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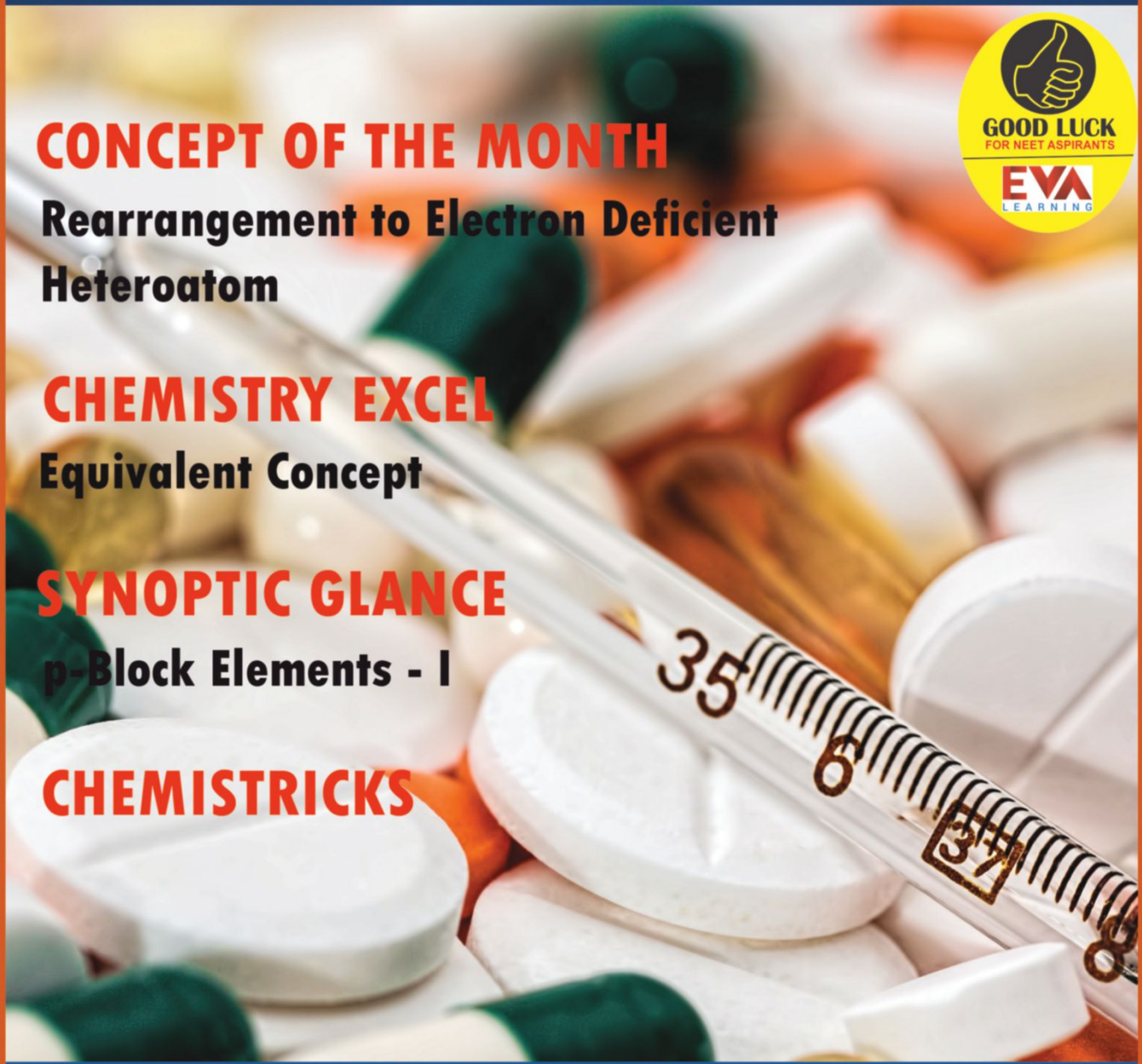

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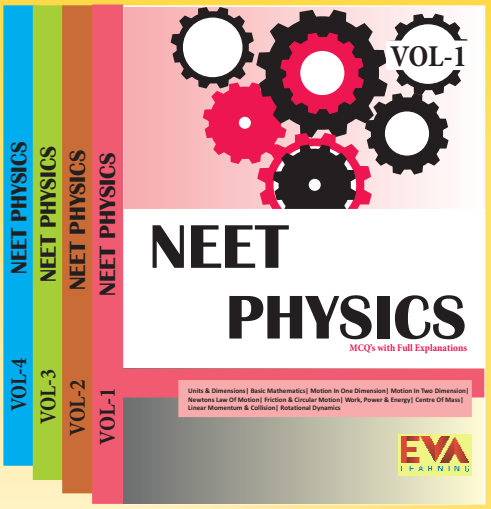

