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**Chemistry
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Problems**

Chemistry Musing

CHEMISTRY today

Vol. XXIII No. 12 December 2014

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These tea polyphenols act as antioxidants and prevent neurodegenerative diseases such as Alzheimer's and Parkinson's diseases, give cardioprotection as well as act as anti-cancer agents. In consonance with our "Made in India Programme," an M.O.U. has been signed with Bajinath Pharmaceuticals Ltd. for transfer of technology for the production of catechins and theaflavins. This is a call to our young students – Do better and better and every time like a Milkha Singh, beat your own record.

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Chemistry Musing was started from August '13 issue of Chemistry Today with the suggestion of Shri Mahabir Singh. The aim of Chemistry Musing is to augment the chances of bright students preparing for JEE (Main and Advanced) / AIPMT / AIIMS / Other PMTs & PETs with additional study material. In every issue of Chemistry Today, 10 challenging problems are proposed in various topics of JEE (Main and Advanced) / AIPMT. The detailed solutions of these problems will be published in next issue of Chemistry Today.

The readers who have solved five or more problems may send their solutions. The names of those who send atleast five correct solutions will be published in the next issue.

We hope that our readers will enrich their problem solving skills through "Chemistry Musing" and stand in better stead while facing the competitive exams.

PROBLEM Set 17

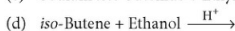
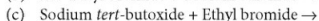
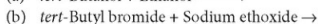
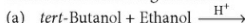
JEE MAIN/PMTs

- Which of the following is not a true peroxide?
 - Hydrogen peroxide
 - Caro's acid
 - Marshall's acid
 - Thiosulphuric acid
- Consider the following statements :
 - During O_2^- formation, one electron is added to the bonding molecular orbital.
 - During N_2^+ formation, one electron is removed from the bonding molecular orbital.
 - d^2sp^3 -hybrid orbitals are directed towards the corners of a regular octahedron.
 - dsp^2 -hybrid orbitals are all at 90° to one another.

Which of the above statements are correct?

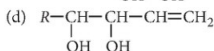
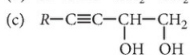
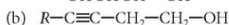
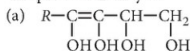
 - (i), (ii) and (iii)
 - (i), (ii) and (iv)
 - (ii), (iii) and (iv)
 - All of these.
- When 2 g of a non-volatile hydrocarbon containing 94.4% carbon is dissolved in 100 g of benzene, the vapour pressure of benzene is lowered from 74.66 torr to 74.01 torr. What will be the molecular formula of the hydrocarbon?
 - C_7H_8
 - C_8H_{16}
 - $C_{14}H_{10}$
 - $C_{10}H_6$

- tert*-Butyl ethyl ether cannot be prepared by which of the following reactions?



- $R-C\equiv C-CH=CH_2 \xrightarrow{HCO_3H} Z$

The product 'Z' may be



Solution Senders of Chemistry Musing

SET 16

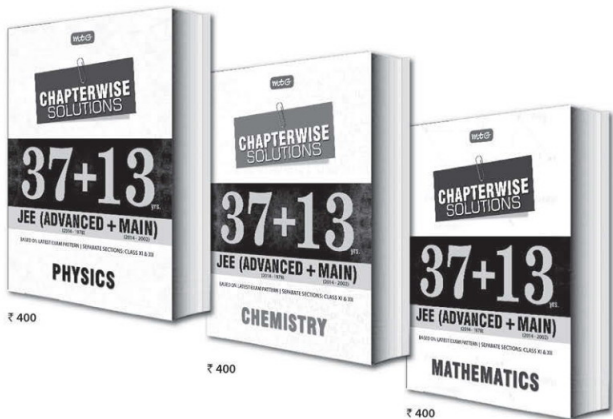
- Rehan Rizvi (Bihar)
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SET 15

- Arun Nayan, Ghazipur (U.P.)
- Rushikesh Joshi, Nagpur (Maharashtra)
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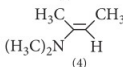
6. A room of $10\text{ m} \times 15\text{ m} \times 4\text{ m}$ dimensions having perfectly insulated walls, ceiling and floor has 60 students seated inside. The air inside the room is at 25°C and 1 atm pressure. If each student loses 200 joules of heat in one second, calculate rise in temperature noticed in 20 minutes?

(Neglect loss of air to the outside as the temperature is raised and C_p for air = $\frac{7}{2}R$).

- (a) 2.02 K (b) 20.2 K
(c) 0.02 K (d) 0.20 K

COMPREHENSION

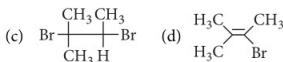
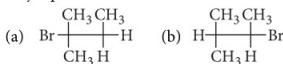
Alkenes are characterized by $\text{C}=\text{C}$ bonds. As such, they are subject to electrophilic addition reactions. Most electrophilic additions obey Markovnikov's rule; however, there are some exceptions. Few alkenes are given below :



7. What is the order of reactivity of the given compounds towards electrophilic addition of HBr?

- (a) $1 > 2 > 3 > 4$ (b) $3 > 1 > 4 > 2$
(c) $4 > 1 > 2 > 3$ (d) $2 > 4 > 1 > 3$

8. When HBr is added to the compound (2), the major product is



INTEGER VALUE

9. An optically active compound (A), $\text{C}_3\text{H}_7\text{O}_2\text{N}$ forms a hydrochloride but dissolves in water to give a neutral solution. On heating with soda lime, (A) yields $\text{C}_2\text{H}_7\text{N}$ (B). Both (A) and (B) react with NaNO_2 and dilute HCl, the former yields a compound (C) $\text{C}_3\text{H}_6\text{O}_3$, which on heating is converted to (D), $\text{C}_6\text{H}_8\text{O}_4$ while the latter yields (E), $\text{C}_2\text{H}_6\text{O}$. In (A) the type of carbon to which N is attached to is z° . The value of z is

10. If the stability constant of $[\text{Zn}(\text{NH}_3)_4]^{2+}$ is 2×10^9 , the ratio of uncomplexed to complexed Zn^{2+} ion in a solution that is 10 M in NH_3 is $x \times 10^{-14}$. The value of x is

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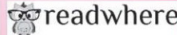
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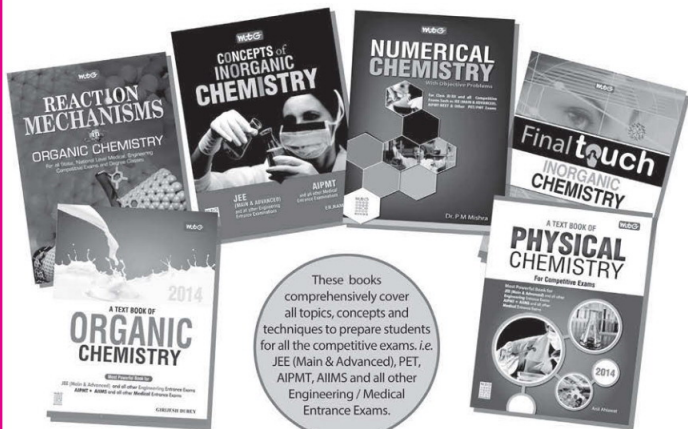
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EXAMINER'S MIND NCERT CLASS XI

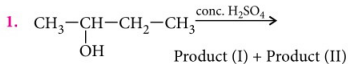
The questions given in this column have been prepared strictly on the basis of NCERT Chemistry for Class XI. This year JEE (Main & Advanced) / AIPMT / AIIMS/other PMTs have drawn their papers heavily from NCERT books.

HYDROCARBONS | ENVIRONMENTAL CHEMISTRY

SECTION - I

Only One Option Correct Type

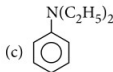
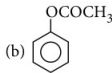
This section contains 20 multiple choice questions. Each question has four choices (a), (b), (c) and (d), out of which ONLY ONE is correct.



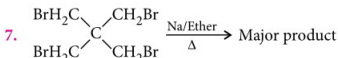
What is not true regarding the products?

- Products I and II are position isomers.
 - Products I and II contain same number of sp^3 and sp^2 carbon atoms.
 - The yield of the products I and II is same.
 - Reaction obeys Saytzeff rule.
2. London smog is found in
- summer during day time
 - summer during morning time
 - winter during morning time
 - winter during day time.
3. Which of the following species is most stable?
- $p\text{-O}_2\text{N}-\text{C}_6\text{H}_4-\overset{+}{\text{C}}\text{H}_2$
 - $\text{C}_6\text{H}_5-\overset{+}{\text{C}}\text{H}_2$
 - $p\text{-Cl}-\text{C}_6\text{H}_4-\overset{+}{\text{C}}\text{H}_2$
 - $p\text{-CH}_3\text{O}-\text{C}_6\text{H}_4-\overset{+}{\text{C}}\text{H}_2$
4. The secondary precursors of photochemical smog are
- SO_2 and NO_2
 - SO_2 and hydrocarbons
 - NO_2 and PAN
 - O_3 and PAN

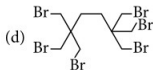
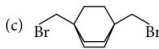
5. Which of the following compounds undergo electrophilic substitution most easily?



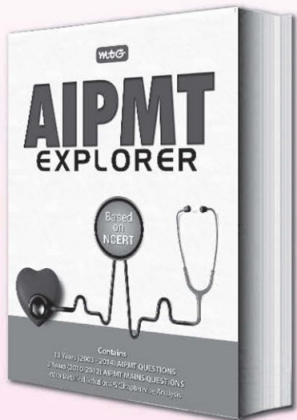
6. The presence of which of the following in drinking water is responsible for mottling of teeth?
- Mercury
 - Iodine
 - Chlorine
 - Fluorine



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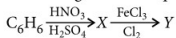
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8. If BOD of river is high, it means that the river is
 (a) not polluted
 (b) very much polluted with inorganic chemicals
 (c) very much polluted with organic matter which is decomposed by microorganisms
 (d) polluted with pesticides.

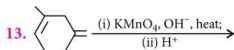
9. In the following reaction sequence,



identify Y.

- (a) 3-Nitrochlorobenzene
 (b) 1-Nitrochlorobenzene
 (c) 4-Nitrochlorobenzene
 (d) 2-Nitrochlorobenzene
10. Regular use of which of the following fertilizers increases the acidity of soil?
 (a) Ammonium sulphate
 (b) Potassium nitrate
 (c) Urea
 (d) Superphosphate of lime.
11. A hydrocarbon with molecular formula C_8H_{18} gives only one monochloro derivative, on chlorination. The compound is
 (a) *n*-octane
 (b) *iso*-octane
 (c) 2,2,4-trimethylpentane
 (d) 2,2,3,3-tetramethylbutane.

12. Measurement of rate of oxygen utilisation by the unit volume of polluted water over a period of time is referred to as
 (a) fermentation
 (b) chemical oxygen demand
 (c) oxidation potential
 (d) biological oxygen demand.



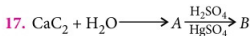
The products obtained are

- (a) $CH_2O + CH_3CO(CH_2)_4COOH$
 (b) $CO_2 + CH_3COCH_2COCH_2CH_2COOH$
 (c) $CH_2O + CH_3COCH_2COCH_2CH_2COOH$
 (d) none of these.

14. The region which is greatly affected by air pollution is
 (a) troposphere (b) stratosphere
 (c) mesosphere (d) thermosphere.

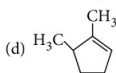
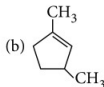
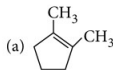
15. 1-Butyne can be distinguished most easily from 2-butyne by
 (a) bromine water
 (b) ozonolysis
 (c) Tollens' reagent
 (d) $KMnO_4$ solution.

16. Excess nitrate in drinking water can cause
 (a) methemoglobinemia
 (b) kidney damage
 (c) liver damage
 (d) laxative effect.



Identify A and B in the above reaction.

- (a) C_2H_6 and CH_3COOH
 (b) C_2H_4 and CH_3COOH
 (c) CH_4 and $HCOOH$
 (d) C_2H_2 and CH_3CHO
18. Lead in water can cause
 (a) eye disease (b) arthritis
 (c) kidney damage (d) hair falling.
19. Which compound will yield 5-keto-2-methylhexanal upon treatment with O_3 ?

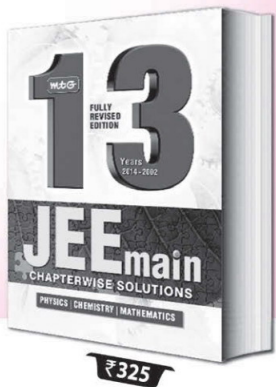
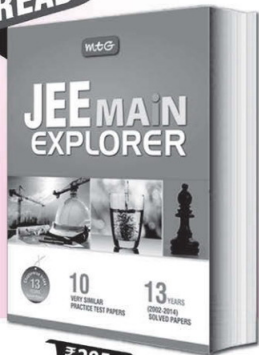


20. Disease caused by eating fish found in water contaminated with industrial wastes having mercury is
 (a) minamata disease
 (b) bright's disease
 (c) hashimoto's disease
 (d) osteosclerosis.

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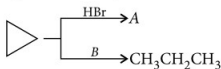
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
SECTION - II

One or More Options Correct Type

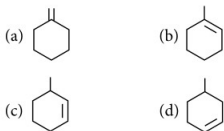
This section contains 5 multiple choice questions. Each question has four choices (a), (b), (c) and (d), out of which ONE or MORE are correct.

21. In the given reactions,

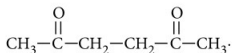


- (a) compound A is 
- (b) compound A is $\text{CH}_3\text{CH}_2\text{CH}_2\text{Br}$
- (c) reagent B is H_2/Ni at 120°C
- (d) reagent B is LiAlH_4 .
22. If the greenhouse effect or global warming remains unchecked, it will alter
- (a) sea levels (b) ozone layer
(c) rainfall (d) temperature.
23. $\text{A} \xrightarrow{\text{dil. H}_2\text{SO}_4/\text{Hg}^{2+}}$ 1-Methylcyclohexanol

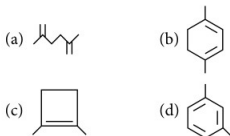
Here A is



24. Ozone layer of stratosphere requires protection from indiscriminate use of
- (a) fungicides, insecticides, bactericides and medicines
(b) aerosols and high flying jets
(c) atomic explosions and industrial wastes
(d) weather balloons.
25. An organic compound on reaction with O_3 followed by Zn and H_2O gives



The possible structure(s) of the compound is/ are



SECTION - III

Paragraph Type

This section contains 2 paragraphs each describing theory, experiment, data, etc. Six questions relate to two paragraphs with three questions on each paragraph. Each question of a paragraph has only one correct answer among the four choices (a), (b), (c) and (d).

Paragraph for Questions 26 to 28

The major water pollutant is organic matter such as leaves, grass, trash, etc. Excessive phytoplankton growth within water is also a cause of water pollution. These wastes are biodegradable. The large population of bacteria decomposes organic matter present in water. They consume oxygen dissolved in water. The amount of oxygen that water can hold in the solution is limited.

26. Biochemical Oxygen Demand, (BOD) is a measure of organic material present in water. BOD value less than 5 ppm indicates a water sample to be
- (a) rich in dissolved oxygen
(b) poor in dissolved oxygen
(c) highly polluted
(d) not suitable for aquatic life.
27. Which of the following statements is false ?
- (a) The main reason for river water pollution is industrial and domestic sewage discharge.
(b) Surface water contains a lot of organic matter, mineral nutrients and radioactive materials.
(c) Oil spill in sea water causes heavy damage to fishery.
(d) Oil slick in sea water increases D.O. value.

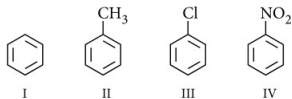
28. Sewage containing organic waste should not be disposed in water bodies because it causes major water pollution. Fish in such a polluted water die because of

- (a) large number of mosquitoes
 (b) increase in the amount of dissolved oxygen
 (c) decrease in the amount of dissolved oxygen in water
 (d) clogging of gills by mud.

Paragraph for Questions 29 to 31

When monosubstituted benzene is subjected to further substitution, three possible disubstituted products are not formed in equal amounts. Two types of behaviour are observed. Either *ortho* and *para* products or *meta* product is predominantly formed. This behaviour depends on the nature of the substituent already present in the benzene ring and not on the nature of the entering group. This is known as directive influence of substituents.

29. Which of the following compounds reacts slower than benzene in electrophilic bromination?
 (a) $C_6H_5NO_2$
 (b) $C_6H_5NH_2$
 (c) C_6H_5OH
 (d) $C_6H_5CH_3$
30. A deactivating group in electrophilic substitution reaction
 (a) deactivates only *ortho*- and *para*- positions.
 (b) deactivates only *meta*- position.
 (c) deactivates *meta*-position more than *ortho*- and *para*- positions.
 (d) deactivates *ortho*- and *para*- positions more than *meta*- position.
31. Identify the correct order of reactivity in electrophilic substitution reactions of the following compounds :



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

SECTION - IV

Matching List Type

This section contains 3 multiple choice questions. Each question has matching lists. The codes for the lists have choices (a), (b), (c) and (d), out of which ONLY one is correct.

32. Match the hydrocarbons in List I with the number of halogen derivatives it can give by monohalogenation in List II and select the correct answer using the code given below the lists :

List I		List II		
P.	<i>neo</i> -Pentane	1.	Five	
Q.	<i>iso</i> -Pentane	2.	Four	
R.	<i>n</i> -Pentane	3.	Three	
S.	Methylcyclohexane	4.	One	
	P	Q	R	S
(a)	4	2	1	3
(b)	1	3	4	2
(c)	2	1	4	3
(d)	4	2	3	1

33. Match the pollutants given in List I with their upper limit concentrations in List II and select the correct answer using the code given below the lists :

List I		List II		
P.	Lead	1.	500 ppm	
Q.	Sulphate	2.	1 ppm	
R.	Nitrate	3.	50 ppb	
S.	Fluoride	4.	50 ppm	
	P	Q	R	S
(a)	2	3	1	4
(b)	3	1	4	2
(c)	1	4	3	2
(d)	4	2	3	1

34. Match the List I with List II and select the correct answer using the code given below the lists :

List I		List II	
P.	Propyne, Propene	1.	Neutral $FeCl_3$ soln.
Q.	Benzene, Ethene	2.	Tollens' reagent
R.	Benzene, Hexane	3.	Baeyer's reagent
S.	Benzene, Phenol	4.	Sooty flame test

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

SECTION - V

Assertion-Reason Type

In the following questions, a statement of assertion is followed by a statement of reason. Mark the correct choice as :

- (a) If both assertion and reason are true and reason is the correct explanation of assertion.
 (b) If both assertion and reason are true but reason is not the correct explanation of assertion.
 (c) If assertion is true but reason is false.
 (d) If both assertion and reason are false.

35. **Assertion** : Staggered conformation of ethane is most stable while eclipsed conformation is least stable.

Reason : Staggered form has the least torsional strain and the eclipsed form has the maximum torsional strain.

36. **Assertion** : Classical smog is oxidising smog whereas photochemical smog is reducing smog.

Reason : Classical smog occurs in warm, dry and sunny climate whereas photochemical smog occurs in cool humid climate.

37. **Assertion** : Benzene reacts with *n*-propyl chloride in presence of AlCl_3 to give *iso*-propyl benzene.

Reason : Benzene undergoes electrophilic substitution readily.

38. **Assertion** : Photochemical smog does not involve the condensation of any kind of fog or smoke particles and hence the word 'smog' is a misnomer.

Reason : Photochemical smog is due to photochemical oxidation of SO_2 to SO_3 which dissolves in moisture of the air to form sulphuric acid droplets which is injurious to health.

39. **Assertion** : Boiling point of pentane is higher than 2,2-dimethylpropane.

Reason : There is steady increase in boiling point with increase in molecular mass.

40. **Assertion** : Lower the concentration of D.O., more polluted is the water sample.

Reason : Oxygen is consumed by microbes for the decomposition of organic matter present in water.

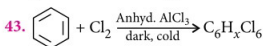
SECTION - VI

Integer Value Correct Type

This section contains 10 questions. The answer to each question is a single digit integer, ranging from 0 to 9 (both inclusive).

41. Total number of the isomeric cyclic compounds having molecular formula C_6H_{12} is

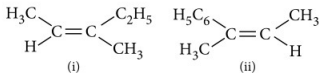
42. The laxative effect is observed only when the sulphates present in water have concentration greater than $x \times 10^2$ ppm. Here x is



The value of x is

44. The number of *cis-trans* isomers with molecular formula C_2BrClFI is

45. Among the given compounds, the number of *E*-isomers are



46. The acid-polluted water with $\text{pH} < y$ is fatal for the aquatic life. The value of y is

47. Two cyclic dienes *A* and *B* have molecular formula, C_6H_8 . On reductive ozonolysis, *A* gives succinaldehyde and glyoxal while *B* gives propane-1,3-dial. *A* and *B* on hydrogenation produce only cyclohexane. The total sum of the positions of the double bonds in compounds *A* and *B* is

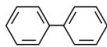
48. The number of aromatic compounds among the following are



(i)



(ii)



(iii)



(iv)

49. Number of different products obtained on reductive ozonolysis of myrcene, a terpenoid is



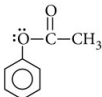
50. In measurement of BOD_x, x is generally taken as

SOLUTIONS

1. (c) : $\text{CH}_3-\underset{\text{OH}}{\text{CH}}-\text{CH}_2-\text{CH}_3 \xrightarrow{\text{conc. H}_2\text{SO}_4}$
 $\text{CH}_3-\text{CH}=\text{CH}-\text{CH}_3$
 Product (I) (Major)
 $+ \text{CH}_2=\text{CH}-\text{CH}_2-\text{CH}_3$
 Product (II) (Minor)
2. (c)
3. (d) : Positive charge on $-\overset{+}{\text{C}}\text{H}_2$ is dispersed due to electron releasing nature of methoxy group.
4. (d)



Activating due to +I and hyperconjugation (weak effects)



Lone pairs of O are in conjugation with $\text{C}=\text{O}$ hence moderate activating group

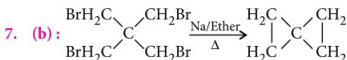


Lone pair on N leads to +M effect (a powerful effect) (Most activating)



Deactivating group

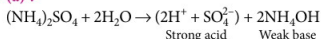
6. (d) : Mottling of teeth is due to the presence of fluorine in drinking water.



8. (c)

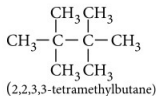
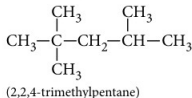
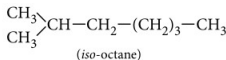


10. (a) :



$(\text{NH}_4)_2\text{SO}_4$ on hydrolysis produces strong acid H_2SO_4 , which increases the acidity of the soil.

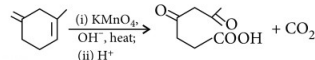
11. (d) : $\text{CH}_3(\text{CH}_2)_6\text{CH}_3$
 (*n*-octane)



Compound in which all hydrogen atoms are equivalent will form one monochloro derivative, which is 2,2,3,3-tetramethylbutane.

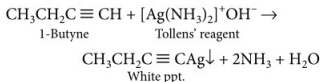
12. (b)

13. (b) : The terminal CH_2 group ($=\text{CH}_2$) is completely oxidised to CO_2 and H_2O ; a monosubstituted atom of a double bond is converted to aldehyde which is further oxidised to carboxylic acid, and the disubstituted atom of a double bond is oxidised to ketone.

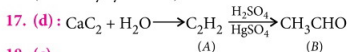


14. (a) : Troposphere is the lowermost region of earth atmosphere and hence greatly affected by air pollution.

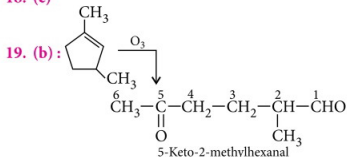
15. (c) : Tollens' reagent is ammoniacal silver nitrate which reacts with 1-alkynes to form white precipitate of silver alkynide.



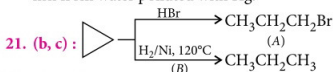
16. (a) : Excess nitrate in drinking water is harmful and can cause methemoglobinemia (blue baby syndrome).



18. (c)

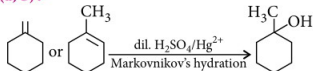


20. (a) : Minamata disease is caused by consuming fish from water polluted with Hg.



22. (a, c, d)

23. (a, b) :



24. (b)

25. (a, b, c)

26. (a) : Clean water rich in dissolved oxygen would have BOD value of less than 5 ppm whereas highly polluted water could have a BOD value of 17 ppm or more.

27. (d)

28. (c) : If the concentration of dissolved oxygen in water is below 6 ppm, the growth of fish gets inhibited.

29. (a) : An electron withdrawing group, $-\text{NO}_2$, deactivates the benzene ring towards electrophilic substitution reaction.

30. (d)

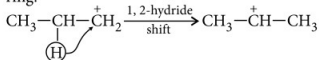
31. (c) : Because $-\text{CH}_3$ group is weakly activating, $-\text{Cl}$ group is weakly deactivating and $-\text{NO}_2$ group is strongly deactivating for electrophilic substitution reaction.

32. (d) 33. (b) 34. (b) 35. (a)

36. (d) : Classical smog occurs in cool humid climate. Chemically it is a reducing mixture and so it is also called as reducing smog.

Photochemical smog occurs in warm, dry and sunny climate. It has high concentration of oxidising agents and is therefore, called as oxidising smog.

37. (b) : When Friedel-Craft's alkylation is carried out with $\text{CH}_3\text{CH}_2\text{CH}_2\text{Cl}$, the product is *iso*-propyl benzene because the initially formed *n*-propyl cation being less stable first rearranges to the more stable *iso*-propyl cation by a 1, 2-hydride shift before attacking the benzene ring.

