

Chemistry Spectrum

JEE Final Touch

Fast Track Revision >>>

HALOALKANES AND
HALOARENES

ALCOHOL, PHENOLS
AND ETHERS

ALDEHYDES, KETONES
AND CARBOXYLIC ACIDS

ORGANIC COMPOUNDS
CONTAINING NITROGEN

BIOMOLECULES
POLYMERS

TEST Tuner

Test Series for JEE Main & Advanced

JEE MAIN Scale Up

JEE MAIN Scale Up

JEE ADVANCED Scale Up

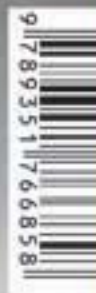
TEST Zoom

Test Series for Board Preparations

TARGET
JEE 2016

REGULARS
CONCEPT MAP
STRATEGIES
FOR YOU

From The Editor's Desk
Exam Tactics:
Tackling JEE
Made Easy

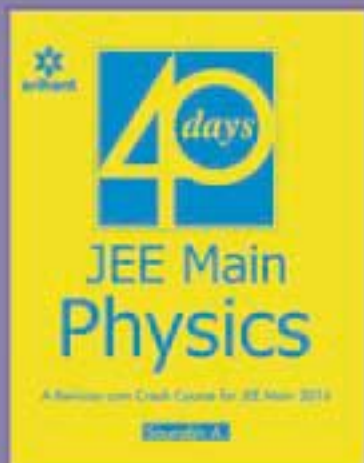


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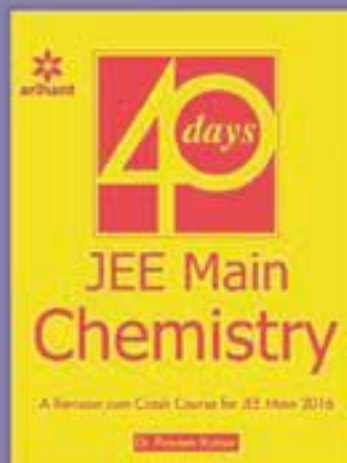
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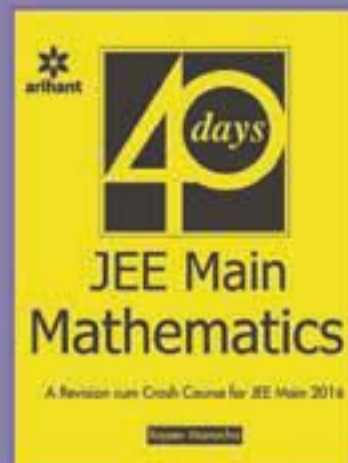
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CONTENTS



02 FROM THE EDITOR'S DESK EXAM TACTICS : TACKLING JEE MADE EASY

04	JEE FINAL TOUCH Fast Track Revision	80	TEST TUNER AIPMT Scale Up
34	TEST TUNER 1 JEE Main Scale Up	84	SPECTRUM FOR YOU
38	TEST TUNER 2 JEE Main Scale Up	86	DO YOU KNOW
43	TEST TUNER 3 JEE Advanced Scale Up	87	STRATEGIES FOR YOU
48	CONCEPT MAP	89	TEST ZOOM Board Exam Scale Up
50	JEE FINAL TOUCH Fast Track Revision	92	TEST ZOOM Board Exam Scale Up
		95	PARTICIPATE & WIN

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EXAM TACTICS: Tackling JEE Made Easy

The present structure of JEE includes a two tier examination system i.e. JEE Mains and JEE Advanced. Let us explore them one by one

JEE MAINS PAPER

In **Chemistry**, the emphasis in the question paper is on verbal (language) presentation of problems. A few numericals and diagrammatic problems are also asked. Some questions with good reasoning are also seen. The best part for this portion of paper is 90-95% questions are directly or indirectly from NCERT Textbook. Although, any fixed pattern is not visible in the question paper, but an approximate weightage of different segments is shown below :

General Chemistry	3-6 questions
Organic Chemistry	8-10 questions
Inorganic Chemistry	6-10 questions
Miscellaneous	2-5 questions

The analysis of 2015 JEE Mains paper suggests 33% questions from class 11th syllabus and 67% questions from class 12th syllabus. The difficulty level wise analysis of 2015 JEE Mains paper suggests the presence of 43% easy questions, 17% tough questions and 40% medium level questions.

MANTRAS TO CRACK JEE MAINS

The two tier examination pattern was introduced in 2013. The weightage of board percentage in final merit was one of the features of this system. The JEE Mains paper of this examination system is comparable with the IIT JEE screening examination of late nineties and early twenties.

For successfully facing this kind of examination try to focus on following points:

- One must prepare for final exam (JEE Advanced) only, i.e. do not target Mains examinations first. In my opinion “**Chote exams target karne se kabhi bhi bade results nahin milte**”, i.e. targeting smaller exams never gives big results. If you consider JEE Advanced as your target then Mains will be cleared automatically. In my opinion Mains is only a screening to differentiate between serious and non-serious aspirants. Thus, if you are among the serious lot than Mains will be of no problem to you.

- The analysis of 2013, 2014 and 2015 JEE Mains paper clearly suggests the importance of class 11th syllabus for this paper, i.e. 46% in Physics, 33% in Chemistry and 57% in Mathematics. So, a real grip over class 11th syllabus is required to succeed in JEE Mains paper.
- Nobody can deny the importance of NCERT Textbooks for this examination. Thus, a good command over NCERT text books is required for a great performance in this examination.
- For capturing NCERT line by line very recently, I saw Master the NCERT. A book, in which objective type questions are framed on each and every line of NCERT. This book can be very helpful to get success in this examination.
- Choose offline or online paper in accordance of your comfort zone and fine preparation. Both the examinations have the own advantages or disadvantages. The difficulty levels are also more or less same in both the formats of JEE Mains but on analysis it is quite visible that the online paper is framed on a slightly tougher side.
- Although, the questions paper contains all the three subjects and merit formation includes total marks obtained in the paper but remember subject wise cut off also exists in JEE. So, a balance in preparation is required subject wise to save you from such a subject wise cut off.
As all the questions are single answer type MCQs hence, use elimination technique in those questions where you don't have clue about the correct option, rather you have clue about incorrect options. Eliminate 3 incorrect options to get the most probable correct option.
- As negative marking is there, hence be cautious in answering the questions. Do not take so much of risks.

JEE ADVANCED PAPER

The JEE Advanced paper is based upon old IIT JEE paper till 2013. It has 2 papers in total, i.e. first in the morning session (9 am to 12 pm) and second in the afternoon session (2 pm-5 pm). Both the papers contain 20 questions per subject, i.e. total 60 questions per paper. The question paper pattern is not at all fixed.

In 2015 Advanced paper following pattern was followed:

PAPER 1

- Section 1 with 8 Integer Type Questions
- Section 2 with 10 MCQs having One or More than One Correct Option
- Section 3 with 2 Matrix Match Questions.

PAPER 2

- Section 1 with 8 Integer Type Questions
- Section 2 with 8 MCQs having One or More than One Correct Option
- Section 3 with 2 Paragraphs having 2 questions each.

In both the papers, section 2 and 3 had a negative marking of 50%.

However, in 2014 JEE Advanced questions paper following pattern was followed :

PAPER 1

- 10 Multiple Choice Questions which are one or more than one answer correct.
- 10 Integer Type Questions. All the 20 questions with 3 marks each with no negative marking.

PAPER 2

- 10 Multiple Choice Questions with only one answer correct.
- 3 paragraphs with 2 question each having only one answer correct.
- A matching type MCQs with one answer correct.
- All the questions with 3 marks each and there is the negative marking of 1/3, i.e. + 3 for correct answer and – 1 for wrong answer.

Thus, the uniqueness of JEE Advanced paper lies in 2 facts i.e.

Its surprising element Every year JEE Advanced paper incorporates one or more surprise elements e.g. in 2014, negative marking in paper 2 was the surprised element. Similarly, the frame of question paper was changed in 2013 as compared to the one seen in 2012 IIT-JEE paper.

Its variety of questions In both 2015 and 2014 JEE Advanced paper following type of questions were asked

- Single answer correct (MCQs)
- More than one answer correct (MCQs)
- Integer type question
- Linked comprehension type
- Matching type

The matrix match type which was the usual component of IIT JEE papers before 2013, become reintroduced in 2015. Likewise comprehension linked questions were 2 per passage in 2015 and 2014, while it was 3 per passage in IIT JEE before 2013.

So, we can say the nature of JEE Advanced paper is very dynamic. No pattern is fixed for the paper. The syllabus wise distribution of marks is more or less same as that seen in JEE Mains paper.

MANTRAS TO CRACK JEE ADVANCED

I personally feel that JEE Advanced is one of the toughest exam, among those of same nature we have worldwide. I also believe in the fact that *more organised examinations are always easier to crack*. So, although it is toughest pattern or frame wise, but if we planned scientifically than we can hit the bull's eye.

For scientific planning following points must be kept in mind:

- Phase wise learning and practice is a must to crack these kinds of examinations. After having the analysis of previous year exams some conclusions can be drawn easily like, those about?
 - (i) the weightage of class 11th syllabus.
 - (ii) the difficulty level distribution among the questions of previous year papers.
 - (iii) the topic wise, question wise distribution of questions
 - (iv) the topic wise, marks wise distribution

Such conclusions will help in strategy development according to your strength and weaknesses.

- If you will be approaching phase wise towards this examination, then it is very clear that till Mains you would be having very less opportunities to practice different question types which are the features of JEE Advanced only. Utilise the period between JEE Mains and JEE Advanced for this purpose. *A mass of students waste their some of this precious time in the wait of Mains result.* Don't ever commit this kind of mistake. Be optimistic, if you have JEE advanced as the target from day 1 in your mind than, you would clear JEE Mains with surety.
- The surprise attack is one of the most lethal weapon of this examination, hence, those aspirants who don't have any kind of premature frame about the pattern of question paper in their mind, has better chances of hitting the target. So, never create the premature frame of question paper in your mind.
- The large time span (9 am to 5 pm) is a very crucial factor in this examination. Such a large time span creates tiredness of all kind (i.e. physical as well as mental) in any person. So during the gap of 2 hrs between Paper 1 and 2 try to relax as much as you can. *Remember! The more you relax, better you perform.*

Last but not the least, a balance between the approaches towards Subjective and Objective formats is required to succeed in IIT as a whole as in present format the final merit also includes the weightage of your Board examinations.

Always keep in mind the words of Sir Winston Churchill

***“The pessimist sees difficulty in every opportunity.
The optimist sees opportunity in every difficulty.”***



JEE Final Touch

Fast Track Revision

Alcohols, Phenols and Ethers

ALCOHOLS

These are hydroxy derivatives of aliphatic hydrocarbons and can be monohydric, dihydric or polyhydric based on the number of —OH groups.

Monohydric Alcohols

These are monohydroxy derivatives of hydrocarbons with general formula $C_nH_{2n+2}O$.

These are prepared through the following methods:

Method	Reaction Involved
1. Hydrolysis of alkyl halides	$RX + aq.KOH \longrightarrow ROH + KX$
2. Hydration of alkenes	$(CH_3)_2C=CH_2 + H_2O \longrightarrow (CH_3)_3C-OH$
3. Hydrolysis of esters	$RCOOR' + H_2O \xrightleftharpoons[H^+]{OH^-} RCOOH + R'OH \quad (\text{Reversible in acidic medium})$ $RCOOR' + H_2O \xrightarrow[OH^-]{OH^-} RCOO^- + R'OH + H_2O \quad (\text{Irreversible in alkaline medium})$
4. Hydrolysis of ethers	$ROR \xrightarrow[\text{Under pressure}]{dil. H_2SO_4 / \Delta} 2ROH$
5. Fermentation	$C_{12}H_{22}O_{11} + H_2O \xrightarrow[\text{Glucose}]{\text{Maltase}} 2C_6H_{12}O_6 \xrightarrow{\text{Zymase}} 2C_2H_5OH + CO_2$
6. Oxymercuration -demercuration	$(CH_3)_2C=CH_2 \xrightarrow[(ii) NaBH_4]{(i) Hg(OAc)_2 / H_2O} (CH_3)_3C-OH$
7. From alkynes	$HC \equiv CH \xrightarrow[Hg^{2+}, H^+]{H_2O} CH_3CHO \xrightarrow{LiAlH_4} CH_3CH_2OH$
8. Hydroboration oxidation	$3R-CH=CH_2 + BH_3 \xrightarrow[DIGLYME]{THF \text{ or}} (RCH_2CH_2)_3B \xrightarrow{H_2O_2} 3RCH_2CH_2OH$

Method	Reaction Involved
9. Reduction of aldehydes, ketones, acids and acid derivatives	<p>LiAlH₄ or H₂/Ni, Pt, Pd, 250°C reduces</p> <p>NaBH₄ reduces</p> $\begin{array}{c} \begin{array}{c} \text{—CHO, —COCl, } >C=O, \text{ —COOH, —(CO)}_2O, \text{ —CO}_2R \\ \downarrow \text{to} \\ \text{—CH}_2OH \end{array} \end{array}$
10. From Grignard's reagent	$RMgX + >C=O \longrightarrow \begin{array}{c} R \\ \\ >C-O^-Mg^+X \end{array} \xrightarrow{H_2O} \begin{array}{c} R \\ \\ >C-OH \end{array}$ $RMgX + \begin{array}{c} \text{—O—} \\ \\ \text{—CH}_2\text{—CH}_2\text{—} \end{array} \longrightarrow \begin{array}{c} RCH_2CH_2O^-Mg^+X \end{array} \xrightarrow{H_2O} RCH_2CH_2OH$
11. Oxo process	$CH_2=CH_2 + CO + H_2 \xrightarrow[\text{High } T \text{ and } p]{Co(CO)_4} CH_3CH_2CHO \xrightarrow{H_2/Ni} CH_3CH_2CH_2OH$
12. Action of nitrous acid	$R-NH_2 + HNO_2 \longrightarrow ROH + N_2 \uparrow + H_2O \quad (1^\circ, 2^\circ \text{ or } 3^\circ)$

Toxicity of Methanol

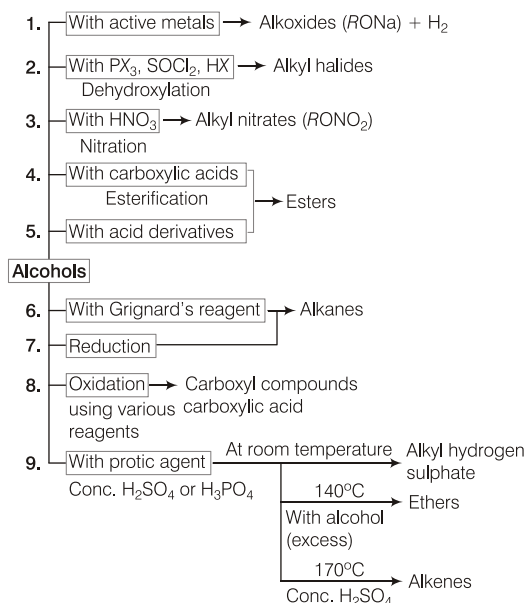
Methanol is highly toxic in nature. Ingestion of even small quantities of it can cause severe diseases like blindness and large quantities cause death. Methanol poisoning can also occur by inhalation of vapours or by prolonged exposure to skin.

{JEE FINAL TOUCH}**Reduction of different functional groups with different reagents**

Group	Product	LiAlH ₄ in ether	NaBH ₄ in EtOH	NaBH ₄ + AlCl ₃ in diglyme	B ₂ H ₆ in THF	H ₂ + catalyst
—CHO	—CH ₂ OH	+	+	+	+	+
>CO	>CHOH	+	+	+	+	+
—CO ₂ H	—CH ₂ OH	+	—	+	+	+ ¹
—CO ₂ R	—CH ₂ OH	+	— ²	—	+	+
—COCl	—CH ₂ OH	+	+	+	—	+ ³
—CONH ₂	—CH ₂ NH ₂	+	—	+	+	+
(RCO) ₂ O	RCH ₂ OH	+	—	+	+	+
Lactone	Diol	+	—	+	+	+
Epoxide	Alcohol	+	—	+	+	+
—CN	—CH ₂ NH ₂	+ ⁵	—	+	+	+
C=NOH	—CH ₂ NH ₂	+	—	—	—	+
RNO ₂	RNH ₂	+	—	—	—	+
ArNO ₂	ArN=NAr	+	—	—	—	+ ⁶
Azoxy	Azo	+	—	—	—	+ ⁶
Alkene	>CH—CH<	—	—	+	+	—
Alkyne	—CH=CH—	— ⁷	—	—	+	+
RX	RH	+	+	—	—	+
ArX	ArH	—	—	—	—	+

1. Only Ru-C and Cu-Br-Cr oxide. 2. Often reduces if use excess of NaBH₄ in MeOH. 3. Give aldehyde at -78°C and with Pd-BaSO₄ - S - quinoline. 4. Reverse addition gives aldehyde. 5. Also to amine. 6. LiAlH₄-AlCl₃ reduces RC≡CH (and ArC≡CH).

- Alcohols show the following chemical reactions:

**Physical and Chemical Properties**

Lower members are colourless toxic liquids, whereas the higher members are waxy solids.

- The boiling point of alcohol is always higher than the corresponding ether, hydrocarbon and haloalkane due to the presence of hydrogen bonding.
- Boiling point ∝ number of —CH₂ groups ∝ $\frac{1}{\text{branching}}$

REMEMBER

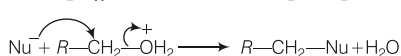
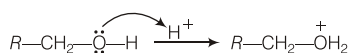
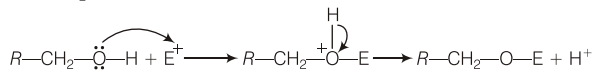
- The chemical properties of alcohols are attributed to the

polar —C—OH bond. Their reactivity is different in

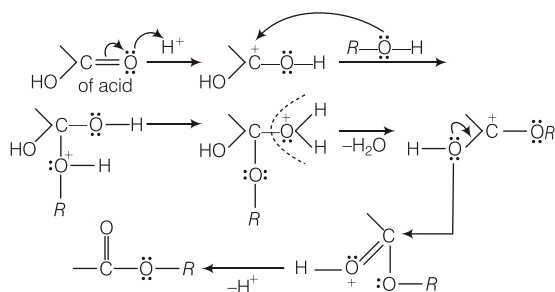
different reactions, e.g.

- The reaction in which O—H bond cleaves, the reactivity order of alcohols is 1° > 2° > 3°.
- The reaction in which C—O bond cleaves, the reactivity order of alcohols is 3° > 2° > 1°.

- Alcohols act as both electrophile (C—O bond breaks) and nucleophile (O—H bond breaks) as shown below:



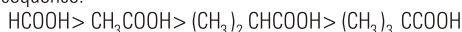
The mechanism of the above reaction can be given as



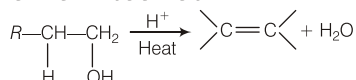
REMEMBER

The same procedure can be applied to acid derivatives also but not named as esterification.

It may be noted that as the size of the group R increases, the rate of esterification reaction decreases due to steric hindrance. Thus, the order of reactivity of alcohols follows the sequence $CH_3OH > CH_3CH_2OH > (CH_3)_2CHOH > (CH_3)_3COH$ and that of the acids follows the sequence:

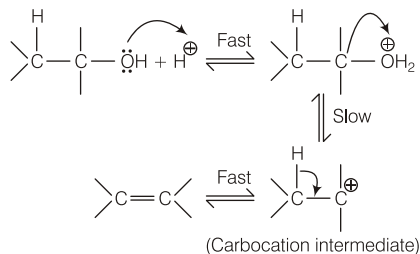


Dehydration of Alcohol

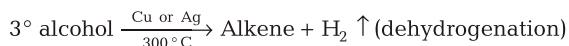
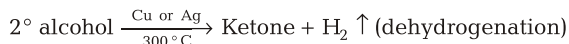
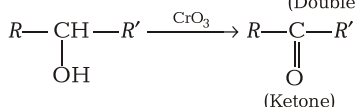
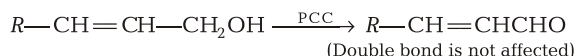
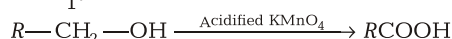
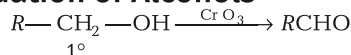


The ease of dehydration of alcohols is $3^\circ > 2^\circ > 1^\circ$ alcohol.

Mechanism (E_1)



Oxidation of Alcohols



Test for 1° , 2° and 3° Alcohols

The following tests are carried out to detect the presence of 1° , 2° and 3° alcohols:

Name of the test and procedure	1° alcohol	2° alcohol	3° alcohol
Victor Meyer's Test The alcohol is treated with P/I ₂ and then with AgNO ₂ and HNO ₂ . The final product obtained is treated with NaOH and the colour is observed.	Blood red colour	Blue colour	No colour
Lucas Test Alcohol is treated with Lucas reagent (equimolar mixture of anhyd. ZnCl ₂ and conc. HCl).	Do not produce turbidity at room temperature	Produce turbidity after 5 min	Produce turbidity immediately
Dehydrogenation Cu or Ag are used for dehydrogenation.	Produce aldehyde	Produce ketone	Dehydrated to give alkene

Dihydric Alcohols

These alcohols contain two—OH groups. Ethylene glycol is the simplest dihydric alcohol. It is a colourless viscous and toxic solid with boiling point $197^\circ C$ and melting point $13^\circ C$.

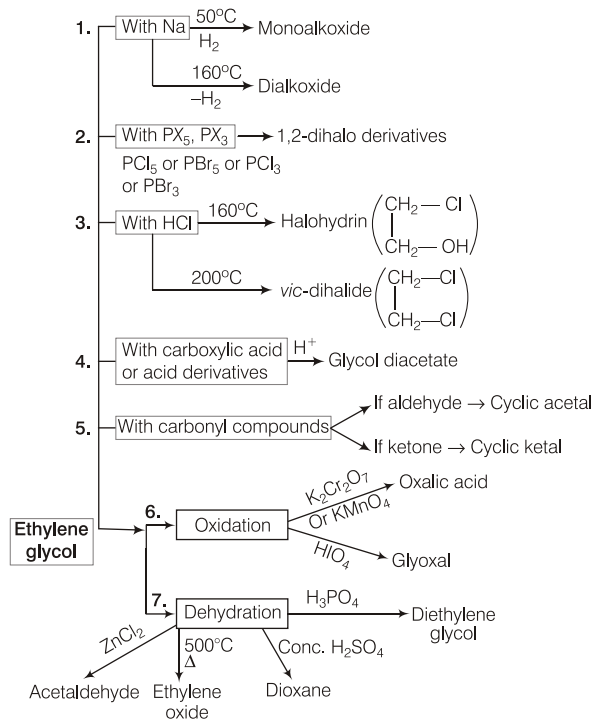
Ethylene glycol is prepared through the following reactions:

S. No.	Method	Reaction Involved
1.	Oxidation of ethylene	$CH_2=CH_2 + \underbrace{KMnO_4 + KOH}_{1\% \text{ alkaline solution}} \rightarrow \begin{array}{c} \\ CH_2OH \\ \\ CH_2OH \end{array}$ (HCOOH is also used for the similar purpose)
2.	Hydrolysis of 1, 2-dibromo ethane	$\begin{array}{c} \\ CH_2-Br \\ \\ CH_2-Br \end{array} + Na_2CO_3 + H_2O \rightarrow \begin{array}{c} \\ CH_2-OH \\ \\ CH_2-OH \end{array} + 2NaBr + CO_2$
3.	Hydrolysis of ethylene halohydrin	$\begin{array}{c} \\ CH_2-OH \\ \\ CH_2-X \end{array} + NaHCO_3 \rightarrow \begin{array}{c} \\ CH_2OH \\ \\ CH_2OH \end{array} + NaX + CO_2 + H_2O$
4.	Hydrolysis of ethylene oxide	$\begin{array}{c} CH_2 \\ \\ CH_2 \end{array} O \xrightarrow[\text{(under pressure)}]{H_2O/H^+, 200^\circ C} \begin{array}{c} \\ CH_2-OH \\ \\ CH_2-OH \end{array}$ Nucleophilic addition
5.	Ethylene diamine deamination	$\begin{array}{c} \\ CH_2-NH_2 \\ \\ CH_2-NH_2 \end{array} + 2HONO \rightarrow \begin{array}{c} \\ CH_2OH \\ \\ CH_2OH \end{array} + 2N_2 + H_2O$
6.	Reductive ozonolysis of ethyne	$\begin{array}{c} CH \\ \\ CH \end{array} \xrightarrow[(ii) H_2O/Zn]{(i) O_3} \begin{array}{c} CHO \\ \\ CHO \end{array} \xrightarrow{LiAlH_4} \begin{array}{c} \\ CH_2OH \\ \\ CH_2OH \end{array}$

{JEE FINAL TOUCH}

Chemical Properties

Ethylene glycol gives the following chemical reactions:



Ethylene Oxide :

A fumigant in Foodstuffs and Textiles

Ethylene oxide is a highly strained molecule (as normal tetrahedral bond angles ($109^\circ 28'$) of both C and O are compressed to approximately 60° in this molecule. It reacts with amino ($-\text{NH}_2$) and sulfhydryl ($-\text{SH}$) groups present in biological materials.

At sufficiently high concentrations, it reacts with enough molecules in cells to cause the death of microorganisms. Because of this property, it is used as a fumigant in foodstuffs and textiles and also to sterilise surgical instruments.

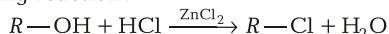
CHEMISTRY IN action

A New form of Frozen Water : The 18th in a Row

A research team has predicted a new molecular form of ice with a record-low density. If this ice can be synthesized, it would become the 18th known crystalline form of water and the first discovered in the US since before World War II. The proposed ice would be about 25 percent less dense than a record-low form synthesized by a European team in 2014. Scientists used a computational algorithm and molecular simulation to determine the ranges of extreme pressure and temperature under which water would freeze into the predicted configuration. That configuration takes the form of a clathrate, essentially a series of water molecules that form an interlocking cage-like structure.

Best Practice SHOTS

1. What is the correct order of reactivity of alcohols in the following reaction?



(a) $1^\circ > 2^\circ > 3^\circ$ (b) $1^\circ < 2^\circ > 3^\circ$ (c) $3^\circ > 2^\circ > 1^\circ$ (d) $3^\circ > 1^\circ > 2^\circ$

2. Which among the following compounds will give a secondary alcohol on reacting with Grignard reagent followed by acid hydrolysis?

- I. HCHO II. $\text{C}_2\text{H}_5\text{CHO}$
III. CH_3COCH_3 IV. HCOOC_2H_5

Select the correct answer.

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

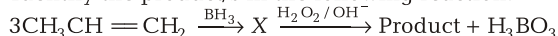
3. The mechanism of the reaction (acid catalysed hydration of alkene) involves the following three steps:

- Nucleophilic attack of water on carbocation.
- Protonation of an alkene to form carbocation by the electrophilic attack of H_3O^+ .
- Deprotonation to form an alcohol.

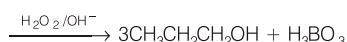
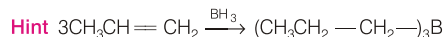
Identify the sequence for the mechanism of reaction in the acid catalysed hydration of alkenes.

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

4. Identify the product/s in the following reaction.



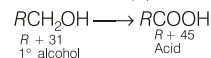
- (a) $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$ (b) $\text{CH}_3\text{CH}(\text{OH})\text{CH}_3$
(c) $\text{CH}_3\text{CH}_2\text{CHO}$ (d) $\text{CH}_3\text{CH}_2\text{OH} + \text{CH}_3\text{OH}$



5. An oxygen containing organic compound upon oxidation forms a carboxylic acid as the only organic product with its molecular mass higher by 14 units. The organic compound is

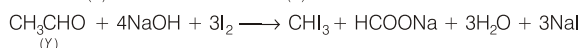
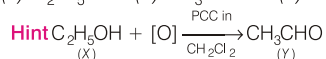
- (a) an aldehyde (b) a primary alcohol
(c) a secondary alcohol (d) a ketone

Hint

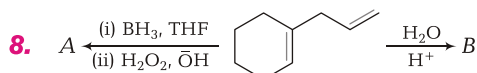
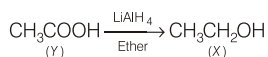
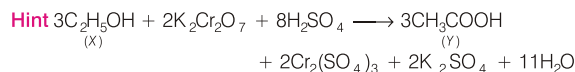


6. An organic compound X on treatment with pyridinium chloro chromate in dichloromethane gives compound Y. Compound Y reacts with I_2 and alkali to form triiodomethane. The compound X is

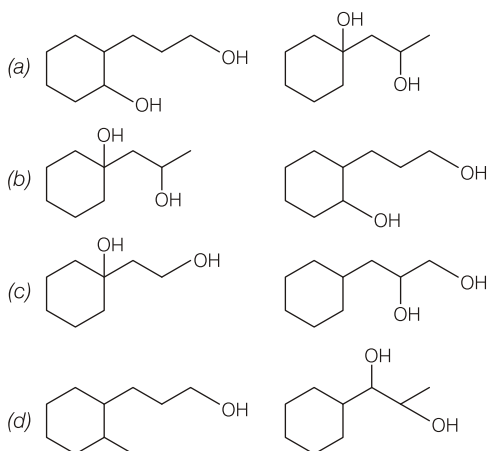
- (a) $\text{C}_2\text{H}_5\text{OH}$ (b) CH_3CHO (c) CH_3COCH_3 (d) CH_3COOH



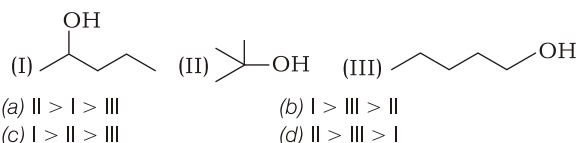
7. When compound X is oxidised by acidified potassium dichromate, compound Y is formed. Compound Y on reduction with LiAlH_4 gives X. X and Y respectively are
- $\text{C}_2\text{H}_5\text{OH}$, CH_3COOH
 - CH_3COCH_3 , CH_3COOH
 - $\text{C}_2\text{H}_5\text{OH}$, CH_3COCH_3
 - CH_3CHO , CH_3COCH_3



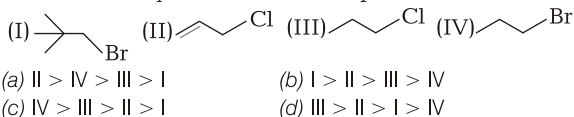
A and B are



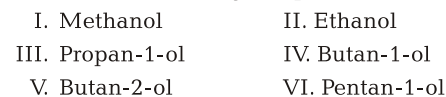
9. Arrange the following in decreasing order of their reaction with Lucas reagent.



10. Which of the following decreasing orders is correct for Williamson's synthesis of the compounds?



11. Consider the following compounds.



Arrange the given compounds in decreasing order of their boiling points and solubilities in H_2O .

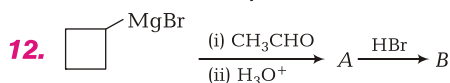
Choose the correct option given below.

Boiling point order

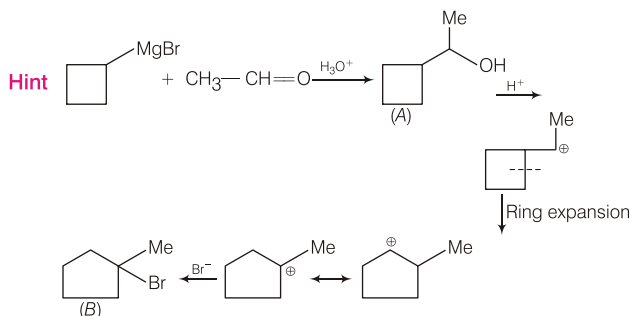
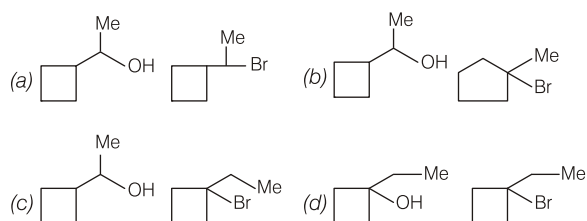
Solubility order

- $\text{VI} > \text{IV} > \text{V} > \text{III} > \text{II} > \text{I}$ $\text{I} > \text{II} > \text{III} > \text{V} > \text{IV} > \text{VI}$
- $\text{VI} > \text{IV} > \text{V} > \text{II} > \text{III} > \text{I}$ $\text{I} > \text{II} > \text{III} > \text{V} > \text{IV} > \text{VI}$
- $\text{VI} > \text{IV} > \text{V} > \text{III} > \text{II} > \text{I}$ $\text{I} > \text{II} > \text{III} > \text{V} > \text{VI} > \text{IV}$
- $\text{I} > \text{II} > \text{III} > \text{IV} > \text{V} > \text{VI}$ $\text{VI} > \text{IV} > \text{V} > \text{III} > \text{II} > \text{I}$

Hint All of them are alcohols. So, all have H-bonding. As the molecular mass and surface area increase, the boiling point increases and solubility decreases.



The compounds A and B, respectively are

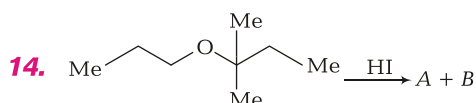


13. Which of the following statements is correct?

- Glycerol on reaction with oxalic acid at 110°C and followed by heating and hydrolysis gives formic acid and glycerol.
- Glycerol on reaction with oxalic acid at 230°C and followed by heating gives allyl alcohol.
- Glycerol on oxidation with dil. HNO_3 gives a mixture of glyceric and tartaric acid.
- Glycerol on oxidation with conc. HNO_3 gives glyceric acid.

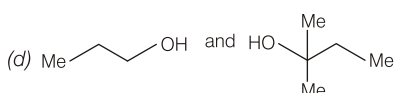
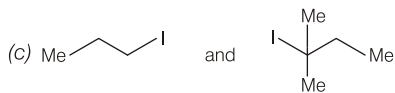
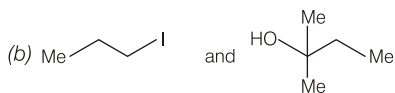
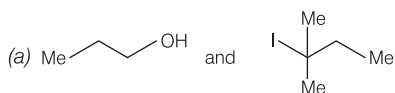
Choose the correct option.

- Both I and II
- Both I and III
- Both III and IV
- All of these

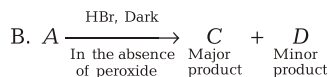
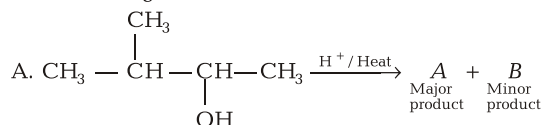


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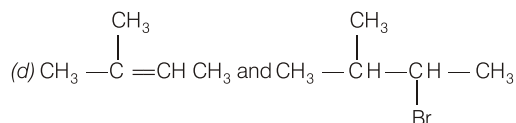
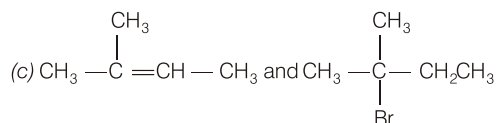
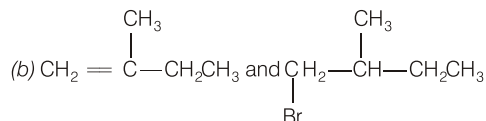
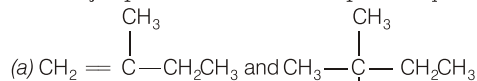
The products A and B respectively are



15. In the following reactions,



The major products A and C respectively are



PHENOLS

These are colourless liquids or solids and are highly toxic in nature.

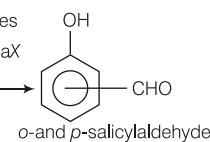
- Their boiling points are higher than alcohols due to the strong intermolecular hydrogen bonding and hence are more miscible with water.
- They have high dipole moment and are more acidic than the corresponding alcohol due to the conjugation between lone pair of oxygen and benzene.
- Phenols are prepared through the following reactions:

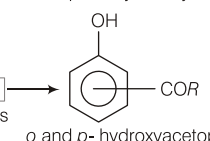
S. No.	Method	Reaction Involved
1.	Dow process (by hydrolysis)	$\text{PhX} \xrightarrow[\text{150 atm}]{\text{aq. NaOH, 340}^\circ\text{C}} \text{PhONa} + \xrightarrow{\text{H}_2\text{O}/\text{H}^+} \text{PhOH}$
2.	Cumene process	$\text{PhCH}(\text{CH}_3)_2 \xrightarrow[\text{H}_2\text{O}/\text{H}^+]{\text{O}_2 \text{ catalyst}} \text{PhOH} + \text{CH}_3\text{COCH}_3$
3.	From diazonium salts	$\text{PhN}^+ \equiv \text{NX}^- \xrightarrow{\text{H}_2\text{O}/\text{H}^+} \text{PhOH} + \text{N}_2 \uparrow + \text{HX}$
4.	Fusion of alkali metal salt of sulphonic acid	$\text{PhSO}_3^-\text{Na}^+ + \text{NaOH} \xrightarrow{\text{Fuse}} \text{PhO}^-\text{Na}^+ \xrightarrow{\text{H}_2\text{O}/\text{H}^+} \text{PhOH}$
5.	From Grignard's reagent	$\text{PhMgBr} \xrightarrow{[\text{O}]} \text{PhOMgBr} \xrightarrow{\text{H}_2\text{O}/\text{H}^+} \text{PhOH}$

S. No.	Method	Reaction Involved
6.	From salt of salicylic acid	$\text{C}_6\text{H}_4(\text{OH})(\text{COO}^-\text{Na}^+) \xrightarrow{\text{NaOH}/\text{CaO}} \text{C}_6\text{H}_5\text{OH} + \text{Na}_2\text{CO}_3$
7.	Hydroxylation of benzene	$\text{C}_6\text{H}_6 + \text{H}_2\text{O}_2 \xrightarrow{\text{HSO}_3\text{F}} \text{PhOH}$
8.	By oxidation of benzene and toluene	$2\text{C}_6\text{H}_6 + \text{O}_2 \xrightarrow[\text{315}^\circ\text{C}]{\text{V}_2\text{O}_5} 2\text{PhOH}$ $\text{C}_6\text{H}_5\text{CH}_3 \xrightarrow[\text{Manganous and cupric salts as catalyst}]{\text{2O}_2 \text{ (air)}} \text{C}_6\text{H}_5\text{OH} + \text{CO}_2 + \text{H}_2\text{O}$
9.	Middle oil fraction of coal tar	<div style="display: flex; align-items: center;"> <div style="border: 1px solid black; padding: 5px; margin-right: 5px;">Middle oil fraction</div> <div style="margin-right: 5px;">Washed H₂SO₄</div> <div style="border: 1px solid black; padding: 5px; margin-right: 5px;">Basic impurities (like pyridine)</div> <div style="margin-right: 5px;">Excessive cooling</div> <div style="border: 1px solid black; padding: 5px; margin-right: 5px;">Naphthalene</div> </div> <div style="margin-left: 100px;"> $\downarrow \text{aq. NaOH, CO}_2, \text{H}_2\text{O}$ </div> <div style="display: flex; align-items: center; margin-top: 10px;"> <div style="margin-right: 10px;">Phenols ← 180°C</div> <div style="margin-right: 10px;">Cresols ← 190-205°C</div> <div style="margin-right: 10px;">Xylois ← 211-235°C</div> <div style="border: 1px solid black; padding: 5px; margin-right: 5px;">Fractional distillation</div> <div style="border: 1px solid black; padding: 5px;">Phenols + Na₂CO₃ (Crude)</div> </div>

Chemical Properties

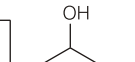

Phenol gives the following chemical reactions:

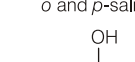
- Esterification** Esters with acid or acid derivatives
- Ether formation** $\text{ArOR} + \text{NaX}$
- Gattermann synthesis** $\text{HCN/HCl, AlCl}_3, 40^\circ\text{C}$


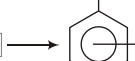
o- and *p*-salicylaldehyde
- Houben-Hoesch reaction** $\text{RCN/HCl, AlCl}_3, \text{hydrolysis}$


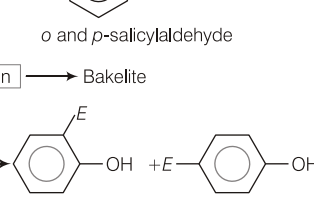
o and *p*-hydroxyacetophenone

Phenol

- Kolbe's reaction** $\text{CO}_2, 140\text{-}200^\circ\text{C}$

- Kolbe-Schmidt reaction** $\text{CO}_2, 5\text{-}7 \text{ atm pressure, } 120\text{-}140^\circ\text{C}$


o and *p*-salicylate ion
- Reimer-Tiemann reaction** $\text{Alkali} + \text{CHCl}_3$


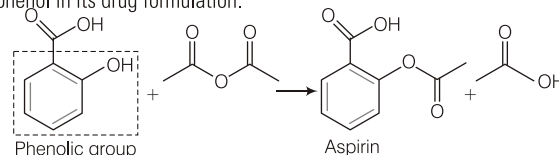
o and *p*-salicylaldehyde
- Lederer-Manasse reaction** HCHO/acid or base


Bakelite
- Electrophilic substitution reactions**


$(E^+ = \text{Electrophile})$

Application of Phenol as a Precursor

Several commercial compounds are synthesised from a precursor containing phenol. For example, aspirin, a well known drug, contains phenol in its drug formulation.



As we can see that phenol is a precursor for making aspirin. The other uses of phenol include the production of plywood, ear and nose drops and disinfectants.

CHEMISTRY IN action

Molecular shielding: A new Perspective

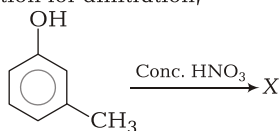
A new study sheds light on unique property of 2-D materials -- ability to shield chemical interactions at the molecular level. Discovery of shielding effect allows scientists to control reactivity of molecules, tune activity of catalysts, and construct new generation of carbon materials as shown in figure.



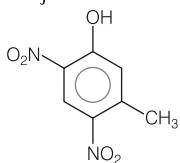
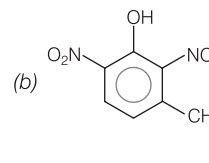
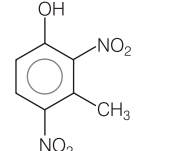
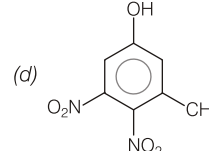
Joint theoretical and experimental study suggested that graphene sheets efficiently shield chemical interactions. One of the promising applications of this phenomenon is associated with improving quality of 2D materials by "de-charging" of charged defect centers on the surface of carbon materials.

Best Practice SHOTS

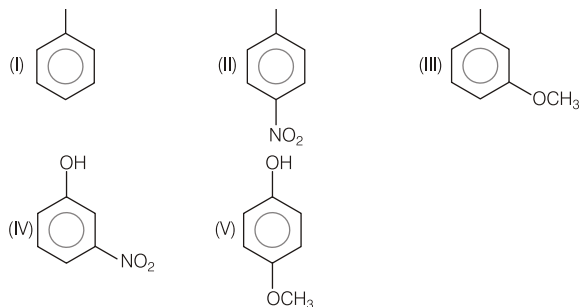
16. In the reaction for dinitration,



The major dinitrated product X is

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

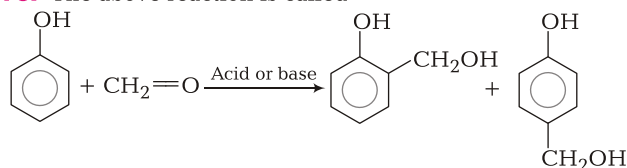
17. Mark the correct order of decreasing acidic strength of the following compounds.



- (a) $\text{V} > \text{IV} > \text{II} > \text{I} > \text{III}$
 (b) $\text{II} > \text{IV} > \text{III} > \text{I} > \text{V}$
 (c) $\text{IV} > \text{III} > \text{II} > \text{I} > \text{V}$
 (d) $\text{I} > \text{II} > \text{III} > \text{IV} > \text{V}$

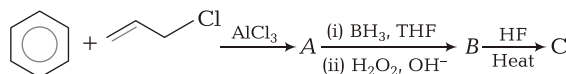
{ JEE FINAL TOUCH }

18. The above reaction is called



- (a) Lederer-Manasse reaction (b) Claisen condensation
(c) Benzoin condensation (d) Etard reaction

19. In the following reaction, identify compounds A, B and C.

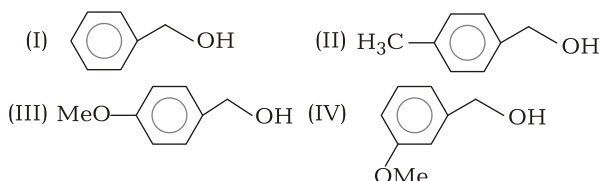


- (a)
- (b)
- (c)
- (d)

20. The reaction of $\text{CH}_3\text{—CH=CH—}$ (with a para-hydroxyphenyl group) with HBr gives

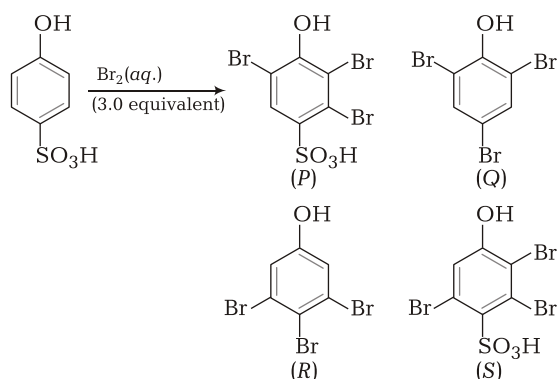
- (a) $\text{CH}_3\text{—CH(Br)—CH}_2\text{—}$ (with a para-hydroxyphenyl group)
- (b) $\text{CH}_3\text{—CH(Br)—CH}_2\text{—}$ (with a para-bromophenyl group)
- (c) $\text{CH}_3\text{—CH}_2\text{—CH(Br)—}$ (with a para-hydroxyphenyl group)
- (d) $\text{CH}_3\text{—CH}_2\text{—CH(Br)—}$ (with a para-bromophenyl group)

21. Identify the correct decreasing order of reactivity of the following compounds with HBr.



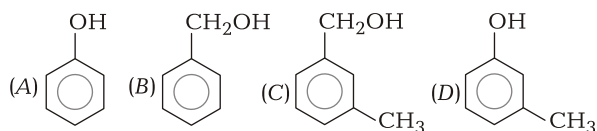
- (a) III > IV > II > I (b) III > II > IV > I
(c) III > II > I > IV (d) II > III > IV > I

22. The major product(s) of the following reaction is (are)



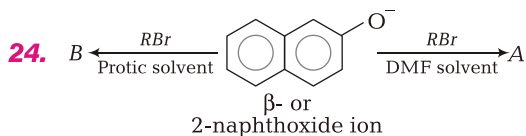
- (a) P and S (b) Only Q (c) R and S (d) S and P

23. Which of the following compounds is an aromatic alcohol?

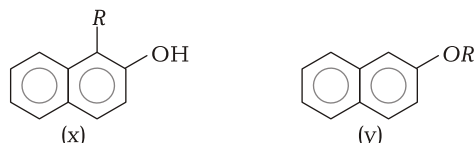


- (a) A, B, C and D (b) A and D
(c) B and C (d) A

Hint Phenol A and compound D, i.e. a derivative of phenol cannot be considered as an aromatic alcohol.



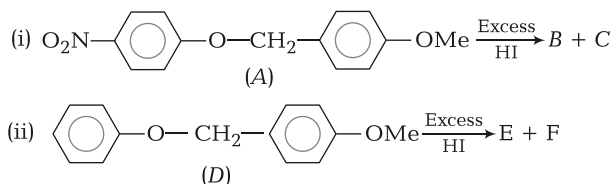
The compounds given are



Consider the following statements and choose the correct option given below.

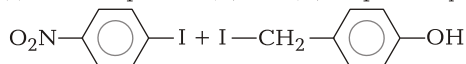
- I. The compound B is x.
II. The compound B is y.
III. The compound A is x.
IV. The compound A is y.
(a) I and III (b) I and IV (c) I and II (d) II and IV

25.

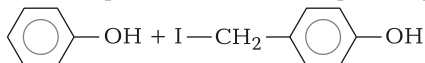


Consider the following statements

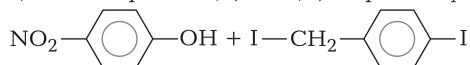
(I) The compounds (B) and (C) respectively are



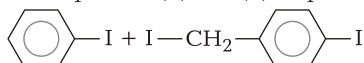
(II) The compounds (E) and (F) respectively are



(III) The compounds (B) and (C) respectively are



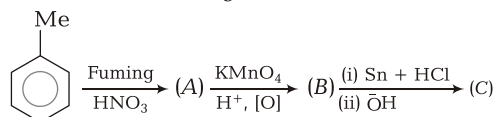
(IV) The compounds (E) and (F) respectively are



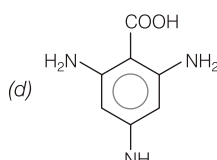
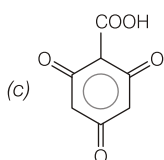
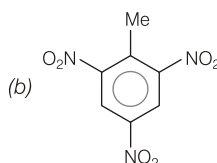
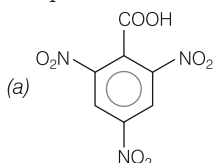
Which of the above statements is/are correct about the reactions (i) and (ii)?

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

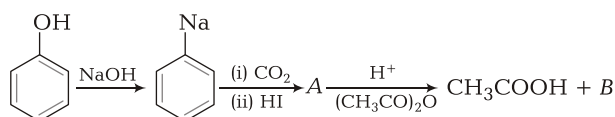
26. Consider the following reaction.



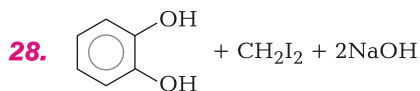
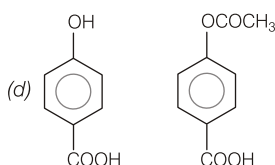
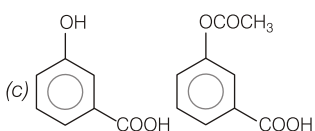
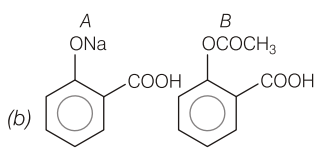
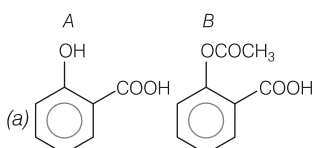
The product C is



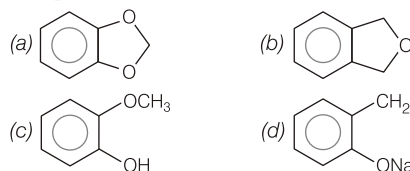
27. Consider the given reaction,



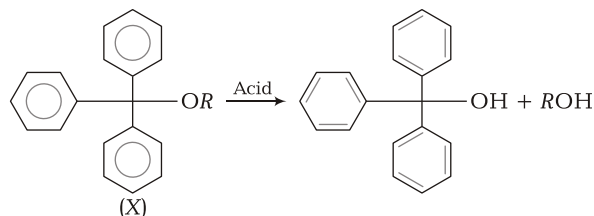
Identify A and B in the above reaction.