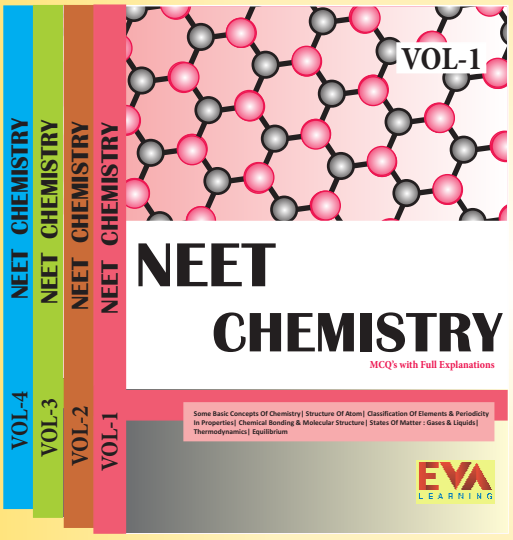

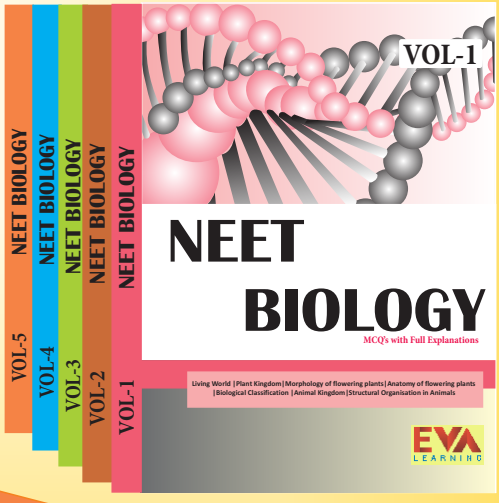

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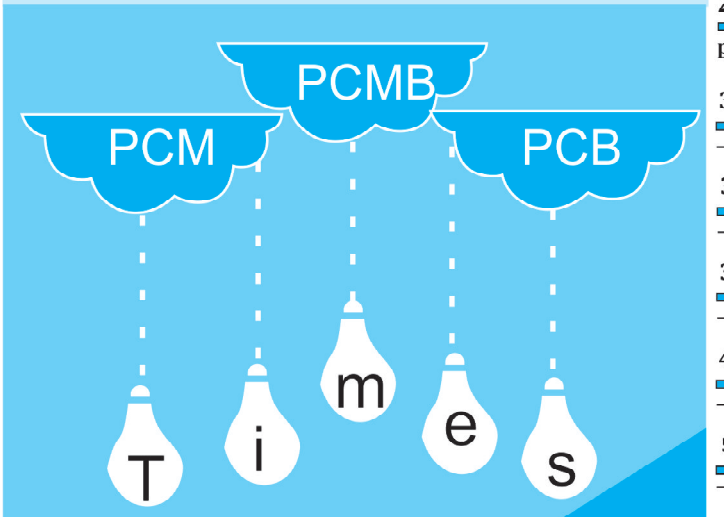

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Balaji Layout, Kodigehalli, Bangalore-560092
PRINTED AT:
JAYAM PRINT SOLUTION, S.NO: 77/A, New Raja Rajeswaripet, Ajith Singh Nagar,
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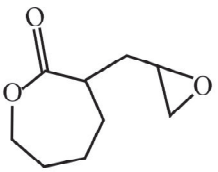


Rearrangement to electron deficient Heteroatom

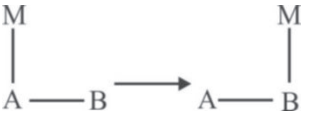
Concept of the month

This column is aimed at preparing students for all competitive exams like JEE, NEET, BITSAT etc. Every concept has been designed by highly qualified faculty to cater to the needs of the students by discussing the most complicated and confusing concepts in Chemistry.

By: P. BRAHMA REDDY
(Alumni of IIT Delhi)

Introduction

Many organic reactions involve changes at functional groups while the molecular skeleton of the reactant remains unchanged. We have, however, encountered some examples in which groups migrate within molecules and carbon skeletons are modified. Such transformations are known as **molecular rearrangements.** The most common kinds of rearrangements involve migration of a group from one atom to the next within the molecule; that is, they are 1,2-rearrangements.



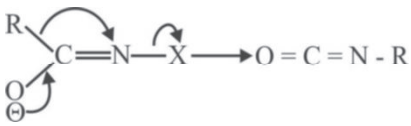
Molecular rearrangements are usually not considered as a separate class of organic reactions. They normally involve intramolecular substitutions with mechanistic features similar to those of their intermolecular counterparts.

Migration of a group from one atom to another atom that is electron deficient is the most common kind of molecular rearrangement. The atom from which migration begins is called the migration origin and the atom to which the migrating group moves is called the migration terminus are usually adjacent to each other.

In this article will discuss about the reactions that involve an electron deficient hetero atom i.e., nitrogen and oxygen atoms which receives electron density in the course of rearrangements.

Rearrangements to electron deficient NITROGEN atom

This group of rearrangements involved the migration of an alkyl or aryl group with its bonding pair of electrons from carbon to the adjacent nitrogen atom. The general mechanism for this type of rearrangement may be sketched below:



The important examples of this type of rearrangements are Beckmann, Hofmann, Curtius, Schmidt and Lossen rearrangements.