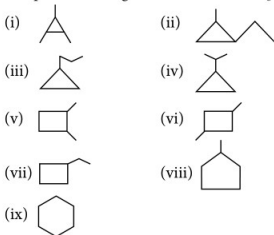


38. (c) : Photochemical smog is due to reaction of NO_2 with hydrocarbons present in the air.

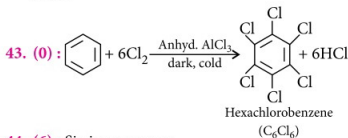
39. (b) : Pentane and 2,2-dimethylpropane are isomers having same molecular formula. Pentane has high boiling point because it is straight chain isomer whereas 2,2-dimethylpropane is branched chain due to which the molecule attains the shape of a sphere. This results in smaller area of contact and therefore, weak intermolecular forces.

40. (a)

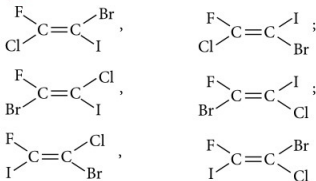
41. (9) : Various possible isomeric cyclic compounds having molecular formula C_6H_{12} are



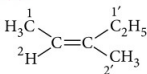
42. (5) : Concentration of sulphates in water greater than $500 (5 \times 10^2 \text{ ppm})$ causes laxative effect.



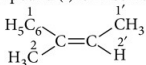
44. (6) : Six isomers are :



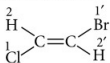
45. (2)



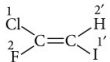
Compound (i) is Z-isomer.



Compound (ii) is Z-isomer.



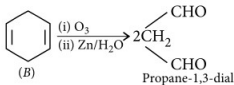
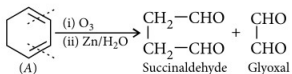
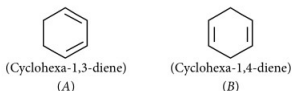
Compound (iii) is E-isomer.



Compound (iv) is E-isomer.

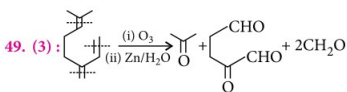
46. (3)

47. (9) : A and B on hydrogenation give cyclohexane. This implies that both A and B should be cyclohexadienes. The ozonolysis products suggest the presence of double bonds at 1 and 3-positions in one and at 1 and 4-positions in the other. Hence, A and B should be



Total sum of the positions of the double bonds in A and B = $1 + 3 + 1 + 4 = 9$.

48. (2) : (i) and (iii) are aromatic. According to Huckel's rule only these two systems follow $(4n + 2)\pi$ electron rule. (iv) is also a $(4n + 2)\pi$ electron system but 6π -electrons are not spread over the entire ring due to presence of sp^3 carbon atom and also it is non-planar. Compound (iii) is aromatic since it contains two benzene rings each one of which contains $(4n + 2)\pi$ electrons with $n = 1$.



50. (5) : We generally measure BOD₅ whereas 5 represents number of days for which the sample is kept, i.e., amount of O₂ consumed in 5 days.

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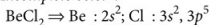
Chemical Bonding and Molecular Structure

- **Chemical bonding** : The combination of two or more atoms involving redistribution of electrons, so that each atom involved in bonding acquires stable configuration in order to gain stability is known as *chemical bonding*. The combination of two atoms involves a decrease in potential energy as a result of net attraction between the atoms.
- There are five types of bonding :
 - Electrovalent bonding or ionic bonding, the strongest bonding
 - Covalent bonding
 - Coordinate bonding
 - Metallic bonding
 - Hydrogen bonding, the weakest among all.
- **Ionic or electrovalent bonding** : The combination of two or more atoms involving complete transfer of one or more electrons from the valence shell of an atom into the valence shell of other atom so that each atom involved in bonding acquires nearest noble gas configuration to gain stability is known as *ionic bonding* or *electrovalent bonding*.
- In ionic bonding, atom losing electrons forms cation and the other gaining electrons forms anion and the electrostatic forces of attraction (coulombic forces) in between oppositely charged ions give rise to evolution of energy, so that resultant molecule acquires lower energy level and gains stability.
- **Characteristics of ionic compounds** :
 - Solid at room temperature
 - have high melting and boiling points
 - hard and brittle
 - soluble in polar solvents
 - conductors of electricity
- **Covalent bonding** : The bond which is formed between two combining atoms by the mutual sharing of electron pair(s) between them is called *covalent bond*.
- **Characteristics of covalent compounds** :
 - Solid, liquid or gas at room temperature
 - have low melting and boiling points
 - soft and waxy
 - soluble in non-polar solvents
 - non-conductors of electricity
- **Coordinate bonding** : It involves one sided sharing of an electron pair in between two atoms or groups or molecules in order to acquire the nearest noble gas configuration.
- **Metallic bonding** : Metallic bond can be defined as the force of attraction between the metallic cations and the mobile electrons and this force holds the metal atoms firmly together in the metallic crystal. e.g., Hg, W.
- **Factors Favouring the formation of metallic bond** :
 - The ionisation energy of the metals should be low.
 - The metals should have low electronegativity.
 - The number of vacant orbitals in a metal should be more than the number of valence electrons in it.
- **Hydrogen bonding** : The attractive force which binds hydrogen atom of one molecule with the electronegative atom (F, O or N) of the same or another molecule is called *hydrogen bond*.
- **Intermolecular hydrogen bonding** is formed between the two different molecules of the same or different compounds e.g., in case of HF, ROH or H₂O, etc.
- **Intramolecular hydrogen bonding** is formed between hydrogen atom and an electronegative atom (F, O or N) within the same molecule e.g., in *o*-nitrophenol.
An intramolecular hydrogen bond results in the cyclization of the molecules and prevents their association.

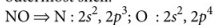
- **Octet rule** : According to octet rule, each atom involved in bonding tries to attain nearest noble gas configuration or to complete its octet.

- **Exceptions to octet rule** :

- *Incomplete octet* :



BeCl_2 has four electrons on Be atom's outermost shell.



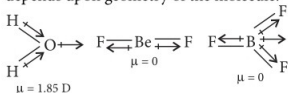
NO has seven electrons on N atom's outermost shell.

- **Isolated dot formulae and dash formulae of some compounds** :

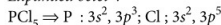
Molecular formula	Electron dot formula	Dash formula or bond formula
C_2H_4	$\begin{array}{c} \text{H} \quad \text{H} \\ \vdots \quad \vdots \\ \text{C} :: \text{C} \\ \vdots \quad \vdots \\ \text{H} \quad \text{H} \end{array}$	$\begin{array}{c} \text{H} \quad \text{H} \\ \quad \\ \text{C} = \text{C} \\ \quad \\ \text{H} \quad \text{H} \end{array}$
MgCO_3	$\text{Mg}^{++} \left[\begin{array}{c} \cdot\ddot{\text{O}} : \text{C} : \ddot{\text{O}} \cdot \\ \cdot\ddot{\text{O}} \cdot \end{array} \right]^{2-}$	$\text{Mg}^{++} \left[\begin{array}{c} \text{O} - \text{C} - \text{O} \\ \\ \text{O} \end{array} \right]^{2-}$
N_2O_5	$\begin{array}{c} \cdot\ddot{\text{O}} : \text{N} : \ddot{\text{O}} : \text{N} : \ddot{\text{O}} \cdot \\ \cdot\ddot{\text{O}} \cdot \quad \cdot\ddot{\text{O}} \cdot \end{array}$	$\begin{array}{c} \text{O} = \text{N} - \text{O} - \text{N} = \text{O} \\ \quad \quad \\ \text{O} \quad \quad \text{O} \end{array}$
$\text{H}_4\text{P}_2\text{O}_7$	$\begin{array}{c} \text{H} \quad \quad \text{H} \\ \cdot\ddot{\text{O}} \cdot \quad \cdot\ddot{\text{O}} \cdot \\ \cdot\ddot{\text{O}} \cdot \quad \cdot\ddot{\text{O}} \cdot \\ \text{H} \cdot \ddot{\text{O}} \cdot \text{P} \cdot \ddot{\text{O}} \cdot \text{P} \cdot \ddot{\text{O}} \cdot \text{H} \\ \cdot\ddot{\text{O}} \cdot \quad \cdot\ddot{\text{O}} \cdot \end{array}$	$\begin{array}{c} \text{H} \quad \quad \text{H} \\ \quad \quad \\ \text{O} \quad \quad \text{O} \\ \quad \quad \\ \text{H} - \text{O} - \text{P} - \text{O} - \text{P} - \text{O} - \text{H} \\ \quad \quad \\ \text{O} \quad \quad \text{O} \end{array}$

- **Dipole moment** : In case of heteroatomic molecules where there is electronegativity difference between two atoms, due to polarisation, the molecule possesses the dipole moment which is the product of the magnitude of charge and the distance between the centres of positive and negative charges.

- Dipole moment is the vector sum of the dipole moments of various bonds, hence it depends upon geometry of the molecule.



- *Expanded octet* :



PCl_5 has ten electrons on P atom's outermost shell.

- **Formal charge on an atom** = Number of valence electrons - number of unshared electrons

$$- \frac{1}{2} \times \text{number of bonding electrons.}$$

- **Fajans rule** : According to Fajans rule, the magnitude of covalent character in the ionic bond depends upon the extent of polarisation caused by cation. In general,

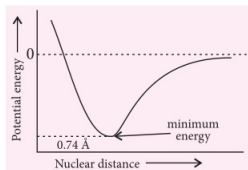
- Smaller the size of cation, larger is its polarising power.
- Larger the size of anion, more will be its polarisability.
- More the charge on cation and anion, more is the covalent character.
- Cations having 18 electrons in the outermost shell bring greater polarisation.

- **Valence Shell Electron Pair Repulsion (VSEPR) Theory** : It predicts the shapes of molecules and ions in which valence shell

electron pairs are arranged about each atom so that electron pairs are kept as far away from one another as possible, thus minimizing electron pair repulsions.

- Electron pairs surrounding a central atom repel each other; this repulsion will be minimized if the orbitals containing these electron pairs point as far away from each other as possible.
- The coordination geometry around the central atom corresponds to the polyhedron whose number of vertices is equal to the number of surrounding electron pairs (coordination number).
- Orbitals that contain non-bonding electrons are more concentrated near the central atom, and therefore offer more repulsion than bonding pairs to other orbitals. The repulsive interactions decreases in the order :
 $lp - lp > lp - bp > bp - bp$
- Repulsive force decreases sharply with increasing angle between the electron pairs. They are strong at 90° , weaker at 120° and weakest at 180° .

- Valence bond theory describes a chemical bond as the overlap of atomic orbitals. Valence bond theory is an approximate theory to explain the formation of covalent bond by quantum mechanics. According to valence bond theory, a bond forms between two atoms when the following conditions are met :
 - An orbital on one atom comes to occupy a portion of the same region of space as an orbital on the other atom. The two orbitals are said to overlap.
 - The total number of electrons in both orbitals is not more than two.
- According to this theory, in the case of hydrogen molecule, the $1s$ orbital of one hydrogen atom overlaps with the $1s$ orbital of the second hydrogen atom to form a molecular orbital called a sigma bond. Attraction increases as the distance between the atoms gets closer but nuclear-nuclear repulsion becomes important if the atoms approach too close.



- Depending upon the types of overlapping, the covalent bond can be divided into :
 - *Sigma (σ) bond* : Bond orbital which is symmetrical about the line joining the two nuclei (internuclear axis) forms a σ -bond. A σ -bond has a cylindrical shape around the bond axis.
 - *Pi (π) bond* : A π -bond has an electron distribution above and below the bond axis.
- Sigma (σ) bonds are formed by head-on overlap of unhybridised, s -orbital- s -orbital, p -orbital- p -orbital, s -orbital- p -orbital or hybridised (sp , sp^2 , sp^3 , sp^3d and sp^3d^2) orbitals, hence σ -bonds are strong bonds, $pi(\pi)$ -bonds are formed by sideways overlap of unhybridised p - and d -orbitals, hence π -bonds are weak bonds.

Orbitals used in bond formation	Overlap of atomic orbitals
s -orbital- s -orbital	
s -orbital- p -orbital	
p -orbital- p -orbital	
p -orbital- p -orbital	
d -orbital- p -orbital	
d -orbital- d -orbital	

- All single bonds are σ -bonds. A double bond consists of one σ and one π -bonds. A triple bond consists of one σ and two π -bonds.
 - Increasing order of bond energy :
Single bond < Double bond < Triple bond
 - Increasing order of bond strength :
Single bond < Double bond < Triple bond
 - Increasing order of bond length :
Triple bond < Double bond < Single bond
 - Increasing order of reactivity :
Single bond < Double bond < Triple bond
- **Hybridisation** : The hybridisation can be defined as a process in which two or more atomic orbitals of the valence shell of an atom (central atom of the molecule or ion) either in its ground state or in its excited state mix (merge or combine or overlap) together and give rise to a set of new orbitals of equal energy which are called *hybrid orbitals* or *hybridised orbitals*. The principles of the valence bond theory for hybridisation derived from Pauling's analysis :
 - Not all of the filled, half-filled, or empty orbitals on any atom need to be used in a hybridisation.
 - Orbitals that are filled, half-filled, or empty do not hybridise with each other. The hybridising orbitals are all half-filled in normal covalent bonding.
 - Orbitals which are all filled or all empty are used in coordinate covalent bonding.
 - The hybridised atomic orbitals on one atom overlap with other normal or hybridised orbitals on another atom, or with both, depending on the molecular geometry.
 - The number of orbitals produced in any hybridisation is equal to the number of original atomic orbitals undergoing hybridisation.
 - Hybridised orbitals have identical shape and energy.
 - Hybridised orbitals show only head-on overlapping and thus form only σ -bond. They never form π -bond.
 - As the s -character increases in hybridised orbitals, electronegativity of the atom involved in hybridisation increases, size

of hybridised orbitals decreases and tendency of overlapping increases giving rise to smaller bond length and higher bond energy.

- **sp -hybridisation** : The hybridisation of one s -orbital and one p -orbital of the central atom gives rise to two sp -hybrid orbitals which are in a linear arrangement and 180° apart.
- **sp^2 -hybridisation** : The hybridisation of one s -orbital and two p -orbitals of the central atom gives rise to three sp^2 -hybrid orbitals which are planar and 120° apart.
- **sp^3 -hybridisation** : The hybridisation of one s -orbital and all the p -orbitals of the central atom gives rise to four sp^3 -hybrid orbitals which are aligned in a tetrahedral configuration and so are 109.5° apart.
- **dsp^2 -hybridisation** : Atoms of the transition metals and of other elements which have d -orbitals available to them can use these d -orbitals in hybridisation. The hybridisation of one s , two p and one d -orbitals of the central metal atom gives rise to four dsp^2 -hybrid orbitals. They are square planar in alignment and 90° apart. The d -orbital used in hybridisation is $d_{x^2-y^2}$.
- **sp^3d or dsp^3 -hybridisation** : The hybridisation of one s , one d and three p -orbitals of the central atom gives rise to five sp^3d or dsp^3 -hybrid orbitals. This hybridisation uses the d_{z^2} -orbital and shape of the molecule becomes trigonal bipyramidal with equatorial bond angle is 120° and axial bond angle is 90° .
- **sp^3d^2 or d^2sp^3 -hybridisation** : Atoms which have two or more d -orbitals available to them can use more than one d -orbital in hybridisation. The hybridisation of two d -orbitals, one s -orbital, and three p -orbitals of the central atom gives rise to six sp^3d^2 or d^2sp^3 -hybrid orbitals. All adjacent orbitals are 90° apart and all non-adjacent orbitals are 180° apart. This form of hybridisation has the geometric structure of an octahedron, with six vertices and eight sides. The d -orbitals used in hybridisation are $d_{x^2-y^2}$ and d_{z^2} .

- **sp^3d^3 -hybridisation** : The hybridisation of three d -orbitals, one s -orbital and three p -orbitals of the central atom gives rise to seven sp^3d^3 -hybrid orbitals which are directed towards the seven corners of a regular pentagonal bipyramid. The orbitals do not lie in one plane, five basal hybrid orbitals lie in the pentagonal

plane and two axial hybrid orbitals lie above and below on the axis passing through the centre of the pentagonal base of the pentagonal bipyramid. The angle between each pair of basal hybrid orbitals is $\frac{360}{5} = 72^\circ$ and between axial and basal hybrid orbitals is 90° .

- **Hybridisation and structures of molecules having bond pairs only :**

Type of hybridisation	No. of hybrid orbitals	Shape of molecule	Bond angle	Examples
sp	2	Linear	180°	BeCl_2 , BeF_2 , CO_2 , CS_2 , C_2H_2 , N_2O , $[\text{Ag}(\text{CN})_2]^-$, HgCl_2 , HCN
sp^2	3	Trigonal planar	120°	BF_3 , BCl_3 , C_2H_4 , NO_3^- , CO_3^{2-} , SO_3 , CH_3^+
sp^3	4	Tetrahedral	109.5°	CH_4 , CCl_4 , SnCl_4 , SiF_4 , NH_4^+ , SO_4^{2-}
dsp^2	4	Square planar	90°	$[\text{PtCl}_4]^{2-}$, $[\text{Ni}(\text{CN})_4]^{2-}$
dsp^3 or sp^3d	5	Trigonal bipyramidal	120° and 90°	PCl_5 , PF_5 , $[\text{Fe}(\text{CO})_5]$
d^2sp^3 or sp^3d^2	6	Octahedral	90°	SF_6 , UF_6 , TeF_6 , $[\text{CrF}_6]^{3-}$, $[\text{Co}(\text{NH}_3)_6]^{3+}$
d^3sp^3 or sp^3d^3	7	Pentagonal bipyramidal	72° and 90°	IF_7

- **Hybridisation and structures of molecules having lone pair(s) :**

Types of molecules	No. of bond pair(s)	No. of lone pair(s)	Hybridisation	Bond angle	Expected geometry	Actual geometry	Examples
AX_2	2	1	sp^2	$<120^\circ$	Trigonal planar	V-shape or Bent	SO_2 , SnCl_2 , PbCl_2 , NO_2^+ , O_3
AX_2	2	2	sp^3	$<109^\circ 28'$	Tetrahedral	V-shape or Bent	H_2O , H_2S , NH_2^- , SCl_2 , OF_2 , Cl_2O , ClO_2^- , ClOF
AX_2	2	3	sp^3d	180°	Trigonal bipyramidal	Linear	XeF_2 , I_3^- , ICl_2^-
AX_3	3	2	sp^3d	90°	Trigonal bipyramidal	T-shape	ClF_3 , IF_3 , BrF_3 , XeOF_2
AX_3	3	1	sp^3	$<109^\circ 28'$	Tetrahedral	Pyramidal	NH_3 , PH_3 , PCl_3 , BiCl_3 , AsCl_3 , XeO_3
AX_4	4	1	sp^3d	120° and 90°	Trigonal bipyramidal	See saw or Distorted tetrahedron	SF_4 , SCl_4 , TeCl_4 , XeO_2F_2

AX_4	4	2	sp^3d^2	—	Octahedral	Square planar	XeF_4, ICl_4^-
AX_5	5	1	sp^3d^2	$<90^\circ$	Octahedral	Square pyramidal	IF_5, BrF_5, SbF_5^{2-}
AX_6	6	1	sp^3d^3		Pentagonal bipyramidal	Distorted octahedral	XeF_6

- The structure of any molecule can be predicted on the basis of hybridisation which can be determined by the following formula :

$$H = \frac{1}{2} [\text{No. of electrons in valence shell of atom} + \text{No. of monovalent atoms} - \text{Charge on cation} + \text{Charge on anion}]$$

Value of H	2	3	4	5	6	7
Hybridisation	sp	sp^2	sp^3	sp^3d	sp^3d^2	sp^3d^3

- For complex ions, hybridisation is determined as :

Ligand	2	3	4	5	6
Hybridisation	sp	sp^2	sp^3 or dsp^2	sp^3d or dsp^3	sp^3d^2 or d^2sp^3

Molecular Orbital Theory

Developed by F. Hund and R. S. Mulliken.

- The electrons in a molecule are present in the various molecular orbitals.
- The atomic orbitals of comparable energy and proper orientation combine to form molecular orbitals.
- The electron in a molecular orbital is influenced by two or more nuclei depending upon the number of atoms in the molecule, thus a molecular orbital is polycentric.
- The number of molecular orbitals formed is equal to the number of combining atomic orbitals.
- The bonding molecular orbital has lower energy and greater stability than the corresponding antibonding molecular orbital.
- The molecular orbital gives electron probability distribution around a group of nuclei in a molecule.
- The molecular orbitals are filled in accordance with Aufbau principle, the Pauli's exclusion

principle and the Hund's rule of maximum multiplicity.

- Order of energy of molecular orbitals for elements with $Z \leq 7$:

$$\sigma 1s < \sigma^* 1s < \sigma 2s < \sigma^* 2s < (\pi 2p_x \approx \pi 2p_y) <$$

$$\sigma 2p_z < (\pi^* 2p_x \approx \pi^* 2p_y) < \sigma^* 2p_z$$

Order of energy of molecular orbitals for elements with $Z \geq 8$:

$$\sigma 1s < \sigma^* 1s < \sigma 2s < \sigma^* 2s < \sigma 2p_z < (\pi 2p_x \approx \pi 2p_y)$$

$$< (\pi^* 2p_x \approx \pi^* 2p_y) < \sigma^* 2p_z$$

- Bond order = $\frac{1}{2} [\text{No. of bonding electrons} - \text{No. of antibonding electrons}]$
- Bond order \propto Bond energy $\propto \frac{1}{\text{Bond length}}$
- Molecules with bond order equal to zero do not exist.
- Species with unpaired electrons are *paramagnetic* and those with all electrons paired are *diamagnetic*.

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(SURFACE CHEMISTRY)

Mukul C. Ray, Odisha

Chemisorption and Physisorption

Many of the surfaces are chemically reactive. With the exception of noble metals, all metals, alloys and many non-metals form surface layers of oxides, nitrides, sulphides, and chlorides depending on the environment to which it is exposed. Besides the chemical corrosion film, there are also adsorbed films that are produced either by physisorption or chemisorption of gases or water vapours from the environment.

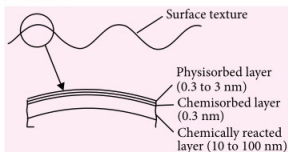
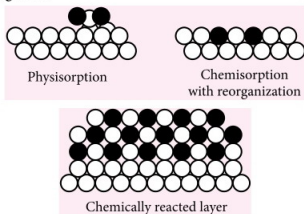


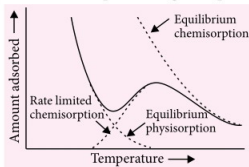
Figure showing the arrangement of different layers on the surface of metals

There is a difference between physisorption, chemisorption and chemically reacted layers, which can be realized from the following schematic diagrams.



With physisorption, no exchange of electrons takes place between adsorbate and adsorbent, it typically involves van der Waals forces. Surfaces are free from physisorption only in high vacuum. In chemisorption, there is actual sharing of electrons. The chemisorbed layer is limited to only monolayer and this is a distinction between chemisorption and chemical reaction. Once the surface is covered with a layer, chemisorption ceases, any subsequent layer formation is by physisorption.

At low temperature physical adsorption process dominates and the amount of chemisorption is insignificant. The extent of physisorption decreases as temperature increases and at one stage the amount of material that can be chemisorbed offsets the loss of physisorbed material and the graph shows an increasing trend. Note that the extent of physisorption is not becoming zero because a surface can remain free from physisorption only at high vacuum. At high temperature, equilibrium can be established with respect to chemisorption. This curve applies to situation where one starts from low temperature. Also, chemisorption is called as activated adsorption as it takes place at high temperature.



Effect of temperature on simultaneous physisorption and chemisorption

Nature of Species in the Adsorbed Form

Nature of oxygen on the adsorbed surface has been extensively studied. Oxygen gets adsorbed on the metal surface as well as on the oxide surface. On the oxide surface both neutral O_2 and O as well as ionic species O^- , O^{2-} and O^{3-} have been reported in equilibrium with each other. Molecular oxygen has been found on platinum at 120 K; at higher temperature oxygen dissociates to atoms indicating the activated nature of chemisorption.

Stability of Colloids

In lyophobic colloids, colloid particles have surface charge. So naturally these identically charged particles repel each other. At the same time van der Waals attraction forces are also there that try to bring the particles together. The figure shows the variation of net resultant force with distance between the colloidal particles. When the net resultant repulsion energy exceeds the kinetic energy, the particles will not coagulate and the dispersion is stable. When the kinetic energy is larger than the repulsion energy, the dispersion is unstable.

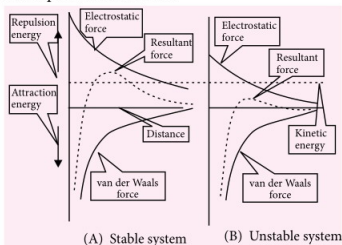


Figure showing the significance of two opposing forces and kinetic energy in explaining the stability of lyophobic colloids

Consequently, if it is required to destabilize a colloid, then the kinetic energy should be made higher or electrostatic repulsion made lower.

Diagram for a negative colloid is given. There is a fixed layer of positive ions on its surface followed by a diffused layer of positive ions. When the colloidal particle moves it takes a small part of the solution with it. The notional boundary that moves with the colloidal particle is called **slip plane**. The potential difference between the slip plane and the bulk of

the solution is called **zeta potential**. If the potential difference between the solid surface and the bulk of the solution is considered, the value is found to be very high. It is not the zeta potential rather it is the surface potential. For a colloidal system to be stable, zeta potential must be more negative than -30 to -40 mV or more positive than $+30$ to $+40$ mV. Also zeta potential without pH value is meaningless like the volume of gas without temperature and pressure. At isoelectric point (or isoelectric pH), zeta potential is zero.