The product is

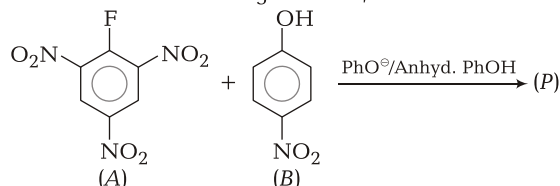


29. The acidic hydrolysis of ether (X) shown below is fastest when

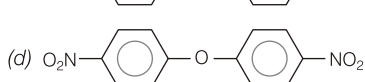
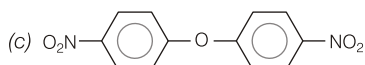
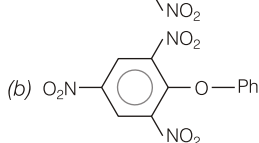
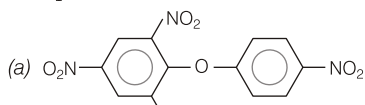


- (a) one phenyl group is replaced by a methyl group
 (b) one phenyl group is replaced by a *para*-methoxy phenyl group
 (c) two phenyl groups are replaced by two *para*-methoxy phenyl groups
 (d) no structural change is made to X

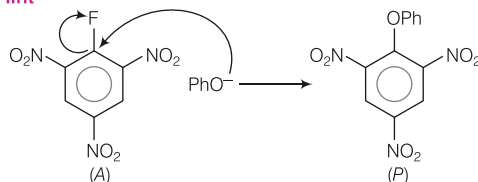
30. Consider the following reaction,



The product (P) is



Hint



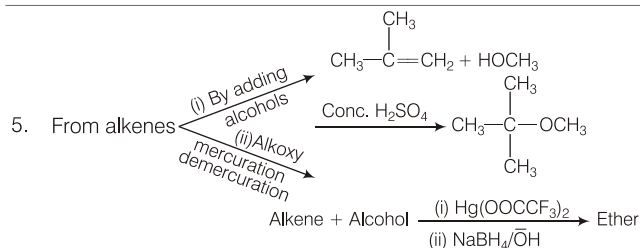


ETHERS

Ethers are organic compounds containing —O— group and having general formula $R-O-R'$.

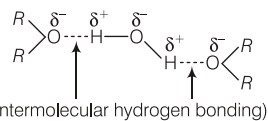
Ethers are prepared through the following reactions:

S. No.	Method	Reaction Involved
1.	Williamson's synthesis	$RO^-Na^+ + R'X \longrightarrow ROR' + Na^+X^-$
2.	By reaction of alkyl halides with dry silver oxide	$2RX + Ag_2O \longrightarrow ROR + 2AgX$
3.	By dehydration of alcohols	$RCH_2OH \xrightarrow[140^\circ C]{\text{conc. } H_2SO_4} RCH_2-O-CH_2R$ (Excess) (Order of dehydration of alcohols $3^\circ < 2^\circ < 1^\circ$) $RCH_2OH \xrightarrow[250^\circ C]{Al_2O_3} RCH_2-O-CH_2R$ (Excess)
4.	By the action of diazomethane on alcohols	$ROH + CH_2N_2 \xrightarrow{HBr} ROCH_3 + N_2 \uparrow$



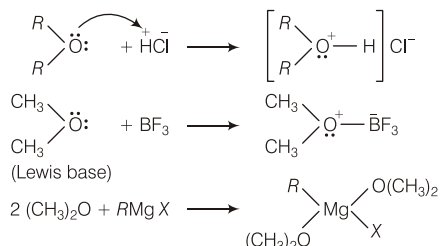
Physical and Chemical Properties

Dimethyl ether and ethyl methyl ether are gases at room temperature while other homologues are colourless liquids with characteristic ether smell and with a dipole moment of 1.15 to 1.3 D. These have the boiling points lower than their isomeric alcohols (due to lesser hydrogen bonding than corresponding alcohols). Ethers upto three C-atoms are soluble in water due to the formation of intermolecular hydrogen bonds as



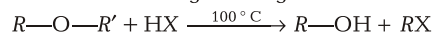
Ethers show the following chemical reactions:

(i) Reaction due to ethereal oxygen



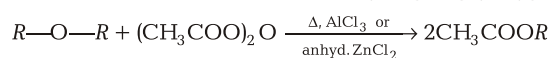
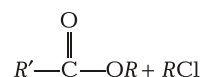
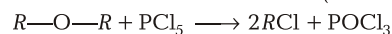
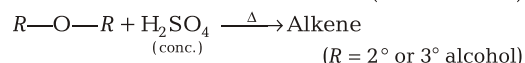
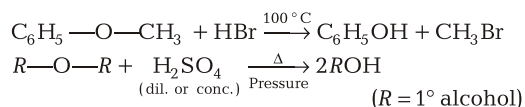
Due to complex formation, Grignard's reagent dissolves in dry ether.

(ii) Reaction involving cleavage of C—O bond.

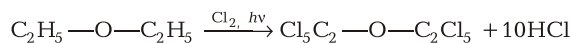
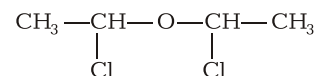
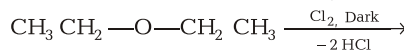
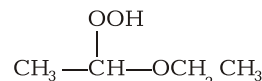
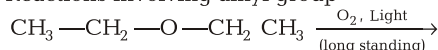


Order of reactivity of different hydrogen halides is $HI > HBr > HCl$.

In case of alkyl aryl ethers, the products are always phenol and an alkyl halide.

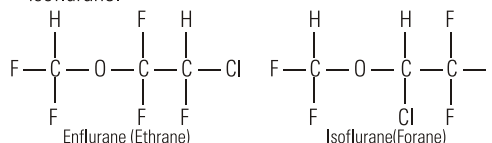


(iii) Reactions involving alkyl group



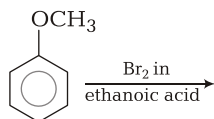
Ether as an Anaesthetic for Surgeries

- Diethyl ether was easy to use and caused excellent muscle relaxation. Blood pressure, pulse rate and respiration were usually only slightly affected.
- The gas's chief drawbacks were its irritating effect on the respiratory passages and its after effect of nausea.
- Among the inhalation anaesthetics used today are several halogenated ethers, the most important being enflurane and isoflurane.



Best Practice SHOTS

31. In the given reaction,

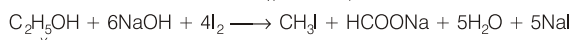
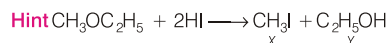


product formed is

- (a) (90% yield) (b) (90% yield)
- (c) (90% yield) (d) (10% yield)

32. One mole of an organic compound A with the formula $\text{C}_3\text{H}_8\text{O}$ reacts completely with two moles of HI to form X and Y. When Y is boiled with aqueous alkali, it forms Z. Z gives the iodoform test. The compound A is

- (a) propan-2-ol (b) propan-1-ol
(c) ethoxyethane (d) methoxyethane

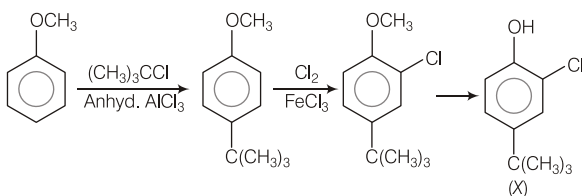


33. Anisole $\xrightarrow{(\text{CH}_3)_3\text{CCl}}$ $\xrightarrow{\text{Cl}_2/\text{FeCl}_3}$ $\xrightarrow[\text{Heat}]{\text{HBr}}$ X

The product X in the above series of reaction is

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

Hint



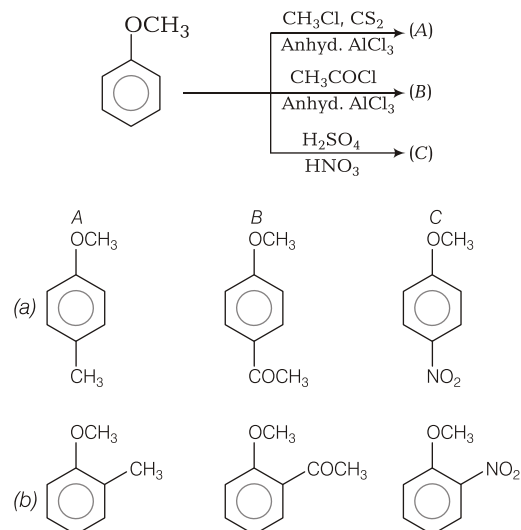
34. Match the following reaction given in Column I with the final product given in Column II and choose the correct option from the codes given below.

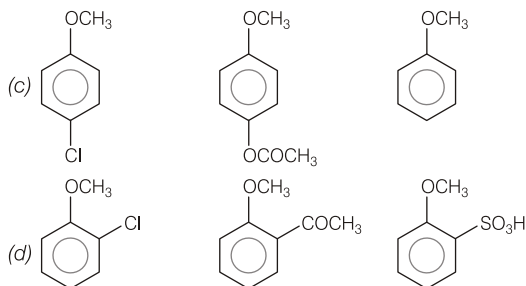
Column I	Column II
A. $\xrightarrow[\text{H}^+]{\text{C}_2\text{H}_5\text{OH}}$ (A)	p. $\text{C}_2\text{H}_5\text{O}-\text{CH}_2-\text{CH}_2-\text{O}-\text{CH}_2-\text{CH}_2-\text{OH}$
$\xrightarrow{\text{H}^+}$ A	
B. $\xrightarrow[\text{H}^+]{\text{H}_2\text{O}}$ (B)	q. $\text{HOH}_2\text{C}-\text{CH}_2-\text{N}(\text{CH}_3)-\text{CH}_2\text{CH}_2\text{OH}$
$\xrightarrow{\text{H}^+}$ B	
C. $\xrightarrow[\text{H}^+]{\text{CH}_3\text{NH}_2}$ (C)	r. $\text{HOCH}_2\text{CH}_2-\text{O}-\text{CH}_2\text{CH}_2\text{OH}$
$\xrightarrow{\text{H}^+}$ C	
D. $\xrightarrow{\text{H}^+}$?	s.

Codes

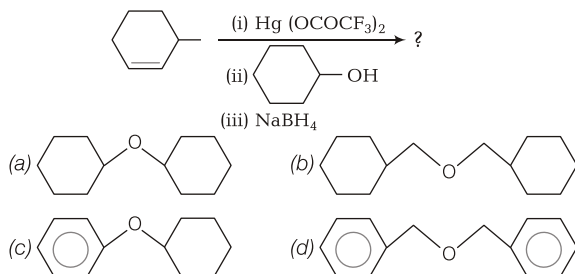
- A B C D A B C D
(a) p q r s (b) s q r p
(c) p r q s (d) p r s q

35. Identify the minor products formed in the given reaction and choose the correct option given below.



{ JEE FINAL TOUCH }

36. What is the structure of product for the following reaction?



37. Consider the following statements and choose the incorrect one.

- When diethyl ether is heated with an excess of PCl_5 , it yields ethyl chloride
- Sometimes explosion occurs while distilling ethers. It is due to the presence of oxides
- On boiling with concentrated hydrobromic acid, phenyl ethyl ether yields phenol and ethyl bromide
- An ether is more volatile than an alcohol having the same molecular formula. This is due to intermolecular hydrogen bonding in alcohols

38. By which of the following procedures, can ethyl *n*-propyl ether be obtained?

- $$\text{C}_2\text{H}_5\text{OH} \xrightarrow{\text{HBr}} \text{I} \xrightarrow[\text{Ether}]{\text{Mg}} \text{II} \xrightarrow[\text{CH}_3\text{CH}_2\text{Br}]{\text{H}_2\text{O}} \text{III} \xrightarrow{\text{Na}}$$
- $$\text{C}_2\text{H}_5\text{OH} \xrightarrow{\text{HBr}} \text{I} \xrightarrow[\text{Ether}]{\text{Mg}} \text{II} \xrightarrow[\text{CH}_3\text{CH}_2\text{Br}]{\text{(i) CH}_2\text{O, (ii) H}_3\text{O}^+} \text{III} \xrightarrow{\text{Na}}$$
- $$\text{C}_2\text{H}_5\text{OH} + \text{H}_2\text{SO}_4 \xrightarrow{140^\circ\text{C}}$$
- $$\text{C}_2\text{H}_5\text{OH} + \text{Conc. H}_2\text{SO}_4 \xrightarrow{180^\circ\text{C}} \text{I} \xrightarrow{\text{CH}_3\text{CH}_2\text{CH}_2\text{Br}}$$

Answers

1. (c) 2. (d) 3. (b) 4. (a) 5. (b) 6. (a) 7. (a) 8. (a) 9. (a) 10. (a)
 11. (a) 12. (b) 13. (d) 14. (a) 15. (c) 16. (a) 17. (b) 18. (a) 19. (a) 20. (c)
 21. (c) 22. (b) 23. (c) 24. (a) 25. (c) 26. (d) 27. (a) 28. (a) 29. (c) 30. (b)
 31. (a) 32. (d) 33. (d) 34. (c) 35. (b) 36. (b) 37. (b) 38. (b)

MASTER STROKE

1. Match the following compounds given in Column I with their names given in Column II and choose the correct option from the codes given below.

Column I	Column II
A. $\text{C}_6\text{H}_5-\text{CH}=\text{CH}-\text{CH}_2\text{OH}$	p. 2-isopropoxybutane
B.	q. (1-cyclopentenyl) methanol
C.	r. 3-cyclohexenyl isopropylether
D.	s. 3-phenyl prop-2-en-1-ol

Codes

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

2. $\text{C}_6\text{H}_5-\text{CH}=\text{CHCHO} \xrightarrow{\text{X}} \text{C}_6\text{H}_5\text{CH}=\text{CHCH}_2\text{OH}$

In the above sequence, X can be

- (a) H_2/Ni (b) NaBH_4 (c) $\text{K}_2\text{Cr}_2\text{O}_7/\text{H}^+$ (d) $(\text{CH}_3)_2\text{CHOH}$

Hint NaBH_4 and LiAlH_4 attack only carbonyl group and reduce it into alcoholic group.

3. Match the items of Column I with items of Column II and choose the correct option from the codes given below.

Column I	Column II
A. Methanol	p. Conversion of phenol to salicylic acid
B. Kolbe's reaction	q. Ethyl alcohol
C. Williamson's synthesis	r. Conversion of phenol to salicylaldehyde
D. Conversion of 2° alcohol to ketone	s. Wood spirit
E. Reimer-Tiemann reaction	t. Heated copper at 573 K
F. Fermentation	u. Reaction of alkyl halide with sodium alkoxide

Codes

- A B C D E F A B C D E F
 (a) s p u t q r (b) s p t u q r
 (c) s p u t r q (d) s p t u r q

4. Consider the following statements and identify them as True (T) and False (F). Choose the correct code given below.

- I. The bond angle in alcohol is slightly more than the tetrahedral angle.

II. Carbon-oxygen bond length of phenol is slightly less than that in methanol.

III. The C—O bond length (141 pm) of ether is almost same as in alcohols.

IV. In ethers, the two bond pairs and two lone pairs of electrons on oxygen are arranged in a planar arrangement.

Codes

I II III IV	I II III IV
(a) T T F T	(b) T T T F
(c) F T T F	(d) F T F T

Hint In ethers, the two bond pairs and two lone pairs of electrons on oxygen are arranged in a tetrahedral arrangement.

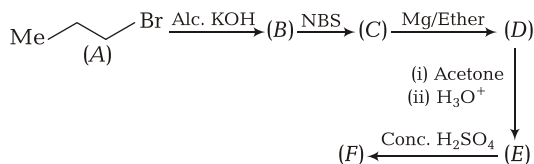
5. Match the items of Column I with items of Column II.

Column I	Column II
A. Antifreeze used in car engine	p. Neutral ferric chloride
B. Solvent used in perfumes	q. Glycerol
C. Starting material for picric acid	r. Methanol
D. Wood spirit	s. Phenol
E. Reagent used for detection of phenolic group	t. Ethylene glycol
F. By product of soap industry used in cosmetics	u. Ethanol

Choose the correct option given below.

A B C D E F
(a) t u s r q p
(b) t u r s p q
(c) t u s r p q
(d) t u q p s r

6. Consider the following reaction



The compounds E and F respectively are

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

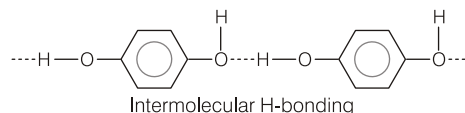
7. Consider the following compounds.

- I. 1, 2-dihydroxy benzene
- II. 1, 3-dihydroxy benzene
- III. 1, 4-dihydroxy benzene
- IV. Hydroxy benzene

The increasing order of boiling points of the above mentioned alcohols is

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

Hint 1, 4-dihydroxy benzene shows the highest boiling point among the given compounds because it forms strong intermolecular hydrogen bond (it does not form intramolecular H-bonding)



8. Match the following reaction given in Column I with the name given in Column II and choose the correct option from the codes given below.

Column I	Column II
A.	p. Elbs oxidation
B.	q. Vilsmeier reaction
C.	r. Kolbe-Schmidt reaction
D.	s. Dakin reaction
	t. Reimer-Tiemann reaction

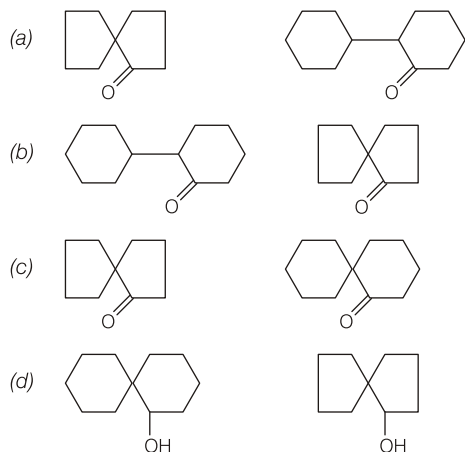
Codes

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

9. Consider the following compounds.



The products of the pinacol-pinacolone rearrangement of the above glycols in acids respectively are

{ JEE FINAL TOUCH }

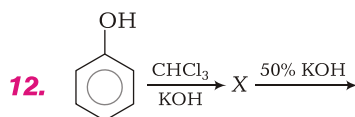
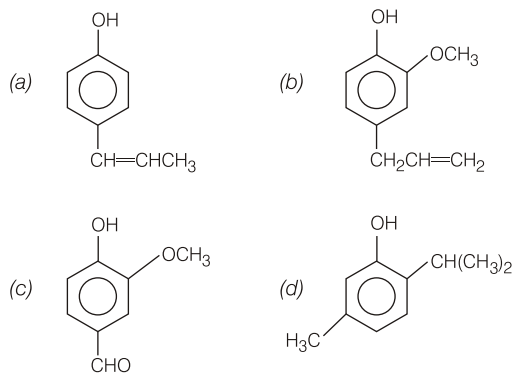
10. Match the following reactants and reagents given in Column I with the products given in Column II and choose the correct option from the codes given below.

Column I	Column II
A.	p.
B. (l) $\xrightarrow{\text{TsCl}}$ followed by Br^-	q.
C. (l) $\xrightarrow{\text{TsCl}}$	r.
D. (l) $\xrightarrow{\text{SOCl}_2}$	s.

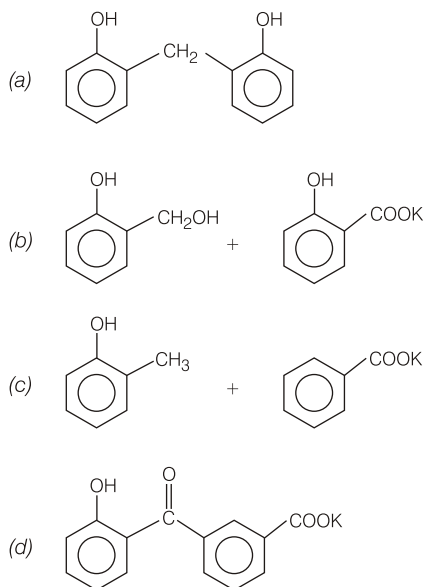
Codes

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

11. Phenols and ethers are used in perfumes and as the flavouring agents. Identify the vanillin from the given below structures.



The final product(s) of this reaction is/are

**Answers**

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

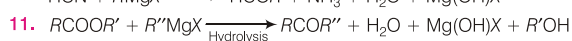
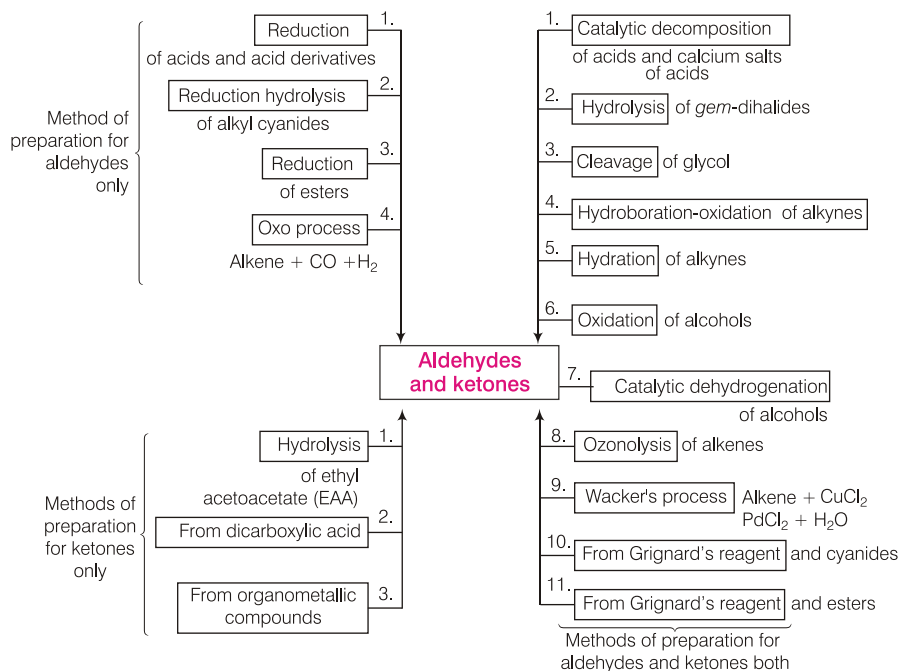
Aldehydes, Ketones and Carboxylic Acids



ALIPHATIC AND AROMATIC ALDEHYDES AND KETONES

Methods of Preparation

Aldehydes and ketones are prepared through the following reactions:

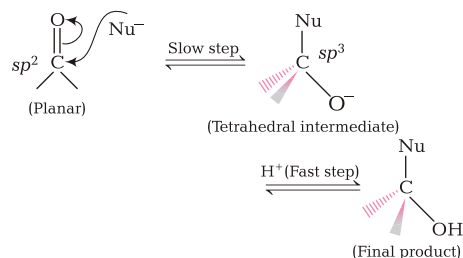


Physical Properties

- HCHO is a gas at room temperature, CH₃CHO is a volatile liquid and the rest are either liquid or solid at room temperature.
- Their boiling points are higher than the corresponding hydrocarbons and ether but less than the corresponding alcohols due to the absence of hydrogen bonding. Hence, the order of boiling points for compounds of comparable molecular masses are alkane < alkene < alkyne < ether < aldehyde < ketone < alcohol.
- Lower members of aldehydes and ketones are soluble in water due to the formation of H-bonding and the solubility decreases as the number of carbons increases in the alkyl chain.

Chemical Properties

- Aldehydes and ketones undergo nucleophilic addition reaction that proceeds through the following mechanism:



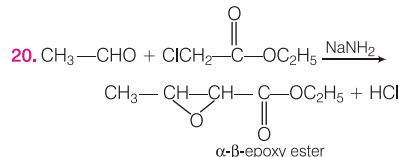
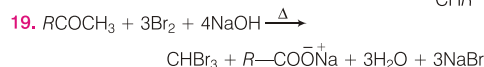
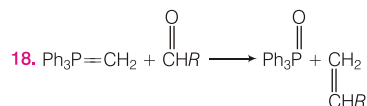
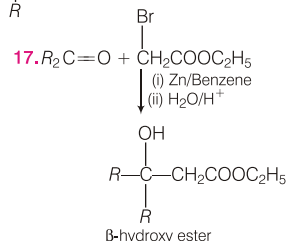
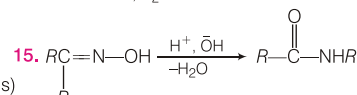
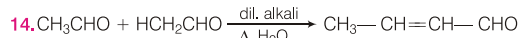
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These show the following chemical properties:

- Miscellaneous reactions**
14. Aldol condensation
 15. Beckmann rearrangement
 16. Reaction with primary amines
 17. Reformatsky reaction
 18. Wittig test
 19. Haloform reaction
 20. Darzen's glycidic ester synthesis
 21. Reduction
 22. Oxidation
 23. Halogenation
 24. With NH_3

Nucleophilic addition reactions

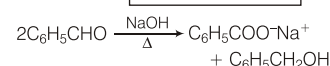
1. With NaHSO_3
 2. With HCN (Cyanohydrin is formed)
 3. With RMgX (Alcohol is formed after hydrolysis)
- Nucleophilic addition elimination reactions**
4. With ammonia derivatives
 4. Hydroxylamine (NH_2OH)—Oxime is formed
 5. Hydrazine ($\text{NH}_2\cdot\text{NH}_2$)—Hydrazone is formed
 6. Phenyl hydrazine ($\text{C}_6\text{H}_5\text{NH}\cdot\text{NH}_2$)—Phenyl hydrazone is formed
 7. Semicarbazide ($\text{NH}_2\text{CONH}\cdot\text{NH}_2$)—Semicarbazone is formed
 8. 2,4-DNP-2,4-DNP hydrazone is formed
9. Addition of water
 10. Addition of alcohols
 11. Addition of thioalcohols
 12. Addition of PX_5
 13. Ethinylation



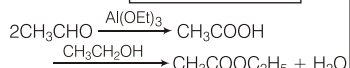
Aldehydes and ketones

Chemical properties of aldehydes only

Cannizzaro reaction



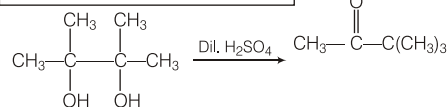
Tischenko reaction



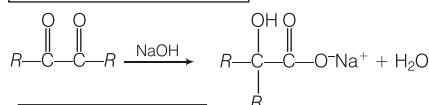
Action of Schiff's reagent

Polymerisation

1. Pinacol-pinacolone rearrangement



2. Benzylic acid rearrangement



3. Addition of chloroform

4. Formation of sodium derivative

Chemical properties of ketones only

Useful Polymers from Formaldehyde

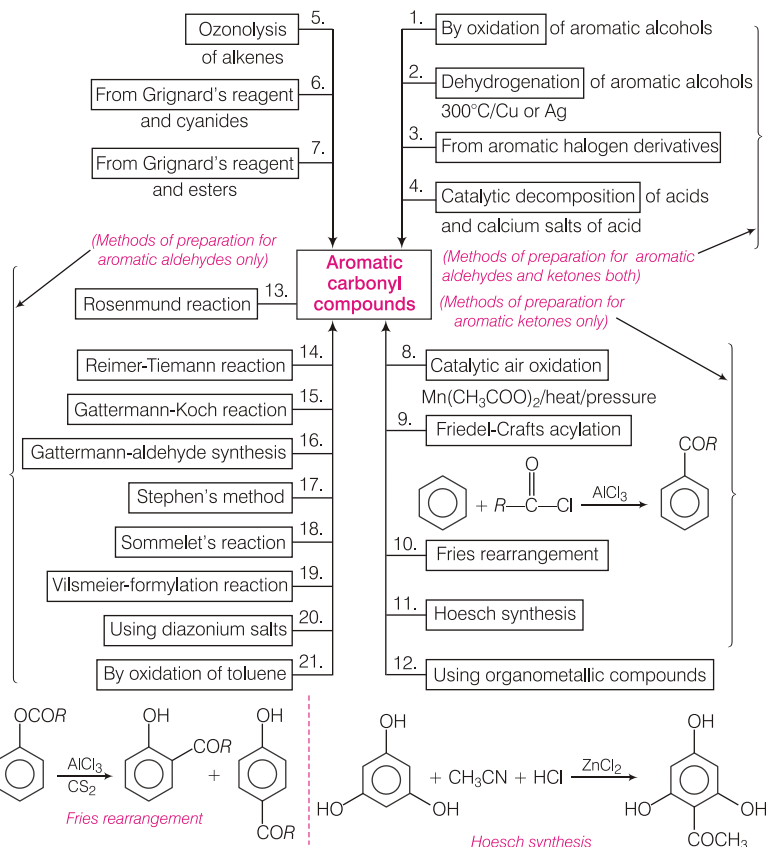
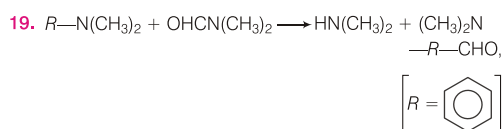
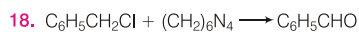
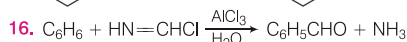
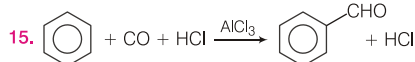
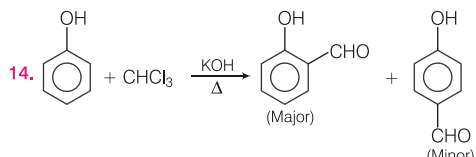
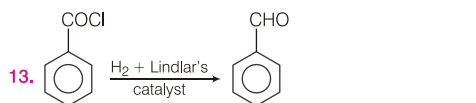
- Formaldehyde has large applications in the production of certain polymeric materials.
- When formaldehyde reacts with phenol, a plastic bakelite with three dimensional structure is formed.
- Similarly, three dimensional polymers are made from formaldehyde and the compounds urea and melamine. These polymers are used not only as plastics but even more importantly as adhesives and coatings.
- Plywood consists of thin sheets of wood glued together by one of these polymers.

Excess of Acetone in the Bloodstream as a Common Symptom of Diabetes

- A person with diabetes is deficient in insulin, the hormone that allows sugars to enter cells.
- Due to lack of insulin in the body, a diabetic is forced to rely on fatty acids and proteins for energy, which produces a large quantity of ketone bodies (acetone, acetoacetic acid and β-hydroxybutyric acid) in the bloodstream.
- This large quantity of ketone bodies can be prevented by monitoring insulin levels within the body.
- When a diabetic body is in stressful situation, it produces hormones such as adrenaline, which increases the rate at which fatty acids are converted to energy. This causes ketone bodies to accumulate.
- When so much acetone builds up in the blood, the body attempts to eliminate it all by causing excessive urination. It can be treated through insulin therapy, replenishing the body with the fluids and electrolytes and diminishing stress.

Aromatic Aldehydes and Ketones

In aromatic aldehydes and ketones, the carbonyl ($>C=O$) group is directly attached to aromatic ring. These are prepared through the following reactions:



Physical Properties

- C_6H_5CHO is a colourless liquid (BP $179^\circ C$) with pleasant almond like odour. It is steam volatile.
- $C_6H_5COCH_3$ is a colourless liquid (BP $202^\circ C$).
- Both are sparingly soluble in water but easily soluble in ethanal and diethyl ether.

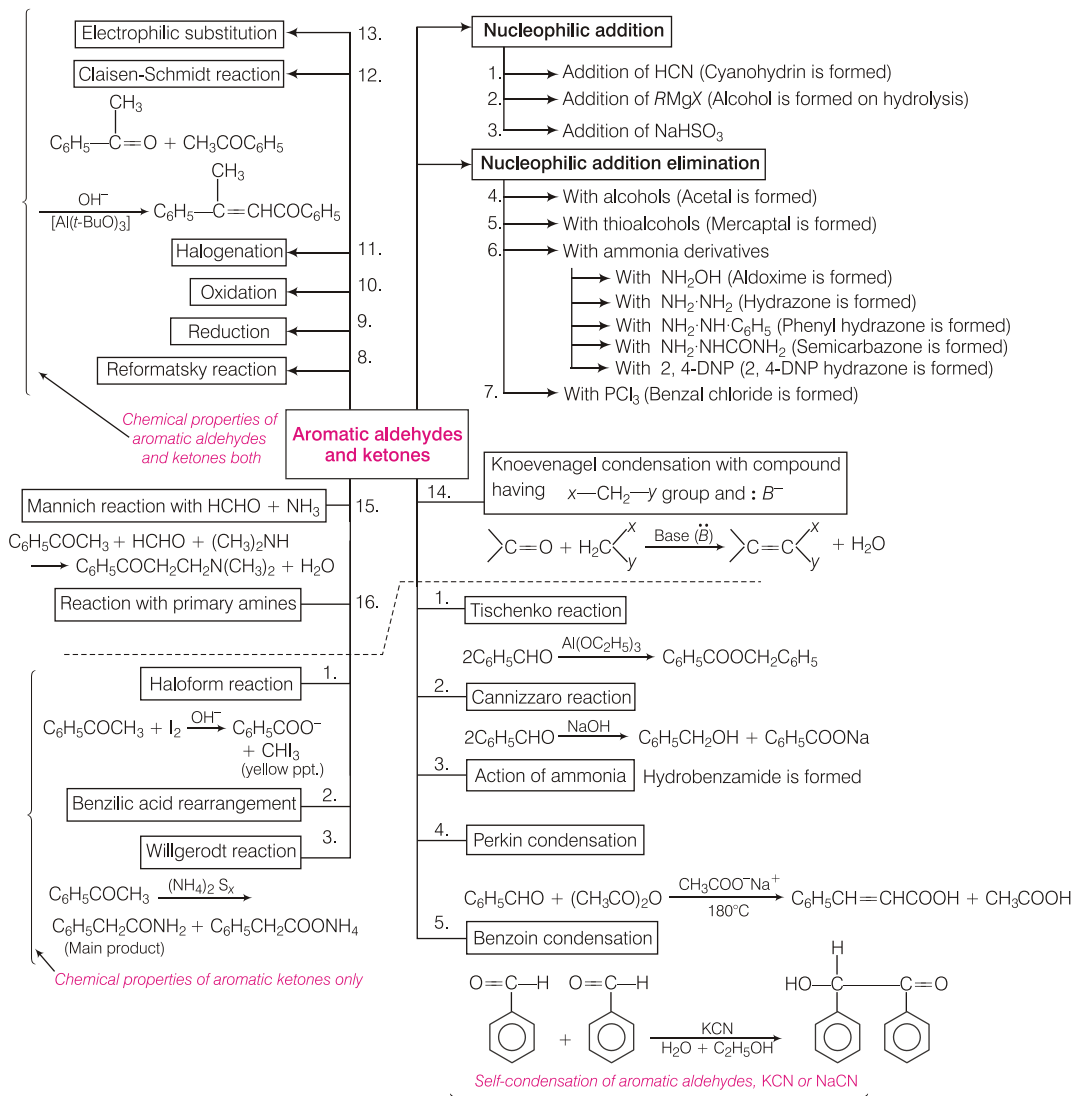
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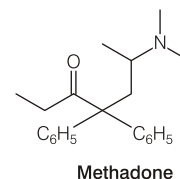
Chemical Properties

Like aliphatic aldehydes and ketones, they also show nucleophilic addition reactions:



Addiction to Opiates and Methadone

- Heroin, opium and morphine are some common opiates.
- All of these drugs cause the body to release excessive amounts of the hormone dopamine. This hormone ends up in the brain, where it attaches to the dopamine receptor and creates a feeling of happiness.
- Opiates are extremely addictive because a person quickly develops a physiological need to have something constantly bounded to the opiate receptor. Otherwise, the addict will experience withdrawal symptoms, which include muscle aches, sweating, vomiting, agitation, abdominal cramping and more.
- To help combat opiate addiction, the oral medication methadone can be prescribed by a medical professional.
- Methadone works by binding to the dopamine receptor in the brain. This eliminates the user's physical dependence on opiates because the user does not need anything else to bind to the dopamine receptor.



Best Practice **SHOTS**

1. Which of the following statements is incorrect?

- (a) Due to dipole-dipole interactions, molecules of carbonyl compounds are held together quite strongly
 (b) Branched carbonyl compounds are more soluble in water than the straight chain carbonyl compounds
 (c) Boiling points of straight chain carbonyl compounds are higher than those of branched carbonyl compounds
 (d) All aldehydes and ketones are used in the preparation of perfumes and flavouring agents

Hint Lower aldehydes have sharp pungent odour. As the size of molecule increases, the odour becomes less pungent and more fragrant.

2. Match the conversions given in Column I with the suitable reagents given in Column II and choose the correct option from the codes given below:

Column I	Column II
A. Ethanenitrile to ethanol	p. O_3/H_2O - Zn dust
B. Allyl alcohol to propanal	q. DIBAL -H
C. But-2-ene to ethanal	r. PCC

Codes

- | | | | | | | | |
|-----|---|---|---|-----|---|---|---|
| A | B | C | A | B | C | | |
| (a) | p | q | r | (b) | r | q | p |
| (c) | q | r | p | (d) | q | p | r |

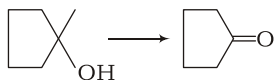
Hint A-q, B-r, C-p

3. An organic compound X gives a red precipitate on heating with Fehling's solution. Which one of the following reactions yields X as a major product?

- (a) $HCHO \xrightarrow[\text{(ii) } H_2O]{\text{(i) } CH_3MgI}$
 (b) $C_2H_5Br + AgOH \xrightarrow{\Delta}$
 (c) $2C_2H_5Br + Ag_2O \xrightarrow{\Delta}$
 (d) $C_2H_2 + H_2O \xrightarrow[1\% HgSO_4, 60^\circ C]{40\% H_2SO_4}$

Hint X = CH_3CHO

4. Name the suitable reagent for following conversion.



- (a) MnO_2
 (b) CrO_3 in glacial acetic acid
 (c) PCC/ CH_2Cl_2
 (d) 3° alcohol is not oxidised

5. Which of the following reagent cannot reduce CH_3COCl to CH_3CHO ?

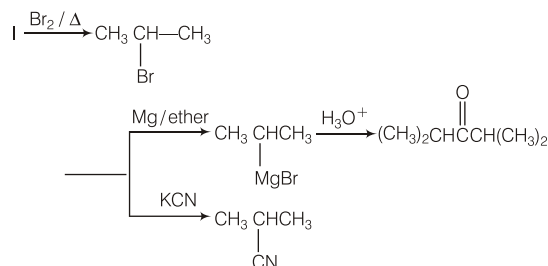
- (a) Pd/ $BaSO_4$, Xylene
 (b) $NaAlH_4$
 (c) DIBAL-H
 (d) $HgSO_4/H_2SO_4$

Hint Hydration of terminal alkynes is catalysed by H_2SO_4 and Hg^{2+} ion.

6. Which of the following reaction conditions is not involved in the steps of conversion of $CH_3CH_2CH_3$ (I) into $(CH_3)_2CH-C(=O)-CH(CH_3)_2$ (II)?

- (a) Br_2/Δ
 (b) Mg/ether + KCN
 (c) H_3O^+
 (d) $H_2SO_4/HgSO_4$

Hint

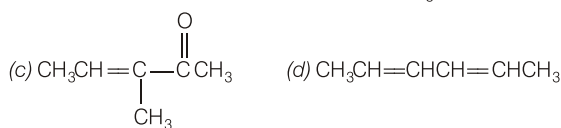
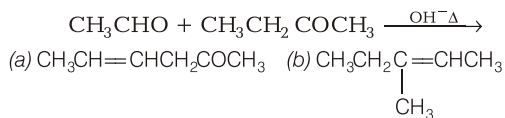


7. Which of the following statements is incorrect?

- (a) The addition of HCN to carbonyl compounds takes place under basic or neutral conditions as HCN is a weak acid and its ionisation increases in neutral/basic medium
 (b) $CH_3CH_2COCH_3$ has larger equilibrium constant than $CH_3CH_2CH_2CHO$
 (c) When acetaldehyde reacts with HCN, there is formation of a chiral carbon but product is optically inactive mixture of two resolvable components
 (d) RCH_2OH is oxidised to $RCHO$ by Cu, some RCH_2OH is left unreacted

Hint Aldehydes being less sterically hindered than ketones, are more reactive.

8. What is the final product of the following crossed aldol condensation?

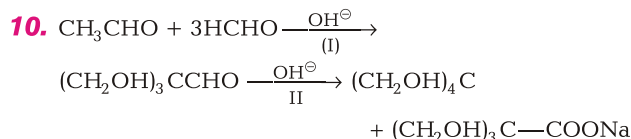


9. Which of the following reactions is not a part of Tischenko reaction?

- (a) $RCHO \longrightarrow RCOOH$
 (b) $RCOOH + RCH_2OH \longrightarrow RCOOCH_2R$
 (c) $RCHO \longrightarrow RCH_2OH$
 (d) $2RCHO \longrightarrow RCH(OH)-R'-CHO$
 ($R' = R$ minus H)

Hint Step 'd' is an aldol condensation reaction.

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Reaction at stages I and II respectively are

- (a) cannizzaro, aldol (b) aldol, aldol
(c) cannizzaro, cannizzaro (d) aldol, cannizzaro

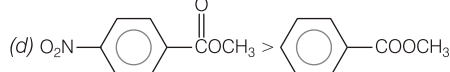
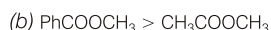
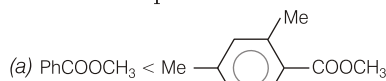
11. Benzophenone can be obtained by

- I. benzoyl chloride + benzene + AlCl_3
II. benzoyl chloride + diphenyl cadmium
III. benzoyl chloride + phenyl magnesium chloride
IV. benzene + carbon monoxide + ZnCl_2

Select an appropriate option.

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

12. Which of the following is arranged in correct order of rate of nucleophilic substitution at its carbonyl group?



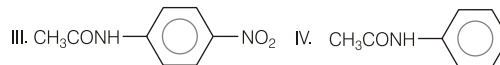
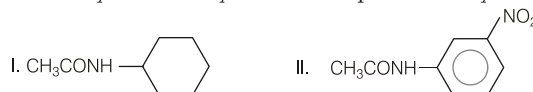
Hint In (a)-steric hindrance

In (b)-benzene ring donates electrons by resonance

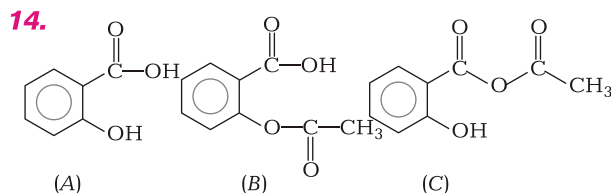
In (c)-electron withdrawing 'F' group

In (d)-electron withdrawing 'NO₂' group

13. List the following amides in order of decreasing reactivity towards hydroxide ion promoted hydrolysis



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



Which of the following statements is incorrect regarding above compounds?

- (a) Salicylic acid (A) has two nucleophilic sites
(b) A on reaction with acetic anhydride produces B and C
(c) B is the structure of aspirin
(d) B is less reactive than C

Hint A on reaction with acetic anhydride forms B rather than C because B (an ester) formed is less reactive than C (an anhydride).

15. Crossed Cannizzaro reaction can be given by following combination.

- (a) CH_3CHO , HCHO (b) $\text{C}_6\text{H}_5\text{CHO}$, CH_3CHO
(c) $\text{C}_6\text{H}_5\text{CHO}$, HCHO (d) All of these

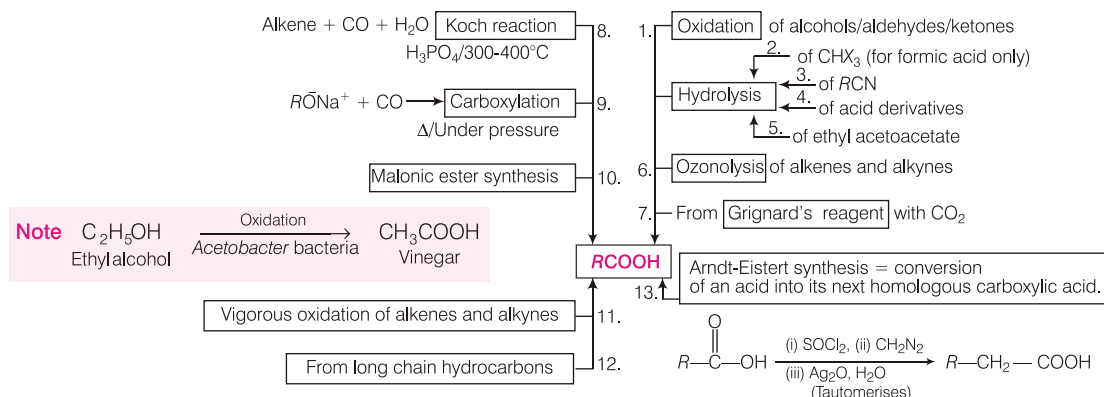
Hint Absence of $\alpha\text{-H}$ in both reactants.



MONOCARBOXYLIC ACIDS, DICARBOXYLIC ACIDS AND AROMATIC CARBOXYLIC ACIDS

Monocarboxylic Acids

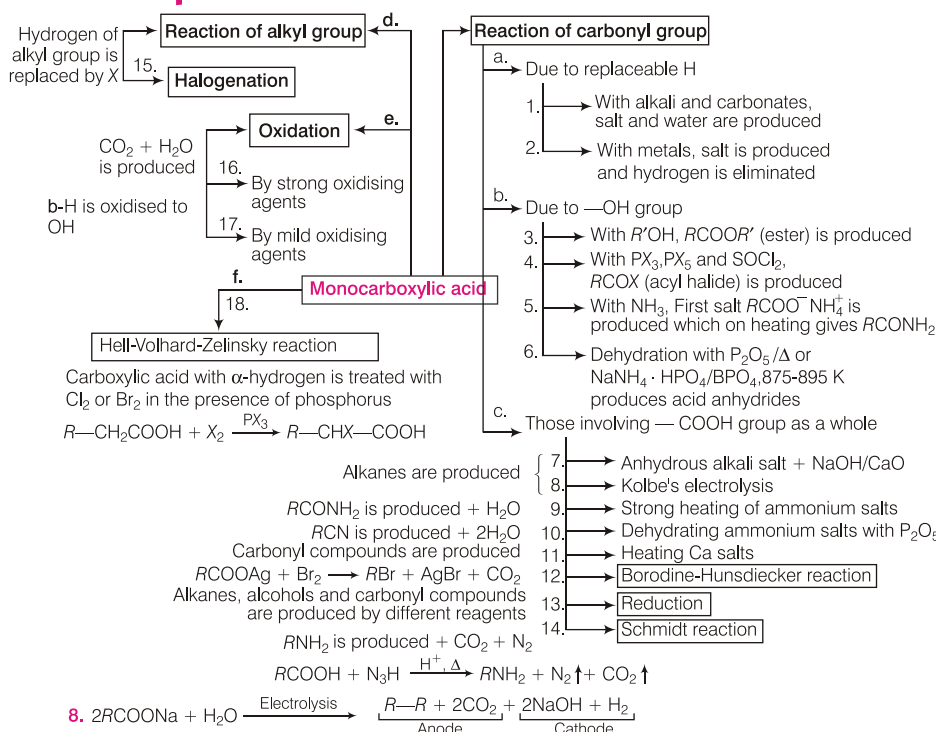
Preparation



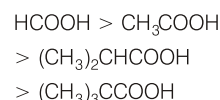
Physical Properties

- Carboxylic acids with unbranched chain of 12-24 carbons are called **fatty acids**.
- First three members are colourless, pungent smelling liquids.
- C₄-C₉ are oily liquids. Higher ones are odourless solids. First four members are miscible with water. Boiling points of acids are higher than corresponding alcohols due to intermolecular H-bonding. Carboxylic acids are stronger acids than phenol but weaker than other mineral acids. The acidic character decreases with increase in molecular weight. Thus, formic acid is the strongest acid among all carboxylic acids.
- The melting points of *n*-monocarboxylic acids : *n* = even = melting point higher, *n* = odd = melting point lower.

Chemical Properties



Note Order of reactivity follows the sequence

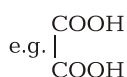


Some Facts about Monocarboxylic Acids

- Formic acid (HCOOH) was first obtained by the distillation of ants. The bites of some ants inject formic acid and the stings of wasps and bees contain formic acid as well as other poisonous materials.
- Acetic acid (CH₃COOH) is made by fermenting cider and honey in the presence of oxygen. This fermentation produces vinegar, a solution containing 4%-10% acetic acid and number of other compounds that add to its flavour.
- Propionic acid (CH₃CH₂COOH) was first found among degradation products of sugar.
- Butyric acid (CH₃(CH₂)₂COOH) is one of the most foul-smelling substance imaginable. It is found in rancid (salted) butter and is one of the ingredients of body odour. By recognising extremely small amounts of this and other chemicals, blood hounds are able to track fugitives.

Dicarboxylic Acids

These acids contain two —COOH groups.



Preparation

- Lab method** By oxidation of cane sugar with HNO₃ in the presence of V₂O₅
 - By heating HCOO⁻Na⁺ to 400°C under pressure
 - By the hydrolysis of cyanogen (CN—CN) with HCl (acid hydrolysis)
 - By heating Na or K in the current of CO₂ at 633 K (sodium salt of oxalic acid is produced)
- Oxalic acid**
- $$\begin{array}{c} \text{COOH} \\ | \\ \text{COOH} \end{array}$$

{ JEE FINAL TOUCH }

Physical Properties

These are crystalline solids with higher melting points than monocarboxylic acids. Lower members are soluble in water.

Chemical Properties

- Sodium salt, i.e. $\begin{array}{c} \text{COO}^- \text{Na}^+ \\ | \\ \text{COO}^- \text{Na}^+ \\ | \\ \text{COOR} \end{array}$ is produced
 - With alkalis and carbonates
 - With alcohols
 - With NH_3
- Ester, i.e. $\begin{array}{c} \text{COOR} \\ | \\ \text{COOR} \\ | \\ \text{CONH}_2 \end{array}$ is produced
 - Heating (a) at 100-150°C (b) at 200°C
 - With glycerol,
- Oxamide, i.e. $\begin{array}{c} \text{CONH}_2 \\ | \\ \text{CONH}_2 \end{array}$ is produced
- Anhydrous form is produced
 - HCOOH is produced + CO_2
- $\begin{array}{c} \text{CH}_2 \\ | \\ \text{CH} \\ | \\ \text{CH}_2\text{OH} \end{array}$ is produced at 110°C and 260°C respectively
 - Dehydration
 - Oxidation
- $\begin{array}{c} \text{COCl} \\ | \\ \text{COCl} \end{array}$ is produced
 - With PCl_5 (in excess)
 - Reduction
- Glycolic acid and glyoxylic acid are formed
- Ethylene oxalate, i.e. $\begin{array}{c} \text{O} \\ / \quad \backslash \\ \text{CH}_2 \quad \text{C}=\text{O} \\ | \quad \quad | \\ \text{CH}_2 \quad \text{C}=\text{O} \\ \backslash \quad / \\ \text{O} \end{array}$ is produced
 - With glycol

Aromatic Carboxylic Acid (Benzoic Acid)

Preparation

- By the oxidation of side chain of aromatic hydrocarbons. (In presence of acidified $\text{K}_2\text{Cr}_2\text{O}_7$, HNO_3 , acidified KMnO_4 , Cl_2 or CO-Mn acetate at 200°C) (Strong oxidising agent)

$$\text{Alcohol} \xrightarrow{\text{K}_2\text{Cr}_2\text{O}_7/\Delta \text{ or } \text{KMnO}_4/\Delta} \text{Acid}$$
- Aldehyde $\xrightarrow[\text{Tollen's reagent}]{\text{Mild oxidising agent}}$ Acid
- By hydrolysis of acid derivatives, nitriles, trihalogen derivatives of arenes ($\text{C}_6\text{H}_5-\text{CCl}_3$).
- By carbocation of organometallic compound
- By haloform reaction
- Addition of CO_2 to benzene
- By means of Friedel-Crafts reaction $\text{C}_6\text{H}_6 + \text{CO}_2 \xrightarrow{\text{AlCl}_3} \text{C}_6\text{H}_5\text{COOH}$
- By phthalic anhydride and steam in the presence of Zn, Cr or Ni at 200-300°C

Physical Properties

- It is a colourless solid and has melting point 122°C.
- It is soluble in hot water, diethyl ether, ethanol and benzene.
- It is steam volatile.

REMEMBER

- It is stronger acid than acetic acid while weaker acid than formic acid.
- It is present in certain resins, i.e. a gum benzoin, balsams, in the urine of horses as hippuric acid.