Beckmann Reaction

$$RR'C = NOH \rightarrow RCONHR'$$

Hofmann reaction

$$RCOOH \rightarrow RCONH_2 \rightarrow RNH_2$$

Curtius reaction

$$RCOOH \rightarrow RCON_3 \rightarrow RNH_2$$

Schmidt reaction

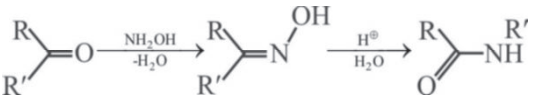
$$RCOOH \rightarrow RCONHN_2^+ \rightarrow RNH_2$$

Lossen reaction $RCHNHOH \rightarrow RNH_2$

If the migrating group in these rearrangements is asymmetric, it retains its configuration indicating that the migrating group never becomes free in solution and therefore the rearrangements are intramolecular.

Beckmann Rearrangement:

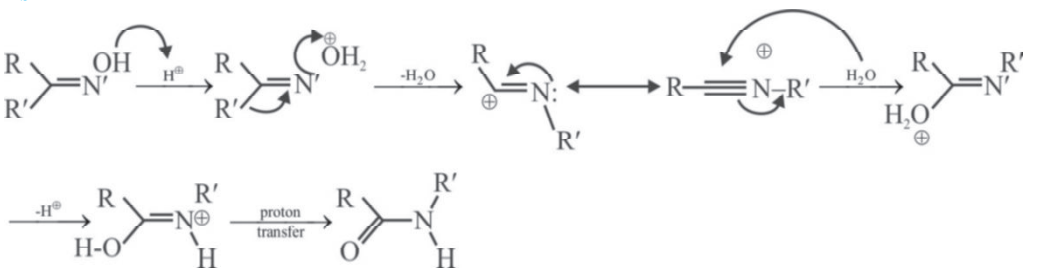
- The Beckmann rearrangement is a reaction of oximes that can result in either amides or nitriles, depending on the starting material (oximes derived from ketones form amides; oximes derived from aldehydes form nitriles).
- The reaction is intramolecular and stereospecific i.e., the substitute *trans* to the leaving groups migrates.



" The reaction can also be carried out with PCl_5, PPA, P_2O_5 or TsCl".

Note that the formation of the oxime is technically not part of the Beckmann rearrangement. The Beckmann rearrangement is the rearrangement of the oxime to amide.

Mechanism



Note: The mechanism of the Beckmann rearrangement follows the same pattern as a pinacol or Baeyer Villiger reaction.

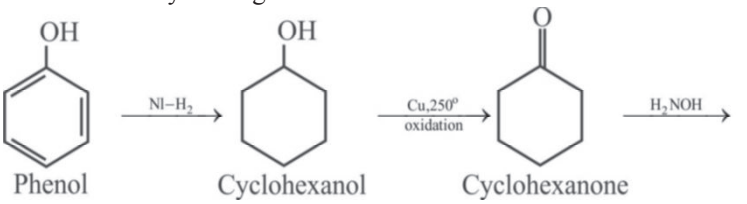
Applications:

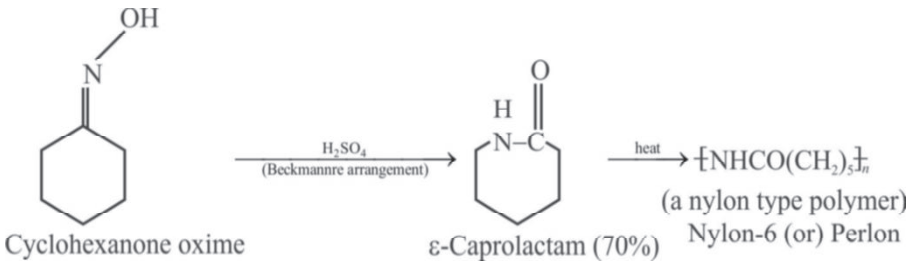
(a) Determination of configuration of ketoximes:

It is based on the fact that the two isomeric ketoximes i.e., syn and anti, give different amides via Beckmann rearrangement. The amide in turn can be identified by their hydrolysis products.

(b) Synthesis of ε - caprolactam:

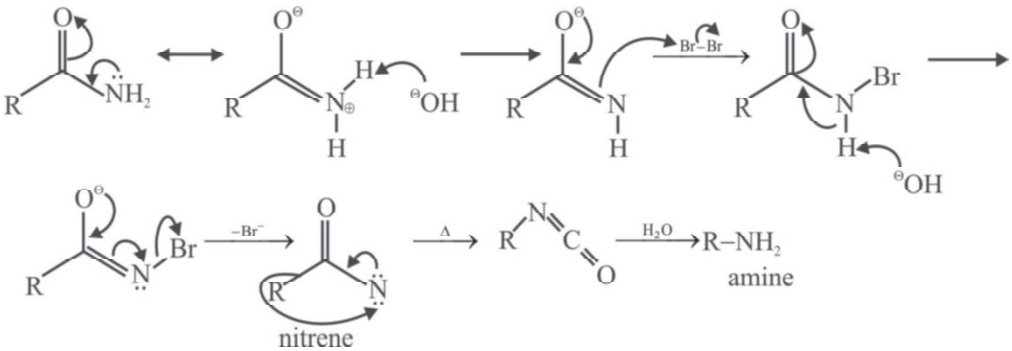
An interersting application of the rearrangement is the synthesis of ε - caprolactam from cyclohexanone oxime and concentrated sulphuric acid. ε caprolactam is the raw material for nylon type of polymers and can be polymerised into latter by heating as shown below.