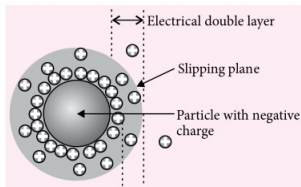


Figure illustrating existence of electrical potential on colloids

For lyophilic colloids, the stability is due to thermodynamic reason in contrast to lyophobic colloid stability, which is due to kinetic factors. Thermodynamics never wants to see the particles with high surface area. In lyophobic colloids the repulsion energy is responsible for preventing them to undergo coagulation. Lyophilic colloid particles are extensively hydrated or solvated. These solvent shells prevent them from undergoing collapse. The interfacial tension (surface tension is defined when the liquid is in contact with air or its own vapour but surface tension when the liquid is in contact with another liquid is interfacial tension) in lyophilic colloids is negative and the colloidal system is formed with lowering in free energy.

Coagulation

For lyophobic colloids, coagulation takes place when an external electrolyte is added. This is explained by two theories, **Charge neutralization theory** and **Double layer compression theory**. The second one says that when the concentration of oppositely charged ions (as compared to charge of colloids) particularly bivalent and trivalent ions increases in the medium there is a more rapid decrease in charge from the surface or the

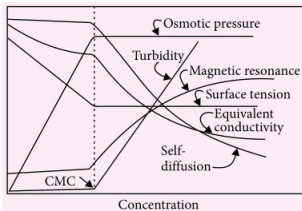
thickness of double layer decreases. The slip plane comes closer to the surface of the colloids and there is a compression of double layer. Now the van der Waals forces would predominate and particles agglomerate. The charge neutralization theory says sometimes oppositely charged ions have a tendency to get adsorbed directly on the particles and hence the ionic cloud dissipates causing the coagulation.

Micelles

Micelles are formed only above Critical Micelle Concentration (CMC) and above Kraft's temperature. Below the Kraft's temperature the soaps or detergent molecules tend to form crystals in the solution and below CMC there are no sufficient molecules to form micelle. In general CMC for soap is 10^{-3} to 10^{-4} moles/litre. The value of CMC also depends on the solvent polarity. Usually CMC increases with decrease in solvent polarity and longer the hydrophobic chain smaller is the CMC.

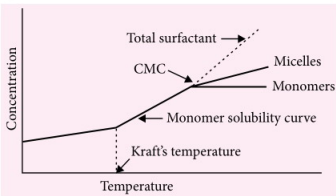
Sodium and potassium soaps are more soluble in water than oil hence, stabilize oil-in-water type emulsion. On the other hand, calcium, aluminium, ferric and magnesium soaps are more soluble in oil than water thus help stabilizing water-in-oil emulsion.

Above CMC, the surfactants form micelle. So concentration of free molecules does not increase. Therefore, properties like osmotic pressure, surface tension become constant. Below CMC, equivalent conductivity shows general behaviour *i.e.*, it decreases with concentration. Surfactants behave like normal electrolytes. Beyond CMC they form micelle and are not free to contribute to conductivity. Turbidity is directly proportional to the concentration.



Variation of different properties with concentration

In the solubility curves, there is sharp change at Kraft's temperature. Below this, the solubility is mainly because of hydration energy and lattice energy. Beyond this Kraft's temperature, lattice energy is not considered and solubility increases till CMC is reached. Above CMC, mostly surfactant molecules exist as micelle but existence of a poor concentration of monomers should not be ruled out.



Solubility curve of surfactant

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UNIT-6

Purification and Characterisation of Organic Compounds | Some Basic Principles of Organic Chemistry | Hydrocarbons | Organic Compounds Containing Halogens

PURIFICATION AND CHARACTERISATION OF ORGANIC COMPOUNDS

- Methods of Purification of Organic Compounds
- Qualitative Analysis
- Quantitative Analysis

TIPS TO REMEMBER

Purification

- ❑ Organic compounds derived from natural sources or prepared in the laboratory are generally impure and need to be purified.
- ❑ Various methods are applied for purification which depend on the nature of the compounds and impurities mixed with them.

Method	Principle	Applications
Crystallization	Different solubilities of a given organic compound and its impurities in the same solvent.	<ul style="list-style-type: none"> • Crystallization of sugar (containing an impurity of common salt) is achieved by shaking the impure solid with hot ethanol at 348 K (sugar dissolves whereas common salt remains insoluble).
Sublimation	Some solid substances change from solid to vapour state without passing through liquid state. Sublimable compounds get separated from non-sublimable impurities.	<ul style="list-style-type: none"> • Iodine from sodium chloride (as iodine sublimes readily leaving behind sodium chloride). • Camphor, naphthalene, anthracene, benzoic acid, etc. are purified.
Distillation	It is used to separate <ul style="list-style-type: none"> • volatile liquids from non-volatile impurities. • liquids having sufficient difference in their boiling points. 	<ul style="list-style-type: none"> • Hexane (b.p. 342 K) and toluene (b.p. 384 K) • Chloroform (b.p. 334 K) and aniline (b.p. 457 K)

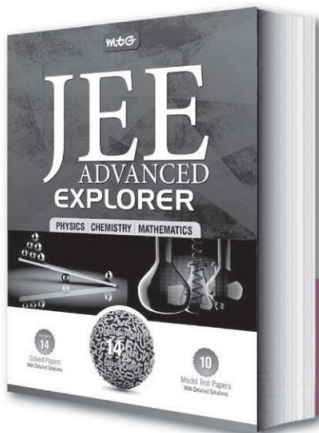
Fractional distillation	If the difference in boiling points of two liquids is not much, this method is used.	<ul style="list-style-type: none"> Crude oil in petroleum industry is separated into various useful fractions such as gasoline, kerosene oil, diesel oil, lubricating oil, etc.
Steam distillation	This method is used to separate substances which are (i) steam volatile, (ii) immiscible with water, (iii) possess a vapour pressure of 10 – 15 mm Hg and (iv) contain non-volatile impurities.	<ul style="list-style-type: none"> Aniline is separated from aniline-water mixture. Essential oils, turpentine oil, <i>o</i>-nitrophenol, bromobenzene, nitrobenzene, etc. can be purified.
Differential extraction	By shaking an aqueous solution of an organic compound with an organic solvent in which the organic compound is more soluble than in water. The organic solvent and the aqueous solution should be immiscible with each other so that they can form two distinct layers which can be separated by using separating funnel.	<ul style="list-style-type: none"> Benzoic acid can be extracted from its water solution using benzene.
Chromatography	Differential movement of individual components of a mixture through a stationary phase under the influence of a mobile phase.	<ul style="list-style-type: none"> Widely used for separation, purification, identification and characterisation of the components of a mixture, whether coloured or colourless.
Adsorption chromatography	Differential adsorption of the various components of a mixture on a suitable adsorbent such as silica gel or alumina.	
– Column chromatography	The mixture is passed through adsorbent packed in glass tube.	<ul style="list-style-type: none"> Mixture of naphthalene and benzophenone
– Thin layer chromatography	The mixture is passed over adsorbent on a thin glass plate.	<ul style="list-style-type: none"> Amino acids can be detected by spraying the plate with ninhydrin solution.
Partition chromatography	Differential partitioning of components of a mixture between stationary and mobile phases.	
– Paper chromatography	A special quality paper known as chromatography paper is used. It contains water trapped in it, which acts as the stationary phase.	<ul style="list-style-type: none"> For separation of sugars and amino acids.

Types of chromatography	Mobile/Stationary phase
Column chromatography	Liquid/Solid
Thin layer chromatography (TLC)	Liquid/Solid
High performance liquid chromatography (HPLC)	Liquid/Solid
Gas-liquid chromatography (GLC)	Gas/Liquid
Partition or paper chromatography	Liquid/Liquid

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KEY POINT

- Retention factor (R_f)

$$R_f = \frac{\text{Distance travelled by the compound from base line}}{\text{Distance travelled by the solvent from base line}}$$
- After purification, an organic compound needs to be tested for purity.
- A pure organic compound possesses characteristic physical properties such as refractive index, specific gravity, boiling point, crystalline structure and melting point.
- In laboratory only melting point (for solids) and boiling point (for liquids) are used as criteria of purity.
- The structure determination and characterisation of an organic compound

involves the following steps:

- Detection of elements (Qualitative analysis)
- Estimation of elements (Quantitative analysis)
- The determination of molecular mass
- Calculation of empirical and molecular formulae

Qualitative Analysis

- An organic compound mainly consists of two elements carbon and hydrogen. In addition to these, it may also contain oxygen, nitrogen, sulphur, halogens and phosphorus.
- The qualitative analysis of organic compounds involves the detection of all these major elements present in it with the help of suitable chemical tests.

Element	Detection	Confirmatory test	Reactions
Carbon	Copper oxide test $2\text{CuO} + \text{C} \xrightarrow{\Delta} 2\text{Cu} + \text{CO}_2 \uparrow$	CO_2 gas turns lime water milky.	$\text{CO}_2 \uparrow + \text{Ca(OH)}_2 \longrightarrow \text{CaCO}_3 \downarrow + \text{H}_2\text{O}$ Lime water Milkiness
Hydrogen	$\text{CuO} + 2\text{H} \xrightarrow{\Delta} \text{Cu} + \text{H}_2\text{O}$	Water droplets appear on the cooler part of the ignition tube and also turns anhydrous CuSO_4 blue.	$\text{CuSO}_4 + 5\text{H}_2\text{O} \longrightarrow \text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ White Blue
Nitrogen	Lassaigne's extract (L.E.) $\text{Na} + \text{C} + \text{N} \xrightarrow{\Delta} \text{NaCN (L.E.)}$	L.E. + $\text{FeSO}_4 + \text{NaOH}$, boil and cool + FeCl_3 + conc. HCl. Gives blue or green colour.	$\text{FeSO}_4 + 2\text{NaOH} \longrightarrow \text{Fe(OH)}_2 + \text{Na}_2\text{SO}_4$ $\text{Fe(OH)}_2 + 6\text{NaCN} \longrightarrow \text{Na}_4[\text{Fe(CN)}_6] + 2\text{NaOH}$ $\text{Na}_4[\text{Fe(CN)}_6] + \text{FeCl}_3 \xrightarrow{\text{HCl}} \text{NaFe[Fe(CN)}_6] + 3\text{NaCl}$ Prussian blue or $3\text{Na}_4[\text{Fe(CN)}_6] + 4\text{FeCl}_3 \longrightarrow \text{Fe}_4[\text{Fe(CN)}_6]_3 + 12\text{NaCl}$ Prussian blue
Sulphur	$2\text{Na} + \text{S} \xrightarrow{\Delta} \text{Na}_2\text{S (L.E.)}$	(i) L.E. + sodium nitroprusside. A deep violet colour. (ii) L.E. + $\text{CH}_3\text{COOH} + (\text{CH}_3\text{COO})_2\text{Pb}$ Gives a black ppt.	(i) $\text{Na}_2\text{S} + \text{Na}_2[\text{Fe(CN)}_5\text{NO}] \longrightarrow \text{Na}_4[\text{Fe(CN)}_5\text{NOS}]$ Sodium nitroprusside Deep violet (ii) $\text{Na}_2\text{S} + (\text{CH}_3\text{COO})_2\text{Pb} \xrightarrow{\text{CH}_3\text{COOH}} \text{PbS} \downarrow + 2\text{CH}_3\text{COONa}$ Black ppt.

Halogens	$\text{Na} + \text{Cl} \xrightarrow{\Delta} \text{NaCl}$ (L.E.)	L.E. + HNO_3 + AgNO_3 (i) White ppt. soluble in aq. NH_3 (or NH_4OH) confirms Cl. (ii) Yellow ppt. partially soluble in aq. NH_3 (or NH_4OH) confirms Br. (iii) Yellow ppt. insoluble in aq. NH_3 (or NH_4OH) confirms I.	$\text{NaX} + \text{AgNO}_3 \xrightarrow{\text{HNO}_3} \text{AgX} \downarrow$ ppt. $\text{AgCl} \downarrow + 2\text{NH}_3(\text{aq.}) \longrightarrow [\text{Ag}(\text{NH}_3)_2] \text{Cl}$ Soluble White ppt.
Nitrogen and sulphur together	$\text{Na} + \text{C} + \text{N} + \text{S} \xrightarrow{\Delta} \text{NaSCN}$ (L.E.) Sodium thiocyanate	Blood red colouration confirms presence of N and S both.	$\text{NaSCN} + \text{FeCl}_3 \longrightarrow [\text{Fe}(\text{SCN})] \text{Cl}_2$ Blood red colour + NaCl
Phosphorus	$\text{P} \xrightarrow[\Delta]{\text{Na}_2\text{O}_2, \text{boil}} \text{Na}_3\text{PO}_4$	Solution is boiled with nitric acid and then treated with ammonium molybdate $(\text{NH}_4)_2\text{MoO}_4$. Formation of yellow ppt. indicates presence of phosphate (hence, phosphorus) in organic compound.	$\text{Na}_3\text{PO}_4 + 3\text{HNO}_3 \longrightarrow \text{H}_3\text{PO}_4 + 3\text{NaNO}_3$ $\text{H}_3\text{PO}_4 + 12(\text{NH}_4)_2\text{MoO}_4 + 21\text{HNO}_3 \longrightarrow (\text{NH}_4)_3\text{PO}_4 \cdot 12\text{MoO}_3 \downarrow +$ Yellow ppt. Ammonium phosphomolybdate $21\text{NH}_4\text{NO}_3 + 12\text{H}_2\text{O}$

KEY POINT

- Presence of oxygen in an organic compound can be detected indirectly by testing the compound containing functional group such as $-\text{OH}$, $-\text{CHO}$, $>\text{C}=\text{O}$, $-\text{COOH}$, $-\text{NO}_2$, etc.

Quantitative Analysis

- Determination of the relative proportions (as percentages) of various elements present in an organic compound is called *quantitative analysis* of the compound. The percentages of the various elements present in the compound are estimated by suitable methods as described.

Element	Method
Carbon and Hydrogen	<p>Liebig's Combustion method : A known mass of an organic compound is burnt in the presence of excess of O_2 and CuO.</p> $\text{C}_x\text{H}_y + \left(x + \frac{y}{4}\right) \text{O}_2 \xrightarrow{\Delta} x\text{CO}_2 + \frac{y}{2} \text{H}_2\text{O}$ <p>CO_2 evolved is absorbed by conc. solution of KOH or ascarite ($\text{NaOH} + \text{CaO}$). H_2O produced is absorbed by anhydrous CaCl_2 or $\text{Mg}(\text{ClO}_4)_2$. Increase in masses of these absorbing compounds gives the masses of CO_2 and H_2O produced.</p> <p>$\% \text{ of C} = \frac{12}{44} \times \frac{\text{mass of } \text{CO}_2 \text{ formed}}{\text{mass of compound taken}} \times 100$, $\% \text{ of H} = \frac{2}{18} \times \frac{\text{mass of } \text{H}_2\text{O} \text{ formed}}{\text{mass of compound taken}} \times 100$</p>

Nitrogen	<p>(i) Dumas method : Nitrogen containing organic compound is heated with CuO in an atmosphere of CO₂. $C_xH_yN_z + \left(2x + \frac{y}{2}\right) CuO \xrightarrow{\Delta} xCO_2 + \frac{y}{2} H_2O + \frac{z}{2} N_2 + \left(2x + \frac{y}{2}\right) Cu$ N₂ evolved gets collected over conc. KOH solution which absorbs all other gases. $\% \text{ of N} = \frac{28}{22400} \times \frac{\text{vol. of N}_2 \text{ at STP}}{\text{mass of compound taken}} \times 100, \text{ Vol. of N}_2 \text{ at STP} = \frac{P_1 V_1 \times 273}{760 \times T_1}$</p> <p>(ii) Kjeldahl's method : $\text{Organic compound} + H_2SO_4 (\text{conc.}) \xrightarrow{\Delta} (NH_4)_2SO_4 \xrightarrow[\Delta]{2NaOH} Na_2SO_4 + 2NH_3 + 2H_2O$ $2NH_3 + H_2SO_4 \longrightarrow (NH_4)_2SO_4$ $\% \text{ of N} = \frac{1.4 \times \text{molarity of acid} \times \text{vol. of acid used} \times \text{basicity of acid}}{\text{mass of compound taken}},$ $\% \text{ of N} = \frac{1.4 \times \text{normality of acid} \times \text{vol. of acid used}}{\text{mass of compound taken}} \quad (\text{for monobasic acid})$</p>
Halogens	<p>Carius method : Halogen in organic compound is precipitated as silver halide by boiling with conc. HNO₃ and then adding AgNO₃.</p> $X \xrightarrow[AgNO_3]{HNO_3, \Delta} AgX \downarrow$ $\% \text{ of Cl} = \frac{35.5}{143.5} \times \frac{\text{mass of AgCl formed}}{\text{mass of compound taken}} \times 100$ $\% \text{ of Br} = \frac{80}{188} \times \frac{\text{mass of AgBr formed}}{\text{mass of compound taken}} \times 100$ $\% \text{ of I} = \frac{127}{235} \times \frac{\text{mass of AgI formed}}{\text{mass of compound taken}} \times 100$
Sulphur	<p>Carius method : Sulphur in organic compound is converted into H₂SO₄ by boiling with Na₂O₂ or conc. HNO₃ and is precipitated as BaSO₄ by adding excess of BaCl₂ solution in water.</p> $S \xrightarrow[\text{(ii) BaCl}_2]{\text{(i) HNO}_3, \Delta} BaSO_4 \downarrow$ <p style="text-align: center;">White ppt.</p> $\% \text{ of S} = \frac{32}{233} \times \frac{\text{mass of BaSO}_4 \text{ formed}}{\text{mass of compound taken}} \times 100$
Phosphorus	<p>Ignition method :</p> $P \xrightarrow[\text{heat}]{HNO_3} H_3PO_4$ $H_3PO_4 + Mg^{2+} + NH_4Cl \xrightarrow{\Delta} MgNH_4PO_4 + HCl$ <p style="text-align: center;">Magnesium ammonium phosphate (white ppt.)</p> $2MgNH_4PO_4 \xrightarrow{\Delta} Mg_2P_2O_7 + 2NH_3 + H_2O$ <p style="text-align: center;">Magnesium pyrophosphate</p> $\% \text{ of P} = \frac{62}{222} \times \frac{\text{mass of Mg}_2\text{P}_2\text{O}_7 \text{ formed}}{\text{mass of compound taken}} \times 100$

Oxygen	Iodine method :
	Organic compound $\xrightarrow{\Delta}$ O ₂ + other gaseous products
	$\frac{[2C + O_2 \xrightarrow{1373\text{ K}} 2CO] \times 5}{[I_2O_5 + 5CO \longrightarrow I_2 + 5CO_2] \times 2}$ $10C + 5O_2 + 2I_2O_5 \longrightarrow 10CO_2 + 2I_2$
	$\% \text{ of O} = \frac{32}{88} \times \frac{\text{mass of CO}_2 \text{ formed}}{\text{mass of compound taken}} \times 100;$ $\% \text{ of O} = \frac{5 \times 16}{2 \times 127} \times \frac{\text{mass of I}_2 \text{ formed}}{\text{mass of compound taken}} \times 100$

✓ SELF CHECK

- For the estimation of nitrogen, 1.4 g of an organic compound was digested by Kjeldahl method and the evolved ammonia was absorbed in 60 mL of $\frac{M}{10}$ sulphuric acid. The unreacted acid required 20 mL of $\frac{M}{10}$ sodium hydroxide for complete neutralization. The percentage of nitrogen in the compound is
 - 5%
 - 6%
 - 10%
 - 3%
 (JEE Main 2014)
- A gaseous hydrocarbon gives upon combustion 0.72 g of water and 3.08 g of CO₂. The empirical formula of the hydrocarbon is
 - C₇H₈
 - C₂H₄
 - C₃H₄
 - C₆H₅
 (JEE Main 2013)

Calculation of Empirical and Molecular Formulae

- **Empirical formula** is the simplest whole number ratio of various atoms present in a compound.
- **Molecular formula** is the exact number of different types of atoms present in a molecule of a compound.
 - Molecular formula = $n \times$ Empirical formula where n is a simplest integer 1, 2, 3, etc. and
$$n = \frac{\text{Molecular mass}}{\text{Empirical formula mass}}$$
 - Molecular mass = $2 \times$ Vapour density

SOME BASIC PRINCIPLES OF ORGANIC CHEMISTRY

- Introduction
- Isomerism
- Electronic Displacement in a Covalent Bond
- Types of Organic Reactions
- Nomenclature

TIPS TO REMEMBER

- Organic chemistry deals with the study of hydrocarbons and their derivatives.
- **Tetravalency of carbon :**

$${}^{12}_6\text{C} : 2, 4$$

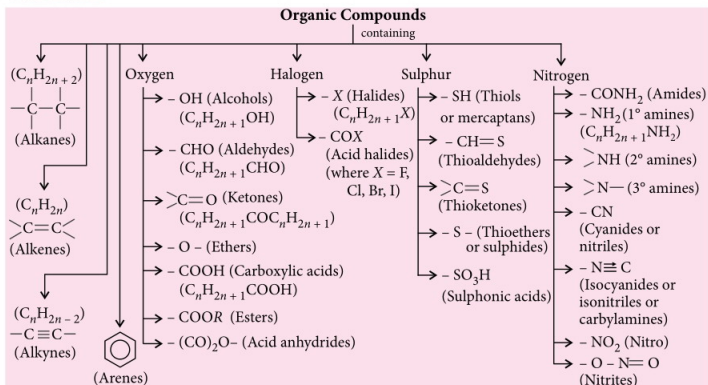
$$1s^2, 2s^1, 2p_x^1, 2p_y^1, 2p_z^1$$
 For carbon, it is very difficult to either gain or lose four electrons, therefore it always shares four electrons and forms four covalent bonds in order to acquire noble gas configuration. Thus, organic compounds are covalent compounds.
- **Shape and hybridisation :**

Molecules	Hybridisation	Shape	Bond angle
Alkane (C _n H _{2n+2})	sp ³	Tetrahedral	109°28'
Alkene (C _n H _{2n})	sp ²	Planar	120°
Alkyne (C _n H _{2n-2})	sp	Linear	180°

📌 KEY POINT

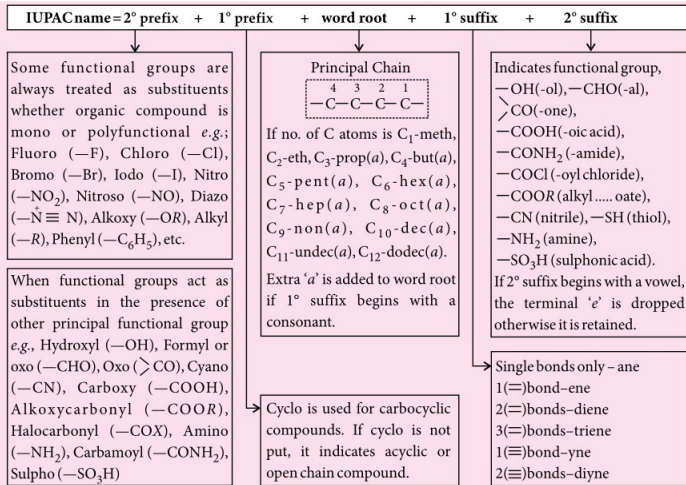
- **s-orbital character :** $sp > sp^2 > sp^3$
- **Size of hybrid orbital :** $sp < sp^2 < sp^3$
- **Bond length of σ-bond :** $sp < sp^2 < sp^3$
- **Electronegativity :** $sp > sp^2 > sp^3$

Classification



Nomenclature

IUPAC nomenclature: The complete IUPAC name of an organic compound consists of five parts.



- Preference order for selection of a principal functional group in polyfunctional compounds is
- COOH, —SO₃H, —COOR, —COCl,
—CONH₂, —CN, —CHO, >C=O, —OH,
—NH₂, >C=C<, —C≡C—.

SELF CHECK

3. The IUPAC name of the compound shown below is



- (a) 2-bromo-6-chlorocyclohex-1-ene
(b) 6-bromo-2-chlorocyclohexene
(c) 3-bromo-1-chlorocyclohexene
(d) 1-bromo-3-chlorocyclohexene.

(AIEEE 2006)

IUPAC nomenclature of aromatic compounds :

- For substituted benzene compounds, the substituent is placed as prefix to the word benzene.
- In disubstituted benzene ring, the substituents are located at the lowest numbers possible while numbering the carbon atoms of the ring.
- In the trivial system of nomenclature, the prefix *ortho* (*o*-) indicates 1,2-, *meta* (*m*-) indicates 1,3- and *para* (*p*-) indicates 1,4-disubstituted benzene ring.
- In case of tri- or higher substituted benzene derivatives, common name of benzene derivatives is taken as the base compound. Number 1 position is assigned to the substituent of the base compound and lowest locant rule is followed for other substituents.
- Benzene ring is considered as substituent [Phenyl (Ph), —C₆H₅] when it is attached to an alkane with a functional group.

KEY POINT

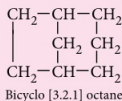
- If the principal chain contains two or more multiple bonds, the numbering is done in accordance with lowest set of locants rule.



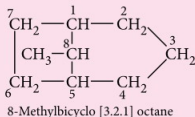
- If both double and triple bonds are present in the parent chain and numbering of parent chain from any end gives the same set of locants, then numbering is done from the end which gives the lowest locant to the double bond.



- Bicyclic compounds are named by adding prefix bicyclo to the name of hydrocarbon corresponding to total number of carbon atoms in two rings. In between the word bicyclo and alkane an expression in the square brackets is placed that represents the number of carbon atoms in each bridge connecting two bridge heads, in descending order separated from one another by full stop.



- If substituent is present, we number the bridged ring system beginning at one bridge head, proceeding first along the longest bridge to the other bridge head, then along the next longest bridge back to the first bridge head. The shortest bridge is numbered last.



