12 Organic Chemistry Some Basic Principles and Techniques

I. Multiple Choice Questions (Type-I)

1. Which of the following is the correct IUPAC name?
   (*i*) 3-Ethyl-4, 4-dimethylheptane
   (*ii*) 4,4-Dimethyl-3-ethylheptane
   (*iii*) 5-Ethyl-4, 4-dimethylheptane
   (*iv*) 4,4-Bis(methyl)-3-ethylheptane

Ans. (*i*)

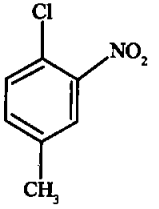
Explanation: In IUPAC naming if different alkyl groups are present, they are written in alphabetical order. Ethyl will be first, followed by methyl. Di, tri, tetra prefixes are not included in alphabetical order.

2. The IUPAC name for $CH_3-\overset{O}{\overset{\|}{C}}-CH_2-CH_2-\overset{O}{\overset{\|}{C}}-OH$ is _____.
   (*i*) 1-hydroxypentane-1,4-dione (*ii*) 1,4-dioxopentanol
   (*iii*) 1-carboxybutan-3-one (*iv*) 4-oxopentanoic acid

Ans. (*iv*)

Explanation: If more than one functional groups are present in the chain, one will be the main functional group on priority basis and mentioned as a sec. suffix, while the others are written as a prefix. Carboxylic group is main functional gp. and suffix is oic acid and ketonic group is prefix mentioned as oxo along with locant.

3. The IUPAC name for

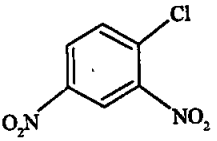


   (*i*) 1-Chloro-2-nitro-4-methylbenzene
   (*ii*) 1-Chloro-4-methyl-2-nitrobenzene
   (*iii*) 2-Chloro-1-nitro-5-methylbenzene
   (*iv*) *m*-Nitro-*p*-chlorotoluene

Ans. (*ii*)

Explanation: Substituent of the base compound is assigned number1 and then the direction of numbering is chosen such that the next substituent

gets the lowest number. The substituents appear in the name in alphabetical order. As for example:



1-Chloro-2, 4-dinitrobenzene

4. Electronegativity of carbon atoms depends upon their state of hybridisation. In which of the following compounds, the carbon marked with asterisk is most electronegative?

(*i*) $CH_3 - CH_2 - {}^*CH_2 - CH_3$ (*ii*) $CH_3 - {}^*CH = CH - CH_3$

(*iii*) $CH_3 - CH_1 - C \equiv {}^*CH$ (*iv*) $CH_3 - CH_2 - CH = {}^*CH_2$

Ans. (*iii*)

Explanation: Electronegativity of carbon atom depends on its hybridized state and percentage of '*s*' character. Electronegativity is directly proportional to percentage of '*s*' character. sp^3 (25% '*s*' character) < sp^2 (33% '*s*' character) < *sp* (50% '*s*' character). Carbon linked through two π bonds is sp hybridized.

5. In which of the following functional group, isomerism is **not** possible?

(*i*) Alcohols (*ii*) Aldehydes

(*iii*) Alkyl halides (*iv*) Cyanides

Ans. (*iii*)

Explanation: Functional isomers have same molecular formula but different functional group. Alcohols are functional isomers of ethers. Aldehydes are functional isomers of ketones. Cyanides are functional isomers of isocyanides. Only alkyl halides do not show functional isomerism.

6. The fragrance of flowers is due to the presence of some steam volatile organic compounds called essential oils. These are generally insoluble in water at room temperature but are miscible with water vapour in vapour phase. A suitable method for the extraction of these oils from the flowers is:

(*i*) Distillation

(*ii*) Crystallisation

(*iii*) Distillation under reduced pressure

(*iv*) Steam distillation

Ans. (*iv*)

Explanation: This technique is applied to separate substances which are steam volatile and are immiscible with water. In steam distillation, steam from a steam generator is passed through a heated flask containing the liquid to be distilled. The mixture of steam and the volatile organic

compound is condensed and collected. The compound is later separated from water using a separating funnel.

7. During hearing of a court case, the judge suspected that some changes in the documents had been carried out. He asked the forensic department to check the ink used at two different places. According to you which technique can give the best results?

(*i*) Column chromatography (*ii*) Solvent extraction
(*iii*) Distillation (*iv*) Thin layer chromatography

Ans. (*iv*)

Explanation: Thin layer chromatography (TLC): It is a method for analyzing mixtures by separating the components of the mixture. TLC can be used to determine the number of components in the mixture, the identity of compounds and the purity of compounds by observing the appearance of a product or the disappearance of a reactant. It can also be used to monitor the progress of a reaction. TLC is a sensitive technique—microgram (0.000001)g quantities can be analyzed by TLC.

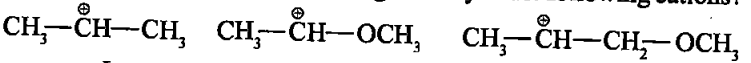
8. The principle involved in paper chromatography is

(*i*) Adsorption (*ii*) Partition
(*iii*) Solubility (*iv*) Volatility

Ans. (*ii*)

Explanation: Partition chromatography is based on continuous differential partitioning of components of a mixture between stationary and mobile phases. Paper chromatography is a type of partition chromatography.

9. What is the correct order of decreasing stability of the following cations?

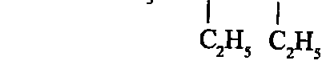


I. II. III.

(*i*) II > I > III (*ii*) II > III > I
(*iii*) III > I > II (*iv*) I > II > III

Ans. (*i*)

Explanation: In (I) case, +vely charged C is attached to two alkyl groups and +I effect stabilize carbocation. In (II) case, +R effect of OCH_3 group stabilize carbocation. In (III) case, –I effect of $-OCH_3$gp. destabilises carbocation hence, the order of stability: II > I >III.

10. Correct IUPAC name for  is _____.

(*i*) 2-Ethyl-3-methylpentane (*ii*) 3, 4-Dimethylhexane
(*iii*) 2-sec-butylbutane (*iv*) 2, 3-Dimethylbutane

Ans. (*ii*)

Explanation: In longest continuous chain both ethyl groups are included and 3rd and 4th carbon have methyl groups present as a substituent.

11. In which of the following compounds the carbon marked with asterisk is expected to have greatest positive charge?

(*i*) $*CH_3—CH_2—Cl$ (*ii*) $*CH_3—CH_2—Mg^+Cl^-$

(*iii*) $*CH_3—CH_2—Br$ (*iv*) $*CH_3—CH_2—CH_3$

Ans. (*i*)

Explanation: Order of electronegativity of the attached group is as follows:

$$Cl > Br > C > Mg.$$

More electronegative group attached to the C will give more positive charge. Therefore, in (*i*) case asterisk C will have greatest positive charge.