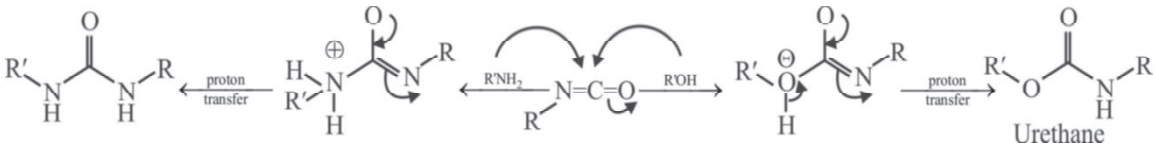
Hofmann Rearrangement

- In the Hofmann rearrangement, an unsubstituted amide is treated with sodium hypobromite or NaOH and Br_2 to give a primary amine that has one carbon fewer than the starting amide.
- The actual product is the isocyanate, but this compound is seldom isolated since it is usually hydrolyzed under the reaction conditions.
- The R group may be alkyl or aryl, but it is an alkyl group of more than about six or seven carbons, low yields are obtained unless Br_2 and NaOMe are used instead of Br_2 and NaOH.



The workup can also be with alcohol or amine to give urethane or urea, respectively.

$(CO_2 + NaOH \rightarrow Na_2CO_3 + H_2O)$



The rate of reaction increases when the migrating group is more electron donating group and decreases when electron with-drawing. If R is an alkyl group with more than eight carbons, low yields are obtained.

Applications:

(a) Formation of amines:

1. Acids and amides to amines

$$RCOOH \xrightarrow{NH_4OH,\Delta} RCONH_2 \xrightarrow{Br_2+KOH} RNH_2$$

$$Me_3CCH_2CONH_2 \xrightarrow{NaOBr} Me_3CCH_2NH_2$$

2. Higher amides (with more than eight carbons) give nitriles which can be reduced to amines

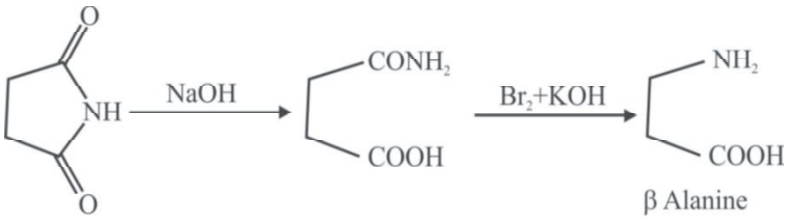
$$RCH_2CONH_2 \xrightarrow{Br_2+KOH} RCH_2CN \xrightarrow{Na+Alcohol} RCH_2CH_2NH_2$$

3. Urea gives the valuable reagent hydrazine

$$H_2N\,CO\,NH_2 \xrightarrow{Br_2+KOH} NH_2NH_2$$

(b) Preparation of β – amino pyridine from nicotinamide

(c) Synthesis of amino acids

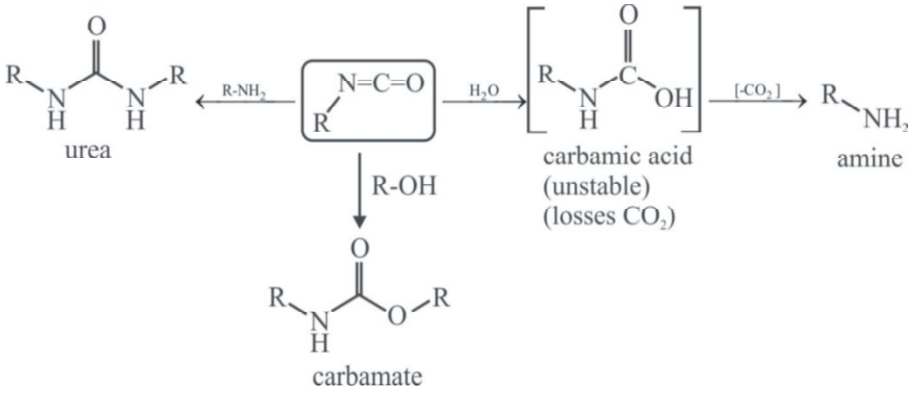


Curtius Rearrangement

- Curtius rearrangement involves the decomposition of acyl azides in an inert solvent (e.g., chloroform, benzene etc) by gentle heat to isocyanate.

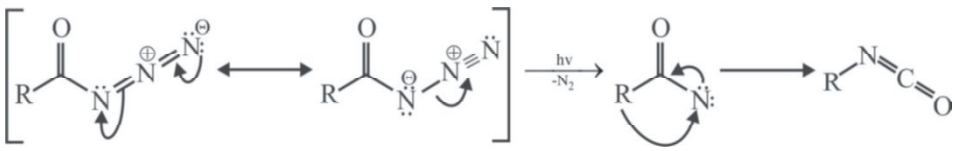
$$RCON_3 \xrightarrow{\Delta} R-N=C=O+N_2$$

- If the reaction is carried out in alcoholic or aqueous medium, the isocyanate further reacts to form urethane, amine or substituted urea.