Chemical Properties

- Salt formation

$$\begin{array}{l} \xrightarrow{\text{NaOH}} \text{C}_6\text{H}_5\text{COO}^- \text{Na}^+ + \text{H}_2\text{O} \\ \xrightarrow{\text{NaHCO}_3} \text{C}_6\text{H}_5\text{COO}^- \text{Na}^+ + \text{CO}_2 + \text{H}_2\text{O} \end{array}$$
- PCl_3 or PCl_5 or $\text{SOCl}_2 \rightarrow \text{ArCOCl}$
- Esterification $\rightarrow \text{C}_6\text{H}_5\text{COOR} + \text{H}_2\text{O}$
- Decarboxylation $\rightarrow \text{C}_6\text{H}_5 + \text{Na}_2\text{CO}_3$
- Reduction $\xrightarrow{\text{LiAlH}_4} \text{C}_6\text{H}_5\text{CH}_2\text{OH}$
- Benzoic acid ($\text{C}_6\text{H}_5\text{COOH}$) $\xrightarrow{\text{NH}_3, \Delta} \text{C}_6\text{H}_5\text{CONH}_2$
- $\text{N}_3\text{H}/\text{H}_2\text{SO}_4 \rightarrow \text{C}_6\text{H}_5\text{NH}_2$ (Schmidt reaction) $-\text{N}_2, \text{CO}_2$
- With organometallic compounds \rightarrow Alkanes are produced
- Electrophilic substitution \rightarrow The benzene ring of benzoic acid undergoes usual electrophilic substitution, $-\text{COOH}$ group is *m*-directing and deactivating.
- Side-chain substitution (HVZ method) $R-\text{CH}_2-\text{COOH} \xrightarrow[\text{(ii) H}_2\text{O}]{\text{(i) X}_2, \text{Red P}} R\text{CHX}-\text{COOH}$ α -halocarboxylic acid
- Hunsdiecker reaction
- Decomposition of acid and calcium salts of acids

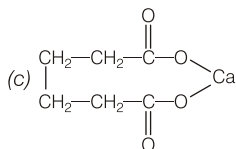
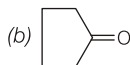
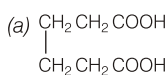
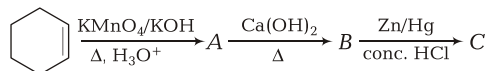
Skin Blemishes and Salicylic Acid

Salicylic acid is used to help clear pimples and skin blemishes in people who have acne. Topical salicylic acid is also used to treat skin conditions that involve scaling or overgrowth of skin cells such as psoriasis (a skin disease in which red, scaly patches form on some areas of the body), ichthyoses (in born conditions that cause skin dryness and scaling), dandruff, corns, calluses and warts on the face, warts with hair growing for them, warts in the nose or mouth, moles or birthmarks.

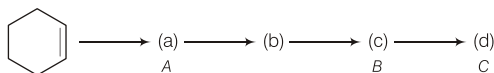
Salicylic acid is in a class of medications called keratolytic agents. Topical salicylic acid treats acne by reducing swelling and redness and unplugging blocked skin pores to allow pimples to shrink. It treats other skin conditions by softening and loosening dry, scaly or thickened skin so that it falls off or can be removed easily.

Best Practice **SHOTS**

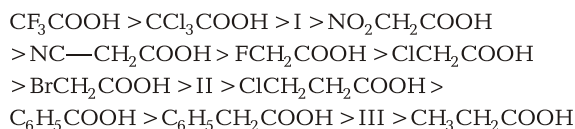
16. Which of the following compounds is not the structure of A or B or C in the reaction that follows:



Hint



17. Consider the order of decreasing acidity of following acids

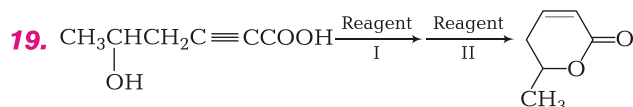


Identify I, II and III and choose the correct option.

- | | I | II | III |
|-----|----------------------------|----------------------------|----------------------------|
| (a) | CHCl_2COOH | H_3CCOOH | HCOOH |
| (b) | CHCl_2COOH | HCOOH | H_3CCOOH |
| (c) | H_3CCOOH | HCOOH | CHCl_2COOH |
| (d) | CH_3COOH | CHCl_2COOH | HCOOH |

18. When aqueous $\text{CH}_3\text{CH}_2\text{COONa}$ is electrolysed, there is formation of various organic products. Which is the major product?

- (a) $\text{CH}_2=\text{CH}_2$ (b) CH_3CH_3
(c) $\text{CH}_3\text{CH}_2\text{COOCH}_2\text{CH}_3$ (d) $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$



Reagents I and II are

- (a) $\text{Pt}/\text{H}_2, \text{H}_3\text{O}^+$ (b) $\text{Li}/\text{NH}_3, \text{H}_3\text{O}^+$
(c) $\text{H}_2/\text{Lindlar's catalyst}, \text{H}_3\text{O}^+$ (d) $\text{H}_2\text{O}/\text{Na}, \text{H}_3\text{O}^+$

Hint Lindlar catalyst changes alkynes to *cis*-alkene.

20. Match the acids given in Column I with their correct IUPAC names given in Column II and choose the correct option from the codes given below.

Column I	Column II
A. Oxalic acid	p. Hexane-1,6-dioic acid
B. Succinic acid	q. Pentane-1, 5-dioic acid
C. Adipic acid	r. Butane-1, 4-dioic acid
D. Glutaric acid	s. Ethane-1, 2-dioic acid

Codes

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

21. Identify the correct methods to convert RBr to RCOOH .



A. I = Mg/ether , II = CO_2 , III = H_3O^+

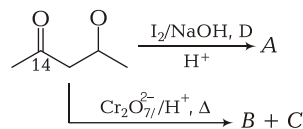
B. I = KCN , II = H_3O^+

C. I = CO_2 , II = Mg/ether , III = H_3O^+

D. I = $\text{HgSO}_4 + \text{H}_2\text{SO}_4$, II = HCN , III = H_3O^+

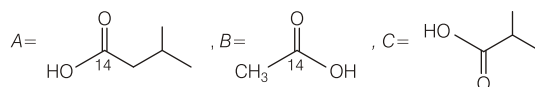
(a) A and B (b) B and C (c) C and D (d) D and A

22. Consider the following reaction with reactants carboxyl carbon as C-14. In which of the following products, this isotopic C-14 has been traced.



- (a) A (b) B (c) C (d) A + B

Hint



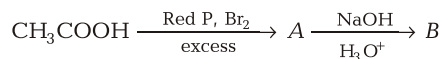
23. $\text{CH}_2 = \text{CH} - \text{CH} = \text{CH}_2 \xrightarrow[\text{(iii) CO}_2]{\text{(i) HBr}} \xrightarrow[\text{(iv) H}_3\text{O}^+]{\text{(ii) Mg/ether}} \text{X}$. What is X?

- (a) $\text{CH}_3\text{C}(=\text{O})\text{CH} = \text{CH}_2$ (b) $\text{CH}_2 = \text{CH} - \text{C}(=\text{O})\text{OH}$
(c) $\text{CH}_3\text{CH} = \text{CHCH}_2\text{COOH}$ (d) $\text{CH}_3\text{CH} = \text{CHCH}_2\text{CHO}$

24. Which of the following statements is incorrect?

- (a) Melting point of dicarboxylic acids are higher than those of monocarboxylic acids
(b) The O—H bond does not lie in the same plane of carbonyl group of carboxylic acid
(c) Molecular mass of acetic acid in benzene is 120 instead of 60
(d) Melting and boiling points of aliphatic acids are usually lower than those of aromatic acids of comparable molecular masses

25. Identify the final product in the following sequence of reaction



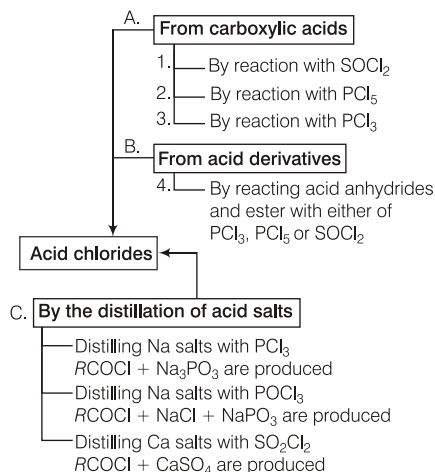
- (a) BrCH_2COOH (b) $\text{CBr}_3 - \text{CH} = \text{CH} - \text{CHO}$
(c) $\begin{array}{c} \text{COOH} \\ | \\ \text{C} \\ | \\ \text{COOH} \end{array}$ (d) $\text{BrCH}_2 - \text{CH} = \text{CH} - \text{COOH}$



ACID DERIVATIVES



Preparation



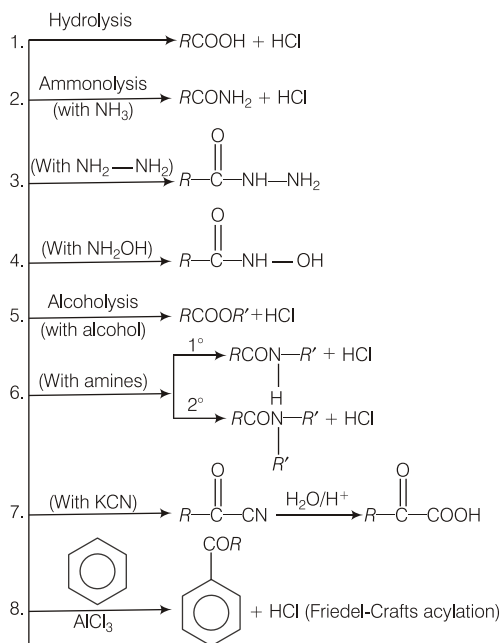
Physical Properties

Acid chlorides are colourless liquids with boiling points lower than corresponding acids with sharp pungent smell.

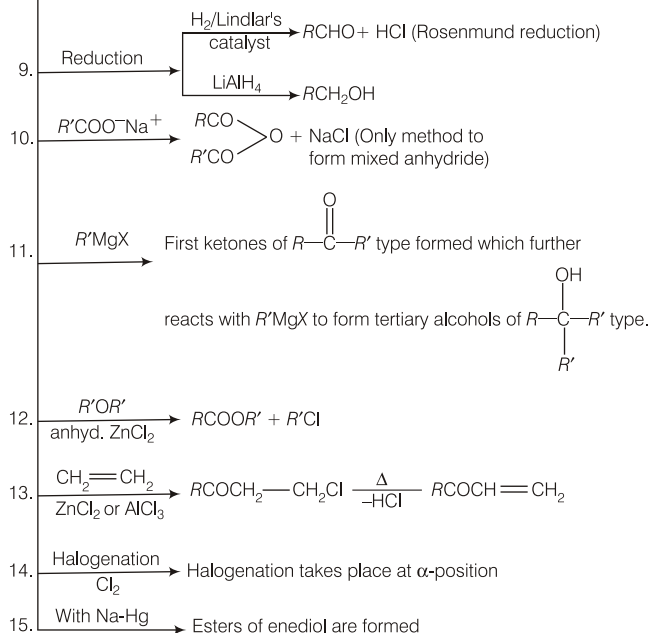
Nucleophilic Reactions (Acyl Chlorides are Preferred over Acetic Acid)

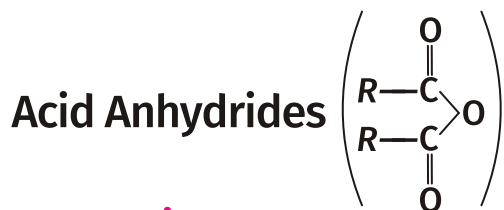
- Acyl chlorides are very reactive as compared to acetic acid. The chloride ion is an excellent leaving group as compared to hydroxide ion under normal conditions.
- Acyl chlorides can be used to prepare carboxylic acid derivatives, such as acid anhydrides, esters and amides, by reacting acid chlorides with salt of carboxylic acid, an alcohol or an amine respectively.
- In case of acyl chlorides, use of base (NaOH or pyridine) or excess amine is required to remove the hydrogen chloride as byproduct and to catalyse the reaction.
- In case of acetic acid, reactions are reversible, often leading to low yields.
- Both of these reactants (CH_3COOH and CH_3COCl) involved in preparing acid derivatives but in case of acyl chlorides, reactions are fast and irreversible. This makes the two steps route often preferable to single step reaction with the carboxylic acids.

Chemical Properties

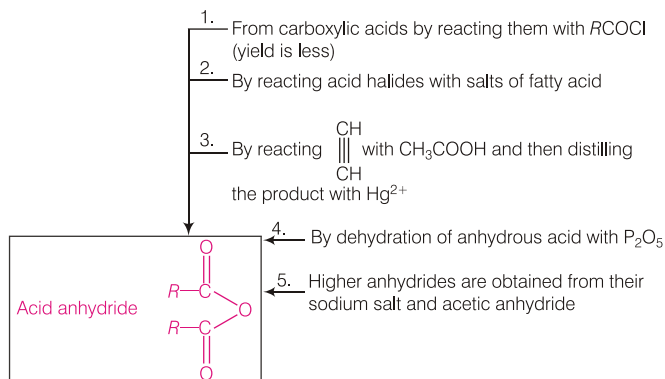


Acid chloride, RCOCl





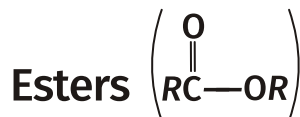
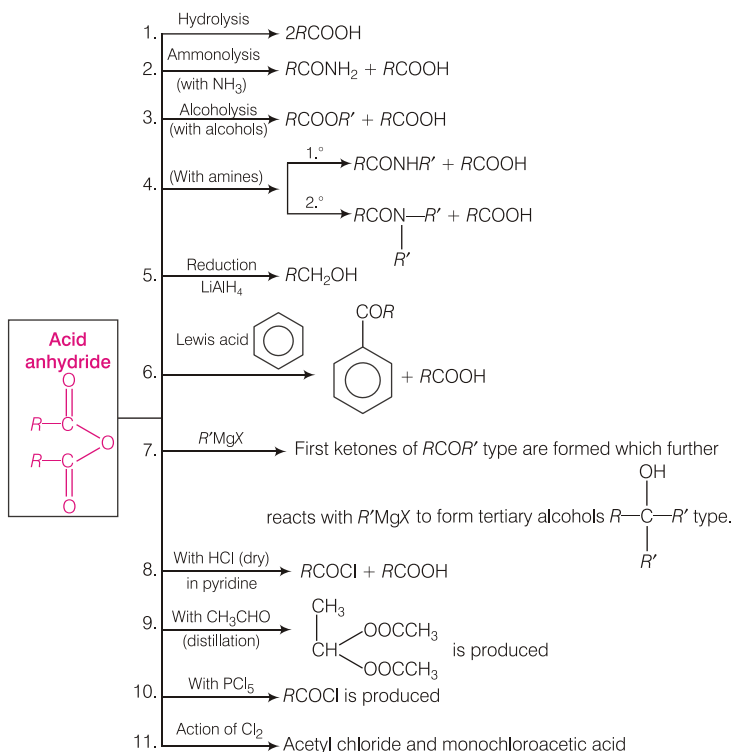
Preparation



Physical Properties

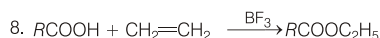
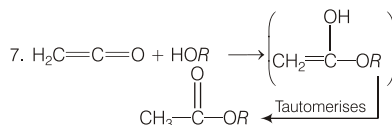
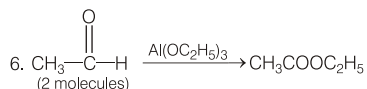
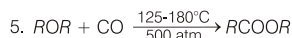
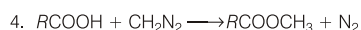
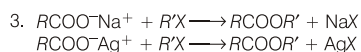
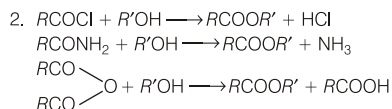
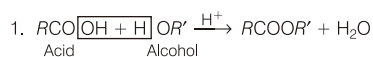
- These are colourless liquids with sharp, pungent smell, insoluble in water.
- Their boiling points are higher than corresponding acids.

Chemical Properties



Preparation

- From carboxylic acid (Fischer-Speier method)
- Reacting acid derivatives with alcohols (Alcoholysis)
- Reacting carboxylic salts with RX
- Reacting carboxylic acid with diazomethane (CH_2N_2)—methyl esters are produced with liberation of N_2 $\text{RCOOH} + \text{CH}_2\text{N}_2 \rightarrow \text{RCOOCH}_3 + \text{N}_2 \uparrow$
- The interaction between an ether and CO at $125-180^\circ\text{C}$ under 500 atm pressure in the presence of $\text{BF}_3 + \text{H}_2\text{O}$
- Tischenko reaction
By condensation of aldehyde in the presence of aluminium ethoxide
- With ketone and alcohols, produce esters.
- Reacting alkene with an acid in the presence of BF_3 .

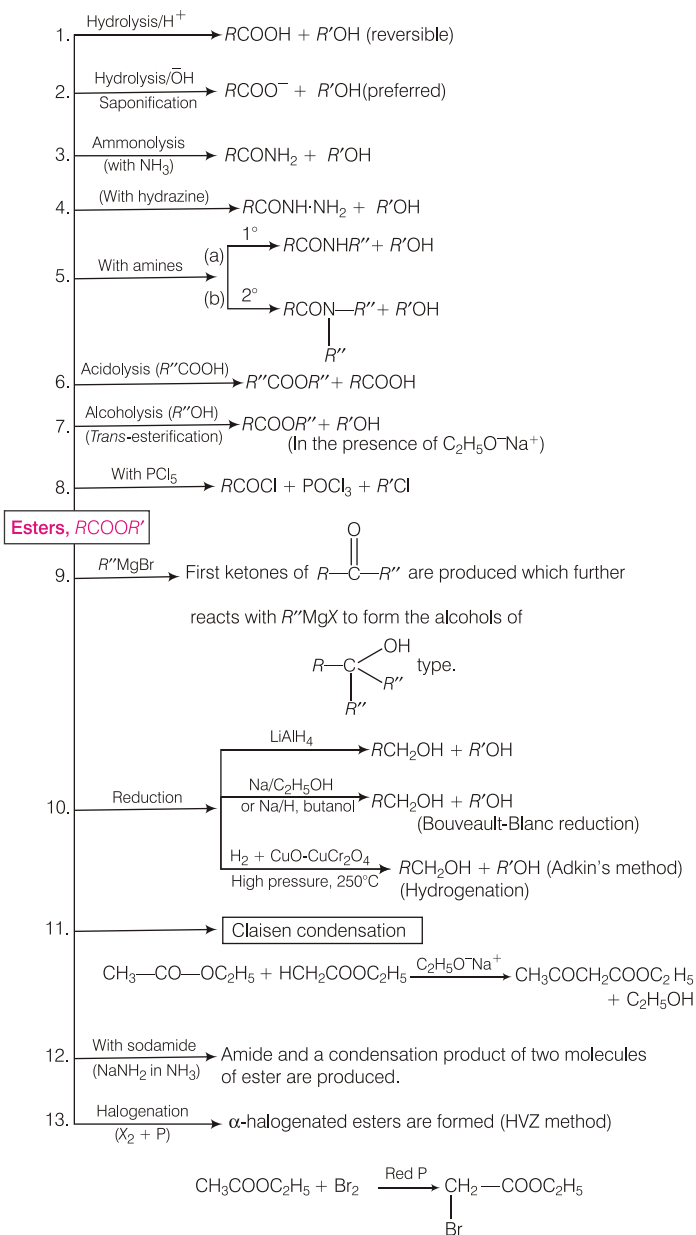


Physical Properties

- Esters are pleasant smelling liquids or solids.
- Boiling points are lower than corresponding acids.
- Insoluble in water but good solvents of other organic compounds.

{JEE FINAL TOUCH}

Chemical Properties



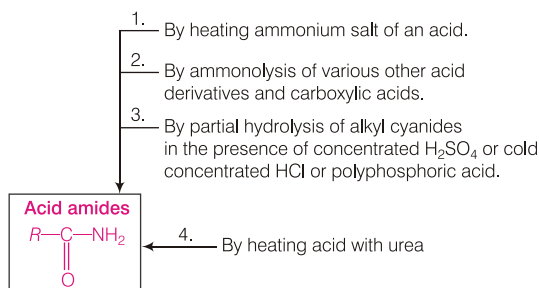
Esters as Flavouring Agents

- Esters have sweet fruity smell with low molecular mass.
- Their properties make them suitable for the preparation of cosmetics and perfumes.
- The lower is molecular mass, stronger are the odours they carry.
- Some esters are given in the following table with different flavour/odour.

Common name	IUPAC name	Flavour/ odour
Ethyl formate	Ethyl methanoate	Rum
<i>n</i> -amyl acetate	Pentyl ethanoate	Pears, bananas
Isoamyl acetate	3-methyl butyl ethanoate	Pears, bananas
<i>n</i> -octyl acetate	Octylethanoate	Oranges
Isobutyl propionate	2-methylpropyl propanoate	Rum
Methyl butyrate	Methylbutanoate	Apples
Ethyl butyrate	Ethylbutanoate	Pineapples
<i>n</i> -butyl butyrate	Butylbutanoate	Pineapples
Methyl <i>trans</i> cinnamate	Methyl (<i>E</i>)-3- phenyl prop-2-enoate	Strawberry

Acid Amides $\left(R-\overset{\overset{O}{\parallel}}{C}-NH_2 \right)$

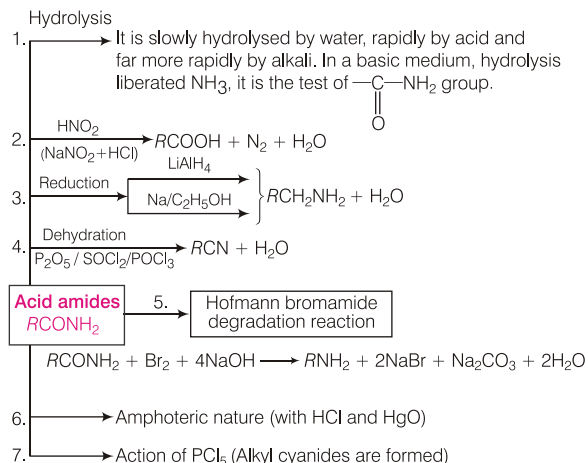
Preparation



Physical Properties

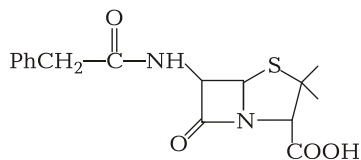
- These are white odourless, crystalline solids with sharp melting points, higher than that of corresponding acids.
- These are soluble in water because they can form H-bonds.

Chemical Properties



Best Practice SHOTS

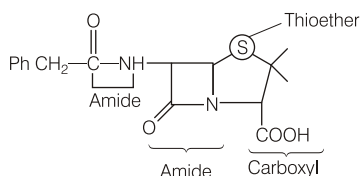
- 26.** Penicillin G is one of the antibiotics and has the following structure,



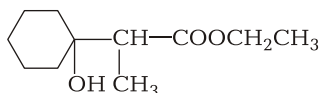
Which of the following functional groups is not present?

- (a) Keto group (b) Amide group
(c) Thioether group (d) Carboxyl group

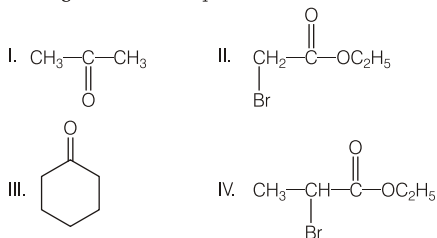
Hint Keto group



- 27.** Which reactants are required to synthesise



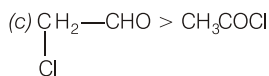
using Reformatsky reaction?



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

- 28.** Which of the following orders of boiling point is correct?

- (a) $\text{CH}_3\text{COOH} > \text{HCOOCH}_3$
(b) $\text{CH}_3\text{CONH}_2 > \text{CH}_3\text{C}(=\text{O})\text{NH}_2$

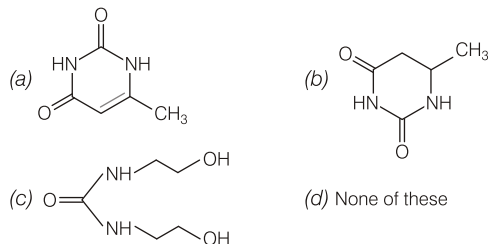


- (d) $\text{CH}_3\text{CN} > \text{CH}_3\text{NC}$

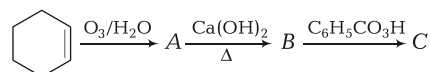
- 29.** Which of the followings is the incorrect order of reactivity of each pair towards hydrolysis?

- (a) $\text{CH}_3\text{COCl} > \text{CH}_3\text{CONH}_2$ (b) $\text{CH}_3\text{COOC}_2\text{H}_5 > \text{CH}_3\text{COCl}$
(c) $(\text{CH}_3\text{CO})_2\text{O} > \text{CH}_3\text{CONH}_2$ (d) $\text{CH}_3\text{COOCH}_3 > \text{CH}_3\text{CONH}_2$

- 30.** Enolic form of acetoacetic ester reacts with urea to form

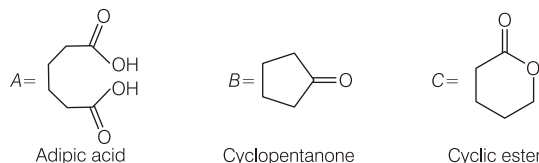


- 31.** Identify C in the following reaction:

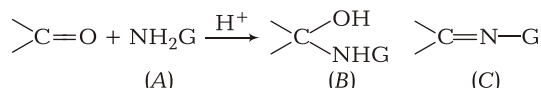


- (a) Adipic acid (b) Cyclopentanone
(c) Cyclic ester (d) Pentanal

Hint



- 32.** Match the following derivatives of ammonia in Column I with the imines formed in Column II when the following addition reaction of aldehydes and ketones taken place



Column I (A)	Column II (B)
A. NH_2OH	p. Semicarbazone
B. $\text{NH}_2\text{-R}$	q. Phenyl hydrazone
C. $\text{NH}_2\text{NHC}_6\text{H}_5$	r. Schiff's base
D. $\text{NH}_2\text{NHCONH}_2$	s. Oxime

Codes

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

- 33.** Acetamide is treated separately with the following reagents. Which one of these would give methyl amine?

- (a) PCl_5 (b) $\text{NaOH} + \text{Br}_2$
(c) Soda lime (d) Hot conc. H_2SO_4

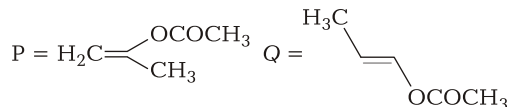
Hint Hofmann bromamide reaction.

- 34.** Benzoyl chloride is prepared from benzoic acid by

- (a) $\text{Cl}_2, h\nu$ (b) SO_2Cl_2
(c) SOCl_2 (d) $\text{Cl}_2, \text{H}_2\text{O}$

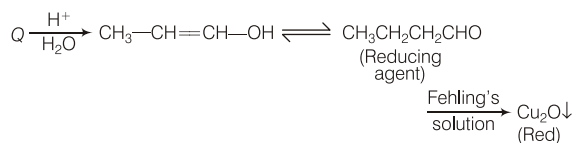
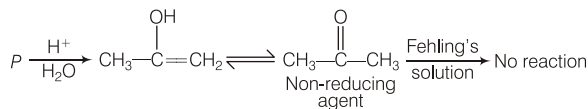
{ JEE FINAL TOUCH }

35. The products of acid hydrolysis of *P* and *Q* can be distinguished by



- (a) Lucas reagent
(c) Fehling's solution
- (b) 2, 4-DNP
(d) NaHSO₃

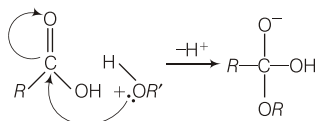
Hint



36. An enantiomerically pure acid is treated with racemic mixture of an alcohol having one chiral carbon. The ester formed will be

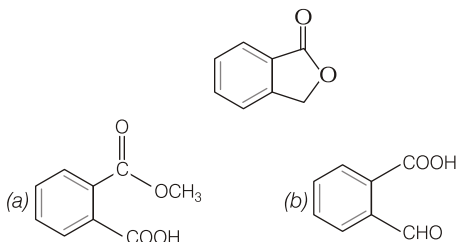
- (a) optically active mixture
(c) meso compound
- (b) pure enantiomer
(d) racemic mixture

Hint

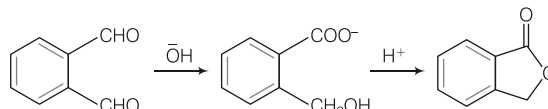


Since, nucleophiles attack at sp^2 -hybridised (planar) carbon atom, therefore it can attack from front or backside of carbon atom.

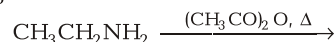
37. Which of the following reactants on reaction with conc. NaOH followed by acidification gives the following lactone as the only product?



Hint



38. What is the structure(s) of the product(s) for the following reaction?



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

39. The correct order of reactivity of acid derivatives towards a nucleophile is

- (a) $\text{RCOCl} > (\text{RCO})_2\text{O} > \text{RCOOR} > \text{RCONH}_2$
(b) $\text{RCOOR} > \text{RCOCl} > \text{RCONH}_2 > (\text{RCO})_2\text{O}$
(c) $\text{RCONH}_2 > (\text{RCO})_2\text{O} > \text{RCOOR} > \text{RCOCl}$
(d) $(\text{RCO})_2\text{O} > \text{RCOCl} > \text{RCOOR} > \text{RCONH}_2$

40. A, A is

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

Answers

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

MASTER STROKE

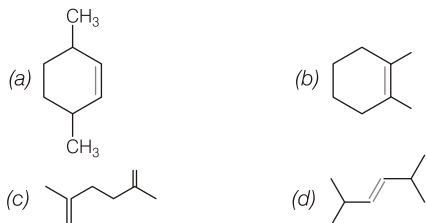
1. C_8H_{14} has three isomers. Oxidative cleavage due to ozonolysis gave the following products.

Isomer A— β , β' -dimethyl adipic acid

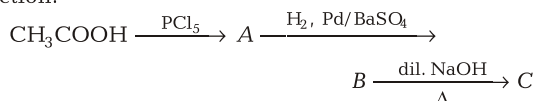
Isomer B—diketone giving iodoform test at both the keto groups.

Isomer C—isobutyric acid

Identify A, B and C and mark the incorrect isomers.



2. Identify the final product in the following sequence of reaction.



- (a) CH_3CHO (b) $CH_3CH=CHCHO$
 (c) $CH_3CH=CH-CH_3$ (d) $HCHO$

3. Select the incorrect pair.

- (a) Methanoic acid—used in rubber, textile, dyeing, leather, etc.
 (b) 2, 4-dichlorophenoxy acetic acid—herbicide
 (c) Sodium benzoate—food preservative
 (d) Vinegar—citric acid

Hint Vinegar—acetic acid

4. Which test gives negative test for CH_3CHO when distinguished with CH_3COCH_3 ?

- (a) Tollen's reagent
 (b) Fehling's solution
 (c) With $CHCl_3$
 (d) With alcohol

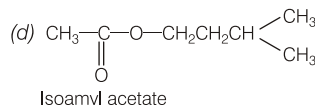
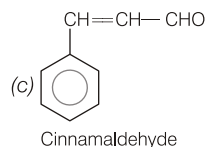
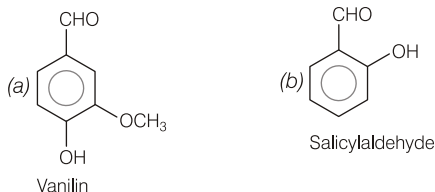
Hint With $CHCl_3$, aldehydes do not react whereas acetone forms chloroform $[CH_3)_2C(OH)CCl_3]$.

5. Cannizzaro reaction is not given by

- (a) $(CH_3)_3C-CHO$ (b) $(CH_3)_2CHCHO$
 (c) C_6H_5CHO (d) $(CH_2OH)_3C-CHO$

Hint Compound 'b' has α -H.

6. Which one of the following carbonyl compound is obtained from the bananas?



7. Which of the following is not the application of aldehydes and ketones?

- (a) Aldehydes and ketones are found in plants and animals as they play a vital role in biochemical processes of life
 (b) They are used in many food products and pharmaceuticals to add flavours
 (c) They are used as solvents and for preparing adhesives, paints, resins, perfumes, plastics, fabrics, etc
 (d) They are used for manufacture of soaps and detergents

Hint Higher fatty acids (carboxylic acids) are used for manufacture of soaps and detergents.

8. Match the common names given in Column I with IUPAC names given in Column II and choose the correct option from the codes given below

Column I	Column II
A. Acetophenone	p. Pentanal
B. Valeraldehyde	q. Prop-2-enol
C. Acrolein	r. 4-methylpent-3-en-2-one
D. Mesityl oxide	s. 1-phenylethanol

Codes

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

9. Which of the following statements are incorrect?

- (a) The C-atom of $C=O$ group is sp^2 -hybridised and forms three σ -bonds and one π -bond formed by the overlap of pure $2p$ -orbitals of C-atom with $2p$ -orbitals of O-atom
 (b) The O-atom has two lone pairs of electrons, thus C-atom of $C=O$ group and three atoms attached to it are on the same plane with bond angle of 120° and the π electron cloud is above and below the plane electron
 (c) The $C=O$ bond is polarised due to high electronegativity of O-atom relative to C-atom. Thus, C-atom acts as an electrophile and O-atom as a nucleophile. On the contrary, $C=C$, π -bond is electron source and acts as nucleophilic site
 (d) Boiling points of carbonyl compounds are lower than hydrocarbons and ethers but higher than alcohols and carboxylic acids

{JEE FINAL TOUCH}

10. Match the following names of reagents given in Column II to bring about the conversions given in Column I and choose the correct option from the codes given below.

Column I	Column II
A. Hexan-1-ol to hexanol	p. $C_6H_5NHCrO_3Cl^-$ (PCC)
B. Cyclohexanol to cyclohexanone	q. CrO_3 in presence of acetic anhydride
C. <i>p</i> -fluorotoluene to <i>p</i> -fluorobenzaldehyde	r. $K_2Cr_2O_7$ in acidic medium

Codes

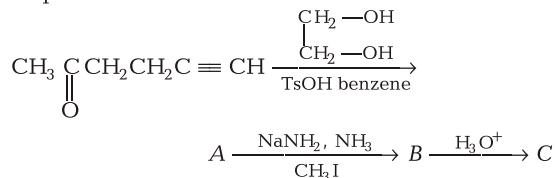
A	B	C	(a)	p	q	r
			(b)	q	r	p
			(c)	p	r	q
			(d)	q	p	r

11. Which of the following statements are wrong about reaction with Grignard's reagent?

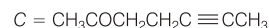
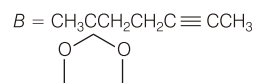
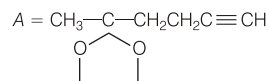
- All aldehydes forms 2° alcohols
- Weak acid is used in hydrolysis
- The reactions of organolithium and sodium acetylide reagents with aldehydes and ketones are similar to the Grignard's reaction
- It is an excellent method of C—C bond formation and can also be used for one carbon chain extension of an alcohol

Hint HCHO being an aldehyde forms 1° alcohol.

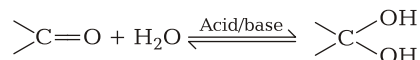
12. Identify compound C in the following reaction sequence



- $CH_3CH(OH)CH_2CH_2C\equiv CH$
- $CH_3C(=O)CH_2CH_2C\equiv CCH_3$
- $CH_3C(=O)CH_2CH_2CH_3$
- $CH_3C(=O)CH_2CH_3$

Hint

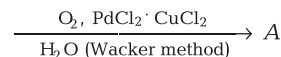
13. Carbonyl compounds form hydrates



K_1, K_2, K_3, K_4 are the equilibrium constants of hydrate formation with $CCl_3CHO, HCHO, CH_3CHO, CH_3COCH_3$. Increasing order of different values is

- $K_3 < K_1 < K_4 < K_2$
- $K_2 < K_1 < K_4 < K_3$
- $K_4 < K_3 < K_2 < K_1$
- $K_1 < K_2 < K_3 < K_4$

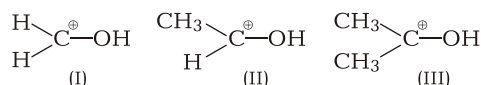
14. $B \xleftarrow[\text{(Oxo method)}]{\text{CO, H}_2} CH_3CH=CH_2$



What is the relation between A and B?

- Position isomers
- Homologues
- Enantiomers
- Functional isomers

15. Protonation of a carboxyl compound is said to increase its electrophilic nature for nucleophilic attack. Arrange the following carboxyl compounds in increasing order of potential energy.



- III < II < I
- I < II < III
- III < I < II
- II < I < III

Answers

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



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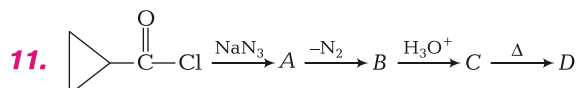
Questions to Measure Your Problem Solving Skills

1. What would be the mass of NaOH added to 200 mL of a 0.16 M HOBr solution to produce a buffer solution of pH 8.3 ? (K_a of HOBr = 2×10^{-9})
 (a) 3.67 g (b) 0.37 g
 (c) 0.037 g (d) 3.07 g
2. The work function of Na-metal is 2.28 eV. If the surface of sodium metal is exposed to a light of wavelength 400nm. The kinetic energy of photoelectrons emitted and threshold wavelength of sodium metal respectively are
 (a) 8.2eV, 545 nm (b) 0.82eV, 545 nm
 (c) 7.2eV, 640 nm (d) 7.2eV, 655 nm
3. Match the following columns.
- | Column I
(Compound) | Column II
(Use) |
|----------------------------|------------------------|
| A. Phenacetin | p. Synthetic detergent |
| B. Luminal | q. Food preservative |
| C. Phosphates | r. Antipyretic |
| D. Ethoxylated nonylphenol | s. Tranquilizer |
| E. Sodium benzoate | t. Neutral detergents |
- Codes
 A B C D E
 (a) r s t p q
 (b) r s p t q
 (c) s r t p q
 (d) p q r s t
4. Choose the correct option from the following.
 (a) Borazole is not isoelectronic and isosteric with benzene
 (b) π -electrons in benzene are completely delocalised while in borazole, they are partially delocalised
 (c) In borazole, B-atom is sp^2 while N-atom is sp^3 -hybridised
 (d) Diborane reacts with excess ammonia and forms boron nitride
5. Which series of reactions correctly represents the chemical reactions related to iron and its compounds?
 (a) $Fe \xrightarrow{\text{Dil. H}_2\text{SO}_4} FeSO_4 \xrightarrow{\text{H}_2\text{SO}_4, O_2} Fe_2(SO_4)_3 \xrightarrow{\text{Heat}} Fe$
 (b) $Fe \xrightarrow{O_2, \text{Heat}} FeO \xrightarrow{\text{Dil. H}_2\text{SO}_4} FeSO_4 \xrightarrow{\text{Heat}} Fe$
 (c) $Fe \xrightarrow{Cl_2, \text{Heat}} FeCl_3 \xrightarrow{\text{Heat, air}} FeCl_2 \xrightarrow{Zn} Fe$
 (d) $Fe \xrightarrow{O_2, \text{Heat}} Fe_3O_4 \xrightarrow{CO, 600^\circ C} FeO \xrightarrow{CO, 700^\circ C} Fe$
6. In a sample of polymer, 20% molecules have molecular mass 20,000, 50% molecules have molecular mass 30,000 and rest molecules have molecular mass 60,000. What would be the PDI for polymer?
 (a) 17.76 (b) 1.761 (c) 1.176 (d) 0.017
7. Excess of KI and dil. H_2SO_4 were mixed in 50 mL H_2O_2 . The I_2 liberated required 20mL of 0.1 N $Na_2S_2O_3$. What would be the strength of H_2O_2 in g/L?
 (a) 6.8 g (b) 0.68 g
 (c) 68 g (d) 0.068 g
8. Match the following Column I which represents biochemical reactions to the Column II representing their corresponding tests.
- | Column I | Column II |
|--|-----------------------|
| A. Protein $\xrightarrow[\text{(ii) Hg(NO}_3)_2 \text{ in HNO}_3]{\text{(i) Hg(NO}_3)_2}$ Red ppt. | p. Millon's test |
| B. Protein $\xrightarrow[\text{HNO}_3]{\text{Conc.}}$ Yellow colour | q. Xanthoproteic test |
| C. Protein + 10% aq. NaOH $\xrightarrow[\text{(ii) CuSO}_4 \text{ solution}]{\text{(i) warm}}$ Reddish-violet colour | r. Biuret test |
- Codes
 A B C A B C
 (a) q r p (b) q p r
 (c) p q r (d) r q p

9. A colourless poisonous gas *A* burns with blue flame is passed through aqueous NaOH at high pressure and temperature conditions, to give a compound *B*. *B* on heating gives *C* and *C* gives white ppt. *D* with CaCl_2 . Both *C* and *D* decolourise acidified KMnO_4 . Product *D* is
 (a) calcium oxalate (b) calcium carbonate
 (c) sodium oxalate (d) calcium sulphate
10. Choose the statements given below as True (T) or False (F) and select the correct option from the given codes.
 A. Entropy decreases in crystallisation of sucrose from solution.
 B. ΔG° tells about how far a reaction will proceed.
 C. If $\Delta H^\circ < E^\circ$, thermodynamic efficiency of a cell becomes more negative.
 D. When average value of poisson's ratio is 1.66 then the molecule is monoatomic.

Codes

	A	B	C	D		A	B	C	D
(a)	T	T	F	T	(b)	T	F	T	T
(c)	T	T	F	F	(d)	F	F	T	T



- (a) *D* is a sterically relieved cyclic ring
 (b) *B* is highly unstable and is the intermediate of this reaction
 (c) *B* is highly stable and explosive to air
 (d) *D* cannot undergo ring extension
12. Match the following columns and choose the correct option from the codes given below.

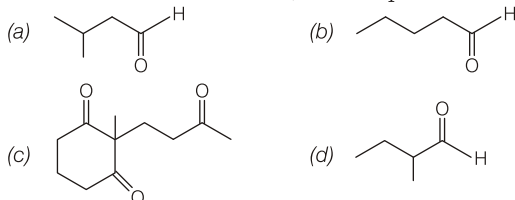
Column I (Acid)	Column II (Nature)
A. Marshall's acid	p. Dibasic
B. Fuming sulphuric acid	q. One P—O—P bond
C. Phosphinic acid	r. One peroxy linkage
D. Pyrophosphoric acid	s. Monobasic

Codes

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

13. A 100 dm^3 flask contains 10 mole each of N_2 and H_2 at 700 K. After equilibrium was reached, partial pressure of H_2 was 1 atm. At this point, 5L of $\text{H}_2\text{O}(l)$ was injected and gas mixture was cooled to 298 K. The value of gaseous pressure would be
 (a) 0.231 atm (b) 2.31 atm (c) 1 atm (d) 5 atm

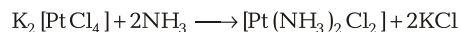
14. One of these compounds can undergoes aldol addition but not aldol condensation, the compound is



15. Among the polyhalides, stability varies as

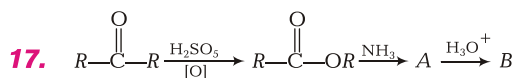
- (a) $[\text{IClBr}]^- < [\text{ICl}_2]^- < [\text{IBr}_2]^-$
 (b) $[\text{IClBr}]^- = [\text{ICl}_2]^- = [\text{IBr}_2]^-$
 (c) $[\text{IClBr}]^- > [\text{IBr}_2]^- > [\text{ICl}_2]^-$
 (d) $[\text{IClBr}]^- > [\text{ICl}_2]^- > [\text{IBr}_2]^-$

16. *cis*-platin is used as an anticancer agent for the treatment of solid tumors. It is prepared as



Given, 83.0 g of $\text{K}_2[\text{PtCl}_4]$ is reacted with 83.0 g of NH_3 . Which is the correct option from the following?

- (a) $\text{K}_2[\text{PtCl}_4]$ is excess reagent
 (b) The number of moles of NH_3 consumed is 0.4
 (c) NH_3 is the limiting reagent
 (d) Number of moles of excess reactant is 2 moles



Choose the correct option regarding this reaction.

- (a) Product *A* is more basic than *B*
 (b) *A* has two alkyl groups whereas *B* has one
 (c) *A* is a tautomeric form of *B*
 (d) *A* is less reactive towards nucleophilic addition reaction

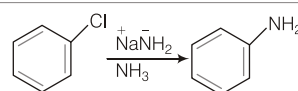
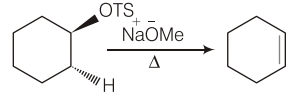
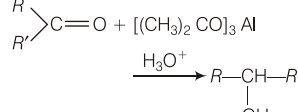
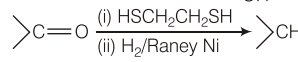
18. Aqueous solution of Ni^{2+} contains $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ and its magnetic moment is 2.83 BM. When ammonia is added in it, the predicted change in the magnetic moment of solution is

- (a) it increases from 2.83 BM
 (b) it decreases from 2.83 BM
 (c) it will remain same
 (d) it cannot be predicted theoretically

19. The rate of a reaction doubles when its temperature changes from 300 K to 310 K. Activation energy of such a reaction will be ($R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}$ and $\log 2 = 0.3010$)

- (a) 53.6 kJ mol⁻¹ (b) 48.6 kJ mol⁻¹
 (c) 58.5 kJ mol⁻¹ (d) 60.5 kJ mol⁻¹

20. Match the following columns.

Column I (Reaction)	Column II (Reaction type)
A. 	p. E ₂ -elimination
B. 	q. Meerwein Ponndorf Verley reduction
C. 	r. Benzyne elimination
D. 	s. Mozingo reduction

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Codes

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

21. Consider the following complex compounds

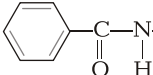
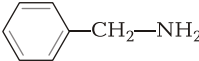


Choose the correct option from the following.

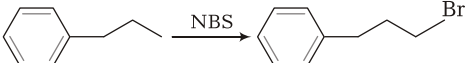
- (a) MnO_4^- , ReO_4^- are coloured but TcO_4^- is colourless
 (b) MnO_4^- , ReO_4^- and TcO_4^- all are coloured
 (c) MnO_4^- is coloured but ReO_4^- and TcO_4^- are colourless
 (d) Only TcO_4^- are coloured
22. Two buffer solutions C and D each made with benzoic acid and sodium benzoate differ in their pH by two units. C has salt: acid = $a:b$. D has salt : acid = $b:a$. If $a > b$ then the correct conclusion is
 (a) benzoic acid raises the value of pH in the solution C
 (b) sodium benzoate raises the value of pH in solution D
 (c) The ratio of a to b is 10
 (d) None of the above

23. Identify the statements given below as True (T) and False (F) and select the correct option from the codes given below.

A. Rate of solvolysis of *tert*-butyl chloride is greater than substituted allyl chloride.

B.  is less basic than 

C. Singlet carbene is more reactive than triplet carbene.

D. 

Codes

	A	B	C	D
(a)	F	T	F	T
(b)	T	F	T	F
(c)	F	T	T	F
(d)	T	T	T	F

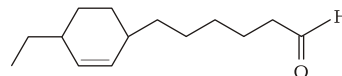
24. Choose the incorrect option from the followings.

- (a) Formation of chromium sesquioxide from ammonium dichromate is known as chemical volcano
 (b) Acidified potassium dichromate solution is used to test for drunken driver
 (c) Chlorides on heating with $\text{K}_2\text{Cr}_2\text{O}_7$ / conc. H_2SO_4 give yellow-blue fumes of chromyl chloride
 (d) Pyrolusite is an ore of manganese

25. What would be the osmotic pressure of a solution that is obtained by mixing 100 cm^3 of 1.5% solution of urea and 100 cm^3 of 3.42% solution by cane sugar at 20°C ?

- (a) 8.3 atm
 (b) 4.2 atm
 (c) 7.1 atm
 (d) 5.0 atm

26. Which one is the correct IUPAC name of the following?



- (a) (4-ethylcyclohex-1-enyl) heptanal
 (b) 6-(4-ethylcyclohex-1-enyl) hexanal
 (c) 6-(4-ethylcyclohex-2-enyl) hexanal
 (d) 4-(6-ethylcyclohex-1-enyl) heptanal

27. Choose the correct option from the followings.

- (a) Anhydrous HCl is a good conductor of electricity
 (b) Pure HI kept in a bottle acquires a brown colour after sometime
 (c) HOCl is less acidic than HOI
 (d) IBr does not exist but ClBr exists

28. CsCl crystallises in body centred cubic lattice. If a is edge length, then which of the following expressions is correct?

- (a) $r_{\text{Cs}^+} + r_{\text{Cl}^-} = 3a$
 (b) $r_{\text{Cs}^+} + r_{\text{Cl}^-} = \frac{3a}{2}$
 (c) $r_{\text{Cs}^+} + r_{\text{Cl}^-} = \frac{\sqrt{3}}{2}a$
 (d) $r_{\text{Cs}^+} + r_{\text{Cl}^-} = \sqrt{3}a$

29. Choose the correct option for the given reaction.



- (a) C is bicarboxylic acid
 (b) A is highly reactive towards nucleophilic reaction
 (c) B is 3-chlorobutanoyl chloride
 (d) This reaction is called Perkin reaction having two active hydrogens in C

30. Match the following columns.

Column I	Column II
A. XeOF_2	p. Square planar, sp^3d^2
B. XeO_2F_2	q. Octahedral, sp^3d^2
C. $\text{Ba}_2[\text{XeO}_6]^{4-}$	r. T-shaped sp^3d
D. XeF_4	s. See-saw, sp^3d

Codes

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

Answers

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

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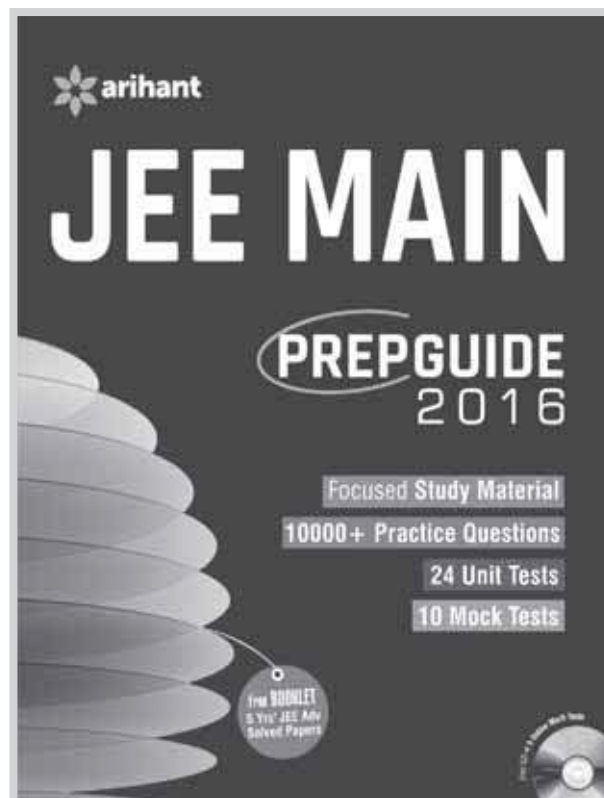
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1. Fill in the blanks.

- Acetamide gives methyl amine on treatment with ...
- Hydrogenation of benzoyl chloride in the presence of Pd and BaSO₄, gives ...
- When propionic acid is treated with aqueous sodium bicarbonate, CO₂ is liberated. The C of CO₂ comes from ...
- Benzoyl chloride is prepared from benzoic acid by ...

