrin is obtained by the reaction of

(a) steam on carbon tetrachloride
(b) nitric acid on chlorobenzene
(c) chlorine on picric acid
(d) nitric acid on chloroform

32. Chlorobenzene on heating with NH_3 under pressure in the presence of cuprous chloride gives

(a) aniline
(b) benzamide
(c) nitrobenzene
(d) *o*- and *p*-chloroamine benzene

33. Conversion of



is an example of which of the following reaction?

(a) Nucleophilic substitution *(b)* Electrophilic substitution
(c) Free radical addition *(d)* Free radical substitution

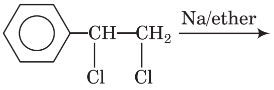
34. The reaction of toluene with Cl_2 in the presence of $FeCl_3$ gives *X* and reaction in the presence of light gives *Y*. Thus, *X* and *Y* are

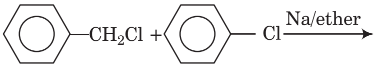
(a) *X* = benzyl chloride, *Y* = *m*-chlorotoluene
(b) *X* = benzyl chloride, *Y* = *o*-chlorotoluene
(c) *X* = *m*-chlorotoluene, *Y* = *p*-chlorotoluene
(d) *X* = *o*- and *p*-chlorotoluene, *Y* = trichloromethyl benzene

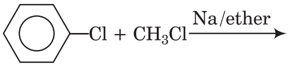
35. Which one of the following statements about benzyl chloride is incorrect?

(a) It is less reactive than alkyl halides
(b) It can be oxidised to benzaldehyde by boiling with copper nitrite solution
(c) It is lachrymatory liquid and gives Beilstein's test
(d) It gives a white precipitate with alcoholic silver nitrite

36. Which of the following is not the Wurtz-fittig reaction?

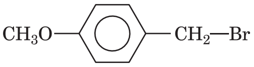
(a)


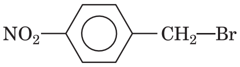
(b)


(c)


(d) None of the above

37. Which one of the following compounds undergoes predominantly S_N2 reaction with aqueous NaOH in polar aprotic solvents?

(a)


(b)


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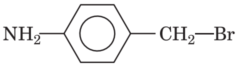

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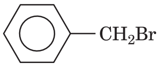
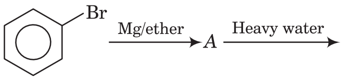
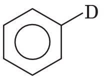
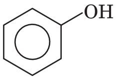


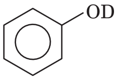
38. Identify the final product obtained in the following reaction.



(a)


(b)


(c)


(d)


39. In the reaction of *p*-chlorotoluene with KNH_2 in liquid NH_3, the major product is

(a) *o*-toluidine *(b)* *m*-toluidine
(c) *p*-toluidine *(d)* *p*-chloroaniline

40. Moth repellent is

(a) perchlorobenzene
(b) *p*-dichlorobenzene
(c) Both (a) and (b)
(d) None of the above

Answers

1. (c)	**2.** (b)	**3.** (c)	**4.** (a)	**5.** (d)
6. (a)	**7.** (d)	**8.** (a)	**9.** (d)	**10.** (c)
11. (d)	**12.** (a)	**13.** (a)	**14.** (a)	**15.** (a)
16. (b)	**17.** (b)	**18.** (c)	**19.** (c)	**20.** (d)
21. (a)	**22.** (b)	**23.** (b)	**24.** (a)	**25.** (a)
26. (a)	**27.** (a)	**28.** (c)	**29.** (d)	**30.** (a)
31. (d)	**32.** (a)	**33.** (b)	**34.** (d)	**35.** (a)
36. (a)	**37.** (b)	**38.** (b)	**39.** (b)	**40.** (c)

ALCOHOLS, PHENOLS AND ETHERS

Alcohols

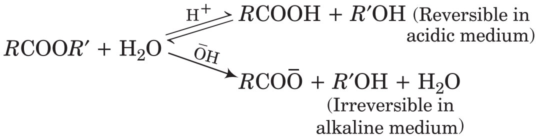
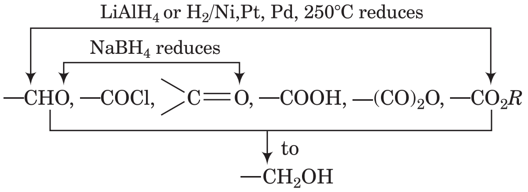
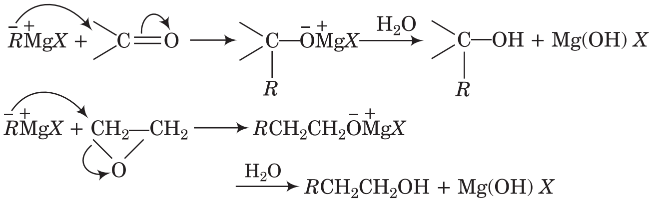
These are hydroxy derivatives of aliphatic hydrocarbons and can be monohydric, dihydric or polyhydric based on the number of —OH groups.

Monohydric Alcohols

These are monohydroxy derivatives of hydrocarbons with general formula, $C_nH_{2n+2}O$ or $C_nH_{2n+1}OH$.

Methods of Preparation

These are prepared through the following methods:

Methods	Reactions involved
1. Hydrolysis of alkyl halides	$RX + aq\cdot KOH \longrightarrow ROH + KX$
2. Hydration of alkenes	$(CH_3)_2C{=}CH_2 + H_2O \longrightarrow (CH_3)_3C{-}OH$
3. Hydrolysis of esters	
4. Hydrolysis of ethers	$ROR \xrightarrow[\text{Under pressure}]{\text{Dil.}H_2SO_4/\Delta} 2ROH$
5. From alkynes	$HC{\equiv}CH \xrightarrow[Hg^{2+},\ H^+]{H_2O} CH_3CHO \xrightarrow{LiAlH_4} CH_3CH_2OH$
6. Oxymercuration-demercuration	$(CH_3)_2C{=}CH_2 \xrightarrow[\text{(ii) }NaBH_4]{\text{(i) }Hg(OAc)_2/H_2O} (CH_3)_3C{-}OH$
7. Hydroboration oxidation	$3R{-}CH{=}CH_2 + BH_3 \xrightarrow[\text{DIGLYME}]{\text{THF or}} (RCH_2CH_2)_3B \xrightarrow{H_2O_2} RCH_2CH_2OH$
8. Reduction of aldehydes, ketones, acids and acid derivatives	
9. Oxo process	$CH_2{=}CH_2 + CO + H_2 \xrightarrow[\text{High } T \text{ and } P]{Co(CO)_4} CH_3CH_2CHO \xrightarrow{H_2/Ni} CH_3CH_2CH_2OH$
10. From Grignard's reagent	
11. Fermentation	$\underset{\text{Maltose}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{\text{Maltase}} \underset{\text{Glucose}}{2C_6H_{12}O_6} \xrightarrow{\text{Zymase}} 2C_2H_5OH + 2CO_2$
12. Deamination	$\underset{(1°,\ 2° \text{ or } 3°)}{R{-}NH_2} + HNO_2 \longrightarrow \underset{(1°,\ 2° \text{ or } 3°)}{ROH} + N_2\uparrow + H_2O$

Reduction of Different Functional Groups with Different Reagents

Group	Product	$LiAlH_4$ in ether	$NaBH_4$ in C_2H_5OH	$NaBH_4 + AlCl_3$ in diglyme	B_2H_6 in THF	H_2 +catalyst
—CHO	$—CH_2OH$	+	+	+	+	+
>CO	>CHOH	+	+	+	+	+
$—CO_2H$	$—CH_2OH$	+	−	+	+	$+^1$
$—CO_2R$	$—CH_2OH$	+	$-^2$		+	+
—COCl	$—CH_2OH$	+	+	+	−	$+^3$
$—CONH_2$	$—CH_2NH_2$	+	−	+	+	+
$(RCO)_2O$	RCH_2OH	+	−	+	+	+
Lactone	Diol	+	−	+	+	+
Epoxide	Alcohol	+	−	+	+	+
—CN	$—CH_2NH_2$	$+^4$	−	+	+	+
>C=NOH	$—CH_2NH_2$	+				+
RNO_2	RNH_2	+	−	−	−	+
$ArNO_2$	ArN=NAr	+	−	−	−	$+^5$
Azoxy	Azo	+				$+^5$
Alkene	>CH—HC<	−	−	+	+	
Alkyne	—CH=CH—	$-^6$			+	+
RX	*R*H	+	+	−	−	+
Ar*X*	ArH			−	−	+

1. Only Ru—C and Cu—Br—Cr oxide. **2.** Often reduces if use excess of $NaBH_4$ in MeOH. **3.** Give aldehyde at −78°C and with Pd—$BaSO_4$—S—quinoline. **4.** Reverse addition gives aldehydes. **5.** Also to amine. **6.** $LiAlH_4$-$AlCl_3$ reduces $RC{\equiv}CH$ (and $ArC{\equiv}CH$).

Physical Properties

(i) Lower alcohols are colourless toxic liquids, whereas the higher members are waxy solids.

(ii) The boiling point of alcohol is always higher than the corresponding ether, hydrocarbon and haloalkane due to the presence of hydrogen bonding.

(iii) Boiling point ∝ number of $—CH_2$ group

$$\propto \frac{1}{\text{Branching}}$$

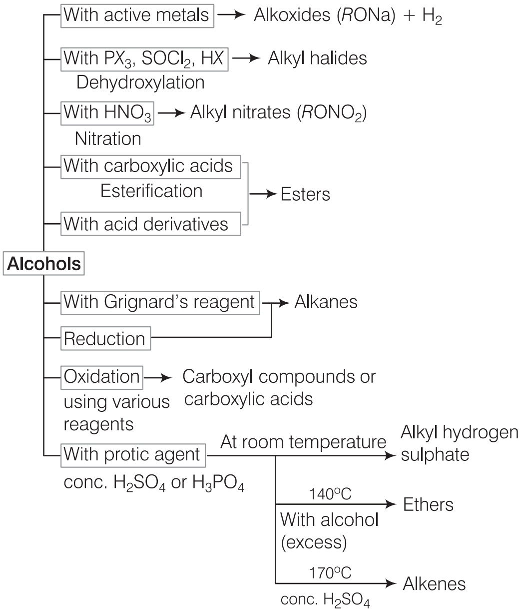
Chemical Properties

- The chemical properties of alcohols are attributed to the polar $-\overset{\delta+}{\underset{|}{\overset{|}{C}}}-\overset{\delta-}{O}H$ bond. Their reactivity is different in different reactions, e.g.

  (i) The reaction in which O—H bond cleaves, the reactivity order of alcohols is 1° > 2° > 3°.

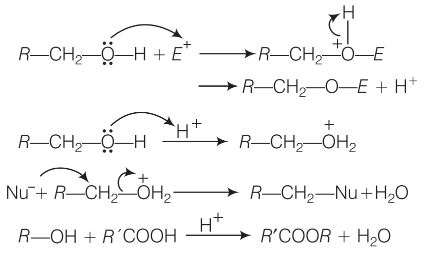
  (ii) The reaction in which C—O bond cleaves, the reactivity order of alcohols is 3° > 2° > 1°.

- Alcohols show the following chemical reactions:



REMEMBER

- Alcohols acts both as electrophile (C—O bond breaks) and nucleophile (O—H bond breaks) as shown below :



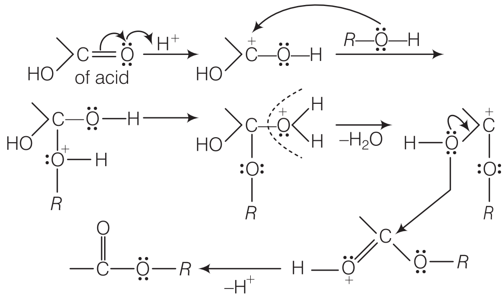
$$R-CH_2-\ddot{O}-H + E^+ \longrightarrow R-CH_2-\overset{+}{O}(H)-E \longrightarrow R-CH_2-O-E + H^+$$

$$R-CH_2-\ddot{O}-H \xrightarrow{H^+} R-CH_2-\overset{+}{O}H_2$$

$$Nu^- + R-CH_2-\overset{+}{O}H_2 \longrightarrow R-CH_2-Nu + H_2O$$

$$R-OH + R'COOH \xrightarrow{H^+} R'COOR + H_2O$$

- The mechanism of the above reaction can be given as



- The same procedure can be applied to acid derivatives also but not named as esterification.
- It may be noted that as the size of the group *R* increases, the rate of esterification reaction decreases due to steric hindrance. Thus, the order of reactivity of alcohols follows the sequence
$CH_3OH > CH_3CH_2OH > (CH_3)_2CHOH > (CH_3)_3COH$ and that of the acids follows the sequence:
$HCOOH > CH_3COOH > (CH_3)_2CHCOOH > (CH_3)_3CCOOH$

Oxidation

The different reagents are used for oxidation and their products are as follows:

(i) Cu or Ag at about 300°C,
1°alcohol $\longrightarrow$ aldehydes + $H_2\uparrow$ (dehydrogenation)
2° alcohol $\longrightarrow$ ketones + $H_2\uparrow$ (dehydrogenation)
3° alcohol $\longrightarrow$ alkenes + H_2O (dehydration)

(ii) $KMnO_4$, $K_2Cr_2O_7$ (acidic as well as alkaline), CrO_3 (in glacial acetic acid), PCC ($C_5H_5\overset{+}{N}ClCrO_3^-$)
1° alcohol $\longrightarrow$ Aldehydes;
2° alcohol $\longrightarrow$ Ketones

(iii) MnO_2 selectively oxidises the —OH group of allylic and benzylic 1°and 2° alcohols to aldehydes and ketones, respectively.

Test for 1°, 2° and 3° Alcohols

The following tests are carried out to detect the presence of 1°, 2° and 3° alcohols.

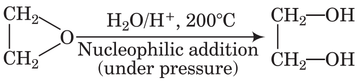
Name of the test and procedure	1° alcohol	2° alcohol	3° alcohol
Victor Meyer's test The alcohol is treated with P/I_2 and then with $AgNO_2$ and HNO_2. The final product obtained is treated with NaOH and the colour is observed.	Blood red colour	Blue colour	No colour
Lucas test Alcohol is treated with Lucas reagent (equimolar mixture of anhyd. $ZnCl_2$ and conc. HCl)	Do not produce turbidity at room temperature	Produce turbidity after 5 min	Produce turbidity immediately
Dehydrogenation Cu or Ag are used for dehydrogenation	Produce aldehydes	Produce ketones	Dehydrated to give alkenes

Dihydric Alcohols

The compounds which contains two —OH groups attached to two successive C-atoms are called glycols. Ethylene glycol is the simplest dihydric alcohol.

Methods of Preparation

These are prepared by the following methods:

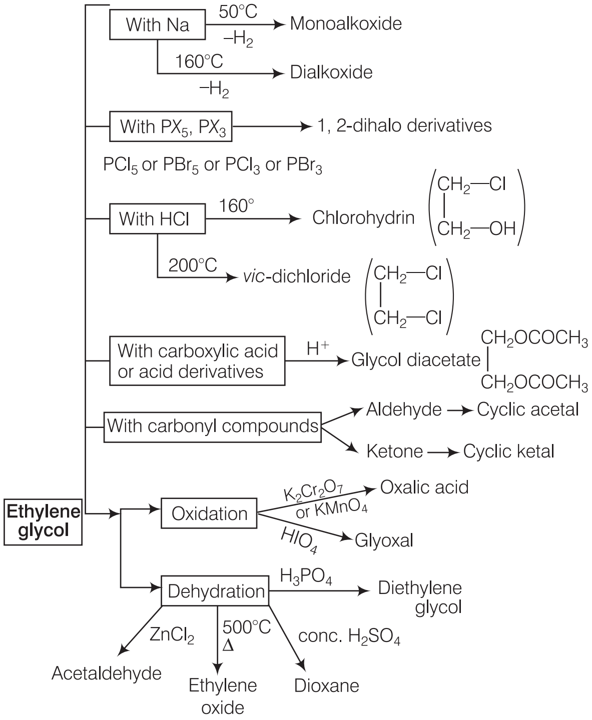
Methods	Reactions involved
1. Oxidation of ethylene	$CH_2{=}CH_2 + \underbrace{KMnO_4 + KOH}_{1\%\ \text{alkaline solution}} \longrightarrow \begin{matrix}CH_2OH\\ \vert\\ CH_2OH\end{matrix}$ HCOOH is also used for the similar purpose.
2. Hydrolysis of 1, 2-dibromo ethane	$\begin{matrix}CH_2-Br\\ \vert\\ CH_2-Br\end{matrix} + Na_2CO_3 + H_2O \longrightarrow \begin{matrix}CH_2-OH\\ \vert\\ CH_2-OH\end{matrix} + 2NaBr + CO_2$
3. Hydrolysis of ethylene halohydrin	$\underset{\text{Halohydrin}}{\begin{matrix}CH_2-OH\\ \vert\\ CH_2X\end{matrix}} + NaHCO_3 \longrightarrow \begin{matrix}CH_2OH\\ \vert\\ CH_2OH\end{matrix} + NaX + CO_2 + H_2O$
4. Hydrolysis of ethylene oxide	 $\begin{matrix}CH_2\\ \vert\\ CH_2\end{matrix}\!\!>O \xrightarrow[\text{Nucleophilic addition (under pressure)}]{H_2O/H^+,\ 200°C} \begin{matrix}CH_2-OH\\ \vert\\ CH_2-OH\end{matrix}$
5. Ethylene diamine deamination	$\begin{matrix}CH_2-NH_2\\ \vert\\ CH_2-NH_2\end{matrix} + 2HONO \rightarrow \begin{matrix}CH_2OH\\ \vert\\ CH_2OH\end{matrix} + 2N_2 + H_2O$
6. Reductive ozonolysis of ethyne	$\begin{matrix}CH\\ \vert\vert\vert\\ CH\end{matrix} \xrightarrow[(ii)\ H_2O/Zn]{(i)\ O_3} \begin{matrix}CHO\\ \vert\\ CHO\end{matrix} \xrightarrow{LiAlH_4} \begin{matrix}CH_2OH\\ \vert\\ CH_2OH\end{matrix}$

Physical Properties

(i) It is colourless viscous solid with bp-197° C, mp-13°C.
(ii) It is sweet in taste, hygroscopic and miscible with water and ethanol in all proportions but insoluble in ether.
(iii) It is as toxic as methyl alcohol when taken orally.

Chemical Properties

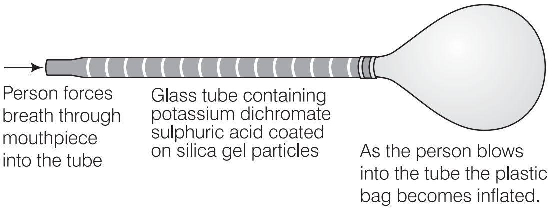
Ethylene glycol gives the following chemical reactions:



Breath-Alcohol Screening

Potassium dichromate oxidation of ethanol to acetic acid is the basis for the original breath-alcohol screening test used by law enforcement agencies to determine a person's Blood Alcohol Content (BAC). The test is based on the difference in colour between the dichromate ion in the reagent and chromium (III) ion in the product.

$$\underset{\text{Ethanol}}{CH_3CH_2OH} + \underset{\substack{\text{(Dichromate}\\\text{reddish orange)}}}{Cr_2O_7^{2-}} \xrightarrow[H_2O]{H_2SO_4} \underset{\text{Acetic acid}}{CH_3\overset{\overset{\displaystyle O}{\|}}{C}OH} + \underset{\substack{\text{Chromium (III)}\\\text{ion (green)}}}{Cr^{3+}}$$



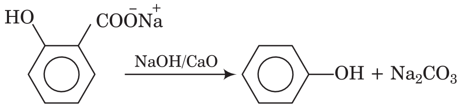
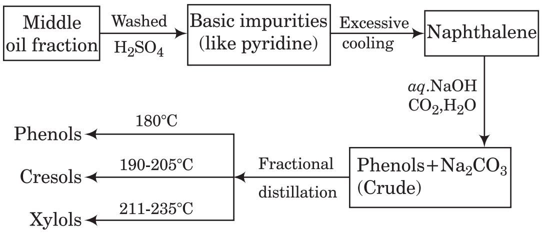
As breath containing ethanol vapour passes through the tube, reddish orange dichromate ion is reduced to green chromium (III) ion. To estimate the concentration of ethanol in the breath, one measures how far the green colour extends along the length of the tube. The correlation between the alcohol content of the breath and in the blood is based on the fact that air deep within the lungs in equilibrium with blood passing through the pulmonary arteries and an equilibrium is established between blood alcohol and breath alcohol.

Phenols

These are the compounds in which a hydroxyl group is attached directly to the aromatic ring. It was discovered by Runge who named it as carbolic acid.