12. Ionic species are stabilised by the dispersal of charge. Which of the following carboxylate ion is the most stable?

(*i*) $CH_3—\overset{\overset{O}{\|}}{C}—O^-$ (*ii*) $Cl—CH_2—\overset{\overset{O}{\|}}{C}—O^-$

(*iii*) $F—CH_2—\overset{\overset{O}{\|}}{C}—O^-$ (*iv*) $\begin{matrix} F \\ \diagdown \\ CH \\ \diagup \\ F \end{matrix}—\overset{\overset{O}{\|}}{C}—O^-$

Ans. (*iv*)

Explanation: The stabilsation of carboxylate ion depends on dispersal of negative charge. The negative charge is dispersed by two factors, *i.e,* +R effect of the carboxylate ion and Inductive effect of the halogens. In all the above structures, +R effect is common but halogen atoms are different. Therefore, dispersal of negative charge depends upon halogen atoms. F is most electronegative, in structure (*iv*) two F atoms are present and more dispersal of negative charge is there.

13. Electrophilic addition reactions proceed in two steps. The first step involves the addition of an electrophile. Name the type of intermediate formed in the first step of the following addition reaction.

$$H_3C—HC = CH_2 + H^+ \longrightarrow ?$$

(*i*) 2° Carbanion (*ii*) 1° Carbocation

(*iii*) 2° Carbocation (*iv*) 1° Carbanion

Ans. (*iii*)

Explanation: When H^+ attacks on propene delocalization of electrons can take place in two possible ways:

$$\overset{3}{H_3C}—\overset{2}{CH}=\overset{1}{CH_2} + H—Br \xrightarrow{H^+}$$

$H_3C—CH_2—\overset{+}{C}H_2 + Br^-$ (*a*) less stable primary carbocation

$H_3C—\overset{+}{C}H—CH_3 + Br^-$ (*b*) more stable secondary carbocation

The secondary carbocation (*b*) is more stable than the primary carbocation (*a*), therefore, the former predominates because it is formed at a faster rate.

14. Covalent bond can undergo fission in two different ways. The correct representation involving a heterolytic fission of CH_3—Br is

(*i*) $CH_3—Br \rightarrow \overset{\oplus}{C}H_3 + \overset{\ominus}{Br}$ (*ii*) $CH_3—Br \rightarrow \overset{\oplus}{C}H_3 + \overset{\ominus}{Br}$

(*iii*) $CH_3—Br \rightarrow \overset{\ominus}{C}H_3 + \overset{\oplus}{Br}$ (*iv*) $CH_3—Br \rightarrow \dot{C}H_3 + \dot{Br}$

Ans. (*ii*)

Explanation: Br is more electronegative than C, hence hetrolytic fission takes place. Electrons displace from carbon to Br. Therefore, CH_3 gets positive charge and Br gets negative charge. Thus, option (*ii*) is correct.

$$H_3C—Br \rightarrow H_3\overset{+}{C} + \overset{-}{Br}$$

15. The addition of HCl to an alkene proceeds in two steps. The first step is the attack of H^+ ion to $>C=C<$ portion which can be shown as

(*i*) $H^+ \rightarrow >C=C<$ (*ii*) $H^+ \leftarrow >C=C<$

(*iii*) H^+ $>C=C<$ (*iv*) All of these are possible

Ans. (*ii*)

Explanation: This effect the π–electrons of the multiple bond are transferred to that atom to which there agent gets attached. For example:

$$>C=C< + H^+ \longrightarrow >\overset{+}{C}—C<_{H}$$

(attacking reagent)

II. Multiple Choice Questions (Type-II)

In the following questions two or more options may be correct.

16. Which of the following compounds contain all the carbon atoms in the same hybridisation state?

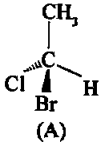
(*i*) H—C ≡ C—C ≡ C—H (*ii*) CH_3—C ≡ C—CH_3

(*iii*) $CH_2 = C = CH_2$ (*iv*) CH_2 = CH—CH = CH_2

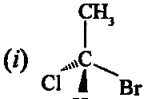
Ans. (*i*) and (*iv*)

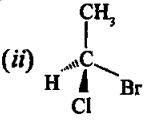
Explanation: Only in these two compounds all carbon atoms are in same hybridisation state *i.e.*, *sp* and sp^2 hybridized, respectively.

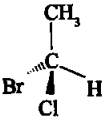
17. In which of the following representations given below spatial arrangement of group/atom **different** from that given in structure 'A'?

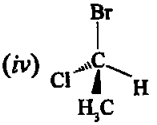


(A)

(*i*) 

(*ii*) 

(*iii*) 

(*iv*) 

Ans. (*i*), (*iii*) and (*iv*)

Explanation: The spatial arrangement of groups or atoms can be checked by doing two interchange and bringing H below the plane of the paper. Find out the sequence of the remaining groups in a particular order whether clockwise or anticlockwise starting from atom with highest atomic number to atom with lower atomic numbers. Hence, option (*ii*) has same spatial arrangement as (A) while in rest three is different.

18. Electrophiles are electron seeking species. Which of the following groups contain only electrophiles?

(*i*) BF_3, NH_3, H_2O

(*ii*) $AlCl_3$, SO_3, NO_2^+

(*iii*) NO_2^+, CH_3^+, $CH_3—\overset{+}{C}=O$

(*iv*) $C_2H_5^-$, $C_2\overset{\bullet}{H}_5$, $C_2H_5^+$

Ans. (*ii*) and (*iii*)

Explanation: Electrophiles are +vely charged or electron deficient species. They are Lewis acids. $AlCl_3$, SO_3 are Lewis acids, NO_2^+, CH_3^+, $CH_3—C^+=O$ are +vely charged species.

Note: Consider the following four compounds for answering questions 19 and 20.

I. $CH_3—CH_2—CH_2—CH_2—\overset{\overset{O}{\|}}{C}—H$

II. $CH_3—CH_2—CH_2—\overset{\overset{O}{\|}}{C}—CH_3$

III. $CH_3—CH_2—\underset{\underset{O}{\|}}{C}—CH_2—CH_3$

IV. $CH_3—\underset{\underset{CH_3}{|}}{CH}—CH_2—\underset{\underset{O}{\|}}{C}—H$

19. Which of the following pairs are position isomers?

(*i*) I and II (*ii*) II and III

(*iii*) II and IV (*iv*) III and IV

Ans. (*ii*)

Explanation: In position isomerism, two or more compounds differ in the position of substituent, functional group or multiple bonds but

molecular formula is same. In pentanone-2 and pentanone-3, position of ketonic group is different.