I	II	III	IV
(a) PCl ₅	benzyl alcohol	methyl group	Cl ₂ , hv
(b) NaOH + Br ₂	benzaldehyde	bicarbonate group	SOCl ₂
(c) Sodalime	benzoic acid	carboxylic acid group	SO ₂ Cl ₂
(d) Hot conc. H ₂ SO ₄	phenol	methylene group	Cl ₂ , H ₂ O

2. Match the extraction processes listed in Column I with metals listed in Column II.

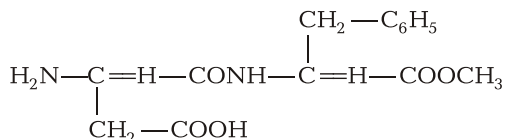
Column I	Column II
A. Self reduction	p. Pb
B. Carbon reduction	q. Ag
C. Displacement by metal	r. Cu
D. Decomposition of iodide	s. B

Codes

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

- For what concentration of Ag⁺ will the emf of the cell at 25° C be zero if concentration of Cu²⁺ is 0.01 M? Given, $E_{\text{Cu}^{2+}/\text{Cu}}^{\circ} = 0.337 \text{ V}$ and $E_{\text{Ag}^{+}/\text{Ag}}^{\circ} = 0.799$.
 (a) $4.31 \times 10^{-9} \text{ M}$ (b) $2.32 \times 10^{-9} \text{ M}$
 (c) $1.53 \times 10^{-9} \text{ M}$ (d) $0.764 \times 10^{-9} \text{ M}$

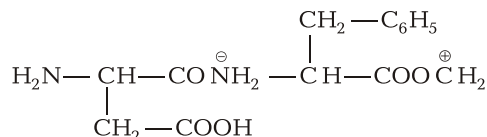
- Aspartame is an artificial sweetener (a peptide) and has the following structure.



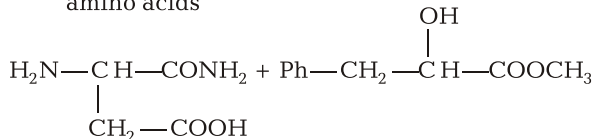
Identify the incorrect statements.

Choose the correct option.

- Four functional groups are amine, acid, amide and esters.
- The Zwitter ionic structure is

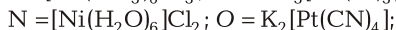
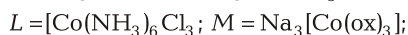


- Hydrolysis of aspartame gives the following amino acids



- One of the amino acids formed is less hydrophobic than other.
 (a) II and III (b) I, II and III
 (c) II, III and IV (d) I and IV

5. Among the following : $K = K_3[Fe(CN)_6]$;



$P = [Zn(H_2O)_6](NO_3)_2$; the diamagnetic complexes are

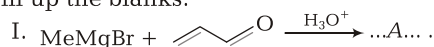
(a) K, L, M, N (b) K, M, O, P

(c) L, M, O, P (d) L, M, N, O

6. When 40 mL of 0.1 M weak base is titrated with 0.1 M HCl, pH of solution at the end point is 5.5. What will be the pH if 10 mL of 0.1 M NaOH is added to the resulting solution?

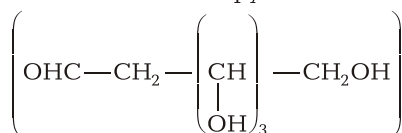
(a) 7 (b) 8 (c) 9 (d) 10

7. Fill up the blanks.

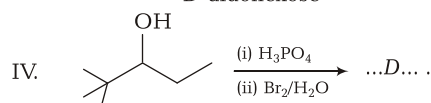


II. $\dots B \dots$ will produce a racemic mixture on chlorination.

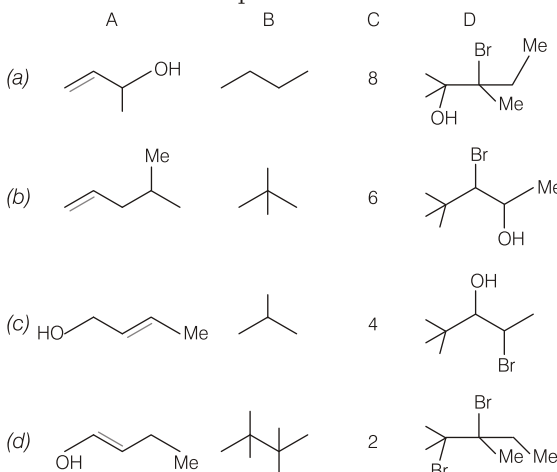
III. The total number of stereoisomers of D-aldohexose in its pyranose form are $\dots C \dots$



D-aldohexose



Choose the correct option.



8. Which of the following arrangements does not represent the correct order of the property stated against it?

(a) $V^{2+} < Cr^{2+} < Mn^{2+} < Fe^{2+}$: Paramagnetic behaviour

(b) $Ni^{2+} < Co^{2+} < Fe^{2+} < Mn^{2+}$: Ionic size

(c) $Co^{3+} < Fe^{3+} < Cr^{3+} < Sc^{3+}$: Stability in aqueous solution

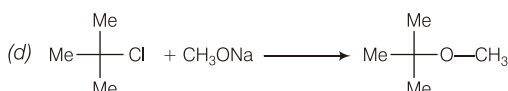
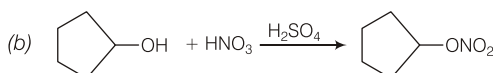
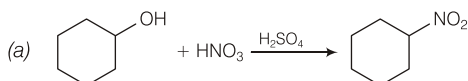
(d) $Sc < Ti < Cr < Mn$: Number of oxidation states

9. A crystal is made up of particles X, Y and Z. X forms fcc packing. Y occupies all octahedral voids of X and Z occupies all tetrahedral voids of X. If all the particles along one body diagonal are removed, then the formula of the crystal would be

(a) XYZ_2 (b) X_2YZ_2

(c) $X_8Y_4Z_5$ (d) $X_5Y_4Z_8$

10. Which of the following reactions is correct?



11. Geometrical shapes of the complexes formed by the reaction of Ni^{2+} with each Cl^- , CN^- and H_2O , respectively are

(a) octahedral, tetrahedral and square planar

(b) tetrahedral, square planar and octahedral

(c) square planar, tetrahedral and octahedral

(d) octahedral, square planar and tetrahedral

12. At 20°C , two balloons of equal volume are porous and filled to pressure of 2 atm, one with 14 kg N_2 and the other with 1 kg of H_2 . The N_2 balloon leaks to pressure of 1/2 atm in 1h. How long will it take for H_2 balloon to reach a pressure of 1/2 atm?

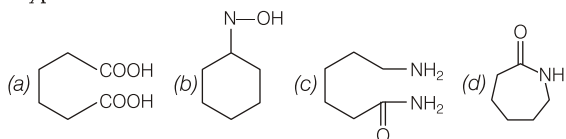
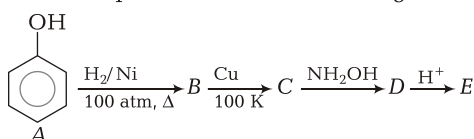
(a) 45 min

(b) 30 min

(c) 10 min

(d) 1 min

13. The final product E in the following reaction is



14. Fill up the blanks. Choose the correct option.

I. A magnesium salt of $\dots A \dots$ anion, when treated with $MgCl_2$ gives white ppt. only on boiling.

II. $\dots B \dots$ is formed upon combustion of sodium metal in excess air.

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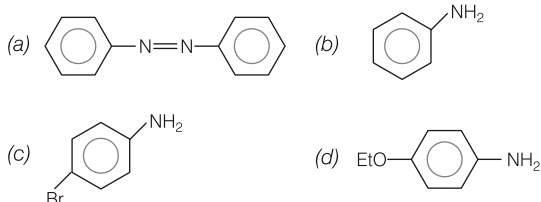
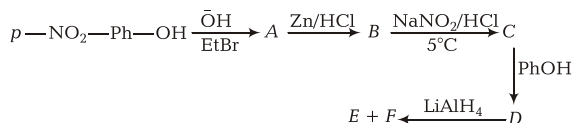
- III. ...C... is not used for softening the temporary hardness of water.
- IV. When zeolite (hydrated sodium aluminium silicate) is treated with hard water, the sodium ions are exchanged with ...D....

A	B	C	D
(a) HCO_3^-	Na_2O_2 and Na_2O	$\text{Ca}_3(\text{PO}_4)_2$	Ca^{2+} and Mg^{2+} ions
(b) SO_4^{2-}	Na_2O_2	$\text{Ca}(\text{OH})_2$	H^+ and OH^- ions
(c) CO_3^{2-}	Na_2O	Na_2CO_3	Ca^{2+} and H^+ ions
(d) NO_3^-	Na_2O and NaOCl	NaO_2	Mg^{2+} and H^+ ions

15. Liquids A and B form an ideal mixture where mole fraction of A is 0.25. At temperature T, a small quantity of the vapour is in equilibrium with the liquid is collected and condensed. This process is repeated for second time with the first condensate. The second condensate now contains 0.645 mole fraction of A. Calculate the mole fraction of B in the third condensate.

(a) 0.191 (b) 0.382 (c) 0.286 (d) 0.143

16. Identify the compound E in the following reaction.



17. Mark the statements as True or False and choose the correct option.

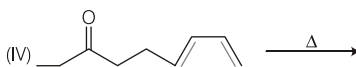
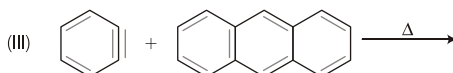
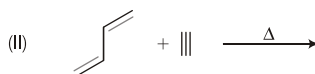
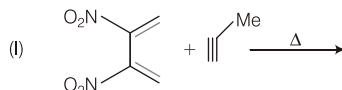
- I. $\text{B}(\text{OH})_3 + \text{NaOH} \rightleftharpoons \text{NaBO}_2 + \text{Na}[\text{B}(\text{OH})_4] + \text{H}_2\text{O}$ Addition of *cis*-1,2-diol will make the reaction to proceed in forward direction.
- II. $(\text{Me})_2\text{SiCl}_2$ on hydrolysis will produce Me_2SiO .
- III. $2(\text{CH}_3)_3\text{N} + \text{B}_2\text{H}_6 \longrightarrow [\text{BH}_2(\text{Me}_3\text{N})]^+ [\text{BH}_4]^-$.
- IV. AlF_3 is insoluble in anhydrous HF but when little KF is added to the compound it becomes soluble.

	I	II	III	IV
(a)	True	False	False	True
(b)	False	True	True	False
(c)	True	True	False	False
(d)	False	False	True	True

18. If equal volumes of solutions A and B are mixed (Resistance of solutions A and B are $R_A = 50\Omega$, $R_B = 100\Omega$) in the same conductivity cell, what will be the resistance of the mixture, using the same cell? Assume that there is no increase in the degree of dissociation of 'A' and 'B' on mixing.

(a) 75.00 Ω (b) 50.00 Ω
(c) 150.0 Ω (d) 66.66 Ω

19. Which of the following reactions would undergo Diels-Alder reaction?



(a) Only II (b) II, III and IV
(c) III and IV (d) All of these

20. Which of the following statements is incorrect? Choose the correct option.

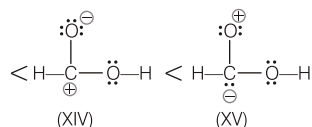
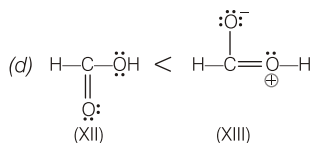
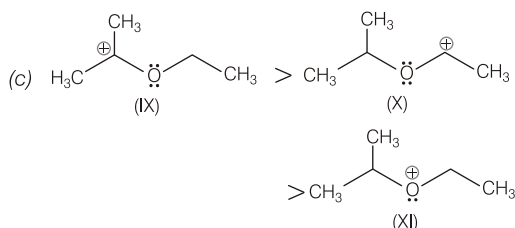
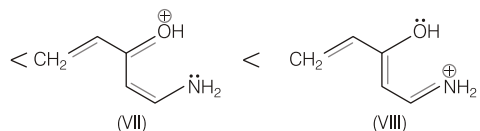
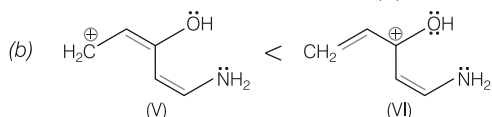
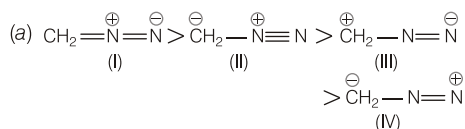
- I. Passing H_2S gas into a mixture of Mn^{2+} , Ni^{2+} , Cu^{2+} and Hg^{2+} ions in an acidified aqueous solution, precipitates of CuS and HgS are obtained.
- II. CuSO_4 decolourises on addition of KCN due to the formation of $\text{Cu}(\text{CN})_2$.
- III. MgSO_4 on reaction with NH_4OH and Na_2HPO_4 forms a white crystalline precipitate, having formula $\text{MgCl}_2 \cdot \text{MgSO}_4$.
- IV. $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ on heating gives a gas which is also given by heating NH_4NO_2 .

(a) Only I (b) Only IV
(c) II and III (d) All are correct

21. A beaker containing 0.020 mole of $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ in 200g of H_2O and a beaker containing 0.040 mole of $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ in 200 g of H_2O are placed in a chamber and allowed to equilibrate. What is the approximate concentration of $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ in the resulting solution?

(a) 0.015
(b) 0.003
(c) 0.051
(d) 0.031

22. The resonating structures of the following compounds are arranged in order of decreasing stabilities. Which option is incorrect?



23. Fill in the blanks. Choose the correct option.

- I. If uranium, $^{238}_{92}\text{U}$ emits an α -particle, the product has mass number and atomic number as ...A...
 II. The radiation from a naturally occurring radioactive substance, as seen after deflection by a magnet in one direction are ...B...
 III. The number of neutrons accompanying the formation of $^{139}_{54}\text{Xe}$ and $^{94}_{38}\text{Sr}$ from the absorption of a slow neutron by $^{235}_{92}\text{U}$, followed by nuclear fission is ...C...
 IV. $^{23}_{11}\text{Na}$ is a stable isotope $^{24}_{11}\text{Na}$ is expected to decay by ...D...

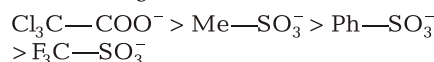
- | | | | | |
|-----|------------|--|---|-----------------------|
| | A | B | C | D |
| (a) | 236 and 92 | α -rays | 0 | β^+ -emission |
| (b) | 238 and 90 | β -rays | 1 | α -emission |
| (c) | 236 and 90 | both α, β -rays | 3 | k -electron capture |
| (d) | 234 and 90 | either α -rays or β -rays | 2 | β^- -emission |

24. A mixture of CuSO_4 and $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ has a mass of 1.245g. After heating to drive off all the water, the mass remains only 0.832 g. What is the mass per cent of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ in the mixture?

- (a) 80%
 (b) 85%
 (c) 92%
 (d) 75%

25. Mark the following statements as True/False. Choose the correct option.

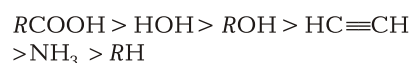
I. Basic strength



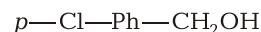
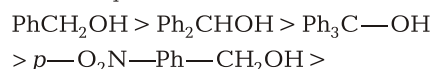
II. Boiling point



III. Acidic character



IV. Reactivity of HBr with alcohols.



- | | | | | |
|-----|-------|-------|-------|-------|
| | I | II | III | IV |
| (a) | False | True | False | True |
| (b) | True | False | True | False |
| (c) | False | True | True | False |
| (d) | True | True | True | False |

26. Match the following Column I with Column II.

Column I Reactions	Column II Equivalent mass of C-atom
A. $2\text{C} + \text{H}_2 \longrightarrow \text{C}_2\text{H}_2$	p. 4.5
B. $2\text{C} + 2\text{H}_2 \longrightarrow \text{C}_2\text{H}_4$	q. 4
C. $2\text{C} + 3\text{H}_2 \longrightarrow \text{C}_2\text{H}_6$	r. 6
D. $3\text{C} + 4\text{H}_2 \longrightarrow \text{C}_3\text{H}_8$	s. 12

Codes

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

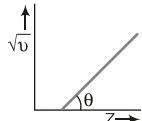
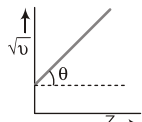
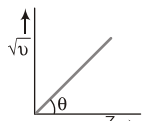
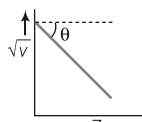
27. Polarising action of Cd^{2+} on anion is stronger than that of Ca^{2+} because

- (a) the charges of the ions are same
 (b) their radii are same
 (c) they have complete electronic energy shells configuration
 (d) All of the above options are correct

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28. Fill in the blanks. Choose the correct option.

- I. ...A... J per photon is the equivalent of energy unit 1.00 cm^{-1}
 II. ...B... is the graph between $\sqrt{\nu}$ and Z in Moseley's equation.
 III. ...C... g orbitals are present in gram subshell.
 IV. Magnetic moment of X^{3+} ion of 3d series is $\sqrt{35}$ BM ...D... is the atomic number of X^{3+} .

	I	II	III	IV
(a)	1.99×10^{-23}		9	26
(b)	1.20×10^{-12}		10	25
(c)	2.89×10^{-23}		8	27
(d)	6.71×10^{-7}		11	24

29. Select the correct pairs. Choose the correct option.

- I. Spontaneous adsorption of a gas on solid surface \rightarrow endothermic process.
 II. Temperature is decreased \rightarrow physisorption speeds up.
 III. Self-stabilising \rightarrow Lyophilic sols.
 IV. Above Critical micelle concentration \rightarrow Conductivity increases

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

30. Two second order reactions A and B have identical frequency factors. The activation energy of A exceeds that of B by 10.46 kJ/mol . At 100°C , the reaction A is 30 per cent completed after 60 min when initial concentration is 0.1 mol/dm^3 . How long will it take reaction B to reach 70 per cent completion at the same temperature of an initial concentration of 0.05 mol/dm^3 ?

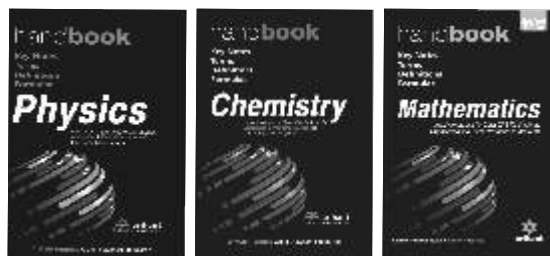
(a) 20.0 min (b) 25.0 min (c) 30.0 min (d) 22.4 min

Answers

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

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Paper I

One or More than One Options Correct Type

1. Choose the correct alternative(s) regarding

I. $[\text{Ni}(\text{CN})_4]^{2-}$ and II. $[\text{Ni}(\text{CO})_4]$.

- | I | II |
|-------------------|-------------|
| (a) Paramagnetic | Diamagnetic |
| (b) Diamagnetic | Diamagnetic |
| (c) Square planar | Tetrahedral |
| (d) Tetrahedral | Tetrahedral |

2. Which of the following compounds will give slow reaction with BuLi?



3. The standard potential of the following cell is 0.23 V at 15°C and 0.21 V at 35°C

$\text{Pt} | \text{H}_2(\text{g}) | \text{HCl}(\text{aq}) | \text{AgCl}(\text{s}) | \text{Ag}(\text{s})$

Given, the standard reduction potential of the $\text{Ag}^+(\text{aq}) | \text{Ag}(\text{s})$ is 0.80 V at 25°C.

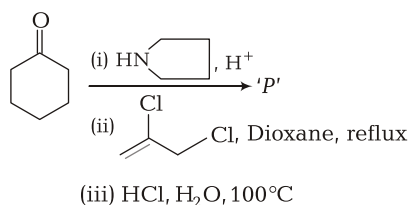
Choose the correct alternative(s) from the following.

- (a) The cell reaction can be written as
- $$\text{AgCl}(\text{s}) + \frac{1}{2} \text{H}_2 \longrightarrow \text{Ag} + \text{H}^+ + \text{Cl}^-$$
- (b) The change in entropy of the reaction is -96.5 JK^{-1}
- (c) The solubility product of AgCl in water at 25°C is 1.6×10^{-10}
- (d) None of the above

4. Choose the correct reactions involving polyhalides.

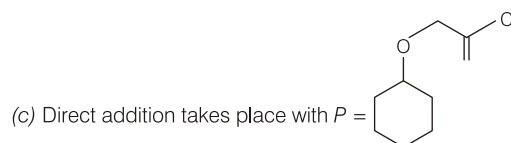
- (a) $3\text{IF}(\text{g}) + \text{BN}(\text{s}) \longrightarrow \text{NI}_3(\text{s}) + \text{BF}_3(\text{g})$
- (b) $2\text{NI}_3 \cdot \text{NH}_3(\text{l}) \longrightarrow \text{N}_2(\text{g}) + 3\text{I}_2(\text{l}) + 2\text{NH}_3(\text{g})$
- (c) $\text{ClF}_3 + \text{SbF}_5 \longrightarrow [\text{ClF}_2^+] [\text{SbF}_6^-]$
- (d) $2\text{I}_3\text{N} \cdot \text{NH}_3(\text{s}) \longrightarrow \text{N}_2(\text{g}) + 3\text{I}_2(\text{g}) + 2\text{NH}_3(\text{g})$

5. In the course of the reaction,



Choose the correct alternative(s) from the followings.

- (a) P is through enolate ion is as an intermediate
- (b) Conjugate addition takes place very rapidly

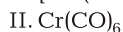
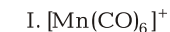


(d) Temperature provides the energy for conjugate addition

6. A 40 mL solution of a weak base, BOH is titrated with 0.1 N HCl solution. The pH of the solution is found to be 10.04 and 9.14 after the addition of 5.0 mL and 20 mL of the acid respectively. The dissociation constant of the base is

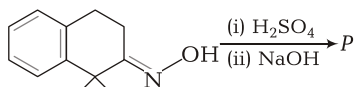
- (a) 1.8×10^{-6}
- (b) 1.8×10^{-5}
- (c) 1.8×10^{-7}
- (d) 7.2×10^{-5}

7. Consider the following complex compounds and choose the correct answer.

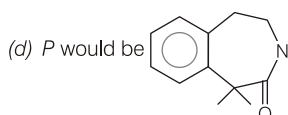
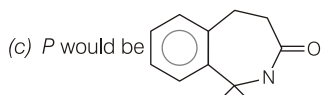


- (a) All follow 16-electron rule
 (b) The increasing order of $M-C$ bond strength is III > II > I
 (c) All follow 18-electron rule
 (d) III behaves as reducing agent

8. Consider the following reaction and choose the correct option(s).

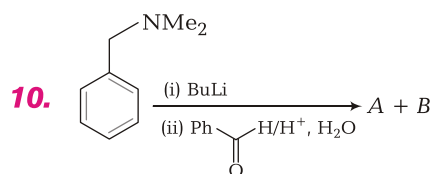


- (a) The driving force of this reaction is position of migrating and leaving group
 (b) The migrating group should be *syn* to the leaving group

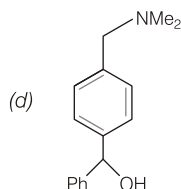
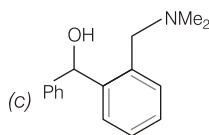
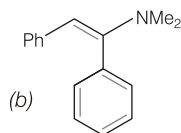
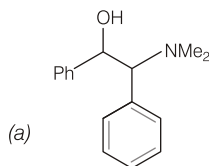


9. Choose the correct statements from the following.

- (a) The solid hydrate, $\text{HClO}_4 \cdot \text{H}_2\text{O}$ conduct electricity
 (b) Bond angle in Cl_2O is less than that in ClO_2
 (c) Cl_2O is expected to decompose spontaneously
 (d) The structure of I_3^- is square pyramidal



The major product *A* for the above reaction is/are



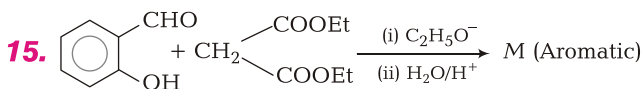
Integer Type Questions

11. A mono atomic ideal gas undergoes a process in which the ratio of p to V at any instant is constant and equal to 1. What is the value of x in the molar heat capacity calculated as $x \times R$?

12. When benzene undergoes nitration, reduction, diazotisation and acidification (H_3PO_2) respectively. If x , I -effect exhibiting groups are present in the final product of this reaction sequence. Find the value of $x + 3$.

13. Compound *X* on reduction with LiAlH_4 gives a hydride *Y* containing 21.72% hydrogen alongwith other products. The compound *Y* reacts with air explosively resulting in boron trioxide. How many water molecules are evolved, when *Y* is exposed to air?

14. It was found experimentally that a metal oxide has formula $M_{0.98}\text{O}$. Metal *M*, presents as M^{2+} and M^{3+} in its oxide. Calculate the fraction of metal approximately which exists as M^{3+} .



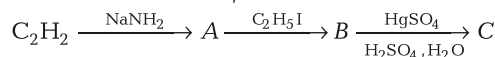
Calculate the number of π -bonds which is/are conjugated with hetero atom in the product *M*.

16. Total number of xenon compounds which contains four sigma bond pairs among the followings are XeF_4 , XeO_2F_2 , XeO_4 , $\text{Ba}_2[\text{XeO}_6]^{4-}$, XeOF_4 , XeO_3 .

17. The equilibrium concentration of carbonate ion is calculated in the form of $x \times 10^{-3} \text{M}$, when equal volumes of 1.0 M sodium carbonate and 1.0 M HCl are mixed. Find out the value of x .

$$\left[\begin{array}{l} K_a = 4.7 \times 10^{-11} \\ K_1 = 4.5 \times 10^{-7} \end{array} \right]$$

18. In the series of reaction,



How many hydrogen atom(s) is/are present in the product *C* which can participate in keto-enol tautomerism?

19. For the elementary reaction, $M \rightarrow N$, the rate of deformation of *M* increases by a factor of 8 upon doubling the concentration of *M*.

Find out the order of the reaction with respect to *M*.

20. How many biomolecules are produced by the reaction of phenol with the following?

Paracetamol, aspirin, sodium laurylsulphate; dulcin, ibuprofen.

Paper 2

Single Answer Correct Type

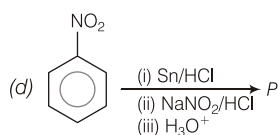
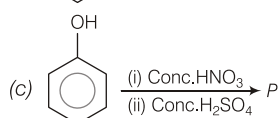
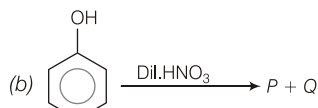
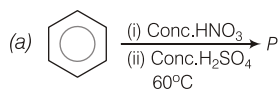
1. At constant temperature and constant pH of 4, the inversion of sucrose proceeds with a constant half-life of 300 min. At the same temperature but pH of 3, the half-life is constant at 30 min. What would be the order of reaction with respect to sucrose and with respect to $[H^+]$, respectively.

- (a) 1, 2 (b) 1, 1
(c) 2, 1 (d) 1, 3

2. Choose the incorrect statement from the following:

- (a) SCl_6 , SBr_6 and SI_6 cannot be prepared
(b) Ozonolysis of alkene gives methanal
(c) SF_6 is unreactive but SF_6 is readily hydrolysed by water
(d) The melting and boiling points vary as $H_2S \gg H_2O > H_2Se > H_2Te$

3. Which of the following reactions forms the most acidic product?



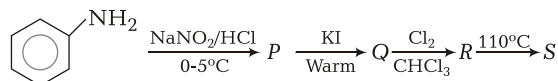
4. What would be the longest wavelength of photons in 'nm', which when made to incident upon a sample of H_2 gas will bring about photochemical decomposition followed by excitation to third Bohr's orbit, if bond energy of H_2 is 436 kg/mol?

- (a) 40.0 nm
(b) 43.3 nm
(c) 47.3 nm
(d) 50.0 nm

5. If Zn pieces are added into aqueous $FeCl_3$ solution, deep yellow colour of $FeCl_3$ fades and changes to light green, whereas, if H_2 gas is passed into $FeCl_3$ solution, there is no change in colour because

- (a) formation of nascent hydrogen in situ
(b) oxidation of Fe^{2+} to Fe^{3+} takes place
(c) Both (a) and (b)
(d) None of the above

6. Consider the following reaction sequence,

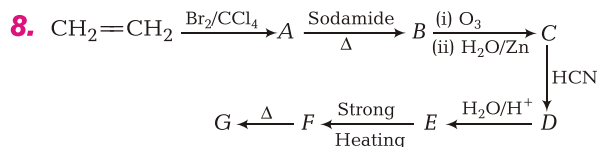


Product 'S' when reacts with sodamide, which reaction intermediate forms?

- (a) Carbocation (b) Carbanion
(c) Free radical (d) Benzyne

7. $N_0/2$ atoms of $X(g)$ are converted into $X^+(g)$ by energy E_1 . $N_0/2$ atoms of $X(g)$ are converted into $X^-(g)$ by energy E_2 . What would be the ionisation potential and electron affinity of $X(g)$ respectively?

- (a) $\frac{E_1 - E_2}{N_0}, \frac{2E_2}{N_0}$ (b) $\frac{2E_1}{N_0}, \frac{2E_2}{N_0}$
(c) $\frac{2E_1}{N_0}, \frac{2(E_1 - E_2)}{N_0}$ (d) Both (b) and (c)



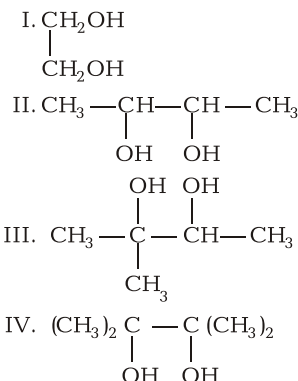
Product G is

- (a) butanoic acid (b) acetaldehyde
(c) methanoyl chloride (d) butanal

9. The complex of iron which is formed in the ring test for nitrate when freshly prepared $FeSO_4$ solution is added to an aqueous solution of NO_3^- followed by the addition of conc. H_2SO_4 . This complex is formed by the charge transfer in which

- (a) Fe^{2+} changes to Fe^{3+} and NO^+ changes to NO
(b) Fe^{2+} changes to Fe^{3+} and NO changes to NO^+
(c) Fe^{2+} changes to Fe^+ and NO changes to NO^+
(d) No charge transfer takes place

10. What would be the correct increasing order of rates of oxidation of diol with HIO_4 ?



- (a) $IV < III < II < I$ (b) $IV < III < I < II$
(c) $I < II < III < IV$ (d) $III < I < II < IV$

Paragraph Type Questions

Paragraph I

Dilute solutions of alkali metals in liquid NH_3 are blue. It is the ammoniated electron which is responsible for the blue colour of the solution and the electrical conductivity is due to the ammoniated cation, $[\text{M}(\text{NH}_3)_x]^+$ as well as the ammoniated electron, $[\text{e}(\text{NH}_3)_y]^-$. Values of x and y depend on the extent of solution. Dilute solutions are paramagnetic due to the free electrons.

- 11.** What happens if alkali metal is allowed to react with concentrated ammonia solution?
- Paramagnetic character of solvated electrons remain retained
 - Reducing character is increased rapidly
 - Reducing character is not taken into account i.e. not affected
 - Solvated electrons associate to form electron-pair and paramagnetic nature decreases
- 12.** Ammoniated solutions of alkali metals are reducing agents due to the presence of free or solvated electrons and can reduce
- $\text{K}_2[\text{Ni}(\text{CN})_4]$ to $\text{K}_4[\text{Ni}(\text{CN})_4]$
 - O_2 to O_2^{2-}
 - Both (a) and (b)
 - None of the above

Paragraph II

An organic compound A is formulated as C_7H_8 is chlorinated in the presence of sunlight to give a product B , which upon hydrolysis gives a compound C . C gives positive test with Tollen's reagent and with sodium acetate and acetic anhydride gives an acid D of equivalent mass 148.15.

- 13.** B on reaction with base gives an unstable compound. The instability of that compound is due to the presence of
- two unsaturated double bonds
 - two aldehydic groups
 - two hydroxyl groups
 - two carboxylic groups
- 14.** What is the compound formed, when the compound C reacts with Tollen's reagent?
- Benzaldehyde
 - Benzoic acid
 - Benzamide
 - Benzyne

Paragraph III

A secondary alkyl halide (P) hydrolysis with alkali (Q) in aqueous medium simultaneously via $\text{S}_{\text{N}}1$ and $\text{S}_{\text{N}}2$ path ways with rate constants k_1 and k_2 respectively. From kinetic data, it was found that a plot of $\frac{-1}{[P]} \frac{d[P]}{dt}$ versus $[Q]$

is straight line with a slope equal to $2.7 \times 10^{-4} \text{ L mol}^{-1}$ and intercept equal to 1.02×10^{-3} . Minimum initial concentration of $[P] = 0.2 \text{ M}$ and $[Q] = 0.5 \text{ M}$.

- 15.** The value of overall rate constant of the hydrolysis of P is,
- 3.29×10^{-4}
 - 1.32×10^{-3}
 - 1.29×10^{-3}
 - 6.74×10^{-5}
- 16.** The initial rate of consumption of isopropyl bromide is
- $2.31 \times 10^{-4} \text{ M min}^{-1}$
 - $2.31 \times 10^{-3} \text{ M min}^{-1}$
 - $1.00 \times 10^{-4} \text{ M min}^{-1}$
 - $5.72 \times 10^{-3} \text{ M min}^{-1}$

Matching Type Questions

- 17.** Match the following.

Column I	Column II
A. $\text{Pt}, \text{H}_2(1 \text{ atm}) \text{H}^+(10^{-3} \text{ M}) \text{H}^+(10^{-6} \text{ M}) \text{H}_2(1 \text{ atm}) \text{Pt}$	p. Spontaneous
B. $\text{Pt}, \text{F}_2(\text{g})(1 \text{ atm}) \text{F}^-(10^{-2} \text{ M}) \text{F}^-(10^{-3} \text{ M}) \text{F}_2(\text{g})(2 \text{ atm}) \text{Pt}, E_{\text{cell}} = 0.699 \text{ V}$	q. Non-spontaneous
C. $\text{Hg}, \text{Hg}_2\text{Cl}_2(\text{s}) \text{KCl}(\text{Saturated solution}) \text{H}^+(\text{pH} = 10) \text{O}, \text{OH}_2 \text{Pt} E_{\text{cell}} = 0.13 \text{ V}$ $E_{\text{SCE}} = 0.24, E_{\text{O}/\text{H}_2\text{O}} = 0.7 \text{ V}$	r. Endergonic
D. $\text{Q} + 2\text{H}^+(\text{pH} = 2) + 2\text{e}^- \longrightarrow \text{H}_2\text{Q}(\text{s})$ $E_{\text{cell}}^\circ = 0.7 \text{ V}, E_{\text{cell}} = 0.582 \text{ V}$	s. Exergonic

Codes

- A B C D
- p,s q,r q,s p,s
 - q,s p,s q,r p,s
 - q p,s r s
 - p,r q,r p,s p,r

- 18.** Match the following.

Column I (Type of sulphur/sulphur containing compound)	Column II (Oxidation state of sulphur/property of compound)
A. Engle's sulphur	p. +6
B. $\text{H}_2\text{S}_2\text{O}_7$	q. Rings, chair conformation
C. $\text{H}_2\text{S}_2\text{O}_8$	r. Crystalline form – yellow crystals
D. Rhombic sulphur	s. +7

Codes

- A B C D
- q p r s
 - q p s r
 - p q r s
 - r p q s

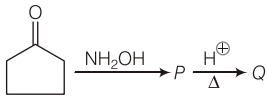
19. Match the followings.

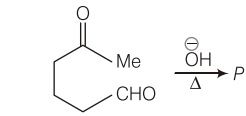
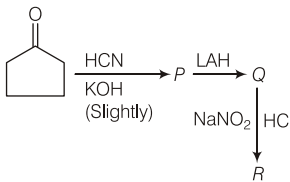
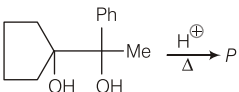
Column I (Statement/Reaction)	Column II (M)
A. M is stable and thermally decomposes at 1300°C.	p. PH_3
B. M is stable and decomposes at 440°C.	q. H_2SO_4
C. Naphthalene \xrightarrow{M} phthalic acid	r. NH_3
D. Perchloric acid \xrightarrow{M} Cl_2O_7	s. H_3PO_4 -10°C.

Codes

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

20. Match the following.

Column I	Column II
A. 	p. Final product is α,β -unsaturated ketone or ketone.

B. 	q. Formation of 6-membered ring.
C. 	r. Final product will give positive Tollen's test.
D. 	s. Ring expansion takes place.

Codes

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

Answers

Paper 1

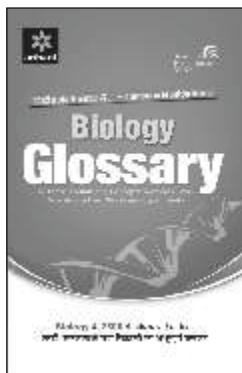
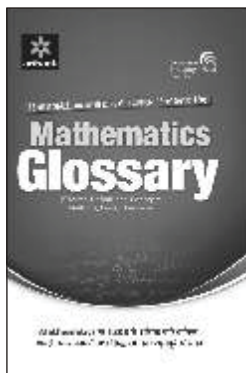
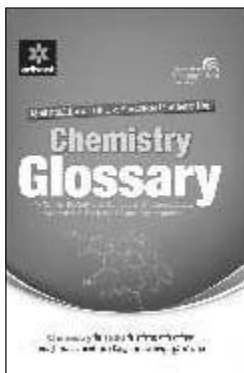
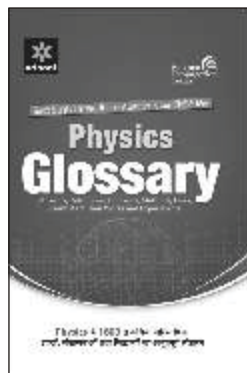
1. (b,c) 2. (a,c,d) 3. (a,b,c) 4. (a,c,d) 5. (a,b,d) 6. (b) 7. (a,c) 8. (a,c) 9. (a,b,c) 10. (c)
11. (2) 12. (3) 13. (3) 14. (4) 15. (4) 16. (3) 17. (5) 18. (5) 19. (3) 20. (2)

Paper 2

1. (b) 2. (d) 3. (c) 4. (b) 5. (a) 6. (d) 7. (b) 8. (b) 9. (c) 10. (a)
11. (d) 12. (c) 13. (c) 14. (b) 15. (c) 16. (a) 17. (b) 18. (b) 19. (c) 20. (c)

GLOSSARIES of

(Physics, Chemistry, Mathematics & Biology)

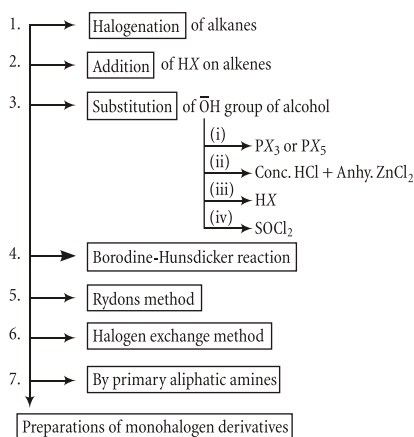


10+2,
इंजीनियरिंग
व मेडिकल
प्रवेश परीक्षाओं में
अध्ययनरत्न विद्यार्थियों
के लिए पारिभाषिक
शब्दों, संकल्पनाओं
तथा सिद्धान्तों का
अभूतपूर्व संकलन

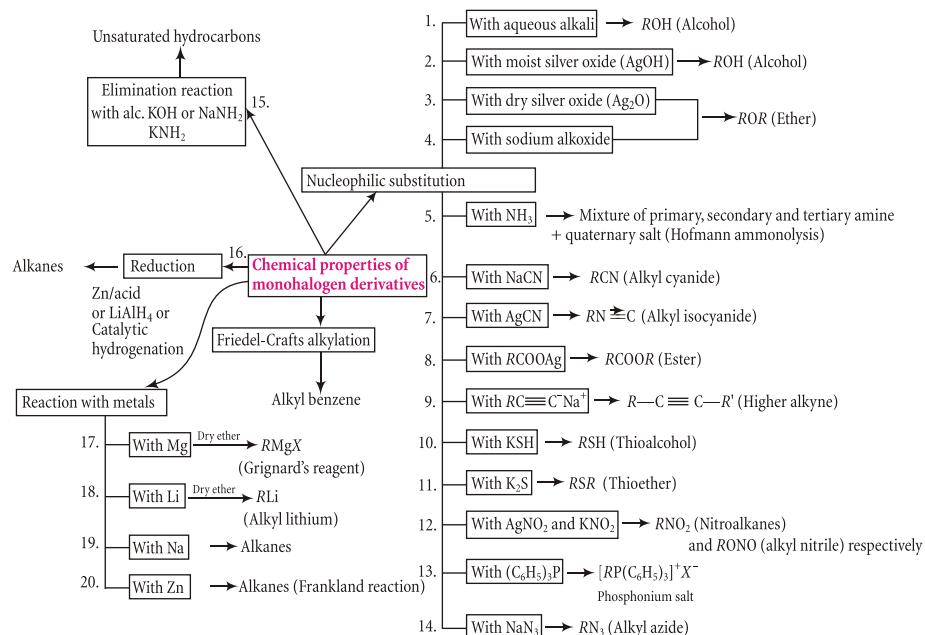
- Organic compounds formed by the replacement of one or more hydrogen atoms from aliphatic and aromatic hydrocarbons by an equal number of halogen atoms are called **haloalkanes** and **haloarenes** respectively.
- These are further classified as primary (1°), secondary (2°) and tertiary (3°) depending upon the fact that hydrogen is attached to primary, secondary or tertiary carbon atom.
- The compounds, in which two halogen atoms are present at the same carbon atom, are called *geminal* (*gem*) dihalides.
- The compounds in which two halogen atoms are present at the adjacent carbon atoms, are called *vicinal* (*vic*) dihalides.
- The compounds in which the two halogen atoms neither occupy the same nor the successive carbon atoms are called α - and ω -dihalogen derivatives.

HALOALKANES

(i) Monohalogen Derivatives



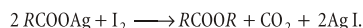
Reaction 3. These reactions are nucleophilic substitution reactions and follow S_N1 or S_N2 mechanism according with alcohol used.



- (i) PBr_5 and PI_5 are highly unstable compounds due to steric hindrance therefore, only chlorides are prepared by this method.
- (ii) Mixture of (1 : 1) dry HCl and anhydrous $ZnCl_2$ is called **Lucas reagent**.
- (iii) The reactivity of alcohols towards HX is, allyl, benzyl $> 3^\circ > 2^\circ > 1^\circ$ and reactivity of halogen acids is, $HI > HBr > HCl > HF$.
- (iv) The reaction of $SOCl_2$ with alcohol is called **Darzens procedure** Bromoalkanes and iodoalkanes are not prepared by this method.

Reaction 4. In this method, when silver salt of fatty acids is treated with Br_2 in refluxing CCl_4 , decarboxylation occurs. This reaction follows free radical mechanism.

- When iodine is used in the place of Br_2 , the reaction is modified as



- This modified reaction is called **Birnbaum Simonini reaction**.

Reaction 5. In this method, alcohol is heated with halogen in the presence of triphenyl phosphate.

Reaction 6. Alkyl chloride or bromide $\xrightarrow{NaI / \text{acetone}}$ Alkyl iodide + Sodium chloride or bromide $\xrightarrow[\text{like } Hg_2F_2]{\text{Inorganic fluorides}}$ Alkyl fluoride + Mercury (I) chloride or bromide

This reaction is called **Finkelstein-reaction**.

Reaction 7. The reaction between 1° aliphatic amines and nitrosyl chloride and bromide gives their corresponding alkyl chloride and alkyl bromide respectively.

Reactions used for distinguishing between vicinal and geminal dihalides

- gem*-dihalides that give aldehyde on hydrolysis, would be terminal dihalides.
- gem*-dihalides that give ketone on hydrolysis, would be non-terminal dihalides.
- When any of dihalide on reaction with KCN, followed by hydrolysis yields an anhydride, it will be a *vic*-dihalide.
- When any dihalide on reaction with KCN, followed by hydrolysis and heat gives a monobasic acid, it will be a *gem*-dihalide.

Revisio CONCE HALOALKANES AND

PHYSICAL PROPERTIES OF HALOALKANES

MONOHALOGEN DERIVATIVES

- CH_3Cl , CH_3Br , CH_3F and C_2H_5Cl are gases at room temperature, rest alkyl halides upto C_{18} are colourless liquids and beyond it, these are colourless solids.
- Soluble in polar solvents like water while insoluble in non-polar solvents like ether, benzene etc.
- Fluoro and chloro compounds are lighter whereas bromo and iodo derivatives are heavier than water.
- The density of alkyl halides decreases, as the size of alkyl group increases.
- Boiling points are in the order $RI > RBr > RCl > RF$, while in case of isomeric halides the order is $1^\circ > 2^\circ > 3^\circ$.

DIHALOGEN DERIVATIVES

- These are colourless, volatile and mildly sweet sour liquids.

HALOFORMS

- $CHCl_3$ and $CHBr_3$ are sickly smelling liquids, while $CHCl_3$ exists in the form of yellow, hexagonal plates.

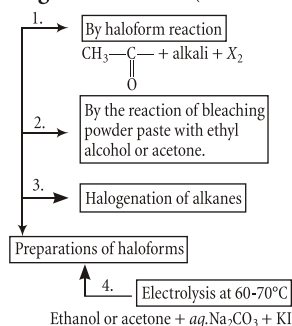
(ii) Dihalogen Derivatives

Alkylene and Alkylidene Dihalides

These can be prepared by the following methods

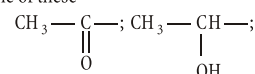
- (i) Addition of halogens to alkenes and alkynes
- (ii) Substitution reaction of *vicinal* glycol with PX_5 or HX
- (iii) Reaction of aldehydes and ketones with PX_5
- These show the following chemical properties
 - (i) With alc. KOH gives alkynes
 - (ii) With Zn dust gives alkenes
 - (iii) With aqueous alkali, *vicinal* dihalides gives glycol and *geminal* dihalides gives ketones.
 - (iv) With KCN and H_2O , *geminal* dihalides gives monobasic acid and *vicinal* dihalides gives dibasic acid.

(iii) Trihalogen Derivatives (Haloforms)



Reaction 1.

- KOH may also be used as alkali.
- The compounds, which can give this test, must contain either one of these



on through PT MAP ND HALOARENES

ALKANES AND HALOARENES

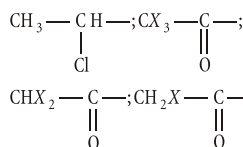
- Their boiling points increase with increase in molecular weights.
- CHCl_3 and CHBr_3 are sparingly soluble in water but more soluble in organic solvents, CHI_3 is insoluble in H_2O but soluble in ether and ethanol.

POLYHALOGEN DERIVATIVES CCl_4

- It is colourless, non inflammable and poisonous liquid with characteristic odour. It has significantly low boiling point (-77°C) and is insoluble in water but soluble in organic solvents.
- **Freons** These are gases at room temperature and liquids when cooled or compressed.
- These are colourless, odourless and non-flammable gases.
- Some freons have ether like smell.

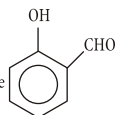
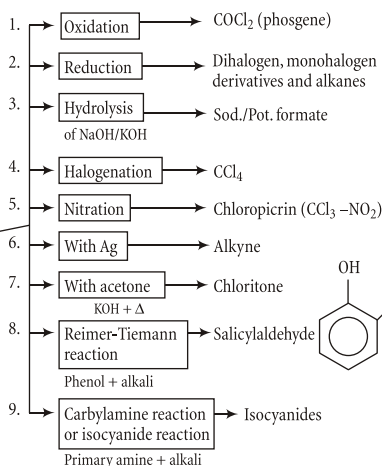
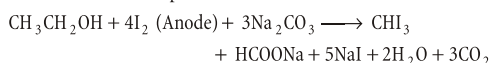
HALOARENES

- Heavier than water, polar but immiscible in water.



Reaction 2. It is a modified form of haloform reaction in which bleaching powder (CaOCl_2) works as the source of halogen (Cl_2) and weak base $\text{Ca}(\text{OH})_2$. This reaction is used for the preparation of only CHCl_3 .

Reaction 4. The complete reaction looks like



Reaction 1

This reaction occurs in the presence of sunlight and as a result of it, a poisonous gas (phosgene) is obtained. Hence, CHCl_3 cannot

be used for anaesthetic purpose. It can be preserved in brown or blue coloured bottles. It is mixed with 1% $\text{C}_2\text{H}_5\text{OH}$ which prevents oxidation or can convert COCl_2 to non-poisonous ethyl carbonate. On oxidation by strong H_2SO_4 and $\text{K}_2\text{Cr}_2\text{O}_7$, following reactions are obtained



Reaction 7

On condensation with acetone, chloretone () is obtained, which is used as hypnotic.

Reaction 8

- Alkaline solution of phenol with CHCl_3 , on refluxing at 60°C and on subsequent acidification gives *o*-hydroxybenzaldehyde.
- A small amount of *p*-isomer is also formed which is separated from *o*-isomer by steam distillation.
- If *o*-position of phenol is occupied, $-\text{CHO}$ group enters at *p*-position.
- Under similar conditions, pyrrole gives pyrrole-2-aldehyde.
- If CCl_4 is used in place of CHCl_3 , the product obtained is salicylic acid (*o*-hydroxy benzoic acid) alongwith a little *p*-hydroxy benzoic acid.

Purity Tests for Chloroform

- It should be absolutely transparent and colourless.
- It should not give yellow colour on shaking with conc. H_2SO_4 .
- It should not turn blue litmus red.

Chemical Tests for Chloroform

- On heating with Fehling's solution gives a brown ppt.
- Gives a grey ppt. of silver with Tollen's reagent.
- Gives pungent smell on heating with 1° amine and KOH.

Dangers of Chloroform to Human Body

- Effects noticed in humans exposed to chloroform *via* anaesthesia include change in respiratory rate, cardiac effects, gastrointestinal effects such as nausea, vomiting and effects on the liver and kidney.
- Chloroform is not currently used as a surgical anesthetic.
- In humans, a fatal oral dose of chloroform may be as low as 10 mL (14.8g), cause death due to respiratory or cardiac arrest.

Uses of Haloforms

- In the synthesis of drug like chlorotone and insecticide like chloropicrin.
- As an anaesthetic.
- Used as a solvent for fats, waxes, rubber, iodine.
- Iodoform is used as an antiseptic for wounds.

(iv) Polyhalogen Derivatives

Carbon Tetrachloride (CCl_4) It is prepared by the chlorination of methane, chloroform, carbon disulphide and propane under different conditions.

Polyhalogen Derivatives CCl_4

- It shows the following chemical properties
- On reduction with $\text{Fe}/\text{H}_2\text{O}$ and Fe/HCl it produces CH_2Cl_2 and CHCl_3 respectively.
- On hydrolysis with *aq.* KOH, it gives K_2CO_3 .
- On oxidation with steam, it produces poisonous phosgene (COCl_2) gas.
- It reacts with phenol and *aq.* KOH to produce salicylic acid. This reaction is called Reimer-Tiemann reaction.
- CFCs and HCFCs are usually produced by the halogen exchange starting from chlorinated methanes and ethanes.
- These are used as a refrigerant in air conditioning system.

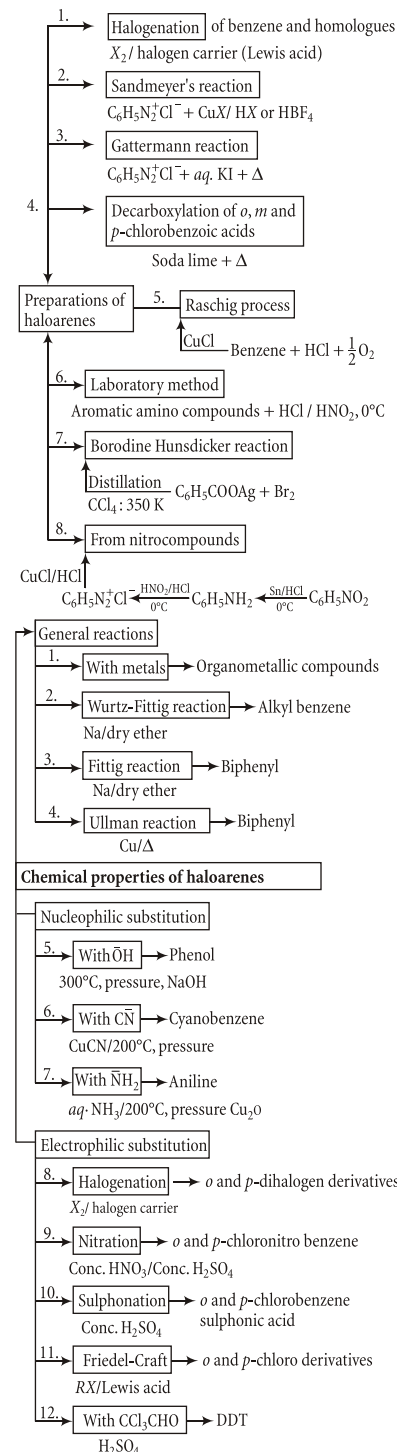
Freons

- These are chlorofluorocarbons (CFCs), contain carbon, chlorine and fluorine and produced as the volatile derivatives of methane and ethane.
- A common subclass is the hydrochlorofluorocarbons (HCFCs), which contains hydrogen as well.