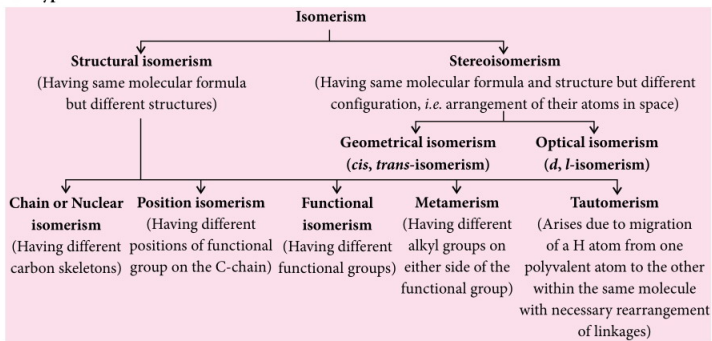
Homologous Series

- A series of organic compounds each containing a characteristic functional group forms a homologous series in which each successive member differs by a —CH₂ group or by 12 + 2 × 1 = 14 mass units. The members of the series are called *homologues* and the phenomenon is called *homology*.

Isomerism

□ The phenomenon of existence of two or more compounds possessing the same molecular formula but different properties is known as *isomerism*.

□ Types of isomerism :



□ Types of structural isomerism :

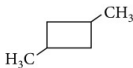
○ Chain isomerism



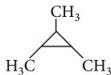
Cyclohexane



Methylcyclopentane



1,3-Dimethylcyclobutane



1,2,3-Trimethylcyclopropane

○ Position isomerism

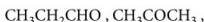


1-Butene



2-Butene

○ Functional isomerism

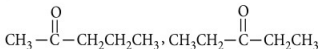


Propanal

Propan-2-one

2-Methyloxirane
(or epoxypropane)

○ Metamerism



Pentan-2-one

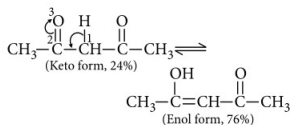
Pentan-3-one

○ Tautomerism

- Isomers exist in dynamic equilibrium.
- It is acid catalysed or base catalysed conversion.

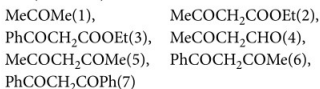
□ Types of tautomerism :

(i) Keto-enol tautomerism :



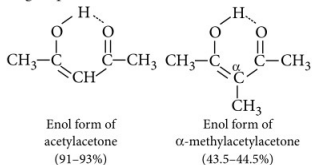
Relative amounts of keto and enol forms depend upon

- stability of the enol formed by intramolecular hydrogen bonding (chelation) and resonance.



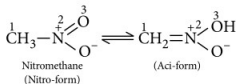
Increasing order of the stability of enol form (i.e., enol content) is 1 < 2 < 3 < 4 < 5 < 6 < 7.

- enol form of α -methylacetylacetone is quite less stable than that of acetylacetone. As there is steric hindrance by α -methyl group.

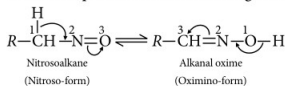


- Polar protic solvents (like water, methanol and acetic acid) decrease the enol content as they stabilise the keto form by forming H-bonding with $>CO$ group. While aprotic solvents (like hexane, benzene) or absence of solvent increase the enol content.

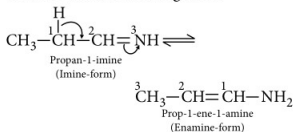
- (ii) **Nitro-acinitro tautomerism** : Shown by 1° and 2° nitroalkanes containing acidic α -Hs.



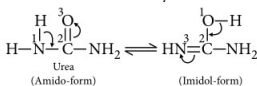
- (iii) **Nitroso-oximino tautomerism** : Shown by nitroso compounds and oximes having α -Hs.



- (iv) **Imine-enamine tautomerism** : Shown by imines and amines having α -Hs.



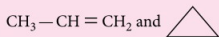
- (v) **Amido-imidol or thioamido-imithiol tautomerism** : Shown by urea and thiourea.



KEY POINT

- Ring-chain isomerism is a part of structural isomerism.

e.g., Alkenes and cycloalkanes (C_nH_{2n})

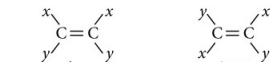


e.g., Alkynes and cycloalkenes (C_nH_{2n-2})



Types of stereoisomerism :

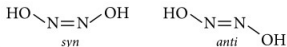
- **Geometrical isomerism** : Geometrical isomers have the same structural formula but they differ in the spatial arrangement of atoms or group of atoms about ($C=C$, $C=N$ or $N=N$) double bond.



(Similar groups on the same side of the double bond)

(Similar groups on the different sides of the double bond)

- In addition to alkenes, compounds containing $C=N$ (aldoxime and ketoxime) and $N=N$ (azo compounds) bonds also show geometrical isomerism. However, in these cases, 'syn' (for *cis*) and 'anti' (for *trans*) are more commonly used.

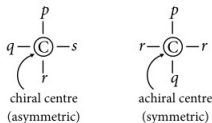


- **E and Z system of nomenclature** : For highly substituted alkenes having four different atoms or groups attached to $C=C$ bond, *cis* and *trans* designations cannot be used. In such cases, E-Z notation is used.



- E is assigned to an isomer in which high priority atoms or groups are on the opposite sides.

- Z is assigned to an isomer in which high priority atoms or groups are on the same side.
- No. of geometrical isomers = 2^n in polyenes. Here, $n = 2$ so, no. of geometrical isomers = $2^2 = 4$.
- **Optical isomerism** : Some substances have the ability to rotate the plane polarised light either to the right (clockwise) or to the left (anticlockwise). These substances are termed as *optically active* substance and the property is called *optical activity*.
- Compounds having similar physical and chemical properties but differing only in the behaviour towards polarised light are called *optical isomers* and the phenomenon is called *optical isomerism*.
- In order to exhibit optical activity, an object must be *chiral*.
- The compound is said to have *chirality* if the central carbon atom is attached to four different groups and this centre is called *chiral (asymmetric) centre* or *stereogenic centre* or *stereocentre*.



- If molecule has a plane of symmetry it is *achiral* (not chiral) and if molecule has no plane of symmetry it is *chiral*.
- **Enantiomers / d and l isomers** are the optical isomers which are non-superimposable mirror images (or dissymmetric).
- **Diastereomers** are the optical isomers which are not mirror images of each other. They have different physical properties and magnitude of specific rotation.

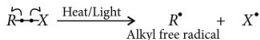
- **Meso compounds** are those compounds which have two or more (even number of chiral carbon atoms and have an internal plane of symmetry. They are optically inactive due to internal compensation.

SELF CHECK

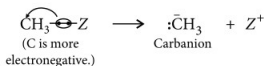
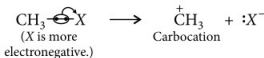
4. The number of structural isomers for C_6H_{14} is
 (a) 3 (b) 4
 (c) 5 (d) 6 (IIT-JEE 2007)
5. The number of stereoisomers possible for a compound of the molecular formula
 $CH_3 - CH = CH - CH(OH) - Me$ is
 (a) 3 (b) 2
 (c) 4 (d) 6 (AIEEE 2009)

Electronic Displacement in a Covalent Bond

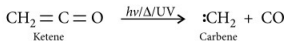
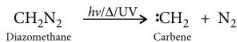
- **Homolytic fission (symmetrical)** : Free radicals are formed by homolytic cleavage of covalent bond in which one of the electrons of the shared pair is moved to each fragment.



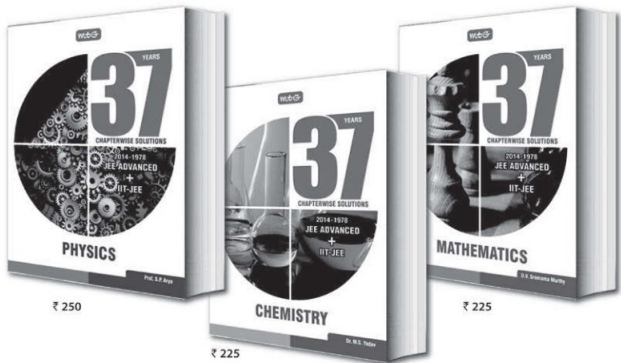
- **Heterolytic fission (unsymmetrical)** : Positive and negative ions are formed by heterolytic cleavage of covalent bond in which both the electrons of the bonding pair are moved to one of the fragments (*i.e.*, towards more electronegative atom).



- **Photolysis or pyrolysis of diazomethane or ketene** :



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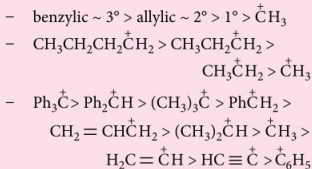
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□ **Reaction intermediates :**

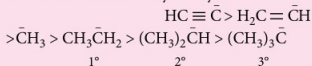
Intermediates	Definition	Hybridisation of carbon and shape	Stability order
Carbocation	Carbon species carrying +ve charge on carbon.	sp^2 hybridised carbon and planar structure.	$3^\circ > 2^\circ > 1^\circ$
Carbanion	Carbon species carrying -ve charge on carbon.	sp^3 hybridised carbon and pyramidal shape.	$1^\circ > 2^\circ > 3^\circ$
Free radical	Atom or group of atoms having odd or unpaired electron.	sp^2 hybridised carbon and planar structure.	$3^\circ > 2^\circ > 1^\circ$

KEY POINT

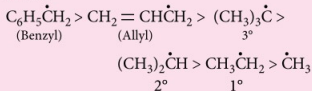
- Relative stabilities of carbocations follow the order :



- Relative stabilities of carbanions follow the order : aromatic > benzyl > allyl >

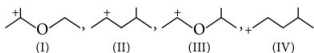


- Relative stabilities of free radicals follow the order :



SELF CHECK

6. The correct stability order for the following species is

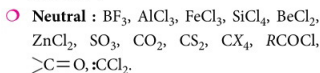
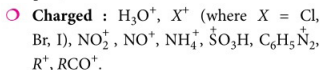


- (a) (II) > (IV) > (I) > (III)
 (b) (I) > (II) > (III) > (IV)
 (c) (II) > (I) > (IV) > (III)
 (d) (I) > (III) > (II) > (IV)

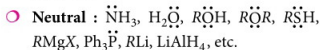
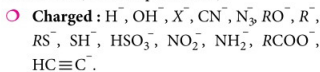
(IIT-JEE 2008)

Attacking Reagents

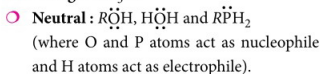
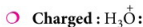
- **Electrophiles :** They are positively charged or neutral molecules having electron deficient atom, seeking a site of high electron density. Electrophiles have an incomplete outer shell and are also called *Lewis acid* (electron-pair acceptor).



- **Nucleophiles :** They are negatively charged or neutral molecules having electron-rich atom with unshared electron pair, seeking electron deficient site to attack. They are also called *Lewis base* (electron-pair donor).



- **Ambiphiles (ambident) :** They behave like both electrophiles and nucleophiles hence, have dual nature (amphoteric).



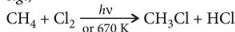
Electron Displacement Effects in Covalent Bonds

- **Inductive effect (I effect)** : Displacement of σ electrons along a saturated carbon chain when an electron donating (+I effect) or when an electron withdrawing (-I effect) group is attached at the end of the carbon chain.
- **Decreasing order of -I effect** : $R_3N- > -NO_2 > -SO_2R > -CN > -COOH > -F > -Cl > -Br > -I > -OR > -COR > -OH > -C_6H_5 > -CH=CH_2 > -H$
 - **Decreasing order of +I effect** : $(CH_3)_3C- > (CH_3)_2C- > CH_3CH_2- > CH_3- > D > H$
- **Electromeric effect (E effect)** : It involves complete transfer of π electrons of a multiple bond towards one of the bonded atoms in the presence of an attacking reagent.
- +E effect when electron transfer takes place towards the atom to which the attacking reagent gets attached.
 - -E effect when electron transfer takes place away from the atom to which the attacking reagent gets attached.
- **Resonance or Mesomeric effect** : It is defined as the polarity produced in the molecule by the interaction of two π bonds or between a π bond and a lone pair of electrons present on adjacent atom.
- **+R or +M effect** : $-Cl, -Br, -I, -NH_2, -NHR, -NR_2, -NHCOR, -OH, -OR, -SR, -SH, -OCH_3, -OCOR, CH_2=CH-CH=CH\ddot{N}H_2, CH_2=CH\ddot{C}l, Ph\ddot{C}l, Ph\ddot{N}H_2, Ph\ddot{O}$
 - **-R or -M effect** : $-NO_2, -CN, >C=O, -CHO, -COOH, -COOR, CH_2=CH-CHO, PhNO_2$
- **Hyperconjugation** : It involves delocalisation of σ electrons of C-H bond of an alkyl group directly attached to an atom of unsaturated system or to an atom with an unshared p -orbital. For an alkyl group attached to unsaturated system it decreases with decrease in number of α -hydrogens :
- $$CH_3- > CH_3CH_2- > (CH_3)_2CH- > (CH_3)_3C-$$

Types of Organic Reactions

- **Substitution reactions (or displacement reactions)** – further classified into three types :

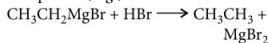
- **Free radical substitution reaction** takes place through free radical intermediates, e.g.,



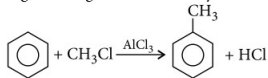
(Here, Cl^\cdot is formed as reaction intermediate)

- **Electrophilic substitution reaction (S_E)** involves the attack by an electrophile. It is of two types :

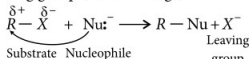
- **Unimolecular (S_{E1})** is first order reaction. These reactions are very rare and generally takes place in aliphatic compounds, e.g.,



- **Bimolecular (S_{E2})** is second order reaction and very common in aromatic compounds where π -electrons of benzene ring are highly delocalised and an electrophile can attack this region of high electron density.



- **Nucleophilic substitution reactions (S_N)** are those reactions in which a stronger nucleophile displaces a weaker nucleophile and the atom or group which departs with its bonding pair of electrons is called the leaving group (or nucleofuge).



Better the leaving group, more facile is the reaction. It is of two types :

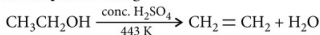
Unimolecular (S_N1)	Bimolecular (S_N2)
It is first order reaction.	It is second order reaction.
Generally carried out in polar protic solvents like water, alcohol and acetic acid.	Carried out in polar aprotic solvents like acetone, DMSO, acetonitrile, or DMF.

Takes place in two steps through carbocation as the intermediate.	Takes place in one step through transition state.
Rate of reaction : $3^\circ > 2^\circ > 1^\circ > \text{CH}_3$ (fastest) (slowest)	Rate of reaction : $\text{CH}_3 > 1^\circ > 2^\circ > 3^\circ$ halides (fastest) (slowest)
Greater the stability of carbocation, faster will be the reaction.	Less the steric hindrance in T.S., faster will be the reaction.
Tends to proceed with weak nucleophiles e.g.; CH_3OH , H_2O , $\text{CH}_3\text{CH}_2\text{OH}$, etc.	Tends to proceed with strong nucleophiles, e.g.; CH_3O^- , CN^- , OH^- , etc.
Configuration is retained but in front attack inversion takes place (racemisation and inversion).	Inversion of configuration takes place (Walden inversion).

□ **Addition reactions :**

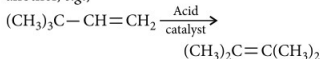
$\text{H}_2\text{C}=\text{CH}_2 + \text{Br}_2 \xrightarrow{\text{CCl}_4} \text{BrCH}_2-\text{CH}_2\text{Br}$
These are also of three types like substitution reactions: Electrophilic addition, Nucleophilic addition and Free radical addition reactions.

□ **Elimination reactions** are opposite of addition reactions in which two atoms or groups of atoms are lost to form compounds with double and triple bonds, e.g.;

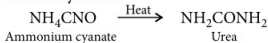


These are of three types : unimolecular elimination (E1), unimolecular conjugate base elimination (E1cB) and bimolecular elimination (E2) reactions.

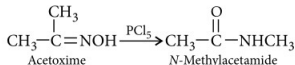
□ **Rearrangements** involve reorganization of the constituent parts of a molecule. In this, functional groups, double bonds, H atoms or alkyl groups are moved from one C atom to another, e.g.;



○ **Wöhler synthesis**

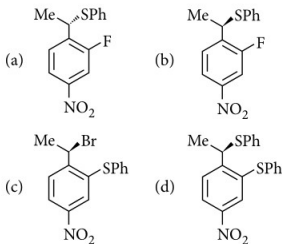
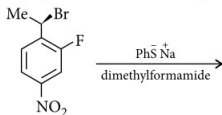


○ **Beckmann rearrangement**



✓ **SELF CHECK**

7. The major product of the following reaction is



(IIT-JEE 2008)

8. $\text{CH}_3\text{Br} + \text{Nu}^- \rightarrow \text{CH}_3-\text{Nu} + \text{Br}^-$
The decreasing order of the rate of the above reaction with nucleophiles (Nu^-) A to D is [$\text{Nu}^- =$ (A) PhO^- , (B) AcO^- , (C) HO^- , (D) CH_3O^-]
(a) $D > C > A > B$ (b) $D > C > B > A$
(c) $A > B > C > D$ (d) $B > D > C > A$.
(AIEEE 2006)

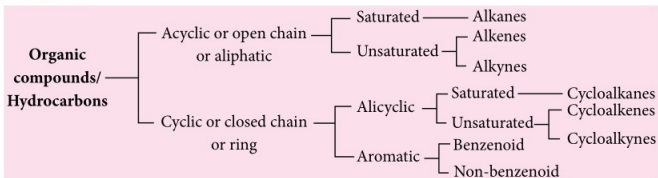
HYDROCARBONS

- Classification
- Conformations (Sawhorse and Newman projections)
- Preparations, properties and reactions (alkanes, alkenes, alkynes and aromatic hydrocarbons)
- Aromaticity

TIPS TO REMEMBER

- Organic compounds composed of only C and H are called *hydrocarbons*.

Classification



Conformations

□ The different arrangements of atoms in space which result from the free rotation of groups about C—C single bond are called *conformations* or *conformers* or *rotamers*.

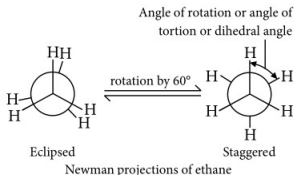
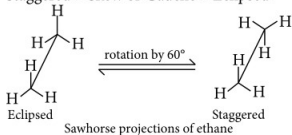
- Among these isomers, basic structure, bond lengths and bond angles remain the same.
- Rotation around a C—C single bond is not completely free due to a weak repulsive interaction between the adjacent bonds, called *torsional strain*.

□ **Conformations of ethane (Sawhorse and Newman projections):**

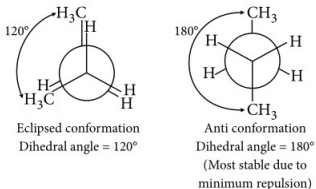
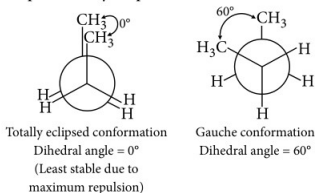
- **Staggered conformation:** The hydrogen atoms attached to two carbons are far apart and experience minimum repulsion.
- **Eclipsed conformation:** The hydrogen atoms attached to two carbons are as close together as possible and experience maximum repulsion.
- **Gauche or Skew form:** A rotation of 60° converts a staggered conformation into an eclipsed conformation, or *vice-versa*. Rotation between 0° to 60° generates one of the many other arrangements in between staggered and eclipsed forms. These arrangements are called *gauche* or *skew form*.

○ **Order of stability:**

Staggered > Skew or Gauche > Eclipsed



□ **Conformations of butane:** The order of stability of different conformations of butane is Staggered (Anti) > Skew or Gauche > Partially eclipsed > Fully eclipsed.



□ **Conformations of cyclohexane:** The order of relative stabilities of various conformations of cyclohexane is

Chair > Twist-boat > Boat > Half-chair

- Conformations of cycloalkanes** : Deviation from normal tetrahedral angle introduces considerable angle strain in cycloalkanes. For example, cyclopropane having bond angle 60° is much strained than cyclobutane having bond angle 90° . Thus, cyclopropane is more reactive than cyclobutane.
 - According to **Baeyer's strain theory**, Strain \propto Angle through which valency bond has deviated from its normal position

Amount of deviation (d) = $\frac{1}{2}(109^\circ 28' - \text{Valency angle})$

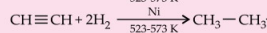
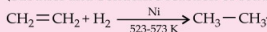
- Cyclopentane has minimum angle strain hence, it is more stable than cyclopropane and cyclobutane.
- Cyclohexane is free from angular strain hence, it is quite stable and unreactive.

Alkanes (Paraffins)

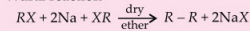
Methods of preparation

By hydrogenation of unsaturated hydrocarbons

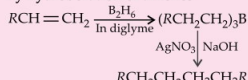
(Sabatier and Sendern's reaction or reduction)



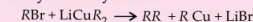
Wurtz reaction



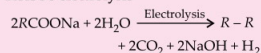
By hydroboration of alkenes



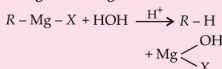
Corey-House synthesis



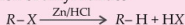
Kolbe's electrolysis



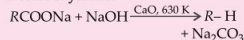
From Grignard's reagent



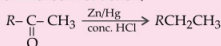
Reduction of alkyl halides



Decarboxylation



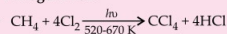
From carbonyl compounds (Clemmensen reduction)



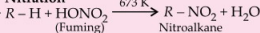
ALKANES

Chemical properties

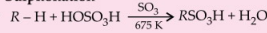
Halogenation



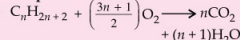
Nitration



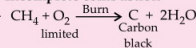
Sulphonation



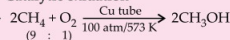
Complete combustion



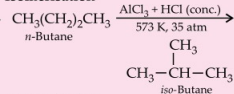
Incomplete combustion



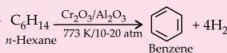
Catalytic oxidation



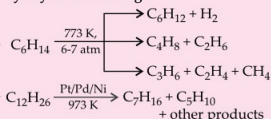
Isomerisation



Aromatisation



Pyrolysis or cracking

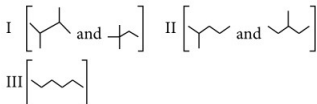


Physical properties

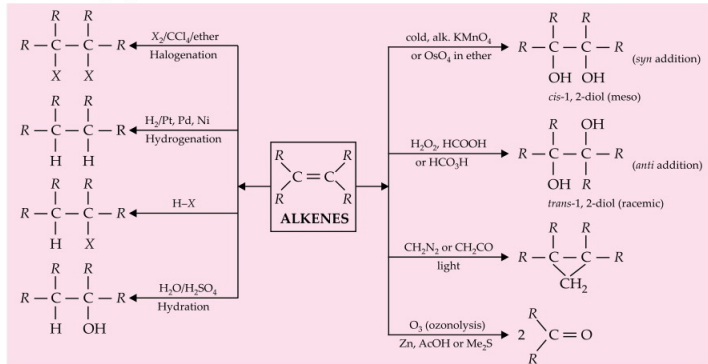
- Due to presence of weak van der Waals forces, the first four members, C_1 to C_4 are gases, C_5 to C_{17} are liquids and C_{18} and above are solids at 298 K.
- All alkanes are colourless and odourless, insoluble in water but dissolve in non polar solvents.
- The boiling point of alkanes increases with increase in molecular mass and for the same alkane the boiling point decreases with branching.
- Alkanes with even number of carbon atoms have higher melting points than those with odd number of carbon atoms due to symmetry.

SELF CHECK

9. Isomers of hexane, based on their branching, can be divided into three distinct classes as shown in the figure.



Chemical properties

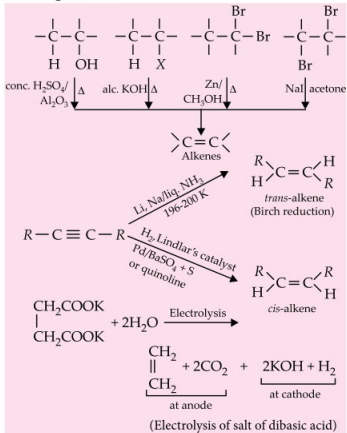


The correct order of their boiling point is

- (a) I > II > III (b) III > II > I
 (c) II > III > I (d) III > I > II
 (JEE Advanced 2014)

Alkenes (Olefins)

Preparation



STRUCTURE OF ATOM

Atom is the smallest indivisible particle of an element that retains the properties of that element.
(By John Dalton, 1808)

Fundamental Particles

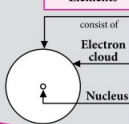
Sub-atomic particles - Like electron, proton, neutron, positron, neutrino, meson, etc.

Three fundamental particles are: Electron, proton and neutron.

Particle	Discovery	Symbol	Mass	Charge	Location
Electron	J.J. Thomson	e	$1/1837$	-1	Electron cloud
Proton	Goldstein	p	1	$+1$	Nucleus
Neutron	Chadwick	n	1	0	Nucleus

Elements

Elements are made up of Atoms combine to form Molecules.



- Contains the *electrons*.
- Makes up most of the volume of the atom.
- Electrons are small and essentially have no mass, so the *electron cloud is mostly empty space*.
- Contains the *protons and neutrons*.
- Contains all the mass of the atom.
- *Extremely dense*.

I. Atomic Models

Different atomic models were proposed to explain the distributions of these charged particles in an atom.

1. Plum Pudding Model, 1904 (By J. J. Thomson)

- Electrons embedded in positive charge.
- Drawback:** Unable to explain:
 - the results of scattering experiments, carried out by Rutherford.



2. Rutherford's Model, 1911

- Tiny, very dense, positive nucleus.
- Diffuse electron cloud (unexplained).

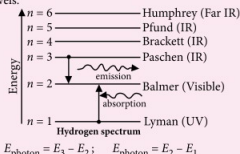
Drawback: Unable to explain:

- the stability of an atom.
- the electronic structure of atoms.