$CH_3—CH_2—CH_2—CO—CH_3$ and $CH_3—CH_2—CO—CH_2—CH_3$

20. Which of the following pairs are **not** functional group isomers?

(*i*) II and III (*ii*) II and IV

(*iii*) I and IV (*iv*) I and II

Ans. (*i*) and (*iii*)

Explanation: Two or more compounds with same molecular formula but different functional groups are called functional isomers. In the given compounds

I. Aldehydic group. II. Ketonic group.

III. Ketonic group. IV. Aldehydic group.

Hence II and III , I and IV are not functional isomers.

21. Nucleophile is a species that should have

(*i*) a pair of electrons to donate (*ii*) positive charge

(*iii*) negative charge (*iv*) electron deficient species

Ans. (*i*) and (*iii*)

Explanation: Nucleophiles are –vely charged or electron rich (lone pair of electrons) species. Hence, options (*i*) and (*iii*) are correct.

22. Hyperconjugation involves delocalisation of _____.

(*i*) electrons of carbon-hydrogen σ bond of an alkyl group directly attached to an atom of unsaturated system.

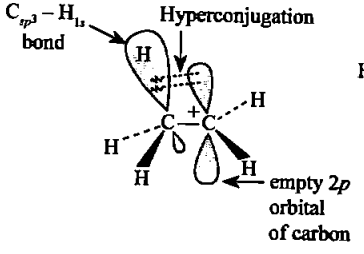
(*ii*) electrons of carbon-hydrogen σ bond of alkyl group directly attached to the positively charged carbon atom.

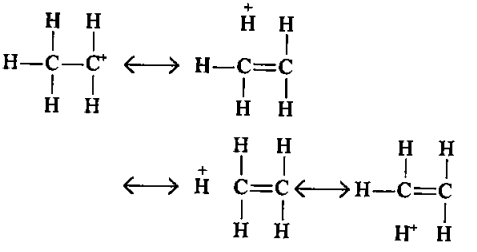
(*iii*) π-electrons of carbon-carbon bond

(*iv*) lone pair of electrons

Ans. (*i*) and (*ii*)

Explanation: Hyperconjugation 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. The σ electrons of C—H bond of the alkyl group enter into partial conjugation with the attached unsaturated system or with the unshared *p* orbital. Hyperconjugation is a permanent effect.





III. Short Answer Type

Note : Consider structures I to VII and answer the questions 23–26.

I. $CH_3—CH_2—CH_2—CH_2—OH$

II. $CH_3—CH_2—\underset{\displaystyle OH}{\underset{|}{CH}}—CH_3$

III. $CH_3—\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle OH}{\underset{|}{C}}}}—CH_3$

IV. $CH_3—\underset{\displaystyle CH_3}{\underset{|}{CH}}—CH_2—OH$

V. $CH_3—CH_2—O—CH_2—CH_3$

VI. $CH_3—O—CH_2—CH_2—CH_3$

VII. $CH_3—O—\underset{\displaystyle CH_3}{\underset{|}{CH}}—CH_3$

23. Which of the above compounds form pairs of metamers?

Ans. When two or more compounds have same molecular formula but different alkyl groups on either side of the functional group, the compounds are called metamers. In the given structures V and VI or VI and VII form a pair of metamers because alkyl groups are different on either side of the functional group –O–.

V. $CH_3—CH_2—O—CH_2—CH_3$ {Metamers}

VI. $CH_3—O—CH_2—CH_2—CH_3$ {Metamers}

and

VI. $CH_3—O—CH_2—CH_2—CH_3$ {Metamers}

VII. $CH_3—O—CH(CH_3)—CH_3$ {Metamers}

24. Identify the pairs of compounds which are functional group isomers.

Ans. Two or more compounds with same molecular formula but different functional groups are called functional isomers. Alcohols are the functional isomers of the ether. In the given structures I, II, III, IV represent alcohols and V, VI, VII are ethers.

Hence, I and V, I and VI, I and VII, II and V, II and VI, II and VII, III and V, III and VI etc.

25. Identify the pairs of compounds that represents position isomerism.

Ans. In position isomerism, two or more compounds differ in the position of substituent, functional group or multiple bonds but molecular formula is same. In the given structures, I and II, III and IV, and VI and VII are position isomers.

I. $CH_3—CH_2—CH_2—CH_2—OH$ and

II. $CH_3—CH_2—CH(OH)—CH_3$ are position isomers.

III. $CH_3—C(CH_3)(OH)—CH_3$ and

IV. $CH_3—CH(CH_3)—CH_2—OH$ are position isomers.
VI. $CH_3—O—CH_2—CH_2—CH_3$ and
VII. $CH_3—O—CH(CH_3)—CH_3$ are position isomers.

26. Identify the pairs of compounds that represents chain isomerism.

Ans. When two or more compounds have similar molecular formula but different carbon skeletons, these are referred to as chain isomers and the phenomenon is termed as chain isomerism.

I. $CH_3—CH_2—CH_2—CH_2—OH$
II. $CH_3—CH_2—CH(OH)—CH_3$
III. $CH_3—C(CH_3)(OH)—CH_3$
IV. $CH_3—CH(CH_3)—CH_2—OH$

27. For testing halogens in an organic compound with $AgNO_3$ solution, sodium extract (Lassaigne's test) is acidified with dilute HNO_3. What will happen if a student acidifies the extract with dilute H_2SO_4 in place of dilute HNO_3?

Ans. Elements like nitrogen, halogens, sulphur and phosphorous present in organic compounds converted into ions by fusing with sodium metal followed by plucking in distilled water getting sodium extract (Lassaigne's test). On adding dil. H_2SO_4 in place of dil. HNO_3 for testing halogens by $AgNO_3$, white precipitate of $AgSO_4$ is formed. This will lead wrong result of chloride. Hence , only HNO_3 is used instead of dil. H_2SO_4.

28. What is the hybridisation of each carbon in $H_2C = C = CH_2$?

Ans. The given structure is of C_3H_4 in which all three carbon atoms are linked to each other by double bonds. Carbons are marked as C1, C2 and C3.C1 and C3 are sp^2 hybridized because of having 3 σ and 1 π bonds. C2 has 2 σ bonds and 2π bonds it is sp hybridized.

$$\overset{1}{CH_2} = \overset{2}{C} = \overset{3}{CH_2}$$

29. Explain, how is the electronegativity of carbon atoms related to their state of hybridisation in an organic compound?

Ans. Electronegativity of carbon is directly proportional to 's' character. If C is sp^3 hybridized then '*s*' character is 25%, sp^2 hybridized then '*s*' character is 33% and if *sp* hybridized then '*s*' character is 50%. Hence, *sp* hybridized carbon has strong hybridization. *s* electrons are more strongly attracted by nucleus than *p*-electrons thus electronegativity of carbon increases with increase in '*s*' character.