Mechanism:

The mechanism of the rearrangement is very similar to Hofmann's rearrangement to isocyanate. The driving force of the rearrangement is the electron deficient nitrogen formed on elimination of nitrogen molecule on heating. Since there is no evidence for the formation of nitrene, all the steps may be concerted.



Applications:

(a) Preparation of primary amines:

The curtius reaction is of interest as it gives a primary amine which is free from secondary and tertiary amines, the impurities which are generally present with other methods of preparation.

$$C_6H_5-CH_2COOC_2H_5 \xrightarrow{1.NH_2NH_2\ 2.HNO_2} C_6H_5CH_2CON_3 \xrightarrow{1.\Delta,C_6H_6\ 2.H_2O} C_6H_5CH_2NH_2$$

Ethylphenylacetate — Benzylamine

(b) Preparation of α - aminoacids

$$NC-CH_2-COOR \xrightarrow[2.RX]{1.NaOEt} RCH(CN)COOR \xrightarrow[2.HNO_2]{1.NH_2NH_2} RCH(COOH)CON_3$$

$$\xrightarrow{\Delta,EtOH} RCH(COOH)NHCOOC_2H_5 \xrightarrow{HCl} RCH(COOH)NH_2$$

(c) Curtius reaction may be used for stepping down the acid series

$$RCH_2COOH \xrightarrow{C_2H_5OH,H^+} RCH_2COOC_2H_5 \xrightarrow[2.HNO_2]{1.NH_2NH_2} RCH_2CON_3$$

$$\xrightarrow{1.\Delta,C_6H_6,2H_2O} RCH_2NH_2 \xrightarrow{HNO_2} RCH_2OH \xrightarrow{Oxidation} RCOOH$$

Schmidt rearrangement

- Schmidt reaction is closely related to Hofmann and Curtius reactions, all of which accomplish the same overall process - conversion of a primary amine with less of the carboxy carbon of the acid.

$$RCOOH + N_3H \xrightarrow{H_2SO_4} RNH_2 + CO_2 + N_2$$

- Free hydrazoic acid is highly toxic and hence sodium azide is slowly added to the solution of the carboxylic acid in sulphuric acid when hydrazoic acid is liberated.
- When treated with hydrazoic acid in sulphuric acid, carbonyl compounds also undergo Schmidt reaction. Ketones form amides while aldehydes generally form a mixture of the correspoding nitrile and N - formyl derivative.

$$RCHO + N_3H \xrightarrow{H_2SO_4} RCN + RNHCHO$$

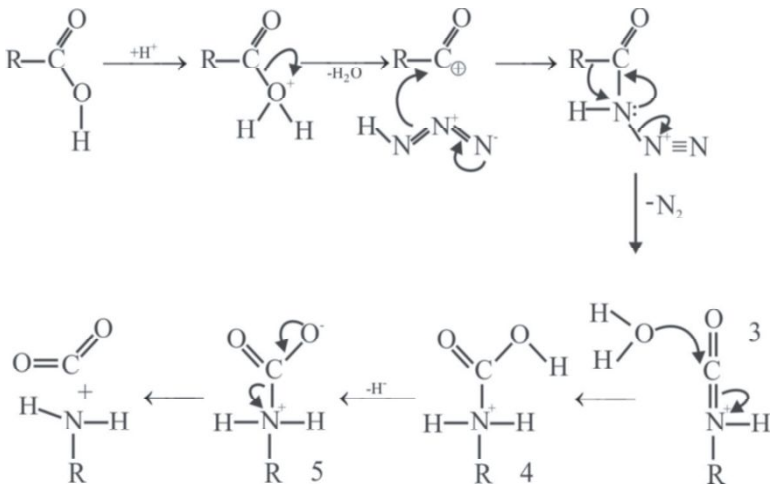
(Formyl derivative of amine)

$$RCOR + N_3H \xrightarrow{H_2SO_4} RCONHR + N_2$$

- The rearrangements in these case closely resemble the Beckmann rearrangement. Dialkyl and cyclic ketones react more readily than alkyl aryl ketones. With alkyl aryl ketones, it is the aryl group which migrates.

Mechanism:

The mechanism of Schmidt reaction with acids has been found to be similar to that the Hofmann and Curtius reactions. The mechanism which is consistent with the experiment observations is as follows:



Sulphuric acid is the most common catalyst for Schmidt reaction but Lewis acids have also been used.