3. Bohr Planetary Model, 1913

- A first explanation of atomic spectra.
- Light can have only discrete quantity of energy.
- Energy is quantized.
- Electric current through a gas in vacuum tube excites the atom of gas.
- As atoms re-emit the light, the light is dispersed through a prism or diffraction grating into its component colours (or wavelengths): **Emission spectrum**.
- Sunlight or incandescent light: **Continuous spectrum**.
- Excited atoms in a vacuum emit a **line spectrum/atomic spectrum**.
- Pattern of emission is different for every element: Serve as "fingerprints" for identification of elements.
- Bohr established H-atom theory.
- The atom can only absorb or emit light having just the right energy to move the electron between certain energy levels.



$$E_{\text{photon}} = E_3 - E_2; \quad E_{\text{photon}} = E_2 - E_1$$

Drawback: Unable to explain:

- the spectra of multielectron atoms.
- fine spectrum of hydrogen.
- Zeeman and Stark effects.

II. Quantum Mechanical Models

1. **de Broglie, 1924:** All material particles possess wave as well as particle character.
2. **Heisenberg's uncertainty principle, 1927:** It is impossible to measure simultaneously both the exact position and exact momentum (or velocity) of an electron.
3. **Schrödinger's model, 1926:** Probability density (ψ^2) \propto probability of finding an electron in an atom. The wave function (ψ) is called *orbital wave function* or simply *atomic orbital*.

III. Subshells

Each orbital can have only two electrons.

Types of orbitals	Shape	Degenerate orbitals
s ($l = 0$)	Spherical	—
p ($l = 1$)	Cartoon dumb-bell	p_x, p_y, p_z
d ($l = 2$)	Double dumb-bell (cloverleaf)	$d_{xy}, d_{yz}, d_{zx}, d_{x^2-y^2}, d_{z^2}$
f ($l = 3$)	Double cloverleaf	$f_{x^3}, f_{y^3}, f_{z^3}, f_{x^2-y^2}z, f_{x^2-z^2}y, f_{y^2-z^2}x, f_{xyz}$

IV. Quantum Numbers

The characteristics of an orbital are expressed in terms of three quantum numbers. Further, to represent the rotation of an electron, spin quantum number is introduced.

Principal (n)	Azimuthal (l)	Magnetic (m_l)	Spin (m_s)
Bohr	Sommerfeld	Lande	Uhlenbeck & Goudsmit
Determines - orbital size and energy.	- orbital shape or type.	- orbital orientation in space.	—
Maximum no. of electrons = $2n^2$ ($n = 1, 2, 3, 4, \dots$)	$l = n - 1$ ($n = 0, 1, 2, 3, \dots$)	$m_l = (2l + 1)$ ($m_l = -l \dots 0 \dots +l$)	For a particular value of $m_l, m_s = \pm 1/2$
Accounts for, - main lines in atomic spectrum.	- the fine lines in the atomic spectrum.	- the splitting of lines in the atomic spectrum.	- magnetic properties of substances.

V. Filling of orbitals in Atom

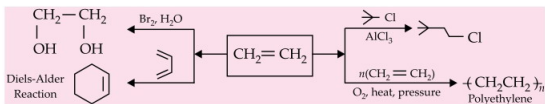
Electrons in various orbitals are filled on the basis of:

Aufbau principle: The order for electron entry into shells and subshells depends on the orbital energy. The lowest energy orbitals will be filled first.

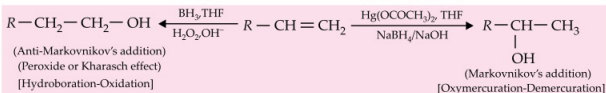
Pauli exclusion principle: No two electrons in an atom can have the same set of four quantum numbers.

Hund's rule: In a subshell with more than one orbital (p, d, f, \dots), electrons should not be spin-paired until every orbital in the subshell contains one electron.

- Atomic number is also known as *proton number* because the charge on the nucleus depends upon the number of protons.
- The Heisenberg's uncertainty and de Broglie concepts are significant only for microscopic systems.
- Schrödinger wave equation does not give *spin quantum number*.
- The letters s, p, d and f come from the spectroscopic terms *sharp, principal, diffused* and *fundamental* which were used to describe the lines in the atomic spectra.
- Electrons in atoms are arranged as: Shells (n) \rightarrow Subshells (l) \rightarrow Orbitals (m_l).
- f -orbitals are found only in the *lanthanide* and *actinide elements*.
- For H-atom, wave function are: Radial nodes $\Rightarrow (n - l - 1)$; Angular nodes $\Rightarrow l$; Total nodes $\Rightarrow (n - 1)$.



○ **Markovnikov's and Anti-Markovnikov's rule**

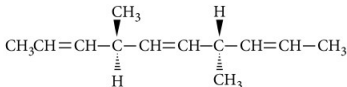


□ **Physical properties**

- The first three members are gases, the next fourteen are liquids and the higher ones are solids.
- All alkenes are colourless and odourless except ethene which has faint sweet smell.
- All alkenes are insoluble in water but fairly soluble in non polar solvents.
- Boiling points of alkenes increase regularly with increase in size and straight chain alkenes have higher boiling points than isomeric branched chain compounds.

✓ **SELF CHECK**

10. The number of optically active products obtained from the complete ozonolysis of the given compound is



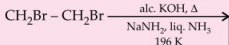
- (a) 0 (b) 1
(c) 2 (d) 4

(IIT-JEE 2012)

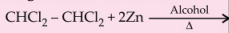
Alkynes (Acetylenes)

□ **Preparation**

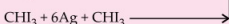
Dehydrohalogenation of dihalides



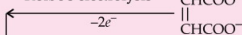
By heating tetrahalides with Zn dust



By heating iodoform with silver



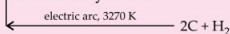
Kolbe's electrolysis



Laboratory method

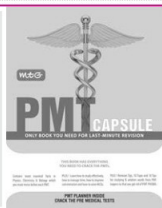


Berthelot synthesis



mtg

PMT
CAPSULE



Essential Facts in
Physics, Chemistry & Biology

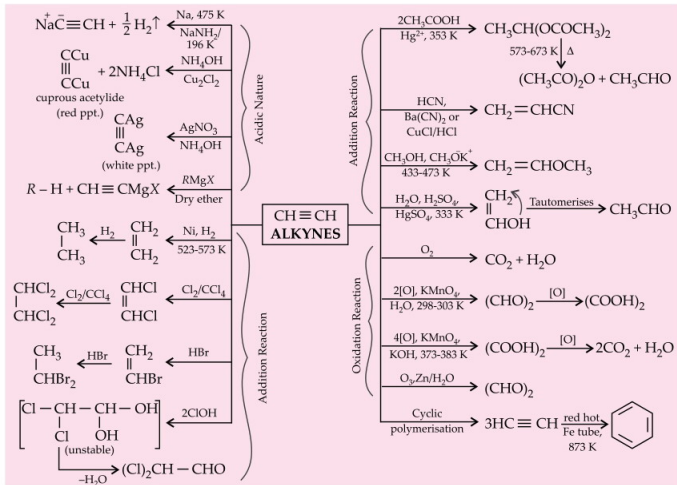
- Learn how to study effectively
- How to manage time
- How to improve concentration
- How to solve MCQ's



MTG BOOKS

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Chemical properties



Physical properties

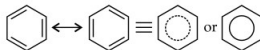
- First three members are gases, the next eight are liquids and the higher ones are solids.
- All alkynes are colourless and odourless except ethyne which has characteristic odour.
- All alkynes are insoluble in water but soluble in non polar solvents.
- Melting points, boiling points and density increase with increase in molar mass.

SELF CHECK

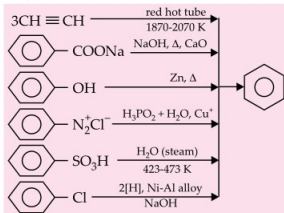
11. The synthesis of 3-octyne is achieved by adding a bromoalkane into a mixture of sodium amide and an alkyne. The bromoalkane and alkyne respectively are
- (a) $\text{BrCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ and $\text{CH}_3\text{CH}_2\text{C} \equiv \text{CH}$
- (b) $\text{BrCH}_2\text{CH}_2\text{CH}_3$ and $\text{CH}_3\text{CH}_2\text{CH}_2\text{C} \equiv \text{CH}$
- (c) $\text{BrCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ and $\text{CH}_3\text{C} \equiv \text{CH}$
- (d) $\text{BrCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ and $\text{CH}_3\text{CH}_2\text{C} \equiv \text{CH}$ (IIT-JEE 2010)

Aromatic Hydrocarbons (Arenes)

- **Structure of benzene** : Kekulé structure of benzene was given by Friedrich August Kekulé in 1865.
- It has high degree of unsaturation and has unusual stability due to resonance stabilisation.



Preparation

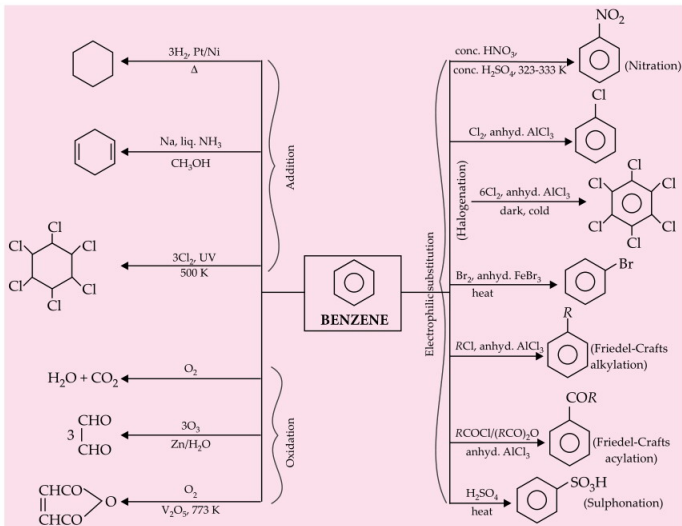


Physical properties

- Aromatic hydrocarbons are non-planar molecules.
- These are colourless liquids or solids with characteristic aroma.
- These are immiscible with water but miscible in organic solvents and burn with sooty flame.

Chemical properties

- B.pt. of arenes increases with increase in the molecular size due to increase in van der Waals forces of attraction.
- M.pt. depends on molecular size and symmetry. Among *o*-, *m*- and *p*-xylenes, *p*-isomer has highest melting point.



KEY POINT

- Benzene undergoes electrophilic substitution while alkenes undergo electrophilic addition.
- **Ortho and para directing groups** also called *activating groups* direct the incoming group to *ortho* and *para* positions of benzene ring. For example, $-\text{CH}_3$, $-\text{C}_2\text{H}_5$, $-\text{C}_6\text{H}_5$, $-\text{X}$, $-\text{OH}$, $-\text{OCH}_3$, $-\text{NH}_2$, $-\text{NHR}$, $-\text{NHCOC}_2\text{H}_5$, etc.

KEY POINT

- $-\text{X}$ groups are *ortho-para* directing due to $+\text{M}$ effect but these groups are deactivating due to $-\text{I}$ effect.
- **Meta directing groups** also called *deactivating groups* direct the incoming group to *meta* position of benzene ring. For example, $-\text{NO}_2$, $-\text{CN}$, $-\text{CHO}$, $-\text{COR}$, $-\text{COOH}$, $-\text{COOR}$, $-\text{SO}_3\text{H}$, $-\text{CF}_3$, $-\text{N}^+(\text{CH}_3)_3$, etc.

- **Huckel rule of aromaticity** is applied to all the ring systems whether they have benzene ring or not and possess the following characteristics :

- Planarity
- Complete delocalisation of π -electrons in the ring.
- Presence of $(4n + 2)\pi$ -electrons in the ring where $n = 0, 1, 2, 3, \dots$

For example,



Benzene



Cyclopentadienyl anion
($n = 1, 6 \pi$ electrons)



Cycloheptatrienyl cation

SELF CHECK

12. The reaction of toluene with Cl_2 in presence of FeCl_3 gives predominantly
- (a) *m*-chlorobenzene
 - (b) benzoyl chloride
 - (c) benzyl chloride
 - (d) *o*- and *p*-chlorotoluene.

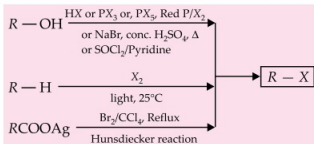
(AIEEE 2007)

ORGANIC COMPOUNDS CONTAINING HALOGENS

- Preparations, properties and reactions
- Nature of C — X bond
- Uses and environmental effects of chloroform, iodoform, freons and DDT

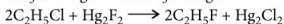
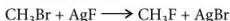
TIPS TO REMEMBER

- **Preparation of haloalkanes**

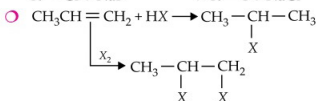


- **By halogen exchange**

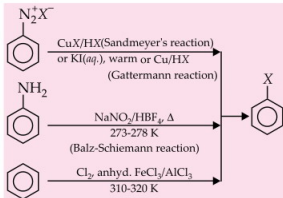
Swarts reaction :



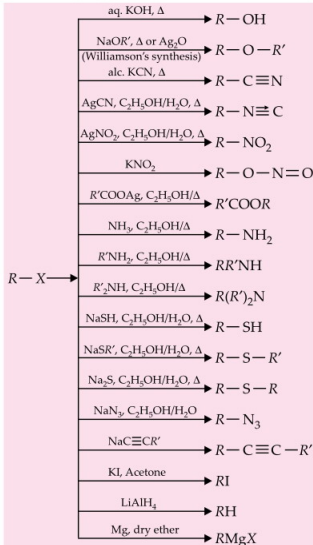
Finkelstein reaction :



- **Preparation of haloarenes**

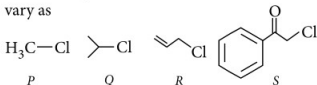


- **Chemical properties**

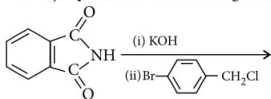


SELF CHECK

13. KI in acetone, undergoes S_N2 reaction with each of P, Q, R and S. The rates of the reaction vary as



- (a) $P > Q > R > S$ (b) $S > P > R > Q$
 (c) $P > R > Q > S$ (d) $R > P > S > Q$
 (JEE Advanced 2013)
14. The major product of the following reaction is



- (a)
- (b)
- (c)
- (d)

(IIT-JEE 2011)

Physical properties

- Lower members (CH_3Cl , CH_3Br and $\text{C}_2\text{H}_5\text{Cl}$) are gases and the others are sweet smelling liquids.
- Alkyl halides are polar in nature but are insoluble in water due to their inability to form H-bonds with water or to break the existing H-bonds between water molecules and are soluble in organic solvents.

- Haloalkanes have higher molecular weights than corresponding alkanes because of which they have considerably higher boiling points.
- Gradation in densities and boiling points of halides for a given alkyl group follows the order: $\text{RI} > \text{RBr} > \text{RCl} > \text{RF}$.
- For a given halogen, the boiling points of alkyl halides increase with the increase in the size of the alkyl group.
- Alkyl iodides usually darken on standing for sometime due to decomposition by light and liberation of iodine.

Nature of C-X bond

- C-X bond is highly polarised because X is more electronegative than C. Thus haloalkanes are highly reactive towards nucleophilic substitution reactions.

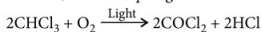


- Order of reactivity:**
 $\text{C}-\text{F} < \text{C}-\text{Cl} < \text{C}-\text{Br} < \text{C}-\text{I}$
- Order of bond length:**
 $\text{C}-\text{F} < \text{C}-\text{Cl} < \text{C}-\text{Br} < \text{C}-\text{I}$
- Order of bond enthalpy:**
 $\text{C}-\text{F} > \text{C}-\text{Cl} > \text{C}-\text{Br} > \text{C}-\text{I}$
- Order of dipole moment:**
 $\text{C}-\text{Cl} > \text{C}-\text{F} > \text{C}-\text{Br} > \text{C}-\text{I}$
- Haloarenes are less reactive towards nucleophilic substitution reactions than haloalkanes.
- This low reactivity can be attributed to the following factors:
 - The C-X bond in halobenzene has a partial double bond character due to involvement of halogen electrons in resonance with benzene ring.
 - The C-X bond in aryl halides is less polar as compared to that in alkyl halides as sp^2 hybridised carbon is more electronegative than sp^3 hybridised carbon.

Chloroform (CHCl_3)

Effects

- It is oxidised to poisonous gas, carbonyl chloride, known as *phosgene*.



Phosgene gas causes liver and kidney damage.

- Inhaling chloroform vapours depresses the CNS, causes dizziness, fatigue and headache.

❑ Uses

- Its major use is in the production of Freon refrigerant, R-22.
- It is used as a solvent for resins, rubbers, oils and fats, alkaloids, iodine and many other substances.
- In the past, it was extensively used as anaesthetic for surgery but now it is rarely used as it causes liver damage.
- It is used in preparation of chloreton (drug) and chloropicrin (insecticide).
- It is used to preserve anatomical species.

Iodoform (CHI_3)

❑ Uses

- Used as an antiseptic in dressing of wounds due to liberation of iodine.
- Used as methylating agent in organic synthesis.

Freons : Chlorofluorocarbons are known as *freons*.

❑ Effects

- Freons cause disruption of ozone layer by initiating radical chain reactions in stratosphere.
- This anthropogenic compound is a greenhouse gas and effect is more than CO_2 .

❑ Uses

- They are used as refrigerants, blowing agents, propellants in medical applications and degreasing solvent.

DDT (*p, p'*-Dichlorodiphenyltrichloroethane)

❑ Uses and Effects

- In 1940, it was used as a pesticide.
- It is a persistent organic pollutant, strongly absorbed by soil.
- It is lipophilic so has a high potential to bioaccumulate.
- It may be directly genotoxic but may also induce enzymes to produce other genotoxic intermediates and DNA adducts.

Carbon tetrachloride (CCl_4) : It is also called *pyrene*.

❑ Effects

- Its exposure causes liver cancer in humans.
- The most common effects are dizziness, light headedness, nausea and vomiting, which can cause permanent damage to nerve cells.
- In severe cases, these effects can lead rapidly to stupor, coma, unconsciousness or death.

❑ Uses

- It is used as feedstock in the synthesis of chlorofluorocarbons and other chemicals, pharmaceutical manufacturing and general solvent use.
- It is used as a cleaning fluid, both in industry, as a degreasing agent, and in the home, as a spot remover and as fire extinguisher.

✓ SELF CHECK

15. What is DDT among the following?
- A fertilizer
 - Biodegradable pollutant
 - Non-biodegradable pollutant
 - Greenhouse gas

(AIEEE 2012)

📌 KEY POINT

- Order of displacement of H from hydrocarbon by halogen :
benzylic \approx allylic $> 3^\circ > 2^\circ > 1^\circ >$ vinylic \approx aryl
- Order of reactivity of halogen acids with alkene : $\text{HI} > \text{HBr} > \text{HCl} > \text{HF}$
- Order of reactivity of alcohols with halogen acid : $\text{Allyl} > 3^\circ > 2^\circ > 1^\circ$
- Order of boiling point: $\text{RI} > \text{RBr} > \text{RCl} > \text{RF}$
 $1^\circ > 2^\circ > 3^\circ$ halides

ANSWER KEYS (SELF CHECK)

1. (c) 2. (a) 3. (c) 4. (c) 5. (c)
6. (d) 7. (a) 8. (a) 9. (b) 10. (a)
11. (d) 12. (d) 13. (b) 14. (a) 15. (c)

Exam Café

QUESTIONS FOR PRACTICE

1. Identify the most stable species in the following sets of ions.



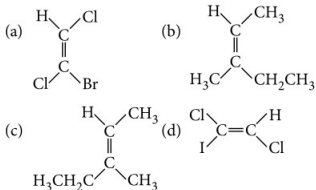
2. An organic compound (0.1840 g) containing nitrogen, when analysed by Dumas method gave 30.0 mL of nitrogen collected at 287 K and 758 mm Hg pressure. The percentage of nitrogen in the organic compound is (Aqueous tension at 287 K is 14 mm Hg.)



3. Which conformer is at a minimum energy on the potential energy diagram in the chair-chair interconversion of cyclohexane?

- (a) Boat
 (b) Half-chair
 (c) Twist-boat
 (d) All conformers are at same energy level.

4. Which of the following have *E*-configuration?



5. Match list I with list II and select the correct answer using the codes given below the lists.

List I
(Compound)

- A. Chloretone
 B. Chloropicrin
 C. Lindane
 D. Teflon

List II
(Use)

- (i) Monomer
 (ii) In war and as insecticide
 (iii) Insecticide
 (iv) Hypnotic

- | A | B | C | D |
|-----------|-------|-------|-------|
| (a) (iii) | (i) | (iv) | (ii) |
| (b) (i) | (ii) | (iii) | (iv) |
| (c) (iv) | (iii) | (ii) | (i) |
| (d) (ii) | (iv) | (i) | (iii) |

6. The reagent which would distinguish between 1-hexyne and 1-hexene is

- (a) $[\text{Ag}(\text{NH}_3)_2]\text{OH}$ (b) KMnO_4
 (c) Br_2 in CCl_4 (d) H_2SO_4

7. The function of boiling the sodium extract with conc. HNO_3 before testing for halogen is

- (a) to make the solution acidic
 (b) to make the solution clear
 (c) to convert Fe^{2+} to Fe^{3+}
 (d) to destroy CN^- and S^{2-} ions.

8. Starting with ethene, which of the following is the best method for preparing ethyne?

- (a) Br_2/CCl_4 ; alc. KOH ; NaNH_2
 (b) HBr ; NaNH_2
 (c) Br_2/CCl_4 ; Zn/H^+ ; H_2/Ni
 (d) HBr ; Zn/H^+ ; H_2/Ni

9. Select the correct IUPAC name of the given compound.



- (a) 1-Bromo-2, 2-dimethylloxacyclobutane
 (b) 3-Bromo-2, 2-dimethylloxacyclobutane
 (c) 3-Bromo-2, 2-dimethylloxocyclobutane
 (d) 1-Bromo-2, 2-methylloxacyclobutane

10. Which of the following compounds has the highest boiling point?

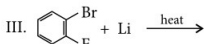
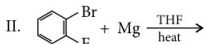
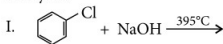
- (a) $\text{CH}_3\text{CH}_2\text{CH}_2\text{Cl}$
 (b) $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Cl}$
 (c) $\text{CH}_3\text{CH}(\text{CH}_3)\text{CH}_2\text{Cl}$
 (d) $(\text{CH}_3)_3\text{CCl}$

11. A compound with no tertiary hydrogen is

- (a) $(\text{CH}_3)_3\text{CCH}(\text{CH}_3)_2$
 (b) $(\text{CH}_3)_3\text{CCH}_2\text{CH}_3$
 (c) $(\text{CH}_3)_2\text{CHCH}_2\text{CH}_2\text{CH}_3$
 (d) none of the above.

12. A compound 'Y' is decomposed at its boiling point, it is purified by
- vacuum distillation
 - steam distillation
 - fractional distillation
 - sublimation.

13. Which of the following reactions can form benzyne?



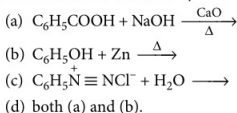
- I
 - II and III
 - All the three
 - None of these.
14. Grignard reagents are
- Strong acids
 - Strong bases
 - Strong electrophiles
 - Strong nucleophiles
- I is correct
 - II is correct
 - I and III are correct
 - II and IV are correct.

15. 6 g of an organic compound containing oxygen is heated with graphite and carbon monoxide formed is quantitatively converted to 8.8 g CO_2 on reaction with I_2O_5 . Percentage of oxygen in the compound is
- 33.33 %
 - 63.33 %
 - 43.33 %
 - 53.33 %

16. Which of the following contains acidic hydrogen?
- Ethene
 - Ethane
 - Both (a) and (b)
 - But-1-yne

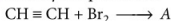
17. CCl_4 is used as fire extinguisher because
- of its covalent bond
 - of its low boiling point
 - of its high melting point
 - it gives incombustible vapours.

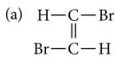
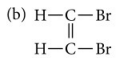
18. Benzene can be obtained by



19. The enolic form of acetone contains
- 9 σ bonds, 1 π bond and 2 lone pairs
 - 8 σ bonds, 2 π bonds and 2 lone pairs
 - 10 σ bonds, 1 π bond and 1 lone pair
 - 9 σ bonds, 2 π bonds and 1 lone pair.

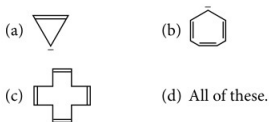
20. Identify the product A.



- 
- 
- Both (a) and (b)
- None of these

21. Chlorobenzene on heating with aqueous NH_3 under pressure in the presence of cuprous oxide gives
- benzamide
 - nitrobenzene
 - aniline
 - chloroaminobenzene.

22. Using the Huckel rule, indicate which of the following species are antiaromatic?

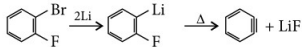
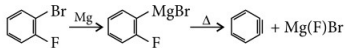


23. Tertiary alkyl halides are practically inert to substitution by $\text{S}_{\text{N}}2$ mechanism because of
- insolubility
 - instability
 - inductive effect
 - steric hindrance.

24. In the reaction of propene with HBr in presence of light, first step involves the
- addition of H atom
 - addition of H^+ ion
 - addition of Br atom
 - none of these.

11. (b) 12. (a)

13. (c) : Chlorobenzene under drastic conditions undergo nucleophilic substitution *via* benzyne mechanism. *o*-Bromofluorobenzene forms benzyne when treated with Mg or Li.



Recall that order of reactivity of aryl halides toward Mg or Li is $\text{ArI} > \text{ArBr} > \text{ArCl} > \text{ArF}$.