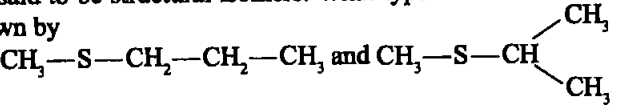
30. Show the polarisation of carbon-magnesium bond in the following structure.

$$CH_3—CH_2—CH_2—CH_2—Mg—X$$

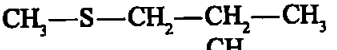
Ans. Carbon is more electronegative than magnesium therefore, Mg has partially positive charge and C has partially negative charge because bonded pair of electrons attracted towards carbon.

$$CH_3—CH_2—CH_2—CH_2—\overset{\delta-}{<}—\overset{\delta+}{Mg}—X$$

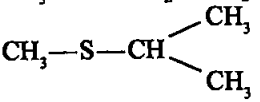
31. Compounds with same molecular formula but differing in their structures are said to be structural isomers. What type of structural isomerism is shown by



Ans. These are position isomers as the functional groups are attached to different carbon atoms in carbon chain. They are not metamers because the number of C atoms on either side of –S– are same.

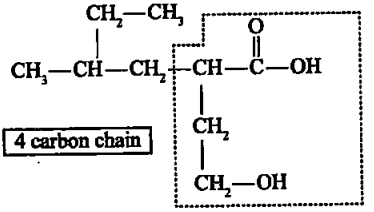


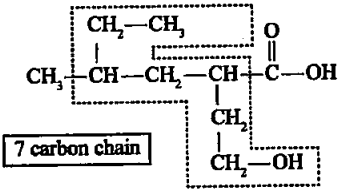
Methyl *n*-propyl thioether.

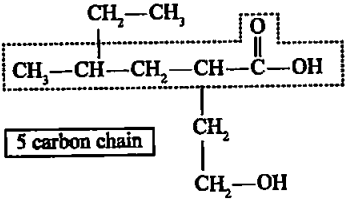


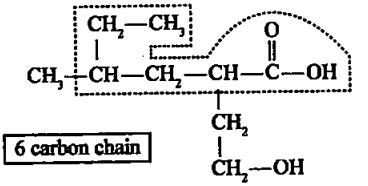
Methyl isopropyl thioether.

32. Which of the following selected chains is correct to name the given compound according to IUPAC system?

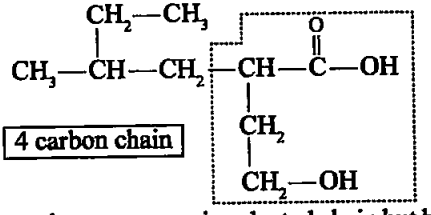








Ans. According to IUPAC nomenclature, the selected longest carbon chain must have maximum functional groups present in the compound. Therefore, only in one selected chain of 4 carbon atoms including both the functional groups is corrected one.



In other three, carbon atoms are in selected chain but both the functional groups are not included.

33. In DNA and RNA, nitrogen atom is present in the ring system. Can Kjeldahl method be used for the estimation of nitrogen present in these? Give reasons.

Ans. In DNA and RNA, nitrogen is present in hetrocyclic base and also present in ring not as a substituent. Therefore, nitrogen present in ring cannot be converted into $(NH_4)_2SO_4$. Hence, cannot be estimated by Kjeldahl method.

34. If a liquid compound decomposes at its boiling point, which method (*s*) can you choose for its purification. It is known that the compound is stable at low pressure, steam volatile and insoluble in water.

Ans. If the compound decomposes at its boiling point but, is steam volatile and insoluble in water and stable at low pressure, steam distillation can be used for its purification.

Note: Answer the questions 35 to 38 on the basis of information given below:

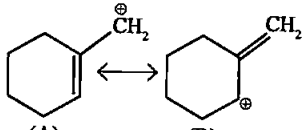
"Stability of carbocations depends upon the electron releasing inductive effect of groups adjacent to positively charged carbon atom involvement of neighbouring groups in hyperconjugation and resonance."

35. Draw the possible resonance structures for $CH_3—O—\overset{+}{C}H_2$ and predict which of the structures is more stable. Give reason for your answer.

Ans. Two resonating structures can be of given carbocation:

In structure I, $CH_3—\ddot{O}—\overset{+}{C}H_2$, CH_2 has +ve charge means octet is not completed, but in structure II, $CH_3—\overset{+}{O}=CH_2$ both the carbon atoms and oxygen atom have octet of electrons hence, more stable.

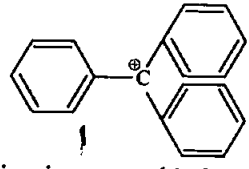
36. Which of the following ions is more stable? Use resonance to explain your answer.



(A) (B)

Ans. Structure A is more stable than B. Carbocation A is more planar and π electrons from the ring shift to side group $\overset{+}{C}H_2$ and stabilized by resonance. Structure (B) is non-planar and does not undergo resonance. Double bond is more stable within the ring as compared to side chain.

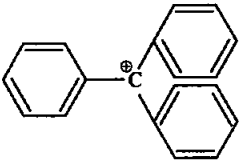
37. The structure of triphenylmethyl cation is given below. This is very stable and some of its salts can be stored for months. Explain the cause of high stability of this cation.



I

Ans. Triphenylmethyl cation is very stable because +ve charge of methyl carbon is delocalized in three phenyl rings. In each phenyl ring, +ve charge is developed on 2 ortho position and para position, *i.e.*, three

resonating structures. Total resonating structures given by triphenylmethyl cation are nine. Hence, it is very stable. These structures can be shown as.



38. Write structures of various carbocations that can be obtained from 2-methylbutane. Arrange these carbocations in order of increasing stability.

Ans. 2-methylbutane gives 4 different carbocations by replacing 1-H atom from different carbons. 2 primary, 1 secondary and 1 tertiary carbocation. Order of stability is as follows:

$CH_3—CH(CH_3)—CH_2—C^+H_2$ I (1° carbocation)

$CH_3—CH(CH_3)—CH^+—CH_3$ II (2° carbocation)

$CH_3—C^+(CH_3)—CH^+—CH_3$ III (3° carbocation)

$^+CH_2—CH(CH_3)—CH^+—CH_3$ IV (1° carbocation)

1° carbocation < 2° carbocation < 3° carbocation

Stability of various carbocations.

I < IV < II < III

39. Three students, Manish, Ramesh and Rajni were determining the extra elements present in an organic compound given by their teacher. They prepared the Lassaigne's extract (L.E.) independently by the fusion of the compound with sodium metal. Then they added solid $FeSO_4$ and dilute sulphuric acid to a part of Lassaigne's extract. Manish and Rajni obtained prussian blue colour but Ramesh got red colour. Ramesh repeated the test with the same Lassaigne's extract, but again got red colour only. They were surprised and went to their teacher and told him about their observation. Teacher asked them to think over the reason for this. Can you help them by giving the reason for this observation? Also, write the chemical equations to explain the formation of compounds of different colours.