DDT (*p, p'*-dichlorodiphenyl trichloroethane)

- It is colourless, tasteless and almost odourless, crystalline organochloride, known for its insecticidal properties.
- It was initially used by the military in world war II to control, malaria, typhus, body lice and bubonic plague.
- It is moderately toxic, can cause cancer and considered as carcinogenic substance.
- Recently, India entered into an agreement with the UN to end the use of insecticide DDT by 2020.

HALOARENES



JEE Final Touch

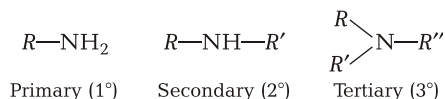
Fast Track Revision

Organic Compounds Containing Nitrogen



ALIPHATIC AMINES

- Amines have general formula RNH_2 , R_2NH or R_3N , where, R is an alkyl or aryl group.
- Amines are classified as primary, secondary or tertiary, according to the number of groups attached to the nitrogen atom.



- These are sp^3 -hybridised and pyramidal in shape with bond angle very close to 109.5° , e.g. the bond angle for trimethyl amine is 108° .

Methods of Preparation of Aliphatic Amines

S.No.	Method	Reaction involved
I For Primary Amines		
1.	By reduction of (i) Alkyl nitriles	$R-C \equiv N \xrightarrow[\text{Alcohol}]{LiAlH_4} RCH_2NH_2$ $R-C \equiv N \xrightarrow[Alcohol]{Na} RCH_2NH_2 \text{ (Mendius reaction)}$
	(ii) Nitroalkanes	$RNO_2 + 3H_2 \xrightarrow[Ni/250^\circ C]{\text{or LAH or } H_2/Pt} RNH_2$
	(iii) Oximes	$R-CH=NOH \xrightarrow[\text{Ether}]{LiAlH_4} RCH_2NH_2 + H_2$
	(iv) Amides	$RCONH_2 \xrightarrow{LiAlH_4} RCH_2NH_2 + H_2O$
2.	Gabriel phthalimide synthesis	

S.No.	Method	Reaction involved
3.	Reductive amination of carbonyl compounds	$RCHO \xrightarrow[-H_2O]{NH_3} R-\overset{\overset{H}{ }}{C}=NH$ <p style="text-align: center;">Imine</p> $\xrightarrow[Ni \text{ or } NaBH_3CN]{H_2} RCH_2NH_2$
4.	Curtius method	$RCOCl \xrightarrow[-N_2]{NaN_3} R-\overset{\overset{O}{ }}{C}-N$ <p style="text-align: center;">Intramolecular alkyl shift</p> $R-N=C=O \xrightarrow{2NaOH} RNH_2$
5.	Hofmann bromamide degradation	$RCONH_2 + Br_2 + 4KOH \xrightarrow{\Delta} RNH_2 + 2KBr + K_2CO_3 + 2H_2O$
6.	Schmidt rearrangement	$R-\overset{\overset{O}{ }}{C}-OH + N_3H \xrightarrow[\Delta]{\text{Conc. } H_2SO_4} RNH_2 + CO_2 + N_2$
II For Secondary Amines		
1.	Reaction of RX with 1° amine	$RNH_2 + RX \xrightarrow{NaOH} R_2NH + NaX + H_2O$
2.	By reduction of (i) isonitriles (ii) N-substituted amides	$RN \equiv C + 2H_2 \xrightarrow[Ni \text{ or } Pt]{} RNHCH_3$ $RCONHR' \xrightarrow[\text{Ether}]{LiAlH_4} RCH_2NHR'$
3.	Reductive amination of carbonyl compounds	$RCHO \xrightarrow{R'NH_2} [R-\overset{\overset{H}{ }}{C}=NR']$ <p style="text-align: center;">Imine</p> $\xrightarrow[Ni]{H_2} R-CH_2-NH-R'$

{ JEE FINAL TOUCH }

S.No.	Method	Reaction involved
III For Tertiary Amines		
1.	Reaction of excess RX with NH_3	$3RX + NH_3 \longrightarrow \left[\begin{array}{c} R_3N^+ \\ \\ H \end{array} \right] X^- \xrightarrow{NaOH} R_3N + NaX + H_2O$
2.	Reduction of N, N-disubstituted amides	$R-\overset{\overset{O}{\parallel}}{C}-NR'_2 \xrightarrow[\text{Ether}]{LiAlH_4} RCH_2NR'_2$
3.	Decomposition of tetraalkyl ammonium hydroxide	$R_4\overset{\oplus}{N}OH \xrightarrow{\Delta} R_3N + H_2O + CH_2=CH_2$
IV For Mixture of Amines		
1.	Hofmann ammonolysis method	$RI \xrightarrow[-HI]{NH_3/393K} R\ddot{N}H_2 \xrightarrow[-HI]{RI} R_2\ddot{N}H \xrightarrow[-HI]{RI} R_3\overset{\oplus}{N} \xrightarrow[-HI]{RI} [R_4\overset{\oplus}{N}]I^-$
2.	By reacting alcohols with ammonia	$ROH + NH_3 \xrightarrow[620K]{Al_2O_3} RNH_2 \xrightarrow[-H_2O]{ROH} R_2NH \xrightarrow[-H_2O]{ROH} R_3N \xrightarrow[-H_2O]{ROH} R_4\overset{\oplus}{N}OH$

Physical Properties

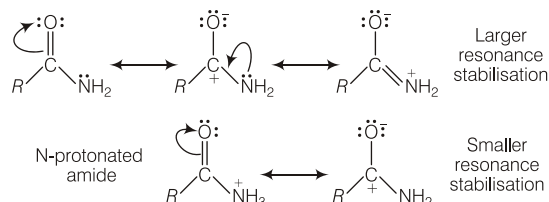
- Aliphatic amines with one or two carbon atoms are gases with fishy odour.
- Primary amines with three or more carbon atoms are liquid due to the presence of intermolecular hydrogen bonding.
- Solubility** These are soluble in water due to intermolecular hydrogen bonding and the order of solubility is 1° amines $>$ 2° amines $>$ 3° amines (due to decrease in extent of H-bonding from 1° to 3° amine).
- Solubility of alcohols $>$ amines (alcohols are more polar than amines).
- Boiling point** 1° amine $>$ 2° amine $>$ 3° amine, alcohols $>$ amines. The reason is same as the reason for the solubility order.
- Basic character of amines** They possess different order of basic strength in gaseous and aqueous phase due to steric hindrance and solvation effect.

Gaseous phase	Aqueous phase
In gaseous phase, the order of basicity is as expected, i.e. $R_3N > R_2NH > RNH_2 > NH_3$ $3^\circ \quad 2^\circ \quad 1^\circ$	Due to solvation effect and steric hindrance by alkyl group in aqueous phase, the order of basic strength is deviated from normal and shows the following order: $(CH_3)_2NH > CH_3NH_2 > (CH_3)_3N > NH_3$ $(C_2H_5)_2NH > (C_2H_5)_3N > C_2H_5NH_2 > NH_3$
where, R = alkyl group	

Basicity of Amines and Amides

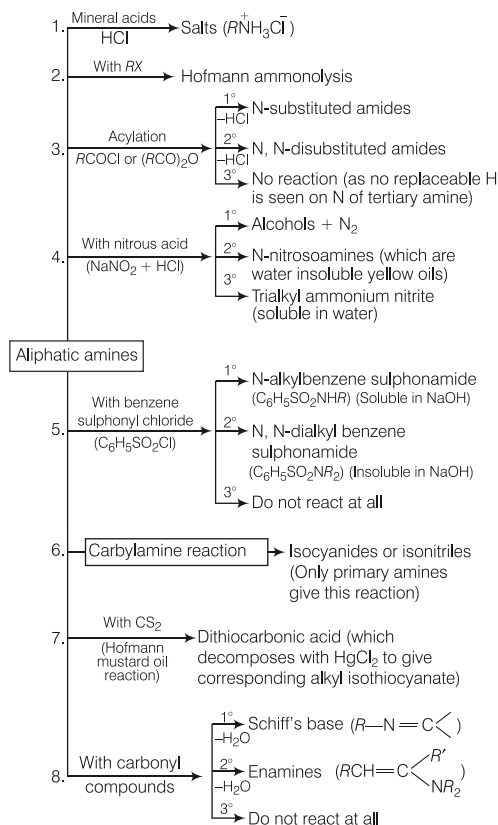
- Amines are far less basic than amides.
- The pK_a value of conjugate acid of a typical amide is about zero.
- This lower basicity of amides can be understood in terms of resonance and inductive effects.
- An amide is stabilised by resonance involving the non-bonding pair of electrons on the nitrogen atom.

Amide



- However, electron-withdrawing nature of the carbonyl group of amide also contribute in its less basic nature.

Chemical Properties



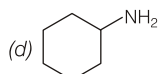
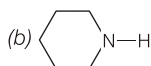
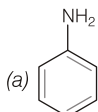
- The above chemical reactions can be used to distinguish among 1° , 2° and 3° amines. The above chemical reactions are also applicable to aromatic amines.

Best Practice **SHOTS**

1. Which of the following is a 3° amine?

- (a) 1-methylcyclohexylamine
 (b) Triethylamine
 (c) *tert*-butylamine
 (d) N-methylaniline

2. Which of the following is the weakest Bronsted base?



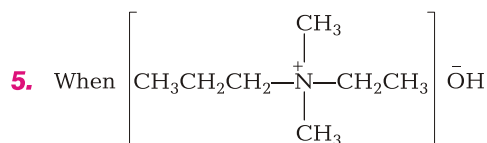
Hint Aniline is weakest Bronsted base among the given four compounds due to resonance present in case of aniline.

3. Amongst the given set of reactants, the most appropriate method for preparing 2° amine is

- (a) 2° R—Br + NH₃
 (b) 2° R—Br + NaCN followed by H₂ / Pt
 (c) 1° R—NH₂ + RCHO followed by H₂ / Pt
 (d) 1° R—Br (2 mol) + potassium phthalimide followed by H₃O⁺ / heat

4. On heating an aliphatic primary amine with chloroform and ethanolic potassium hydroxide, the organic compound formed is

- (a) an alkanol
 (b) an alkanediol
 (c) an alkyl cyanide
 (d) an alkyl isocyanide



is heated, then

- (a) propane is the major product
 (b) ethene and C₃H₇N(CH₃)₂ are the only products
 (c) ethene and propane are obtained while ethene as the major product
 (d) equimolar amounts of ethene and propene are obtained

6. Isopropyl amine $\xrightarrow{\text{KMnO}_4} \text{X} \xrightarrow{\text{H}_3\text{O}^+} \text{Y}$.

In this sequence, X and Y respectively are

- (a) acetaldimine, ethanal
 (b) ethanal, ketimine
 (c) ketimine, acetone
 (d) acetone, propan-2-ol

7. (A) C₂H₅NH₂ $\xrightarrow[\text{(ii) AgNO}_2]{\text{(i) NOCl}} \text{W}$

(B) (CH₃)₂CH(NH₂) $\xrightarrow[\text{(ii) AgNO}_2]{\text{(i) NOCl}} \text{X}$

(C) (CH₃)₃C(NH₂) $\xrightarrow[\text{(ii) AgNO}_2]{\text{(i) NOCl}} \text{Y}$

(D) CH₃CH(NH₂)C₂H₅ $\xrightarrow[\text{(ii) AgNO}_2]{\text{(i) NOCl}} \text{Z}$

Which product will not show tautomerism?

- (a) W (b) X (c) Y (d) Z

8. Which of the following reactions is given by primary amines?

- (a) Reaction with HONO
 (b) Reaction with chloroform and alcoholic KOH
 (c) Reaction with acetyl chloride
 (d) Reaction with Grignard's reagent

9. An organic amino compound reacts with aqueous nitrous acid at low temperature to produce an oily nitrosoamine. The compound is

- (a) CH₃NH₂
 (b) CH₃CH₂NH₂
 (c) (CH₃CH₂)₃N
 (d) CH₃CH₂NHCH₂CH₃

Hint Secondary amines give oily nitrosoamine with nitrous acid.

10. A compound of molecular formula C₃H₉N when reacts with benzene sulphonyl chloride gives a product soluble in dilute NaOH solution. The compound should be

- (a) (CH₃)₃N
 (b) (CH₃)₂CH—NH₂
 (c)
 (d) All of the above

11. Ethyl isocyanide on hydrolysis in acidic medium generates

- (a) ethylamine salt and methanoic acid
 (b) propanoic acid and ammonium salt
 (c) ethanoic acid and ammonium salt
 (d) methylamine salt and ethanoic acid

12. A $\xrightarrow{\text{H}_2\text{NOH}} \text{B} \xrightarrow{\text{Reduction}} \text{C} \xrightarrow{\text{NOCl}} \text{CH}_3\text{CH}_2\text{Cl}$

In the above sequence, A and C are

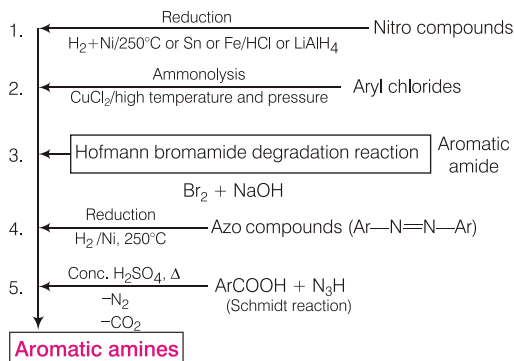
- (a) methanal, methylamine
 (b) acetone, ethylamine
 (c) ethanal, dimethylamine
 (d) acetaldehyde, ethylamine



AROMATIC AMINES

In aromatic amines, the N-atom is directly attached to the benzene ring, e.g. aniline, *o*-toluidine, diphenylamine, etc. These are also divided into 1°, 2° and 3° amines based on the number of H-atoms of NH₃ replaced by aryl group.

Methods of Preparation

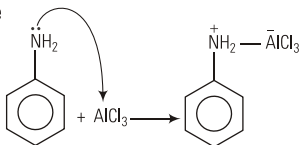


Physical and Chemical Properties

- These are colourless liquids or solids having characteristic odour. They turn brown in air due to oxidation.
- They are soluble in water due to intermolecular hydrogen bonding. They are less basic than the corresponding aliphatic amines due to electron withdrawing nature of benzene ring and the basicity decreases as the number of benzene ring directly attached to N-atom increases.
- Aromatic amines also give most of chemical reactions that are given by aliphatic amines and the only difference is that the alkyl group is substituted by the aryl group. Apart from they give electrophilic aromatic substitution reactions.

REMEMBER

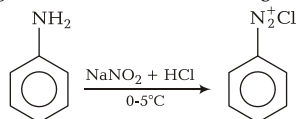
Aniline does not undergo Friedel-Crafts alkylation and acetylation due to the formation of salt with AlCl₃, the reagent used in Friedel-Crafts reaction. After formation of salt, the N-atom of aniline acquires positive charge and acts as a strong deactivating group for further reaction.



Benzene Diazonium Salts (ArN₂⁺X⁻)

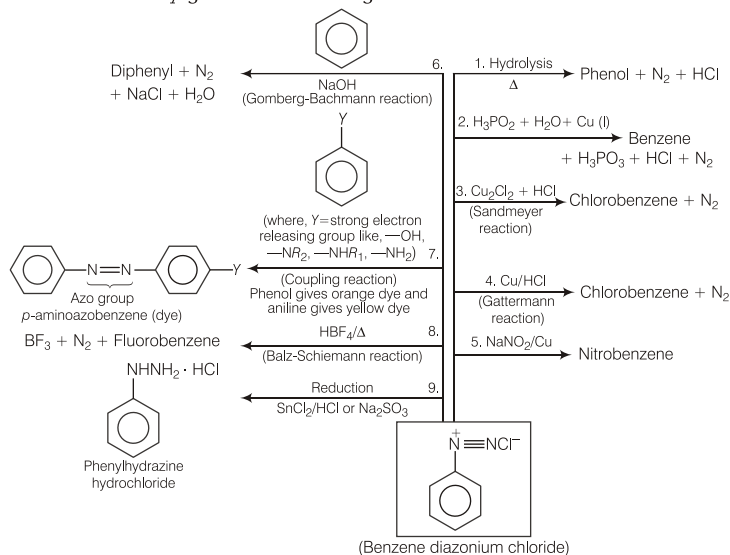
These salts contain benzene diazonium (ArN₂⁺) ion that is stabilised by resonance.

- Presence of electron releasing groups like —NR₂, —OR, etc., at *o*/*p*-position stabilises the benzene diazonium salt.
- It is prepared through diazotisation reaction given below:



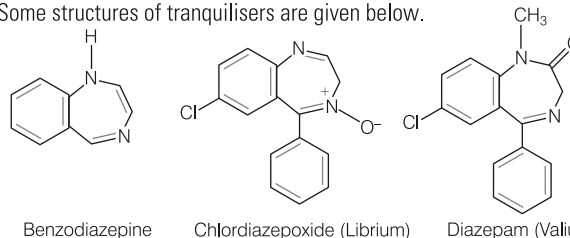
Physical and Chemical Properties

These are colourless crystalline solids and are soluble in water due to their ionic nature. They give the following chemical reactions:



Amines as Tranquillisers

- Usually people have experienced anxiety and stress at sometimes in their lives. Each person develops various ways to cope with these factors such as meditation, or exercise or psychotherapy or drugs. One modern way of coping is to use tranquilisers.
- The first modern tranquilisers were derivatives of a compound called benzodiazepine. Librium, valium and other benzodiazepines are central nervous system sedatives/hypnotics. As sedatives, they diminish activity and excitement, thereby exerting a calming effect. As hypnotics, they produce drowsiness and sleep. Some structures of tranquilisers are given below.



Benzodiazepine

Chlordiazepoxide (Librium)

Diazepam (Valium)

Best Practice **SHOTS**

13. Benzamide on treatment with POCl_3 gives

- (a) aniline (b) benzonitrile
(c) chlorobenzene (d) benzylamine

Hint POCl_3 brings dehydration of primary amide.

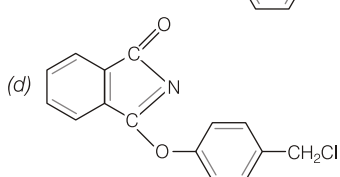
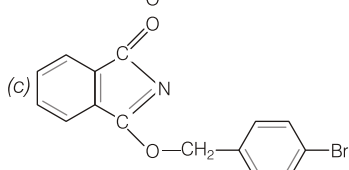
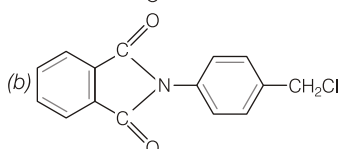
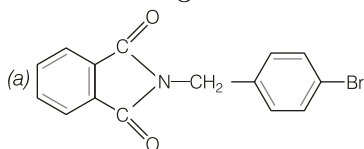
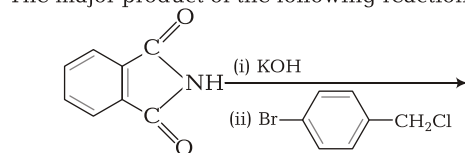
14. *p*-chloroaniline and anilinium hydrochloride can be distinguished by

- (a) Sandmeyer reaction (b) NaHCO_3
(c) AgNO_3 (d) carbylamine test

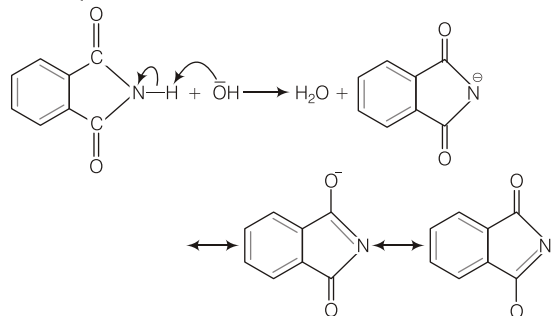
Hint $\text{C}_6\text{H}_5\text{NH}_3^+\text{Cl}^- + \text{AgNO}_3 \longrightarrow \text{C}_6\text{H}_5\text{NH}_3^+\text{NO}_3^- + \text{AgCl}\downarrow$
Anilinium hydrochloride

In case of *p*-chloroaniline, no such precipitates of AgCl are obtained.

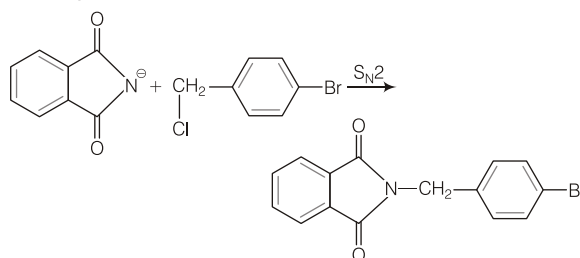
15. The major product of the following reaction is



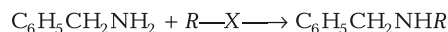
Hint Step 1



Step 2



16. Benzylamine may be alkylated as shown in the following equation



Which of the following alkyl/aryl halides is best suited for this reaction through $\text{S}_{\text{N}}1$ mechanism?

- (a) CH_3Br (b) $\text{C}_6\text{H}_5\text{Br}$ (c) $\text{C}_6\text{H}_5\text{CH}_2\text{Br}$ (d) $\text{C}_2\text{H}_5\text{Br}$

Hint $\text{C}_6\text{H}_5\text{CH}_2^+$ is the most stable carbocation among all given in the options.

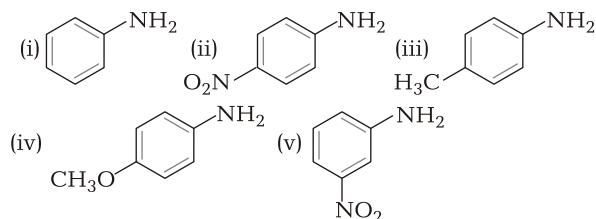
17. Which of the following reagents would not be a good choice for reducing an aryl nitro compound to an amine?

- (a) H_2 (excess)/ Pt (b) LiAlH_4 in ether
(c) Fe and HCl (d) Sn and HCl

18. Aniline reacts with ... to yield ... as the final product.

- (a) bromine; 2-bromoaniline
(b) bromine; 2, 4, 6-tribromoaniline
(c) chloroform/KOH; phenyl cyanide
(d) acetyl chloride; benzanilide

19. The correct increasing order of basic nature of the following bases is



- (a) (ii) < (v) < (i) < (iii) < (iv) (b) (v) < (ii) < (i) < (iii) < (iv)
(c) (ii) < (v) < (i) < (iv) < (iii) (d) (v) < (ii) < (i) < (iv) < (iii)

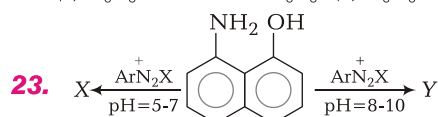
Hint $-\text{OCH}_3$ is strongest electron releasing group (+M-effect) which opposes most the dispersion of lone pair of electron on nitrogen into the ring. Thus, $-\text{OCH}_3$ being at *para*-position imparts highest basicity.

$-\text{NO}_2$ being at *meta*-position stabilises the electron pair of nitrogen only by $-I$ -effect.

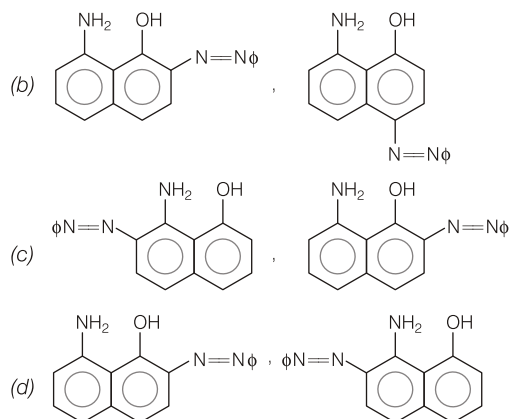
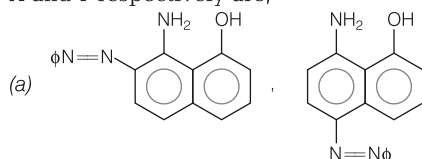
$-\text{NO}_2$ being at *para*-position due to $-M$ -effect and $-I$ -effect stabilises the lone pair of electron on nitrogen most and imparts least basicity.

{ JEE FINAL TOUCH }

- 20.** Benzene diazonium chloride on treatment with hypophosphorous acid and water in the presence of Cu^+ catalyst produces
(a) benzene (b) toluene (c) aniline (d) chlorobenzene
- 21.** The basicity of aniline is less than that of cyclohexylamine. This is due to
(a) +R-effect of $-\text{NH}_2$ group (b) -I-effect of $-\text{NH}_2$ group
(c) -R-effect of $-\text{NH}_2$ group (d) hyperconjugation effect
- 22.** Nitrobenzene is reduced by Zn and alcoholic potash mixture to get
(a) $\text{C}_6\text{H}_5-\text{NH}_2$ (b) $\text{C}_6\text{H}_5-\text{NH}-\text{NH}-\text{C}_6\text{H}_5$
(c) $\text{C}_6\text{H}_5-\text{N}=\text{N}-\text{C}_6\text{H}_5$ (d) $\text{C}_6\text{H}_5-\text{NH}-\text{CO}-\text{C}_6\text{H}_5$



X and Y respectively are,



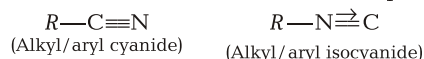
- 24.** During diazotisation of benzenamine with sodium nitrite and hydrochloric acid, the excess of hydrochloric acid is used primarily to
(a) check the hydrolysis of $\phi-\text{OH}$
(b) ensure a stoichiometric amount of nitrous acid
(c) check the concentration of free aniline
(d) neutralise any base formed during reaction



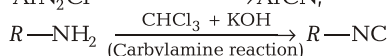
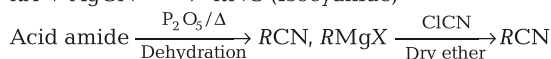
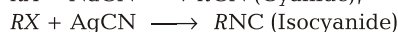
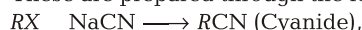
CYANIDES, ISOCYANIDES AND NITRO COMPOUNDS

Cyanides and Isocyanides

- There are two isomeric derivatives of HCN represented as:

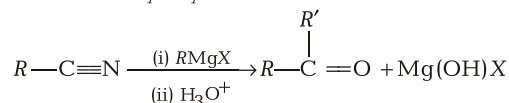
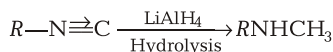
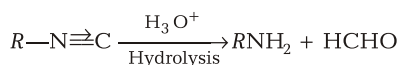
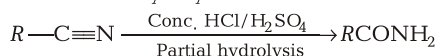
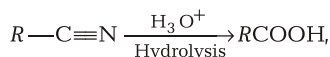


- These are prepared through the following reactions:



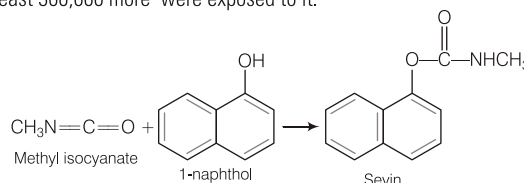
Physical and Chemical Properties

- Lower members are colourless liquids, whereas higher members are crystalline solids. Cyanides have pleasant odour, whereas isocyanides have unpleasant odour.
- Cyanides have higher boiling points than the corresponding isocyanides.
- They show the following chemical properties:



Bhopal Tragedy

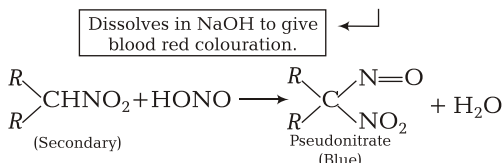
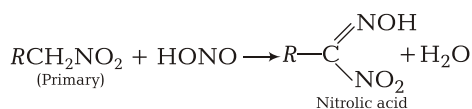
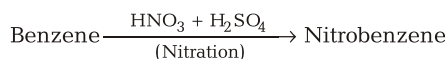
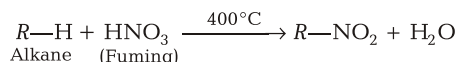
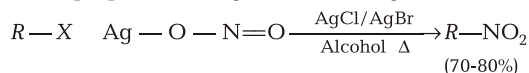
This tragedy was happened in India, in 1984, in the city Bhopal. There was a massive leak of methyl isocyanate, used in the preparation of insecticide, Sevin. It resulted in the deaths of more than 2000 people, atleast 300,000 more were exposed to it.



This catastrophe, the worst chemical industrial accident in history, led to a complete reappraisal of the safety measures for the handling of large quantities of toxic chemicals. The toxicity of the isocyanate function derives from its rapid reaction with nucleophilic sites in biological molecules. Indiscriminate attack on the hydroxy, amino and thiol groups in, e.g. peptides and proteins inactivates them with respect to their biological function, other substances, which would be similarly affected by such attack, include small molecules taking part in the transmission of nerve impulses and various aspects of cell regulation.

Nitro Compounds

These are alkyl or aryl compounds containing $-\text{NO}_2$ group. These are prepared through the following reactions:

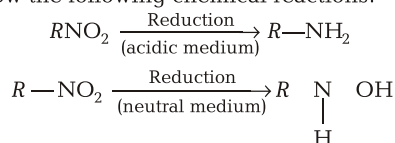


Dissolves in NaOH to give blood red colouration.

Does not dissolve in alkali

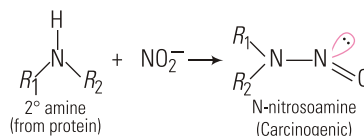
Physical and Chemical Properties

- Nitroalkanes are colourless pleasant smelling liquids, whereas aromatic nitro compounds are pale yellow liquids or solids with distinct odour.
- They have higher boiling points than the corresponding hydrocarbons. These are more soluble in non-polar solvents than polar solvents due to the absence of hydrogen bonding.
- They show the following chemical reactions:



N-Nitrosoamines: A Powerful Carcinogen

Sodium nitrite is added to meat as a preservative to inhibit the growth of *Clostridium botulinum* and to prevent the meat from turning brown. However, inside our stomach, the low pH stimulates the reaction of nitrite ion with secondary amine found in meat to produce carcinogenic N-nitrosoamines.



- Some common N-nitrosoamines are N-nitrosodimethyl amine and N-nitrosopyrrolidine.
- Cigarette smoke also contains carcinogenic N-nitrosodimethyl amine.

Best Practice [SHOTS]

25. Which of the following statements is not correct?

- Alkyl isocyanides have bad odours while alkyl cyanides have pleasant odours
- Alkyl cyanides are not poisonous as KCN
- Alkyl cyanides have lower boiling points than the corresponding alkyl isocyanides
- Acetonitrile is soluble in water but not in methyl carbonylamine

26. Treatment of nitrobenzene with acetyl chloride in the presence of anhydrous AlCl_3 gives

- 2-nitroacetophenone
- 3-nitroacetophenone
- 4-nitroacetophenone
- None of the above

27. The conversion, $\text{C}_6\text{H}_5\text{NO}_2 \longrightarrow \text{C}_6\text{H}_5\overset{\text{O}}{\text{N}}=\text{N}-\text{C}_6\text{H}_5$ can be brought about reduction with

- $\text{Na}_3\text{AsO}_3 / \text{NaOH}$
- glucose/HCl
- Zn/NaOH
- $\text{LiAlH}_4 / \text{ether}$

28. The gas leaked from a storage tank of the Union Carbide plant in Bhopal gas tragedy was

- methyl isocyanate
- methylamine
- ammonia
- phosgene

29. $\text{CH}_3\text{CN} \longrightarrow \text{CH}_3\text{CH}_2\text{NH}_2$

Which of the following cannot be used for the above conversion?

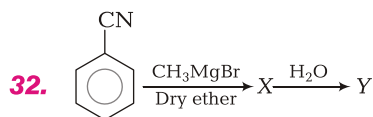
- Pt / H_2
- LiAlH_4
- Na / $\text{C}_2\text{H}_5\text{OH}$
- $\text{SnCl}_2 / \text{HCl}$

30. Phenyl cyanide cannot be obtained by

- $\text{C}_6\text{H}_5\text{CONH}_2 \xrightarrow{\text{P}_2\text{O}_5, \Delta}$
- $\text{C}_6\text{H}_5-\text{CH}=\text{NOH} \xrightarrow{\text{Ac}_2\text{O}, \Delta}$
- $\text{C}_6\text{H}_5\text{Cl} \xrightarrow{\text{Alc. KOH}}$
- $\text{C}_6\text{H}_5\text{NH}_2 \xrightarrow[\text{(ii) CuCN}]{\text{(i) NaNO}_2/\text{HCl}}$

31. Tertiary nitroalkanes cannot tautomerise because

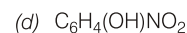
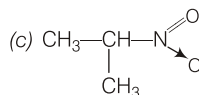
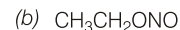
- their tautomeric forms are highly unstable
- they do not contain any multiple bond
- they do not have labile H-atom
- they are not basic in nature



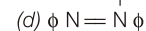
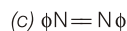
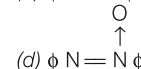
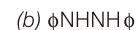
Identify Y.

- (a) Benzophenone
(b) Acetophenone
(c) Benzoic acid
(d) Phenol

33. Which of the following is not a nitro derivative?



34. In the reduction of nitrobenzene, which of the following is the intermediate?

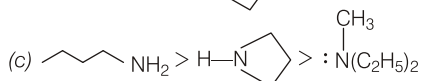
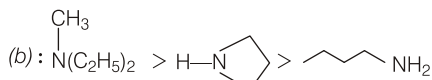
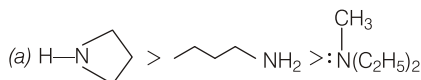


Answers

1. (b) 2. (a) 3. (c) 4. (d) 5. (c) 6. (c) 7. (c) 8. (b) 9. (d) 10. (b)
11. (a) 12. (d) 13. (b) 14. (c) 15. (a) 16. (c) 17. (b) 18. (b) 19. (a) 20. (a)
21. (a) 22. (b) 23. (c) 24. (c) 25. (c) 26. (c) 27. (a) 28. (a) 29. (d) 30. (c)
31. (c) 32. (b) 33. (b) 34. (a)

MASTER STROKE

1. Which of the following decreasing order of boiling points is correct?



(d) None of the above

2. Acetamide is treated separately with the following reagents.

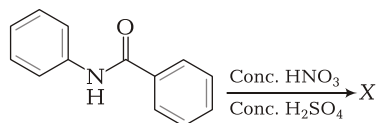
Which of these would give methylamine?

- (a) PCl_5 (b) Soda lime
(c) $NaOH + Br_2$ (d) Hot, conc. H_2SO_4

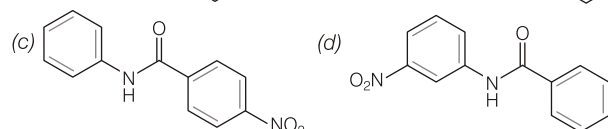
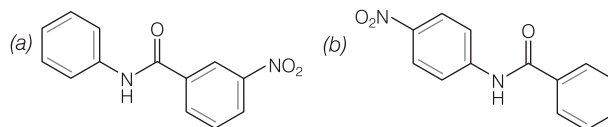
3. An aliphatic nitro compound turns red with the addition of a conc. $NaOH$ solution, followed by the addition of an excess of $NaNO_2$ solution and then dil. H_2SO_4 . The colour disappears with the addition of the excess of an acid but reappears, if the solution is made alkaline. The aliphatic nitro compound is

- (a) $CH_3CH_2NO_2$ (b) $(CH_3)_2CHNO_2$
(c) $(CH_3)_3CNO_2$ (d) All of these

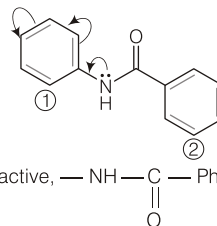
4. In the following reaction:



The structure of the major product X is



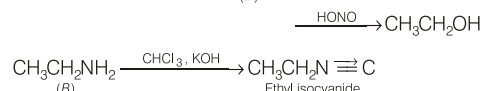
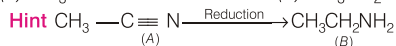
Hint



Ring 1 is more active, $—NH—C(=O)—Ph$

is *ortho-para* directing, *para* product is predominating.

5. An organic compound A having molecular formula C_2H_3N , on reduction, gave another compound B. Upon treatment with nitrous acid, B gave ethyl alcohol. On warming with chloroform and alcoholic KOH, it formed an offensive smelling compound C. The compound C is



6. An aliphatic amine with molar mass 73 g mol^{-1} on heating with excess of CH_3I gave a quaternary salt. The amine can be

I. N, N-diethyl ethanamine

II. N-methyl propanamine

III. 2-butanamine

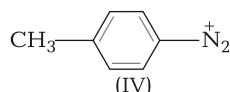
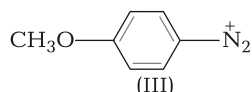
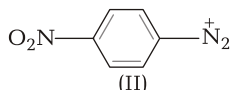
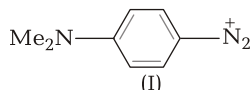
IV. Neo-pentylamine

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

Hint Let the amine be $\text{C}_n\text{H}_{2n+3}\text{N}$.

The molar mass $= (14n + 17) = 73$, $n = 4$

7. Consider the following diazonium ions.



The order of reactivity of the above diazonium ions towards diazo coupling with phenol in the presence of dil. NaOH is

(a) I < IV < II < III

(b) I < III < IV < II

(c) III < I < II < IV

(d) III < I < IV < II

Hint Diazonium ion acts as an electrophile in coupling reaction. Greater the electron withdrawing power, higher the electrophilicity.

8. Which of the following options is correct with respect to decreasing order of basic nature?

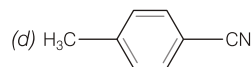
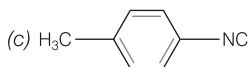
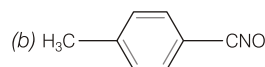
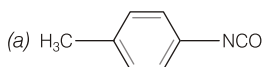
(a) $\text{C}_6\text{H}_5\text{NH}_2 > \text{NH}_3 > \text{CH}_3\text{NH}_2 > (\text{CH}_3)_2\text{NH}$

(b) $\text{NH}_3 < \text{C}_6\text{H}_5\text{NH}_2 > \text{CH}_3\text{NH}_2 > (\text{CH}_3)_2\text{NH}$

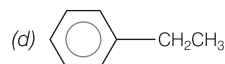
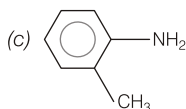
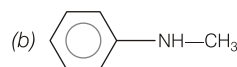
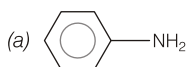
(c) $(\text{CH}_3)_2\text{NH} > \text{CH}_3\text{NH}_2 > \text{NH}_3 > \text{C}_6\text{H}_5\text{NH}_2$

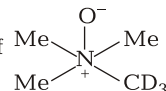
(d) $\text{CH}_3\text{NH}_2 > (\text{CH}_3)_2\text{NH} > \text{C}_6\text{H}_5\text{NH}_2 > \text{NH}_3$

9. The reaction of CHCl_3 and alcoholic KOH with *p*-toluidine gives



10. Which of the following is the strongest base?



11. Pyrolysis of  would give

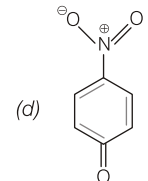
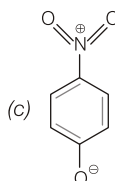
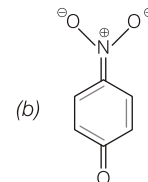
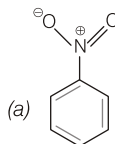
(a) mixture of $\text{CH}_2=\text{CH}-\text{CD}_3$ and $\text{CH}_3-\text{CH}=\text{CD}_2$

(b) $\text{CH}_3-\text{CH}=\text{CD}_2$

(c) $\text{Me}_2\text{N}^+=\text{C}(\text{CD}_3)(\text{CH}_3)$

(d) $\text{CH}_2=\text{CH}-\text{CD}_3$

12. The most unlikely representation of resonance structure of *p*-nitrophenoxide ion is



Hint N-atom forms five bonds and contains positive charge.

13. An amine on treatment with HNO_2 evolved N_2 . The amine on exhaustive methylation with CH_3I formed a quaternary salt containing 59.07% iodine. The amine is likely to be

(a) CH_3NH_2

(b) $(\text{CH}_3)_2\text{NH}$

(c) $\text{C}_2\text{H}_5\text{NH}_2$

(d) $(\text{CH}_3)_3\text{N}$

Hint Evolution of N_2 with HNO_2 means amine should be primary. 59.07 g of iodine is present in 100 g of compound.

\therefore 127 g of iodine, i.e. 1 mole will present in

$$\frac{100 \times 127}{59.07} = 215 \text{ g of compound}$$

14. A compound X has the molecular formula $\text{C}_7\text{H}_7\text{NO}$. On treatment with Br_2 and KOH, X gives an amine Y. Y gives carbylamine test and upon diazotisation and coupling with phenol gives an azo dye Z. X is

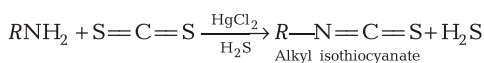
(a) PhCONH_2

(b) PhCONHCOCH_3

(c) PhNO_2

(d) PhCOONH_4

15. Consider the following reaction,



This reaction constitutes

(a) mustard oil reaction

(b) test for 3° amine

(c) test for 2° amine

(d) test for CS_2

Answers

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

Biomolecules



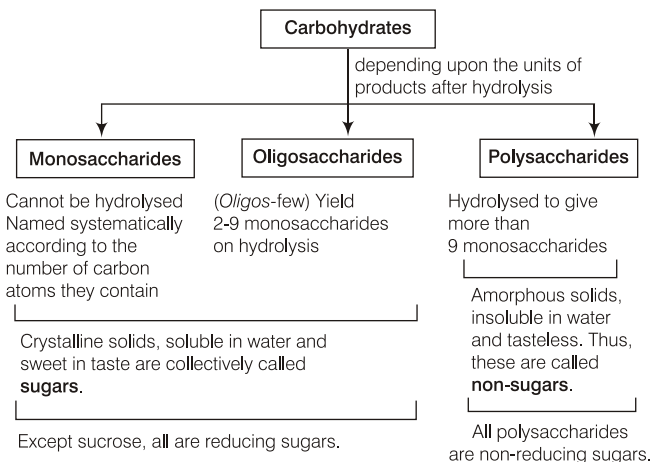
CARBOHYDRATES

Biomolecules are essential complex molecules found in and synthesised by living organisms.

These include carbohydrates, amino acids, proteins, enzymes, vitamins, nucleic acids, etc.

Carbohydrates

These are optically active polyhydroxy aldehydes or ketones or the compounds that produce such units on hydrolysis. These are also called saccharides and are classified as

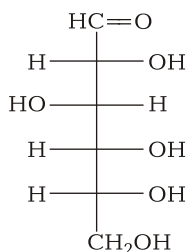


Monosaccharides

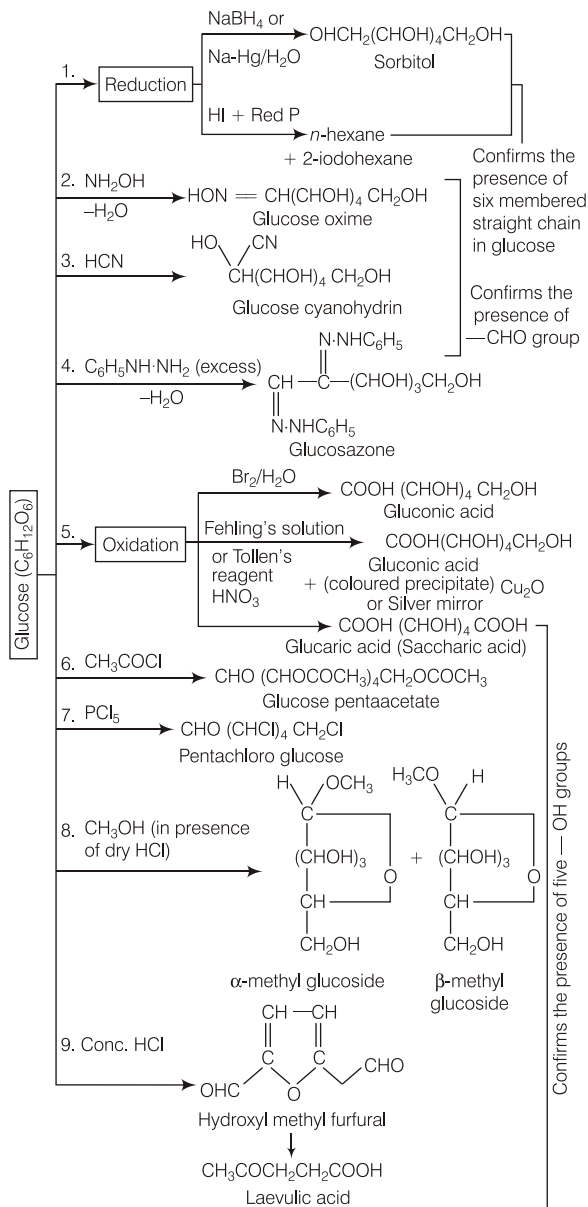
- These are the simplest carbohydrates which cannot be hydrolysed further.
- These are polyhydroxy compounds containing either an aldehyde group (aldose) or a ketone group (ketose, the keto group is present next to the terminal carbon).
- The simplest monosaccharides are trioses such as glyceraldehyde, dihydroxy acetone. Naturally occurring monosaccharides are pentoses (ribose and deoxyribose sugar) and hexoses (glucose and fructose).

Glucose (C₆H₁₂O₆)

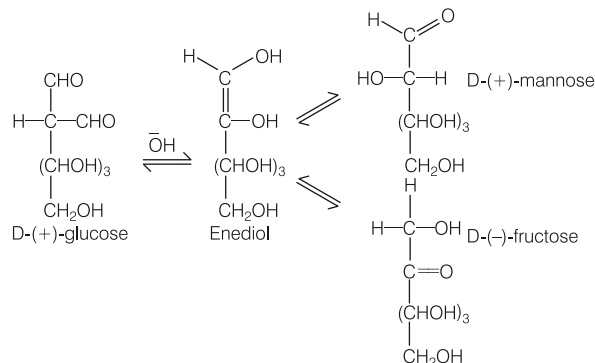
- It is an aldohexose reducing sugar that occurs freely and in combined state in nature.
- It is prepared by the hydrolysis of sucrose, starch, lactose, etc.
- It is a white crystalline solid, highly soluble in water but insoluble in ether. It is also called dextrose as it is dextrorotatory and belongs to D-series.



- The chain structure of glucose can be drawn as the structure shown in right side.
- Chemical properties of glucose are given below:



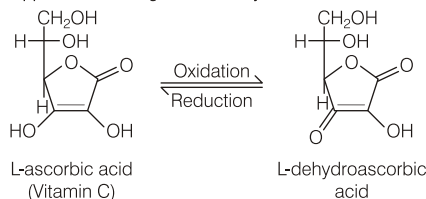
10. Metallic hydroxide \rightarrow $\text{CHO}(\text{CHOH})_4\text{CH}_2\text{O}-\text{Ca}-\text{OH}$
Calcium glucosate
11. $\text{HIO}_4 \rightarrow$ $\text{HCOOH} + \text{HCHO}$
12. Fermentation \rightarrow Ethanol + CO_2
13. Dehydration \rightarrow Black mass or sugar carbon (6C)
14. Alkali (dil.) \rightarrow Yellow \rightarrow Brown \rightarrow Resinous mass
 \rightarrow Lobry-de-Bruyn-van Ekenstein rearrangement



Vitamin C versus a Monosaccharide

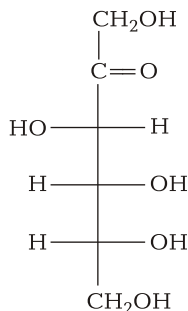
The structure of vitamin C (L-ascorbic acid) resembles to that of a monosaccharide. This vitamin can be synthesised by both biochemically (from plants and animals) and commercially (from D-glucose).

Humans do not have the enzymes required to carry out this synthesis. That is why, we obtain vitamin C in the food we eat as a vitamin supplement. Oranges are a major source of vitamin C.

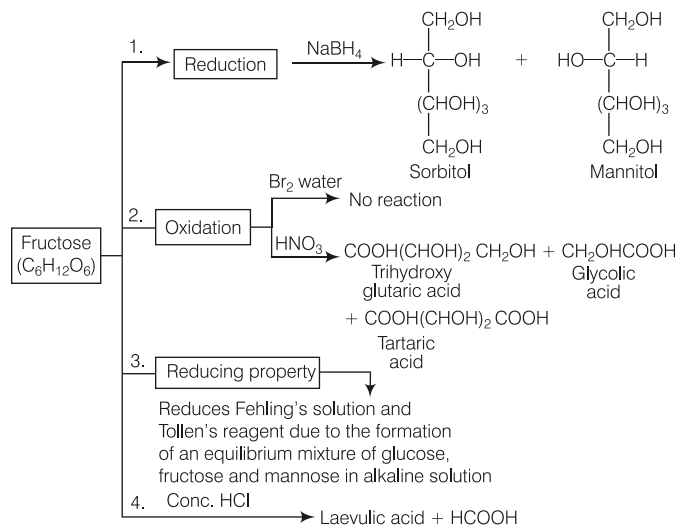


Fructose (Fruit Sugar, $\text{C}_6\text{H}_{12}\text{O}_6$)

- It is also called ketohexose due to the presence of a keto group at C-2 position.
- It also belongs to D-series of sugars and is laevorotatory. It is prepared by the hydrolysis of cane sugar.
- Its open chain structure can be shown as in right.
- It is a colourless crystalline compound, soluble in water (less soluble than glucose) but insoluble in ether, benzene, etc.

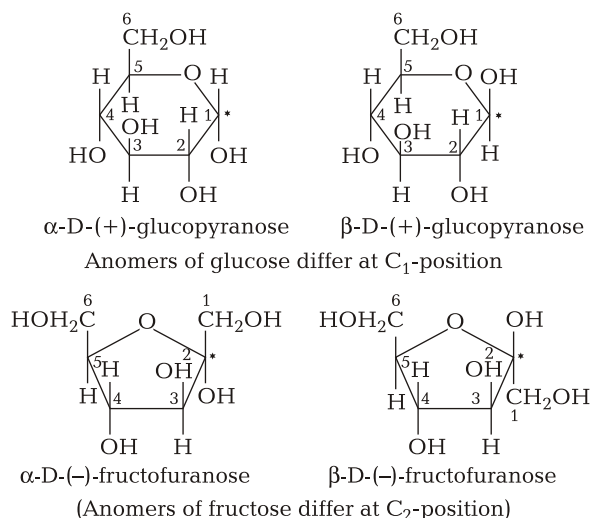


- Fructose shows the following chemical properties:



Cyclic Structures of Glucose and Fructose

- The straight chain structure of glucose is unable to explain the following properties of glucose:
 - Despite having $-\text{CHO}$ group, it does not give 2, 4-DNP test, Schiff's test and hydrogen sulphite with NaHSO_3 .
 - It does not also react with NH_2OH .
- Later it was found that glucose exists as six membered ring structure (pyranose) and fructose exists as five membered ring structure (furanose). Their structures are given below:



Disaccharides

- These are formed when two monosaccharide units are joined together through oxide linkage (glycosidic linkage) by the loss of water molecule.