14. (d)

15. (d) : Percentage of oxygen

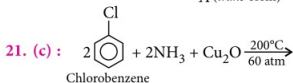
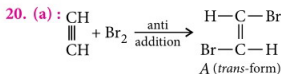
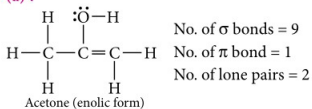
$$\begin{aligned} &= \frac{16}{44} \times \frac{\text{mass of CO}_2}{\text{mass of organic compound}} \times 100 \\ &= \frac{16}{44} \times \frac{8.8}{6} \times 100 = 53.33\% \end{aligned}$$

16. (d)

17. (d) : CCl_4 is used as fire extinguisher under the name 'pyrene'. The dense vapours form a protective layer on the burning objects and prevent the oxygen or air to come in contact with the burning objects.

18. (d)

19. (a) :



21. (c) :

22. (d) : The number of π electrons in the species is counted, if it corresponds to $(4n + 2)$, then the species is aromatic (Huckel rule), otherwise antiaromatic.

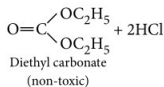
(a) $2 + 2 = 4$ (antiaromatic)(b) $6 + 2 = 8$ (antiaromatic)

(c) 8 (antiaromatic).

23. (d)

24. (c) : In presence of light addition of HBr takes place through free radical mechanism where addition of bromine atom (bromine radical, $\dot{\text{Br}}$) is the first step.

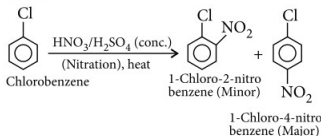
25. (c)

26. (d) : $\text{COCl}_2 + 2\text{C}_2\text{H}_5\text{OH} \longrightarrow$ 

27. (d) : Carbocations are sp^2 hybridised, simple (unconjugated) carbanions are sp^3 hybridised but conjugated carbanions are sp^2 hybridised because here delocalization of electrons results in the formation of a double bond which requires all involved atoms to lie in the same plane (coplanar), *i.e.* the molecule becomes flat.

28. (b)

29. (a) :



The $-\text{Cl}$ group in chlorobenzene is *o*-, *p*-director and deactivating. However, because of steric hindrance at the *o*-position, the *p*-product usually predominates over the *o*-product.

30. (c)

2015

CBSE-B^oARD

CHAPTERWISE PRACTICE PAPER

Series-7**Aldehydes, Ketones and Carboxylic Acids**

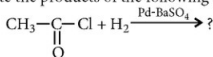
Time : 3 hrs.

Marks : 70

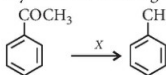
GENERAL INSTRUCTIONS

- (i) All questions are compulsory.
- (ii) Question numbers 1 to 5 are very short-answer questions and carry 1 mark each.
- (iii) Question numbers 6 to 10 are short-answer questions and carry 2 marks each.
- (iv) Question numbers 11 to 22 are also short-answer questions and carry 3 marks each.
- (v) Question number 23 is value based question and carries 4 marks.
- (vi) Question numbers 24 to 26 are long-answer questions and carry 5 marks each.
- (vii) Use Log Tables, if necessary. Use of calculator is not allowed.

1. Write the products of the following reaction:

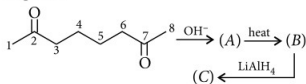


2. Identify 'X' in the following reaction:

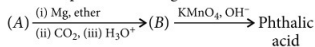


3. Write the Hell-Volhard-Zelinsky reaction.
 4. Write the IUPAC name of the following :
 $(\text{CH}_3)_2\text{C}=\text{CHCOCH}_3$
 5. How is benzoic acid obtained from bromobenzene?
 6. CH_3CHO is more reactive than CH_3COCH_3 towards reaction with HCN . Why?
 7. Write the products of oxidation of
 - (i) 2-pentanone and
 - (ii) 3-pentanone.
 Are the major products same or different? Explain.
 8. Carboxylic acids do not give reactions of carbonyl group. Explain.
 9. Hydrazones of aldehydes and ketones are not prepared in highly acidic medium. Give reason.
 10. Give reasons:
 - (i) *p*-Nitrobenzoic acid has higher K_a value than benzoic acid.
 - (ii) Chloroacetic acid has lower pK_a value than acetic acid.
- OR**
- (i) Arrange the following in increasing order of acidic character. Also give reason.
 HCOOH , ClCH_2COOH , CF_3COOH , CCl_3COOH
 - (ii) Account for the following observation:
 Melting point of an acid with even number of carbon atoms is higher than those of its neighbours with odd number of carbon atoms.
 11. State one chemical method each to distinguish between the following pairs of organic compounds:
 - (i) Acetaldehyde and acetone
 - (ii) Phenol and benzoic acid
 - (iii) Propanone and ethanol

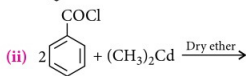
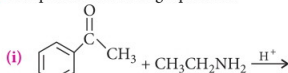
12. Identify A, B and C in the following reactions sequence:



13. Assign structure to the compound (A), C_8H_9Br which responds following series of reactions.



14. Complete the following equations:



Convert:

- (i) Acetaldehyde to crotonaldehyde
 - (ii) Cyclohexanecarbaldehyde to cyclohexylphenylcarbinol
 - (iii) Acetic acid to acetone
15. How will you bring about the following conversions in not more than two steps?
- (i) Benzaldehyde to 3-phenylpropan-1-ol
 - (ii) Benzaldehyde to α -hydroxyphenylacetic acid
 - (iii) Benzoic acid to *m*-nitrobenzyl alcohol
16. (i) Although phenoxide ion has more number of resonating structures than carboxylate ion, carboxylic acid is a stronger acid than phenol. Why?
- (ii) Benzoic acid does not undergo Friedel-Crafts reaction. Why?
- (iii) Carbonyl carbon is an electrophilic whereas carbonyl oxygen is a nucleophilic centre. Why?
17. How will you convert ethanal into the following compounds?

- (i) Butan-2-one
- (ii) Butan-1-ol
- (iii) Butanoic acid

18. (i) An organic compound (A) with molecular formula $C_5H_8O_2$ is reduced to *n*-pentane on treatment with Zn-Hg/HCl. (A) forms a dioxime with hydroxylamine and gives a positive iodoform and Tollens' test. Identify the compound (A).

- (ii) *m*-Hydroxybenzoic acid is a stronger acid than benzoic acid while *p*-hydroxybenzoic acid is weaker. Explain.

19. Write the following reactions:

- (i) Cannizzaro reaction
- (ii) Gatterman-Koch reaction
- (iii) Stephen reaction

20. Give reasons for the following:

- (i) Formic acid shows reducing properties.
- (ii) β -Ketoacids undergo decarboxylation easily.
- (iii) Highly branched carboxylic acids are much less acidic than unbranched acids.

21. How would you account for the following:

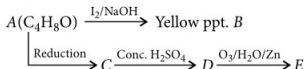
- (i) The boiling points of aldehydes and ketones are lower than the corresponding acids.
- (ii) The aldehydes and ketones undergo a number of addition reactions.
- (iii) There are two $-NH_2$ groups in semicarbazide. However, only one is involved in the formation of semicarbazones.

22. (i) Benzaldehyde gives a positive test with Tollens' reagent but not with Fehling's and Benedict's solutions. Explain.

- (ii) The addition of hydrogen cyanide to carbonyl compounds is accelerated by bases and retarded by acids. Explain.

23. A class XII student, Kiran observed a specific smell of bitter almonds in her chemistry laboratory. She immediately informed her class teacher about the leakage.

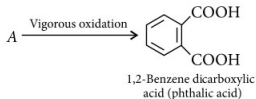
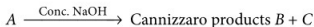
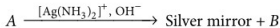
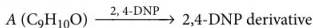
- (i) What could be the reason for specific smell of bitter almonds?
 (ii) What would be the products when this compound is treated with concentrated KOH?
 (iii) Does this compound reduce Fehling's solution?
 (iv) What values are displayed by Kiran?
24. Identify *A*, *B*, *C*, *D* and *E* in the following sequence of reactions:



(*E*) also gives iodoform test.

OR

Identify *A*, *B* and *C* in the following sequence of reactions.



25. A ketone (*A*) (C_4H_8O) undergoes haloform reaction. (*A*) on reduction gives (*B*) which on reaction with conc. H_2SO_4 forms (*C*). (*C*) forms mono-ozonide (*D*) with O_3 . (*D*) on hydrolysis with Zn dust gives only (*E*). Identify *A* to *E*.

OR

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 NH_3 gives (*E*). (*E*) on dehydration produces HCN. Identify *A* to *E*.

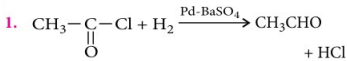
26. Compound '*A*' $C_6H_{12}O_2$ on reduction with $LiAlH_4$ yields two compounds '*B*' and '*C*'. The

compound '*B*' on oxidation gives '*D*' which on further oxidation gives CH_3COOH . The acid on treatment with aqueous alkali and subsequent heating furnished '*E*'. Deduce the structures of *A*, *B*, *C*, *D* and *E*.

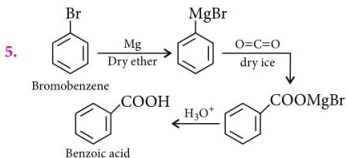
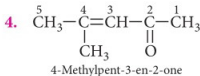
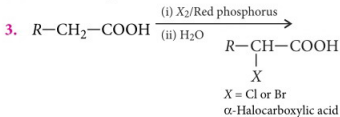
OR

An organic compound (*A*) (C_3H_6O) is resistant to oxidation but forms compound (*B*) (C_3H_8O) on reduction. (*B*) reacts with HBr to form the compound (*C*). (*C*) with Mg forms Grignard reagent (*D*) which reacts with (*A*) to form a product which on hydrolysis gives (*E*). Identify *A* to *E*.

SOLUTIONS

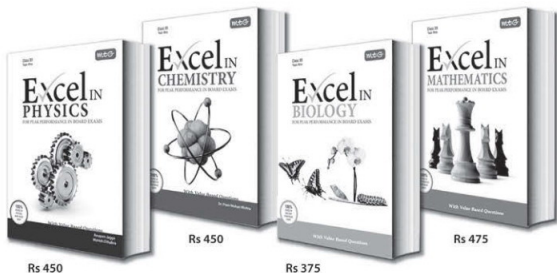


2. '*X*' is Zn-Hg, conc. HCl



6. This is due to the presence of two electron releasing methyl groups attached to the carbonyl carbon that hinder the approach of nucleophile to carbonyl carbon and reduce the electrophilicity of the carbonyl group in CH_3COCH_3 .
7. In case of unsymmetrical ketones, the keto group stays preferentially with the smaller alkyl group (Popoff's rule).

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- Comprehensive theory strictly based on NCERT, complemented with illustrations, activities and solutions of NCERT questions
- Practice questions & Model Test Papers for Board Exams
- Value based questions
- Latest CBSE Board Sample Papers (Solved)
- Previous years' CBSE Board Examination Papers (Solved)



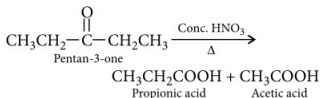
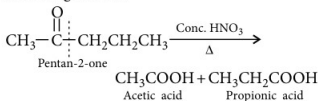
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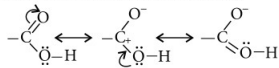
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In case of symmetrical ketones, only one mode of cleavage occurs.

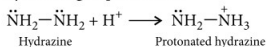


The major products in both are same.

8. The carboxylic carbon is less electrophilic than carbonyl carbon because of the possible resonance structures shown below:



9. In highly acidic medium, the $-\text{NH}_2$ group of hydrazine gets protonated.



Due to electron withdrawing effect of NH_3^+ group, the lone pair of electrons on the $-\text{NH}_2$ group of protonated hydrazine is not available for nucleophilic attack on $>\text{C}=\text{O}$ and hence hydrazone formation does not occur.

10. (i) *p*-Nitrobenzoic acid is a stronger acid than benzoic acid or has higher K_a value due to $-I$ and $-R$ effects of the $-\text{NO}_2$ group, which weakens the $\text{O}-\text{H}$ bond and also due to dispersal of the $-ve$ charge, *p*-nitrobenzoate ion becomes more stable than benzoate ion.
- (ii) The presence of electron withdrawing group ($-\text{Cl}$) in chloroacetic acid increases its acidic strength so, it has lower pK_a value than acetic acid.

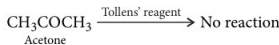
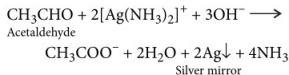
OR

- (i) $\text{HCOOH} < \text{ClCH}_2\text{COOH} < \text{CCl}_3\text{COOH} < \text{CF}_3\text{COOH}$
Electron withdrawing group stabilises the carboxylate anion and strengthens the

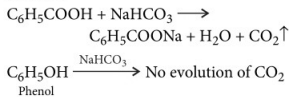
acid through delocalisation of the negative charge through inductive effect. More the number of electron withdrawing groups and more the electronegativity of the atom attached to the carboxyl group more will be the acidic strength.

- (ii) Acids containing even number of carbon atoms have carboxyl and terminal methyl groups on the opposite sides of the zig-zag carbon chain and hence they fit closely into crystal lattice than odd ones that is why they have higher lattice energy and higher melting point.

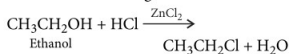
11. (i) Acetaldehyde reduces Tollens' reagent to silver mirror but acetone does not.



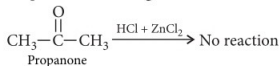
- (ii) Benzoic acid being a stronger acid than phenol, decomposes NaHCO_3 to evolve CO_2 with brisk effervescence but phenol does not.



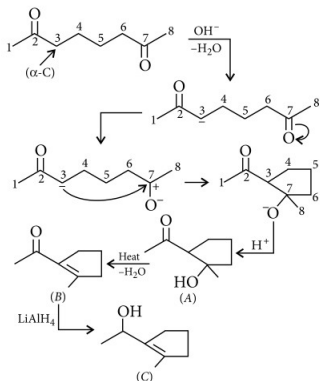
- (iii) When treated with Lucas reagent (conc. $\text{HCl} + \text{anhyd. ZnCl}_2$) ethanol gives cloudiness on heating.



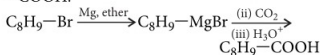
Propanone does not give Lucas test.



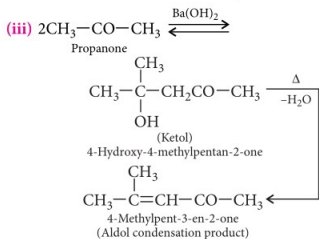
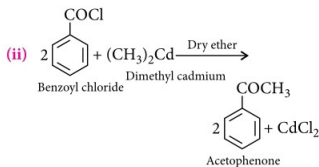
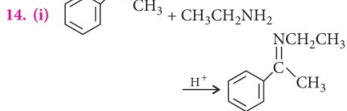
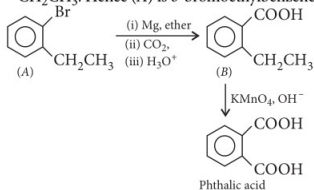
12. Di-ketone can undergo internal aldol condensation reaction to form (A) which on heating loses a water molecule and give (B). (B) upon reduction with LiAlH_4 forms (C). The sequence of reactions is as follows:



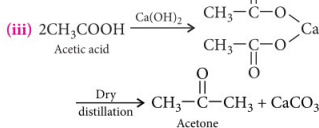
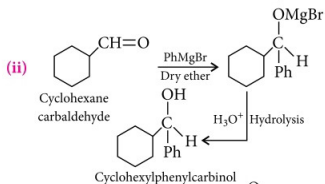
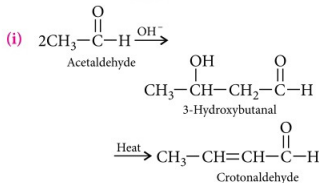
13. Reaction of compound (A) with Mg in ether followed by CO_2 points out the conversion of $-\text{Br}$ to $-\text{MgBr}$ which reacts with CO_2 to form $-\text{COOH}$.

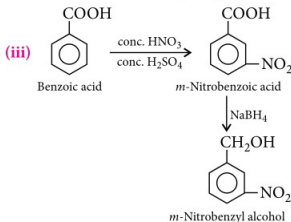
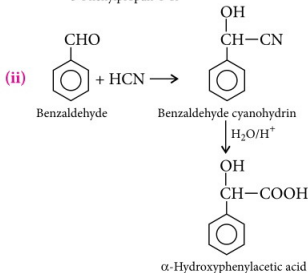
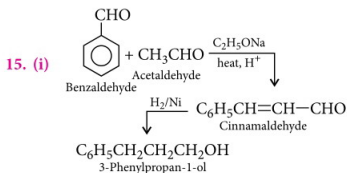


Since the final product has two $-\text{COOH}$ groups, the second must have been introduced through the oxidation of the side chain, which should be $-\text{CH}_2\text{CH}_3$. Hence (A) is *o*-bromoethylbenzene.



OR

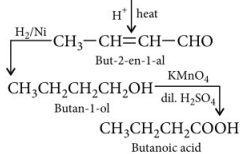
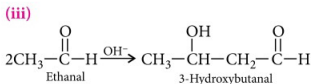
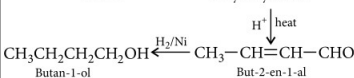
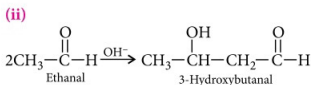
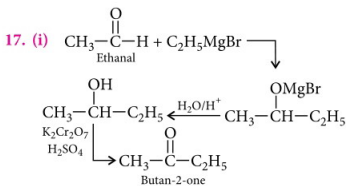
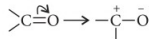




16. (i) The conjugate base of carboxylic acid, a carboxylate ion, is stabilised by two equivalent resonance structures. The negative charge in these structures is delocalised over two more electronegative oxygen atoms. The conjugate base of phenol, a phenoxide ion, has non-equivalent resonance structures in which the negative charge is at the less electronegative carbon atom.

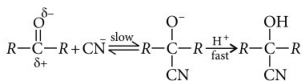
- (ii) Carboxylic group is deactivating group and the catalyst aluminium chloride (Lewis acid) used in Friedel-Crafts reaction gets bonded to the carboxyl group.

- (iii) Due to higher electronegativity, electron density shifts towards oxygen and carbon becomes electron deficient and hence acts as electrophilic centre whereas oxygen acts as nucleophilic centre.



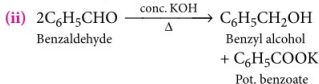
18. (i) The organic compound (A) (C₅H₈O₂) is reduced to *n*-pentane on treatment with Zn-Hg/HCl which means that it may be an aldehyde or ketone containing chain of five carbon atoms. Since it gives positive iodoform and Tollens' test, it must be an aldehyde.

- (ii) The addition of HCN to $>C=O$ compounds proceeds as follows:



In basic medium, CN^- is formed from HCN while in acidic medium, the ionization of HCN to give CN^- is suppressed.

23. (i) Benzaldehyde has a smell of bitter almonds and there might have been leakage from benzaldehyde bottle.



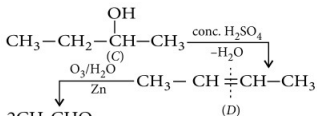
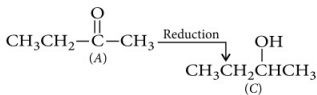
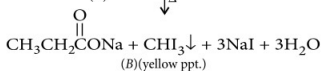
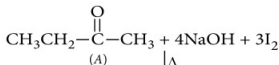
- (iii) No, aromatic aldehydes do not reduce Fehling's solution.

- (iv) Awareness, responsibility

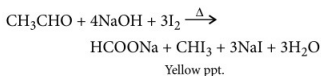
24. (A) gives iodoform test.

Thus, (A) has $\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_3$ where, R is C_2H_5 .

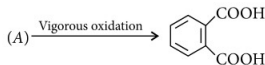
Thus, (A) is $\text{CH}_3\text{CH}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_3$



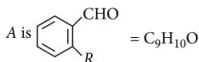
(E) also gives iodoform test.



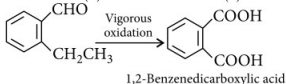
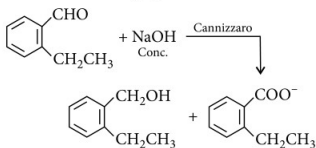
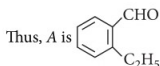
OR



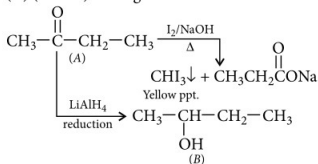
Thus, (A) has benzene ring and two groups in 1,2-position. (A) forms 2, 4-DNP derivative thus carbonyl group is present. (A) reduces Tollens' reagent, thus (A) has $-\text{CHO}$ group. (A) shows Cannizzaro reaction thus $-\text{CHO}$ is directly attached to benzene nucleus. Thus,

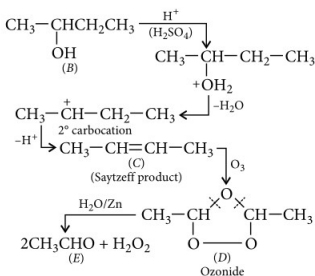


Thus, R is C_2H_5 .

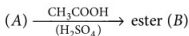


25. (A) (ketone) undergoes haloform reaction.

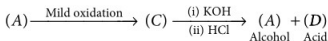




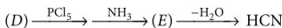
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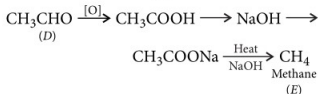
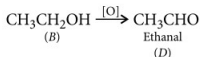
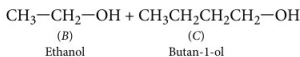
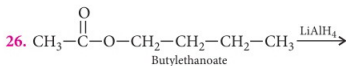
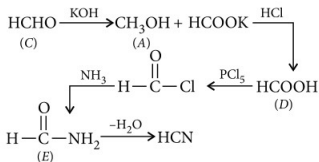
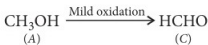
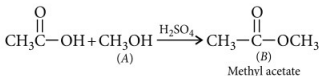
Thus, (A) is an alcohol.



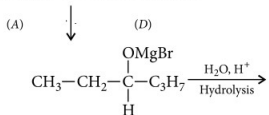
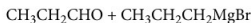
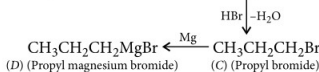
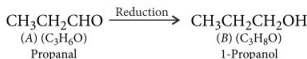
Thus, (C) undergoes Cannizzaro reaction.



Thus, (E) is $\text{H}-\overset{\text{O}}{\parallel}{\text{C}}-\text{NH}_2$.



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EXAMINER'S MIND NCERT CLASS XII


The questions given in this column have been prepared strictly on the basis of NCERT Chemistry for Class XII. This year JEE (Main & Advanced) / AIPMT / AIIMS / other PMTs have drawn their papers heavily from NCERT books.

POLYMERS | CHEMISTRY IN EVERYDAY LIFE

SECTION - I

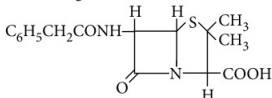
Only One Option Correct Type

This section contains 20 multiple choice questions. Each question has four choices (a), (b), (c) and (d), out of which ONLY ONE is correct.

- Rayon is chemically known as
 - cellulose nitrate
 - cellulose
 - cellulose acetate
 - resins.
- The class of drugs used for the treatment of stress is
 - analgesics
 - antiseptics
 - antihistamines
 - tranquilizers.
- Cross-linked or network polymers are usually formed by
 - bifunctional monomer
 - trifunctional monomer
 - monofunctional monomer
 - both (a) and (b).
- Tincture of iodine is
 - aqueous solution of I_2
 - solution of I_2 in aqueous KI
 - alcoholic solution of I_2
 - aqueous solution of KI.
- Nylon-6, 6 is obtained by condensation polymerisation of
 - adipic acid and ethylene glycol
 - adipic acid and hexamethylenediamine
 - terephthalic acid and ethylene glycol
 - adipic acid and phenol.
- A drug that is antipyretic as well as analgesic is
 - chlorpromazine hydrochloride
 - para-acetamidophenol
 - chloroquine
 - penicillin.
- Arrange the following polymers in the increasing order of intermolecular forces :
Fibre, Plastic, Elastomer.
 - Elastomer < Fibre < Plastic
 - Elastomer < Plastic < Fibre
 - Plastic < Elastomer < Fibre
 - Fibre < Elastomer < Plastic
- Which of the following soaps/detergents is least biodegradable?
 - $C_{17}H_{35} - COONa$
 - $CH_3 - (CH_2)_{11} - OSO_3Na$
 - $CH_3 - (CH_2)_9 - \overset{\overset{CH_3}{|}}{CH} - \text{C}_6\text{H}_4 - SO_3Na$
 - $CH_3 - \overset{\overset{CH_3}{|}}{CH} - (CH_2CH_2)_2 - CH_2 - \overset{\overset{CH_3}{|}}{CH} - CH_3$

- Which one of the following is a thermosetting polymer?
 - Nylon-6
 - Nylon-6, 6
 - Bakelite
 - SBR
- Antiseptics and disinfectants either kill or prevent growth of microorganisms. Identify which of the following statements is not true.
 - Dilute solutions of boric acid and hydrogen peroxide are strong antiseptics.
 - Disinfectants harm the living tissues.
 - 0.2% solution of phenol is an antiseptic while its 1% solution acts as a disinfectant.
 - Chlorine and iodine are used as strong disinfectants.

11. Terylene is the polyester of
 (a) hexamethylenediamine and adipic acid
 (b) vinyl chloride and formaldehyde
 (c) melamine and formaldehyde
 (d) ethylene glycol and terephthalic acid.