Ans. If organic compound contains N and S both, then on fusion with Na metal compound gives NaSCN or NaCN and Na_2S depending on the quantity of Na metal. If Na metal is less then only NaSCN is formed. In that case L.E on treating with $FeSO_4$ and H_2SO_4 gives red colour due to the formation of ferric thiocyanide $Fe(SCN)_3$. In case of NaCN, L.E on treating with $FeSO_4$ and H_2SO_4 gives prussian blue colour.

Chemical reactions:

$Fe^{2+} \rightarrow Fe^{3+}$ (Oxidation)

$Fe^{3+} + 3NaSCN \rightarrow Fe(SCN)_3 + 3Na^+$

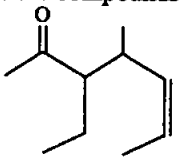
Red colour

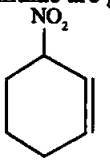
If Na is in excess then : $NaSCN + 2Na \xrightarrow{\Delta} NaCN + Na_2S$

$$6CN^- + F^{2+} \rightarrow [Fe(CN)_6]^{4-}$$

$$3[Fe(CN)_6]^{4-} + 4Fe^{3+} \xrightarrow{xH_2O} \underset{\text{Prussian blue}}{Fe_4[Fe(CN)_6]_3.xH_2O}$$

40. Name the compounds whose line formulae are given below:

(*i*) 

(*ii*) 

Ans. (*i*) 3-ethyl, 4-methylhept-5-en-2-one. (Longest chain of carbon atoms selected in such a way that the functional group > C = O gets lowest possible locant.

(*ii*) 3-nitrocyclohex-1-en (Carbon atoms of the ring are numbered in such a way that double bonded carbon gets the lowest number followed by the nitro group $-NO_2$.

41. Write structural formulae for compounds named as—

(*a*) 1-Bromoheptane (*b*) 5-Bromoheptanoic acid

Ans. (*i*) $\underset{\text{1-Bromoheptane}}{CH_3—CH_2—CH_2—CH_2—CH_2—CH_2—CH_2Br}$

(*ii*) $\underset{\text{5-Bromoheptanoic acid}}{CH_3—CH_2—CH(Br)—CH_2—CH_2—CH_2—COOH}$

42. Draw the resonance structures of the following compounds;

(*i*) $CH_2=CH—\ddot{\underset{\cdot\cdot}{Cl}}:$

(*ii*) $CH_2=CH—CH=CH_2$

(*iii*) $CH_2=CH—\underset{\displaystyle H}{\overset{\displaystyle O}{\overset{\|}{\underset{|}{C}}}}$

Ans. (*i*) $CH_2=CH—Cl \leftrightarrow {}^-CH_2—CH=Cl^+$

(*ii*) $CH_2=CH—CH=CH_2 \leftrightarrow {}^+CH_2—CH=CH—CH_2^- \leftrightarrow CH_2—CH=CH—CH_2^+$

(*iii*) $CH_2=CH—CHO \leftrightarrow {}^+CH_2—CH=CHO^-$

43. Identify the most stable species in the following set of ions giving reasons:

(*i*) $\overset{+}{C}H_3, \overset{+}{C}H_2Br, \overset{+}{C}HBr_2, \overset{+}{C}Br_3$

(*ii*) $\overset{\ominus}{C}H_3, \overset{\ominus}{C}H_2Cl, \overset{\ominus}{C}HCl_2, \overset{\ominus}{C}Cl_3$

Ans. (*i*) CH_3^+ is most stable species because replacement of H atom by Br (–Inductive effect) increases +ve charge on carbon atom and destabilizes the species.

(*ii*) $^-CCl_3$ is most stable because –ve charge on carbon atom is dispersed due to –I effect of Cl. More Cl atoms, more dispersal of –ve charge and more stabilized.

44. Give three points of differences between inductive effect and resonance effect.

Ans.

S.No.	Inductive effect	Resonance effect
1.	It involves displacement of σ electrons in saturated compounds.	It involves displacement of π electrons or lone pair of electrons in unsaturated and conjugated compounds.
2.	In inductive effect, there is slight displacement of σ electrons and partial +ve or –ve charge develops.	In this effect, there is complete transfer of π electrons and as a result, complete +ve or –ve charge develops.
3.	Inductive effect can move only upto 3 to 4 carbons.	In this case, movement of electrons all along the length of conjugated system takes place.

45. Which of the following compounds will not exist as resonance hybrid. Give reason for your answer:

(*i*) CH_3OH (*ii*) $R—CONH_2$ (*iii*) $CH_3CH = CHCH_2NH_2$

Ans. (*i*) **CH_3OH:** It does not show resonance because of absence of π electrons.

(*ii*) **$RCONH_2$:** It shows resonance due to the presence of lone pair on N atom and π electrons on C = O bond. Hence, amide can be represented by three resonating structures.

(*iii*) **$CH_3CH = CHCH_2NH_2$:** As the lone pair of electrons on N atom, is not conjugated with the π electrons of double bond. Hence, it does not show resonance.

46. Why does SO_3 act as an electrophile?

Ans. SO_3 acts as an electrophile because three highly electronegative oxygen atoms are attached to sulphur atom in SO_3 which makes sulphur atom electron deficient. It can be shown by resonance. Sulphur gets +ve charge and acts as an electrophile.

47. Resonance structures of propenal are given below. Which of these resonating structures is more stable? Give reason for your answer.

$$\underset{\text{I}}{CH_2=CH—CH=O} \longleftrightarrow \underset{\text{II}}{\overset{\oplus}{C}H_2—CH=CH—\overset{\ominus}{O}}$$

Ans. Structure I of propenal is more stable because structure having more covalent bonds in a resonating structure, has more stability. In structure II, the terminal carbon has only six electrons which makes it less stable.

$CH_2=CH—CH=O$ [Structure I] $\leftrightarrow {}^{+}CH_2—CH=CH—O^{-}$ [Structure II]

48. By mistake, an alcohol (boiling point 97°C) was mixed with a hydrocarbon (boiling point 68°C). Suggest a suitable method to separate the two compounds. Explain the reason for your choice.

Ans. Mixture of alcohol and hydrocarbon can be separated by simple distillation because both the components have large difference in their

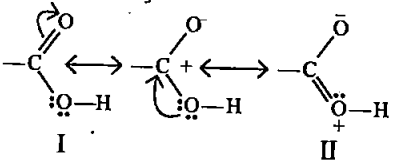
boiling points. When temperature is raised to the low boiling liquid *i.e.*, hydrocarbon, the vapours consist only hydrocarbon without any contamination of alcohol.