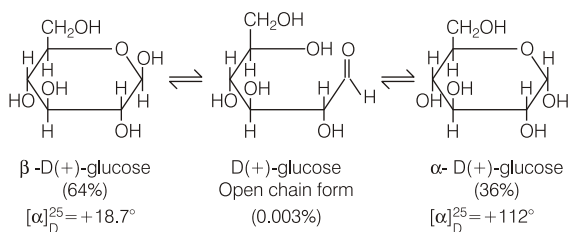
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- Some important disaccharides are given below:

Disaccharides	Structure
(a) Sucrose Formed by glycosidic linkage between C-1 of α -D-glucose and C-2 of β -D-fructose.	<p style="text-align: center;">α-D-glucose β-D-fructose</p>
(b) Maltose Formed by glycosidic linkage between C-1 and C-4 of two different α -D-glucose.	<p style="text-align: center;">(I) (II) α-D-glucose α-D-glucose</p>
(c) Lactose Formed by glycosidic linkage between C-1 of β -D-galactose and C-4 of β -D-glucose.	<p style="text-align: center;">β-D-galactose β-D-glucose</p>

Mutarotation

Mutarotation is the change in specific rotation that accompanies to maintain the equilibrium of α - and β - anomers in aqueous solution, e.g. a solution is prepared by dissolving crystalline α -D-glucopyranose in water, has a specific rotation of $+112^\circ$, which gradually decreases to an equilibrium value of $+52.7^\circ$ as α -D-glucopyranose also undergoes mutarotation, during which the specific rotation changes from $+18.7^\circ$ to the same equilibrium value of $+52.7^\circ$. Mutarotation is common to all carbohydrates that exist in hemiacetal forms.



Inversion of Sugar

Natural sucrose is dextrorotatory but on hydrolysis, it gives dextrorotatory glucose ($+52.5^\circ$) and laevorotatory fructose (-92.4°), making the mixture laevorotatory (since, the magnitude of laevorotation is more than dextrorotation).

Hence, hydrolysis brings a change in the sign of rotation of sucrose from *dextro* to *laevo* and the sugar formed is called inverted sugar.

Polysaccharides

- These are condensation polymers of monosaccharides that are joined together by glycosidic linkages with evolution of water.
- These can be either homopolysaccharides (polymer of one type of monosaccharide) or heteropolysaccharide (polymer of more than one types of saccharide).
- Some important polysaccharides are given in the table below:

Name and function of polysaccharides	Structure and monomers
(a) Starch Plants store food as starch after photosynthesis. Also consumed by animals.	<p>It is a polymer of α-D-glucose and contains two components such as:</p> <p>(i) Amylose (15-20%) It is a long unbranched straight chain polymer of 200-1000 α-D-glucose units that are held by C_1-C_4 glycosidic linkage.</p> <p>It is a water soluble component of starch.</p> <p>(ii) Amylopectin (80-85%) It is a branched chain polymer of α-D-glucose units that are held by C_1-C_4 glycosidic linkage, however branching occurs through C_1-C_6 glycosidic linkage.</p>
(b) Cellulose It is the main constituent of plant cell wall.	<p>It is a straight chain polymer of β-D-glucose units that are held by C_1-C_4 glycosidic linkage.</p>
(c) Glycogen Carbohydrate in animal body is stored as glycogen. It is also found in yeast and fungi.	<p>It is a branched chain polymer of α-D-glucose having structure similar to amylopectin, however glycogen is even more branched (contains lesser monomer units).</p>

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Best Practice **SHOTS**

- 1.** When a monosaccharide forms a ring by interaction of one of its hydroxyl group with its aldehyde group, the bond is referred to as a (an) linkage.
(a) ether (b) ester (c) acetal (d) hemiacetal
- 2.** Ketones do not reduce Tollen's reagents, but fructose with a keto group reduces it. It is attributed to
(a) enolisation of keto group of fructose and then, its transformation into aldehyde group in the presence of OH⁻ which is present in Tollen's reagent
(b) >CH—OH group which is also oxidised to keto group
(c) Both (a) and (b) statements are correct
(d) None of the above statement is correct
- 3.** Which of the following show mutarotation?
(a) Glucose (b) Fructose
(c) Both (a) and (b) (d) None of these
- 4.** The monosaccharides having anomeric carbon atom are
(a) geometrical isomers (b) α and β -optical isomers
(c) having symmetrical carbon atoms
(d) None of the above
- Hint** C₁ carbon of monosaccharides is called anomeric carbon. When the —OH group attached with C₁ carbon towards right, called α -form. When the —OH group is attached towards left, it is called β -form.
- 5.** Which of the following compounds is obtained, when glucose reacts with excess C₆H₅—NHNH₂?
(a) Glucosazone (b) Gluconic acid
(c) Glucose phenyl hydrazone (d) Saccharic acid
- Hint**
- $$\begin{array}{ccc}
 \begin{array}{c} \text{CHO} \\ | \\ \text{CHOH} \\ | \\ (\text{CHOH})_3 \\ | \\ \text{CH}_2\text{OH} \\ \text{Glucose-(+)} \end{array} & \xrightarrow{3\text{C}_6\text{H}_5\text{NHNH}_2} & \begin{array}{c} \text{CH}=\text{N-NHC}_6\text{H}_5 \\ | \\ \text{C}=\text{N-NHC}_6\text{H}_5 \\ | \\ (\text{CHOH})_3 \\ | \\ \text{CH}_2\text{OH} \\ \text{Glucosazone} \end{array} + \text{C}_6\text{H}_5\text{NH}_2 + \text{NH}_3 + 2\text{H}_2\text{O}
 \end{array}$$
- 6.** Which of the following does not form an oxime?
(a) Glucose (b) Glucose pentaacetate
(c) Arabinose (d) Galactose
- 7.** The two forms of D-glucopyranose obtained from the solution of D-glucose are called
(a) isomers (b) anomers (c) epimers (d) enantiomers
- 8.** Identify the product C in the following series of reactions.
Glucose $\xrightarrow{\text{HCN}}$ A $\xrightarrow{\text{H}_2\text{O}}$ B $\xrightarrow{\text{HI}}$ C
(a) Heptanoic acid (b) Hexanoic acid
(c) α -methyl caproic acid (d) None of these
- Hint**
- $$\begin{array}{ccc}
 \begin{array}{c} \text{CHO} \\ | \\ (\text{CHOH})_4 \\ | \\ \text{CH}_2\text{OH} \end{array} & \xrightarrow[\text{(iii) HI}]{\text{(i) HCN}} & \begin{array}{c} \text{COOH} \\ | \\ (\text{CH}_2)_5 \\ | \\ \text{CH}_3 \end{array} \\
 & \xrightarrow[\text{(ii) H}_2\text{O}]{\text{(i) HCN}} & \\
 & & \text{Heptanoic acid}
 \end{array}$$
- 9.** An optically active compound A, gave an $[\alpha]_D^{25} = 30^\circ$, while a mixture of A and its enantiomer B, gave $[\alpha]_D^{25} = +15^\circ$. The ratio of A to B in the mixture is
(a) 1 : 3 (b) 3 : 1 (c) 1 : 2 (d) 2 : 1
- Hint** $\frac{15}{30} \times 100 = 50$
- Thus, the mixture is 50% optically pure. Hence, the amount of
A = 50 + 25 = 75, B = 0 + 25 = 25 \Rightarrow A : B = 3 : 1
- 10.** Sucrose (cane sugar) is a disaccharide, one molecule of sucrose on hydrolysis gives
(a) 2 molecules of glucose
(b) 2 molecules of glucose + 1 molecule of fructose
(c) 1 molecule of glucose + 1 molecule of fructose
(d) 2 molecules of fructose
- 11.** Synthesis of each molecule of glucose in photosynthesis involves
(a) 18 molecules of ATP (b) 10 molecules of ATP
(c) 8 molecules of ATP (d) 6 molecules of ATP
- 12.** Sucrose is not a reducing sugar because its
(a) hemiacetal groups cannot be converted to aldehyde groups
(b) disaccharide bond has an α -1, 4 anomeric linkage
(c) disaccharide bond has a β -1, 4 anomeric linkage
(d) disaccharide bond has a α -1, 2 anomeric linkage
- 13.** Complete hydrolysis of cellulose gives
(a) D-fructose (b) D-ribose
(c) D-glucose (d) L-glucose
- Hint** $(\text{C}_6\text{H}_{10}\text{O}_5)_n + n\text{H}_2\text{O} \xrightarrow{\text{H}^+} n\text{C}_6\text{H}_{12}\text{O}_6$
Cellulose D-glucose
- 14.** D-fructose is used for sweetening cold drinks but not hot ones because
(a) it is not a true carbohydrate
(b) on heating, it converts into pyranose form
(c) on heating, it converts into furanose form
(d) on heating, it gets decomposed into D-fructose
- Hint** The sweeter form of D-fructose is fructopyranose. The high temperature causes a shift in the pyranose \rightleftharpoons furanose equilibrium towards the less sweet D-fructose.
- 15.** A $\xrightarrow{\text{HOH}/\text{H}^+}$ glucose + fructose
B $\xrightarrow{\text{HOH}/\text{H}^+}$ glucose + glucose
C $\xrightarrow{\text{HOH}/\text{H}^+}$ glucose + galactose
the disaccharides A, B and C respectively are
(a) lactose, sucrose and maltose
(b) sucrose, maltose and lactose
(c) sucrose, lactose and maltose
(d) maltose, sucrose and lactose
- Hint** Sucrose $\xrightarrow{\text{HOH}/\text{H}^+}$ glucose + fructose
Maltose $\xrightarrow{\text{HOH}/\text{H}^+}$ 2 - molecules of glucose
Lactose $\xrightarrow{\text{HOH}/\text{H}^+}$ glucose + galactose



AMINO ACIDS AND PROTEINS

Amino Acids

As name suggest, these contain both amine (—NH_2) and carboxylic acid (—COOH) groups and are classified into α , β , γ , δ , etc., amino acids, based on the position of —NH_2 group. These are colourless, crystalline, water soluble high melting solids.

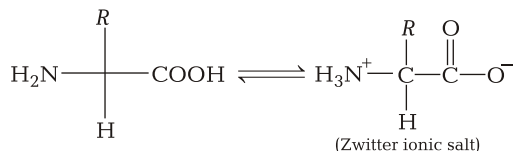
20 different types of α -amino acids have been found in living beings which are classified as

- Essential amino acids** (these are not synthesised in our body and are obtained through diet), e.g. valine, leucine, isoleucine, arginine, lysine, threonine, methionine, phenylalanine, tryptophan and histidine.
- Non-essential amino acids** (these are synthesised in our body), e.g. rest of the 10 amino acids, i.e. glycine, alanine, glutamic acid, aspartic acid, glutamine, asparagine, serine, cysteine, tyrosine, proline.

These can be further classified into sulphur containing amino acids-cysteine and methionine, heterocyclic amino acids-tryptophan, histidine and proline.

Zwitter Ionic Structure of Amino Acid

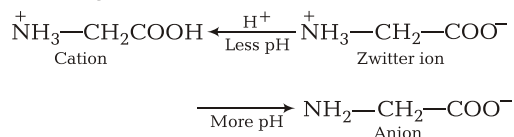
Amino acids exist as Zwitter ion (a bipolar ion) due to transfer of a proton from —COOH group to —NH_2 group as shown below:



Hence, amino acids are amphoteric. These are also optically active (except glycine-simplest amino acid) and mostly exist as L-isomer.

Isoelectric Point

- In aqueous solution, Zwitter ions are stable only over a certain pH range. At high H^+ ions concentration (low pH), the —COO^- group picks up a proton and forms a cation (due to the presence of NH_3^+ group) with a positive charge. At low H^+ ions concentration (high pH), the NH_3^+ group loses a proton and forms an anion (due to the presence of —COO^- group) with a negative charge.



The point (pH range) at which the amino acid molecule has equal positive and negative charges is called the **isoelectric point**. At this point, the amino acids do not migrate in an electric field.

- All amino acids do not have the same isoelectric point. Neutral amino acids have isoelectric points from pH 5.5 to 6.3 (e.g. glycine = 6.1). Acidic amino acids have isoelectric point around pH 3 (e.g. aspartic acid = 3) and basic amino acids have isoelectric point from pH 7.6 to 10.8 (e.g. lysine = 9.7).
- Amino acids usually show their lowest solubility in a solution at the isoelectric point because of their highest concentration of dipolar ion. This property has been used in the separation of different amino acids obtained from the hydrolysis of proteins.
- The acidity and basicity constants of amino acids are very low as compared to carboxylic acids and aliphatic amines. The reason being that in α -amino acids, —NH_3^+ and —COO^- groups which acts as acid and base respectively.

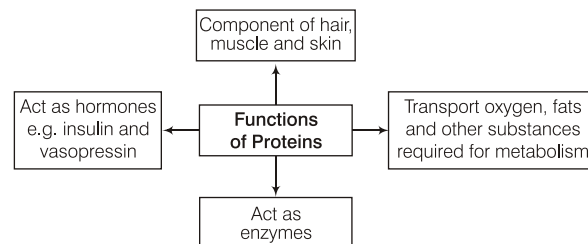
Amino Acids and Disease

During World War II, the Chamorro people of Guam have a high incidence of a syndrome that resembles Amyotrophic Lateral Sclerosis (ALS) with elements of Parkinson's disease and dementia. This syndrome was developed as a result of food shortages, the tribe ate large quantities of the seeds of cycas circinalis.

These seeds contain β -methylamino-L-alanine, an amino acid, that binds to glutamate receptors. When monkeys are given; β -methylamino-L-alanine, they develop some of the features of this syndrome. We may gain an understanding of how ALS and Parkinson's disease arise by studying the mechanism of action of β -methylamino-L-alanine.

Proteins

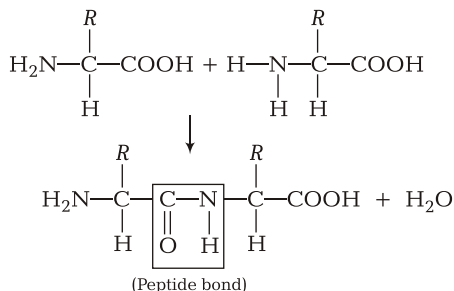
These are polymers of amino acids (specifically α - amino acids) and make upto 15% by mass of our body.



Proteins are important components of most foods. In the digestive system, proteins are broken down into small molecules called α - amino acids. These molecules are then reassembled in cells to form other proteins required by the body.

Structure of Proteins

Proteins are condensed polymer of α -amino acids which are joined together through a peptide bond with the release of water molecule.



Based on the shape and orientation of the peptide bond, proteins are classified into the following types:

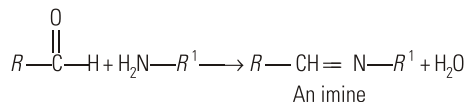
Name and definition of structure	Characteristics of the structure and examples
(a) Primary structure (1°) The number and sequence of different amino acids in a protein constitute primary structure.	Any change in the primary structure (change in the sequence of amino acid) creates a new amino acids.
(b) Secondary structure (2°) This structure is due to shape obtained by the folding of polypeptide chain in space. The folding is due to hydrogen bonding between $-\text{NH}-$ group of one amino acid and $>\text{C}=\text{O}$ group of an adjacent turn.	Secondary structure are of two types such as α -helix which is the most common secondary structure and β -helix.

- (c) **Tertiary structure** (3°) Further folding of secondary structure gives tertiary structure which represents overall folding of the polypeptide chain. Fibrous proteins and globular proteins are examples of tertiary structure of protein. Secondary and tertiary structures are stabilised by hydrogen bond, disulphide linkage, van der Waals' and electrostatic force of attraction.
- (d) **Quaternary structure** The spatial arrangement of different subunits (made of 2° quaternary structures are or 3° polypeptide chains) with respect to each other represents quaternary structure. During denaturation of proteins, secondary, tertiary and quaternary structures are destroyed but primary structure remains intact.

Enzymes Enzymes are biomolecules, mostly made of globular proteins, that catalyse a particular reaction in our body. Enzymes are highly specific for a particular reaction and for a particular substrate.

Advanced Glycation End (AGE) Products and Ageing

1° amine and an aldehyde or a ketone can react by linking two molecules as shown below:



As in our body, proteins have $-\text{NH}_2$ group and carbohydrates have aldehyde or keto groups, they can undergo this reaction by establishing a link between a sugar and a protein molecules. When this reaction is not catalysed by enzymes, it is called *glycation of proteins*.

The process, however does not stop here, When these linked products are heated in a test tube, high molecular weight, water insoluble, brownish complexes are formed.

These complexes are called advanced glycation end products (AGE). In the body, they cannot be heated, but the same result happens over long periods of times.

Best Practice SHOTS

16. Which of the following is involved in the formation of heme?

- (a) Lysine (b) Glycine
(c) Tyrosine (d) Arginine

Hint The heme ring system is synthesised from glycine and succinyl-CoA.

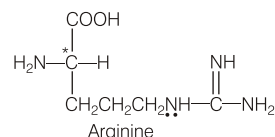
17. Which of the following is not an essential amino acid for man?

- (a) Tyrosine (b) Leucine
(c) Lysine (d) Valine

18. Which amino acid have more than one stereogenic centre?

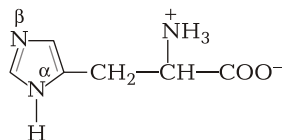
- (a) Aspartic acid (b) Lysine
(c) Arginine (d) Histidine

Hint



{ JEE FINAL TOUCH }

19. Which of the nitrogen of histidine is first protonated?



- (a) α (b) β
(c) Both (a) and (b) (d) None of these

Hint Protonation of β -N leads to imidazolium ion, which is stabilised by two equivalent resonating structures.

20. Which of the following is a heterocyclic amino acid?

- (a) Glycine (b) Alanine
(c) Phenylalanine (d) Tryptophan

21. Give the pOH range for the isoelectric point of the amphoteric ion of an amino acid.

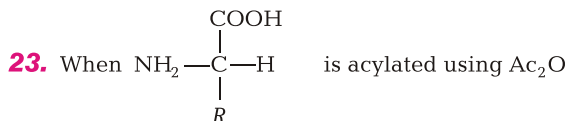
- (a) 5.5 to 6.3 (b) 2.5 to 5.0
(c) 7.7 to 8.5 (d) 9.0 to 10.7

Hint The pH range for the isoelectric point is from 5.5 to 6.3 or the pOH range for the isoelectric point is from 7.7 to 8.5.

22. At pH = 4, glycine exists as

- (a) $\text{NH}_3^+ - \text{CH}_2 - \text{COO}^-$ (b) $\text{NH}_3^+ - \text{CH}_2 - \text{COOH}$
(c) $\text{NH}_2 - \text{CH}_2 - \text{COOH}$ (d) $\text{NH}_2 - \text{CH}_2 - \text{COO}^-$

Hint At pH = 4, an amphoteric zwitter ion structure changes into cation when an acid is added to it.



- (a) its configuration is retained
(b) its configuration is inverted

- (c) it becomes unstable
(d) no reaction takes place

24. Isoelectric point is a

- (a) specific temperature
(b) suitable concentration of amino acid
(c) hydrogen ion concentration that does not allow migration of amino acid under electric field
(d) melting point of an amino acid under the influence of electric field

25. Ninhydrin is a reagent used to detect when separated by ion exchange chromatography.

- (a) amino acid (b) amines
(c) Both a and b (d) None of these

26. Which is the neutral amino acid?

- (a) Serine (b) Glutamic acid
(c) Lysine (d) Histidine

27. Which amino acid can form covalent sulphur - sulphur bonds?

- (a) Cysteine (b) Glycine (c) Proline (d) Histidine

28. Which amino acid has phenyl —OH group?

- (a) Lysine (b) Arginine
(c) Proline (d) Tyrosine

29. An achiral amino acid is

- (a) alanine (b) valine (c) leucine (d) glycine

30. In the tetrapeptide ala - lys - val - leu, the C - terminal amino acid is

- (a) ala (b) cys (c) val (d) leu

Answers

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

MASTER STROKE

1. Some of the following are parts of essential amino acids

A : Valine, B: Leucine

C : Serine, D: Proline

E : Lysine, F: Aspartic acid

Select essential amino acid.

- (a) A, B, C (b) B, C, F
(c) A, C, D (d) A, B, E

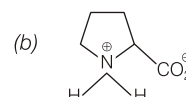
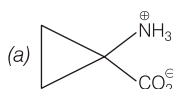
2. Select the correct statement.

- (a) Oligopeptide is generally used for the peptide containing about four to ten amino acids residue

- (b) Steric hindrance causes the *trans* configuration to be more stable than the *cis* configuration so that α -carbons of adjacent amino acids are *trans* to each other

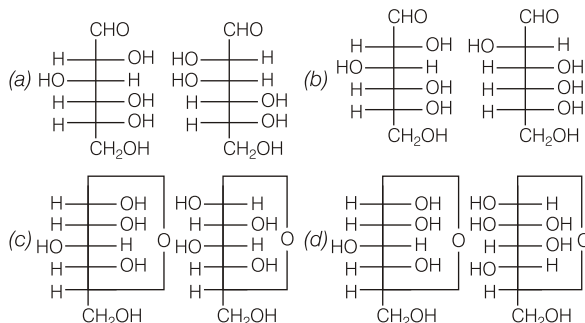
- (c) Both of the above are correct
(d) None of the above is correct

3. Which is α -amino acid?



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

4. Which of the following pairs represents anomers?



5. A compound gives negative test with ninhydrin and positive test with Benedict's solution. The compound is

- (a) a protein (b) an amino acid
(c) a lipid (d) a monosaccharide

6. Which of the following statements is not true about glucose?

- (a) It is an aldohexose
(b) On heating with HI, it forms *n*-hexane
(c) It is present in furanose form
(d) It does not give 2, 4-DNP test

Hint Glucose is present in pyranose form.

7. Biuret test is not given by

- (a) carbohydrate (b) polypeptides
(c) urea (d) protein

Hint Biuret test is characteristically given by the compound having



8. Which of the following monosaccharides is present as five cyclic membered structure (furanose structure)?

- (a) Ribose (b) Glucose
(c) Mannose (d) Galactose

9. Which one of the following is involved in the formation of nicotinamide and indole-3-acetic acid?

- (a) Lysine (b) Glycine (c) Tyrosine (d) Arginine

10. Which of the following statement(s) is/are true?

I. All amino acids contain one chiral centre.

II. Some amino acids contain one, while some contain more chiral centre or even no chiral centre.

III. All amino acids found in protein have L-configuration.

IV. All amino acids found in proteins have amino group.

- (a) II, III and IV (b) II and III
(c) I, III and IV (d) I and IV

11. Which of the following statements is incorrect?

- (a) α -D-glucose and β -D-glucose are enantiomers
(b) D-glyceraldehyde and L-glyceraldehyde are epimers
(c) The reserve carbohydrate of animals is glycogen
(d) Few aldohexoses which react with phenylhydrazine to give identical osazones are epimers

12. Which of the following carbohydrates cannot be directly utilised by the human body as a source of energy?

- (a) Glucose (b) Sucrose
(c) Glycogen (d) Cellulose

13. The α -amino acid which contains the aromatic side chain is

- (a) proline (b) tyrosine
(c) valine (d) tryptophan

14. Cellulose is a straight-chain polysaccharide composed of only

- (a) D- glucose units joined by α - glycosidic linkage
(b) D- glucose units joined by β - glycosidic linkage
(c) D- galactose units joined by α -glycosidic linkage
(d) D- galactose units joined by β -glycosidic linkage

15. The pH value of the solution in which a particular amino acid does not migrate under the influence of an electric field is called the

- (a) eutectic point (b) neutralisation point
(c) effusion point (d) isoelectric point

16. The Kiliani's synthesis is used to increase the carbon chain in

- (a) acid (b) alcohol
(c) aldose (d) ketose

17. α - and β - glucose differ in the orientation of the (—OH) group around

- (a) C₁ (b) C₂ (c) C₃ (d) C₄

18. Which of the following carbohydrates is an essential constituent of plant cells?

- (a) Starch (b) Cellulose
(c) Sucrose (d) Vitamins

19. Glucose molecule reacts with x number of molecule(s) of phenylhydrazine to yield osazone. The value of x is

- (a) three (b) two
(c) one (d) four

20. Which is the correct statement?

- (a) Starch is a polymer of α - glucose
(b) Amylose is a component of cellulose
(c) Lactose made up by galactose unit
(d) In cyclic structure of furanose, there are four carbon atoms and one oxygen atom

Answers

1. (d) 2. (c) 3. (c) 4. (b) 5. (d) 6. (c) 7. (a) 8. (a) 9. (b) 10. (b)
11. (a) 12. (d) 13. (d) 14. (b) 15. (d) 16. (c) 17. (a) 18. (b) 19. (a) 20. (a)

Polymers



CLASSIFICATION AND MOLECULAR MASS OF POLYMERS

Polymers are macromolecules with high molecular mass which are formed by the joining of one or more than one repeating structural units. Polymers are classified into different categories based on source, structure, molecular force etc., and is shown in the table below.

Classification of Polymers

Base of classification	Polymer types
Based on source	(a) Natural polymers These occur naturally in plants and animals, e.g. cellulose, starch, rubber etc.
	(b) Semi-synthetic polymers These are synthesised from natural polymers, e.g. cellulose nitrate, cellulose acetate (rayon).
	(c) Synthetic polymers These are synthesised artificially, e.g. polythene, buna-S etc.
Based on structure	(a) Linear polymers These are long and straight chain polymers, e.g. polyvinyl chloride etc.
	(b) Branched chain polymers These are linear chains having some branches, e.g. low density polythene, etc.
	(c) Cross-linked or network polymers These are formed from bi-functional or tri-functional monomers which are joined through covalent bond, e.g. melamine, bakelite etc.
Based on mode of polymerisation	(a) Addition polymers These are formed by repeated addition of monomers containing double or triple bonds. These are further classified as: (i) Homopolymers These are formed by the polymerisation of single monomeric units, e.g. polythene. (ii) Copolymers These are formed by the polymerisation of two monomeric units, e.g. buna-S, buna-N etc.
	(b) Condensation polymers These are formed by condensation reaction between two different bi-functional or tri-functional monomeric units with the elimination of small molecules such as H_2O , ROH , HCl etc., e.g. nylon-6,6, dacron, etc.
	(c) Thermoplastic polymers These possess intermolecular forces intermediate between elastomers and fibres. These can be made softer or harder repeatedly by heating and cooling respectively, e.g. polythene, PVC etc.
Based on molecular forces (decides the mechanical strength)	(a) Elastomers These are held together by weakest intermolecular forces that make them stretched showing elastic properties. e.g. neoprene, buna-S, buna-N etc.
	(b) Fibres These are held together by strong intermolecular forces like hydrogen bonding that gives them high tensile strength and elasticity, e.g. polyamides, polyesters etc.
	(c) Thermosetting polymers These are cross-linked polymers which on heating undergo extensive cross-linking. These cannot be reused, e.g. bakelite, urea-formaldehyde resin etc.
	(d) Thermoplastic polymers These possess intermolecular forces intermediate between elastomers and fibres. These can be made softer or harder repeatedly by heating and cooling respectively, e.g. polythene, PVC etc.
Based on biodegradation	(a) Biodegradable polymers These can be degraded by microbes, e.g. all natural polymers, PHBV, nylon-2-nylon-6 etc.
	(b) Non-biodegradable polymers Most of the artificially synthesised polymers like polythene, PVC etc. These cause pollution to environment.

Biologically Compatible Polymers

These polymers functionalised with a biological surface reactive moiety and a bridging molecule to provide a medical adhesive. Some examples of these are given below:

- The polymer used in making contact lenses must be quite hydrophilic to permit easy lubrication of the eye. Therefore, a hydrogel in which free alcohol groups are attached to a poly (methyl methacrylate) is used.
- Polymers for making dental impressions, on the other hand, should not form local hydrous pockets but must be moderately hydrophilic in order to wet the oral tissue effectively. These polymers will solidify, because these are capped with groups that can react by a ring opening polymerisation.

Molecular Mass of Polymers

There are two ways of expressing molecular mass of a polymer. These are number average molecular mass and weight average molecular mass.

Number Average Molecular Mass

The expression for number average molecular mass is $\bar{M}_n = \frac{\sum N_i M_i}{\sum N_i}$. Osmotic pressure method is used to determine

number average molecular mass.

Weight Average Molecular Mass

The expression for weight average molecular mass is

$$\bar{M}_w = \frac{\sum N_i M_i^2}{\sum N_i M_i}$$

It is determined by light scattering and ultracentrifugation methods.

where, N_i = number of molecules of molecular mass M_i

Polydispersity Index (PDI)

The ratio of weight average molecular mass and number average molecular mass is called polydispersity index (PDI).

$$PDI = \frac{\bar{M}_w}{\bar{M}_n}$$

For natural polymers, PDI = 1

∴ $\bar{M}_w = \bar{M}_n$ and polymer is monodispersed.

For synthetic polymers, PDI > 1,

∴ $\bar{M}_w > \bar{M}_n$ and polymer is polydispersed.

Best Practice [SHOTS]

- Which of the following are examples of polymer?

I. Plastics	II. Proteins
III. Paints	IV. Polythene

 Choose the correct option.

(a) I, II and III	(b) II, III and IV
(c) I, II and IV	(d) All of these
- Which of the following polymers behave as semi-synthetic polymers?

(a) Cellulose and starch	(b) Cellulose acetate and cellulose nitrate
(c) Buna-N and buna-S	(d) Cellulose nitrate and buna-S
- Examples of linear polymers are

(a) HDP, PVC	(b) HDP, LDP
(c) LDP, PVC	(d) PVC, bakelite
- Cross-linked polymers are usually formed by

(a) bifunctional monomer	(b) trifunctional monomer
(c) monofunctional monomer	(d) Both (a) and (b)
- Among the following polymers, the strongest intermolecular forces of attraction are present in

(a) elastomers	(b) fibres
(c) thermoplastics	(d) thermosetting
- The polymer that shows elastic property is

(a) neoprene	(b) polyesters
(c) nylon-2-nylon-6	(d) polythene
- Identify the example(s) of thermoplastic polymer.

(a) Polythene	(b) Polystyrene
(c) Polyvinyl	(d) All of these
- Three dimensional molecule with cross-links is formed in the case of

(a) thermoplastic	(b) thermosetting plastic
(c) Both (a) and (b)	(d) None of these
- Low density polythene is an example of

(a) cross-linked polymer	(b) natural polymer
(c) linear polymer	(d) branched polymer
- What is full form of HDP?

(a) High density polyethylene	(b) High density polythene
(c) High density polypropene	(d) High density polypropylene
- Which of the following monomers forms biodegradable polymers?

(a) Glycine-amino caproic acid	(b) Caprolactam
(c) 3-hydroxybutanoic acid + 3-hydroxypropanoic acid	(d) Ethylene glycol + phthalic acid
- What is the similarity between buna-N and PHBV?

(a) Both are copolymers	(b) Both are biodegradable
(c) Both have one same monomeric unit	(d) Peroxide catalyst is used in their preparations
- PHBV stands for

(a) poly β -hydroxybutyrate valerate	(b) poly α -hydroxybutyrate valerate
(c) poly β -hydroxybutyrate-co- β -hydroxy valerate	(d) poly α -hydroxybutyrate - co- β -hydroxy valerate
- The number average molecular mass and weight average molecular mass of a polymer are respectively 30, 000 and 40, 000. The polydispersity index of the polymer is

(a) < 1	(b) > 1	(c) 1	(d) 0
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- Number average molecular mass (\bar{M}_n) and weight average molecular mass (\bar{M}_w) of the synthetic polymers are related as

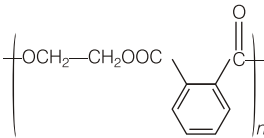
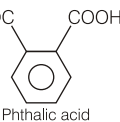
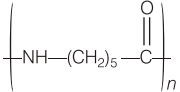
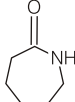
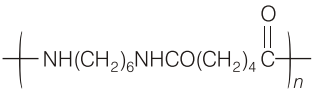
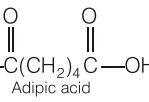
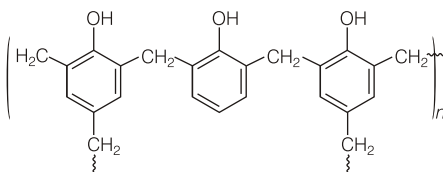

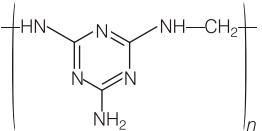
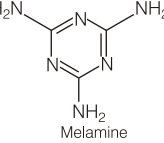
(a) $\bar{M}_n = (\bar{M}_w)^{1/2}$	(b) $\bar{M}_n = \bar{M}_w$
(c) $\bar{M}_w > \bar{M}_n$	(d) $\bar{M}_w < \bar{M}_n$

{ JEE FINAL TOUCH }**TYPES OF POLYMERS AND VULCANISATION OF RUBBER****(a) Addition Polymers**

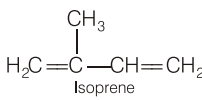
Polymer name and structure	Monomers	Uses
Polythene $\text{-(CH}_2\text{-CH}_2\text{)}_n\text{-}$	$\text{CH}_2\text{=CH}_2$ (Ethene)	As an insulator, anticorrosive, packing material, household and laboratory wares.
Polystyrene $\left[\begin{array}{c} \text{C}_6\text{H}_5 \\ \\ \text{---CH---CH}_2\text{---} \\ \\ \text{---} \end{array} \right]_n$	$\begin{array}{c} \text{CH=CH}_2 \\ \\ \text{C}_6\text{H}_5 \\ \text{(Styrene)} \end{array}$	As an insulator, wrapping materials, in manufacture of toys and household articles.
Polyvinyl chloride (PVC) $\left[\begin{array}{c} \text{Cl} \\ \\ \text{---CH}_2\text{---CH---} \\ \\ \text{---} \end{array} \right]_n$	$\text{CH}_2\text{=CHCl}$ Vinyl chloride	In manufacture of raincoats, handbags, vinyl flooring and leather clothes.
Polytetrafluoroethylene (PTFE) or Teflon $\text{-(CF}_2\text{-CF}_2\text{)}_n\text{-}$	$\text{CF}_2\text{=CF}_2$ Tetrafluoroethene	As lubricant, insulator and in making cooking wares.
Polymethyl methacrylate (PMMA or plexiglass) $\left[\begin{array}{c} \text{CH}_3 \\ \\ \text{---CH}_2\text{---C---} \\ \\ \text{COOCH}_3 \\ \text{---} \end{array} \right]_n$	$\begin{array}{c} \text{CH}_2\text{=C COOCH}_3 \\ \\ \text{CH}_3 \\ \text{Methyl methacrylate} \end{array}$	As substitute of glass and making decorative materials.
Polyacrylonitrile (Orlon) $\left[\begin{array}{c} \text{CN} \\ \\ \text{---CH}_2\text{---CH---} \\ \\ \text{---} \end{array} \right]_n$	$\text{CH}_2\text{=CHCN}$ Vinyl cyanide	In making synthetic fibres and synthetic wool.
Neoprene $\left[\begin{array}{c} \text{---CH}_2\text{---C=CH---CH}_2\text{---} \\ \\ \text{Cl} \\ \text{---} \end{array} \right]_n$	$\begin{array}{c} \text{CH}_2\text{=C---CH=CH}_2 \\ \\ \text{Cl} \\ \text{Chloroprene} \end{array}$	As an insulator, in making conveyor belts and printing rollers.
Buna-S (styrene-butadiene rubber, SBR) $\left[\begin{array}{c} \text{---CH}_2\text{---CH=CH---CH}_2\text{---CH---CH}_2\text{---} \\ \\ \text{C}_6\text{H}_5 \\ \text{---} \end{array} \right]_n$	(a) $\text{CH}_2\text{=CH---CH=CH}_2$ Buta-1, 3-diene (b) $\begin{array}{c} \text{CH=CH}_2 \\ \\ \text{C}_6\text{H}_5 \\ \text{Styrene} \end{array}$	In making automobile tyres, footwear and bubble gums.
Buna-N (nitrile rubber, NBR) $\left[\begin{array}{c} \text{---CH}_2\text{---CH=CHCH}_2\text{---CH---CH}_2\text{---} \\ \\ \text{CN} \\ \text{---} \end{array} \right]_n$	(a) $\text{CH}_2\text{=CH---CH=CH}_2$ Buta-1, 3-diene (b) $\begin{array}{c} \text{CH=CH}_2 \\ \\ \text{CN} \\ \text{Acrylonitrile} \end{array}$	In making oil seals, manufacture of hoses and tank linings.

(b) Condensation Polymers

Polymer name and structure	Monomer(s)	Uses
Terylene or dacron $\left[\begin{array}{c} \text{O} \quad \text{O} \\ \quad \\ \text{---C---C}_6\text{H}_4\text{---C---CO---CH}_2\text{CH}_2\text{---O---} \\ \text{---} \end{array} \right]_n$	(a) $\text{HO---CH}_2\text{---CH}_2\text{---OH}$ Ethylene glycol or ethane -1, 2-diol (b) $\begin{array}{c} \text{O} \quad \text{O} \\ \quad \\ \text{HO---C---C}_6\text{H}_4\text{---C---OH} \\ \text{Terephthalic acid} \\ \text{or benzene-1,4-dicarboxylic acid} \end{array}$	For making wash and wear fabrics, tyre cords, safety belts, tents, sea belts and sails.

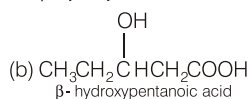
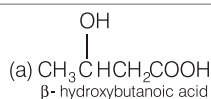
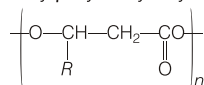
Polymer name and structure	Monomer(s)	Uses
Glyptal or alkyl resin 	(a) $\text{HO}-\text{CH}_2-\text{CH}_2-\text{OH}$ Ethylene glycol (b)  Phthalic acid	As binding material in preparation of mixed plastics and paints.
Nylon-6 or Perlon 	 Caprolactam	In making fibres, plastics, tyre cords and ropes.
Nylon-6, 6 	(a)  Adipic acid (b) $\text{H}_2\text{N}-(\text{CH}_2)_6-\text{NH}_2$ Hexamethylenediamine	In making bristles for brushes, synthetic fibres, parachutes, ropes and carpets, as a substitute for metal in bearings and gears. Crinkled nylon is used for making elastic hosiery.
Bakelite 	(a) HCHO Formaldehyde (b) $\text{C}_6\text{H}_5\text{OH}$ Phenol	For making gears, protective coatings and electrical fittings.
Urea formaldehyde resin 	(a) HCHO Formaldehyde (b) NH_2CONH_2 Urea	For making unbreakable cups and laminated sheets.
Melamine-formaldehyde resin or melmac 	(a)  Melamine (b) HCHO Formaldehyde	In making plastic crockery, unbreakable cups and plates.
Kelvar (nylon polymer)	(a) Terephthalic acid (b) 1, 4-diaminobenzene	For making bulletproof vests.
Lexan or polycarbonate (polyester)	(a) Diethyl carbonate (b) Bisphenol-A	In making bulletproof windows and safety helmets.

(c) Biodegradable Polymers

Polymer name and structure	Monomer(s)	Uses
Amylose (straight chain polymer)	α -D-glucose	A component of starch.
Amylopectin (branched chain polymer) cellulose	α -D-glucose, β -D-glucose	A component of starch.
Natural rubber (straight chain polymer)	 Isoprene	Plant cell wall is made of cellulose.

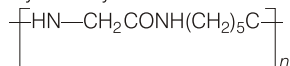
{ JEE FINAL TOUCH }

Poly- β -hydroxybutyrate-co- β -hydroxy valerate (PHBV)



Used to make packaging material, orthopaedic devices and in controlled release of drugs.

Nylon-2-nylon-6



Used to make nylon ropes, fishing nets, parachutes, etc.

Mechanisms Involved in Addition Polymerisation for Three Different Cases

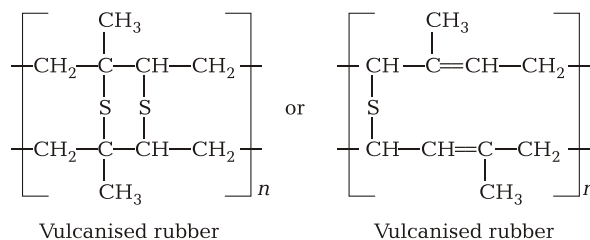
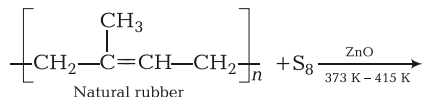
Free radical addition polymerisation	Cationic addition polymerisation	Anionic addition polymerisation
<p>Step I Initiation</p> $(\text{RCOO})_2 \rightarrow 2\text{RCOO}^\bullet \rightarrow \text{R}^\bullet + \text{CO}_2$ <p>Alkyl peroxide (Free radical)</p> $\text{R}^\bullet + \text{CH}_2=\underset{\text{Y}}{\text{CH}} \rightarrow \text{RCH}_2-\underset{\text{Y}}{\overset{\bullet}{\text{C}}}\text{H}$ <p>(Excited monomer)</p> <p>(Y=H, Cl, CN, -R etc)</p> <p>Step II Propagation</p> $\text{RCH}_2-\underset{\text{Y}}{\overset{\bullet}{\text{C}}}\text{H} + \text{CH}_2=\underset{\text{Y}}{\text{CH}} \rightarrow \text{RCH}_2-\underset{\text{Y}}{\text{CH}}-\underset{\text{Y}}{\text{CH}}-\underset{\text{Y}}{\overset{\bullet}{\text{C}}}\text{H}$ $\text{RCH}_2-\underset{\text{Y}}{\text{CH}}-\underset{\text{Y}}{\text{CH}}-\underset{\text{Y}}{\overset{\bullet}{\text{C}}}\text{H} + n\text{CH}_2=\underset{\text{Y}}{\text{CH}} \rightarrow \text{R}-\left[\underset{\text{Y}}{\text{CH}_2}-\underset{\text{Y}}{\text{CH}} \right]_n-\underset{\text{Y}}{\text{CH}_2}-\underset{\text{Y}}{\overset{\bullet}{\text{C}}}\text{H}$ <p>Step III Termination</p> $\text{R}-\left[\underset{\text{Y}}{\text{CH}_2}-\underset{\text{Y}}{\text{CH}} \right]_n-\underset{\text{Y}}{\text{CH}_2}-\underset{\text{Y}}{\overset{\bullet}{\text{C}}}\text{H} + \text{R}^\bullet \rightarrow \text{R}-\left[\underset{\text{Y}}{\text{CH}_2}-\underset{\text{Y}}{\text{CH}} \right]_n-\underset{\text{Y}}{\text{CH}_2}-\underset{\text{Y}}{\text{CH}}-\text{R}$	$\text{H}_2\text{SO}_4 \rightleftharpoons \text{H}^+ + \text{HSO}_4^-$ $\text{H}^+ + \text{CH}_2=\underset{\text{CH}_3}{\text{C}}(\text{CH}_3) \rightarrow \text{H}_3\text{C}-\underset{\text{CH}_3}{\overset{\oplus}{\text{C}}}(\text{CH}_3)$ <p>(Carbocation)</p> $\text{BF}_3 + \text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{BF}_3(\text{OH}^-)$ $\text{H}_3\text{C}-\underset{\text{CH}_3}{\overset{\oplus}{\text{C}}}(\text{CH}_3) + \text{CH}_2=\underset{\text{CH}_3}{\text{C}}(\text{CH}_3) \rightarrow \text{H}_3\text{C}-\underset{\text{CH}_3}{\text{C}}(\text{CH}_3)-\underset{\text{CH}_3}{\overset{\oplus}{\text{C}}}(\text{CH}_3)$ $\text{H}_3\text{C}-\underset{\text{CH}_3}{\text{C}}(\text{CH}_3)-\underset{\text{CH}_3}{\overset{\oplus}{\text{C}}}(\text{CH}_3) + n\text{CH}_2=\underset{\text{CH}_3}{\text{C}}(\text{CH}_3) \rightarrow \text{H}_3\text{C}-\left[\underset{\text{CH}_3}{\text{C}}(\text{CH}_3)-\underset{\text{CH}_3}{\text{CH}_2} \right]_n-\underset{\text{CH}_3}{\overset{\oplus}{\text{C}}}(\text{CH}_3)$ <p>Step III $-\text{H}^+$</p> $\text{H}_3\text{C}-\left[\underset{\text{CH}_3}{\text{C}}(\text{CH}_3)-\underset{\text{CH}_3}{\text{CH}_2} \right]_n-\underset{\text{CH}_3}{\overset{\oplus}{\text{C}}}(\text{CH}_3) \xrightarrow{-\text{H}^+} \text{H}_3\text{C}-\left[\underset{\text{CH}_3}{\text{C}}(\text{CH}_3)-\underset{\text{CH}_3}{\text{CH}_2} \right]_n-\text{CH}=\underset{\text{CH}_3}{\text{C}}(\text{CH}_3)$	$\text{KNH}_2 \rightarrow \text{K}^+ + \text{NH}_2^-$ $\text{H}_2\text{N} + \text{CH}_2=\underset{\text{CN}}{\text{C}}\text{H} \rightarrow \text{H}_2\text{N}-\underset{\text{CN}}{\overset{\ominus}{\text{C}}}\text{H}$ <p>Carbanion</p> $\text{H}_2\text{N}-\underset{\text{CN}}{\overset{\ominus}{\text{C}}}\text{H} + \text{CH}_2=\underset{\text{CN}}{\text{C}}\text{H} \rightarrow \text{H}_2\text{N}-\underset{\text{CN}}{\text{CH}}-\underset{\text{CN}}{\overset{\ominus}{\text{C}}}\text{H}$ $\text{H}_2\text{N}-\underset{\text{CN}}{\text{CH}}-\underset{\text{CN}}{\overset{\ominus}{\text{C}}}\text{H} + n\text{CH}_2=\underset{\text{CN}}{\text{C}}\text{H} \xrightarrow{+\text{H}^+} \text{H}_2\text{N}-\underset{\text{CN}}{\text{CH}}-\left[\underset{\text{CN}}{\text{CH}_2}-\underset{\text{CN}}{\text{CH}} \right]_n-\underset{\text{CN}}{\text{CH}_2}-\underset{\text{CN}}{\overset{\ominus}{\text{C}}}\text{H}$ <p>Step III $+\text{H}^+$</p> $\text{H}_2\text{N}-\underset{\text{CN}}{\text{CH}}-\left[\underset{\text{CN}}{\text{CH}_2}-\underset{\text{CN}}{\text{CH}} \right]_n-\underset{\text{CN}}{\text{CH}_2}-\underset{\text{CN}}{\overset{\ominus}{\text{C}}}\text{H} \xrightarrow{+\text{H}^+} \text{H}_2\text{N}-\underset{\text{CN}}{\text{CH}}-\left[\underset{\text{CN}}{\text{CH}_2}-\underset{\text{CN}}{\text{CH}} \right]_n-\underset{\text{CN}}{\text{CH}_2}-\underset{\text{CN}}{\text{CH}_2}$

Difference between High Density and Low Density Polythenes

Low density polythene	High density polythene
Polymerisation is done under very high pressure of 1000-2000 atm and temperature of 350 K to 570 K.	Polymerisation is done at a low pressure of 6-7 atm and temperature of 333 to 343 K in the presence of hydrocarbon solvent.
A peroxide initiator is used as a catalyst.	$\text{Al}(\text{C}_2\text{H}_5)_3$ and TiCl_4 (Ziegler-Natta catalyst) are used as catalysts.
Density is low due to highly branched structure. It is less tougher and harder.	Density is high due to linear structure and close packing. It is more tougher and harder.

Vulcanisation of Rubber

In order to improve the physical properties of natural rubber, it is heated with sulphur and a suitable additive at a temperature range between 373 to 415 K. S-atom forms cross-links at reactive sites of double bond making it stiffer.



Best Practice SHOTS

16. Which of the following type of forces are present in vulcanised rubber?
 - (a) Weakest intermolecular forces
 - (b) Hydrogen bonding
 - (c) Three dimensional network of bonds
 - (d) Metallic bonding
17. Baby feeding bottles and soft drink bottles are usually made up of
 - (a) polyurethane
 - (b) polyester
 - (c) polyamide
 - (d) polyethylene-HDPE
18. Terylene is the polymer of
 - (a) ethylene glycol and terephthalic acid
 - (b) hexamethylenediamine and adipic acid
 - (c) phenol and formaldehyde
 - (d) urea and formaldehyde
19. Which one of the following is not a condensation polymer?
 - (a) Melamine
 - (b) Glyptal
 - (c) Dacron
 - (d) Orlon
20. In the addition polymerisation, the molecules of the different monomers add together to form a
 - (a) chain growth polymer
 - (b) homopolymer
 - (c) copolymer
 - (d) None of these
21. Which one of the followings is a chain growth polymer?
 - (a) Starch
 - (b) Nucleic acid
 - (c) Polystyrene
 - (d) Protein
22. Teflon, styron and neoprene all are
 - (a) copolymers
 - (b) condensation polymers
 - (c) homopolymers
 - (d) monomers
23. Which one of the following is used to make non-stick cookware?
 - (a) PVC
 - (b) Polystyrene
 - (c) Polyethylene
 - (d) Polytetrafluoroethylene
24. Which of the following polymers is currently used as a tyre cord?
 - (a) Polyethylene
 - (b) Polypropylene
 - (c) Bakelite
 - (d) Nylon-6
25. PVC polymer can be prepared by which of the following monomer?
 - (a) $\text{CH}_3\text{CH}=\text{CH}_2$
 - (b) $\text{C}_6\text{H}_5\text{CH}=\text{CH}_2$
 - (c) $\text{CH}_2=\text{CH}_2$
 - (d) $\text{CH}_2=\text{CH}-\text{Cl}$
26. Bakelite is a product of the reaction between
 - (a) formaldehyde and NaOH
 - (b) aniline and urea
 - (c) phenol and methanol
 - (d) phenol and chloroform
27. Novolac and bakelite are those polymers which come under the category of
 - (a) melamine-formaldehyde polymer
 - (b) phenol-formaldehyde polymer
 - (c) polyester
 - (d) polyamide
28. Which of the following is not a polyamide?
 - (a) Wool
 - (b) Leather
 - (c) Nylon
 - (d) Natural rubber
29. Which of the following is used to harden the rubber for tyre manufacture?
 - (a) 1, 2-butadiene
 - (b) CaC_2
 - (c) Wax
 - (d) Carbon black

Answers

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

MASTER STROKE

1. Given polymers, A = nylon-6, B = buna-S, C = polythene. Arrange these in decreasing order of their intermolecular forces.

(a) $A > B > C$ (b) $B > C > A$ (c) $B < A < C$ (d) $C < A < B$

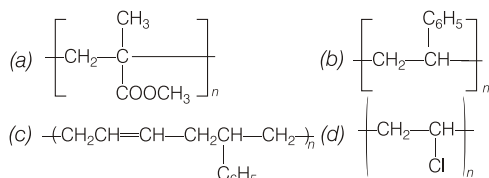
Hint In nylon-6,6, amide linkage is present. Amide linkage is polar, hence is strongest. Out of buna-S and polythene, buna-S has greater surface area. Hence, it has stronger intermolecular forces.

2. Which of the following is a condensation polymer?

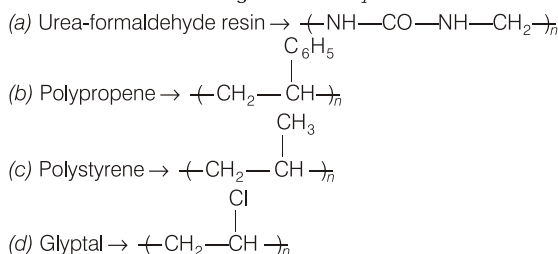
(a) Nylon-6 (b) Rubber
(c) Polyvinyl chloride (d) Polyethylene

Hint Nylon-6 has amide linkage, formed by condensation of $-\text{COOH}$ group with $-\text{NH}_2$ group. It is accompanied by loss of water. So, it is a condensation polymer.