Methods of Preparation

These are prepared through the following reactions:

Methods	Reaction involved
1. Dow process (by hydrolysis)	$PhX \xrightarrow[\text{340°C, 150 atm}]{aq.\ NaOH} Ph\overset{-}{O}\overset{+}{Na} \xrightarrow{H_2O/H^+} PhOH$
2. Cumene process	$PhCH(CH_3)_2 \xrightarrow[H_2O/H^+]{O_2,\ \text{catalyst}} PhOH + CH_3COCH_3$
3. From diazonium salts	$Ph\overset{+}{N} \equiv NX^- \xrightarrow{H_2O/H^+} PhOH + N_2\uparrow + HX$
4. Fusion of alkali metal salt of sulphonic acid	$PhSO_3^-Na^+ + NaOH \xrightarrow{\text{Fuse}} Ph\overset{-}{O}\overset{+}{Na}$ $\xrightarrow{H_2O/H^+} PhOH$
5. From Grignard's reagent	$PhMgBr \xrightarrow{[O]} PhOMgBr \xrightarrow{H_2O/H^+} PhOH$
6. From salt of salicylic acid	
7. Hydroxylation of benzene	$C_6H_6 + H_2O_2 \xrightarrow{HSO_3F} PhOH$
8. By oxidation of benzene and toluene	$2C_6H_6 + O_2 \xrightarrow[315°C]{V_2O_5} 2PhOH$ $C_6H_5CH_3 \xrightarrow[\text{Manganous and cupric salts and catalyst}]{2O_2(\text{air})} C_6H_5OH + CO_2 + H_2O$
9. Middle oil fraction of coal tar	

Physical Properties

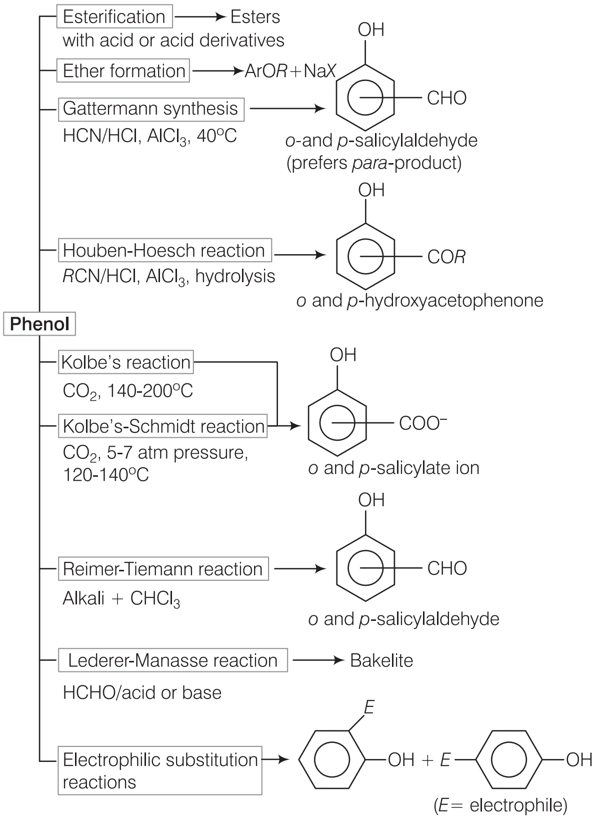
(i) These are colourless liquids or solids and are highly toxic in nature.

(ii) Their boiling points are higher than corresponding alcohols due to stronger intermolecular hydrogen bonding and hence are more miscible with water.

(iii) They have high dipole moments and are more acidic than the corresponding alcohol due to the conjugation between lone pair of oxygen and benzene.

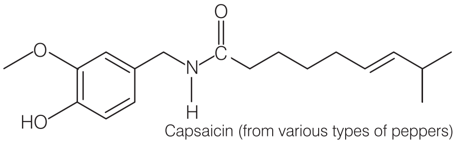
Chemical Properties

Phenol gives the following chemical reactions:



Capsaicin, For Those Who Like It Hot

Capsaicin, the pungent principal from the fruit of various species of peppers (Capsicum and Solanaceae) was isolated in 1876. Capsaicin contains both phenol and a phenol ether.



Capsaicin (from various types of peppers)

The inflammatory properties of capsaicin are well known; the burning sensation in the mouth and sudden tearing in the eyes caused by a good dose of hot chilli peppers. For this reason, capsaicin, containing extracts from these flaming foods are used in sprays to ward off dogs or other animals that might nip at your heels while you are running or cycling.

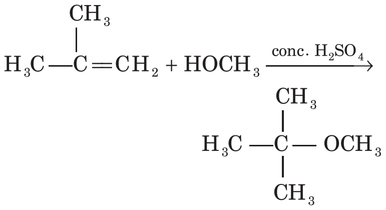
Ironically, capsaicin is able to both cause and relieve pain. Currently,two capsaicin-containing creams, Mioton and Zostrix, are prescribed to treat the burning pain. They are also prescribed for diabetics to relieve persistent foot and leg pain.

Ethers

These are the organic compounds having —O— functional group and having general formula, $R-O-R'$.

Methods of Preparation

Ethers are prepared through the following methods:

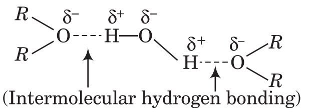
	Methods	Reaction involved
1.	Williamson's synthesis	$R\overset{-}{O}\overset{+}{Na} + R'X \longrightarrow ROR' + \overset{+}{Na}\overset{-}{X}$
2.	By reaction of alkyl halides with dry silver oxide	$2RX + Ag_2O \longrightarrow ROR + 2AgX$
3.	By dehydration of alcohols	$\underset{(Excess)}{RCH_2OH} \xrightarrow[140°C]{conc.\ H_2SO_4} RCH_2-O-CH_2R$ (Order of ease of dehydration of alcohols 3°<2°<1°) $\underset{(Excess)}{RCH_2OH} \xrightarrow[250°C]{Al_2O_3} RCH_2-O-CH_2R$
4.	By the action of diazomethane of alcohols	$ROH + CH_2N_2 \xrightarrow{HBF_4} ROCH_3 + N_2\uparrow$
5.	From alkenes (i) By adding alcohols (ii) Alkoxy mercuration demercuration	 $H_3C-\overset{\overset{CH_3}{\vert}}{C}=CH_2 + HOCH_3 \xrightarrow{conc.\ H_2SO_4} H_3C-\underset{\underset{CH_3}{\vert}}{\overset{\overset{CH_3}{\vert}}{C}}-OCH_3$ $\text{Alkene} + \text{Alcohol} \xrightarrow[(ii)\ NaBH_4/\overline{O}H]{(i)\ Hg(OOCCF_3)_2} \text{Ether}$

Physical Properties

(i) Dimethyl ether and ethyl methyl ether are gases at room temperature while other homologues are colourless liquids with characteristics ether smell and with a dipole moment of 1.15 to 1.3 D.

(ii) These have the boiling points lower than their isomeric alcohols (due to lesser hydrogen bonding than corresponding alcohols).

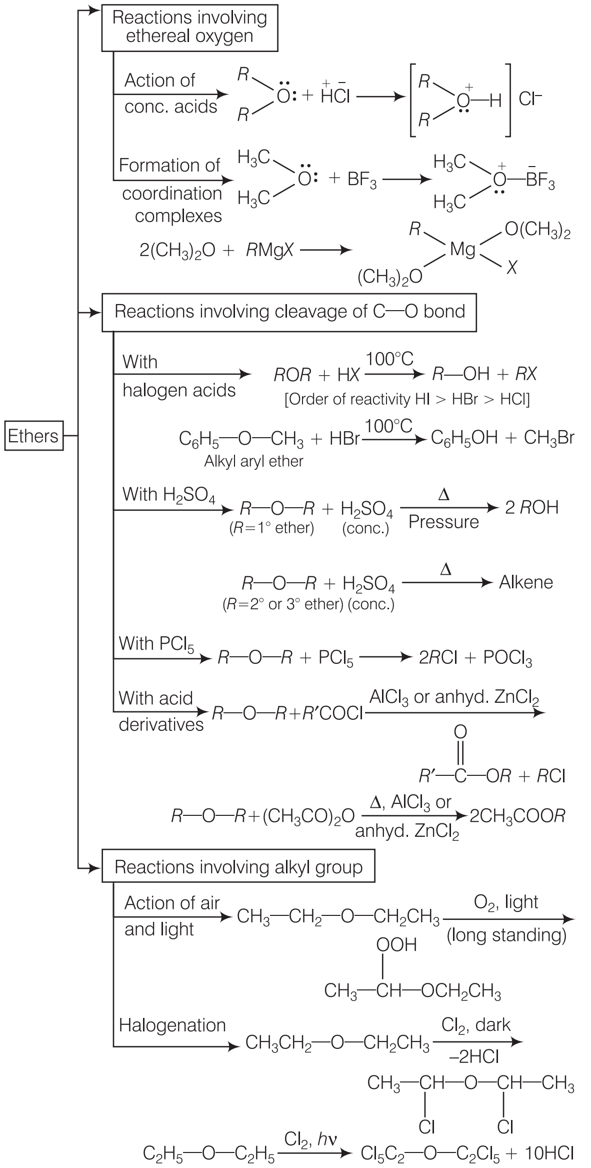
(iii) Ethers upto three C-atoms are soluble in water due to the formation of intermolecular hydrogen bonds as:



(Intermolecular hydrogen bonding)

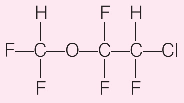
Chemical Properties

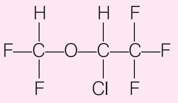
These show the following chemical properties :



Ether as an Anaesthetic for Surgeries

- Diethyl ether was easy to use and caused excellent muscle relaxation. Blood pressure, pulse rate and respiration were usually only slightly affected.
- The gas's chief drawbacks were its irritating effect on the respiratory passages and its after effect of nausea.
- Among the inhalation anaesthetic used today are several halogenated ether, the most important being enflurane and isoflurane.


Enflurane (ethrane)


Isoflurane (forane)

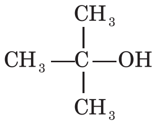
MASTER STROKES

1. The gas evolved on heating CH_3MgBr in methanol is **[JEE Main 2016]**

(a) propane (b) ethane
(c) HBr (d) methane

2. Which of the following alcohols cannot be oxidised by potassium dichromate in the presence of sulphuric acid?

(a) CH_3CH_2OH (b) $C_6H_5CH_2OH$
(c) $C_6H_5CHOHCH_3$ (d)


$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-OH$

3. In the following reaction sequence,

$$R-OH \xrightarrow{P\,+\,I_2} R-I \xrightarrow{AgNO_3} RNO_2 \xrightarrow{HNO_2} \text{No reaction}$$

The alcohol is a

(a) primary alcohol (b) secondary alcohol
(c) tertiary alcohol (d) phenol

4. An unknown alcohol is treated with the "Lucas reagent" to determine whether the alcohol is primary, secondary or tertiary. Which alcohol reacts fastest and by which mechanism? **[JEE Main 2013]**

(a) Secondary alcohol by S_N1
(b) Tertiary alcohol by S_N1
(c) Secondary alcohol by S_N2
(d) Tertiary alcohol by S_N2

5. The compound which reacts fastest with Lucas reagent at room temperature is

(a) butan-2-ol (b) butan-1-ol
(c) 2-methylpropan-1-ol (d) 2-methylpropan-2-ol

6. An industrial method for 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 nickel catalyst
(c) by reducing formaldehyde with $LiAlH_4$
(d) by reacting formaldehyde with aqueous sodium hydroxide solution

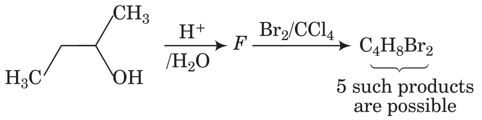
7. When phenyl magnesium bromide reacts with *tert* butanol, which of the following is formed?

(a) *Tert* butyl methyl ether
(b) Benzene
(c) *Tert* butylbenzene
(d) Phenol

8. HBr reacts fastest with

(a) 2-methylpropan-2-ol (b) propan-1-ol
(c) propan-2-ol (d) 2-methylpropan-1-ol

9.



How many structures of *F* are possible?

(a) 2 (b) 5 (c) 6 (d) 3

RAPID CONCEPT REVISION

10. The mechanism of the reaction (acid catalysed hydration of alkene) involves the following three steps :

I. Nucleophilic attack of water on carbocation.
II. Protonation of an alkene to form carbocation by the electrophilic attack of H_3O^+.
III. Deprotonation to form an alcohol.

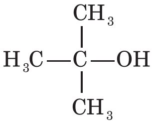
Identify the sequence for the mechanism of reaction in the acid catalysed hydration of alkenes.

(a) I, II and III
(b) II, I and III
(c) III, I and II
(d) III, II and I

11. Propan-1-ol and propan-2-ol can be best distinguished by

(a) oxidation with alk$\cdot$$KMnO_4$ followed by reaction with Fehling solution
(b) oxidation with acidic dichromate followed by reaction with Fehling solution
(c) oxidation by heating with copper followed by reaction with Fehling solution
(d) oxidation with conc. H_2SO_4 followed by reaction with Fehling solution

12. On treatment with a concentrated solution of zinc chloride in conc$\cdot$HCl at room temperature, an alcohol immediately gives, an oily product. The alcohol can be

(a) $C_6H_5CH_2OH$
(b) $CH_3CHOHCH_3$
(c) 
$H_3C—C(CH_3)_2—OH$
(d) Any of these

13. Which among the following compounds will give a secondary alcohol on reacting with Grignard's reagent followed by acid hydrolysis?

I. HCHO
II. C_2H_5CHO
III. CH_3COCH_3
IV. $HCOOC_2H_5$

Select the correct option.

(a) Only II
(b) Only III
(c) Both I and IV
(d) Both II and IV

14. An organic compound X on treatment with pyridinium chloro chromate in dichloromethane gives compound Y. Compound Y reacts with I_2 and alkali to form triiodomethane. The compound X is

(a) C_2H_5OH
(b) CH_3CHO
(c) CH_3COCH_3
(d) CH_3COOH

15. Which of the following statements is/are correct?

I. Glycerol on reaction with oxalic acid at 110°C and followed by heating and hydrolysis gives formic acid and glycerol.
II. Glycerol on reaction with oxalic acid at 230°C and followed by heating gives allyl alcohol.
III. Glycerol on oxidation with dil. HNO_3 gives a mixture of glyceric and tartonic acid.
IV. Glycerol on oxidation with conc. HNO_3 gives glyceric acid.

Choose the correct option.

(a) I and II (b) I and III (c) III and IV (d) All of these

16. Consider the following compounds,

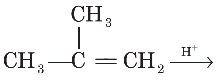
I. Methanol
II. Ethanol
II. Propan-1-ol
IV. Butan-1-ol
V. Butan-2-ol
VI. Pentan-1-ol

Arrange the given compounds in decreasing order of their boiling points and solubilities in H_2O.

Choose the correct option given below.

	Boiling point order	Solubility order
(a)	VI > IV > V > III > II > I	I > II > III > V > IV > VI
(b)	VI > IV > V > II > III > I	I > II > III > V > IV > VI
(c)	VI > IV > V > III > II > I	I > II > III > V > VI > IV
(d)	I > II > III > IV > V > VI	VI > IV > V > III > II > I

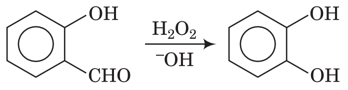
17. Which of the following reaction will not yield *p*-*tert*-butylphenol?

(a) Phenol + 
$CH_3—C(CH_3)=CH_2 \xrightarrow{H^+}$
(b) Phenol + $(CH)_3COH \xrightarrow{H^+}$
(c) Phenol + $(CH_3)_3C\cdot Cl \xrightarrow{AlCl_3}$
(d) Phenol + $CHCl_3 \xrightarrow{NaOH}$

18. Phenol $\xrightarrow[\text{(ii) } CO_2/140°C]{\text{(i) NaOH}} A \xrightarrow{H^+/H_2O} B \xrightarrow{Ac_2O} C$

In this reaction, the end-product C is

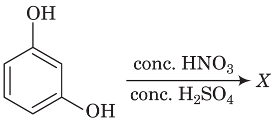
(a) salicylaldehyde
(b) salicylic acid
(c) phenyl acetate
(d) aspirin

19. 

The above reaction is called

(a) Reimer Tiemann reaction
(b) Liebermann's nitroso reaction
(c) Darkin reaction
(d) Lederer-Manasse reaction

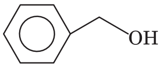
20. Consider the following reaction,

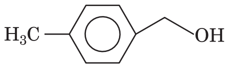


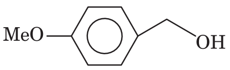
Product X is

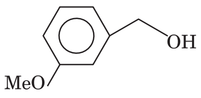
(a) picric acid
(b) styphnic acid
(c) salicylic acid
(d) benzoic acid

21. Identify the correct decreasing order of reactivity for the following compounds with HBr.

I. 

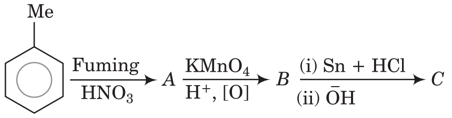
II. 

III. 

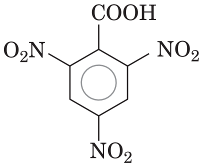
IV. 

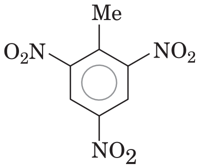
(a) III > IV > II > I
(b) III > II > IV > I
(c) III > II > I > IV
(d) II > III > IV > I

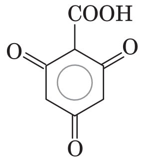
22. Consider the following reaction,

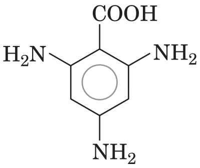


The product C is

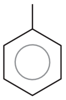
(a) 

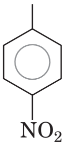
(b) 

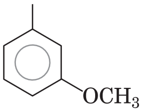
(c) 

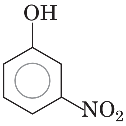
(d) 

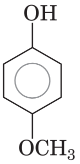
23. The correct order of decreasing acidic strength of the following compounds is

I. 

II. 

III. 

IV. 

V. 

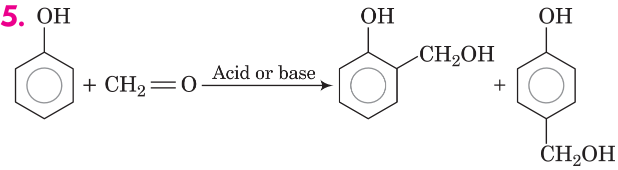
(a) V > IV > II > I > III (b) II > IV > III > I > V
(c) IV > III > II > I > V (d) I > II > III > IV > V

24. Consider the following reaction,

$$\text{Phenol} \xrightarrow{\text{Zn dust}} X \xrightarrow[\text{Anhyd· AlCl}_3]{CH_3Cl} Y \xrightarrow{\text{Alk. KMnO}_4} Z$$

The product Z is

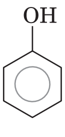
(a) toluene (b) benzaldehyde (c) benzoic acid (d) benzene

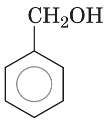
25. 

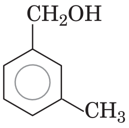
The reaction is called

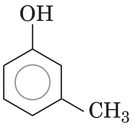
(a) Lederer-Manasse reaction (b) Claisen condensation
(c) Benzoin condensation (d) Etard reaction

26. Which of the following compound(s) is/are aromatic alcohol?

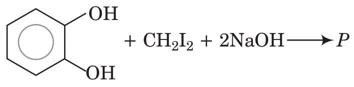
A. 

B. 

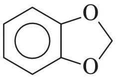
C. 

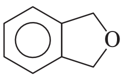
D. 

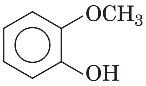
(a) A, B, C and D (b) A and D (c) B and C (d) Only A

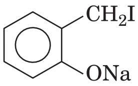
27. 

The product P is

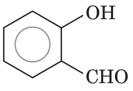
(a) 

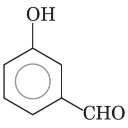
(b) 

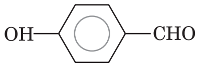
(c) 

(d) 

28. In which of the following compound —OH group is least reactive?

(a) 

(b) 

(c) 

(d) All are equally reactive

29. The following reaction is known as

(a) Perkin reaction (b) Gattermann reaction
(c) Kolbe reaction (d) Gattermann-aldehyde reaction

30. Phenol reacts with bromine in carbon disulphide at low temperature to give

(a) *m*-bromophenol (b) *o* and *p*-bromophenol
(c) *p*-bromophenol (d) 2, 4, 6-tribromophenol

31. When phenol is treated with excess of bromine water, it gives

(a) *m*-bromophenol (b) *o*-and *p*-bromophenol
(c) 2,4-bromophenol (d) 2, 4, 6-tribromophenol

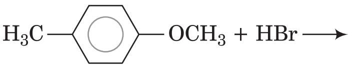
32. When diethyl ether is heated with an excess of PCl_5, it yields

(a) ethyl chloride (b) diethyl ether peroxide
(c) ethanoyl chloride (d) perchlorodiethyl ether

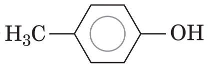
33. Sometime explosion occurs while distilling ethers. It is due to the presence of

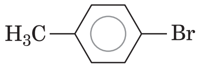
(a) oxides (b) ketones (c) aldehydes (d) peroxides

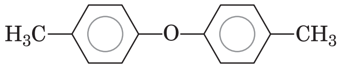
34. The final product obtained in the reaction



is

(a) 

(b) 

(c) 

(d) None of these

35. Diethyl ether on heating with conc. HI gives two moles of

(a) ethanol (b) iodoform
(c) ethyl iodide (d) methyl iodide

RAPID CONCEPT REVISION

36. *A* reacts with C_2H_5I giving *B* and NaI. Here *A* and *B* respectively, are

(a) CH_3COONa, CH_3OCH_3 *(b)* $C_2H_5OC_2H_5$, $C_2H_5COOC_2H_5$
(c) C_2H_5ONa, $C_2H_5OC_2H_5$ *(d)* C_2H_5OH, $C_2H_5OC_2H_5$

37. An organic compound, C_3H_6O does not give a precipitate with 2, 4-dinitrophenyl hydrazine reagent and does not react with metallic sodium. It could be

(a) $CH_3—CH_2—CHO$ *(b)* $CH_2=CH—CH_2OH$
(c) $CH_3—CO—CH_3$ *(d)* $CH_2=CH—O—CH_3$

38. One mole of an organic compound *A* with the formula C_3H_8O reacts completely with two moles of HI to form *X* and *Y*. When *Y* is boiled with aqueous alkali, it forms *Z*. *Z* gives the iodoform test. The compound *A* is

(a) propan-2-ol *(b)* propan-1-ol
(c) ethoxyethane *(d)* methoxyethane

39. I. 1, 2-dihydroxy benzene
II. 1, 3-dihydroxy benzene
III. 1, 4-dihydroxy benzene
IV. Hydroxy benzene

The increasing order of boiling points of above mentioned alcohol is

(a) I < II < III < IV *(b)* I < II < IV < III
(c) IV < I < II < III *(d)* IV < II < I < III

40. By which of the following procedures, can ethyl *n*-propyl ether be obtained?

(a) $C_2H_5OH \xrightarrow{HBr} I \xrightarrow[Ether]{Mg} II \xrightarrow{H_2O} III \xrightarrow[CH_3CH_2Br]{Na}$

(b) $C_2H_5OH \xrightarrow{HBr} I \xrightarrow[Ether]{Mg} II \xrightarrow[(ii)\ H_3O^+]{(i)\ CH_2O} III \xrightarrow[CH_3CH_2Br]{Na}$

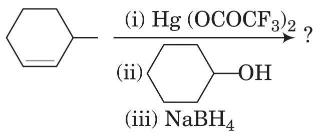
(c) $C_2H_5OH + H_2SO_4 \xrightarrow{140°C}$

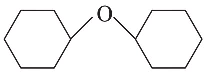
(d) $C_2H_5OH + conc\cdot H_2SO_4 \xrightarrow{180°C} I \xrightarrow{CH_3CH_2CH_2Br}$

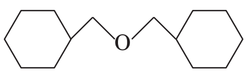
41. Consider the following statements and choose the incorrect one.