49. Which of the two structures (A) and (B) given below is more stabilised by resonance? Explain.

CH_3COOH and $CH_3COO^{\ominus}$

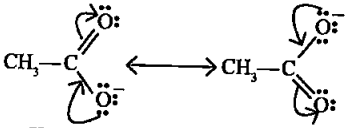
(A) (B)

Ans. Resonating structure of CH_3COOH



I II

Resonating structure of CH_3COO^-.



III IV

Structure II is less stable than I because in structure II separation of +ve and –ve charges is there. Therefore, contribution of structure (II) is less than that of (I), these hybrid of compound (A) *i.e.*, CH_3COOH. While structure (III) and (IV) are of equal energy and also contribute equally towards resonance hybrid of compound (B). Therefore, CH_3COO^- is more stable.

IV. Matching Type

In the following questions more than one correlation is possible between options of Column I and Column II. Make as many correlations as you can.

50. Match the type of mixture of compounds in Column I with the technique of separation/purification given in Column II.

Column I	Column II
(*i*) Two solids which have different solubilities in a solvent and which do not undergo reaction when dissolved in it.	(*a*) Steam distillation
(*ii*) Liquid that decomposes at its boiling point	(*b*) Fractional distillation
(*iii*) Steam volatile liquid	(*c*) Simple distillation
(*iv*) Two liquids which have boiling points close to each other	(*d*) Distillation under reduced pressure
(*v*) Two liquids with large difference in boiling points.	(*e*) Crystallisation

Ans. (*i*) → (*e*); (*ii*) → (*d*); (*iii*) → (*a*); (*iv*) → (*b*); (*v*) → (*c*)

Explanation:

Column I	Column II
(*i*) Two solids which have different solubilities in a solvent and which do not undergo reaction when dissolved in it.	On dissolving in solvent, the solid which is insoluble is separated out by filtration and the soluble solid is separated by crystallisation.
(*ii*) Liquid that decomposes at its boiling point	Distillation under reduced pressure is done, because at low pressure vapours are formed below its boiling point and decomposition does not take place.
(*iii*) Steam volatile liquid	Liquid is converted into vapours by passing steam followed by condensation.
(*iv*) Two liquids which have boiling points close to each other	The vapours of such liquids are formed within the same temperature range and are condensed simultaneously. The technique of fractional distillation is used in such cases. In this technique, vapours of a liquid mixture are passed through a fractionating column before condensation. The fractionating column is fitted over the mouth of the round bottom flask.
(*v*) Two liquids with large difference in boiling points.	Liquids having different boiling points vaporise at different temperatures. The vapours are cooled and the liquids so formed are collected separately.

51. Match the terms mentioned in Column I with the terms in Column II.

Column I	Column II
(*i*) Carbocation	(*a*) Cyclohexane and 1- hexene
(*ii*) Nucleophile	(*b*) Conjugation of electrons of C–H σ bond with empty p-orbital present at adjacent positively charged carbon.
(*iii*) Hyperconjugation	(*c*) sp^2 hybridised carbon with empty *p*-orbital
(*iv*) Isomers	(*d*) Ethyne
(*v*) *sp* hybridisation	(*e*) Species that can receive a pair of electrons
(*vi*) Electrophile	(*f*) Species that can supply a pair of electrons

Ans. (*i*) → (*c*); (*ii*) → (*f*); (*iii*) → (*b*); (*iv*) → (*a*); (*v*) → (*d*); (*vi*) → (*e*)

Explanation:

Column I	Column II
(*i*) Carbocation	Carbocation is formed by the loss of one electron from '*p*'orbital. Therefore, Carbon is sp^2 hybridized.
(*ii*) Nucleophile	Nucleophiles are negatively charged or electron rich ready to donate electrons to electron deficient species.
(*iii*) Hyperconjugation	The σ electrons of C—H bond of the alkyl group enter into partial conjugation with the attached unsaturated system or with the unshared *p* orbital. Hyperconjugation is a permanent effect.
(*iv*) Isomers	Isomers have same molecular formula but different structure and different properties. C_6H_{12} molecular formula gives two structures, cyclohexane and *n*-hexene.
(*v*) *sp* hybridisation	In C_2H_2(ethyne), C is *sp* hybridized, because C has 2σ bond and 2π bonds.
(*vi*) Electrophile	Electron loving *i.e.*, +ve charge species or electron deficient species.

52. Match Column I with Column II.

Column I	Column II
(*i*) Dumas method	(*a*) $AgNO_3$
(*ii*) Kjeldahl's method	(*b*) Silica gel
(*iii*) Carius method	(*c*) Nitrogen gas
(*iv*) Chromatography	(*d*) Free radicals
(*v*) Homolysis	(*e*) Ammonium sulphate

Ans. (*i*) → (*c*); (*ii*) → (*e*); (*iii*) → (*a*); (*iv*) → (*b*); (*v*) → (*d*)

Explanation:

Column I	Column II
(*i*) Dumas method	Compounds containing N are estimated.
(*ii*) Kjeldahl's method	In Kjeldahl's method, N present in compound is converted into $(NH_4)_2SO_4$.
(*iii*) Carius method	In Carius method, halogens are estimated as a silver halide by using $AgNO_3$.

(*iv*) Chromatography	In chromatography, silica gel is used as a fixed phase and acts as an adsorbent.
(*v*) Homolysis	As a result of hemolytic fission of bond, shared pair of electrons equally distributed and free radicals are formed.

53. Match the intermediates given in Column I with their probable structure in Column II.

Column I	Column II
(*i*) Free radical	(*a*) Trigonal planar
(*ii*) Carbocation	(*b*) Pyramidal
(*iii*) Carbanion	(*c*) Linear

Ans. (*i*) → (*a*); (*ii*) → (*a*); (*iii*) → (*b*)

Explanation:

Column I	Column II
(*i*) Free radical	Free radical is formed as a result of hemolytic fission and C becomes sp^2 hybridized. Shape of free radical is trigonal planar.
(*ii*) Carbocation	In carbocation, positively charged C is sp^2 hybridized and shape is trigonal planar.
(*iii*) Carbanion	In carbanion, negatively charged C is sp^3 hybridized with lone pair and shape is pyramidal.

54. Match the ions given in Column I with their nature given in Column II.

Column I	Column II
(*i*) $CH_3—\ddot{O}—\overset{\oplus}{C}H—CH_3$	(*a*) Stable due to resonance
(*ii*) $F_3—C^{\oplus}$	(*b*) Destablished due to inductive effect
(*iii*) $CH_3—\underset{CH_3}{\overset{CH_3}{C}}\ominus$	(*c*) Stabilised by hyperconjugation
(*iv*) $CH_3—\overset{\oplus}{C}H—CH_3$	(*d*) A secondary carbocation

Ans. (*i*) → (*a*); (*ii*) → (*b*); (*iii*) → (*b*); (*iv*) → (*c, d*)

Explanation:

Column I	Column II
(*i*) $CH_3—\ddot{O}—\overset{\oplus}{C}H—CH_3$	Stabilize due to resonance. Stability is related to resonating structure.
(*ii*) $F_3—C^{\oplus}$	In $^+CF_3$, F atoms show –I effect and decreases electron density of C. Hence, instability increases and $^+CF_3$ is destabilized.