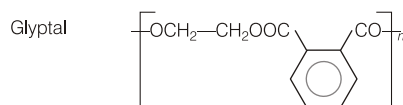
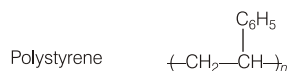
3. Which of the following is a copolymer?



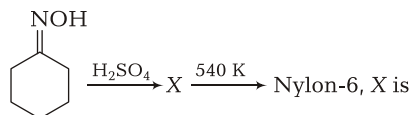
4. Which of the following is correctly matched?



Hint Urea-formaldehyde resin $\left(\text{NH}-\text{CO}-\text{NH}-\text{CH}_2 \right)_n$

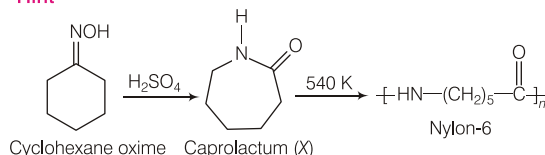


5. In the reaction sequence,



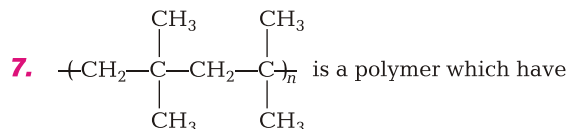
- (a) cyclohexanone
(b) caprolactam
(c) hexamethylenediamine
(d) hexamethylene diisocyanate

Hint

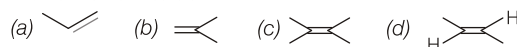


6. Plexiglass, also known as PMMA, is a polymer of

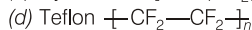
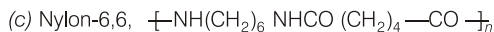
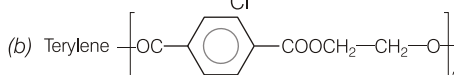
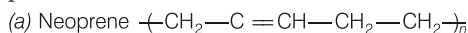
(a) methyl acrylate (b) methyl methacrylate
(c) acrylic acid (d) None of these



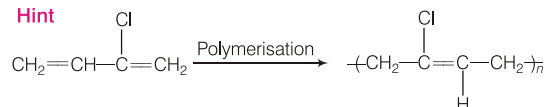
monomer units as



8. Structures of some common polymers are given below alongwith their names. Which one is not correctly presented?



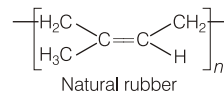
Hint



9. Which one of the following statements is not true?

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

Hint Natural rubber is *cis*-, 1,4-polyisoprene and has only *cis*-configuration about the double bond.



10. I. Caprolactam is the monomer of nylon-6.

II. Dacron is the monomer of ethylene glycol.

III. Orlon is the monomer of polyacrylonitrile.

IV. Tetrafluoroethene is the monomer of teflon.

Which of the above mentioned statement(s) is/are correct? Choose the correct option.

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

Hint Dacron is the polymer of ethylene glycol and terephthalic acid. Orlon is another term used for polyacrylonitrile.

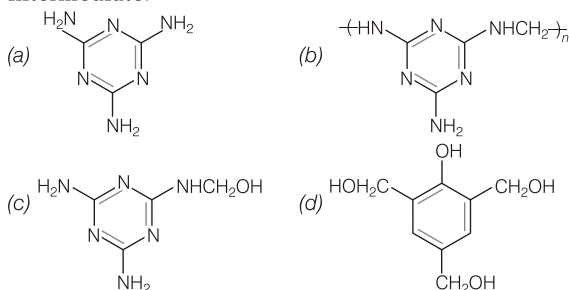
11. Match the following columns and choose the correct option from the codes given below.

Column I (Polymer)	Column II (Monomer)
A. HDP	p. Acrylonitrile
B. Natural rubber	q. Tetrafluoroethene
C. Teflon	r. Isoprene
D. Acrilan	s. Chloroprene
E. Neoprene	t. Ethene

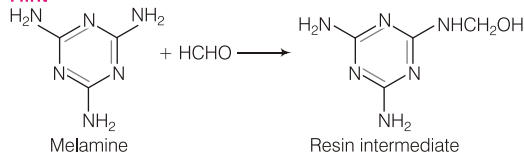
Codes

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

12. When melamine and formaldehyde polymerise, a resin intermediate is formed. Identify the structure of this intermediate.



Hint



13. A polydisperse mixture of a polymer can be described by the following composition molar mass data

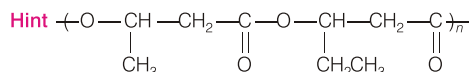
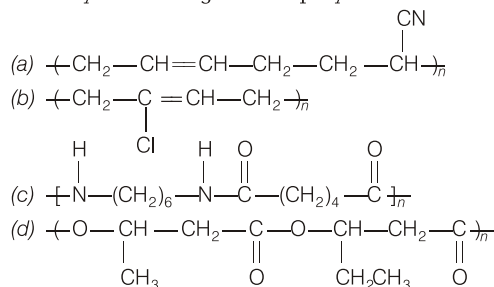
N_i (mol)	0.10	0.20	0.40	0.20	0.10
M_i (kg mol ⁻¹)	1.00	1.20	1.40	1.60	1.80

Calculate the mass average of this mixture.

- (a) 1.43 kg mol⁻¹ (b) 1.21 kg mol⁻¹
 (c) 2.41 kg mol⁻¹ (d) 6.27 kg mol⁻¹
14. A polymeric sample in which 30% molecules have a molecular mass 20,000, 40% have 30,000, and the rest 30% have 60,000. The \bar{M}_n and \bar{M}_w of this sample are
 (a) 36,000; 43,000 (b) 43,333; 36,000
 (c) 72,000; 86,666 (d) 86,666; 72,000
15. Which of the following is used as a catalyst in the manufacture of polythene by Ziegler-Natta method?
 (a) Titanium dioxide
 (b) Titanium tetrachloride and triphenyl aluminium
 (c) Titanium isoperoxide
 (d) Titanium tetrachloride and triethyl aluminium

Hint Titanium tetrachloride and triethyl aluminium are used as Ziegler-Natta catalyst.

16. Identify the biodegradable polymer.



PHBV Poly-β hydroxybutyrate-co-β-hydroxyvalerate is a biodegradable polymer.

17. Which of the following statements is false?

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

Hint Nylon-6,6 is an example of fibre.

18. Consider the following statements,

- I. PVC is useful in making unbreakable cups and laminated sheets.
 II. Glyptal is useful in making paints and lacquers.
 III. Polypropene is useful in making ropes, toys, pipes, fibres, etc.
 IV. Bakelite is useful in making combs, electrical switches, etc.

Which of the above statement(s) is/are correct?

- (a) I and II (b) II and III (c) III and IV (d) II, III and IV

Hint PVC is useful in making raincoats, handbags etc.

19. How will you get the monomer for manufacturing PVC?

- (a) By adding Cl₂ to C₂H₂ (b) By adding HCl to C₂H₄
 (c) By adding Cl₂ to C₂H₄
 (d) By adding HCl to C₂H₂ (in presence of Hg²⁺ salts)

Hint By adding HCl to ethylene in presence of Hg²⁺ salts, the monomer vinyl chloride is obtained for the manufacture of PVC.

20. Consider the following statements about PHBV and identify the correct one.

- (a) It is obtained by the copolymerisation
 (b) It is used specially in packaging, orthopaedic devices
 (c) It undergoes bacterial degradation in the environment
 (d) All of the above

Hint PHBV is obtained by the copolymerisation and is used special in packaging. It undergoes bacterial degradation in the environment.

Answers

1. (a) 2. (a) 3. (c) 4. (a) 5. (b) 6. (b) 7. (b) 8. (a) 9. (d) 10. (c)
 11. (b) 12. (c) 13. (a) 14. (a) 15. (d) 16. (d) 17. (b) 18. (d) 19. (d) 20. (d)

Haloalkanes and Haloarenes

These questions are sync with the concepts given in concept map. Follow concept map to solve these questions,

HALOALKANES

Best Practice SHOTS

1. Which is more reactive towards HCl?

- (a) $\text{CH}_2=\text{CH}-\text{CH}_2-\text{OH}$ (b) $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$
 (c) $\text{CH}_3-\underset{\text{OH}}{\underset{|}{\text{C}}}-\text{H}-\text{CH}_3$ (d) $\text{CH}_2=\text{CH}-\text{OH}$

Hint $\text{CH}_2=\text{CH}-\overset{+}{\text{C}}\text{H}_2$ (intermediate) is resonance stabilised.

2. Which mechanism ($\text{S}_{\text{N}}1$ or $\text{S}_{\text{N}}2$) is followed in the protonation of $\text{CH}_3\text{CH}_2\text{OH}$ and $(\text{CH}_3)_2\text{CHOH}$ respectively?

- (a) $\text{S}_{\text{N}}1$ in both (b) $\text{S}_{\text{N}}2$ in both
 (c) $\text{S}_{\text{N}}1$ and $\text{S}_{\text{N}}2$ (d) $\text{S}_{\text{N}}2$ and $\text{S}_{\text{N}}1$

3. Which of the followings gives racemic mixture on halogenation?

- (a) $(\text{CH}_3)_4\text{C}$ (b) $(\text{CH}_3)_2\text{CHCH}_2\text{CH}(\text{CH}_3)_2$
 (c) $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$ (d) $(\text{CH}_3\text{CH}_2)_4\text{C}$

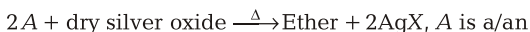
Hint $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3 \xrightarrow{\text{Cl}_2} \text{CH}_3-\overset{*}{\underset{\text{Cl}}{\text{C}}}-\text{CH}_2-\text{CH}_3$ *C is

chiral carbon. Thus, racemic mixture.

4. Reactivity of halogens towards alkanes is in order

- (a) $\text{F}_2 > \text{Br}_2 > \text{Cl}_2 > \text{I}_2$ (b) $\text{F}_2 > \text{Cl}_2 > \text{I}_2 > \text{Br}_2$
 (c) $\text{Cl}_2 > \text{I}_2 > \text{Br}_2 > \text{F}_2$ (d) $\text{F}_2 > \text{Cl}_2 > \text{Br}_2 > \text{I}_2$

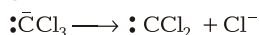
5. In the following reaction



- (a) primary alcohol (b) acid
 (c) alkyl halide (d) alcohol

Hint $2R-X + \text{Ag}_2\text{O} \xrightarrow{\Delta} R-O-R + 2\text{AgX}$
Alkyl halide (Dry) Ether

6. Following reaction is of the type

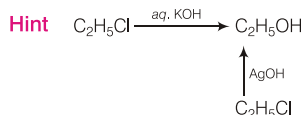


- (a) β -elimination (b) α -elimination
 (c) 1, 2-elimination (d) E_2 -elimination

7. Identify A and B in the following reaction



- (a) A = aqueous KOH; B = AgOH
 (b) A = alcoholic KOH/ Δ ; B = Aqueous NaOH
 (c) A = aqueous NaOH; B = AgNO₂
 (d) A = AgNO₂; B = KNO₂



8. Chloropicrin is obtained when chloroform reacts with _____ and reaction is _____ type.

- (a) nitrous acid, S_{N} (b) nitric acid, S_{E}
 (c) picric acid, S_{E} (d) nitric acid, S_{N}

9. Tertiary alkyl halides are practically inert to substitution by $\text{S}_{\text{N}}2$ mechanism because of

- (a) steric hindrance (b) inductive effect
 (c) instability (d) insolubility

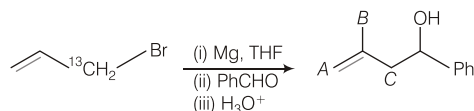
10. Select the reagent that will yield the greater amount of substitution on reaction with 1-bromobutane.

- (a) $\text{CH}_3\text{CH}_2\text{O}^-\text{K}^+$ in dimethyl sulphoxide (DMSO)
 (b) $(\text{CH}_3)_3\text{C}^-\text{O}^-\text{K}^+$ in dimethyl sulphoxide (DMSO)
 (c) Both (a) and (b) will give comparable amount of substitution
 (d) Neither (a) nor (b) will give any appreciable amount of substitution

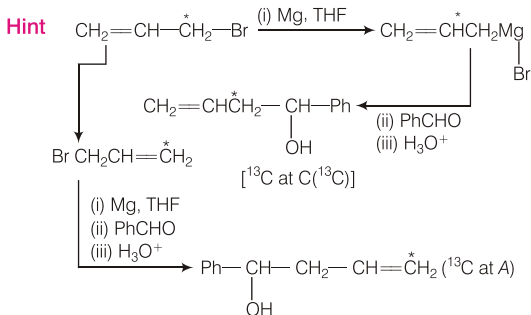
11. Iodoform is formed on warming iodine and Na₂CO₃ with

- (a) $\text{C}_2\text{H}_5\text{OH}$ (b) CH_3OH (c) CH_3COOH (d) HCOOCH_3

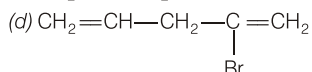
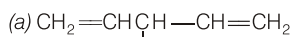
12. In the following reactions isotopic (¹³C) appears at



- (a) A (b) B (c) C (d) Both A and C



13. $\text{CH}_2 = \text{CHCHCH} = \text{CH}_2 \xrightarrow{\text{NBS}}$ A, A is

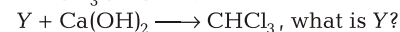


14. Which of the following compounds is used in antiknock composition to prevent the deposition of oxides of lead on spark plug combustion chamber and exhaust pipe?

(a) Glycol
(c) Benzene

(b) Glycerol
(d) 1, 2-dibromoethane

15. $\text{CaOCl}_2 + \text{H}_2\text{O} \longrightarrow \text{Ca(OH)}_2 + \text{X}$

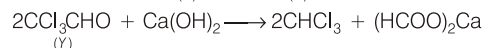
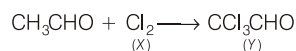
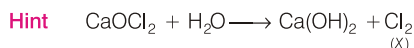


(a) $\text{CH}_3\text{CH(OH)}_2$

(b) CH_2Cl_2

(c) CCl_3CHO

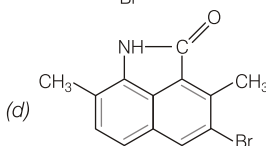
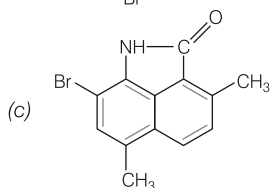
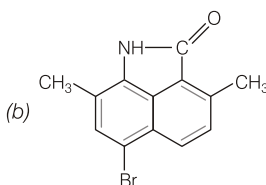
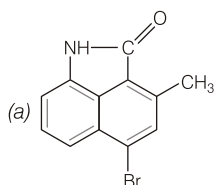
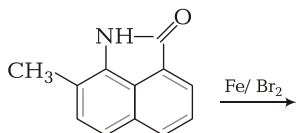
(d) $\text{CCl}_3\text{COCH}_3$



HALOARENES

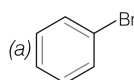
Best Practice SHOTS

16. Product on monobromination of following compound is

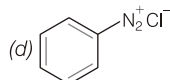
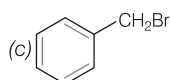


17. X $\xrightarrow[\text{HNO}_3]{\text{AgNO}_3}$ yellow or white ppt.

Which of the followings cannot be X?

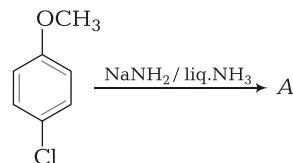


(b) $(\text{CH}_3)_2\text{CHCl}$

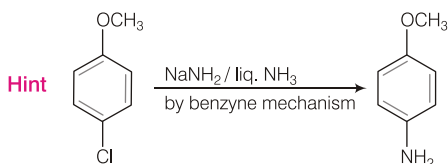
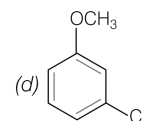
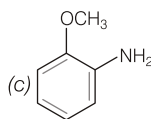
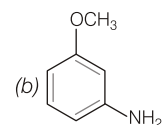
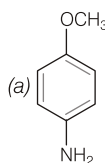


Hint Aryl halides are less reactive towards nucleophilic substitution, hence this reaction is not given by bromobenzene.

18. In the following reaction,

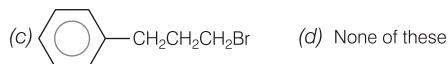
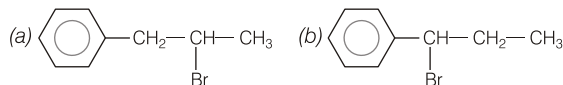


The major product A is



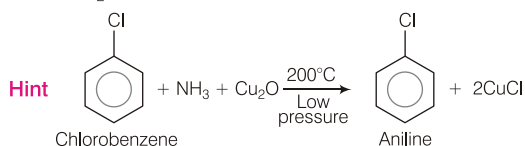
19.

Major product of the above reaction is

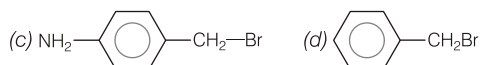
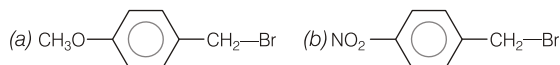
{ JEE FINAL TOUCH }

20. Chlorobenzene gives aniline with

- (a) $\text{NH}_3 / \text{Cu}_2\text{O}$ (b) $\text{NH}_3 / \text{H}_2\text{SO}_4$
 (c) NaNH_2 (d) None of these



21. Which one of the following compounds undergoes predominantly $\text{S}_{\text{N}}2$ reaction with aqueous NaOH in polar aprotic solvents?



22. Which one of the following cannot undergo nucleophilic substitution reaction under ordinary condition?

- (a) Allyl chloride (b) Benzyl chloride
 (c) *n*-propyl chloride (d) Vinyl chloride

23. Which one of the following chlorohydrocarbons readily undergoes solvolysis?

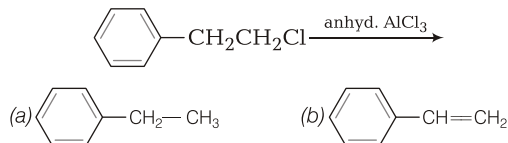


24. Which one of the following statements about benzyl chloride is incorrect?

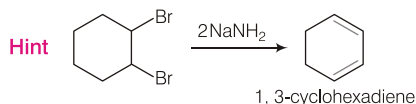
- (a) It is less reactive than alkyl halides
 (b) It can be oxidised to benzaldehyde by boiling with copper nitrite solution
 (c) It is a lachrymatory liquid and gives Beilstein's test
 (d) It gives a white precipitate with alcoholic silver nitrite

Hint Benzyl chloride is more reactive than alkyl halides because benzyl carbocation is stabilised by resonance.

25. What is the predominant product in the following reaction?



26. 1, 2-dibromocyclohexane on dehydrogenation gives



27. The compound formed on heating chlorobenzene with chloral in the presence of concentrated sulphuric acid is

- (a) gammexane (b) DDT
 (c) freon (d) hexachloroethane

28. Which is not the intermediate in the halogenation of toluene at benzylic position?



- (c) Both of these (d) None of these

29. Which of the following reacts with chloroform and base to form phenyl isocyanide?

- (a) Phenol
 (b) Benzene
 (c) Nitrobenzene
 (d) Aniline

Hint Carbylamine reaction

30. Moth repellent is

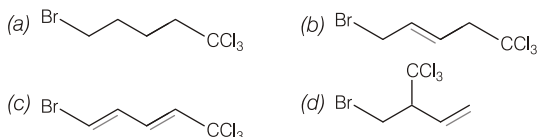
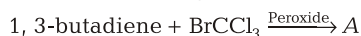
- (a) perchloroethane
 (b) *p*-dichlorobenzene
 (c) Both (a) and (b)
 (d) None of the above

Answers

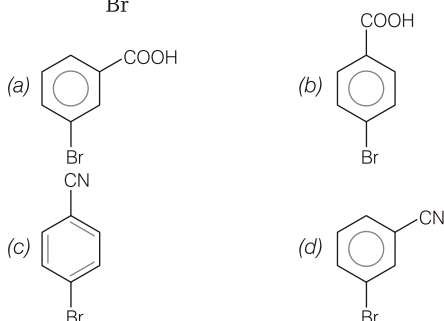
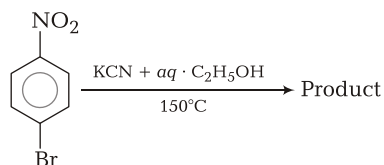
1. (a) 2. (a) 3. (c) 4. (d) 5. (c) 6. (b) 7. (a) 8. (b) 9. (a) 10. (a)
 11. (a) 12. (d) 13. (b) 14. (d) 15. (c) 16. (b) 17. (a) 18. (a) 19. (b) 20. (a)
 21. (b) 22. (d) 23. (c) 24. (a) 25. (b) 26. (b) 27. (b) 28. (b) 29. (d) 30. (c)

MASTER STROKE

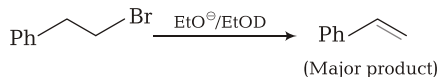
1. In the following reaction, identify product (A)



2. Identify the product in the following reaction.

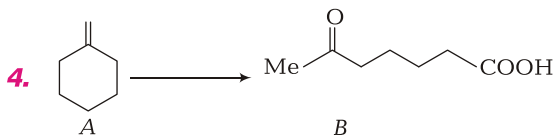


3. In the following reaction,



by which mechanism does the reaction proceed?

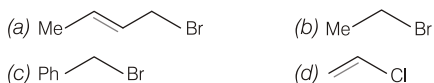
- (a) E_1 (b) E_2
(c) E_{cb} (d) α -elimination



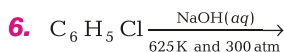
The above conversion can be carried out by which reagents?

- (a) (i) HBr + peroxide (ii) $\text{Me}_3\text{CO}^\ominus, \Delta$ (iii) $\text{O}_3/\text{H}_2\text{O}$
(b) (i) HBr (ii) $\text{C}_2\text{H}_5\text{O}^\ominus, \Delta$ (iii) $\text{O}_3/\text{H}_2\text{O}$
(c) (i) HI (ii) $\text{MeO}^\ominus, \Delta$ (iii) $\text{O}_3/\text{Zn, acid}$
(d) HCl + peroxide

5. Which one of the following compounds gives S_N1 and S_N2 mechanisms?

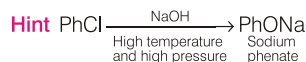


Hint Allyl halides undergo S_N1 and S_N2 .



The product can be

- (a) benzal (b) sodium benzoate
(c) benzol (d) sodium phenate



7. When iodoform is heated with silver powder, the gaseous product formed is

- (a) ethene (b) ethyne
(c) ethane (d) silver iodide

8. Pick up the correct statement about alkyl halide.

- (a) These are associated with each other by H-bonds
(b) These dissolve in water quickly
(c) These dissolve easily in organic solvent
(d) These do not contain any polar bonds in their molecules

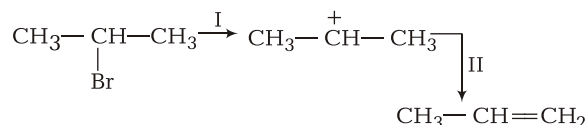
9. Which one of the following cannot be used for the preparation of iodoform?

- (a) Acetone (b) Methanol
(c) Ethanol (d) Acetaldehyde

10. In order to get ethanethiol from bromoethane, the reagent used is

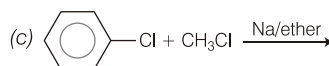
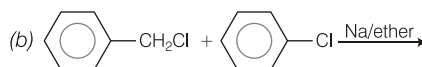
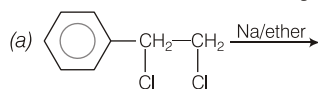
- (a) sodium bisulphide
(b) sodium sulphide
(c) potassium thiocyanate
(d) potassium sulphide

11. In the following reaction sequence, slow and fast steps respectively are



- (a) I and II
(b) II and I
(c) Both are slow steps
(d) Both are fast steps

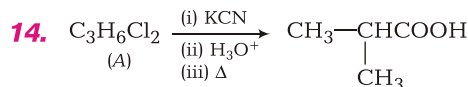
12. Which is not the Wurtz-fittig reaction?



- (d) None of the above

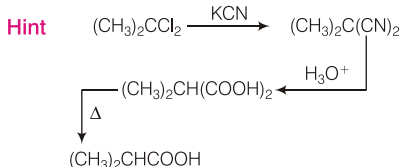
{ JEE FINAL TOUCH }**13.** $\text{CH}_3\text{CH}_2\text{Cl}$ by Wurtz reaction forms

- (a) ethane, ethene and butane (b) ethene and butane
(c) Only butane (d) Only ethane



Here, A is

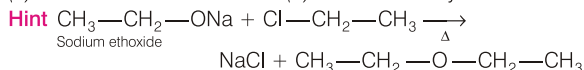
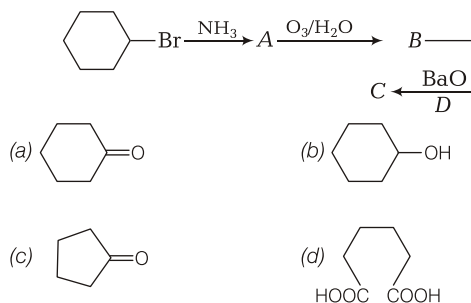
- (a) 1,1-dichloropropane (b) 1,2-dichloropropane
(c) 2,2-dichloropropane (d) 1,3-dichloropropane

**15.** Westron has the formula

- (a) CF_2Cl_2 (b) CHCl_3
(c) $\text{C}_2\text{H}_2\text{Cl}_4$ (d) CHF_3

16. Ethyl chloride is converted into diethyl ether by

- (a) Wurtz reaction (b) Grignard's reagent
(c) Perkin's reaction (d) Williamson's synthesis

**17.** End product of the following sequence of reactions is**18.** Which is highly selective?

- (a) Chlorination of hydrocarbons
(b) Bromination of hydrocarbons
(c) Both (a) and (b)
(d) None of the above

19. 2-bromopentane is heated with potassium ethoxide in ethanol. The major product obtained is

- (a) 2-ethoxy pentane (b) 1-pentene
(c) *trans*-2-pentene (d) *cis*-2-pentene

20. When chlorine reacts with ethyl alcohol, it forms

- (a) chloroform (b) chloral
(c) ethyl chloride (d) carbon tetrachloride

Answers

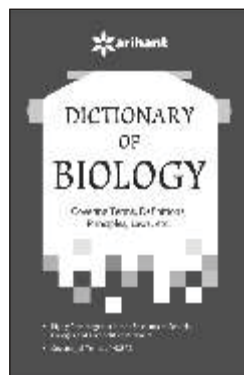
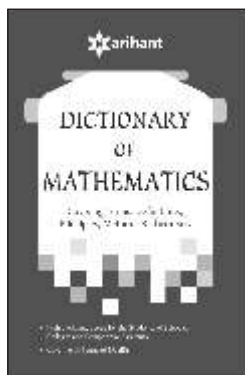
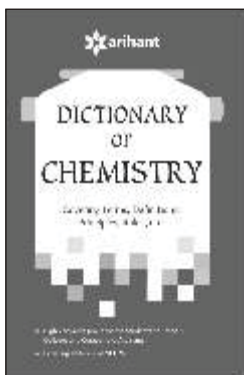
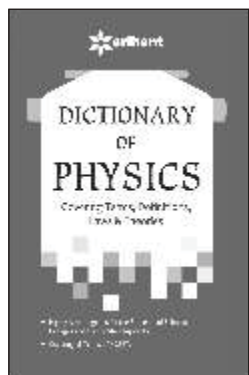
1. (b) 2. (a) 3. (b) 4. (b) 5. (a) 6. (d) 7. (b) 8. (c) 9. (b) 10. (a)
11. (a) 12. (a) 13. (c) 14. (c) 15. (c) 16. (d) 17. (c) 18. (b) 19. (c) 20. (b)

SCIENCE DICTIONARIES *in*

(Physics, Chemistry, Mathematics & Biology)



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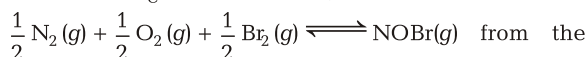
Questions to Measure Your Problem Solving Skills

- Instructions**
- This test consists of 45 questions and each question is allotted 4 marks for correct response.
 - Candidates will be awarded marks as stated above for correct response of each question. 1/4 marks will be deducted for indicating incorrect response of each question. No deduction from the total score will be made if no response is indicated for an item in the answer sheet.
 - There is only one correct response for each question. Filling up more than one response in any question will be treated as wrong response and marks for wrong response will be deducted according as per instructions.

1. When 1.763g of hydrated BaCl_2 is heated, 1.505 g of anhydrous salt is remained, what is the formula of hydrate?

(a) $\text{BaCl}_2 \cdot 5\text{H}_2\text{O}$ (b) $\text{BaCl}_2 \cdot \text{H}_2\text{O}$
(c) $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ (d) None of these

2. Determine K_C for the reaction,

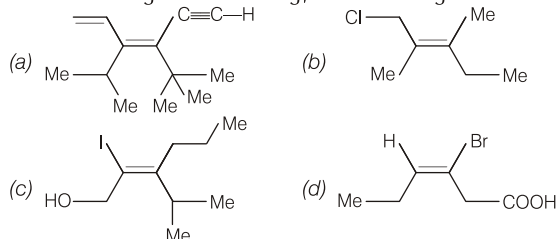


from the following data at 298K. The equilibrium constant for the following reactions, $2\text{NO}(g) \rightleftharpoons \text{N}_2(g) + \text{O}_2(g)$ and $\text{NO}(g) + \frac{1}{2} \text{Br}_2(g) \rightleftharpoons \text{NOBr}(g)$ are 2.4×10^{30}

and 1.4 respectively

(a) 8.352×10^{12} (b) 9.037×10^{-16}
(c) 9.037×10^{16} (d) 8.352×10^{-12}

3. Which among the following, has Z-configuration?

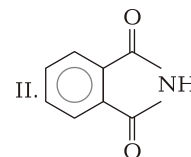
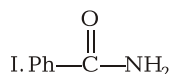


4. Which one of the following statements about the zeolites is false?

(a) They are used as cation exchangers
(b) They have open structure which enables them to take up small molecules
(c) Zeolites are aluminosilicates having three-dimensional network

(d) Some of the SiO_4^{4-} units are replaced by AlO_4^{5-} and AlO_6^{9-} ions in zeolites

5. The decreasing order of acidic character of the following organic compound is



III. PhNH_2

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

6. A hydrocarbon C_6H_{12} decolourises bromine solution and yield *n*-hexane on hydrogenation. On oxidation with KMnO_4 , it gives two different monobasic acids of the type $R\text{---COOH}$. The compound is

(a) cyclohexene (b) 2-hexene (c) 1-hexene (d) 3-hexene

7. Match the following Column I with Column II.

Column I (Compounds)	Column II ($\text{p}K_a$)
A.	p. 4.69
B.	q. 5.12
C.	r. 4.58
D.	s. 4.39

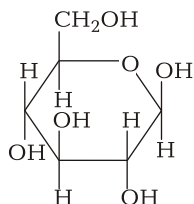
Codes

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

8. The correct order of ionic radii of Yb^{3+} , La^{3+} , Eu^{3+} and Lu^{3+} is

- (a) $\text{Yb}^{3+} < \text{La}^{3+} < \text{Eu}^{3+} < \text{Lu}^{3+}$
 (b) $\text{Lu}^{3+} < \text{Eu}^{3+} < \text{La}^{3+} < \text{Yb}^{3+}$
 (c) $\text{La}^{3+} < \text{Eu}^{3+} < \text{Lu}^{3+} < \text{Yb}^{3+}$
 (d) $\text{Yb}^{3+} < \text{Lu}^{3+} < \text{Eu}^{3+} < \text{La}^{3+}$

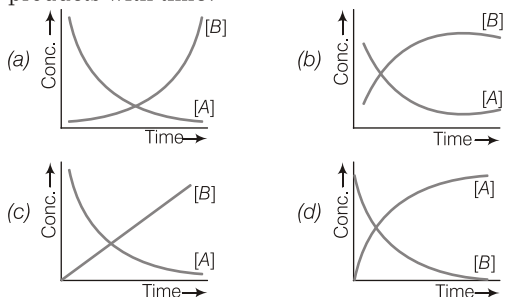
9. The following carbohydrate is very important for human body,



Anomeric carbon present in the carbohydrate are

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

10. Consider the reaction, $A \rightarrow B$. The concentration of both the reactant and the product varies exponentially with time. Which of the following figures correctly describe the change in concentration of reactants and products with time?



11. The difference between two heats of reaction at constant pressure and a constant volume for the reaction, $2\text{C}_6\text{H}_6(l) + 15\text{O}_2(g) \rightarrow 12\text{CO}_2(g) + 6\text{H}_2\text{O}(l)$ at 25°C in kJ is

- (a) -7.43 (b) +3.72 (c) -3.72 (d) +7.43

12. What is the mass of carbon present in 0.1 mole of sodium ferricyanide $\text{Na}_3[\text{Fe}(\text{CN})_6]$?

- (a) 7.2 g (b) 4.5 kg (c) 4.5 g (d) 7.2 kg

13. The transition state from $n=4$ to $n=3$ in a He^+ ion results in UV radiation. Infrared radiation will be obtained in the transition from

- (a) $n=2 \rightarrow n=1$ (b) $n=3 \rightarrow n=2$
 (c) $n=5 \rightarrow n=4$ (d) $n=8 \rightarrow n=6$

14. At 1.10 atm and 298 K, a gas undergoes a reversible adiabatic expansion to 1.00 atm and 287 K. What is the molar heat capacity of the gas?

- (a) 5 cal mol^{-1} (b) 6 cal mol^{-1}
 (c) 7 cal mol^{-1} (d) 8 cal mol^{-1}

15. In a 15 L vessel, HI was heated to attain equilibrium. At equilibrium, 2523.5 g HI, 305.6 g I_2 , 20.6 g H_2 were present in the mixture. The K_C will be

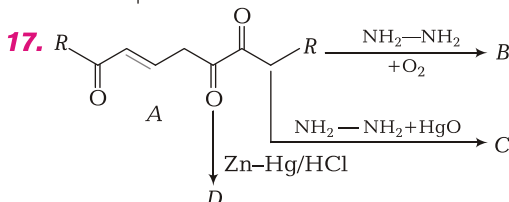
- (a) 0.3 (b) 0.03 (c) 3.0 (d) None of these

16. Which of the following statements is wrong?

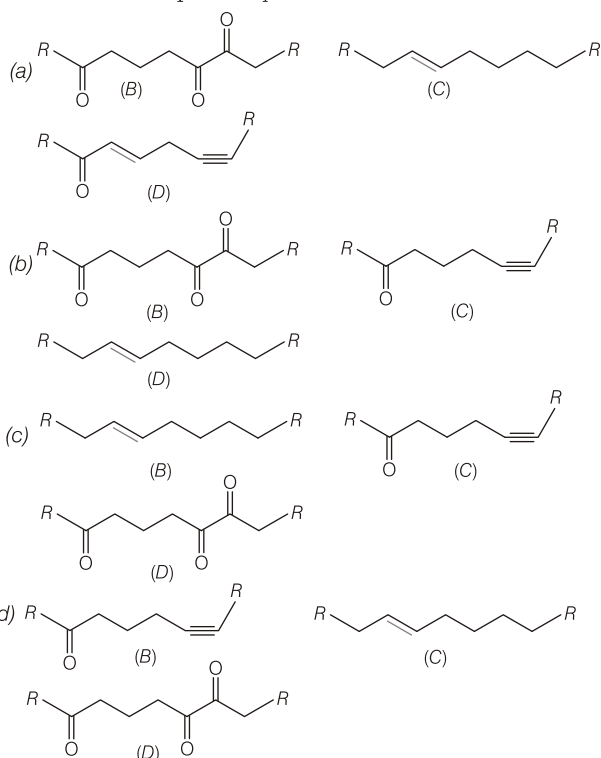
- (a) The decreasing order of the numerical value of heat of combustion is



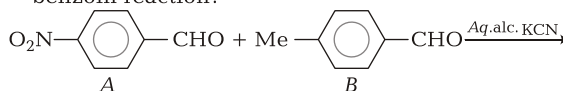
- (b) Cycloalkanes are planar
 (c) Cyclopropane has higher heat of combustion per methylene ($-\text{CH}_2-$) group than that of cyclobutane
 (d) With the exception of cyclopropane, cycloalkanes are non-planar



B, C and D respectively are



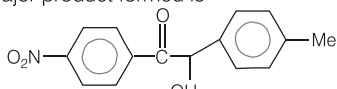
18. Which of the following statements are true about the benzoin reaction?



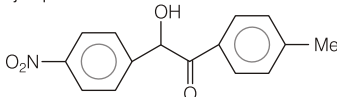
- (a) $\text{C}\bar{\text{N}}$ attacks at the ($-\text{N}-\text{O}$ group) of A
 (b) $\text{C}\bar{\text{N}}$ attacks at ($>\text{C}=\text{O}$ group) of B

AIPMT PREP UP

(c) The major product formed is



(d) The major product formed is



19. Pick up the incorrect statement.

- (a) The boiling points of alkyl halides are more than those of the corresponding alkanes
 (b) In water, the solubility order of alcohols is, $\text{CH}_3\text{OH} > \text{C}_2\text{H}_5\text{OH} > \text{C}_6\text{H}_5\text{OH}$
 (c) $\text{C}_6\text{H}_5\text{NH}_2$ is a weaker base than NH_3
 (d) All of the above statements are wrong

20. How many geometrical isomers can be formed from $[\text{Pt}(\text{NH}_3)(\text{Br})(\text{Cl})(\text{Py})]$?

- (a) 3 (b) 4 (c) 5 (d) 6

21. A transition metal A has 'spin-only' magnetic moment value of 1.8 BM. When it is reacted with dilute sulphuric acid in the presence of air, a compound B is formed. B reacts with compound C to give compound D with the liberation of iodine. Then, the metal A and compounds B, C and D respectively are

- (a) Ti, TiSO_4 , KI and TiI_2 (b) Zn, ZnSO_4 , KI and Zn_2I_2
 (c) Cu, CuSO_4 , KI and Cu_2I_2 (d) Cu, CuSO_4 , Cu_2I_2 and CuI_2

22. Which of the followings is not correctly matched?

- | Polymer | Monomer(s) |
|----------------|------------------------------|
| (a) Teflon | Tetrafluoro ethylene |
| (b) Plexiglass | Methyl methacrylate |
| (c) Orlon | Glycerol, phthalic anhydride |
| (d) Buna-S | Styrene, 1, 3-butadiene |

23. If 50% of a radioactive substance dissociates in 15min, then the time taken by the substance to dissociate 99% will be

- (a) 50 min (b) 100 min (c) 99 min (d) 150 min

24. $\text{CH}_3\text{CN} + \text{H}_2\text{O} \xrightarrow{\text{H}^+} \text{A} \xrightarrow[\text{Red P}]{\text{Excess Cl}_2} \text{B}$

In the above reactions, A and B respectively are

- (a) CH_3COOH , CCl_3COOH (b) $\text{CH}_3\text{CH}_2\text{OH}$, $\text{CH}_3\text{CH}_2\text{Cl}$
 (c) CH_3CHO , CCl_3CHO (d) CH_3COCH_3 , $\text{CCl}_3\text{COCH}_3$

25. Match the following Column I with Column II.

Column I	Column II
A. Leclanche cell	p. Cell reaction, $2\text{H}_2 + \text{O}_2 \longrightarrow 2\text{H}_2\text{O}$
B. Ni-Cd cell	q. does not involve any ion in solution and is used in hearing aids.
C. Fuel cell	r. Rechargeable
D. Mercury cell	s. Reaction at anode, $\text{Zn} \longrightarrow \text{Zn}^{2+} + 2\text{e}^-$
	t. Converts energy of combustion into chemical energy.

Codes

- | | A | B | C | D | A | B | C | D |
|-----|---|---|---|---|-----|---|---|---|
| (a) | p | q | r | t | (b) | t | r | s |
| (c) | s | r | t | q | (d) | s | r | q |

26. C and Si belong to the same group in the periodic table. Then, what is the reason behind $\text{Me}_3\text{SiCH}_2\text{COOH}$ and $\text{Me}_3\text{CCH}_2\text{COOH}$ being different in acidic character?

- (a) Si has larger atomic size than C
 (b) Si is more electronegative than C
 (c) Si is more electropositive than C
 (d) Si has lower atomic volume than C

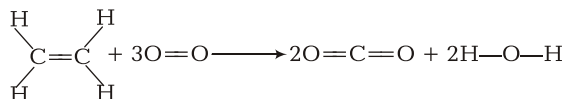
27. 16 g of oxygen at 300K occupies volume of 5 dm^3 , what will be the workdone in expanding it isothermally until the volume becomes 25 dm^3 ?

- (a) $+ 2.30 \times 10^4 \text{ J}$ (b) $- 2.01 \times 10^3 \text{ J}$
 (c) $+ 2.01 \times 10^3 \text{ J}$ (d) $- 2.30 \times 10^4 \text{ J}$

28. When a light of wavelength ' λ ' falls on a metal surface with intensity 'X', the metal emits Y electrons per second of average energy Z. What will happen to Y and Z, if X is doubled?

- (a) Y will be doubled and Z will become half
 (b) Y will remain same and Z will be doubled
 (c) Both Y and Z will be doubled
 (d) Y will be doubled but Z will remain same

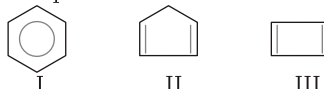
29. Calculate the heat of combustion of ethene from following bond energy data,



Different bonds	C=C	C—H	O=O	C=O	O—H
Bond energy (kJ mol^{-1})	619	414	499	724	460

- (a) $- 865 \text{ kJ mol}^{-1}$ (b) $+ 964 \text{ kJ mol}^{-1}$
 (c) $- 964 \text{ kJ mol}^{-1}$ (d) $+ 865 \text{ kJ mol}^{-1}$

30. The correct order of stability of the following compounds is



- (a) $\text{I} > \text{II} > \text{III}$ (b) $\text{III} > \text{II} > \text{I}$ (c) $\text{II} > \text{I} > \text{III}$ (d) $\text{I} > \text{III} > \text{II}$

31. Match the following Column I with Column II.

Column I	Column II
A.	p. Williamson's synthesis
B.	q. Intramolecular dehydration
C.	r. $\text{Ph}-\text{CH}=\text{CH}_2$
D.	s.

Codes

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

- 32.** A new carbon-carbon bond formation is possible in
 (a) Cannizzaro reaction (b) Decarboxylation reaction
 (c) Clemmensen reduction (d) Reimer-Tiemann reaction
- 33.** Which of the following amines will form stable diazonium salt at 273 to 283 K?
 (a) $C_2H_5NH_2$ (b) $C_6H_5NH_2$
 (c) $C_6H_5CH_2NH_2$ (d) $C_6H_5N(CH_3)_2$
- 34.** A M^{n+} metal ion has d^4 electronic configuration and it forms a complex with three bidentate ligand. If $\Delta_o > P$, then hybridisation of M^{n+} is
 (a) d^2sp^3 (b) sp^3 (c) sp^3d^2 (d) sp^2
- 35.** All the following statements about the transition elements are correct except one which is
 (a) Most of the transitional elements are predominantly metallic
 (b) In aqueous solution many of their simple ions are coloured
 (c) Most of the transitional elements have partially filled d -orbitals
 (d) Most of transitional elements show only one valence state
- 36.** Chargaff's rule said that in an organism
 (a) amount of adenine (A) is equal to that of cytosine (C) and the amount of thymine (T) is equal to that of guanine (G)
 (b) amount of all bases are equal
 (c) amount of adenine (A) is equal to that of thymine (T) and the amount of guanine (G) is equal to that of cytosine (C)
 (d) amount of adenine (A) is equal to that of guanine (G) and the amount of thymine (T) is equal to that of cytosine (C)
- 37.** Which one of the followings is not a true statement?
 (a) α -carbon of α -amino acid is asymmetric
 (b) All proteins are found in L -form
 (c) Human body can synthesise all proteins that we need
 (d) At pH = 7, both amino group and carboxylic group exist in ionised form

- 38.** Match the following Column I with Column II.

Column I (Colloidal of dispersion)	Column II (Nature of dispersion)
A. Milk	p. Solid in liquid
B. Clouds	q. Liquid in gas
C. Paints	r. Solid in solid
D. Jellies	s. Liquid in liquid
	t. Liquid in solid

Codes

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

- 39.** 25g of a solute of molar mass 250g mol^{-1} is dissolved in 100 mL of water to obtain a solution, whose density is 1.025 g mol^{-1} . The molarity and molality of the solution respectively are
 (a) 0.75 and 1 (b) 0.8 and 1
 (c) 1 and 0.8 (d) 1 and 0.75
- 40.** What volume of air containing 21% of oxygen by volume, is required to completely burn 1kg of sulphur (S_8) which contains 4% incombustible material? Sulphur burns according to the reaction, $\frac{1}{8} S_8 + O_2 \longrightarrow SO_2$.
 (a) 1800 L (b) 4800 L (c) 3200 L (d) 5800 L
- 41.** At what partial pressure, oxygen will have a solubility of 0.05 g L^{-1} in water at 293 K? Henry's constant (K_H) for O_2 is 34.86 K bar.
 (a) 2 bar (b) 0.98 bar (c) 1.2 bar (d) 2.5 bar
- 42.** KI and sucrose solution with 0.1M concentration have osmotic pressure of 0.465 atm and 0.245 atm respectively. What is the degree of dissociation?
 (a) 84.6% (b) 82.3%
 (c) 89.8% (d) 85.2%
- 43.** Match the following Column I with Column II.

Column I (Physical quantity)	Column II (SI unit)
A. Resistance	p. Sm^{-1}
B. Conductance	q. $\text{Sm}^2\text{mol}^{-1}$
C. Molar conductivity	r. ohm (Ω)
D. Cell constant	s. m^{-1}
E. Conductivity	t. siemen (S)

Codes

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

- 44.** If the molar conductivities at infinite dilution of NaCl, HCl and CH_3COONa are 126.4, 425.9 and $91.0\text{ S cm}^2\text{ mol}^{-1}$ respectively, what will be the molar conductivity of acetic acid?
 (a) $295.3\text{ S cm}^2\text{ mol}^{-1}$ (b) $300.5\text{ S cm}^2\text{ mol}^{-1}$
 (c) $295.0\text{ S cm}^2\text{ mol}^{-1}$ (d) $390.5\text{ S cm}^2\text{ mol}^{-1}$
- 45.** The rate constant for the decomposition of a hydrocarbon is $2.418 \times 10^{-5}\text{ s}^{-1}$ at 546 K. If the energy of activation is 179.9 kJ/mol, what will be the value of pre-exponential factor?
 (a) $3.9 \times 10^{12}\text{ s}^{-1}$ (b) $5.6 \times 10^{-12}\text{ s}^{-1}$
 (c) $6.2 \times 10^{-12}\text{ s}^{-1}$ (d) $2.5 \times 10^{12}\text{ s}^{-1}$

Answers

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

CHEMISTRY

SPECTRUM

for You

Q1 Sir, I had read the Le-Chatelier's principle many times. But still get confused about the direction of reaction by varying the temperature, in case of exothermic reactions. Please explain me in an easy way to clear my confusion.

[Rahul Singh, Delhi]

Dear Rahul, do not get confused, keep in mind that at equilibrium, system is being held at a specific temperature, so that net reaction does not actually change the temperature of the system. Now, as we increase the temperature of the system, this increase in temperature will increase heat of the system. For exothermic reactions (produce heat when proceed in forward direction), as we increase the temperature of the system, this system will try to maintain its equilibrium temperature. For this, the system tends to move in reverse or backward direction (converting products back to reactants) so that temperature remains same. On the other hand, when we decrease the temperature of the system, it tends to move in forward direction and maintain its equilibrium temperature.

Q2 Sir, burning of wood is a spontaneous or feasible process according to thermodynamic laws. But wood cannot burn itself, it starts burning only after igniting it. Please explain.

[Pooja Sharma, Meerut]

Wood could not burn itself. It first undergoes thermal degradation or pyrolysis. Some of the products of pyrolysis are, combustible gases, vapours and mists. Under the influence of heat, wood produces gaseous substances that react very fast with oxygen leading to high inclination of wood to ignite and burn. Combustion takes place as a reaction between oxygen and gases released from the organic material. Gaseous substances react with each other and oxygen, releasing a large amount of heat that further induces pyrolysis and combustion reactions. The burning may continue of its own until the wood has been consumed except for inorganic products left as ashes.

Q3 Sir, I have solved many problems in which mixture of an acid and a base is given.

But in some problems I could not get which species should act as an acid or a base and unable to find out the direction of the reaction. Explain me how can I solve such type of problems?

[Rachna Bansal, Pune]

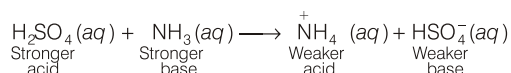
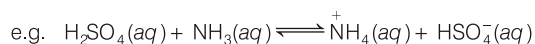
The direction of reaction in such type of problems depends upon the relative strengths of conjugate acid-base pair. You can use following table to find out the relative strength of conjugate acid-base pairs.

Acid (HA)		Base (A ⁻)	
↑ Acidic strength	$\left. \begin{array}{l} \text{HClO}_4 \\ \text{HCl} \\ \text{H}_2\text{SO}_4 \\ \text{HNO}_3 \\ \text{H}_3\text{O}^+ \end{array} \right\} \text{Strong acids} \\ \text{(100\% dissociated in aqueous solution)}$	$\left. \begin{array}{l} \text{ClO}_4^- \\ \text{Cl}^- \\ \text{HSO}_4^- \\ \text{NO}_3^- \\ \text{H}_2\text{O} \end{array} \right\} \text{Very weak bases. (Negligible tendency to protonated in aqueous solution)}$	↓ Basic strength
↑ Acidic strength	$\left. \begin{array}{l} \text{HSO}_4^- \\ \text{H}_3\text{PO}_4 \\ \text{HNO}_2 \\ \text{HF} \\ \text{CH}_3\text{COOH} \\ \text{H}_2\text{CO}_3 \\ \text{H}_2\text{S} \\ \text{NH}_4^+ \\ \text{HCN} \\ \text{HCO}_3^- \\ \text{H}_2\text{O} \end{array} \right\} \text{Weak acids} \\ \text{(exists in solution as a mixture of HA, A}^- \text{ and H}_3\text{O}^+)$	$\left. \begin{array}{l} \text{SO}_4^{2-} \\ \text{H}_2\text{PO}_4^- \\ \text{NO}_2^- \\ \text{F}^- \\ \text{CH}_3\text{CO}_2^- \\ \text{HCO}_3^- \\ \text{HS}^- \\ \text{NH}_3 \\ \text{CN}^- \\ \text{CO}_3^{2-} \\ \text{OH}^- \end{array} \right\} \text{Weak bases} \\ \text{(Moderate tendency to be protonated in aqueous solution)}$	↓ Basic strength
	$\left. \begin{array}{l} \text{NH}_3 \\ \text{OH}^- \\ \text{H}_2 \end{array} \right\} \text{Very weak acids}$	$\left. \begin{array}{l} \text{NH}_2^- \\ \text{O}^{2-} \\ \text{H}^- \end{array} \right\} \text{Strong bases 100\% protonation in aqueous solution}$	



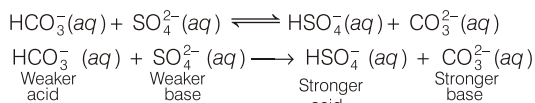
To predict the direction of reaction, use the balanced equation to identify the acids and bases and then use the above table to identify stronger acid and stronger base.

When equal concentrations of reactants and products are present, proton transfer occurs from the stronger acid to stronger base.



Hence, direction of reaction should be forward.

Again, for



Hence, direction of reaction should be backward.

104 Sir, please explain me the energies of the atomic orbitals for hydrogen atom.

[Anuj, Kanpur]

Dear Anuj, for hydrogen atom the energies of the atomic orbitals are related only to the principal quantum number (n) and not the azimuthal quantum number (l), so for hydrogen atom, the $2s$ and $2p$ orbitals are degenerate, i.e. have equal energy levels. This is not the case for many electron atoms where, the $2s$ orbital has lower energy than $2p$ orbital.