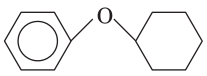
(a) When diethyl ether is heated with an excess of PCl_5, it yields ethyl chloride
(b) Sometimes explosion occurs while distilling ethers which is due to the presence of oxides
(c) On boiling with concentrated hydrobromic acid, phenyl ethyl ether yields phenol and ethyl bromide
(d) An ether is more volatile than an alcohol having the same molecular formula. This is due to intermolecular hydrogen bonding in alcohols

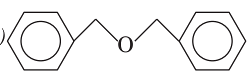
42. What is the structure of product for the following reaction?



(a)


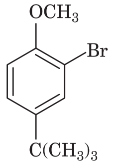
(b)


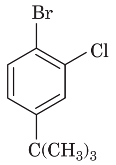
(c)


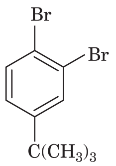
(d)


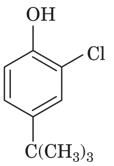
43. Anisole $\xrightarrow{(CH_3)_3CCl} \xrightarrow{Cl_2/FeCl_3} \xrightarrow[Heat]{HBr} X$

The product *X* in the above series of reaction is

(a)


(b)


(c)


(d)


44. Match the items of Column I with items of Column II and choose the correct option from the codes given below.

Column I	Column II
A. Anti-freeze used in car engine	p. Neutral ferric chloride
B. Solvent used in perfumes	q. Glycerol
C. Starting material of picric acid	r. Methanol
D. Wood spirit	s. Phenol
E. Reagent used for detection of phenolic group	t. Ethylene glycol
F. By product of soap industry used in cosmetics	u. Ethanol

Codes

	A	B	C	D	E	F		A	B	C	D	E	F
(a)	t	u	s	r	q	p	*(b)*	t	u	r	s	q	p
(c)	t	u	s	r	p	q	*(d)*	t	u	q	p	s	r

45. Match the items of Column I with items of Column II and choose the correct option from the codes given below.

Column I	Column II
A. Methanol	p. Conversion of phenol to salicylic acid
B. Kolbe's reaction	q. Ethyl alcohol
C. Williamson's synthesis	r. Conversion of phenol to salicylaldehyde
D. Conversion of 2° alcohol to ketone	s. Wood spirit
E. Reimer-Tiemann reaction	t. Heated copper at 573 K
F. Fermentation	u. Reaction of alkyl halide with sodium alkoxide

Codes

	A	B	C	D	E	F		A	B	C	D	E	F
(a)	s	p	u	t	q	r	*(b)*	s	p	t	u	q	r
(c)	s	p	u	t	r	q	*(d)*	s	p	t	u	r	q

Answers

1. (d)	**2.** (d)	**3.** (c)	**4.** (b)	**5.** (d)
6. (a)	**7.** (b)	**8.** (a)	**9.** (d)	**10.** (b)
11. (c)	**12.** (c)	**13.** (a)	**14.** (a)	**15.** (d)
16. (a)	**17.** (d)	**18.** (d)	**19.** (c)	**20.** (b)
21. (c)	**22.** (d)	**23.** (b)	**24.** (c)	**25.** (a)
26. (c)	**27.** (a)	**28.** (a)	**29.** (d)	**30.** (c)
31. (d)	**32.** (a)	**33.** (d)	**34.** (a)	**35.** (c)
36. (c)	**37.** (d)	**38.** (d)	**39.** (c)	**40.** (b)
41. (b)	**42.** (b)	**43.** (d)	**44.** (c)	**45.** (c)

ALDEHYDES, KETONES AND CARBOXYLIC ACIDS

Aliphatic Aldehydes and Ketones

Organic compounds containing $>C{=}O$ group are called carbonyl compounds. In **aldehydes**, the carbonyl group is bonded to a carbon and hydrogen while in **ketones**, it is bonded to the two carbon atoms.

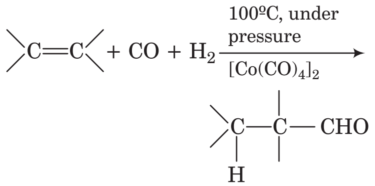
Methods of Preparation

Aldehydes and ketones are prepared through the following reactions.

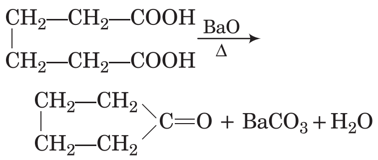
(I) Both Aldehydes and Ketones

Methods	Reaction involved
1. Catalytic decomposition	$2RCOOH \xrightarrow[300°C]{\text{Mn or Th oxide}} RCOR + H_2O + CO_2$
2. Hydrolysis	$\underset{\textit{Gem}\text{-dihalides}}{RCHX_2} \xrightarrow[-H_2O]{\text{aq.NaOH}} RCHO$
3. Cleavage	$2°\text{ glycol} \xrightarrow{Pb(OOCCH_3)_4} \text{Aldehydes}$ $3°\text{ glycol} \xrightarrow{Pb(OOCCH_3)_4} \text{Ketones}$
4. Hydroboration -oxidation	$3RC{\equiv}CH \xrightarrow[\text{DIGLYME (ii) } H_2O_2/\bar{O}H]{\text{(i) } BH_3 \text{ in TMF}} \underset{\text{Aldehyde}}{RCH_2CHO}$ $\xrightleftharpoons{\text{Tautomerisation}} \underset{\text{Enol}}{RCH{=}\overset{OH}{CH}}$
5. Hydration	$RC{\equiv}CH \xrightarrow[\text{1\% } HgSO_4 \text{, 42\% } H_2SO_4]{H_2O/60\text{-}70°C} R{-}\overset{OH}{C}{=}CH_2$ $\xrightleftharpoons{\text{Tautomerisation}} R{-}\overset{O}{\overset{\|}{C}}{-}CH_3$
6. Oxidation	$1°\text{ alcohol} \xrightarrow[K_2Cr_2O_7]{\text{Acidified}} \text{Aldehydes}$ $2°\text{ alcohol} \xrightarrow[K_2Cr_2O_7]{\text{Acidified}} \text{Ketones}$
7. Catalytic dehydrogenation	$\begin{matrix}R\\R'\end{matrix}{>}CHOH \xrightarrow[300°C]{Cu} \begin{matrix}R\\R'\end{matrix}{>}C{=}O+H_2$
8. Ozonolysis	$RCH{=}CHR' \xrightarrow[\text{(ii) } Zn/CH_3COOH]{\text{(i) } O_3 \text{ in } CHCl_3} RCHO+R'CHO$ $R_2C{=}CR_2' \xrightarrow[\text{(ii) } Zn/CH_3COOH]{\text{(i) } O_3 \text{ in } CHCl_3} R_2C{=}O+R_2'C{=}O$
9. Grignard's reagent	$HCN + RMgX \xrightarrow{H_2O} HCOR + NH_3 + H_2O + Mg(OH)X$ $RCN + R'MgX \xrightarrow{H_2O} R{-}\underset{R'}{\underset{\|}{C}}{=}O+NH_3+H_2O + Mg(OH)X$

(II) Only Aldehydes

Methods	Reactions involved
1. Reduction (i) Acids and acid derivatives (ii) Esters	$RCOCl + H_2 \xrightarrow[\text{in xylene or quinolene}]{Pd/BaSO_4 \text{ or } CaCO_3} RCHO + HCl$ $RCOOR' \xrightarrow[\text{(ii) } H_2O]{\text{(i) DIBAL-H}} RCHO + R'OH$
2. Reduction hydrolysis	$RCN \xrightarrow{SnCl_2/H_2O} RCH{=}NH{:}HCl$ $\xrightarrow{\text{Hydrolysis}} RCHO + NH_4Cl + H_2O$
3. Oxo process	

(III) Only Ketones

Methods	Reactions involved
1. Hydrolysis	$CH_3COCH_2COOH \xrightarrow{\Delta} CH_3COCH_3 + CO_2 + H_2O$
2. From dicarboxylic acids	
3. From organometallic compounds	$R'{-}\overset{R'}{\overset{\|}{C}}uLi + R{-}COCl \longrightarrow RCOR' + R'CuLiCl$

Physical Properties

(i) HCHO is a gas at room temperature, CH_3CHO is a volatile liquid and the rest are either liquid or solid at room temperature.

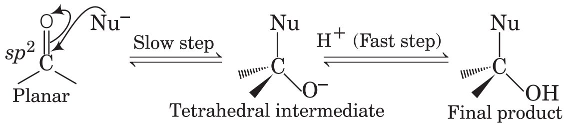
(ii) Their boiling points are higher than the corresponding hydrocarbons and ether but less than the corresponding alcohols due to the absence of hydrogen bonding. Hence, the order of boiling points for compounds of comparable molecular masses are alkane < alkene < alkyne < ether < aldehyde < ketone < alcohol.

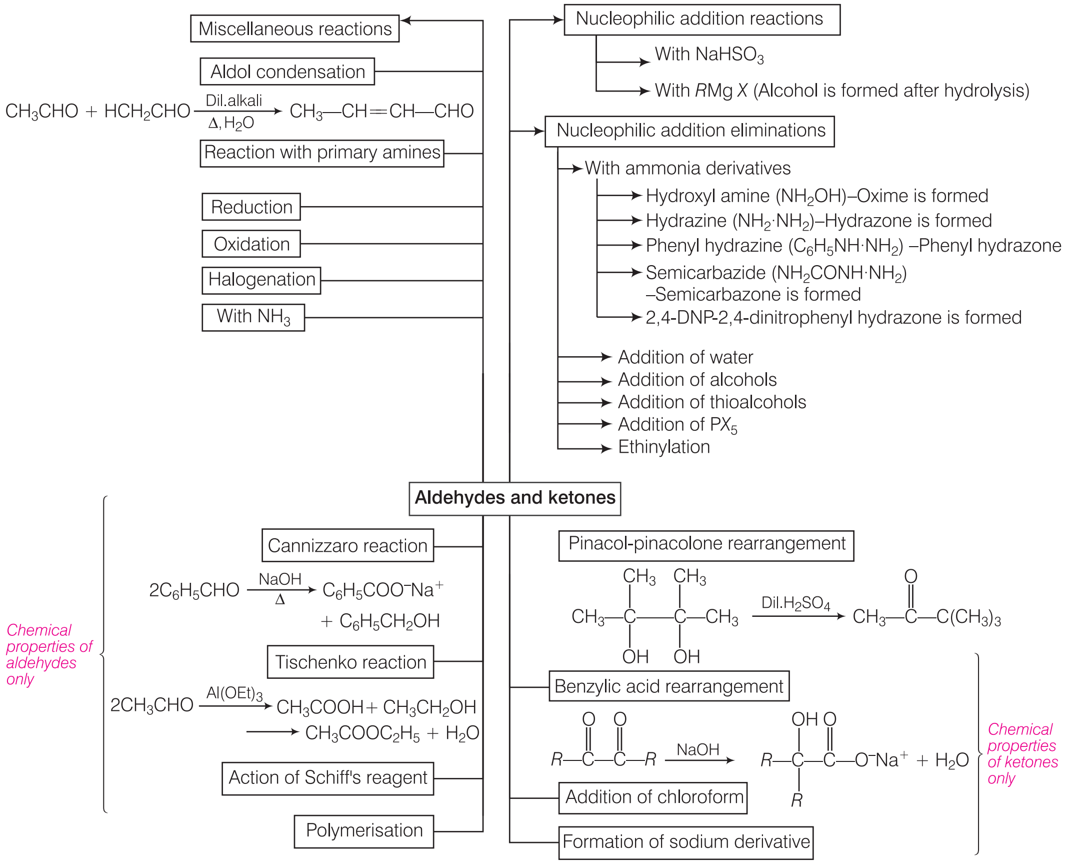
(iii) The lower members are miscible with water and soluble in organic solvents while miscibility with water decreases as molecular weight increases.

Chemical Properties

Aldehydes and ketones undergo nucleophilic addition reaction that prceeds through the following mechanism.

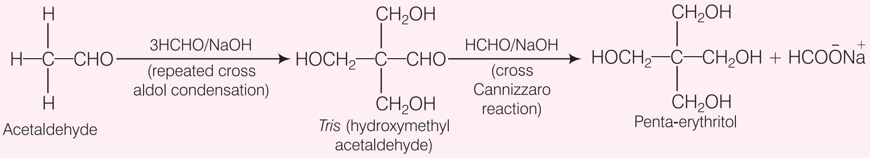
These show the following chemical properties:





PETN: The Deadly Explosive (Delhi High Court, 8-Sep-2011)

The terrorist attack which occured in Delhi High Court on September 8, 2011 used PETN as the deadly explosive. PETN stands for pentaerythritol tetranitrate. The preparation of PETN takes place as follows



PETN mixed with ammonium nitrate is used as a deadly explosive.

AMAZING REALITIES

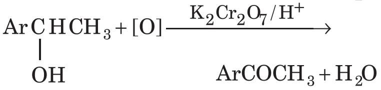
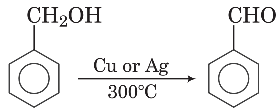
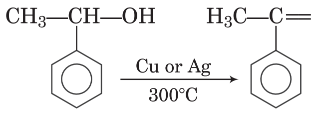
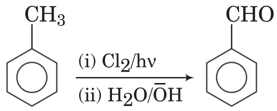
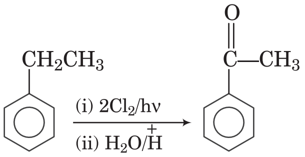
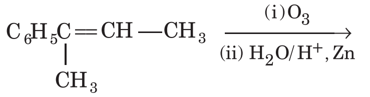
- **Just one atomic layer thick, the 'miracle material' Graphene is a better conductor of electricity and heat than any material.**
- **The element Californium is often called the most expensive substance in the world. Its cost is as much as $68 million for one gram.**

Aromatic Aldehydes and Ketones

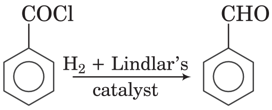
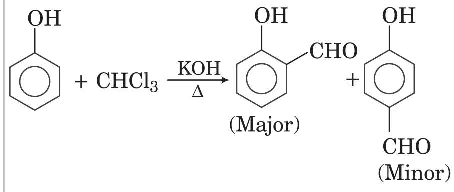
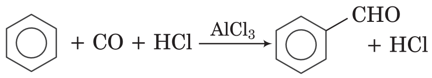
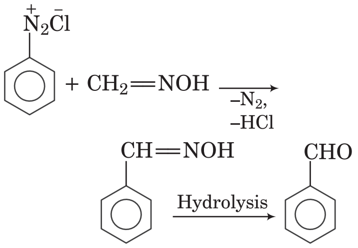
In aromatic aldehydes and ketones, the carbonyl ($>C{=}O$) group is directly attached to aromatic ring.

Methods of Preparation

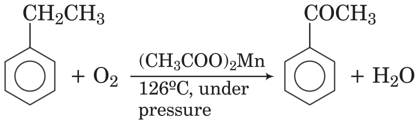
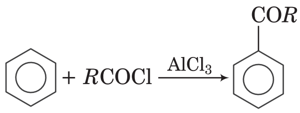
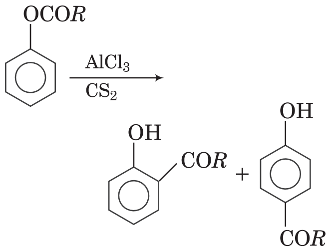
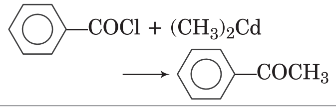
(I) Both Aromatic Aldehydes and Ketones

Methods	Reactions involved
1. Oxidation	$ArCH_2OH + [O] \xrightarrow{K_2Cr_2O_7/H^+} ArCHO + H_2O$  $Ar\underset{OH}{\underset{\vert}{C}}HCH_3 + [O] \xrightarrow{K_2Cr_2O_7/H^+} ArCOCH_3 + H_2O$
2. Dehydrogenation	 
3. Aromatic halogen derivatives	 
4. Ozonolysis	$C_6H_5CH{=}CH_2 \xrightarrow[(ii)\ H_2O/H^+, Zn]{(i)\ O_3} C_6H_5CHO + HCHO + H_2O_2$  $C_6H_5\underset{CH_3}{\underset{\vert}{C}}{=}CH-CH_3 \xrightarrow[(ii)\ H_2O/H^+, Zn]{(i)\ O_3} C_6H_5COCH_3 + CH_3CHO + H_2O_2$
5. Grignard reagent	$HCN + C_6H_5MgX \xrightarrow{H_2O} C_6H_5CHO + NH_3 + Mg(OH)X$ $CH_3CN + C_6H_5MgX \xrightarrow{H_2O} C_6H_5COCH_3 + NH_3 + Mg(OH)X$
6. Catalytic decomposition	$C_6H_5COOH + HCOOH \xrightarrow[300°C]{MnO_2} C_6H_5CHO + H_2O + CO_2$ $C_6H_5COOH + C_6H_5COOH \xrightarrow[300°C]{MnO_2} C_6H_5COC_6H_5 + H_2O + CO_2$

(II) Only Aromatic Aldehydes

Methods	Reactions involved
1. Rosenmund reaction	
2. Reimer-Tiemann reaction	
3. Gattermann -Koch reaction	
4. Gattermann -Aldehyde synthesis	$C_6H_6 + HN{=}CHCl \xrightarrow[H_2O]{AlCl_3} C_6H_5CHO + NH_3$
5. Stephen's method	$C_6H_5CN \xrightarrow{Sn/HCl} C_6H_5\ CHO + NH_4Cl + H_2O$
6. Using diazonium salts	

(III) Only Aromatic Ketones

Methods	Reactions involved
1. Catalytic air oxidation	
2. Friedel Craft's acylation	
3. Fries rearrangement	
4. Using organometallic compounds	

Physical Properties

- C_6H_5CHO is colourless liquid, bp 179°C with pleasant almond like odour, soluble in ethanol and diethyl ether, steam volatile.
- $C_6H_5COCH_3$ is a colourless liquid, bp 202°C, sparingly soluble in water but dissolves readily in ethanol and diethyl ether.

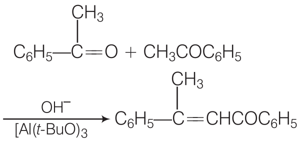
Chemical Properties

These show the following chemical properties:

Aromatic aldehydes and ketones

Electrophilic substitution

Claisen-Schmidt reaction



$$C_6H_5-\overset{CH_3}{\overset{|}{C}}{=}O + CH_3COC_6H_5 \xrightarrow[{[Al(t\text{-}BuO)_3]}]{OH^-} C_6H_5-\overset{CH_3}{\overset{|}{C}}{=}CHCOC_6H_5$$

Halogenation

Oxidation

Reduction

Chemical properties of aromatic aldehydes and ketones both

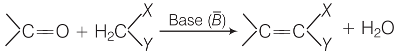
Nucleophilic additions

- Addition of HCN (Cyanohydrin is formed)
- Addition of *R*MgX (Alcohol is formed on hydrolysis)
- Addition of $NaHSO_3$

Nucleophilic addition elimination

- With alcohols (Acetal is formed)
- With ammonia derivatives
  - With NH_2OH (Aldoxime is formed)
  - With $NH_2{\cdot}NH_2$ (Hydrazone is formed)
  - With $NH_2{\cdot}NH{\cdot}C_6H_5$ (Phenyl hydrazone is formed)
  - With $NH_2{\cdot}NHCONH_2$ (Semicarbazone is formed)
  - With 2, 4-DNP (2, 4-DNP hydrazone is formed)
- With PCl_5 (Benzal chloride is formed)

Knoevenagel condensation with compound having $X-CH_2-Y$ group and $:B^-$



$$\rangle C{=}O + H_2C\langle^{X}_{Y} \xrightarrow{\text{Base }(\bar{B})} \rangle C{=}C\langle^{X}_{Y} + H_2O$$

Mannich reaction with HCHO + NH_3

$$C_6H_5COCH_3 + HCHO + (CH_3)_2NH \longrightarrow C_6H_5COCH_2CH_2N(CH_3)_2 + H_2O$$

Reaction with primary amines

Haloform reaction

$$C_6H_5COCH_3 + I_2 \xrightarrow{OH^-} C_6H_5COO^- + \underset{\text{(Yellow ppt.)}}{CHI_3}$$

Chemical properties of aromatic ketones only

Tischenko reaction

$$2C_6H_5CHO \xrightarrow{Al(OC_2H_5)_3} C_6H_5COOCH_2C_6H_5$$

Cannizzaro reaction

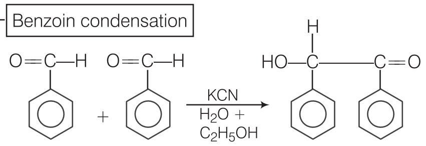
$$2C_6H_5CHO \xrightarrow{NaOH} C_6H_5CH_2OH + C_6H_5COONa$$

Action of ammonia — Hydrobenzamide is formed

Perkin condensation

$$C_6H_5CHO + (CH_3CO)_2O \xrightarrow[180^\circ]{CH_3COO^-Na^+} C_6H_5CH{=}CHCOOH + CH_3COOH$$

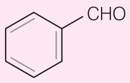
Benzoin condensation



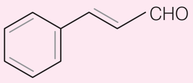
Self-condensation of aromatic aldehydes, KCN or NaCN

Chemical Properties of aromatic aldehydes only

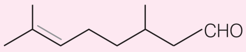
Some Naturally Occurring Aldehydes and Ketones



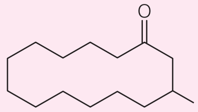
Benzaldehyde (oil of almonds)



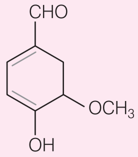
Cinnamaldehyde (oil of cinnamon)



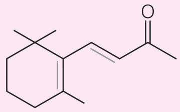
Citronellal (citronella oils; also in lemon and lemon grass oils)



Muscone (From the musk deer; used in perfumes)



Vanillin (vanilla bean)



β-Ionone (from violets)

AMAZING REALITIES

There's enough gold in the Earth's crust to cover the entire land surface knee-deep.