(*iii*) $CH_3-\overset{CH_3}{\underset{CH_3}{\overset{|}{\underset{|}{C}}}}\ominus$	In $(\overline{CH_3})\ \overline{C}^-$, CH_3 groups show +I effect and increases electron density of C and destabilized $(CH_3)\ C^-$.
(*iv*) $CH_3-\overset{\oplus}{C}H-CH_3$	Secondary carbocation is stabilized due to hyperconjugation and +I effect of $2CH_3$ groups.

V. Assertion and Reason Type

In the following questions a statement of Assertion (A) followed by a statement of Reason (R) is given. Choose the correct option out of the choices given below each question.

55. Assertion (A) : Simple distillation can help in separating a mixture of propan-1-ol (boiling point 97°C) and propanone (boiling point 56°C).

Reason (R) : Liquids with a difference of more than 20°C in their boiling points can be separated by simple distillation.

(*i*) Both A and R are correct and R is the correct explanation of A.
(*ii*) Both A and R are correct but R is not the correct explanation of A.
(*iii*) Both A and R are not correct.
(*iv*) A is not correct but R is correct.

Ans. (*i*)

Explanation: The liquids are having sufficient difference in their boiling points. Liquids having different boiling points vaporise at different temperatures. The vapours are cooled and the liquids so formed are collected separately.

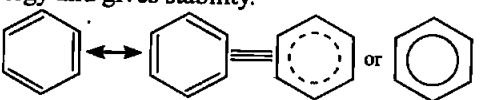
56. Assertion (A) : Energy of resonance hybrid is equal to the average of energies of all canonical forms.

Reason (R) : Resonance hybrid cannot be presented by a single structure.

(*i*) Both A and R are correct and R is the correct explanation of A.
(*ii*) Both A and R are correct but R is not the correct explanation of A.
(*iii*) Both A and R are not correct.
(*iv*) A is not correct but R is correct.

Ans. (*iv*)

Explanation: Canonical structures always have more energy than resonance hybrid. Resonance hybrids are always more stable than any of the canonical structures. The delocalization of electrons lowers the orbitals energy and gives stability.



(A) (B) (C)

Canonical Structures Resonance Hybrid

57. **Assertion (A) :** Pent-1-ene and pent-2-ene are position isomers.
Reason (R) : Position isomers differ in the position of functional group or a substituent.
(*i*) Both A and R are correct and R is the correct explanation of A.
(*ii*) Both A and R are correct but R is not the correct explanation of A.
(4) Both A and R are not correct.
(*iv*) A is not correct but R is correct.

Ans. (*i*)

Explanation: When two or more compounds differ in the position of substituent atom or functional group on the carbon skeleton, they are called position isomers and this phenomenon is termed as position isomerism. Pent-2-ene and pent-1-ene are position isomers because differ in the position of double bond.

58. **Assertion (A) :** All the carbon atoms in $H_2C=C=CH_2$ are sp^2 hybridised.
Reason (R) : In this molecule all the carbon atoms are attached to each other by double bonds.
(*i*) Both A and R are correct and R is the correct explanation of A.
(*ii*) Both A and R are correct but R is not the correct explanation of A.
(*iii*) Both A and R are not correct.
(*iv*) A is not correct but R is correct.

Ans. (*iv*)

Explanation: Hybridization of C can be find out by counting σ bonds and π bonds present on C atom.

$$\underset{1\pi}{CH_2}\overset{3\sigma}{=}\underset{2\pi}{C}\overset{2\sigma}{=}\underset{1\pi}{CH_2}\quad\overset{3\sigma}{}$$

If C has 3σ bonds, it is sp^2 hybridized. If C has 2σ bonds, it is *sp* hybridized.

59. **Assertion (A) :** Sulphur present in an organic compound can be estimated quantitatively by Carius method.
Reason (R) : Sulphur is separated easily from other atoms in the molecule and gets precipitated as light yellow solid.
(*i*) Both A and R are correct and R is the correct explanation of A.
(*ii*) Both A and R are correct but R is not the correct explanation of A.
(*iii*) Both A and R are not correct.
(*iv*) A is not correct but R is correct.

Ans. (*iii*)

Explanation: Sulphur is estimated by Carius method in the form of white precipitate of $BaSO_4$ on heating with fuming HNO_3 and $BaCl_2$. If light yellow solid is obtained means impurities are present. It is filtered washed and then dried to get pure $BaSO_4$.

60. **Assertion (A) :** Components of a mixture of red and blue inks can be separated by distributing the components between stationary and mobile phases in paper chromatography.

Reason (R) : The coloured components of inks migrate at different rates because paper selectively retains different components according to the difference in their partition between the two phases.

(*i*) Both A and R are correct and R is the correct explanation of A.

(*ii*) Both A and R are correct but R is not the correct explanation of A.

(*iii*) Both A and R are not correct.

(*iv*) A is not correct but R is correct.

Ans. (*i*)

Explanation: In paper chromatography, a special quality paper known as chromatography paper, is used. Chromatography paper contains water trapped in it, which acts as the stationary phase. A strip of chromatography paper spotted at the base with the solution of the mixture is suspended in a suitable solvent or a mixture of solvents. This solvent acts as the mobile phase. The solvent rises up the paper by capillary action and flows over the spot. The paper selectively retains different components according to their differing partition in the two phases. The paper strip so developed is known as a chromatogram. The spots of the separated coloured compounds are visible at different heights from the position of initial spot on the chromatogram.

VI. Long Answer Type

61. What is meant by hybridisation? Compound $CH_2 = C = CH_2$ contains *sp* or sp^2 hybridised carbon atoms. Will it be a planar molecule?

Ans. The atomic orbitals combine to form new set of equivalent orbitals known as hybrid orbitals. Unlike pure orbitals, the hybrid orbitals are used in bond formation. The phenomenon is known as hybridisation which can be defined as the process of intermixing of the orbitals of slightly different energies so as to redistribute their energies, resulting in the formation of new set of orbitals of equivalent energies and shape. In $CH_2{=}C{=}CH_2$(allene) carbon atom 1and 3 are sp^2 hybridized as each one has 3σ bonds while carbon atom 2 has 2σ bonds and it is *sp* hybridized. Allene molecule as a whole is non-planar.