In an atom with more than one electron, there are electron-electron repulsions in addition to attractive interactions between the protons of nucleus and the electrons. These electron-electron repulsions serve shielding of electrons from nuclear charge.

e.g. In lithium the two electrons in $1s$ -orbital lie largely between the nucleus and the $2s$ electron. This means the charge felt by the $2s$ electron, known as the **effective nuclear charge** (Z_{eff}), is considerably less than the actual charge of $+3$.

105 Sir, alcohols always considered as causing ill effects to health, economy and society. But are there any uses which alcohols can find in our daily life? Please explain.

[Nisha Gupta, Saharanpur]

Dear Nisha, alcohols are not always harmful for us. Heavy consumption of it, can damage the body organs and systems, especially liver, stomach and brain.

These have many uses in our daily life that are give below :

As fossil fuels These burn very cleanly, producing only carbon dioxide and water. Ethanol is considered a renewable fuel as it can be made from renewable sources such as sugarcane.

In perfumes Ethanol is least toxic among alcohols. It is used in perfumes to stop the plant and animal extracts from going off.

As an antiseptic Alcohol is safe for use on the skin, because it works at lower concentration (65-82%).

As a good solvent Alcohols act as good solvents. Ethanol is often used to dissolve chemicals that are insoluble in water, e.g. perfumes, cosmetics and vegetable essences such as vanilla extract.

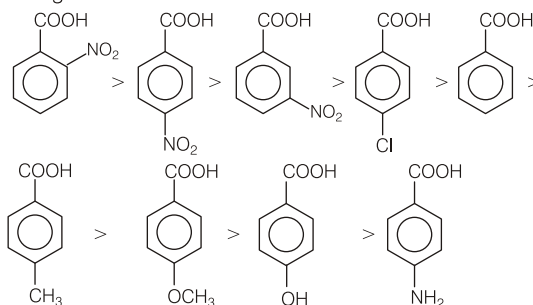
As a cleaner These are used to get rid of bacteria and oil. Alcohols are also used in mouthwash.

106 Sir, please explain me how can I solve problems related to order of acidic strengths of aliphatic and aromatic carboxylic acids?

[Rupali Singh, Dehradun]

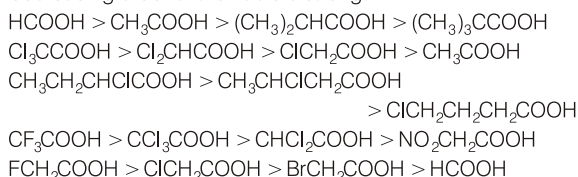
Dear Rupali, strength of acids is indicated by pK_a value. Higher the value of K_a or lower the value of pK_a , stronger is the acid.

Aromatic acids are more acidic than aliphatic acids **Effect of substituents on acidity of aromatic and aliphatic carboxylic acids.** Electron donating groups decrease the acidify and electron withdrawing groups increase the acidity of carboxylic acid. Among substituted aromatic acids the strength decreases as follows:



The effect of a substituent group is maximum at *ortho* position due to nearness. It is called *ortho* effect.

For aliphatic carboxylic acids you may consider the following decreasing order of their acidic strength :



DO YOU KNOW?



Amazing facts with proper explanation.

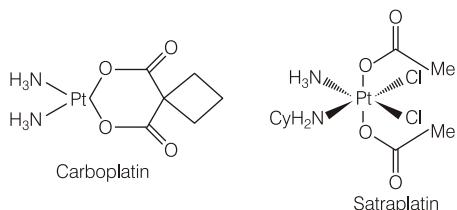
d- and f-block Elements

Why is *cis*-platin not used as an anticancer drug now-a-days?

Although *cis*-platin [$\text{cis-PtCl}_2(\text{NH}_3)_2$] has proved very successful, but there are many problems with its use. It only affects a narrow range of tumors and some become resistant to it. It also has severe toxic effects that gives rise to many side effects such as

- An increased risk of getting an infection due to drop in white blood cells which make it harder to fight infections and one can become very ill.
- Tiredness and weakness (fatigue) during and after treatment.
- It can cause kidney damage, nausea, hair loss and some hearing loss especially with high pitched sounds.
- One may not be able to become parent after treatment with this drug.
- It can cause numbness or tingling in fingers or toes, which results difficulty with fiddly things such as doing up bottoms.
- It can cause loss of taste or a metallic taste.

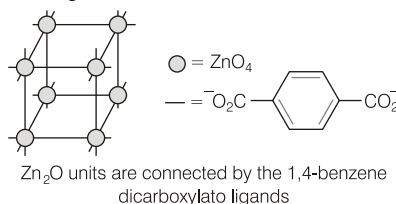
The toxicity occurs because *cis*-platin does not selectively target tumors but affects all cells. The platinum coordinates to other molecules in the body, such as proteins, in addition to DNA. There has been a great effort to find other platinum compounds that work as well, or even better, but have fewer side effects. Carboplatin and satraplatin are both examples of newer platinum anti-cancer drugs. Carboplatin contains a bidentate dicarboxylate ligand instead of the two chloro ligands. The dicarboxylate ligand is less labile which makes carboplatin less toxic, so larger doses are possible. Satraplatin is a platinum (IV) complex, and is more soluble in water than *cis*-platin. This allows it to be taken orally rather than as an injection.



Enough hydrogen can be stored in zinc based networks.

Basic zinc ethanoate has the formula $[\text{Zn}_4\text{O}(\text{O}_2\text{CMe})_6]$. If the ethanoate ligands are replaced by 1,4-benzenedicarboxylate ligands, the benzene rings link adjacent complexes together into a network structure. This is an example of a coordination network known as Metal Organic Framework (MOF). The coordination network crystallises from solution with solvent molecules in the pores, but these can be removed by heating. The network formed with dicarboxylates are particularly robust and often stable to over 300°C . Once the solvent molecules have been removed, the pores can be used to store gas molecules.

Hydrogen uptake into such zinc based networks has been studied to see whether these materials can be used to safely store hydrogen and the results are promising.

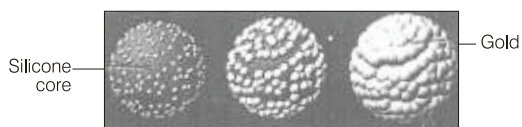


Gold and silver are the only d-block metals that occur naturally in the elemental form.

Gold, silver, copper and platinum metals occur in nature in larger amounts. There are very few metals that can resist natural weathering processes like oxidation. That is why silver and gold are found as native metals. Gold is the most well known native metal. Mostly gold is mined as native and can be found as nuggets, veins or wires of gold in a rock matrix, or fine grains of gold, mixed with sediments or bound with rock. Native silver may also occur as cubic, octahedral or dodecahedral crystals. It may occur alloyed with gold as electrum. Silver nuggets, wires and grains are relatively common but there are also a larger number of silver compound minerals owing to silver being more reactive than gold.

Gold nanoparticles are used in drug delivery.

Nanoparticles have comparable size as that of many biological materials. Thus, they can be used for drug delivery system. These nanoparticles are used in the form of nanoshells. Nanoshells are very tiny spheres with a silica core covered by a layer of gold nanoparticles. Such nanoshells have tunnable optical wavelengths. The tunnability depends on the thickness of the gold nanoparticle layer. The researchers have adjusted this thickness for the wavelength to fall in the near infrared region, a region where human blood and tissue are relatively transparent. One such nanoshell system is used for insulin delivery. In this case, the tunnable nanoshells are embedded into polymers that respond to temperature change. The polymers form a capsule like container in which drugs such as insulin can be held. Irradiating the polymer with the proper wavelength causes the embedded nanoshells to heat up, which in turn activates the polymer and causing it to collapse and release the drug.



Gold plated nanoshells, used for drug delivery system. The gold is layered around a silicone core.

STATES OF MATTER

We read some topics from this chapter in Physics also. So, this chapter is important from exam point of view as we can cover up both Chemistry and Physics. Different types of problems may be asked in exams from this chapter. We are providing problem solving strategies for some selected important topics as below

Ideal Gaseous Laws

TYPE 1 When one quantity is constant in the problem and asked to find out another one.

- If temperature (T) is constant, apply Boyle's law
($p_1V_1 = p_2V_2 = p_3V_3 = \dots$)

- If pressure (p) is constant, apply Charles' law
($\frac{V_1}{T_1} = \frac{V_2}{T_2} = \frac{V_3}{T_3} = \dots$)

- If volume (V) is constant, apply Gay Lussac's law

$$\frac{p_1}{T_1} = \frac{p_2}{T_2} = \frac{p_3}{T_3} = \dots$$

- If number of moles (n) is constant, apply

$$\frac{p_1V_1}{T_1} = \frac{p_2V_2}{T_2}$$

TYPE 2 When there is no constant quantity given in the problem

- If n is asked to find out apply, $pV = nRT$
- If density (d) is asked to find, apply $pM = dRT$
(M = molar mass)

TYPE 3 When, in a gaseous mixture, partial pressures and volumes are given and asked to find out total pressure (p) apply Dalton's law of partial pressures,

$$p = \frac{p_1V_1 + p_2V_2}{V_1 + V_2}$$

- When partial pressure of single species is asked to find, apply $p_i = X_iP$

(X_i = Mole fraction of single species)

- $X_i = \frac{\text{Number of moles of one species}}{\text{Total number of moles of all species present in gaseous mixture}}$

TYPE 4 When pressures of moist gas and water vapour or aqueous tension is given and asked to find out pressure of dry gas, apply.

Pressure of dry gas = Pressure of moist gas – Pressure of water vapour or aqueous tension.

CHEMISTRY CONCENTRATE

PRACTICE PROBLEMS

- 1.22 g of a gas measured over water at 288 K temperature and 775 mm pressure of mercury occupied 900 mL volume, calculate the volume of dry gas at NTP. Vapour pressure of water at 15°C is 14 mm.
- Find the total pressure exerted by 1.6 g methane and 2.2 g CO₂ contained in a 1 L flask at 27°C.

Graham's Law of Diffusion or Effusion

Generally, questions are not asked directly from this topic. Some quantities are provided in the problem and asked to find out some other interlinked quantities. We can solve them as follows :

TYPE 1 When rates of effusion or diffusion of two gases are provided and asked to find out ratio of densities. Apply, $\frac{r_1}{r_2} = \sqrt{\frac{d_2}{d_1}}$

TYPE 2 When densities of two gases and molecular mass of one gas are provided and asked to find out the molecular mass of other gas apply,

$$\sqrt{\frac{d_2}{d_1}} = \sqrt{\frac{M_2}{M_1}}$$

TYPE 3 When volumes and rates of two gases are provided and asked to find out time, apply, $\frac{r_1}{r_2} = \frac{V_2t_2}{V_1t_1}$

TYPE 4 When rates and molecular masses of two gases and pressure of one gas are provided and asked to find out pressure of another gas, apply

$$\frac{r_1}{r_2} = \frac{p_1}{p_2} \sqrt{\frac{M_1}{M_2}}$$

CHEMISTRY CONCENTRATE

PRACTICE PROBLEMS

- What will be the ratio of diffusion of helium and methane under identical conditions of pressure and temperature?
- 100 cm³ of NH₃ diffuses through a pin hole in 32.5 s. How much time will 60 cc of N₂ take to diffuse under the same conditions?
- At 27°C, hydrogen is leaked through a tiny hole into a vessel for 20 min. Another unknown gas at the same temperature and pressure as that of hydrogen leaked through the same hole for 20 min. After the effusion of the gases the mixture exerts a pressure of 6 atm. The hydrogen content of the mixture is 0.7 mole. If the volume of the container is 3 L, what is the molecular mass of the unknown gas?

STRATEGIES FOR YOU

Kinetic Theory of Gases

Generally, direct formula based questions have been asked from this topic. Different types of problems that can be asked given below

TYPE 1 When two or three quantities are provided in the problem and asked to find out average (\bar{v}) or root mean square (v_{rms}) or most probable velocity (v_p), apply formulae,

$$\bar{v} = \frac{v_1 + v_2 + \dots + v_N}{N} = \sqrt{\frac{8RT}{\pi M}} = \sqrt{\frac{8pU}{\pi M}} = \sqrt{\frac{8p}{\rho}}$$

$$v_{rms} = \sqrt{\frac{v_1^2 + v_2^2 + \dots + v_N^2}{N}} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3pU}{M}} = \sqrt{\frac{3p}{\rho}}$$

$$v_p = \sqrt{\frac{2RT}{M}} = \sqrt{\frac{2pU}{M}} = \sqrt{\frac{2p}{\rho}}$$

$$v_p : \bar{v} : v_{rms} = \sqrt{2} : \frac{\sqrt{8}}{\pi} : \sqrt{3},$$

$$(v_p < \bar{v} < v_{rms} = 1 : 1.128 : 1.224)$$

TYPE 2 If v_{rms} , volume (U), total number of gas molecules (N), and mass of gas molecule (m) are given and asked to find out pressure, apply $p = \frac{1}{3} \frac{m}{U} N v_{rms}^2$

TYPE 3 When pressure (p) and volume (U) or temperature (T) are provided and asked to find out average kinetic energy (E_{KE}) apply,

$$\text{For 1 mole of gas } (N = N_A) \Rightarrow E_{KE} = \frac{3}{2} RT = \frac{3}{2} pU$$

$$\text{For } n \text{ mole of gas, } E_{KE} = \frac{3}{2} nRT = \frac{3}{2} pU$$

$$\text{For a single molecule, } E_{KE} = \frac{3RT}{2N_A} = \frac{3}{2} kT$$

- k = Boltzmann's constant
- At absolute zero there is no molecular motion of gas occurs.

TYPE 4 When velocities of different gases are provided and asked to find out some other quantities or vice-versa apply,

$$\frac{v_1}{v_2} = \sqrt{\frac{M_2}{M_1}} \text{ (At same temperatures and different molecular masses)}$$

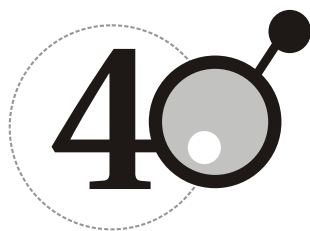
$$\frac{v_1}{v_2} = \sqrt{\frac{T_1}{T_2}} \text{ (At different temperatures and same molecular masses)}$$

$$\frac{v_1}{v_2} = \sqrt{\frac{T_1 M_2}{T_2 M_1}} \text{ (At different temperatures and different molecular masses)}$$

CHEMISTRY CONCENTRATE

PRACTICE PROBLEMS

- Calculate the root mean square, average and most probable speed of N_2 at 25°C .
- Calculate the pressure exerted by 10^{23} gas molecules each of mass 10^{-22} g in a gas container of volume 1 L, the rms speed is 10^5 cms^{-1} .
- A gas bulb of 1 L capacity contains 2.0×10^{21} molecules of nitrogen exerting a pressure of $7.57 \times 10^3 \text{ Nm}^{-2}$. Calculate the root mean square speed and temperature of the gas molecules. If the ratio of most probable speed to the root mean square speed is 0.82, calculate the most probable speed of these molecules at this temperature.

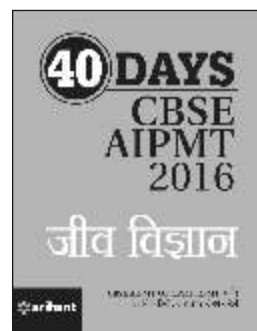
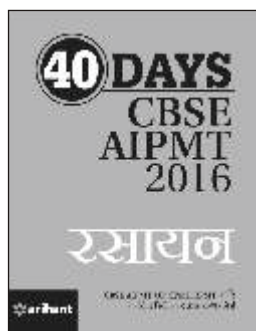
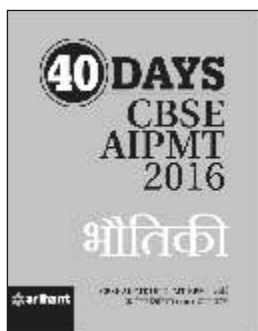


40 days रिवीजन cum क्वैश कोर्स

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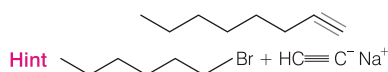
Prototype Question Paper toward CBSE 2016

1 Very Short Answer Type Questions

1. What does 'pyrometallurgy' mean?

Hint Extraction of metal by using reductant and heat with metal oxide.

2. Using a haloalkane and a nucleophile, synthesise



3. Give reason

Reactivity towards Lucas reagent, decreases in the following order

2-methyl-2-propanol > butan-2-ol > butan-1-ol.

Hint Order of reactivity of carbocation towards lucas reagent $3^\circ > 2^\circ > 1^\circ$.

4. Which reducing agent is employed to get copper from the leached low grade copper ore?

Hint Scrap iron or H_2

5. Define peptisation.

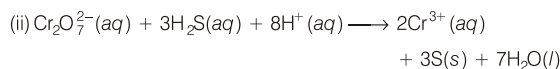
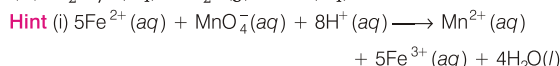
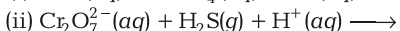
2 Short Answer Type I Questions

6. Arrange the hydrides of group 15 elements in the increasing order of their boiling points.

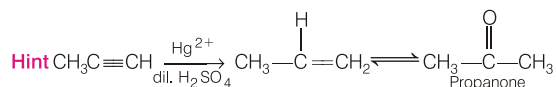
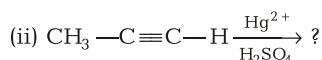
Hint As the molecular mass of elements increases van der Waals' force increases. Intermolecular H-bonding in ammonia is maximum. Hence, boiling point of ammonia is greater than PH_3 and AsH_3 .

Order of boiling points : $PH_3 < AsH_3 < NH_3 < SbH_3 < BiH_3$

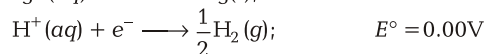
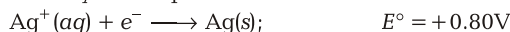
7. Complete the following chemical equations.



8. (i) Aldehydes are more reactive than ketones, Complete the above reaction.



9. (a) Following reactions occur at cathode during the electrolysis of aqueous silver chloride solution.



On the basis of their standard reduction electrode potential (E°) values, which reaction is feasible at the cathode and why?

(b) Define limiting molar conductivity. Why conductivity of an electrolyte solution decreases with the decrease in concentration? [Delhi 2015]

Hint (a) Reduction of Ag^+ is feasible.

(b) On dilution, the number of ions per unit volume that carry the current in a solution decreases.

10. (i) What are fibrous proteins?

(ii) Name the purines present in DNA.

3 Short Answer Type II Questions

11. Explain the role of each of the followings in the extraction of metals from their ores.

(i) CO in the extraction of nickel.

(ii) Zinc in the extraction of silver.

(iii) Silica in the extraction of copper.

Hint (i) Impure Ni reacts with CO to form volatile $Ni(CO)_4$, which on heating gives pure Ni.

(ii) Zn acts as a reducing agent in the extraction of Ag.

(iii) Used to remove iron oxide impurity as iron silicate.

{ BOARD EXAM SCALE UP }

12. Explain each of the followings.

- (i) Nitrogen is much less reactive than phosphorus.
- (ii) The stability of +5 oxidation state decreases down the group 15.
- (iii) The bond angles (O—N—O) are not same in NO_2^- and NO_2^+ . [Delhi 2012]

Hint (i) More stable triple bond is present in N_2 molecule whereas phosphorus forms only P—P single bond.
 (ii) Due to inert pair effect.
 (iii) NO_2^+ has linear shape but NO_2^- has bent shape.

13. Give reasons.

- (i) $E_{\text{Mn}^{2+}/\text{Mn}}$ values are not regular for first row transition metals. (3d series).
- (ii) KMnO_4 has deep purple colour.
- (iii) Basic character of oxides and hydroxides of lanthanides decreases as atomic number increases.

Hint (i) As sum of IE_1 and IE_2 increases, stability of +2 oxidation state decreases along the period.

Exceptions Mn (Mn^{2+} has half-filled *d*-sub shells), Zn (completely filled *d*-subshells)

- (ii) Due to charge transfer from O to Mn.
- (iii) Due to lanthanoid contraction.

14. 208g of an element A has 4.283×10^{24} atoms. If the element A crystallises in fcc structure with edge length of the unit cell being 408 pm, calculate its density.

Hint Density (d) = $\frac{Z \times M}{a^3 \times N_0} = 2.86 \text{ g cm}^{-3}$

15. The boiling point (bp) elevation of 0.402°C is observed when 0.5126g naphthalene is dissolved in 50g of CCl_4 , while bp elevation of 0.647°C is observed when 0.6216 g of an unknown solute is dissolved in same mass of same solvent.

(Molar mass of naphthalene = 128g/mol). Find the molecular mass of unknown solute.

Hint $\Delta T_b = k_b \cdot m$

Where $m = \frac{w_2 \times 1000}{M_2 \times w_1}$; $M_2 = 96.43 \text{ g/mol}$

16. When a certain conductivity cell was filled with 0.020M KCl which has specific conductivity of $0.2768 \Omega^{-1} \text{m}^{-1}$, it had a resistance of 82.40Ω at 25°C . With 0.0025M K_2SO_4 , it had a resistance of 326.0Ω . Calculate.

- (i) Cell constant
- (ii) Conductivity of K_2SO_4 solution

Hint Specific conductance = $\frac{\text{Cell constant}}{\text{Resistance}}$

17. Convert ethanol into

- (i) butane-1, 3-diol, (ii) but-2-enol
- (iii) but-2-enoic acid.

Hint (i) Aldol condensation followed by reduction (with LiAlH_4)
 (ii) Aldol condensation followed by heating (removal of H^+)
 (iii) Aldol condensation followed by heating (removal of H^+) and then oxidation by Tollen's reagent.

18. How can you synthesise phenol from

- (i) cumene? (ii) chlorobenzene? (iii) benzene?

Hint (i) **Steps** : (a) oxidation, (b) hydrolysis
 (ii) Dow's process

(iii) **Steps** : (a) Sulphonation (by oleum), (b) treatment with NaOH, and then with dil. HCl.

19. What happens when

- (i) *n*-propyl chloride is treated with alcoholic KOH?
- (ii) *n*-butyl bromide is treated with aqueous KOH?
- (iii) ethyl bromide is treated with sodium in presence of dry ether?

Hint (i) elimination occurs (ii) substitution occurs
 (iii) Wurtz reaction

20. Define the followings with suitable examples.

- (i) Sulpha drugs (ii) Analgesics
- (iii) Antimicrobials.

or

- (i) Give one important use of meprobamate.
- (ii) Name the main constituents of dettol.
- (iii) Name a substance that can be used as an antiseptic as well as disinfectant.

Hint (i) Used as mild tranquilizer suitable for relieving tension

- (ii) Chloroxylenol and α -terpineol.
- (iii) Phenol 0.2% solution of phenol is used as antiseptic while 1% solution of phenol is used as disinfectant.

21. Write (a) name of monomers, (b) structures of the following polymers. [Delhi 2011, All India 2011]

- (i) Buna-S (ii) Dacron (iii) Glyptal

22. (i) Why are carbohydrates generally optically active?

- (ii) What is "Zwitter ion"?
- (iii) Which enzyme deficiency causes scurvy?

Hint (i) Because of the presence of chiral carbon atom and absence of plane of symmetry.

- (iii) Vitamin C

23. Yameeni was working in a paint company as a formulation scientist. She used to process paint using various chemicals such as TiO_2 powder, polymers, emulsions and various types of surfactants. She used to wear gloves, face mask and safety shoes with lab coat while working in paint processing laboratory. When her work was finished in the laboratory, she always ensured that chemical wastes are properly treated before effluxing to the environment.

As a student of chemistry, answer the following questions.

- (i) Paint is a colloidal emulsion of polymer, TiO_2 powder and surfactant. What principle is employed for stabilising the paint?
- (ii) What are the ingredients, used in stabilising the paint emulsion?
- (iii) Why such safety measures were taken by her?
- (iv) What values can be associated with activities performed by Yameeni?

BOARD EXAM SCALE UP

- Hint** (i) Micelle formation at critical micelle concentration stabilises the oil in water emulsion of paint.
- (ii) Surfactants (having the hydrophobic-hydrophilic parts) are used for micelle formation.
- (iii) TiO_2 powder, if inhaled, gets adsorbed in lungs and causes respiratory diseases. Surfactants and chemicals can cause damage to skin. Hence, face mask, gloves, shoes and labcoats are used.
- (iv) She is knowledgeable, concerned about the safety and environment.

5 Long Answer Type Questions

24. Write short notes on

- (i) Carbylamine reaction
 (ii) Diazotisation
 (iii) Hofmann's bromamide reaction
 (iv) Coupling reaction
 (v) Acetylation (5×1=5)

or

- (i) Give reasons (2 × 2 = 4)
- (a) Aromatic primary amines cannot be prepared by Gabriel phthalimide synthesis.
- (b) Nitro compounds have higher boiling points compared to other compounds of same molecular mass.
- (ii) Why is an aqueous solution of amines basic in nature? (1)

- Hint** (i) (a) Aryl halides do not undergo nucleophilic substitution (with potassium phthalimide)
- (b) High polarity due to strong electrostatic force of attraction between nitrogen and oxygen of nitro group.
- (ii) In aqueous solution, amines accept a proton from water and liberate OH^- ions.

25. For the hydrolysis of methyl acetate in aqueous solution, the following results were obtained.

Time/s	0	30	60
$[\text{CH}_3\text{COOCH}_3]/\text{molL}^{-1}$	0.60	0.30	0.15

- (i) Show that it follows pseudo first order reaction, as the concentration of water remains constant.
- (ii) Calculate the average rate of reaction between the time interval 30 to 60 s. (Given, $\log 2 = 0.3010$, $\log 4 = 0.6021$) [Delhi 2015]

Hint (i) The rate constant for pseudo first order reaction,

$$K = \frac{2.303}{t} \log \frac{[\text{C}]_0}{[\text{C}]} \quad \text{where, } K = K'(\text{H}_2\text{O})$$

(ii) Average rate = $\frac{[\text{CH}_3\text{COOCH}_3]_{t_2} - [\text{CH}_3\text{COOCH}_3]_{t_1}}{t_2 - t_1}$

or

- (i) What is the effect of adding catalyst on the equilibrium constant and Gibbs free energy change of a reaction?
- (ii) The rate constant of a reaction is $1.2 \times 10^{-3} \text{ s}^{-1}$ at 30°C and $2.1 \times 10^{-3} \text{ s}^{-1}$ at 40°C . Calculate the energy of activation of the reaction.
- (iii) Calculate the disintegration constant and average life of a radioactive element if its half-life is 100 s. How much time will it take to lose its activity by 90%?

Hint (i) $\Delta G \propto K$ and catalyst increases rate of both forward and backward reaction. Hence, no effect.

$$(ii) \log \frac{K_2}{K_1} = \frac{E_a}{2.303R} \left(\frac{T_2 - T_1}{T_1 T_2} \right)$$

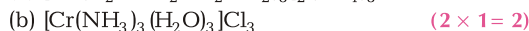
$$\therefore E_a = 44.13 \text{ kJ/mol}$$

$$(iii) K = \frac{0.693}{t_{1/2}} = 0.00693 \text{ s}^{-1}$$

$$\tau = \frac{1}{K} = 144.3 \text{ s} \quad (\tau = \text{average life})$$

$$t = \frac{2.303}{K} \log \frac{N_0}{N} = 332.3 \text{ s}$$

26. (i) Write the IUPAC name of



(ii) Indicate the optically active isomers of $[\text{Cr}(\text{H}_2\text{O})_2(\text{C}_2\text{O}_4)_2]$

(iii) Give reason.

(a) $[\text{NiCl}_4]^{2-}$ is paramagnetic, whereas $[\text{Ni}(\text{CO})_4]$ is diamagnetic though both are tetrahedral.

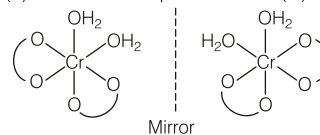
(b) $[\text{Co}(\text{NH}_3)_6]^{+3}$ is orange yellow in colour and $[\text{CoF}_6]^{3-}$ is blue in colour. [2 × 1 = 2]

or

- (i) Discuss the nature of M—C bonding (σ and π , both in) organometallic compounds with examples.
- (ii) Discuss the factors that affect the stability of coordination compounds.

Hint (i) (a) *Tris*-(ethane-1,2-diamine) cobalt(III) sulphate

(b) Triamminetriaquachromium(III) chloride



Cis-isomer is optically active

- (iii) (a) $[\text{NiCl}_4]^{2-}$ — Ni^{2+} with weak field ligand (Cl^-), no pairing, paramagnetic.
 $[\text{NiCl}_4]^{2-}$ — $\text{Ni}^{(0)}$ with strong field ligand, (CO), pairing, diamagnetic.
- (b) CFSE of F^- is less than that of NH_3 .



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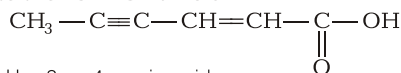
Prototype Question Paper toward CBSE 2016

1 Very Short Answer Type Questions

1. What is the basicity of $H_4P_2O_7$?

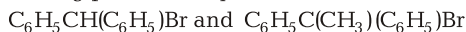
Hint Basicity of oxoacids of phosphorus is equal to the number of P—OH bonds present in the molecule.

2. Write the IUPAC name of



Hint Hex-2-en-4-ynoic acid.

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



Hint Greater the stability of carbocation, greater will be its ease of formation from alkyl halide and faster will be the rate of S_N1 reaction.

4. A delta is formed at the meeting point of sea water and river water. Why? **[All India 2015]**

Hint Clay and sand present in the river water are neutralised by electrolytes present in sea water.

5. A compound is formed by two elements P and Q . What is the formula of a compound if atoms of Q forms cubic close packing and atoms of P occupy one-third of tetrahedral voids?

Hint The formula of the compound is P_2Q_3 .

2 Short Answer Type I Questions

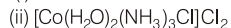
6. What are interstitial compounds? Write two characteristics of these compounds.

Hint Compound formed when atom of sufficiently small radius occupies an interstitial site in a metal lattice.

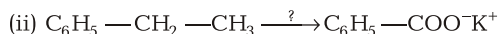
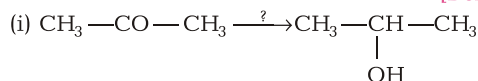
7. (i) Write down the IUPAC name of the complex, $[Pt(NH_3)_3Br(NO_2)Cl]Cl$

(ii) Write the formula for the following complex. Chlorodiaquatrimminecobalt (III) chloride

Hint (i) Triaminebromochloronitroplatinum (iv) chloride



8. Name the reagents used in the following reactions. **[Delhi 2015]**



Hint (i) $NaBH_4$ (ii) $KMnO_4 - KOH$

9. What is meant by negative deviations from Raoult's law? Give an example. What is the sign of ΔH_{mix} for negative deviation? or

What concentration of nitrogen should be present in a glass of water at room temperature? Assume a temperature of $25^\circ C$, a total pressure of 1 atmosphere and mole fraction of nitrogen in air is 0.78 [K_H for nitrogen = $8.42 \times 10^{-7} M/mmHg$]?

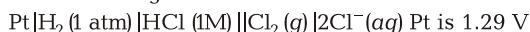
[Ans = $4.99 \times 10^{-4} M$]

Hint ρ_{N_2} = mole fraction of N_2 in air $\times \rho_{total}$

As K is in the unit of $M(mm)^{-1}$, Henry's law is applied.

Concentration of N_2 in solution = $K_H \rho_{N_2}$

10. The emf of a galvanic cell



Calculate the partial pressure of $Cl_2 (g)$.

$$E_{Cl_2 / Cl^-}^\circ = 1.36 \text{ V}$$

[Ans. $\rho_{Cl_2} = 424 \times 10^{-3} \text{ atm}$]

Hint $\frac{1}{2}H_2(g) + \frac{1}{2}Cl_2(g) \longrightarrow H^+(aq) + Cl^-(aq)$

$$E_{cell} = E_{cell}^\circ - \frac{0.059}{1} \log \frac{[H^+][Cl^-]}{[\rho_{H_2}]^{1/2}[\rho_{Cl_2}]^{1/2}}$$

3 Short Answer Type II Questions

11. Determine the osmotic pressure of a solution prepared by dissolving 25 mg of K_2SO_4 in 2L of water at $25^\circ C$, assuming that it is completely dissociated.

[Ans. $527 \times 10^{-3} \text{ atm}$]

Hint Apply van't Hoff equation

$\pi = i CRT$ where, i = numbers of ions produced by K_2SO_4 .

BOARD EXAM SCALE UP

12. (i) Why is an external emf of more than 2.2 V required for the extraction of Cl_2 from brine?
 (ii) Although carbon and hydrogen are better reducing agents but they are not used to reduce metallic oxide at high temperature. Why?

(iii) What is the role of flux in metallurgical process?

Hint

- (i) For a spontaneous reaction, ΔE° should be positive.
 (ii) They form carbides and hydrides respectively.
 (iii) Mixing of concentration ore in order to remove basic and acidic impurities.

13. An element crystallises as face-centred cubic lattice with density as 5.20 g/cm^3 and edge length of the side of cell as 300 pm. Calculate the mass of the element which contains 3.01×10^{24} atoms.

Hint 6.023×10^{23} atoms are contained in one mole of the element (its molar mass). We have to calculate the mass of element containing 3.01×10^{24} atoms. Atomic mass of element can be calculated using following equation d (density) = MZ/Na^3

14. (i) Account for the following.

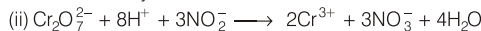
- (a) Cu^+ is unstable in an aqueous solution.
 (b) Transition metals form complex compounds.

(ii) Complete the following equation.



Hint (i) (a) In aqueous solution Cu^+ undergoes disproportionation reaction.

(b) Due to their small sizes, high ionic charges and availability of vacant d -orbitals.



15. (i) Draw the geometrical isomers of complex $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]^+$.

(ii) If CFSE for octahedral $[\text{CoCl}_6]^{4-}$ is $18,000 \text{ cm}^{-1}$. Calculate the CFSE for tetrahedral $[\text{CoCl}_4]^{2-}$.

(iii) Write the hybridisation and magnetic behaviour of the complex $[\text{Ni}(\text{CO})_4]$. (At. no. of Ni = 28)

Hint (ii) CFSE for tetrahedral = $4/9$ CFSE for octahedral.

16. A voltaic cell is set up at 25°C with the following half cells.

Al/Al^{3+} (0.001 M) and Ni/Ni^{2+} (0.50M).

Write an equation for the reaction that occurs, when the cell generates an electric current and determine the cell potential. **[All India 2012]**

$$E_{\text{Ni}^{2+}/\text{Ni}}^\circ = -0.25\text{V}$$

$$E_{\text{Al}^{3+}/\text{Al}}^\circ = -1.66\text{V} \quad (\log 8 \times 10^{-6} = -5.0969)$$

Hint Cell reaction, $2\text{Al}(s) + 3\text{Ni}^{2+}(aq) \longrightarrow 2\text{Al}^{3+}(aq) + 3\text{Ni}(s)$

$$E_{\text{cell}} = E_{\text{cell}}^\circ - \frac{0.0591}{n} \log \frac{[\text{Al}^{3+}]^2}{[\text{Ni}^{2+}]^3}$$

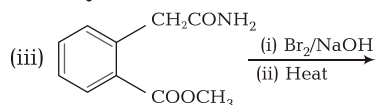
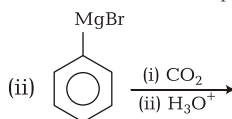
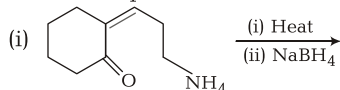
17. Give reasons for the following observations.

- (i) Lyophilic colloid is more stable than lyophobic colloid.
 (ii) Coagulation power of Al^{3+} is more than Na^+ .
 (iii) On dilution of soap solution, micelles may revert to individuals.

18. Distinguish between addition and condensation polymers. Classify the following into addition and condensation polymers.

- (i) Polyethene (ii) PTFE (iii) Polybutadiene
 (iv) Bakelite

19. Predict the products of the following reactions.

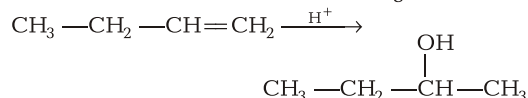


20. How will you convert the following?

- (i) Propionamide to acetamide
 (ii) Propanal to butanone
 (iii) Propanoic acid to propenoic acid

or

- (i) Write the mechanism of the following reaction.



(ii) Why is the $\text{C}-\text{O}-\text{H}$ bond angle in alcohols slightly less than the tetrahedral angle whereas the $\text{C}-\text{O}-\text{C}$ bond angle in ether is slightly greater?

21. (i) How will you explain the presence of all the six carbon atoms in glucose in a straight chain?

(ii) During curdling of milk, what happens to sugar present in it?

(iii) Name two fat soluble vitamins, their sources and the diseases caused due to their deficiency in diet.

22. Give reason

(i) Reaction of $\text{C}_6\text{H}_5\text{CH}_2\text{Br}$ with aqueous sodium hydroxide follows $\text{S}_{\text{N}}1$ mechanism.

(ii) Haloarenes are less reactive than haloalkanes and haloalkenes.

(iii) Phosphorus chloride (tri and penta) are preferred over thionyl chloride for the preparation of alkyl chlorides from alcohols.

23. Seema, a domestic helper of Rajni, fainted while mapping the floor. Rajni immediately took her to the nearby hospital where she was diagnosed with 'Pernicious anaemia' by the doctor. The doctor prescribed an iron rich diet and multivitamins supplement to her. Rajni helped her financially to get the medicines. After sometime Seema was diagnosed to be normal. Answer the following questions based on the above passage:

(i) Name the vitamin whose deficiency causes pernicious anaemia.

BOARD EXAM SCALE UP

- (ii) Give an example of a fat soluble vitamin.
 (iii) Write down the examples of iron rich diet.
 (iv) What are the values shown by Rajni?

5 Long Answer Type Questions

24. (i) Account for the followings.

- (a) PH_3 forms bubbles when passed slowly in water but NH_3 dissolves.
 (b) Ozone is thermodynamically less stable than oxygen.
 (c) N_2 is less reactive than P_4 .

(ii) Draw the structure of the followings.

- (a) BrO_3^- (b) NH_4^+

or

- (i) In the preparation of H_2SO_4 by contact process. Why is SO_3 not absorbed directly in water to form H_2SO_4 ?
 (ii) Give one reason to explain why ClF_3 exists but FCl_3 does not exist?
 (iii) Out of H_2O and H_2S which one has higher bond angle and why?
 (iv) What is the oxidation state of central atom in the anion of compound NaH_2PO_2 ?
 (v) Complete the equation $2\text{HI} + \text{H}_2\text{SO}_4 \longrightarrow$

Hint (i) (a) PH_3 does not form hydrogen bond in water as NH_3 forms.

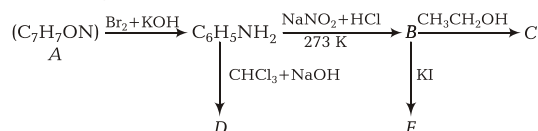
(b) Decomposition of ozone results in the liberation of heat and increase in entropy. These two factors give large negative values of Gibbs free energy change for the decomposition of ozone to oxygen.

(c) N_2 has high bond dissociation energy due to the presence of triple bond.

or

- (i) Because the reaction is highly exothermic.
 (ii) Fluorine is more electronegative than chlorine and has smaller size. Thus, one large Cl-atom can accommodate three smaller F-atoms but reverse is not true.
 (iii) Bond angle of H_2O ($\text{H}-\text{O}-\text{H} = 104.5^\circ$) is larger than that of H_2S ($\text{H}-\text{S}-\text{H} = 92^\circ$) because oxygen is more electronegative than sulphur.

25. An aromatic compound A of molecular formula $\text{C}_7\text{H}_7\text{ON}$ undergoes a series of reactions as shown below. Write the structures of A, B, C, D and E in the following reactions. [Delhi 2015]



Hint $\text{A} = \text{C}_6\text{H}_5\text{CONH}_2$, $\text{B} = \text{C}_6\text{H}_5\text{N}_2^+\text{Cl}^-$, $\text{C} = \text{C}_6\text{H}_6$.

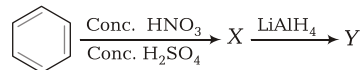
$\text{D} = \text{C}_6\text{H}_5\text{N} \equiv \text{C}$, $\text{E} = \text{C}_6\text{H}_5\text{I}$

or

(i) Write the structure of main product when benzenediazonium chloride reacts with the following reagents:

- (a) $\text{H}_3\text{PO}_2 + \text{CuCl}$ (b) $\text{CuBr} + \text{HBr}$

(ii) Write the product formed Y in the following reaction sequence:



(iii) Why do primary aromatic amines are not prepared by Gabriel phthalimide synthesis?

26. A reaction between substance A and B is represented stoichiometrically by, $\text{A} + \text{B} \longrightarrow \text{C}$. Observations on the rate of reaction in three separate experiments are as follows

S.No.	Initial concentrations		Duration of experiment	Final concentration
	$[\text{A}]_0$, M	$[\text{B}]_0$, M	Δt (h)	$[\text{A}]_f$, M
1.	0.1000	1.0	0.50	0.0975
2.	0.1000	2.0	0.50	0.0900
3.	0.0500	1.0	2.00	0.0450

(i) What is the order with respect to each reactant?

(ii) What is the value of rate constant?

Hint (i) $\text{Rate} = k[\text{A}]^x[\text{B}]^y$

$$\text{Rate} = -\frac{d[\text{A}]}{dt} = -\frac{d[\text{B}]}{dt} = \frac{d[\text{C}]}{dt}$$

(ii) $k = 5 \times 10^{-2} \text{ M}^{-2} \text{ h}^{-1}$.

or

(i) The curie was originally intended to be the activity of one gram of radium (At. mass-226). Calculate the actual mass of radium which is equal to one curie.

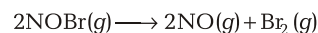
t_{50} (Radium-226) = 1620 yr

One curie = 3.7×10^{10} disintegration (of atoms) per second (dps).

One year = 3.154×10^7 s

[Ans. 1.024 g]

(ii) The gas phase decomposition of NOBr is second-order with $k = 0.810 \text{ M}^{-1} \text{ s}^{-1}$ at 10°C . The reaction starts with $4.00 \times 10^{-3} \text{ M}$ NOBr in a flask at 10°C . How many seconds does it takes to use up $1.50 \times 10^{-3} \text{ M}$ NOBr ?



$$\text{Rate} = k[\text{NOBr}]^2$$

Hint (i) From t_{50} (half-life), K can be calculated.

$$\frac{dx}{dt} = k \frac{m}{A} N_0, \quad (\text{A is atomic mass of radium})$$

$$m = 1.024 \text{ g}$$

(ii) Reaction follows second-order kinetics.

Initial $[\text{NOBr}]_0 = 4.00 \times 10^{-3} \text{ M}$

After time t , $[\text{NOBr}]_t = [\text{NOBr}]_0 - [\text{NOBr}]_{\text{used}}$

Since, coefficient of reactant (y) = 2,

hence we use equation

$$k = \frac{1}{t} \left[\frac{1}{[\text{NOBr}]_t} - \frac{1}{[\text{NOBr}]_0} \right]$$

$$t = 92.65 \text{ s}$$

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Knowledge Coefficient

Quizzer (No.16)



1. Aspartame is a widely used artificial sweetener. It is almost 200 times sweeter than sucrose. One sample of aspartame, $C_{14}H_{18}N_2O_5$, has a mass of 1.80g another contains 0.220 mole aspartame. How many grams of aspartame are in the 0.220 mole sample?

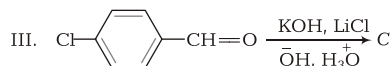
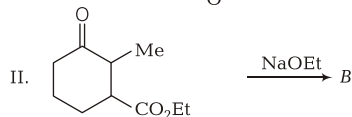
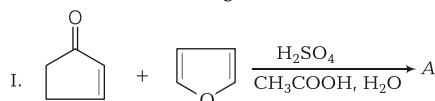
(a) 74.6 g (b) 64.7 g (c) 84.3 g (d) 92.4 g

2. *cis*-Platin is an anti-cancer drug used for the treatment of tumors. It can be produced by reacting ammonia with potassium tetrachloroplatinate.

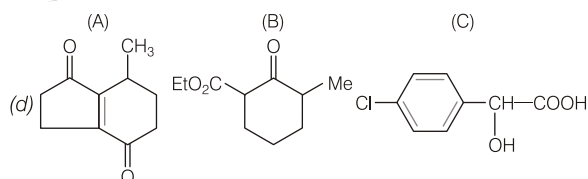
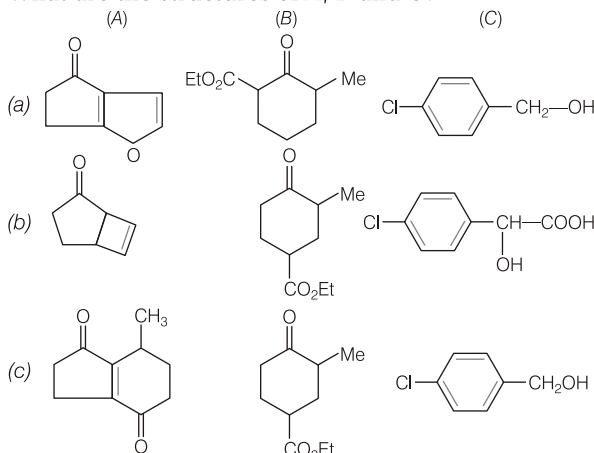
If the reaction, starts with 5.00 g of ammonia and 50.0 g of potassium tetrachloroplatinate, how many grams of *cis*-platin are produced? Assuming that all the limiting reactant is converted to *cis*-platin.

(a) 44.4 g (b) 39.0 g (c) 36.0 g (d) 52.7 g

3. Consider the following reactions,



What are the structures of A, B and C?



4. The dimerisation of acetaldehyde in a weakly alkaline solution produces a compound A which can be dehydrated to give B, C_6H_6O . Condensation of B with malonic acid in the presence of organic base gives a compound C, which loses carbon dioxide on heating to yield a compound D. When D is treated with ozone and the resulting ozonide decomposed with cold hydrogen peroxide solution, acetic acid and oxalic acid are obtained as major products. Elucidate the structure of D.

- (a) $CH_3-CH=CH-COOH$
 (b) $COOH-CH=CH-CH=CHCOOH$
 (c) $CH_3-CH=CH-CH=CHCOOH$
 (d) $CH_3-C(CH_3)=CH-CH=COOH$

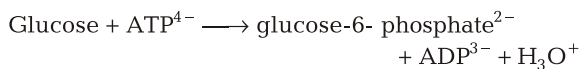
5. A person claimed that his stomach ruptured when he took a full teaspoon of baking soda in a glass of water to relieve heartburn after a full meal ($\frac{1}{2}$ tsp = 2.5 g of $NaHCO_3$).

Assume that the pH of stomach acid is 1 and the stomach has the volume of 1L, when expanded fully. Body temperature is $37^\circ C$. What volume of CO_2 gas was generated by the reaction of baking soda with stomach acids?

(a) 0.76 L (b) 0.82 L (c) 0.29 L (d) 0.36 L

6. Many biochemical processes involve reactions that take place at a temperature of $37^\circ C$ and a pH of 7 in body fluids. Under these conditions the Gibbs free energy change is specified as ΔG° , where the prime specifies that all substances are at their standard state concentrations excepts for H_3O^+ , which is at biological concentration of 10^{-7} mol/L (pH = 7). What is ΔG° (1 mol/L H_3O^+) for this reaction?

MAGAZINE QUIZZER



$$\Delta G^\circ = -16.7 \text{ kJ/mol}$$

(a) 2.48 kJ/mol (b) 27.9 kJ/mol (c) 92.9 kJ/mol (d) 20.2 kJ/mol

7. Which of the following statements is incorrect?

- (a) Bromine can be displaced by iodine in aqueous medium but iodine cannot be displaced by bromine in acetone medium
 (b) $\text{CH}_3\text{CH}_2\text{OH}$ does not react with aq. NaBr to form $\text{CH}_3\text{CH}_2\text{Br}$ but readily reacts with HBr to form $\text{CH}_3\text{CH}_2\text{Br}$
 (c) Nucleophilic catalysts are those nucleophilic species that accelerate the rate of $\text{S}_{\text{N}}2$ reaction
 (d) DMF and DMSO do not favour $\text{S}_{\text{N}}2$ reaction because they are polar solvents

8. The melting point of sodium is 97.8°C at 1.00 atm pressure. The densities at this temperature of solid and liquid sodium are 0.952 g cm^{-3} and 0.929 g cm^{-3} respectively. The enthalpy change of fusion is 3.00 kJ mol^{-1} . Calculate the melting temperature of sodium at a pressure of 120 atm.

- (a) 272 K (b) 293 K
 (c) 372 K (d) 300 K

9. Consider the following statements,

- I. Crystal field theory is an electrostatic model of bonding in coordination complexes that considers the ligands as point charges.

II. In an octahedral complex, the d -orbitals are splitted into two sets, with three orbitals stabilised and two orbitals destabilised.

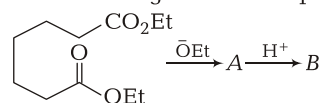
III. The crystal field splitting energies Δ_o and Δ_t are related by the expression $\Delta_t = \frac{4}{9} \Delta_o$.

IV. The d -orbital splitting diagram for a square planar complex is obtained from that for an octahedral complex by stabilising all the orbitals with a Z -component and destabilising those without a Z -component.

Find out the correct statement(s).

- (a) I, II and III (b) Only IV
 (c) II and IV (d) All of these

10. Consider the following reaction sequence,



Find the structure of B.

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

KNOWLEDGE Coefficient Quizzer (No. 16)

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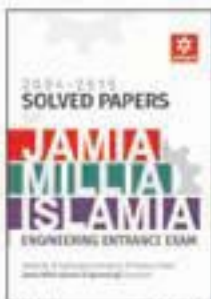
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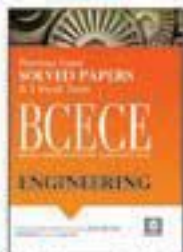
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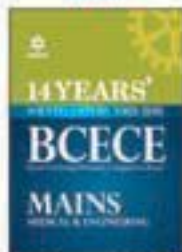
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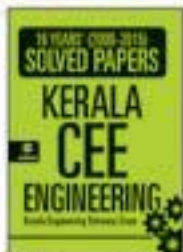
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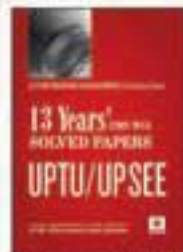
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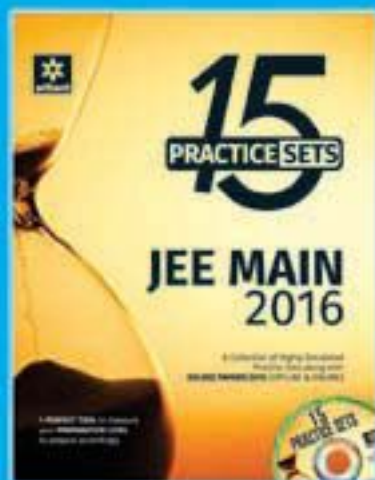
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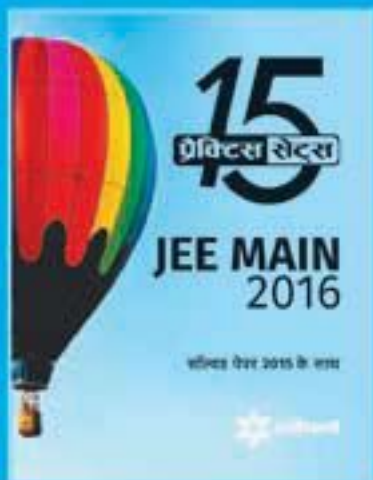
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