Carboxylic Acid

Organic compounds which contain carboxylic group (—COOH) are called **carboxylic acids**. Depending upon the number of —COOH group present in the compound, the carboxylic acids are classified into monocarboxylic acids, dicarboxylic acids, tricarboxylic acids, etc.

Monocarboxylic Acids

The general formula of monocarboxylic acid is R—COOH or $C_nH_{2n+1}COOH$.

RAPID CONCEPT REVISION

Methods of Preparation

These are prepared through the following methods:

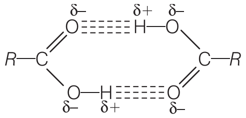
Methods	Reaction involved
1. Oxidation	$RCH_2OH \xrightarrow{[O]} RCHO + H_2O \xrightarrow{[O]} RCOOH$
2. Hydrolysis of (i) CHX_3 (ii) RCN (iii) Acid derivatives	 $CHX_3 + 3NaOH \xrightarrow[-H_2O]{} HCOOH$ $RCN \xrightarrow{H_2O} RCOOH + NH_3$ $RCOOR' \xrightarrow{H_2O/\bar{O}H} RCOO^- + R'OH$
3. Ozonolysis	$CH_2{=}CH_2 + O_2 \xrightarrow[AgO]{H_2O_2} 2\,HCOOH + H_2O_2$ $CH{\equiv}CH + O_2 \xrightarrow{Zn/H_2O} 2\,HCOOH$
4. Grignard's reagent	$RMgX + CO_2 \xrightarrow{\text{Hydrolysis}} RCOOH + Mg(OH)X$
5. Koch reaction	$CH_2{=}CH_2 + CO + H_2O \xrightarrow[300-400°C]{H_3PO_4} CH_3CH_2COOH$
6. Carboxylation	$R\bar{O}Na^+ + CO \xrightarrow[\text{Under pressure}]{\Delta} RCO\bar{O}Na^+ \xrightarrow{H_2O/H^+} RCOOH$
7. From long chain hydrocarbons	$2RCH_3 + 3O_2 \longrightarrow 2RCOOH + 2H_2O$

Physical Properties

(i) Carboxylic acids with unbranched chain of 12-24 carbons are called fatty acids.

(ii) First three members are colourless, pungent smelling liquids.

(iii) C_4-C_9 are oily liquids. Higher ones are odourless solids. First four members are miscible with water and this miscibility decreases with increase in molecular weight.



(iv) Boiling points of acids are higher than corresponding alcohols due to intermolecular H-bonding.

(v) Carboxylic acids are stronger acids than phenol but weaker than other mineral acids. The acidic character decreases with increase in molecular weight.

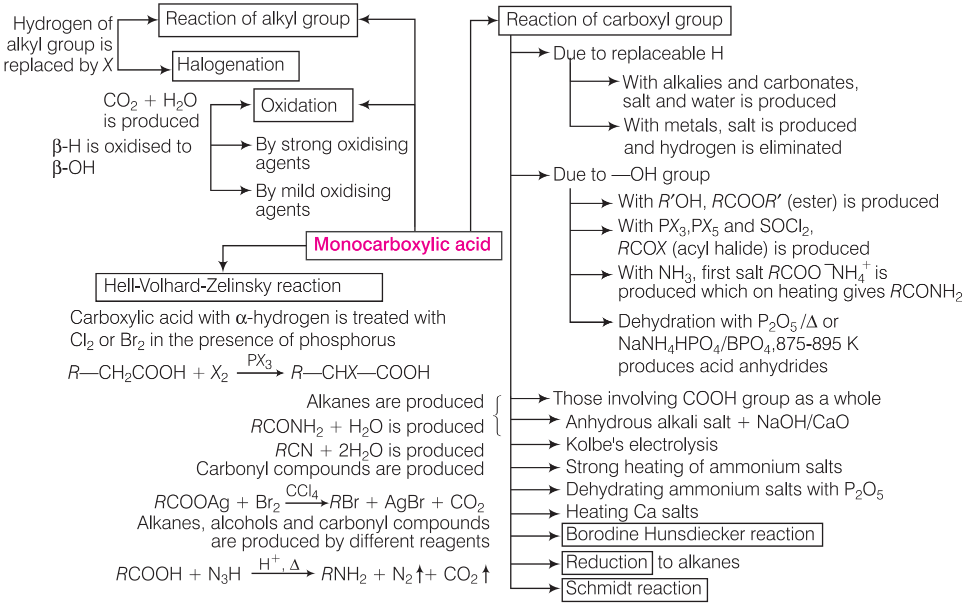
(vi) The melting points of *n*-monocarboxylic acids;
n = even = melting point higher,
n = odd = melting point lower.

SOME FACTS ABOUT MONOCARBOXYLIC ACIDS

Formic acid (HCOOH) was first obtained by the distillation of ants. The bites of some ants inject formic acid and the stings of wasps and bees contain formic acid as well as other poisonous materials.

- Acetic acid (CH_3COOH) is made by fermenting cider and honey in the presence of oxygen. This fermentation produces vinegar, a solution containing 4%-10% acetic acid and number of other compounds that add to its flavour.
- Propionic acid (CH_3CH_2COOH) was first found among degradation products of sugar.
- Butyric acid ($CH_3(CH_2)_2COOH$) is one of the most foul-smelling substance imaginable. It is found in rancid (salted) butter and is one of the ingredients of body odour. By recognising extremely small amounts of this and other chemicals, blood hounds are able to track fugitives.

Chemical Properties



AMAZING REALITIES

- **It is estimated that a plastic container can resist decomposition for as long as 50000 years.**
- **A bee sting is acidic and a wasp sting is alkaline. To treat a sting by one of these you should use the opposite type of chemical.**

Dicarboxylic Acid

The general formula of saturated dicarboxylic acids is $C_nH_{2n}(COOH)_2$ ($n = 0$ for oxalic acid).

Methods of Preparation

Methods	Reactions involved
1. Oxidation of cane sugar (Lab method)	$C_{12}H_{22}O_{11} + 18[O] \xrightarrow[V_2O_5]{HNO_3} 6(COOH)_2 + 5H_2O$
2. Heating $HCO\bar{O}Na^+$	$2HCOONa \xrightarrow{\Delta} \begin{array}{c}COONa\\ \vert \\ COONa\end{array} + H_2$
3. Hydrolysis of cynogen	$CN—CN + 4H_2O \longrightarrow \begin{array}{c}COOH\\ \vert \\ COOH\end{array} + 2NH_3$
4. Heating Na or K in the presence of CO_2	$2CO_2 + 2Na \xrightarrow{\Delta} \begin{array}{c}COONa\\ \vert \\ COONa\end{array}$

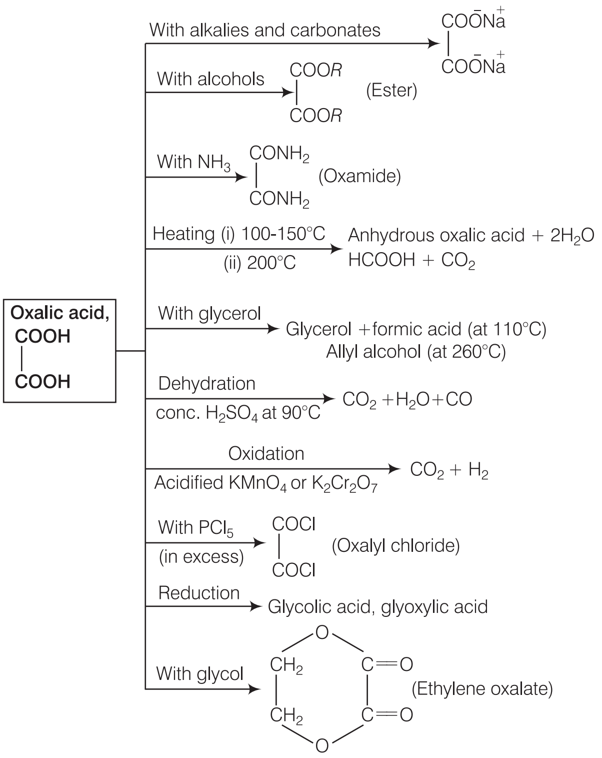
Physical Properties

(i) Dicarboxylic acids are crystalline solids with mp higher than corresponding monocarboxylic acids.

(ii) Lower members are readily soluble in water and solubility decreases with increase in molecular weight.

Chemical Properties

These show the following chemical properties:

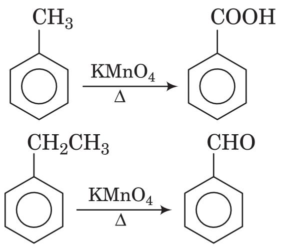
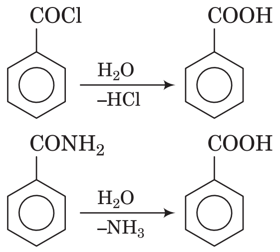
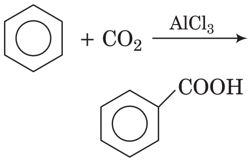
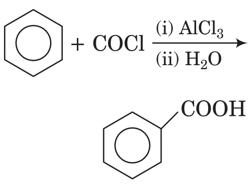


Aromatic Carboxylic Acid (Benzoic Acid)

These are compounds in which one or more carboxyl groups (—COOH) is attached to the ring directly.

Methods of Preparation

These are prepared through the following methods:

Methods	Reactions involved
1. Oxidation of side chain aromatic hydrocarbons	
2. Oxidation of primary alcohols or aldehydes	$\text{Alcohol} \xrightarrow[KMnO_4/\Delta]{\substack{\text{Strong oxidising agent}\\ K_2Cr_2O_7/\Delta \text{ or}}} \text{Acid}$ $\text{Aldehyde} \xrightarrow[\text{Tollen's reagent}]{\text{Mild oxidising agent}} \text{Acid}$
3. Hydrolysis of acid derivatives, nitriles	
4. Addition of CO_2 to benzene	
5. Friedel Craft's reaction	

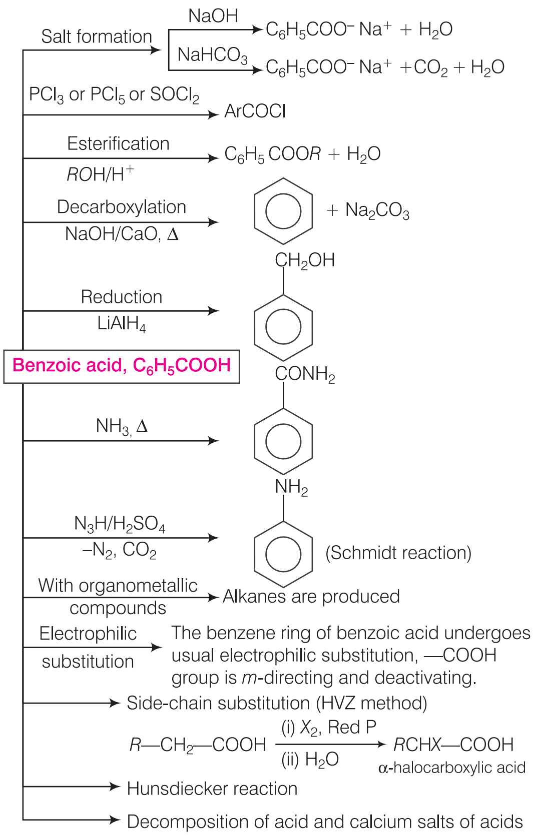
Physical Properties

(i) It is a colourless solid, mp is 122°C, soluble in hot water, diethyl ether, ethanol and benzene.

(ii) It is present in certain resins, particularly Agum-benzoin, belsams, in the urine of horses as hippuric acid.

Chemical Properties

These show the following chemical properties:

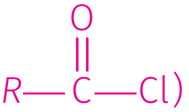


Acid Derivatives

The group of compounds obtained from acids by the replacement of —OH of carboxyl group by other atoms or groups (e.g. —Cl, —NH_2, —OCO*R*, —O*R*) are called acid derivatives.

Acid Chlorides

(Acyl Chlorides, $R—\overset{\displaystyle O}{\overset{\|}{C}}—Cl$)



Methods of Preparation

These are prepared by the following methods:

Methods	Reactions involved
1. From carboxylic acid	
(i) using $SOCl_2$	$RCOOH + SOCl_2 \longrightarrow RCOCl + SO_2 + HCl$
(ii) using PCl_5	$RCOOH + PCl_5 \longrightarrow RCOCl + HCl + POCl_3$
(iii) using PCl_3	$3RCOOH + PCl_3 \longrightarrow 3RCOCl + H_3PO_3$
2. From acid derivatives	$(RCO)_2O + PCl_5 \longrightarrow 2RCOCl + POCl_3$
3. By distillation of acid salts	
(i) distilling Na salts with PCl_3	$3RCOONa + PCl_3 \longrightarrow 3RCOCl + Na_3PO_3$
(ii) distilling Na salts with $POCl_3$	$3RCOONa + POCl_3 \longrightarrow 3RCOCl + NaCl + NaPO_3$
(iii) distilling Ca salts with SO_2Cl_2	$(RCOO)_2Ca + SO_2Cl_2 \longrightarrow 2RCOCl + CaSO_4$

Physical Properties

(i) These are colourless liquids with boiling points lower than corresponding acids (due to the absence of intermolecular H-bonding).

(ii) They have sharp pungent smell.

(iii) The higher members are colourless solids.

Nucleophilic Reactions
(Preference of Acyl chloride over Acetic Acid)

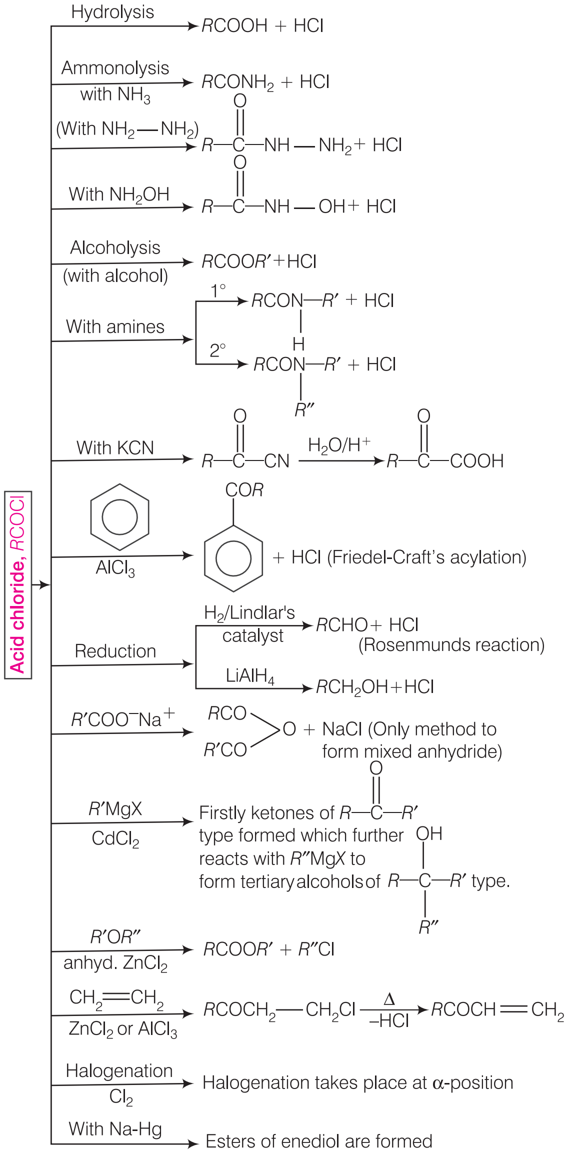
- Acyl chlorides are very reactive as compared to acetic acid. The chloride ion is an excellent leaving group as compared to hydroxide ion under normal conditions.
- Acyl chlorides can be used to prepare carboxylic acid derivatives, such as acid anhydrides, esters and amides, by reacting acid chlorides with salts of carboxylic acid, an alcohol or an amine respectively.
- In case of acyl chlorides, use of base (NaOH or pyridine) or excess amine is required to remove the hydrogen chloride as by-product and to catalyse the reaction.
- In case of acetic acid, reactions are reversible, often leading to low yields.
- Both of these reactants (CH_3COOH and CH_3COCl) involved in preparing acid derivatives but in case of acyl chlorides, reactions are fast and irreversible. This makes the two steps route often preferable to single step reaction with the carboxylic acid.

AMAZING REALITIES

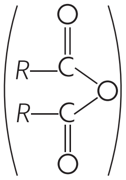
The Eiffel Tower can be 15 cm taller during the summer due to thermal expansion.

Chemical Properties

These show the following chemical properties:



Acid Anhydrides



Methods of Preparation

These are prepared by the following methods:

Methods	Reactions involved
1. From carboxylic acid by reacting with RCOCl	$RCOCl + R'COOH \xrightarrow{\text{Pyridine}} \left.\begin{matrix}RCO\\R'CO\end{matrix}\right\rangle O + HCl$
2. By reacting $CH\equiv CH$ with CH_3COOH followed by distillation	$CH\equiv CH + 2CH_3COOH \longrightarrow$ $CH_3—CH\left\langle\begin{matrix}OOCCH_3\\OOCCH_3\end{matrix}\right. \xrightarrow[\text{distillation}]{Hg^{2+}}$ $\underset{CHO}{\overset{CH_3}{|}} + \left.\begin{matrix}CH_3CO\\CH_3CO\end{matrix}\right\rangle O$
3. Dehydration of anhydrous acid	$2RCOOH \xrightarrow[P_2O_5]{\Delta}$ $\left.\begin{matrix}RCO\\R'CO\end{matrix}\right\rangle O + H_2O$
4. By reaction of acid halides with salts of fatty acids	$RCOONa + R'COCl \xrightarrow{\text{Pyridine}}$ $\left.\begin{matrix}RCO\\R'CO\end{matrix}\right\rangle O + NaCl$

Physical Properties

(i) These are colourless liquids with sharp, pungent smell, insoluble in water but dissolves due to hydrolysis.

(ii) Their boiling points are higher than corresponding acids.

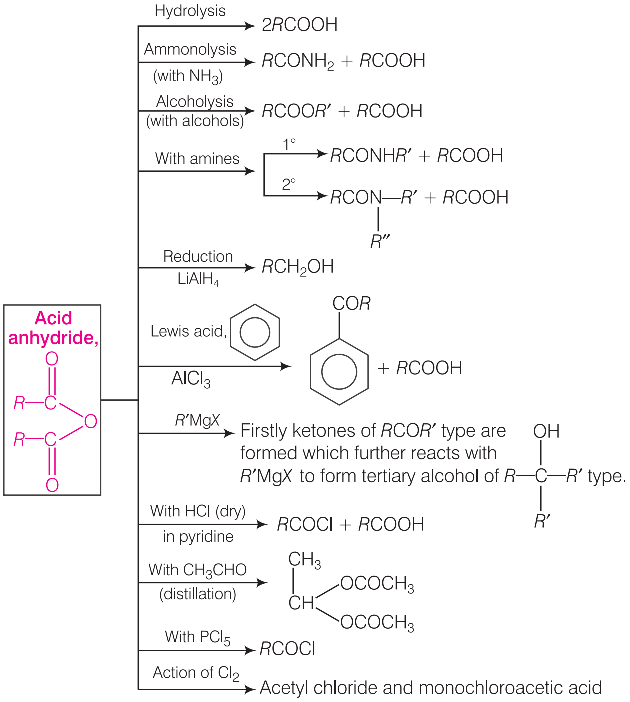
CHEMISTRY IN action

Teen Wins Big for a Homemade Polymer

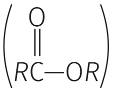
Kiara Nirghin a high school junior in Johannesburg created a biodegradable and superabsorbent material that can be planted alongside crops to create mini reservoirs of water in the soil. First, she boiled orange peels in water to produce a liquid rich in pectin, a highly absorbent carbohydrate. Then, she combined the pectin with pieces of dried orange peels and avocado skins, baked the mixture to remove moisture and crushed it all into a powder. Finally, she mixed the powder with more peels and skins. The resulting polymer could hold 300 times its weight in water. In tests, the invention kept soil moist and plants grown with it were taller and healthier and produced more flowers. Nirghin hopes her material will help drought-stricken communities improve their food security.

Chemical Properties

These show the following chemical properties:



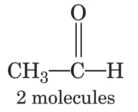
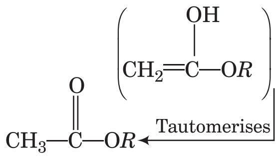
Esters



$$\left(R\overset{O}{\overset{\|}{C}}—OR\right)$$

Methods of Preparation

These are prepared by the following methods:

Methods	Reactions involved
1. From carboxylic acid (Esterification)	$RCO\boxed{OH + H}OR'$ Acid Alcohol $\xrightarrow{H^+} RCOOR' + H_2O$
2. Reacting acid derivatives with alcohols (alcoholysis)	$RCOCl + R'OH \longrightarrow RCOOR' + HCl$ $RCONH_2 + R'OH \longrightarrow RCOOR' + NH_3$ $\left.\begin{matrix}RCO\\RCO\end{matrix}\right\rangle O + R'OH \longrightarrow RCOOR' + RCOOH$
3. Reacting carboxylate salts with RX	$RCOO^-Na^+ + R'X \longrightarrow RCOOR' + NaX$ $RCOO^-Ag^+ + R'X \longrightarrow RCOOR' + AgX$
4. Reacting carboxylic acid with diazomethane (CH_2N_2).	$RCOOH + CH_2N_2 \longrightarrow RCOOCH_3 + N_2\uparrow$
5. By condensation of aldehyde in the presence of aluminium ethoxide.	 $CH_3—\overset{O}{\overset{\|}{C}}—H$ 2 molecules $\xrightarrow{Al(OC_2H_5)_3} CH_3COOC_2H_5$
6. With ketene and alcohols.	$H_2C{=}C{=}O + HOR \longrightarrow$  $\left(CH_2{=}\overset{OH}{\overset{\mid}{C}}—OR\right) \xrightarrow{\text{Tautomerises}} CH_3—\overset{O}{\overset{\|}{C}}—OR$
7. Reacting alkene with an acid in the presence of BF_3.	$RCOOH + CH_2{=}CH_2 \xrightarrow{BF_3} RCOOC_2H_5$

Physical Properties

(i) These are pleasant smelling liquids or solids.