12. The structure given below is known as



- (a) penicillin F (b) penicillin G
 (c) penicillin K (d) ampicillin.
13. The bakelite is made from phenol and formaldehyde. The initial reaction between the two compounds is an example of
 (a) aromatic electrophilic substitution
 (b) aromatic nucleophilic substitution
 (c) free radical reaction
 (d) aldol condensation.
14. Which of the following are not target molecules for drug function in the body?
 (a) Carbohydrates (b) Lipids
 (c) Vitamins (d) Proteins
15. The process involving heating of rubber with sulphur is called
 (a) galvanisation (b) vulcanization
 (c) bessemerisation (d) sulphonation.
16. Class of drugs interferes with the natural action of histamine is
 (a) tranquilizers (b) diuretics
 (c) analgesics (d) anti-allergic.
17. Arsenic drugs are mainly used in the treatment of
 (a) jaundice (b) typhoid
 (c) syphilis (d) cholera.
18. Which of the following statements is not correct?
 (a) Some antiseptics can be added to soaps.
 (b) Dilute solutions of some disinfectants can be used as antiseptics.
 (c) Disinfectants are used for sterilisation of inanimate objects.
 (d) Antiseptic medicines can be ingested.

19. Which of the following statements is not correct regarding free radical addition polymerization?

- (a) It involves free radical addition.
 (b) Chain terminating steps involve combination or disproportionation of free radicals.
 (c) The presence of Lewis acids increases the polymerization process.
 (d) The presence of O_2 acts as radical initiator.
20. Cetyltrimethylammonium bromide is a popular
 (a) anionic detergent
 (b) cationic detergent
 (c) non-ionic detergent
 (d) sweetener.

SECTION - II

One or More Options Correct Type

This section contains 5 multiple choice questions. Each question has four choices (a), (b), (c) and (d), out of which ONE or MORE are correct.

21. Which of the following are characteristics of thermosetting polymers?
 (a) Heavily branched cross-linked polymers.
 (b) Linear slightly branched long chain molecules.
 (c) Become infusible on moulding so cannot be reused.
 (d) Soften on heating and harden on cooling, can be reused.
22. Which of the following antibiotics is/are the modification of penicillin?
 (a) Ofloxacin (b) Ampicillin
 (c) Amoxycillin (d) Tetracycline
23. Which of the following monomers form biodegradable polymers?
 (a) 3-Hydroxybutanoic acid + 3-Hydroxyphen-tanoic acid
 (b) Glycine + ϵ -Aminocaproic acid
 (c) Ethylene glycol + Phthalic acid
 (d) Caprolactum
24. Which of the following is not correctly matched?
 (a) Dysentery--Amoebic

- (b) Typhoid–Bacterial
 (c) AIDS–Viral
 (d) Malaria–Fungal

25. Which of the following is false?

- (a) Artificial silk is derived from cellulose.
 (b) Nylon-6, 6 is an example of elastomer.
 (c) The repeating unit in natural rubber is isoprene.
 (d) Both starch and cellulose are polymers of glucose.

SECTION - III

Paragraph Type

This section contains 2 paragraphs each describing theory, experiment, data, etc. Six questions relate to two paragraphs with three questions on each paragraph. Each question of a paragraph has only one correct answer among the four choices (a), (b), (c) and (d).

Paragraph for Questions 26 to 28

Rubber is a natural polymer. It is also termed as elastomer and has a variety of uses. It can be stretched like a spring and exhibits elastic properties. To improve upon its physical properties, a process of vulcanization is carried out. Synthetic rubber is any vulcanizable rubber like polymer, which is capable of getting stretched to twice its length. However, it returns to its original shape and size as soon as the external stretching force is released.

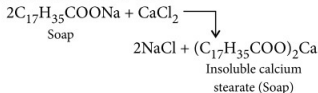
26. Which of the following statements is not true?
 (a) Buna-S is a copolymer of 1, 3-butadiene and styrene.
 (b) Natural rubber is a 1,4-polymer of isoprene.
 (c) In vulcanization, the formation of sulphur bridges between different chains make rubber harder and stronger.
 (d) Natural rubber has the *trans*-configuration at every double bond.
27. Structure of monomer unit of synthetic rubber is
- $$\begin{array}{c} \text{Cl} \\ | \\ \text{H}_2\text{C}=\text{C}-\text{CH}=\text{CH}_2 \end{array}$$
- (a) $\text{H}_2\text{C}=\text{C}-\text{CH}=\text{CH}_2$
 (b) $\text{F}_2\text{C}=\text{CF}_2$
 (c) $\text{CH}_2=\text{CH}_2$
 (d) None of these.

28. Which of the following is used in vulcanization of rubber?

- (a) SF_6
 (c) Cl_2F_2
 (b) CF_4
 (d) C_2F_4

Paragraph for Questions 29 to 31

Hard water contains calcium and magnesium ions. These ions form insoluble calcium and magnesium soaps respectively when sodium or potassium soaps are dissolved in hard water.



These insoluble soaps separate as scum in water and are useless as cleansing agent.

29. Soaps are

- (a) sodium salts of long chain fatty acids
 (b) potassium salts of long chain fatty acids
 (c) potassium salts of short chain fatty acids
 (d) both (a) and (b).

30. Detergents are better than soaps because

- (a) they are less affected by hard water
 (b) they can be used in acidic solution
 (c) both (a) and (b)
 (d) they wash clothes better.

31. The role of phosphate in detergent powder is to

- (a) control pH level of the detergent water mixture
 (b) remove Ca^{2+} and Mg^{2+} ions from the water that cause the hardness of water
 (c) provide whiteness to the fabrics
 (d) form solid detergents as phosphateless detergents are liquid in nature.

SECTION - IV

Matching List Type

This section contains 3 multiple choice questions. Each question has matching lists. The codes for the lists have choices (a), (b), (c) and (d), out of which ONLY ONE is correct.

32. Match the List I (Artificial sweetener) with List II (Sweetness value as compared to cane sugar) and select the correct answer using the code given below the lists :

List I		List II	
P. Aspartame		1.	100
Q. Alitame		2.	550
R. Sucralose		3.	600
S. Saccharin		4.	2000

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

33. Match the List I (Monomers) with List II (Polymers) and select the correct answer using the code given below the lists :

List I		List II	
P. Phthalic acid and ethylene glycol		1.	Buna-N
Q. Terephthalic acid and ethylene glycol		2.	Nylon-6, 6
R. Hexamethylenediamine and adipic acid		3.	Dacron
S. Acrylonitrile and 1, 3-butadiene		4.	Glyptal

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

34. Match the functions given in List I with the class of compounds given in List II and select the correct answer using the code given below the lists :

List I		List II	
P. Communicate message between two neurons and that between neurons to muscles		1.	Antagonists
Q. Bind to the receptor site and inhibit its natural function		2.	Agonists
R. Crucial to body's communication process		3.	Chemical messenger
S. Mimic the natural messenger		4.	Receptors

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

SECTION - V

Assertion-Reason Type

In the following questions, a statement of assertion is followed by a statement of reason. Mark the correct choice as :

- (a) If both assertion and reason are true and reason is the correct explanation of assertion.
 (b) If both assertion and reason are true but reason is not the correct explanation of assertion.
 (c) If assertion is true but reason is false.
 (d) If both assertion and reason are false.

35. **Assertion** : Teflon has high thermal stability and chemical inertness.

Reason : Teflon is thermoplastic.

36. **Assertion** : Chemical messenger gives message to the cell without entering the cell.

Reason : Chemical messengers are received at the binding sites of receptor proteins.

37. **Assertion** : Molecular mass of polymer is expressed as an average.

Reason : Polymer sample contains chains of varying lengths.

38. **Assertion** : Detergents are preferred to soaps for washing purposes.

Reason : Detergents having branched hydrocarbon chains are non-biodegradable.

39. **Assertion** : Buta-1, 3-diene is the monomer of natural rubber.

Reason : Natural rubber is formed through anionic addition polymerization.

40. **Assertion** : Aspirin can cause ulcer in the stomach.

Reason : The ester group in aspirin gets hydrolysed to acid group in the stomach where the pH is 2.

SECTION - VI

Integer Value Correct Type

This section contains 10 questions. The answer to each question is a single digit integer, ranging from 0 to 9 (both inclusive).

- Total number of lone pairs present in monomer melamine is
- Amongst the following, the total number of preservatives are
Sodium stearate, Sodium acetate, Sodium benzoate, Sodium sulphite, Sodium metabisulphite, Sodium sulphate, Sodium thiosulphate.
- Number of double bonds present in the repeating structural unit of polythene is
- Number of non-narcotic analgesics out of the following is
Morphine, Paracetamol, Aspirin, Codeine, Naproxen, Ibuprofen, Heroin.
- The total number of condensation homopolymers among the following is
Polyester, Bakelite, Nylon 6, PVC, Starch, Nylon-6, 6, Glyptal, Natural rubber.
- Number of C-atoms in saccharin is
- Formation of polythene from calcium carbide takes place as follows :

$$\text{CaC}_2 + 2\text{H}_2\text{O} \longrightarrow \text{Ca(OH)}_2 + \text{C}_2\text{H}_2$$

$$\text{C}_2\text{H}_2 + \text{H}_2 \longrightarrow \text{C}_2\text{H}_4$$

$$n\text{C}_2\text{H}_4 \longrightarrow -(\text{CH}_2-\text{CH}_2-)_n$$
 The amount of polythene (in g) obtained from 16 kg of CaC_2 is
- x % solution of phenol acts as a disinfectant. The value of x is
- Percentage of sulphur used in vulcanization of rubber is
- Number of phenolic groups present in codeine is

SOLUTIONS

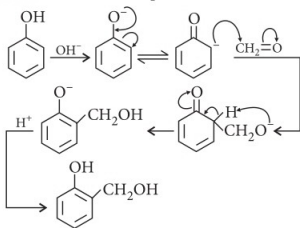
- (c) : Rayon is chemically known as cellulose acetate.
- (d)

- (d) : Cross-linked or network polymers are formed from bifunctional and trifunctional monomers and contain strong covalent bonds between different linear polymer chains, e.g., bakelite, melamine, etc.
- (c) : Tincture of iodine is 2–3% solution of iodine in alcohol and water mixture.
- (b) : Nylon-6, 6 is prepared by condensation polymerisation of adipic acid and hexamethylenediamine.

$$n\text{HOOC}(\text{CH}_2)_4\text{COOH} + n\text{H}_2\text{N}-(\text{CH}_2)_6-\text{NH}_2$$

$$\xrightarrow[\text{High pressure}]{553 \text{ K}}$$

$$\left[\text{CO}-(\text{CH}_2)_4-\text{CONH}-(\text{CH}_2)_6-\text{NH} \right]_n$$
- (b) : Para-acetamidophenol (paracetamol) is used as an antipyretic as well as analgesic.
- (b) : Elastomers or rubbers have the weakest intermolecular forces of attraction while fibres have the strongest intermolecular forces of attraction. Plastics possess intermolecular forces of attraction intermediate between elastomers and fibres.
- (d) : More branching in the molecular structure leads to less biodegradability.
- (c) 10. (a) 11. (d)
- (b) : The given structure depicts penicillin G (benzyl penicillin).
- (a) : Aromatic electrophilic substitution



Similarly, substitution occurs at the p -position.

- (c)
- (b) : Heating of rubber with sulphur to improve its properties is called vulcanization.

16. (d) : Antihistamines or anti-allergic drugs interfere with the natural action of histamine.

17. (c)

18. (d) : Antiseptics cannot be ingested.

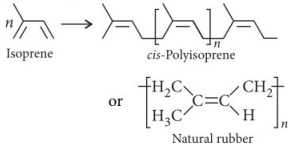
19. (c) : Lewis acids such as AlCl_3 , BF_3 etc. in presence of a trace of water act as initiator in cationic polymerization.

20. (b) 21. (a, c) 22. (b, c) 23. (a, b)

24. (d) : Malaria is not a fungal disease. Rather it is a protozoan disease.

25. (b) : Nylon-6, 6 is a fibre and not an elastomer.

26. (d) : Natural rubber is *cis*-polyisoprene, and has only *cis*-configuration about the double bond.



27. (a) 28. (a)

29. (d) : Soaps are sodium and potassium salts of long chain fatty acids.

30. (c)

31. (b) : Between 20–45% of tripolyphosphate is added to detergent powder and liquid detergents which remove Ca^{2+} and Mg^{2+} ions from hard water by forming stable soluble complexes. It also makes the solution alkaline and helps to remove grease.

32. (d) : Aspartame is 100 times sweeter than cane sugar

Saccharin is 550 times sweeter than cane sugar

Sucralose is 600 times sweeter than cane sugar

Alitame is 2000 times sweeter than cane sugar.

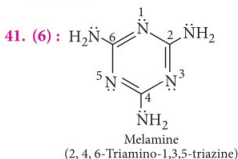
33. (d) 34. (b) 35. (b) 36. (a)

37. (a)

38. (b) : Detergents are preferred to soaps for washing purposes because the calcium and magnesium salts of detergents unlike those of soaps are soluble in water.

39. (d)

40. (a) : At pH 2, the ester group of aspirin gets hydrolysed to acid which causes ulcer in the stomach.

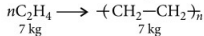
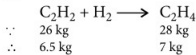
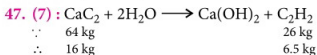
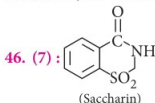


42. (2) : Sodium benzoate and sodium metabisulphite

43. (0) : The repeating structural unit of polythene is $-\text{CH}_2\text{CH}_2-$. It has no double bond.

44. (4) : Paracetamol, aspirin, naproxen and ibuprofen.

45. (2) : Nylon-6, starch

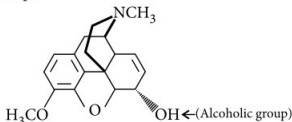


During addition, nothing is lost. Therefore, 7 kg of C_2H_4 will give 7 kg of polyethene.

48. (1) : 0.2% solution of phenol acts as an antiseptic whereas its 1% solution acts as a disinfectant.

49. (5)

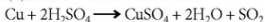
50. (0) : Structure of codeine is given below which contains only an alcoholic group not phenolic group.



CHEMISTRY MUSING

SOLUTION SET 16

1. (a): The reaction would be:



1 mole of Cu reacts with 2 moles of H_2SO_4 .
Since we have only 1 mole of H_2SO_4 so, it is the limiting reagent.

From the above equation we observe that

2 moles of H_2SO_4 react with Cu to produce
1 mole of SO_2

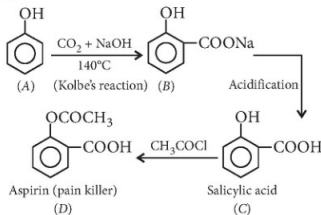
\therefore 1 mole of H_2SO_4 reacts with Cu to produce
 $\frac{1}{2}$ mole of SO_2

Now, 1 mole of $\text{SO}_2 = 6.023 \times 10^{23}$ molecules

$\therefore \frac{1}{2}$ mole of $\text{SO}_2 = \frac{6.023 \times 10^{23}}{2}$ molecules
 $= 3 \times 10^{23}$ molecules of SO_2

2. (a): Reaction (a) is a redox reaction since oxidation state of I changes from -1 to 0 and that of Cu changes from +2 to +1.

3. (c): 'A' gives characteristic colour with FeCl_3 , hence it has -OH group attached to sp^2 hybridised C-atom. Also it has vapour density 47 hence, its molecular mass will be 94 which corresponds to mass of phenol. Thus, 'A' is phenol. Other reactions are represented as:



4. (a): $\text{HOCl} \rightleftharpoons \text{H}^+ + \text{OCl}^-$

$$K_a = \frac{[\text{H}^+][\text{OCl}^-]}{[\text{HOCl}]} \quad \dots(i)$$

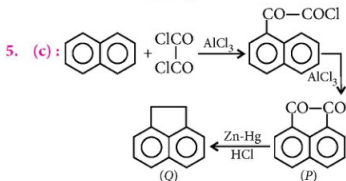
$$\text{OCl}^- + \text{H}_2\text{O} \rightleftharpoons \text{HOCl} + \text{OH}^-$$

$$K_{eq} = \frac{[\text{HOCl}][\text{OH}^-]}{[\text{OCl}^-]} \quad \dots(ii)$$

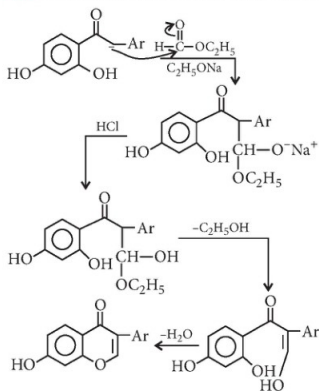
Multiply equation (i) by (ii), we get

$$K_a K_{eq} = [\text{H}^+][\text{OH}^-] = K_w = 1 \times 10^{-14}$$

$$\therefore K_a = \frac{K_w}{K_{eq}} = \frac{1.0 \times 10^{-14}}{3.6 \times 10^{-7}} = 2.8 \times 10^{-8}$$



6. (d): This is an example of Claisen condensation.

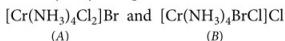


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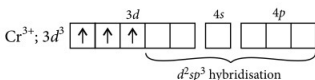
Log on to <http://test.pcmbody.com>

7. (c): The two isomers are ionisation isomers and they may be represented as



'A' forms yellow precipitate of AgBr with AgNO₃. 'B' forms white precipitate of AgCl with AgNO₃. Since in solution both the isomers produce 2 ions, so their aqueous solutions will show approximately same conductivity.

8. (b): In both the isomers, chromium is in +3 oxidation state and the number of unpaired electrons is three.



9. (7): $2\text{H}^+ + 2e^- \rightarrow \text{H}_2; Q = \frac{1}{[\text{H}^+]^2}$

$$E = E_{\text{SHE}}^\circ - \frac{0.0591}{2} \log \frac{1}{[\text{H}^+]^2}$$

$$-0.413 = 0 - \frac{0.0591}{2} \log [\text{H}^+]^{-2}$$

$$-0.413 = 0.0591 \log [\text{H}^+],$$

$$0.413 = 0.0591 (-\log [\text{H}^+])$$

$$= 0.0591 \text{ pH} \quad [\because -\log [\text{H}^+] = \text{pH}]$$

$$\text{pH} = \frac{0.413}{0.0591} = 6.988 \approx 7$$

10. (3): Be_nAl₂Si₆O₁₈: It is Beryl, with formula Be₃Al₂Si₆O₁₈, where, n = 3. It is a blue coloured gemstone. It is an aluminosilicate, with Be as impurity.

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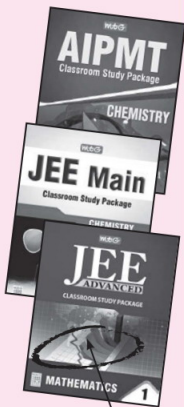
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The best questions and their solutions will be printed in this column each month.

- Q1.** Two different aqueous solutions of 0.5 M HCl and 0.5 M NaCl are given. Which has the highest value of molar conductance?
—Mohd. T. Khan, Ghazipur, U.P.

Ans. In general, the molar conductivity is expressed as

$$\Lambda_m = \frac{1000\kappa}{\text{Molarity (M)}}$$

On applying the values of given electrolytes—

Electrolyte	Concentration	Λ_m
HCl	0.5 M	2000 κ
NaCl	0.5 M	2000 κ

Mathematically, the value of Λ_m for both the electrolytes are same. But, it depends on—

- The concentration of the ions :** Here, the concentration of both the ions (H^+ and Na^+) are same in solution.
- Nature of electrolyte :** HCl is a strong electrolyte. NaCl being water soluble ionic salt, dissociates completely thus, it is also a strong electrolyte.
- The charges carried by each ion :** Both electrolytes are of 1 – 1 type electrolytes i.e., having the same charges (H^+ and Cl^- ; Na^+ and Cl^-).
- Ionic size and mobility :** The ionic mobility decreases with increase in the size of the ion and hence, conductivity also decreases. The conductivity of HCl is greater than that of NaCl since the size of H^+ ion is smaller than that of Na^+ ion.

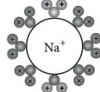
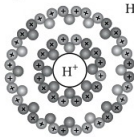
Free ions



Smaller and moves faster Larger and moves slowly
However, in aqueous solution the *extent of hydration* affects the mobility of the ion, which in turn affects the conductivity. **Heavily hydrated ions show low conductance values due to large size.**

e.g., in aqueous solutions, H^+ ion with high charge density is heavily hydrated than Na^+ ion with low charge density. Hence, hydrated H^+ ion is bigger in size than hydrated Na^+ ion. As a result, NaCl shows high molar conductivity compared to HCl in water.

Hydrated ions



Larger and moves slowly Smaller and moves faster

- Q2.** What gases are emitted from garbage actually?
—S. Majumdar, Howrah, W. B.

Ans. Landfill gas is a complex mixture of different gases created by the action of microorganisms within a landfill.

- It contains *six greenhouse gases* such as carbon dioxide (40 – 45%), methane (50 – 55%) and nitrous oxide (N_2O) along with three fluorinated gases.

[Methane is a naturally-occurring gas created by the decay of organic matter inside a landfill. It traps over 21 times more heat than carbon dioxide, and nitrous oxide absorbs 310 times more heat than carbon dioxide.]

- Some varying amounts of N_2 , O_2 gas, water vapour and H_2S are also present.
- Some inorganic (Hg) and radioactive (tritium, ^3H) contaminants are also found.
- Ten toxic gases such as vinyl chloride, C_6H_6 , ethylene dibromide, ethylene dichloride, methylene chloride, perchloroethylene, CCl_4 , methyl chloroform, trichloroethylene and CHCl_3 are also present.

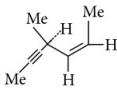
PRACTICE PROBLEMS 2015

Chemistry Olympiad

1. During micelle formation

(a) $\Delta H = +ve$; $\Delta S = +ve$
 (b) $\Delta H = -ve$; $\Delta S = -ve$
 (c) $\Delta H = -ve$; $\Delta S = +ve$
 (d) $\Delta H = +ve$; $\Delta S = -ve$

2. Hydrogenation of the given compound in the presence of poisoned palladium catalyst gives



(a) optically active compound
 (b) an optically inactive compound
 (c) a racemic mixture
 (d) a diastereomeric mixture.

3. The non-stoichiometric compound, $Fe_{0.94}O$ is formed when x % of Fe^{2+} ions are replaced by as many $2/3 Fe^{3+}$ ions, x is

(a) 18 (b) 12
 (c) 15 (d) 6

4. Gold number of few colloids are given below: Gelatin = 0.005; Starch = 25; Egg albumin = 0.08; Gum arabic = 0.10. Which is the best protective colloid?

(a) Gelatin (b) Starch
 (c) Egg albumin (d) Gum arabic

5. Insulin has 51 amino acids in two polypeptide chains, which are cross-linked by

(a) peroxide bond
 (b) disulphide bond
 (c) diazo bond
 (d) two carbon-carbon double bonds.

6. The wavelength of light required to break the bond between two chlorine atoms in a chlorine molecule is

(Given : $Cl - Cl$ bond energy = 243 kJ/mol)

(a) 8.18×10^{-31} m (b) 6.26×10^{21} m
 (c) 4.93×10^{-7} m (d) 4.11×10^{-6} m

7. Degree of dissociation of NH_4OH in water is 1.8×10^{-5} , then degree of hydrolysis of NH_4OH in NH_4Cl is

(a) 1.8×10^{-5} (b) 1.8×10^{-10}
 (c) 5.55×10^{-5} (d) 5.55×10^5

8. The potential of a hydrogen electrode at pH = 10 is

(a) 0.59 V (b) 0.0 V
 (c) -0.59 V (d) 0.059 V

9. Let p and p_s be the partial pressure and saturated partial pressure of water respectively. Then the relative humidity is given by

(a) $\frac{p_s + p}{p_s} \times 100$ (b) $\frac{p}{p_s} \times 100$

(c) $\frac{p_s}{p} \times 100$ (d) $(p + p_s) \times 100$

10. Which of the following molecular orbitals has no nodal plane?

(a) σ_{2s} (b) $\pi^* 2p_x$
 (c) $\pi^* 2p_y$ (d) $\sigma^* 2p_z$

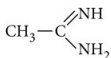
11. An alloy which does not contain copper is

(a) invar (b) bronze
 (c) brass (d) bell metal.

12. Liquid hydrocarbons can be converted to a mixture of gaseous hydrocarbons by

(a) oxidation
 (b) cracking
 (c) distillation under reduced pressure
 (d) hydrolysis.

13. The correct order of basic strength of the following compounds is



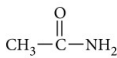
(I)



(II)



(III)



(IV)

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

14. 7.5 g of a gas occupies 5.6 L of volume at STP. The gas is

- (a) NO (b) N₂O
(c) CO (d) CO₂

15. Which would be the most stable conformation of *trans*-1-ethyl-3-methylcyclohexane?

- (a) Equatorial (methyl) – equatorial (ethyl)
(b) Axial (methyl) – equatorial (ethyl)
(c) Axial (methyl) – axial (ethyl)
(d) Axial (ethyl) – equatorial (methyl)

16. The ratio of Boyle's temperature and critical temperature for a gas is

- (a) 8/27 (b) 27/8
(c) 1/2 (d) 2/1

17. A bottle of dry ammonia and a bottle of dry hydrogen chloride connected through a long tube are opened simultaneously at both ends, the white ammonium chloride ring first formed will be

- (a) at the centre of the tube
(b) near the hydrogen chloride bottle
(c) near the ammonia bottle
(d) throughout the length of the tube.

18. Which of the following is a negatively charged bidentate ligand?

- (a) Dimethylglyoximate
(b) Cyano
(c) Ethylenediamine
(d) Acetate

19. Haemoglobin contains 0.33% of iron by weight. The molecular weight of haemoglobin is approximately 67,200. The number of iron atoms (at. wt. of Fe = 56) present in one molecule of haemoglobin is

- (a) 6 (b) 1
(c) 4 (d) 2

20. 'Oil of mirbane' is another name for
(a) aniline (b) nitrobenzene
(c) toluene (d) toluidine.