Applications:

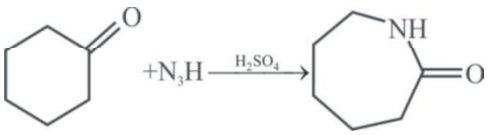
(a) Preparation of amines:

Primary amines in good yield are obtained directly from the acids, provided the acids do not contain groups sensitive to conc. Sulphuric acid. The reagent, however, is dangerous to handle due to its poisonous and explosive nature.

$$C_6H_5CH_2COOH + N_3H \xrightarrow[CHCL_3]{H_2SO_4} C_6H_5CH_2NH_2 + N_2 + CO_2$$

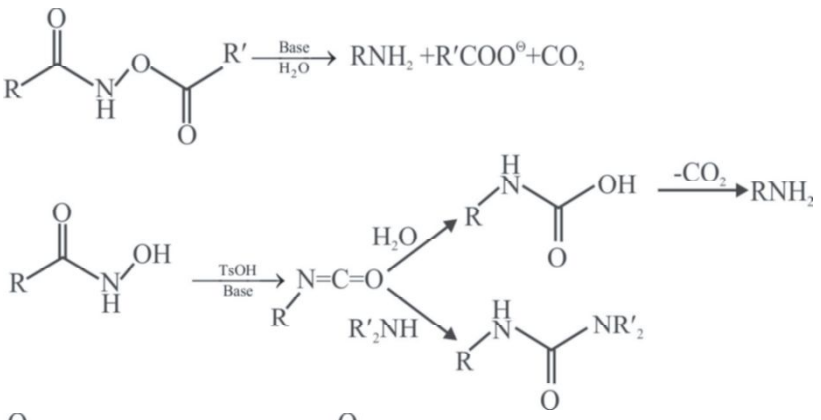
(b) Preparation of lactams

Cyclic ketones react to give lactams. Cyclohexanone gives $\varepsilon-$ caprolactam.

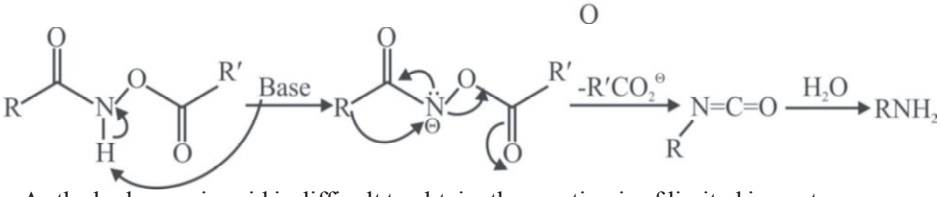


Lossen Rearrangement

Ester of hydroxamic acid reacts with base to give isocyanate that could be converted into amine as shown in Hofmann rearrangement.



Mechanism:



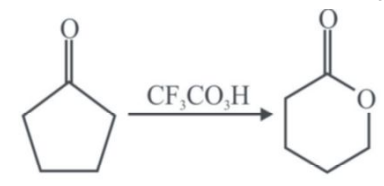
Applications: As the hydroxamic acid is difficult to obtain, the reaction is of limited importance.

Rearrangements to electron deficient OXYGEN atom

Baeyer Villiger Rearrangement:

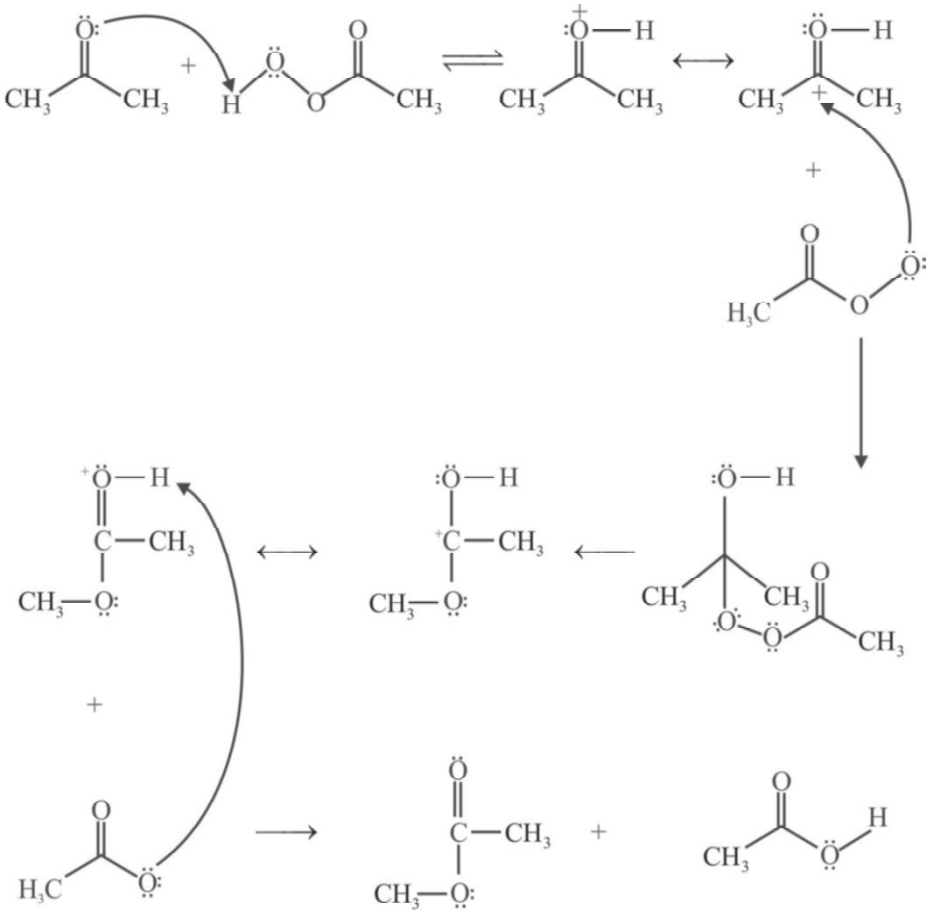
- Baeyer Villiger rearrangement is an example of the migration of a group from carbon to electron deficient oxygen.
- The reaction involves the oxidation of ketones to esters by the treatment with peracids such as peracetic acid, pertrifluoroacetic acid, permonosulphuric acid, etc.