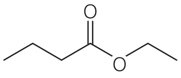
(ii) The boiling point of esters is lower than corresponding acids.

(iii) They are insoluble in water but good solvents of other organic compounds.

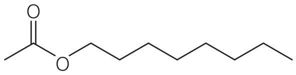
Fragrant Esters

Naturally occurring esters are present in both animals and plants. Small sized esters, alongwith other volatile organic compounds are responsible for the smells of fruits. Often, one compound plays a major role in producing the fruity smell. Different esters have different fragrances and flavours and various synthetic esters are used as flavourings in the food industry.

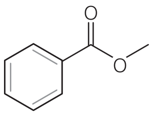
(i) Pineapple flavouring—Ethyl butanoate,



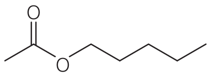
(ii) Orange odour—octyl ethanoate,



(iii) Marzipan odour—methyl benzoate,

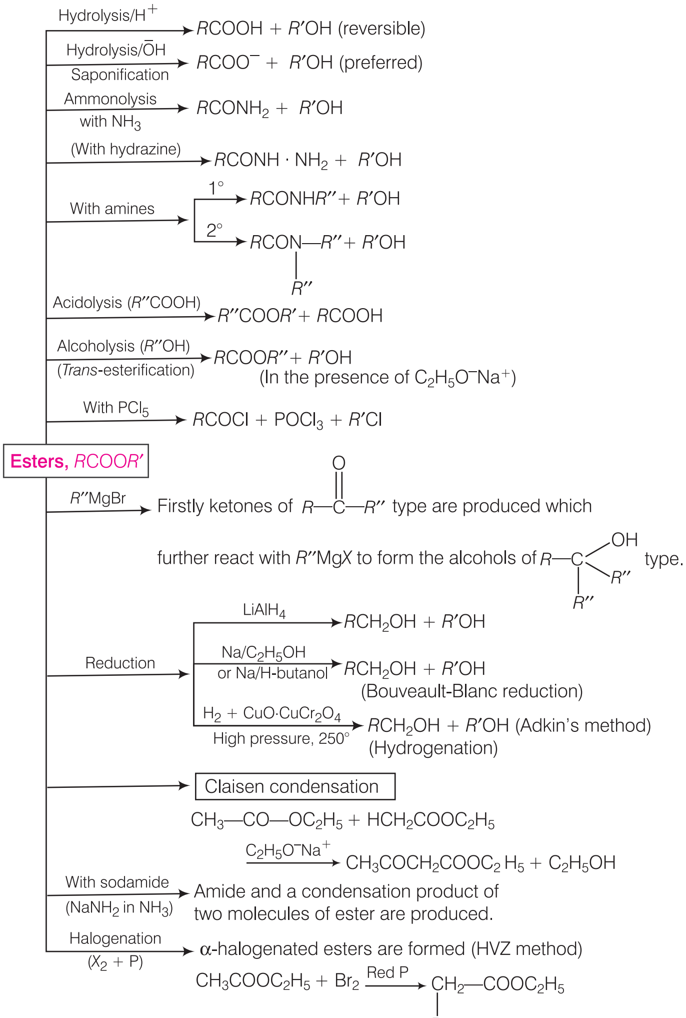


(iv) Banana odour—pentyl ethanoate,



Chemical Properties

These show the following chemical properties:



Esters, *RCOOR′*

- Hydrolysis/H^+ → $RCOOH + R'OH$ (reversible)
- Hydrolysis/$\bar{O}H$ Saponification → $RCOO^- + R'OH$ (preferred)
- Ammonolysis with NH_3 → $RCONH_2 + R'OH$
- (With hydrazine) → $RCONH \cdot NH_2 + R'OH$
- With amines → 1° $RCONHR'' + R'OH$; 2° $RCON(R'')—R'' + R'OH$
- Acidolysis ($R''COOH$) → $R''COOR' + RCOOH$
- Alcoholysis ($R''OH$) (*Trans*-esterification) → $RCOOR'' + R'OH$ (In the presence of $C_2H_5O^-Na^+$)
- With PCl_5 → $RCOCl + POCl_3 + R'Cl$
- $R''MgBr$ → Firstly ketones of $R—\overset{O}{\overset{\|}{C}}—R''$ type are produced which further react with $R''MgX$ to form the alcohols of $R—C(OH)(R'')R''$ type.
- Reduction →
  - $LiAlH_4$ → $RCH_2OH + R'OH$
  - Na/C_2H_5OH or Na/H-butanol → $RCH_2OH + R'OH$ (Bouveault-Blanc reduction)
  - $H_2 + CuO{\cdot}CuCr_2O_4$ High pressure, 250° → $RCH_2OH + R'OH$ (Adkin's method) (Hydrogenation)
- → Claisen condensation

$$CH_3—CO—OC_2H_5 + HCH_2COOC_2H_5 \xrightarrow{C_2H_5O^-Na^+} CH_3COCH_2COOC_2H_5 + C_2H_5OH$$

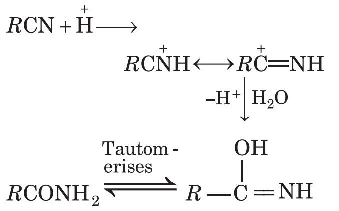
- With sodamide ($NaNH_2$ in NH_3) → Amide and a condensation product of two molecules of ester are produced.
- Halogenation ($X_2 + P$) → α-halogenated esters are formed (HVZ method)

$$CH_3COOC_2H_5 + Br_2 \xrightarrow{\text{Red P}} \underset{\substack{|\\ Br}}{CH_2}—COOC_2H_5$$

Acid Amides $\left(R\underset{\substack{\|\\ O}}{C}—NH_2\right)$

Methods of Preparation

These are prepared by the following methods:

Methods	Reactions involved
1. By heating ammonium salt of an acid	$RCO\bar{O}\overset{+}{N}H_4 \xrightarrow{\Delta} RCONH_2 + H_2O$
2. By partial hydrolysis of alkyl cyanides	 $RCN + \overset{+}{H} \longrightarrow RC\overset{+}{N}H \longleftrightarrow R\overset{+}{C}{=}NH \xrightarrow{-H^+,\ H_2O} R—\overset{OH}{\overset{\vert}{C}}{=}NH \underset{}{\overset{\text{Tautomerises}}{\rightleftharpoons}} RCONH_2$
3. By heating acid with urea	$RCOOH + H_2N\overset{O}{\overset{\|}{C}}NH_2 \longrightarrow RCONH_2 + CO_2 + H_2O$

Physical Properties

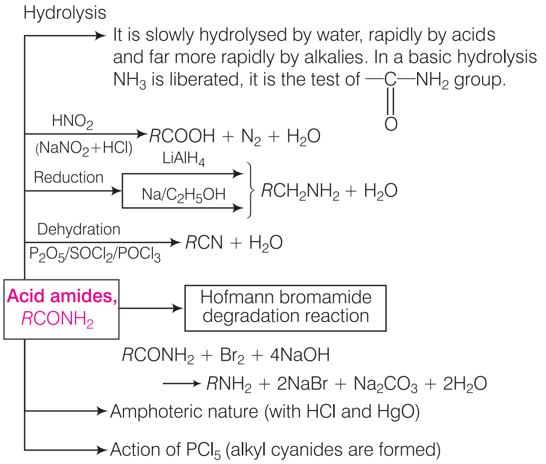
(i) These are white odourless, crystalline solids with sharp mp, higher than that of corresponding acids.

(ii) These are soluble in water

$$\cdots H—HN—CR = O\cdots H—HN—CR = O\cdots$$

Chemical Properties

These show the following chemical properties:



Acid amides, *RCONH₂*

- Hydrolysis → It is slowly hydrolysed by water, rapidly by acids and far more rapidly by alkalies. In a basic hydrolysis NH_3 is liberated, it is the test of $—\underset{\substack{\|\\ O}}{C}—NH_2$ group.
- HNO_2 ($NaNO_2$+HCl) → $RCOOH + N_2 + H_2O$
- Reduction → $LiAlH_4$ / Na/C_2H_5OH → $RCH_2NH_2 + H_2O$
- Dehydration $P_2O_5/SOCl_2/POCl_3$ → $RCN + H_2O$
- → Hofmann bromamide degradation reaction

$$RCONH_2 + Br_2 + 4NaOH \longrightarrow RNH_2 + 2NaBr + Na_2CO_3 + 2H_2O$$

- → Amphoteric nature (with HCl and HgO)
- → Action of PCl_5 (alkyl cyanides are formed)

CHEMISTRY IN action

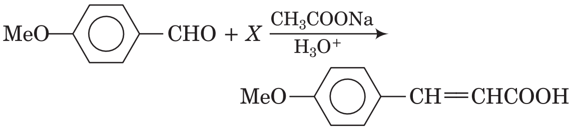
Some catalysts contribute their own oxygen for reactions

Chemical reactions that release oxygen in the presence of a catalyst are known as **oxygen-evolution reactions**. These reactions are a crucial part of chemical energy storage processes, including water splitting, electrochemical carbon dioxide reduction, and ammonia production. The kinetics of this type of reaction are generally slow, but compounds called metal oxides can have catalytic activities that vary over several orders of magnitude, with some exhibiting the highest such rates reported to date. The physical origin of these observed catalytic activities is not well-understood. Now scientists have shown that in some of these catalysts oxygen doesn't come only from the water molecules surrounding the catalyst material instead some of it comes from within the crystal lattice of the catalyst material itself. The procedure used for the experiment was tracer technique. This was proved by first using water with a heavier isotope of oxygen (oxygen 18), and later switching to ordinary water (made with oxygen 16). The detection of the heavier oxygen 18 in the resulting gas proves that this came out of the catalyst.

MASTER STROKES

1. Etard's reaction involves the preparation of benzaldehyde from
(*a*) toluene (*b*) ethyl benzene
(*c*) benzoyl chloride (*d*) sodium benzoate

2.



The compound *X* is
(*a*) CH_3COOH (*b*) $BrCH_2—COOH$
(*c*) $(CH_3CO)_2O$ (*d*) CHO —COOH

3. Which of the following reagent is used to bring about the following transformation: But-2-ene to ethanal?
(*a*) $K_2Cr_2O_7$ in acidic medium (*b*) CrO_2Cl_2 / H_3O^+
(*c*) PCC (*d*) O_3/H_2O—Zn dust

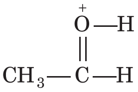
4. The compound with which ethanal does not react is
(*a*) HCl (*b*) Cl_2
(*c*) PCl_5 (*d*) *aq.* $NaHSO_3$

5. The most reactive compound towards formation of cyanohydrin on treatment with HCN followed by acidification is
(*a*) benzaldehyde (*b*) *p*-nitrobenzaldehyde
(*c*) phenylacetaldehyde (*d*) *p*-hydroxybenzaldehyde

6. Consider the following aldol condensation reaction,

$$CH_3—CHO \xrightarrow{H_2SO_4} CH_3—CH=CH—CHO$$

The nucleophile is
(*a*) $\bar{C}H_2—CHO$ (*b*) $CH_2=CH—\bar{O}$
(*c*) $CH_2 = CH—OH$ (*d*)



$CH_3—\overset{\overset{\overset{+}{O}—H}{\|}}{C}—H$

7. The major organic product in the following reaction is

$$CH_2O(\text{excess}) + CH_3CH_2CHO \xrightarrow{\text{conc. NaOH}} \xrightarrow{H_3O^+}$$

(*a*) $CH_3—C(CH_2OH)_3$ (*b*) CH_3OH
(*c*) HCOOH (*d*) Both (a) and (c)

8. Match the conversions given in Column I with the suitable reagents given in Column II and choose the correct option from the codes given below.

Column I	Column II
A. Ethanenitrile to ethanol	p. O_3/H_2O-Zn dust
B. Allyl alcohol to propanal	q. DIBAL-H
C. But-2-ene to ethanol	r. PCC

Codes

	A	B	C
(*a*)	p	q	r
(*b*)	r	q	p
(*c*)	q	r	p
(*d*)	q	p	r

9. An organic compound *X* gives a red precipitate on heating with Fehling's solution. Which one of the following reactions yields *X* as a major product?
(*a*) $HCHO \xrightarrow[\text{(ii) } H_2O]{\text{(i) } CH_3MgI}$
(*b*) $C_2H_5Br + AgOH \xrightarrow{\Delta}$
(*c*) $2C_2H_5Br + Ag_2O \xrightarrow{\Delta}$
(*d*) $C_2H_2 + H_2O \xrightarrow[1\%\ HgSO_4,\ 60°C]{40\%H_2SO_4}$

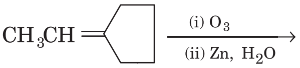
10. One of the following named reaction is an example of "disproportionation reaction". Identify it.
(*a*) Birch reduction
(*b*) Aldol condensation
(*c*) Reimer-Tiemann reaction
(*d*) Cannizzaro reaction

11. $A \xrightarrow{\text{Dil. NaOH}} (CH_3)_2C = CHCOCH{=}C(CH_3)_2.$

Identify '*A*'
(*a*) Acetone (*b*) Acetaldehyde
(*c*) Propionaldehyde (*d*) Formaldehyde

12. In the conversion of Grignard reagent into an aldehyde, the other component used is
(*a*) ethyl formate (*b*) ethyl acetate
(*c*) ethyl cyanide (*d*) hydrogen cyanide

13. Acetaldehyde is not obtained in which of the following reactions.
(*a*) $CH_2=CH—CH=CH_2 \xrightarrow[\text{(ii) Zn, } H_2O]{\text{(i) } O_3}$
(*b*)



(*c*) $HC \equiv CH + H_2O \xrightarrow[H_2SO_4]{HgSO_4}$
(*d*) $CH_3COCl + H_2 \xrightarrow{Pd\text{-}BaSO_4}$

14. Which of the following statements is incorrect?
(*a*) The addition of HCN to carbonyl compounds takes place under basic or neutral conditions as HCN is a weak acid and its ionisation increases in neutral/basic medium
(*b*) $CH_3CH_2COCH_3$ has larger equilibrium constant than $CH_3CH_2CH_2CHO$
(*c*) When acetaldehyde reacts with HCN, there is formation of a chiral carbon but product is optically inactive mixture of two resolvable components
(*d*) RCH_2OH is oxidised to $RCHO$ by Cu, some RCH_2OH is left unreacted

15. The most suitable reagent for the conversion of $R—CH_2—OH \rightarrow R—CHO$ is **[JEE Main 2014]**
(*a*) $KMnO_4$
(*b*) $K_2Cr_2O_7$
(*c*) CrO_3
(*d*) PCC (pyridinium chlorochromate)

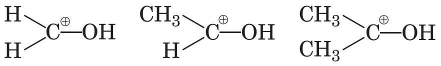
16. The Cannizzaro's reaction is not given by

(a) trimethyl acetaldehyde *(b)* acetaldehyde
(c) benzaldehyde *(d)* formaldehyde

17. Which of the following gives an aldehyde on dry distillation?

(a) Calcium formate + calcium acetate
(b) Calcium acetate + calcium benzoate
(c) Calcium acetate
(d) Calcium benzoate

18. Protonation of a carboxyl compound is said to increase its electrophilic nature for nucleophilic attack. Arrange the following carboxyl compounds in increasing order of potential energy.

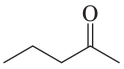
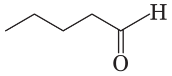
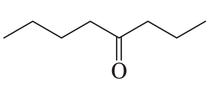
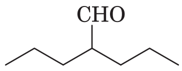


(I) (II) (III)

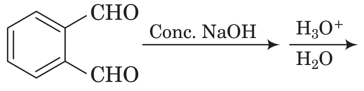
(a) III < II < I *(b)* I < II < III
(c) III < I < II *(d)* II < I < III

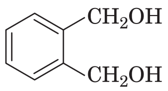
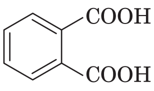
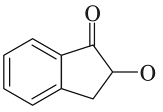
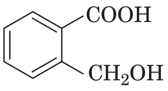
19. What is the final major product of the following sequence of reaction ,

$$CH_3—CH_2—CH_2—C\equiv C—H \xrightarrow{NaNH_2} \xrightarrow{CH_3CH_2CH_2—Br} \xrightarrow[H_2SO_4]{HgSO_4} ?$$

(a) 
(b) 
(c) 
(d) 

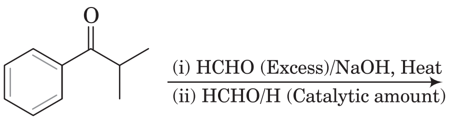
20. Predict the major organic product in the following reaction.

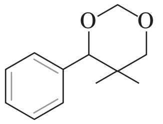
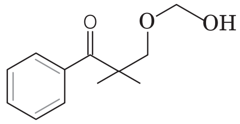
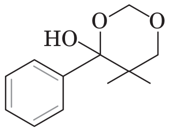
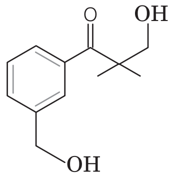


(a) 
(b) 
(c) 
(d) 

21. The major product of the following reaction sequence is

[JEE Advanced 2016]



(a) 
(b) 
(c) 
(d) 

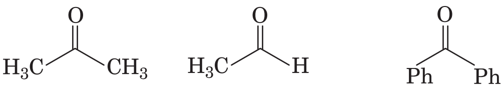
22. Which is necessary for the conversion of butane-2-one into propanoic acid?

(a) Tollen's reagent *(b)* Fehling solution
(c) $NaOH/I_2/H^+$ *(d)* $NaOH/NaI/H^+$

23. Butan-2-one can be converted to propanoic acid by which of the following?

(a) $NaOH, NaI/H^+$ *(b)* Fehling's solution
(c) $NaOH, I_2/H^+$ *(d)* Tollen's reagent

24. The order of reactivity of phenyl magnesium bromide with the following compounds is

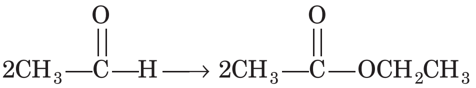


(I) (II) (III)

(a) II > III > I *(b)* I > III > II
(c) II > I > III *(d)* All of these

25. Which reagent given below can differentiate propanal from propanone?

(a) Schiff's reagent
(b) $NaHSO_3$
(c) 2, 4-dinitrophenyl hydrazine
(d) NaCN/HCN

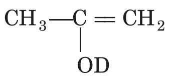
26. 

$$2CH_3—\overset{O}{\overset{\|}{C}}—H \longrightarrow 2CH_3—\overset{O}{\overset{\|}{C}}—OCH_2CH_3$$

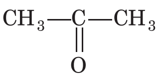
The name of the reaction and reagent used for it is

(a) Cannizzaro reaction, NaOH
(b) Aldol condensation, $\bar{O}H$
(c) Tischenko reaction, $Al(OC_2H_5)_3$
(d) Perkin reaction, $(CH_3CO)_2O$

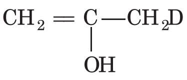
27. The enol form of acetone after treatment with D_2O gives

(a) 

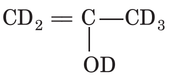
$CH_3—\underset{OD}{\underset{|}{C}}=CH_2$

(b) 

$CH_3—\underset{O}{\underset{\|}{C}}—CH_3$

(c) 

$CH_2=\underset{OH}{\underset{|}{C}}—CH_2D$

(d) 

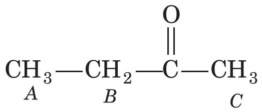
$CD_2=\underset{OD}{\underset{|}{C}}—CD_3$

28. If the enolate ion combines with carbonyl group of ester, we get

(a) aldol *(b)* α, β-unsaturated ester
(c) β-keto ester *(d)* acid

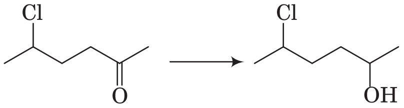
RAPID CONCEPT REVISION

29. In the given compound, which of the following marked hydrogen(s) is most acidic?


$CH_3—CH_2—\overset{O}{\overset{\|}{C}}—CH_3$ (A, B, C)

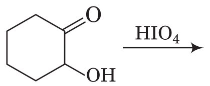
(a) Only A
(b) Only B
(c) Only C
(d) Both B and C

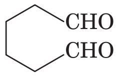
30. The reagent which can best bring about the following transformation is



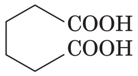
(a) $LiAlH_4$
(b) $NaBH_4$
(c) Zn(Hg)-HCl
(d) $Al[(CH_3)_2CHO]_3$

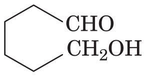
31. The product obtained in the following reaction is



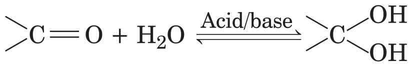
(a)


(b)


(c)


(d)


32. Carbonyl compounds form hydrates

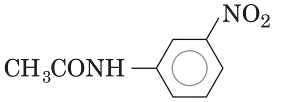

$$>C=O + H_2O \xrightleftharpoons{\text{Acid/base}} >C<\begin{matrix}OH\\OH\end{matrix}$$

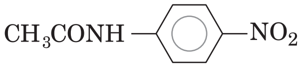
K_1, K_2, K_3, K_4 are the equilibrium constants of hydrate formation with CCl_3CHO, HCHO, CH_3CHO, CH_3COCH_3. Increasing order of equilibrium constants is

(a) $K_3 < K_1 < K_4 < K_2$
(b) $K_2 < K_1 < K_4 < K_3$
(c) $K_4 < K_3 < K_2 < K_1$
(d) $K_1 < K_2 < K_3 < K_4$

33. The decreasing reactivity order of the following amides towards hydroxide ion which promoted hydrolysis is

I.

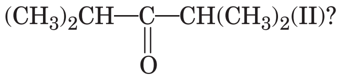

II.