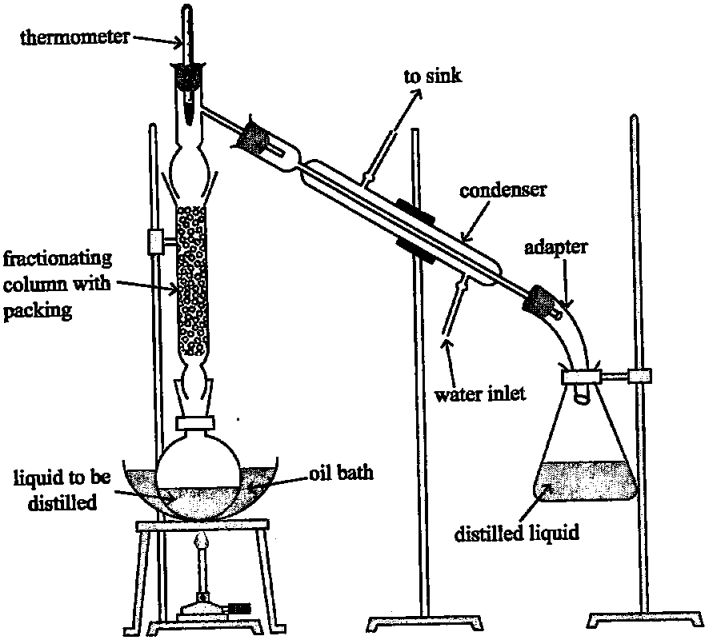
62. Benzoic acid is an organic compound. Its crude sample can be purified by crystallisation from hot water. What characteristic differences in the properties of benzoic acid and the impurity make this process of purification suitable?

Ans. Impurities present in benzoic acid are either insoluble in water or more soluble in water to such an extent that they remain in solution. Benzoic acid crystallizes from mother liquor.

63. Two liquids (A) and (B) can be separated by the method of fractional distillation. The boiling point of liquid (A) is less than boiling point of

liquid (B). Which of the liquids do you expect to come out first in the distillate? Explain.

Ans. If the difference in boiling points of two liquids is not much, simple distillation cannot be used to separate them. The vapours of such liquids are formed within the same temperature range and are condensed simultaneously. The technique of fractional distillation is used in such cases. In this technique, vapours of a liquid mixture are passed through a fractionating column before condensation. The fractionating column is fitted over the mouth of the round bottom flask. The liquid [A] with low boiling point will distill first.

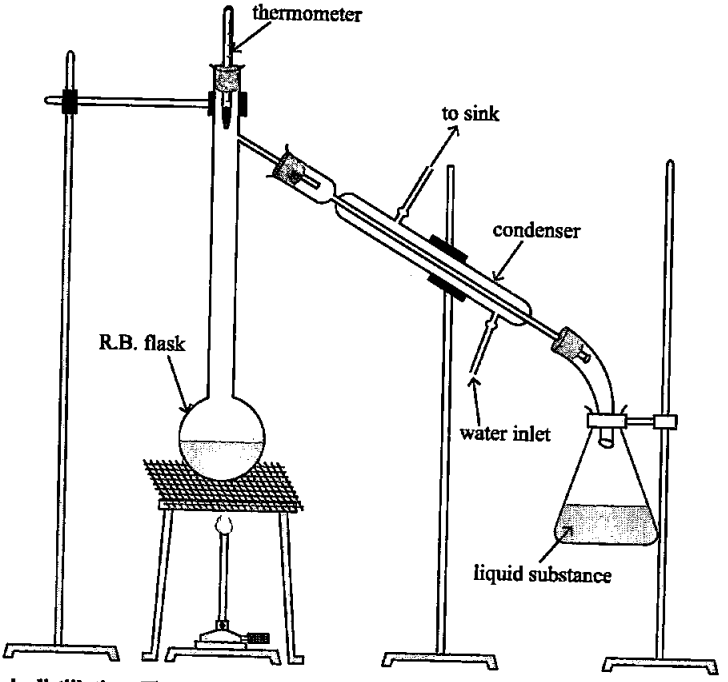


Fractional distillation: The vapours of lower boiling fraction reach the top of the column first followed by vapours of higher boiling fractions.

64. You have a mixture of three liquids A, B and C. There is a large difference in the boiling points of A and rest of the two liquids i.e., B and C. Boiling point of liquids B and C are quite close. Liquid A boils at a higher temperature than B and C and boiling point of B is lower than C. How will you separate the components of the mixture? Draw a diagram showing set up of the apparatus for the process.

Ans. Liquids having different boiling points vaporise at different temperatures. The vapours are cooled and then liquids so formed are collected separately. Liquid A can be separated from B and C because of large difference in boiling point. Liquid B and C have boiling points very close to each other and cannot be separated by simple distillation hence

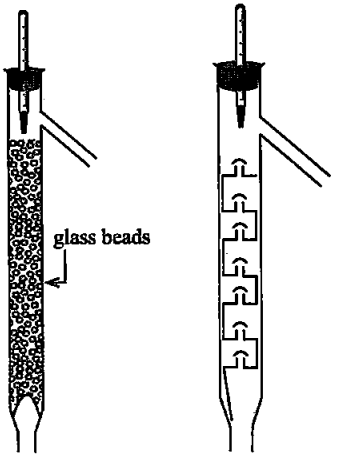
separated by fractional distillation. Liquid B distilled first because the order of boiling points of A, B and C are as follows: B < C < A.



Simple distillation: The vapours of a substance formed are condensed and the liquid is collected in conical flask.

65. Draw a diagram of bubble plate type fractionating column. When do we require such type of a column for separating two liquids? Explain the principle involved in the separation of components of a mixture of liquids by using fractionating column. What industrial applications does this process have?

Ans. If the difference in boiling points of two liquids is not much, simple distillation cannot be used to separate them. The vapours of such liquids are formed within the same temperature range and are condensed simultaneously. The technique of fractional distillation is used in such cases. In this technique, vapours of a liquid mixture are passed through a fractionating column before condensation. The fractionating column is fitted over the mouth of the round bottom flask. Vapours of the liquid with higher boiling point condense before the vapours of the liquid with lower boiling point. The vapours rising up in the fractionating column become richer in more volatile component. By the time the vapours reach to the top of the fractionating column, these are rich in more volatile component.



simple packed column bubble plate column

66. A liquid with high boiling point decomposes on simple distillation but it can be steam distilled for its purification. Explain how is it possible?

Ans. Steam distillation is a special type of separation process for temperature sensitive materials like natural organic compounds. Some organic compounds tend to decompose at higher temperature and normal distillation does not suit this purpose. So steam/water is added to the apparatus and the temperature of the compounds are depressed, evaporating them at lower temperature. Once the distillation is accomplish, the vapours are condensed and hence there is the separation of the constituents at ease.

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