$$RCOR' \xrightarrow{CF_3COOOH} RCOOR' + CF_3COOH$$



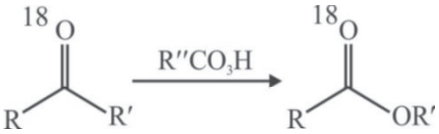
- The overall reaction is an insertion of oxygen atom between the carbonyl group and the adjacent carbon in ketone.
- The choice of solvent depends upon the solubility of the reactants. Commonly used solvents are glacial acetic acid and chloroform.

Mechanism:



Electron releasing groups in the ketone and electron withdrawing groups in peracids promote the reaction rate. Pertrifluoroacetic acid is very effective because trifluoroacetate ion is a good leaving group.

- The mechanism is supported by the fact that the labelled oxygen atom of the ketone is entirely present in the carbonyl oxygen of the ester.



- The migrating group retains its configuration as in other concerted reactions. For acyclic compounds the migrating group, $R^{'}$ must be $2^{o}, 3^{o}$ or vinylic. However, migration of 1^{o} alkyl group may be brought about by using CF_3CO_3H or $BF_3H_2O_2$ as reagent.
- In unsymmetrical ketones, that group migrates which is more electron releasing.

Applications:

(a) Preparation of esters

Esters which are difficult to synthesize can be prepared by this method.

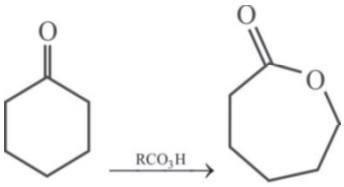
$$C_6H_5COCH_3 \xrightarrow{CF_3CO_3H} CH_3COOC_6H_5$$

$$\underset{\text{Pinacolone}}{CH_3COC(CH_3)_3} \xrightarrow{CF_3CO_3H} \underset{\text{t-butylacetate}}{CH_3COOC(CH_3)_3}$$

(b) Preparation of anhydrides

$$CH_3COCOCH_3 \xrightarrow{RCO_3H} CH_3COOCOCH_3$$

(c) Preparation of Lactones



(d) Elucidation of Structure

The ester obtained as a result of the rearrangement may be hydrolysed to acid and alcohol from which the structure of the substrate can be determined. The reaction is not successful with aldehydes. Aliphatic aldehydes are oxidized to acids by the migration of the hydrogen.

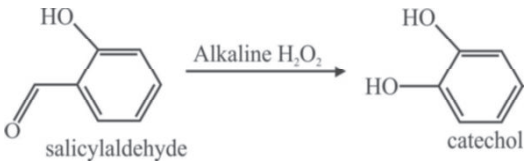
$$RCHO \xrightarrow{R'CO_3H} RCOOH$$

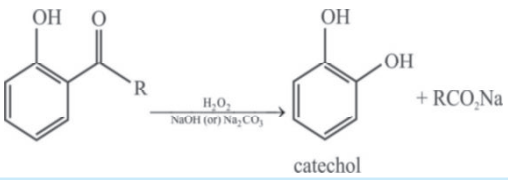
A few aromatic aldehydes have been converted to formates by the migration of the aryl group.

$$ArCHO \xrightarrow{R'CO_3H} HCOOAr$$

Dakin reaction

The replacement of the aldehyde group of o- and p- hydroxy and o- amino benzaldehyde or ketone by a hydroxyl group on reaction with alkaline hydrogen peroxide is called Dakin reaction. This reaction is closely related to Baeyer Villiger oxidation.