III.


IV.

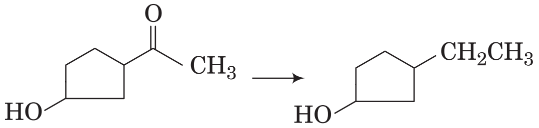

(a) II > III > IV > I
(b) III > II > IV > I
(c) I > IV > III > II
(d) IV > I > II > III

34. Which of the following reaction conditions is not involved in the steps of conversion of $CH_3CH_2CH_3$(I) into $(CH_3)_2CH—\underset{\underset{O}{\|}}{C}—CH(CH_3)_2$(II)?



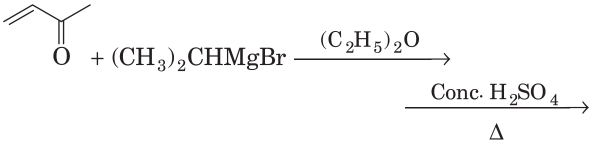
(a) Br_2/Δ
(b) Mg/ether + KCN
(c) H_3O^+
(d) $H_2SO_4/HgSO_4$

35. The appropriate reagent for the following transformation is

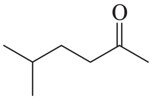


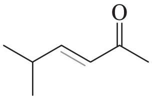
(a) Zn(Hg), HCl
(b) NH_2NH_2, OH^-
(c) H_2/Ni
(d) $NaBH_4$

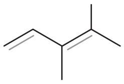
36. In the reaction given below.

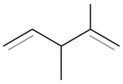


The final major product is

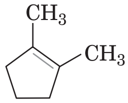
(a)


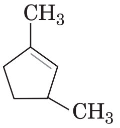
(b)


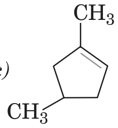
(c)


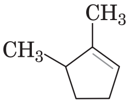
(d)


37. Which compound would give 5-keto-2-methyl hexanal upon ozonolysis? **[JEE 2015 Main]**

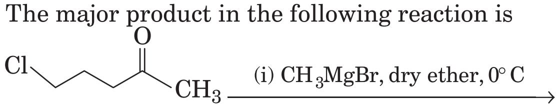
(a)


(b)


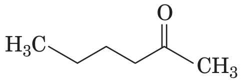
(c)


(d)


38. The major product in the following reaction is



[JEE Advanced 2014]

(a)


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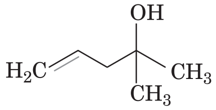
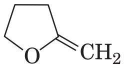
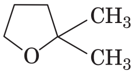


(c)


(d)


39. Which of the following on treatment with Baeyer's reagent will give *meso*-tartaric acid?

(a) Fumaric acid *(b)* Maleic acid

(c) Both (a) and (b) *(d)* None of these

40. Which of the following carboxylic acids is not reduced to the corresponding 1° alcohol by $LiAlH_4$?

(a) $BrCH_2CH_2CH_2COOH$

(b) Cyclohexane carboxylic acid

(c) $(Z)—CH_3CH = CHCH_2COOH$

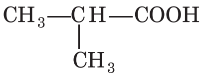
(d) $CH_3CH(CH_3)CH_2COOH$

41. An organic compound *A* upon reacting with NH_3 gives *B*. On heating, *B* give *C*. *C* in the presence of KOH reacts with Br_2 to give $CH_3CH_2NH_2$. *A* is

[JEE Main 2013]

(a) CH_3COOH *(b)* $CH_3CH_2CH_2COOH$

(c)



$CH_3—\underset{CH_3}{\underset{|}{C}}H—COOH$

(d) CH_3CH_2COOH

42. When benzene sulphonic acid and *p*-nitrophenol are treated with $NaHCO_3$, the gases released are respectively

(a) SO_2, NO_2 *(b)* SO_2, NO

(c) SO_2, CO_2 *(d)* CO_2, CO_2

43. The compound that does not liberate CO_2, on treatment with aqueous sodium bicarbonate solution, is [JEE Advanced 2013]

(a) benzoic acid *(b)* benzenesulphonic acid

(c) salicylic acid *(d)* carbolic acid (phenol)

44. Benzamide on treatment with $POCl_3$ gives

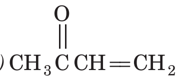
(a) aniline *(b)* benzonitrile

(c) chlorobenzene *(d)* benzyl amine

45. $CH_2{=}CH—CH{=}CH_2 \xrightarrow[\substack{\text{(ii) Mg / ether} \\ \text{(iii) } CO_2 \\ \text{(iv) } H_3O^+}]{\text{(i) HBr}} X.$

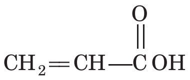
What is *X* ?

(a)



$CH_3\overset{\overset{O}{||}}{C}CH{=}CH_2$

(b)



$CH_2{=}CH—\overset{\overset{O}{||}}{C}OH$

(c) $CH_3CH = CHCH_2COOH$ *(d)* $CH_3CH = CHCH_2CHO$

46. Which of the following statements is incorrect?

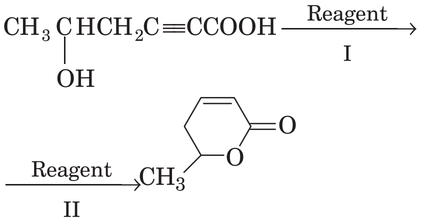
(a) Melting point of dicarboxylic acids are higher than those of monocarboxylic acids

(b) The O—H bond does not lie in the same plane of carbonyl group of carboxylic acid

(c) Molecular mass of acetic acid in benzene is 120 instead of 60

(d) Melting and boiling points of aliphatic acids are usually lower than those of aromatic acids of comparable molecular masses

47.



$CH_3\underset{OH}{\underset{|}{C}}HCH_2C{\equiv}CCOOH \xrightarrow[\text{I}]{\text{Reagent}} \xrightarrow[\text{II}]{\text{Reagent}}$

Reagents I and II are

(a) $Pt / H_2, H_3O^+$

(b) $Li / NH_3, H_3O^+$

(c) H_2/Lindlar's catalyst, H_3O^+

(d) H_2O / Na, H_3O^+

48. When aqueous CH_3CH_2COONa is electrolysed, there are formation of various organic products. Which is the major product?

(a) $CH_2{=}CH_2$

(b) CH_3CH_3

(c) $CH_3CH_2COOCH_2CH_3$

(d) $CH_3CH_2CH_2CH_3$

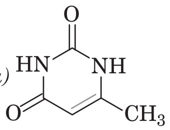
49. Acetamide is treated separately with the following reagents. Which one of these would give methyl amine?

(a) PCl_5 *(b)* $NaOH + Br_2$

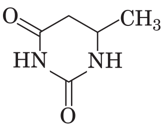
(c) Soda lime *(d)* Hot conc.H_2SO_4

50. Enolic form of acetoacetic ester reacts with urea to form

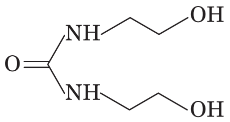
(a)



(b)



(c)



(d) None of these

Answers

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

AMPLIFIER

COORDINATION COMPOUNDS

Innovative problems targetted to improve your conceptual learning.

1. *Why geometrical isomerism is not possible in tetrahedral complexes having two different types of unidentate ligands with the central metal ion?*

- The tetrahedral complexes do not show geometrical isomerism because the relative positions of the unidentate ligands attached to the central metal atom are same with respect to each other.

2. *Oxalic acid is commonly used to remove rust stains. Justify.*

- Rust is hydrated iron (III) oxide, $Fe_2O_3 \cdot xH_2O$. Iron (III) forms soluble complex with chelating oxalate ion furnished by oxalic acid.

$$Fe_2O_3 + 6C_2O_4^{2-} + 6H_3O^+ \longrightarrow \underset{\text{Soluble complex}}{2[Fe(C_2O_4)_3]^{3-}} + 9H_2O$$

3. *Why does NH_3 readily form complexes but NH_4^+ does not?*

- NH_3 contain a lone pair of electrons which coordinates with the metal ion to form the complex compound. However, in NH_4^+ ion, the lone pair is bound to H^+ and therefore, not available for bonding to metal ion. Therefore, NH_4^+ does not form complexes readily.

4. *Why $K_4[Fe(CN)_6]$ is non-toxic whereas KCN is highly toxic.*

- The compound $K_4[Fe(CN)_6]$ ionises in water as:

$$K_4[Fe(CN)_6] \rightleftharpoons 4K^+ + [Fe(CN)_6]^{4-}$$

whereas KCN ionises as,

$$KCN \longrightarrow K^+ + CN^-$$

The free CN^- ion is highly toxic. Thus, KCN which gives free CN^- ions is also highly toxic. On the other hand, the solution of $K_4[Fe(CN)_6]$ gives $[Fe(CN)_6]^{4-}$ ion which does not contain free CN^- ions and hence it is non-toxic.

5. *$Cu(OH)_2$ is soluble in NH_4OH, but not in NaOH solution. Why?*

- $Cu(OH)_2$ is soluble in NH_4OH due to the formation of soluble complex, $[Cu(NH_3)_2](OH)_2$. But no such complex is formed by the reaction of $Cu(OH)_2$ with NaOH.

6. *In case of lead poisoning, calcium dihydrogen salt of EDTA is used. Explain.*

- EDTA coordinates with lead in the body because of more soluble lead-EDTA complex, which can be eliminated in urine without causing any harmful effects. The calcium salt of EDTA is used so that any excess EDTA will not remove Ca^{2+} ions from the body.

7. *Why only transition metals are known to form π-complexes?*

- Transition metals/ions have empty *d*-orbitals into which the electron pairs can be donated by ligands containing π-electrons, i.e. electrons in their π molecular orbitals, e.g. $CH_2{=}CH_2$, C_5H_5 and C_6H_6, etc.

8. *Is metal carbonyls and organometallics are same?*

- Yes, metal carbonyls are called organometallics because C-atom of CO linked to the metal. In fact, the metal-carbon bonds have both σ and π-character.

9. *The values of dissociation constants of $[Cu(NH_3)_4]^{2+}$ and $[Co(NH_3)_6]^{3+}$ are 1.0×10^{-12} and 6.2×10^{-36}, respectively. Which complex would be more stable and why?*

- Smaller the value of the dissociation constant, more stable is the complex in the solution. Thus, $[Co(NH_3)_6]^{3+}$ is more stable than $[Cu(NH_3)_4]^{2+}$ ion.

10. *Why the two complexes, $PtCl_4 \cdot 2NH_3$ and $PtCl_4 \cdot 2KCl$ does not give precipitate of AgCl with $AgNO_3$ solution?*

- $PtCl_4 \cdot 2NH_3$ has the structural formula, $[Pt(NH_3)_2Cl_4]$ and $PtCl_4 \cdot 2KCl$ has the structural formula, $K_2[PtCl_6]$. In both cases, the Cl^- ions are present in the coordination sphere and are not ionisable. Therefore, both of these does not give tests for Cl^- ions with $AgNO_3$ solution.

11. *Crystal field splitting in tetrahedral complexes (Δ_t) is smaller than octahedral complexes (Δ_o). Why?*

- (i) In tetrahedral complexes there are four ligands while there are six ligands in octahedral complexes. Therefore, lesser number of ligands will produce less crystal field splitting.
  (ii) In tetrahedral complexes, none of the orbitals is pointing directly towards the ligands and therefore, splitting is less.

12. *In the synergic bonding of metal carbonyls, which orbitals are involved in the overlap?*

(i) Filled bonding π_{2p} orbital of CO with empty metal d-orbital resulting in σ-bond between metal atom and carbon atom of CO.

(ii) Filled metal d-orbital with empty anti-bonding π^*_{2p} orbital of CO resulting in additional π-bond between the metal and same CO molecule (back bonding).

13. *$[Co(CN)_6]^{3-}$ and $[CoF_6]^{3-}$ both are octahedral complexes. Then, what is the difference between the two?*

$[Co(CN)_6]^{3-}$ is an inner orbital or low spin complex (containing strong field ligand) involving the hybridisation d^2sp^3 while $[CoF_6]^{3-}$ is an outer orbital or high spin complex (containing weak field ligand) involving sp^3d^2-hybridisation.

14. *Why a chelating complex is more stable than unchelated complex?*

Chelating complex is more stable than unchelated complex because the ligand in chelated complex is attached to the metal ion from many points. Thus, there is a strong force of attraction between the metal ion and the ligand.

15. *Why complexes are preferred over simple metal ions in the electrolytic bath for electroplating?*

Complexes dissociate slowly and hence give a smooth and even deposit on articles, e.g. articles can be electroplated with silver or gold much more smoothly and evenly from solutions of the complexes, $[Ag(CN)_2]^-$ and $[Au(CN)_2]^-$, than from the solutions of the simple ions.

16. *$[Ti(H_2O)_6]^{3+}$ is coloured while $[Sc(H_2O)_6]^{3+}$ is colourless. Why?*

In $[Ti(H_2O)_6]^{3+}$, Ti^{3+} ion has one electron in the d-subshell (lower energy, t_{2g} d-orbitals) which can absorb light in the visible region resulting into d-d transition (jump into higher energy, e_g-orbitals). As a result, green and yellow portions of light are absorbed. The complex has the complementary colour, *viz.* purple. In $[Sc(H_2O)_6]^{3+}$, Sc^{3+} has no d-electron. Hence, no light is absorbed for d-d transition. Hence, it is colourless.

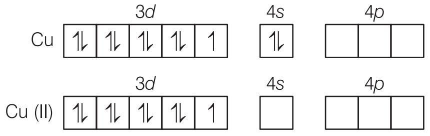
17. *Account for the different magnetic moment of hexacyanoferrate (III) ion and hexafluoridoferrate (III) ion.*

Magnetic moment ($\mu = \sqrt{n(n+2)}$ BM, where n = number of unpaired electrons) depends upon unpaired electrons. Higher the number of unpaired electrons greater will be the magnetic moment. In $[Fe(CN)_6]^{3-}$, CN^- is a strong field ligand and therefore, electrons pair up in d-subshell leaving one unpaired electron. The complex is inner orbital complex.

On the other hand, in $[FeF_6]^{3-}$, F^- is a weak field ligand and therefore, electrons in $3d$-subshell do not get pair up. It is outer orbital complex and has 5 unpaired electrons. Thus, $[FeF_6]^{3-}$ has greater magnetic moment than $[Fe(CN)_6]^{3-}$.

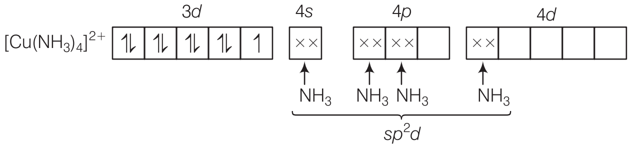
18. *According to X-ray studies, the complex $[Cu(NH_3)_4]^{2+}$ has a square planar geometry, hence involve dsp^2-hybridisation, but actually it involve sp^2d-hybrid orbitals. Explain.*

The oxidation state of copper in $[Cu(NH_3)_4]^{2+}$ is $+2$ with $3d^9$ outer electronic configuration.



The X-ray studies have shown that this complex ion has a square planar geometry with dsp^2-hybridisation. This can be achieved by promoting one electron from one of the $3d$-orbitals into higher energy vacant $4p$-orbitals. This means that the complex could be easily oxidised, i.e. Cu^{2+} will change into Cu^{3+}. However, this is not true because Cu^{3+} ions are rare.

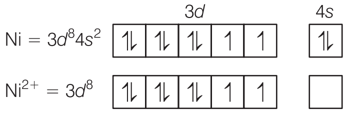
The spectroscopic studies have also shown that electron is not present in the $4p$-orbital. To solve this anomaly, the electron in $3d$-orbitals remain undistributed and it involves the use of outer $4d$-orbitals for hybridisation.



19. *Explain, why platinum (II) and palladium (II) form square planar complexes almost exclusively, but only a few nickel (II) complexes are square planar?*

Platinum (II) and palladium (II) complexes have greater value of Δ. The greater Δ values imply greater stabilisation of the square planar configuration, because the d^8 ions have CFSE = 2.456 *vs* $-1.20\ \Delta$ for octahedral coordination spheres. The greater the magnitude of Δ, the greater is the difference in CFSE. When the difference in CFSE is sufficient to overcome the loss of bonding energy in two bonds (6 or 4), the square complex is stabilised.

20. *Why nickel does not form low spin octahedral complexes?*



For low spin, electrons should pair up. This will produce only one empty d-orbital. Hence, d^2sp^3-hybridisation is not possible to form octahedral complexes.

TARGET NEET 2017

MEDI QUEST

Comprehensive Simulator Test Series for NEET & AIIMS

NEET
SCALE UP

Mock Questions from Complete Syllabus with Answer key.

FULL TEST
2
(Complete Syllabus)
WITH ANSWER KEY

INSTRUCTIONS

- This test consists of 45 questions and each question is allotted 4 marks for correct response.
- Candidates will be awarded marks as stated above for correct response of each question. 1/4 marks will be deducted for indicating incorrect response of each question. No deduction from the total score will be made if no response is indicated for an item in the answer sheet.
- There is only one correct response for each question. Filling up more than one response in any question will be treated as wrong response and marks for wrong response will be deducted according as per instructions.

1. The increasing order of CFSE value for the following compounds is

$\underset{\text{(I)}}{[Rh(NH_3)_6]^{3+}}$; $\underset{\text{(II)}}{[Ir(NH_3)_6]^{3+}}$; $\underset{\text{(III)}}{[Co(NH_3)_6]^{3+}}$

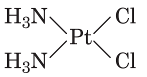
(a) I < II < III
(b) II < I < III
(c) III < I < II
(d) III < II < I

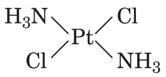
2. Which one of the following statements related to lanthanides is incorrect?

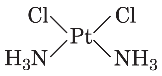
(a) La^{3+} and Lu^{3+} are diamagnetic
(b) Lanthanides are strong electropositive elements
(c) The basic character of oxides and hydroxides increases from $La(OH)_3$ to $Lu(OH)_3$
(d) Cerium shows +4 oxidation state

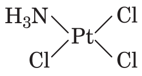
3. Identify the product (P) in the following reaction,

$$[Pt(NH_3)_4]^{2+} \xrightarrow{2Cl^-} \text{Product (P)}$$

(a)


(b)


(c)


(d)


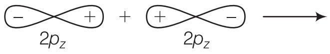
4. Among the following, which one is an incorrect statement?

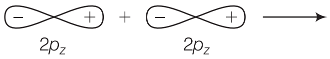
(a) Fluorine does not form oxide with oxygen but it forms oxy-fluoride
(b) Bromine does not show + 7 oxidation state
(c) $(SiH_3)_3N$ is stronger base than $(CH_3)_3N$
(d) Nitric oxide is paramagnetic

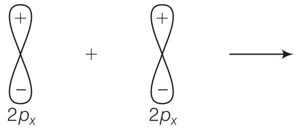
5. Which one of the following sets of orbitals is include in the t_{2g} orbital?

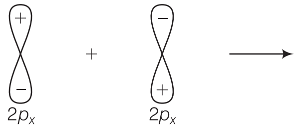
(a) $d_{x^2-y^2}, d_{z^2}$
(b) d_{xy}, d_{yz}, d_{z^2}
(c) d_{xy}, d_{yz}, d_{xz}
(d) $d_{x^2-y^2}, d_{xz}, d_{yz}$

6. Which one of the following *p*-orbitals combination forms two nodal planes?

(a)


(b)


(c)


(d)


7. The correct geometry of ClF_3 and $_3^-$ respectively are

(a) trigonal bipyramidal; trigonal bipyramidal
(b) trigonal bipyramidal; linear
(c) octahedral; trigonal planar
(d) trigonal planar; linear

8. Which of the following reactions does not undergoes disproportionation reaction?

(a) $Cl_2 + 2\bar{O}H(aq) \longrightarrow ClO^-(aq) + Cl^-(aq) + H_2O(l)$
(b) $2H_2O_2(aq) \longrightarrow 2H_2O(l) + O_2(g)$
(c) $2F_2(g) + 2H_2O(l) \longrightarrow 4HF(aq) + O_2(g)$
(d) $2F_2(g) + 2OH^-(aq) \longrightarrow 2\ {}^-(aq) + OF_2(g) + H_2O(l)$

9. Which one of the following statements is incorrect regarding the behaviour of lithium?

(a) Li is the strongest reducing agent among all the alkali metals
(b) Li nitrate when heated gives Li nitrite, whereas other alkali metal nitrates give the corresponding oxide
(c) Lithium reacts with N_2 to form Li_3N
(d) Lithium reacts directly with carbon to form an ionic carbide

10. Which of the following reactions does not used for the preparation of diborane?

(a) $BF_3 + LiH \xrightarrow{\Delta}$
(b) $BF_3 + LiAlH_4 \longrightarrow$
(c) $NaBH_4 + I_2 \longrightarrow$
(d) $BCl_3 + H_2O \longrightarrow$

11. The geometry of the adduct formed from the following acid-base reaction is

$$BF_3 + NH_3 \longrightarrow \text{Adduct}$$

(a) square planar
(b) linear
(c) tetrahedral
(d) trigonal bipyramidal

12. The bond order and magnetic behaviour of C_2 molecule respectively are

(a) 2, paramagnetic
(b) 2, diamagnetic
(c) 3, paramagnetic
(d) 1, diamagnetic

13. Which one of the following substance gives brick red colour in flame test and breaks down on heating to form oxygen and a brown gas is evolved?