21. The energy of activation for a reaction is 150 kJ mol⁻¹. Presence of a catalyst lowers the energy of activation by 60%. What will be the effect on rate of reaction at 25°C, if other things remain same?

(r₂ → with catalyst, r₁ → without catalyst)

- (a) r₂ = r₁ (b) $\frac{r_2}{r_1} = \frac{1}{2} \times 10^5$
(c) $\frac{r_2}{r_1} = 5.97 \times 10^{15}$ (d) $\frac{r_2}{r_1} = 2.93 \times 10^{10}$

22. The ionic product of water will increase, if
(a) pressure is decreased
(b) OH⁻ is added
(c) H⁺ is added
(d) temperature is increased.

23. The following data are given for the decomposition of ammonium nitrite in aqueous solution.

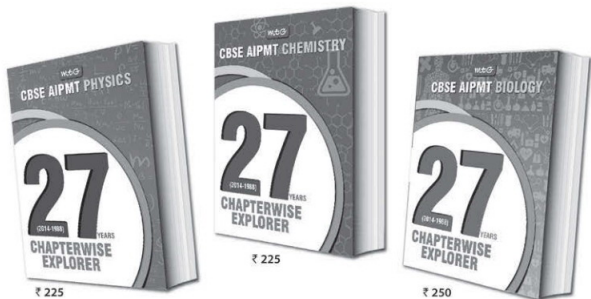
Vol. of N ₂ (in cc)	Time (min.)
6.25	10
9.00	15
11.40	20
13.65	25
35.65	∞

The order of reaction is

- (a) zero (b) one
(c) two (d) three.

24. Rate of a reaction can be expressed by Arrhenius equation as: $k = Ae^{-E/RT}$. In this equation, E represents

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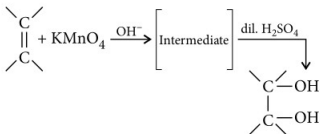


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- (a) the energy above which all the colliding molecules will react
 (b) the energy below which colliding molecules will not react
 (c) the fractional energy of the reacting molecules at a temperature, T
 (d) the fraction of molecules with energy greater than the activation energy of the reaction.
25. In the oxidation of alkenes with a dilute KMnO_4 solution followed by acidification with dilute H_2SO_4 to give diol,



the —OH groups come from

- (a) NaOH (b) H_2O
 (c) KMnO_4 (d) H_2SO_4
26. What is the equivalent mass of IO_3^- , when it gets converted into I_2 in acidic medium?
 (a) $M/6$ (b) $M/7$
 (c) $M/5$ (d) $M/4$
27. Urotropine has the composition of
 (a) $(\text{CH}_2)_4\text{N}_6$ (b) $(\text{CH}_2)_5\text{N}_5$
 (c) $(\text{CH}_2)_6\text{N}_4$ (d) $(\text{CH}_3)_6\text{N}_5$

28. Which step is not involved in hydrometallurgical process?
 (a) $\text{Cu}_2\text{S} + 2\text{Cu}_2\text{O} \rightarrow 6\text{Cu} + \text{SO}_2$
 (b) $\text{CuFeS}_2 + 2\text{H}_2\text{SO}_4 \rightarrow \text{CuSO}_4 + \text{FeSO}_4 + 2\text{H}_2\text{S}$
 (c) $\text{CuSO}_4 + \text{Fe} \rightarrow \text{FeSO}_4 + \text{Cu}$
 (d) $\text{CuCO}_3 + \text{H}_2\text{SO}_4 \rightarrow \text{CuSO}_4 + \text{H}_2\text{O} + \text{CO}_2$
29. Rectified spirit contains
 (a) 95.6% ethanol and 4.4% methanol
 (b) 100% ethanol
 (c) 95.6% ethanol and 4.4% water
 (d) 95.6% ethanol and 4.4% benzene.

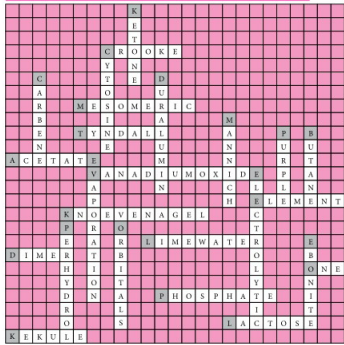
30. Which of the following nuclear processes are identical?

- (a) β^+ -emission and β^- -emission
 (b) α -emission and γ -emission
 (c) β^+ -emission and electron capture
 (d) γ -emission and production of X-rays

ANSWER KEY

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

SOLUTIONS TO NOVEMBER 2014 CROSSWORD



Winners of November 2014 Crossword

Santosh Kumar (Mumbai): Crossword puzzle in chemistry is the 'different concept' which helps in building up students' knowledge.

Geetika Sharma (Delhi): Crossword puzzle is 'awesome'. It covers all the syllabus of chemistry. After solving it 'I must say chemistry is never difficult'.

Senders of November 2014 Crossword

Tushar Chatterjee, Anurag Bera (West Bengal), Yash Khuman, Chintan Gondaliya, Dhanraj Hirpara, Parth Jakasaniya (Gujrat)

Senders of October 2014 Crossword

Tushar Chatterjee (West Bengal), Jaykishan Pipaliya, Dhanraj Hirpara (Gujrat)



CONCEPT BOOSTER

Dear students!! In this series of Inorganic Chemistry, group 16 along with group 15 is given. I hope that you again can find the 'catch' of every reaction and reasoning. Take care and sharpen your rationale in Chemistry.

*Arunava Sarkar

PHOSPHORUS

In general, the most important ores of phosphorus are :

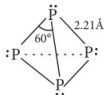
- Phosphorite *i.e.* $\text{Ca}_3(\text{PO}_4)_2$
- Chlorapatite *i.e.* $3\text{Ca}_3(\text{PO}_4)_2 \cdot \text{CaCl}_2$
- Fluorapatite *i.e.* $3\text{Ca}_3(\text{PO}_4)_2 \cdot \text{CaF}_2$

Phosphorus shows a number of allotropic forms like red, black and white phosphorus.

White Phosphorus

White phosphorus exists as P_4 units. P_4 takes the shape of a regular tetrahedron where phosphorus atoms take the vertices.

$\angle \text{PPP} = 60^\circ$ which is much lesser than the normal tetrahedral angle which is $109^\circ 28'$. This is why P_4 is a strainful structure and wants to come out from this. This is the reason white phosphorus is 'hyperactive' in nature. Even at the normal temperature, phosphorus comes in contact with O_2 and ablates to give P_2O_5 eventually.



Some important points regarding white phosphorus :

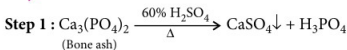
- Phosphorus is a soft non-metal. It is like wax and can be cut with a knife.
- Many P_4 units are connected through weak van der Waals forces of attraction and this is why phosphorus has low melting point (316.58 K) and boiling point (554 K).
- Phosphorus is poisonous in nature. It causes a disease called *Phossy jaw* which is responsible for the decay of jaw bones.

- Above 1070 K, P_4 molecule is unstable and gives P_2 on dissociation.

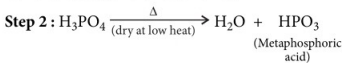
Preparation of White Phosphorus

$\text{Ca}_3(\text{PO}_4)_2$ is the main source of phosphorus. It is available in bone ash. There are two ways for obtaining phosphorus from $\text{Ca}_3(\text{PO}_4)_2$.

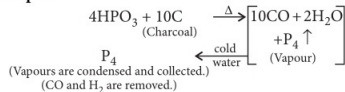
Way 1



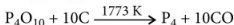
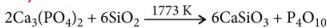
Remove CaSO_4 and collect H_3PO_4 .



Step 3 :



Way 2

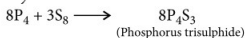


Uses and Common Reactions of White Phosphorus

Uses

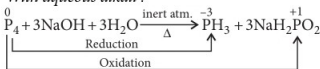
- To prepare rat killing poison.
- To prepare fire bombs.
- To prepare 'Strike anywhere Matches'.

Actually, phosphorus when combines with sulphur gives a number of sulphides like P_2S_3 , P_2S_5 , P_4S_3 , P_4S_7 and to some extent P_4S_{10} also. Out of all these P_4S_3 is mainly used in 'Strike anywhere Matches'.



Reactions

○ With aqueous alkali :

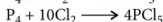
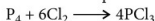


For the same element, both oxidation and reduction occurs. This is known as disproportionation reaction.

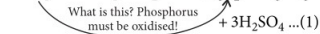
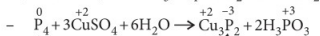
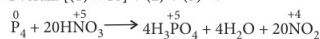
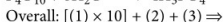
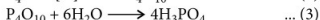
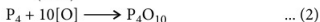
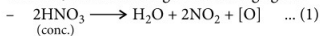
○ With metals : Phosphorus gives metal phosphides.



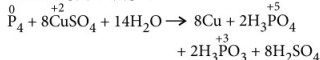
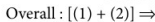
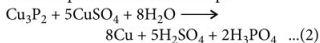
○ With halogens : Phosphorus gives phosphorus trihalides and pentahalides.



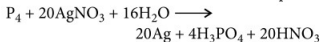
○ Reducing property : As phosphorus can easily be oxidised, it can act as a good reducing agent.



This is explained in the next step.

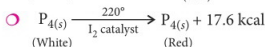
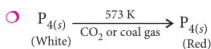


With silver nitrate similar reaction takes place.

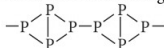


Red Phosphorus

Red phosphorus is obtained from white phosphorus only. Two main ways are :



Red phosphorus has also got tetrahedral structure but here P_4 units are connected through covalent bonds which create a strong network as follows :

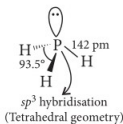


Differences between white and red phosphorus :

White phosphorus	Red phosphorus
Highly reactive	Comparatively very less reactive
Reacts with caustic alkalis	Does not react with caustic alkalis
Less density	Higher density
Poisonous	Non-poisonous
Insoluble in water but soluble in organic solvents	Insoluble in both water and organic substances
Lower melting and boiling points	Higher melting and boiling points
Less stable, lower ignition temperature	More stable, higher ignition temperature

PHOSPHINE

Structure

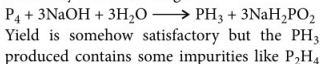


Properties

- At normal temperature, it is a gas.
- It has rotten fish like smell.

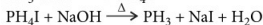
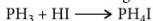
Preparation

○ **Laboratory method :** The best reaction used in laboratory is the following one.

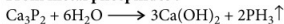


(diphosphine). This P_2H_4 is highly inflammable and it can catch fire. So, at first in the flask CO_2 or coal gas is passed to displace air.

Now to remove P_2H_4 from PH_3 , the gas is passed through a U-tube placed in an ice-cold atmosphere. PH_3 condenses at -185.5 K , which is very low in comparison to the condensation point of P_2H_4 and hence under the condition P_2H_4 condenses but PH_3 comes out. However, there is another way to purify PH_3 . Pass the gas through HI. This gives PH_4I which is due to the reaction between PH_3 and HI. PH_4I (phosphonium iodide) on reaction with strong alkali like NaOH gives PH_3 back.

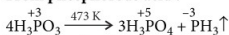


○ **From metal phosphides :**



Instead of water, dilute acid like dilute HCl can also be used. As a metal phosphide, AlP is also a good choice.

○ **From phosphorous acid :**



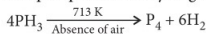
This is another disproportionation reaction.

Frequently asked questions based on the comparison of NH_3 and PH_3 :

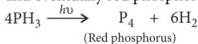
- Which is more basic, NH_3 or PH_3 ?
- Which has higher value $\angle HNH$ or $\angle HPH$?
- Which bond length is more, N—H in NH_3 or P—H in PH_3 ?

Some Important Reactions of PH_3

○ **Dissociation :** At around 713 K , PH_3 dissociates into phosphorus and hydrogen.

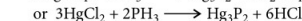
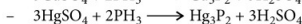


This is found to be white phosphorus. However, if the decomposition is carried under water in presence of light then allotropic change occurs and eventually red phosphorus is obtained.

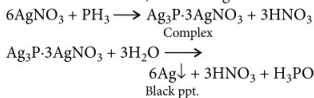


○ **Reaction with solutions of metallic salts (where the metal is below hydrogen) :**

Metallic phosphides are produced during the course of such reactions. For example,

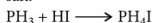


Silver complexes always have the tendency to get converted to metallic silver (comparatively stable than others in its own zone metals). Reaction goes as below:



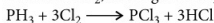
○ **Reaction with mineral acids :**

Due to its weak basic nature, PH_3 reacts with mineral acids like HI to give the corresponding salt.



○ **4Reaction with Cl_2 :**

PH_3 when burns in Cl_2 , depending on the amount of Cl_2 , either gives PCl_3 or PCl_5 .



Halides of Phosphorus

PCl_3

It has pyramidal structure and phosphorus is sp^3 hybridised. P—Cl bond length is larger than that of the P—H bond. This is due to the larger size of Cl atoms. $\angle ClPCl$ is 100.4° and this is also larger than that of $\angle HPH$ because of two things :

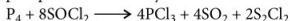
- Larger size of chlorine atoms.
- Donation of electron pair from Cl to vacant orbital of P.



○ **Preparation :** Laboratory preparation is simple which is the reaction between P_4 and dry Cl_2 under heat.



Another good way is reaction between phosphorus and thionyl chloride.

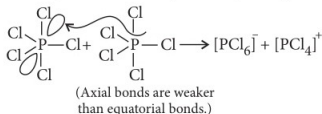


○ **Some important reactions of PCl_3 :**

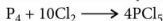


PCl₅

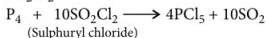
Phosphorus is sp^3d hybridised and the shape is trigonal bipyramidal. Why does PCl₅ conduct electricity? The reason behind this is in the solid state, PCl₅ exists as an ion pair $[\text{PCl}_4]^+[\text{PCl}_6]^-$.



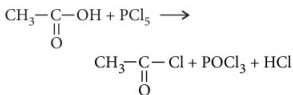
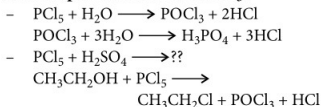
- **Preparation** : One process is the normal reaction between P₄ and Cl₂.



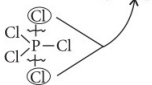
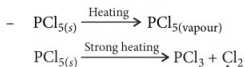
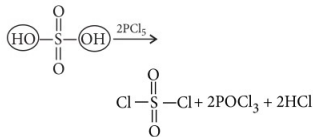
Another is the reaction between P₄ and SO₂Cl₂.



- **Some important reactions of PCl₅** :



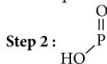
What is happening here? —OH is replaced by —Cl. The same funda is applied with H₂SO₄.

**Oxoacids of Phosphorus**

- Q.** What will be the increasing order of acidic strength of H₃PO₄, H₃PO₃ and H₃PO₂ when it is known that the following acidic order of oxoacids of chlorine is absolutely correct?
HClO₄ > HClO₃ > HClO₂ > HClO

Few tricks to draw the structures of oxoacids of phosphorus are :

- P must contain a double bonded oxygen. This will be the first step.
- Now, put a single —OH group attached with P. If required, more number of —OH groups can be added.
- If more number of P atoms are there, then do the same trick with all the phosphorus atoms. If now some oxygen atoms are left, then put it in between the phosphorus atoms to construct the peroxy bond.
- If the formula is given in the following form : (HPO_n)_n i.e. the polymeric form, and value of *n* is 3 to 5 then generally the structure is cyclic but if the value of *n* is not given then in general it is a long straight chain polymer.

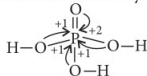
H₃PO₄ :

- Step 3 :** Count the remaining H atoms. It is 2. Count the remaining O atoms. It is 2. They can be grouped as two —OH groups.

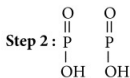
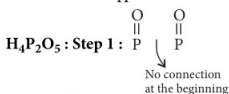
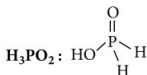
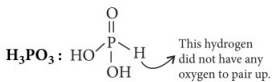


- Step 4 :** It is a very important step.

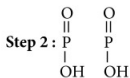
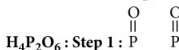
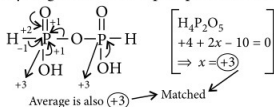
Compare the oxidation states as in the structure and it can be calculated normally as +5.



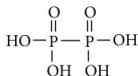
Actually, it is also +5.



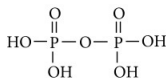
Step 3: Two hydrogen atoms and one oxygen atom left. These cannot be paired. So, put oxygen in between two phosphorus atoms and add hydrogen atoms with phosphorus atoms.



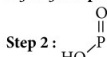
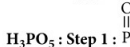
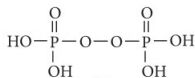
Step 3: Two hydrogen atoms and two oxygen atoms left. These can be paired.



$\text{H}_4\text{P}_2\text{O}_7$: This can be obtained from $\text{H}_4\text{P}_2\text{O}_6$ only.

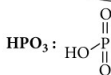
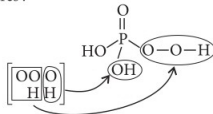


$\text{H}_4\text{P}_2\text{O}_8$: This can be obtained from $\text{H}_4\text{P}_2\text{O}_6$ only.



Step 3: Three oxygen atoms and two hydrogen atoms left.

There are no two phosphorus atoms so no question to put an extra oxygen in between two phosphorus atoms. So go with the following structures:



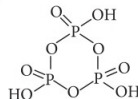
$(\text{HPO}_3)_3$:

- It has to be cyclic.
- Atoms present in the cycle must be atleast bivalent. So, H cannot be a part here. As the number of phosphorus atoms is 3 so make the ring with three phosphorus and three oxygen atoms.

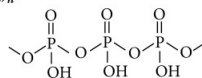


Now, oxygen atoms left is 6.

So,



$(\text{HPO}_3)_n$:

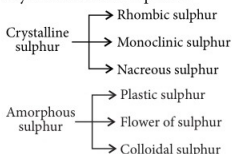


GROUP 16 ELEMENTS

Under this group, oxygen and sulphur families are main.

Sulphur and its Compounds

Sulphur exists in two allotropic forms : crystalline and amorphous.



Basically, rhombic and monoclinic sulphur come under the category of homocyclic structures where general formula can be given as S_n where $n = 6$ to 20 . Rhombic sulphur is basically yellow coloured at normal temperature. It is also known as α -sulphur. Rhombic sulphur has S_8 form and its structure is as follows :

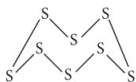


Rhombic sulphur is the stable form of sulphur and it is insoluble in water but soluble in CS_2 . In a China dish or Porcelain dish solution of roll sulphur in CS_2 is taken and it is slowly evaporated. Octahedral crystals of rhombic sulphur come out.

Basically, monoclinic sulphur is prepared from rhombic sulphur.

Above 369 K, rhombic sulphur gets converted to monoclinic sulphur. In fact monoclinic sulphur is stable only above 369 K.

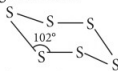
Monoclinic sulphur is known as β -sulphur and it can also be prepared through cooling the molten sulphur in a China dish. Monoclinic sulphur has the following structure :



Monoclinic sulphur has dull yellow colour and it is soluble in CS_2 but not in H_2O .

As below 369 K, rhombic sulphur and above 369 K monoclinic sulphur exists, therefore, it is understandable that at 369 K, both the forms coexist. This temperature is therefore known as *transition temperature*.

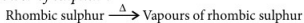
Another form of sulphur under the category of homocyclic sulphur which is obtained is known as Engel's sulphur or ϵ sulphur. Its formula is S_8 and it has the following structure :



This is the chair form. The category of amorphous sulphur is overall known as catena sulphur.

- *Plastic or x-sulphur* : On adding molten and boiling sulphur slowly into the cold water, rubber like plastic sulphur comes out. If this form is allowed to stand for long, then it changes into rhombic sulphur. Plastic sulphur has S_8 units and it consists of spiral chain.

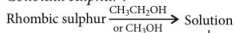
Flower of sulphur :



↓ Allow to cool in a container slowly

This is flower of sulphur. ← Flower like solid sulphur

Colloidal sulphur :



↓ Pour into cold H_2O

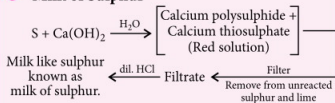
Sulphur exists in suspended form in water and does not precipitate.

This is known as colloidal sulphur.

So far the sulphur allotropes which have overall S_6 to S_{20} sulphur atoms in their chain or ring have been mentioned but it is also possible to have small molecules of sulphur *i.e.* S_n where $n = 2$ to 5 . These are unstable indeed. For example, S_2 is such a molecule which is blue coloured, paramagnetic in nature and stable above 1000 K.

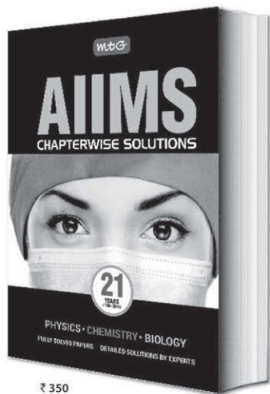
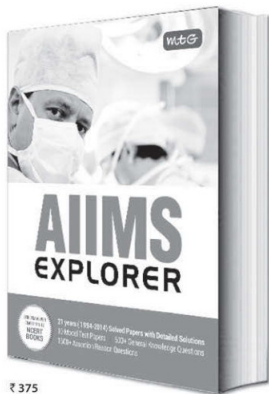
Add to Your Knowledge

- **Milk of Sulphur**





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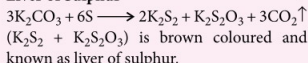
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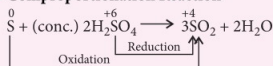
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○ Liver of Sulphur



○ Comproportionation Reaction

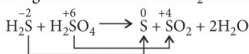


Both oxidation and reduction at the LHS lead to the same product in RHS.

H₂S



Conc. H_2SO_4 cannot be used as, due to its strong oxidising nature it will oxidise H_2S as below :



Important reactions of H₂S



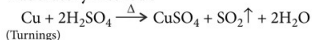
This is why when aqueous solution of H_2S is kept for long it becomes opaque as the sulphur formed remain in suspended form.



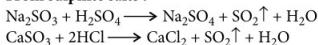
SO₂

Preparation

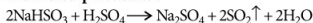
○ Laboratory method :



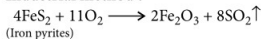
○ From sulphite salts :



○ From bisulphite salts :



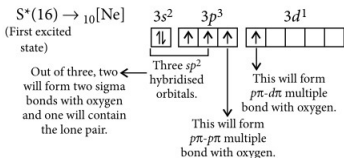
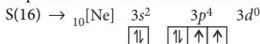
○ Industrial method :



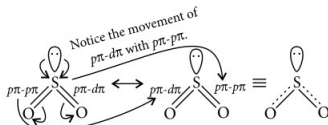
Structural Formation of SO₂ and SO₃

SO_2 is a gas at normal temperature. Here, the molecules are combined with weak van der Waals forces of attraction.

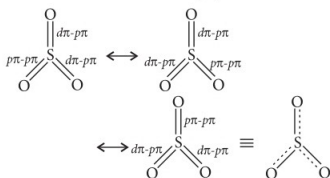
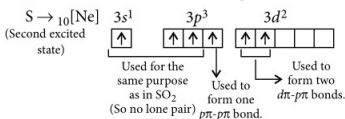
Sulphur in its first excited state forms SO_2 .



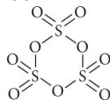
So, the following structure is opt for SO_2 .



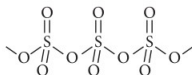
SO_3 on the other hand, has two $d\pi-p\pi$ bonds.



SO_3 , however can have other two forms also, one is cyclic trimer i.e. $(SO_3)_3$ which looks as below :



The another one is linear structure of SO_3 which is as below:



...To be continued on the next issue.

C R O S S W O R D

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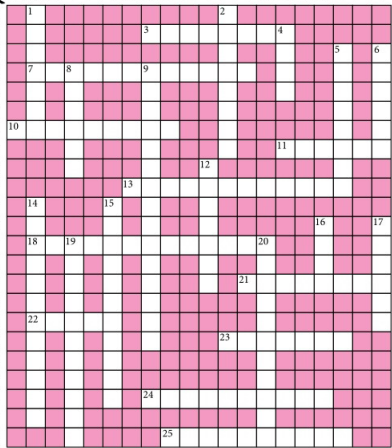
ACROSS

- A 'rogue element'. (8)
- Stomach acid. (12)
- A type of alcohols obtained by reduction of ketones. (9)
- Metal, useful in diagnosing stomach ulcers. (6)
- Smells like bitter almonds. (12)
- A substitution reaction by which C_6H_5Cl is synthesised from C_6H_6 . (13)
- First transition series element, having total five electrons in $3d$ and $4s$ -orbitals. (8)
- The term 'vitamine' was changed to 'vitamin' because most of them did not contain the _____ groups. (5)
- The cross-linking agent, used in manufacturing of tyre rubber. (7)
- A term applied to reactions which exhibit dynamic equilibrium. (10)
- A type of mixture containing insoluble particles mixed evenly through a liquid. (10)

DOWN

- The main constituent of CNG. (7)
- A sub-atomic particle, having mass same as that of an electron. (8)
- An inert gas used in street signs. (4)
- A yellowish-green gas manufactured from salt and used in disinfectants and plastics. (8)
- The Latin word for 'iron'. (6)
- The term used to describe a molecule with an unequal charge distribution. (6)
- Carboxylic acids have exceptionally high boiling points due to (15)

Cut Here



- The liquefied metal which expands on solidification. (7)
- An equipment, which detects the driver's ethanol level. (12)
- This gas is prepared by the catalytic oxidation of ammonia. (11)
- Element that does not show catenation. (4)
- Name of catalyst used for the preparation of Grignard reagent. (6)
- A type of reaction in which a reaction intermediate, carbene is formed. (11)
- The process, by which muddy water can be purified. (11)

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