(a) Magnesium carbonate
(b) Magnesium nitrate
(c) Barium nitrate
(d) Calcium nitrate

14. Which of the following complex species involves d^2sp^3-hybridisation?

(a) $[Fe(CN)_6]^{3-}$
(b) $[Cr(NH_3)_6]^{2+}$
(c) $[FeF_6]^{3-}$
(d) $[CoF_6]^{3-}$

15. Which of the following statements about $AlCl_3$ is incorrect?

(a) Its aqueous solution conducts electricity
(b) It involves back bonding between Cl and Al
(c) It exists as a dimer
(d) It is a covalent compound

16. 10 g of acetic acid is dissolved in 1 L ethyl alcohol. If they do not react chemically with each other, then the molality of solution is
(Given, $d_{C_2H_5OH} = 0.789\ g\ mL^{-1}$)

(a) $0.28\ mol\ kg^{-1}$
(b) $0.4\ mol\ kg^{-1}$
(c) $0.3\ mol\ kg^{-1}$
(d) $0.2\ mol\ kg^{-1}$

17. The solubility of M_2X_3 in pure water, assuming that neither kind of ion reacts with H_2O if the solubility product of M_2X_3, $(K_{sp} = 1.1 \times 10^{-23})$ is

(a) $1.0 \times 10^{-23}\ mol\ L^{-1}$
(b) $1.0 \times 10^{-25}\ mol\ L^{-1}$
(c) $1.0 \times 10^{-5}\ mol\ L^{-1}$
(d) $2.0 \times 10^{-5}\ mol\ L^{-1}$

18. Select the correct arrangement of cubic unit cell in their increasing coordination number.

(a) scc < fcc < bcc
(b) bcc < fcc < scc
(c) scc < bcc < fcc
(d) fcc < scc < bcc

19. Equal volumes of three acidic solutions of pH 3, 4 and 5 are mixed in a vessel. What will be the H^+ ion concentration in the mixture?

(a) 1.11×10^{-4} M
(b) 3.7×10^{-4} M
(c) 3.7×10^{-3} M
(d) 1.11×10^{-8} M

20. For the following combustion reaction at 298 K,

$$C(s) + \frac{1}{2}O_2(g) \longrightarrow CO(g)$$

Which of the following alternative is correct?

(a) $\Delta H > \Delta U$
(b) $\Delta H = \Delta U$
(c) $\Delta H < \Delta U$
(d) ΔH and ΔU does not exhibit any relation with each other

21. Which one of the following sets of quantum numbers represents the highest energy level in an atom?

(a) $n = 4, l = 0, m = 0, s = +1/2$
(b) $n = 3, l = 1, m = 1, s = +1/2$
(c) $n = 3, l = 2, m = -2, s = +1/2$
(d) $n = 3, l = 0, m = 0, s = +1/2$

22. Which of the following compounds does not show the intramolecular hydrogen bond?

(a) *o*-nitrophenol
(b) Ethylene glycol
(c) *o*-hydroxy benzaldehyde
(d) Conc. acetic acid

23. Specific conductance of a 0.05 N solution of weak acid is 5.25×10^{-4} mho cm^{-1}. At this dilution, degree of dissociation is 0.0825. The equivalent conductivity of weak acid at infinite dilution is

(a) 172.3 mho cm^{2}eq^{-1}
(b) 273.3 mho cm^{2}eq^{-1}
(c) 150.5 mho cm^{2}eq^{-1}
(d) 127.3 mho cm^{2}eq^{-1}

24. If current strength of 125 A is passed through a solution of Al_2O_3, how much time will be required to liberate 100 g of Al?

(a) 96500 s
(b) 8755.77 s
(c) 8577.77 s
(d) 8500 s

25. Arsenic (III) sulphide forms a sol with a negative charge. Which of the following ionic substances should be most effective in coagulating the sol ?

(a) Na_3PO_4
(b) $Al_2(SO_4)_3$
(c) KCl
(d) $MgCl_2$

26. Elevation in boiling point of an aqueous urea solution is 0.52°C ($K_b = 0.52$°C mol^{-1} kg). The mole fraction of urea in this solution is

(a) 0.982 *(b)* 0.018
(c) 0.0567 *(d)* 0.942

27. In which of the following case, van't Hoff factor (*i*) remains unchanged?

(a) $KMnO_4$ reduced to MnO_2 in alkaline medium
(b) $PtCl_4$ reacts with KCl
(c) *aq.* $ZnCl_2$ reacts with *aq.* NH_3
(d) *aq.* $FeCl_3$ reacts with *aq.* $K_4[Fe(CN)_6]$

28. One ampere of current strength is being passed through a metallic wire. The number of electrons flowing per minute through a point in the wire is

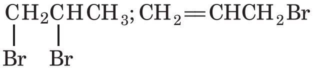
(a) 6.24×10^{18} *(b)* 62.4×10^{18}
(c) 6.24×10^{23} *(d)* 6.24×10^{19}

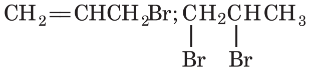
29. Consider the following chemical reactions,

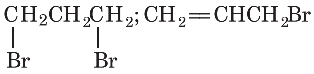
$$\text{I. } CH_2{=}CHCH_3 + Br_2 \xrightarrow{\text{High temp.}} A$$

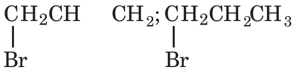
$$\text{II. } CH_2{=}CHCH_3 + Br_2 \xrightarrow[CCl_4]{\text{Room temp.}} B$$

A and *B* respectively are

(a)

$\underset{Br}{CH_2}\underset{Br}{CH}CH_3; CH_2{=}CHCH_2Br$

(b)

$CH_2{=}CHCH_2Br; \underset{Br}{CH_2}\underset{Br}{CH}CH_3$

(c)

$\underset{Br}{CH_2}CH_2\underset{Br}{CH_2}; CH_2{=}CHCH_2Br$

(d)

$\underset{Br}{CH_2}CH\quad CH_2; \underset{Br}{CH_2}CH_2CH_3$

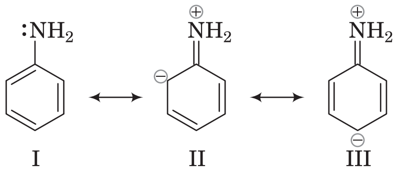
30. How many stereoisomers are possible for 2, 4-heptadiene?

(a) 2 *(b)* 4 *(c)* 6 *(d)* 8

31. Which of the following polymers is produced when caprolactum is partially hydrolysed and then heated to 250°C?

(a) Nylon-6,6 *(b)* PVC
(c) Nylon-6 *(d)* Dacron

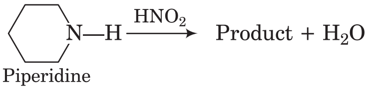
32. The resonating structures of aniline are given below,

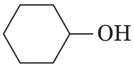


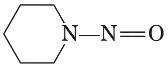
The correct order of stability is

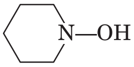
(a) I < II < III *(b)* I > II > III
(c) II > I > III *(d)* II < III > I

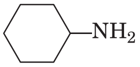
33. Identify the product for the following transformation,



(a)


(b)


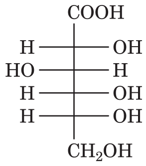
(c)


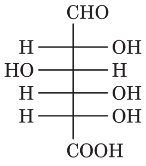
(d)


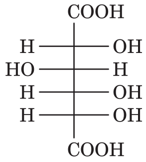
34. D-glucose on warming with nitric acid form a product *A*.

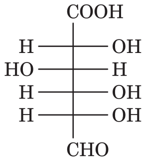
$$\text{D-glucose} + HNO_3 \longrightarrow A$$

The correct structure of *A* is

(a)


(b)


(c)


(d)


35. Some amino acids are given below, Phenylalanine (I), Threonine (II), Cystein (III), Tyrosine (IV)

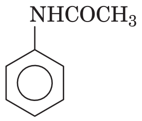
Which amino acids contain aromatic rings?

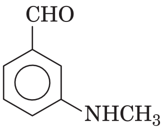
(a) I and II *(b)* I and IV *(c)* II and III *(d)* I, II and IV

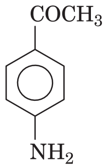
36. Electrolysis of an aqueous solution of sodium salt of a fatty acid gives an alkane having

(a) one carbon more than that of parent salt
(b) one carbon less than that of parent salt
(c) same carbon as parent salt
(d) two carbon more than that of parent salt

37. A compound *A*, C_8H_9NO, was boiled with NaOH, an oily liquid *B* was obtained alongwith a salt *C*. Liquid *B* gave carbylamine reaction, while *C* on heating with soda lime produced methane. The structure of compound *A* was

(a)


(b)


(c)


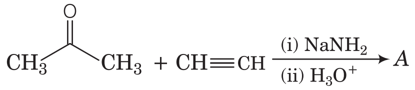
(d) Both (a) and (c)

38. Arrange the following alkyl halides in order of increasing reactivity to S_N2 displacement.

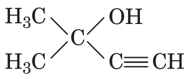
I. $CH_3CH_2CH_2Cl$
II. $CH_3CH_2CH_2CH_3Br$
III. $CH_3CH_2CHBrCH_3$
IV. $(CH_3)_2CClCH_2CH_3$

(a) II < I < III < IV (b) IV < I < II < III
(c) IV < III < I < II (d) III < IV < I < II

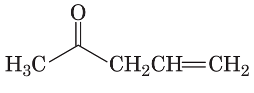
39. Identify the correct structure of the product *A* formed in the reaction,



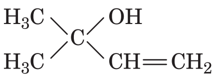
(a)



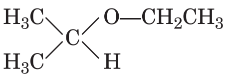
(b)



(c)

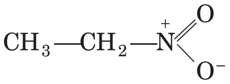


(d)

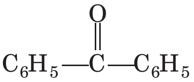


40. Which among the given molecules can exhibit tautomerism?

I.

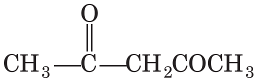


II.



$C_6H_5-\overset{\overset{O}{\|}}{C}-C_6H_5$

III.

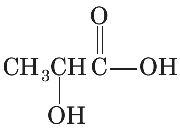


$CH_3-\overset{\overset{O}{\|}}{C}-CH_2COCH_3$

(a) Only II (b) I and II
(c) I and III (d) Only III

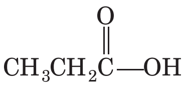
41. The correct order of acidic strength of the following carboxylic acids is

I.



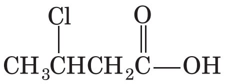
$CH_3\underset{\underset{OH}{|}}{CH}\overset{\overset{O}{\|}}{C}-OH$

II.



$CH_3CH_2\overset{\overset{O}{\|}}{C}-OH$

III.

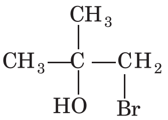


$CH_3\overset{\overset{Cl}{|}}{C}HCH_2\overset{\overset{O}{\|}}{C}-OH$

(a) I > II > III
(b) I > III > II
(c) III > II > I
(d) II > I > III

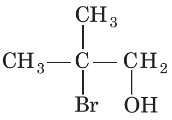
42. The structure of the product formed when 2-methylpropene is treated with Br_2/H_2O is

(a)



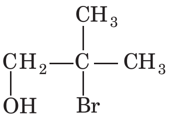
$CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{HO}{|}}{C}}-\underset{\underset{Br}{|}}{CH_2}$

(b)



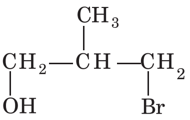
$CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{Br}{|}}{C}}-\underset{\underset{OH}{|}}{CH_2}$

(c)



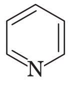
$\underset{\underset{OH}{|}}{CH_2}-\overset{\overset{CH_3}{|}}{\underset{\underset{Br}{|}}{C}}-CH_3$

(d)

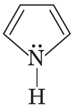


$\underset{\underset{OH}{|}}{CH_2}-\overset{\overset{CH_3}{|}}{CH}-\underset{\underset{Br}{|}}{CH_2}$

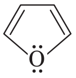
43. Which among the given heterocyclic compounds, imparting the properties of a (weak) base



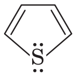
(I)



(II)



(III)



(IV)

(a) Only I (b) Only III
(c) Only IV (d) Only II

44. Which one of following statements is/are correct?

(a) In the extraction of metals, the value of standard oxidation potentials of metal should be low in aqueous solution
(b) On electrolysis, metal dissolves from anode and deposits on cathode
(c) Electroplating of tin on iron sheets protects rusting of iron
(d) All of the above

45. Which of the following statement is correct?

(a) Reactions with low activation energy are usually exothermic
(b) The rate law sometimes enables to deduce the mechanism of a reaction
(c) The rate law for a reaction is an algebraic expression relating the forward reaction rate to product concentration
(d) Increase in the total pressure of a gas phase reaction increase the fraction of collisions effective in producing reaction

Answers

1. (c)	**2.** (c)	**3.** (b)	**4.** (c)	**5.** (c)
6. (d)	**7.** (a)	**8.** (c)	**9.** (b)	**10.** (d)
11. (c)	**12.** (b)	**13.** (d)	**14.** (a)	**15.** (b)
16. (d)	**17.** (c)	**18.** (c)	**19.** (b)	**20.** (a)
21. (c)	**22.** (d)	**23.** (d)	**24.** (c)	**25.** (b)
26. (b)	**27.** (c)	**28.** (a)	**29.** (b)	**30.** (b)
31. (c)	**32.** (b)	**33.** (b)	**34.** (c)	**35.** (b)
36. (a)	**37.** (a)	**38.** (c)	**39.** (a)	**40.** (c)
41. (b)	**42.** (a)	**43.** (a)	**44.** (d)	**45.** (d)

TARGET CBSE 2017

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BOARD EXAM

(PAPER ONE PREP UP)

Typical Questions with Crispy Solutions.

FULL TEST
3
(COMPLETE SYLLABUS)
WITH SOLUTIONS

INSTRUCTIONS

- All questions are compulsory.
- Question numbers 1 to 5 are very short answer type questions and carry 1 mark each.
- Question numbers 6 to 10 are short answer type I questions and carry 2 marks each.
- Question numbers 11 to 22 are also short-answer type II questions and carry 3 marks each.
- Question numbers 23 is a value based type question and carry 4 marks.
- Question numbers 24 to 26 are long-answer type questions and carry 5 marks each.
- Use log tables, if necessary. Use of calculators is not allowed.

Very Short Answer Type Questions [1 Mark]

1. Why is it that only sulphide ores are concentrated by "froth floatation process"?

2. What is the reason for the stability of colloidal sols? [All India 2016]

3. Give an example each of a molecular solid and an ionic solid.

4. How copper is extracted from a low grade ore of it? [All India 2011]

5. The reaction, $A + 2B \longrightarrow C$, obeys the rate $= k[A]^{1/2}[B]^{3/2}$. What is the order of reaction?

Short Answer Type I Questions [2 Marks]

6. (i) In non-ideal solution, what type of deviation shows the formation of maximum boiling azeotropes?

(ii) At same temperature, H_2 is more soluble in water than He. Which of them has higher value of K_H and why?

7. If the radius of bromide ion is 0.182 nm, how large a cation can fit in each of the tetrahedral hole?

8. Hess's law is just an extension of the law of conservation of energy. Justify this statement.

9. (i) Write the structures of the following compounds.

(a) BrF_3 (b) XeF_4

(ii) What happens when

(a) SO_2 gas is passed through an aqueous solution of Fe^{3+} salt?

(b) XeF_4 reacts with SbF_5? [All India 2016]

10. PH_3 forms bubbles when passed slowly in water but NH_3 dissolves. Why?

Short Answer Type II Questions [3 Marks]

11. $MgSO_4$ gives a precipitate with NH_4OH but not with the mixture of NH_4Cl and NH_4OH. Why?

12. Depict the galvanic cell in which the reaction,

$$Zn(s) + 2Ag^+(aq) \longrightarrow Zn^{2+}(aq) + 2Ag(s)$$

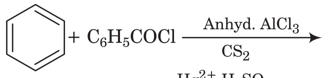
takes place and also answer the following questions.

(i) Which of the electrode is negatively charged?
(ii) The carriers of the current in the cell.
(iii) Individual reaction at each electrode.

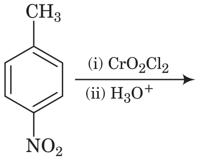
13. Give reasons for the following.

(i) Aniline does not undergo Friedel-Crafts reaction.
(ii) $(CH_3)_2NH$ is more basic than $(CH_3)_3N$ in an aqueous solution.
(iii) Primary amines have higher boiling point than tertiary amines.

14. Write the structures of the main products of the following reactions. [Delhi 2012]

(i) 

(ii) $H_3C-C\equiv C-H \xrightarrow{Hg^{2+}, H_2SO_4}$

(iii) 

Or

Aldehydes are generally more reactive than ketones in nucleophilic addition reactions. Why?

15. (i) Name the drug which prevents the interaction of histamine with the receptors present in the stomach wall.

(ii) On electrolysing $CuSO_4$ solution in presence of Pt, the solution becomes colourless. Why?

(iii) Why NH_4Cl is added in the precipitation of group III hydroxides before the addition of NH_4OH ?

16. An element crystallises in a bcc lattice with edge length of 500 pm. The density of the element is 7.5 g cm^{-3}. How many atoms are present in 300 g of the element?

17. A balloon of diametre 20 m weighs 100 kg. Calculate its pay-load, if it is filled with He at 1.0 atm and 27°C. Density of air is 1.2 kg m^{-3} (R = 0.0821 dm^3 atm K^{-1} mol^{-1}).

18. Why guanidine is the strongest organic N-base ($K_b \cong 1$)?

19. How will you convert the following,

(i) Propanone to propan-2-ol

(ii) Ethanal to 2-hydroxy propanoic acid

(iii) Toluene to benzoic acid

20. Hydrogen peroxide (H_2O_2) decomposes according to the equation,

$$H_2O_2\,(l) \longrightarrow H_2O(l) + \frac{1}{2}O_2(g)$$

Given, that $\Delta H^\circ = -98.2$ kJ mol^{-1} and

$\Delta S^\circ = +70.1$ $JK^{-1}mol^{-1}$. Is this reaction spontaneous at

25°C, how?

21. Account for the fact that the tendency of catenation decreases down the group 14 elements?

22. (i) Give one example of polyester used as a synthetic fibre.

(ii) Name the compounds from which polyester is prepared.

(iii) What type of polymerisation takes place in the formation of the polyester from these compounds?

Value Based Type Question [4 Marks]

23. Mr. Robin works in a large university's physical plant department which oversees the day-to-day operation of the building on campus. The university currently maintains 14 days scale air conditioning units that still use CFCs production. A member of the committee comes to Mr. Robin, because she is concerned about the potential costs of replacing so many units.

She ask to Mr. Robin following questions. Answer the following questions by assuming that you are Mr. Robin.

(i) Since, a cooling is sealed (the refrigerant is kept under pressure in a sealed system), why does the continuously use of CFCs risk to the environment?

(ii) Will the university simply buy a different refrigerant to replace the CFCs and use in the existing units.

(iii) What would be the concern associated with such refrigerant replacement?

Long Answer Type Questions [5 Marks]

24. (i) How will you convert phenol to benzoic acid?

(ii) An organic compound A having molecular formula C_6H_6O gives a characteristic colour with aqueous $FeCl_3$ solution. A on treatment with CO_2 and NaOH at 400 K under pressure gives B which on acidification gives a compound C. The compound C reacts with acetyl chloride to give D which is a popular pain killer. Deduce the structure of A, B, C and D.

Or

(i) Ethereal solution of an organic compound A when treated with Mg gives B. B on treatment with ethanol followed by acid hydrolysis gave propan-2-ol. Identify the compound A and B.

(ii) How will you distinguish between the following pairs?

(a) CH_3OH and C_2H_5OH

(b) Propan-1-ol and 2-methyl propan-2-ol

(c) Ethanol and propan-1-ol

25. Calculate the average volume available to a molecule in a sample of nitrogen gas at STP. What is the average distance between neighbouring molecule if a nitrogen molecule is assumed to be spherical?

Or

What kind of isomerism are exhibited by following pair of compounds?

(i) *n*-butyl alcohol and isobutyl alcohol

(ii) *sec*-butyl alcohol and *t*-butyl alcohol

(iii) Maleic acid and fumaric acid

(iv) *d* and *l*-forms of lactic acid

(v) *o*-hydroxy toluene and benzyl alcohol

26. (i) Account for the following.

(a) Mn shows the highest oxidation state of +7 with oxygen but with fluorine, it shows the highest oxidation state of +4.

(b) Cr^{2+} is a strong reducing agent.

(c) Cu^{2+} salts are coloured while Zn^{2+} salts are white.

(ii) Complete the following equations.

(a) $2MnO_2 + 4KOH + O_2 \xrightarrow{\Delta}$

(b) $Cr_2O_7^{2-} + 14H^+\ 6I^- \longrightarrow$

Or

The elements of 3*d*-transition series are given as

Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn.

Answer the following questions.

(i) Write the element which shows maximum number of oxidation states. Give reason.

(ii) Which element has the highest melting point?

(iii) Which element shows only +3 oxidation state?

(iv) Which element is a strong oxidising agent in +3 oxidation state and why?

Answers with Explanation

1. Because pine oil preferentially wets the sulphide ores and hence brings it to the froth and impurities (gangue) are wetted by water.

2. The presence of equal and similar charges on the colloidal particles prevents coagulation.

3. Molecular solid $\longrightarrow$ Solid CO_2, Ionic solid $\longrightarrow Na^+Cl^-$

4. Copper is extracted by hydrometallurgy from low grade ores. It is leached out using acid or bacteria.

$$Cu + H_2SO_4 \longrightarrow CuSO_4 + H_2\uparrow$$

5. Order of reaction $= \frac{1}{2} + \frac{3}{2} = \frac{4}{2} = 2$

6. (i) Negative deviation from Raoult's law.

(ii) He has higher value of K_H because if the gas has more solubility, its K_H value will be more.

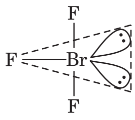
7. For tetrahedral voids, $\frac{r^+}{r^-} = 0.414$

For maximum value of r^+,

$$r^+ = 0.414 \times 0.182$$
$$= 7.5 \times 10^{-2} \text{ nm}$$

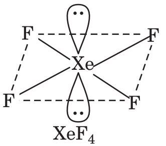
8. The law of conservation of energy states that energy can neither be created nor destroyed. Hess's law also predicts the similar fact that total energy change during the same course of reaction is independent of the path by which reaction is achieved.

9. (i) (a)



BrF_3
(T-shaped)

(b)



XeF_4
(Square planar)

(ii) (a) SO_2 gas reduces Fe^{3+} to Fe^{2+}

$$2SO_2 + 2Fe^{3+} + 4H_2O \longrightarrow 2Fe^{2+} + 2SO_4^{2-} + 8H^+$$

(b) XeF_4 reacts with covalent pentafluoride (SbF_5) to form an adduct.

10. NH_3 forms H-bond with water but PH_3 does not form H-bond with water.

11. The dissociation of NH_4OH is suppressed in presence of NH_4Cl and thus $[OH^-]$ diminishes to such an extent that $[Mg^{2+}][OH^-]^2 < K_{sp}$.

12. $Zn|Zn^{2+}||Ag^+|Ag$ is Daniel cell.

(i) Anode of Zn with negative charge; cathode of Ag with positive charge.

(ii) Zn to Ag in outer circuit and Ag to Zn inside the cell.

(iii) **Anode** $Zn \longrightarrow Zn^{2+} + 2e^-$ (Oxidation)

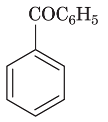
Cathode $2Ag^{2+} + 2e^- \longrightarrow 2Ag$ (Reduction)

13. (i) $\underset{\substack{\text{Aniline}\\\text{(Lewis base)}}}{C_6H_5\ddot{N}H_2} + \underset{\text{(Lewis acid)}}{AlCl_3} \longrightarrow \underset{\text{(Complex)}}{[C_6H_5NH_2]^+[AlCl_3]^-}$

(ii) Basic strength of $(CH_3)_2NH$ and $(CH_3)_3N$ depends upon the stabilisation of their conjugate acids by a number of factors such as H-bonding, steric hindrance of alkyl groups and $+I$-effect of alkyl groups.

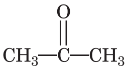
(iii) Intermolecular H-bonding is present in primary amines but not in tertiary amines.

14. (i)



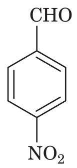
Benzophenone

(ii)



$\underset{\text{Acetone}}{CH_3-\overset{\overset{O}{\|}}{C}-CH_3}$

(iii)



para-nitrobenzaldehyde

Or

Aldehydes are more reactive towards nucleophilic addition reactions than ketones due to inductive effect and steric effect.

15. (i) Cimetidine (Tagamet).

(ii) Because the coloured $Cu^{2+}(aq)$ ions are reduced to Cu.

(iii) To control the concentration of $\bar{O}H$ (common ion effect) otherwise hydroxides of IV group will precipitate.

16. Density of unit cell $(\rho) = \frac{Z \times M}{a^3 \times N_A}$

where, Z = number of atoms present per unit cell (for bcc lattice, $Z = 2$)

M = atomic mass of the element, a = edge length

N_A = Avogadro's number

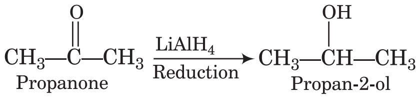
17. Volume of balloon $= \frac{4}{3}\pi r^3$

Mass of He in balloon $(w) = \frac{pVM}{RT}$

Payload = mass of air displaced – total mass

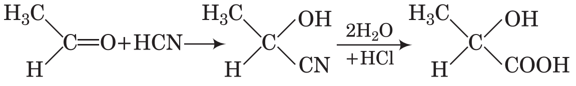
18. Both guanidine and its conjugate acid, the guanidinium ion, are stabilised by delocalisation.

19. (i)



$\underset{\text{Propanone}}{CH_3-\overset{\overset{O}{\|}}{C}-CH_3} \xrightarrow[\text{Reduction}]{LiAlH_4} \underset{\text{Propan-2-ol}}{CH_3-\overset{\overset{OH}{|}}{CH}-CH_3}$

(ii)



Ethanal

Acetaldehyde cyanohydrin

2-hydroxy propanoic acid

(iii) $\underset{\text{Toluene}}{C_6H_5CH_3} \xrightarrow[\text{(oxidation)}]{K_2Cr_2O_7+H_2SO_4} \underset{\text{Benzoic acid}}{C_6H_5COOH}$

20. $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$

21. In case of group 14 elements, the atomic size increases down the group, as a result of which, the bond dissociation enthalpy decreases steadily.

22. (i) Terylene

(ii) It is a condensation polymer of ethylene glycol and terephthalic acid.

(iii) Condensation polymerisation.

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Typical Questions without Solutions

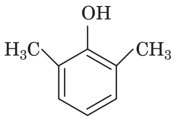
INSTRUCTIONS

- All questions are compulsory.
- Questions number 1 to 5 are very short answer type questions and carry 1 mark each.
- Questions 6 to 10 are short answer type I questions and carry 2 marks each.
- Question number 11 to 22 are also short answer type II questions and carry 3 marks each.
- Question number 23 is a value based type questions and carry 4 marks.
- Question number 24 to 26 are long-answer type questions and carry 5 marks each.
- Use log table, if necessary. Use of calculators is not allowed.

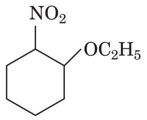
Very Short Answer Type Questions [1 Mark]

1. Give the IUPAC names of the following compounds.

(i)



(ii)



2. Sodium salts of some acids are very useful as food preservatives. Give the name of two such acids.

3. What is denaturation and renaturation of proteins?

4. $Pb(NO_3)_2$ on heating gives a brown gas which undergoes dimerisation on cooling. Identify the gas. [All India 2016]

5. Out of *o* and *p*-dibromobenzene which one has higher melting point and why?

Short Answer Type I Questions [2 Marks]

6. When a coordination compound, $CoCl_3 \cdot 6NH_3$ is mixed with $AgNO_3$, three moles of AgCl are precipitated per mole of the compound. Write,

(i) structural formula of the complex.
(ii) IUPAC name of the complex.

7. A 0.1539 molal aqueous solution of cane sugar (molar mass = 342 g mol^{-1}) has a freezing point of 271 K while the freezing point of pure water is 273.13 K. What will be the freezing point of an aqueous solution containing 5 g of glucose (mol. mass = 180 g mol^{-1}) per 100 g of solution? [All India 2007]

8. Explain the following observations:

(i) Co^{2+} is easily oxidised to Co^{3+} in the presence of a strong ligand.
(ii) CO is a stronger complexing reagent than NH_3. [Delhi 2012]

9. On increasing the temperature, solubility of lead nitrate in water increases while solubility of lead acetate decreases. Why?

10. Metals *A* and *B* have reduction potentials of – 0.76 V and + 0.80 V, respectively. Which of these metals will react with H_2SO_4 liberating H_2 and why?

Or

The + 3 oxidation states of lanthanum (Z = 57), gadolinium (Z = 64) and lutetium (Z = 71) are especially stable. Why?

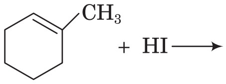
Short Answer Type II Questions [3 Marks]

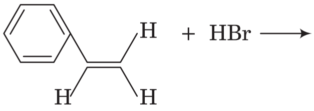
11. Electrolysis of a solution of $MnSO_4$ in aqueous sulphuric acid is a method for the preparation of MnO_2 as per reaction,

$$Mn^{2+}(aq) + 2H_2O \longrightarrow MnO_2(s) + 2H^+(aq) + H_2(g)$$

On passing a current of 27 A for 24 h, 1 kg of MnO_2 is formed. What is the value of current efficiency? Write the reaction taking place at the cathode and anode, respectively?

12. Complete the following reactions.

(i) 

(ii) 

(iii) $CH_3CH_2CH{=}CH_2 + HBr \longrightarrow$ [Foreign 2012]

Or

Answer the following questions.

(i) Why soaps does not work in hard water?

(ii) What are the main constituents of dettol?

(iii) How do antiseptics differ from disinfectants? [Delhi 2011, 2009]

13. How could you achieve the following conversion?

(i) Nitrobenzene to aniline.

(ii) Alkyl halide to quaternary ammonium salt.

(iii) Aniline to benzonitrile. [Delhi 2007]

14. The hexaaqua manganese (II) ion contains five unpaired electrons while the hexacyano manganese (II) ion contains only one unpaired electron. Explain using crystal field theory.

15. The rate constant for the first order decomposition of H_2O_2 is given by the following equation:

$$\log k = 14.2 - \frac{1.0 \times 10^4}{T} \text{K}$$

Calculate E_a and rate constant (K) if its half-life period is 200 minutes.

16. A mixture of SO_3, SO_2 and O_2 gases is maintained in a 10 L flask at a temperature at which the equilibrium constant for the reaction is 100.

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$

If the number of moles of SO_2 and SO_3 in the flask are equal, how many moles of O_2 are present?

17. Calcium metal crystallises in a face-centred cubic lattice with edge length of 0.556 nm. Calculate the density of the metal if it contains (i) 0.5% Frenkel defects and (ii) 0.2% Schottky defects.

18. (i) What does designation 66 in nylon-6,6 polymer means?

(ii) Which polymer is obtained when free radical polymerisation of chloroprene occurs? Write the structure of the polymer thus obtained. [Foreign 2011]

19. Give reason for the following observations.

(i) *p*-dichlorobenzene has higher melting point than those of *o* and *m*-isomers.

(ii) Haloarenes are less reactive than haloalkanes towards nucleophilic substitution reaction.

(iii) The treatment of alkyl chloride with aqueous KOH leads to the formation of alcohol but in the presence of alcoholic KOH, alkene is the major product. [All India 2009 C, Delhi 2008, 2008 C]

20. At temperature of 380°C, the half-life period for the first order decomposition of H_2O_2 is 360 min. Activation energy of the reaction is 200 kJ mol^{-1}. Then, find the time required for 75% decomposition of H_2O_2 at temperature of 450°C.

21. Tendency to form pentahalides decreases down the group 15 of the periodic table. Account for this observation. [CBSE 2011]

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

Value Based Type Question [4 Marks]

23. Nimisha and Ankita were two good friends study in the same school. One day both were going school through the street of Rajeev chowk. One worker standing on 3rd floor of a building was painting the building. Suddenly, some drops of paint dropped to Ankita's shirt. She became worried regarding stain of paint. Nimisha has advised her to use the ethyl alcohol which is used in laboratory to remove the stains of paint?

Answer the following questions.

(i) What is the colour of ethanol used in laboratory?

(ii) Write one method of preparation of ethanol.

(iii) Why Nimisha had advised Ankita to use ethanol for removing stains of paints?

(iv) What values has shown by Nimisha?

Long Answer Type Questions [5 Marks]

24. (i) An organic compound with molecular formula $C_9H_{10}O$ forms 2,4-DNP derivative, reduces Tollen's reagent and undergoes Cannizaro's reaction. On vigorous oxidation, it gives 1, 2-benzenedicarboxylic acid. Identify the compound.

(ii) Give the chemical test to distinguish between

(i) propanol and propanone.

(ii) benzaldehyde and acetophenone.

(iii) Arrange the following compounds in an increasing order of their property as indicated:

Acetaldehyde, acetone, methyl *tert*-butyl ketone (reactivity towards HCN) [All India 2012]

Or

Give one chemical test to distinguish between the following pair of compounds.

(i) Methylamine and dimethylamine
(ii) Secondary and tertiary amines
(iii) Ethylamine and aniline
(iv) Aniline and N-methylamine
(v) Aniline and benzylamine

25. An organic compound *A* on treatment with acetic acid in the presence of sulphuric acid produces an ester *B*. *A* on mild oxidation gives *C*. *C* with 50% KOH followed by acidification with dil. HCl generates '*A*' and *D*. *D* with PCl_5 followed by reaction with ammonia gives *E*. *E* on dehydration produces hydrocyanic acid. Identify the compound *A*, *B*, *C*, *D* and *E*. [Delhi 2009 C]

Or

An amorphous solid *A* burns in air to form a gas *B* which turns lime water milky. The gas is also produced as a by-product during roasting of sulphide ore. This gas decolourises acidified $KMnO_4$ solution and reduces Fe^{3+} to Fe^{2+}. Identify the solid *A* and the gas *B* and write the reaction involved.

26. (i) Give reasons for the following.

(a) Only xenon is known to form real compounds of the noble gases.
(b) Bismuth is a strong oxidising agent in the pentavalent state.
(c) H_2S is less acidic than H_2Te.

(ii) Complete the following chemical equations.

(a) $XeF_2 + H_2O \longrightarrow$
(b) $PH_3 + HgCl_2 \longrightarrow$

Or

A strip of nickel metal is placed in a one molar solution of $Ni(NO_3)_2$ and a strip of silver metal is placed in a one molar solution of $AgNO_3$. An electrochemical cell is created when the two solutions are connected by a salt bridge and the two strips are connected by wires to a voltameter.

(i) Write the balanced equations for the overall reactions occurring in the cell and calculate the cell potential.

(ii) Calculate the cell potential, *E*, at 25°C for the cell if the initial concentration of $Ni(NO_3)_2$ is 0.100 molar and the initial concentration of $AgNO_3$ is 1.00 molar.
$[E_{Ni^{2+}/Ni} = -0.25\,V;\ E_{Ag^+/Ag} = 0.80\,V]$

[Foreign 2012]

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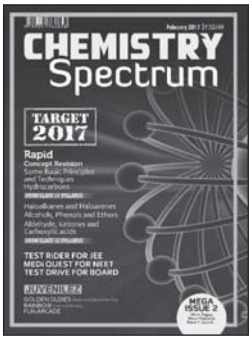

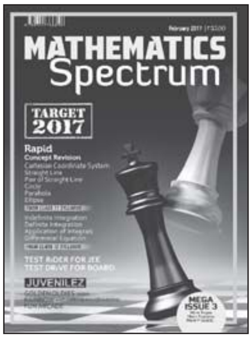

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FUN ARCADE

Irving langmuir

(31/1/1881-16/8/1957)

Irving Langmuir was born in Brooklyn, New York, on January 31, 1881, as the third of four children of Charles Langmuir and Sadie, née Comings. His early education was obtained in various schools and institutes in USA and Paris (1892-1895). He graduated high school from Chestnut Hill Academy, an elite private school located in the affluent Chestnut Hill area in Philadelphia. He graduated with a Bachelor of Science degree in metallurgical engineering from the Columbia University School of Mines in 1903. Postgraduate work in Chemistry under **Nernst** in Göttingen earned him the degrees of M.A and Ph.D in 1906.

Returning to America, Dr. Langmuir became instructor in Chemistry at Stevens Institute of Technology, Hoboken, New Jersey where he taught until July 1909. He then entered the research laboratory of the General Electric Company at Schenectady, New York where he eventually became associate director. Langmuir's studies embraced chemistry, physics and engineering and were largely the out growth of studies of vacuum phenomena. His initial contributions to science came from his study of light bulbs (a continuation of his Ph.D work). In 1932, he was awarded by Nobel Prize "for his discoveries and investigations in surface chemistry".

After a short illness, he died in Woods Hole, Massachusetts from a heart attack on August 16, 1957.

CROSSWORD

ACROSS

1. In ...., the bond breaks in such a fashion that the shared pair of electrons remains with one of the fragments. (11)

2. A reagent that takes away an electron pair is called .... (12)

4. The chemical substances, used to control the growth of pests are called .... (10)

7. The ratio of the radioactive to non-radioactive molecules in the solution .... till it attains a constant value. (9)

8. The hydrogen molecule is more stable than that of .... hydrogen atoms. (8)

10. In case of a non-polar (covalent) solvent, solvation enthalpy is .... (5)

12. All the proteins are laevorotatory due to the presence of asymmetric .... in α-amino acids. (6)

13. Antacids in .... form are more effective than that in the form of tablets. (6)

14. An alkaline substance corrosive towards organic matter .... (7)

DOWN

3. A paste of suspended solid particles in a liquid is .... (6)

5. A molecule having partial positive and negative charges separated by a distance .... (6)

6. To pour away the clear liquid above a precipitate or sediment carefully .... (6)

9. Capable of killing bacteria .... (13)

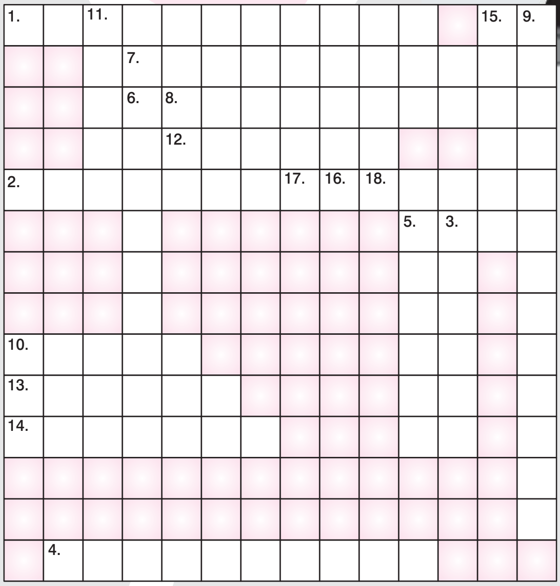
11. Most of the long polypeptide chain are folded or coiled to produce specific .... dimensional structures. (5)

15. CCl_4 is used as a fire extinguisher under the name, ... (6)

16. Mercury cannot form any .... (9)

17. Treatment of phosphonium iodide with 30% KOH solution gives .... (9)

18. .... wastes involves combustion of a substance into its ash at a high temperature and in a plentiful supply of O_2. (10)



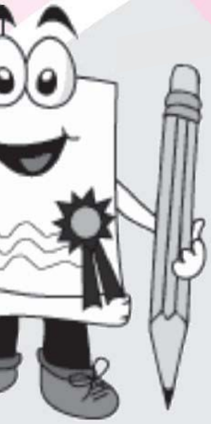
Puzzles to Puzzle You

① A solution of palmitic acid ($M = 245$ g mol^{-1}) in benzene contains 4.24 g of acid per dm^3. When this solution is dropped on a water surface the benzene evaporates and the palmitic acid forms a mono molecular film of the solid type. If we wish to cover an area of 500 cm^2 with a monolayer, what volume of solution should be used? The area covered by one palmitic acid molecule may be taken to be 0.21 nm^2.

② A compound (X) reacts with three molecules of aqueous bromine to give yellowish white precipitate of 2, 4, 6-tribromophenol. Find the number of carbon atoms present in compound (X).

③ A beam of specific kind of particles with velocity 2.1×10^7 m/s is scattered by a gold ($Z = 79$) nuclei. Find out specific charge (charge/mass) of this particle if the distance of closest approach is 2.4×10^{-14} m.

④ A solute undergoes a reversible trimerisation when dissolved in a certain solvent. The boiling point elevation of its 0.1 molal solution was found to be identical to the boiling point elevation in case of a 0.08 molal solution of a solute which neither undergoes association nor dissociation. To what percent had the solute undergoes trimerisation?



January 2017 issue Answer

Crossword

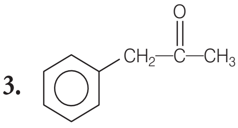
1, 2 D	E	C	R	E	A	S	I	N	G			4. Z	20. H
15. E	T	H	E	R		14. L	A	C	T	O	S	E	Y
S				13. G	E	N	E	T	I	C		R	P
16. T	E	R	T	I	A	R	Y	A	M	I	N	O	E
3. R	A	D	I	O	A	C	T	I	V	E	18. B	12. S	R
U							8. L		17. C	6. C	E	T	C
5. C	H	A	R	G	E	10. F	I		A	A	C	A	O
T						I	V		V	T	K	B	N
7. I	N	C	R	E	A	S	E	19. S	I	H	M	I	J
9. V						H	R	C	T	O	A	L	U
11. E	N	T	R	O	P	Y		H	I	D	N	I	G
C								O	E	E	N	T	A
T								T	S	S		Y	T
O								T					I
R								K					O
								Y					N

Puzzles to Puzzle Answers

1. 0.955 : 1

2. $K_c = 32$

3.

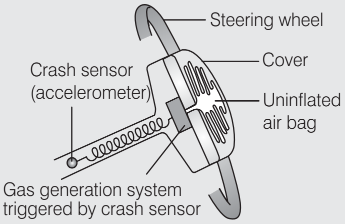


1-phenylpropanone

4. 4 kg

CHEMICAL CONNECT : CAR AIR BAGS

- Most cars are fitted with a supplementary restraint system, more commonly known as an air bag.
- This is designed to inflate within a few milliseconds in a collision to prevent an occupant hitting the steering wheel or front windscreen.



- On impact, an accelerometer detects that the car has slowed down violently and sends an electrical signal.
- This triggers a chemical reaction that produces a gas to inflate the folded bag.
- There are several gas generation systems in use, but a common one uses the decomposition of sodium azide (NaN_3).
- The reaction is extremely fast and releases a large volume of unreactive nitrogen gas

$$2NaN_3(s) \longrightarrow 2Na(s) + 3N_2(g)$$

- There are some drawbacks with the system.
- The reaction is very exothermic and releases heat. This is absorbed by the metal surroundings, which prevent the gas from getting too hot.
- In addition, the other product of the decomposition is sodium, a highly reactive metal.
- To make the products safe, the NaN_3 is mixed with potassium nitrate (KNO_3) and silica (SiO_2). As the NaN_3 decomposes, the sodium metal formed is oxidised by the potassium nitrate to sodium oxide (Na_2O) which combines with the silica to make sodium silicate (Na_2SiO_3), a safe unreactive powder.

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QUIZZER (NO. 27)

1. A student has an aqueous solution of $Ca(OH)_2$ that is approximately 0.1 M. She titrated a 50 mL sample of the $Ca(OH)_2$ solution with a standardised solution of 0.3 M $HNO_3(aq)$. To reach the end-point, 41.4 mL of the HNO_3 solution was needed. What is the molarity of $Ca(OH)_2$ solution?

2. Why it takes so much more energy to extract aluminium from bauxite than to recycle it?

3. 1-methylcyclohex-1-ene is treated with diborane and then with a solution of hydrogen peroxide in aqueous sodium hydroxide. Give the major product of the reaction.

4. An electric current of 2 A was passed through a platinum salt solution for 3 h and 10.9 g of metallic platinum was formed at the cathode. What is the charge on the platinum ions in the solution?

5. ^{40}Ca is a product of the decay of ^{40}K. Then, why the ratio of ^{40}K to ^{40}Ca cannot be used to date rocks?

Fill in the blanks

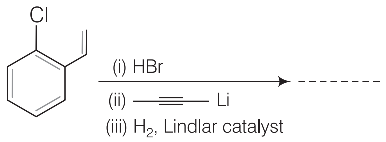
6. Stalactites are natural stone formation which are formed by the interaction of .... and ....

7. Liquid oxygen present between the poles of magnet is suspended because ....

8. The coordinate covalent bonds formed by the cyclam (which can act as a ligand) with a central metal ion is ....

9. $^{55}_{26}Fe + ... \longrightarrow ^{55}_{25}Mn$

10.



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