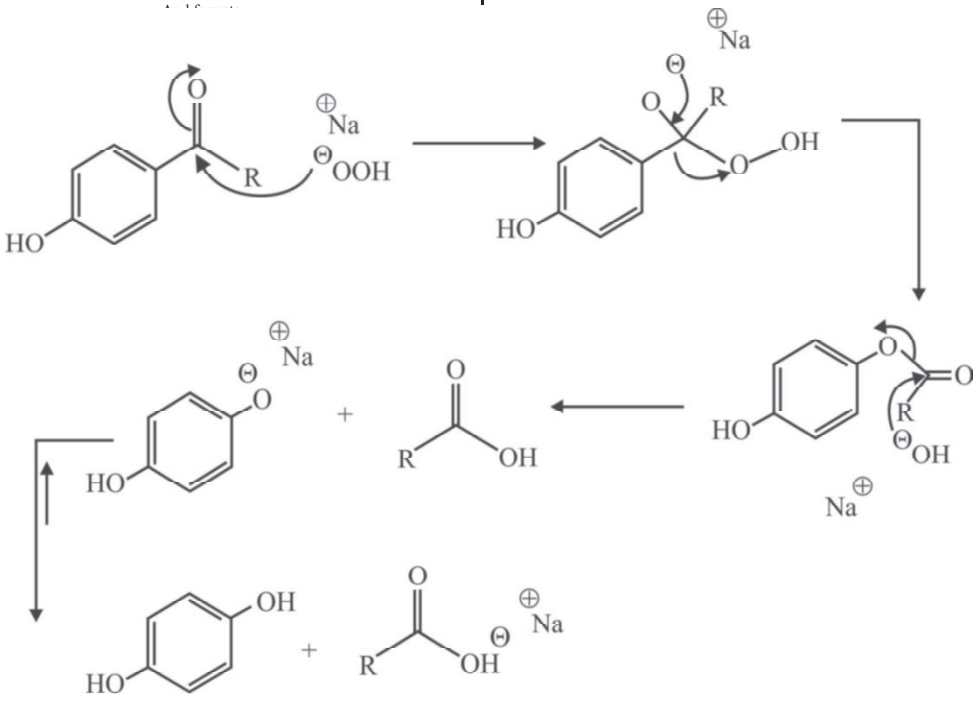
The product formed depends on the starting material. If ortho substituted phenol is the starting material, then catechol is formed. In mechanism, para substitued phenol is explained which results in the formation of quinol.

Mechanism:

During the reaction, the formyl group will be removed as formate ion and then replaced by the hydroxyl group.

1. $H_2O_2 + NaOH \rightleftharpoons HOONa + H_2O$

2.



Exercise

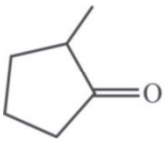
(SINGLE ANSWER TYPE)

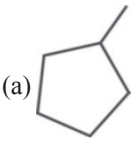
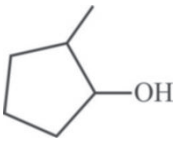
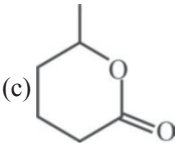
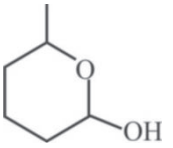
1. When an amide is treated with alcoholic solution of KOH and Br_2, the carbon atom of amide group is removed as

(a) CO_2 (b) CO_3^{2-} (c) HCO_3^- (d) CO

2. Which of the following reaction is involved in the preparation of perlon polymer from oximes?

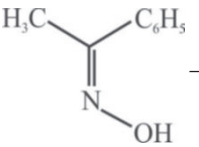
(a) Beckmann rearrangement
(b) Curtius rearrangement
(c) Schmidt rearrangement
(d) Lossen rearrangement

3.  Product. The product is

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

4. Identify the correct migratory aptitude during Baeyer Villiger oxidation?

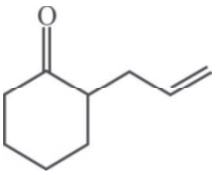
(a) t - alkyl > Cyclohexyl = 2^o alkyl = benzyl = phenyl
(b) t - alkyl > Cyclohexyl > 2^o alkyl > benzyl = phenyl
(c) t - alkyl > Cyclohexyl < 2^o alkyl > benzyl > phenyl
(d) t - alkyl > Cyclohexyl > 2^o alkyl < benzyl < phenyl

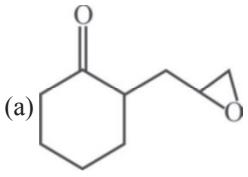
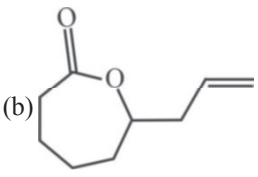
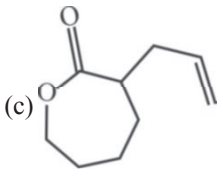
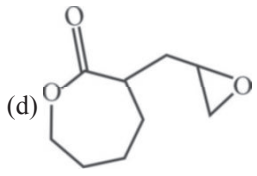
5.  A+B. The products A and B are, respectively

(a) $C_6H_5COOH + CH_3NH_2$
(b) $C_6H_5NH_2 + CH_3COOH$
(c) $C_6H_5CONHCH_3$
(d) $CH_3CONHC_6H_5$

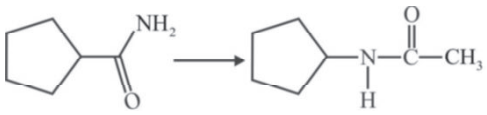
6. Which of the following reaction may be used for stepping down the acid series?

(a) Beckmann rearrangement
(b) Curtius rearrangement
(c) Lossen rearrangement
(d) Schmidt rearrangement

7.  A. The product A is

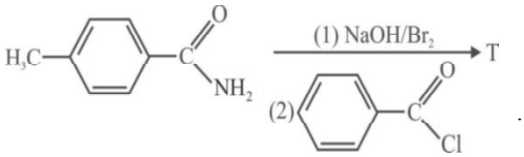
(a) 
(b) 
(c) 
(d) 

8. Select the correct sequence of reagents for the following conversion.

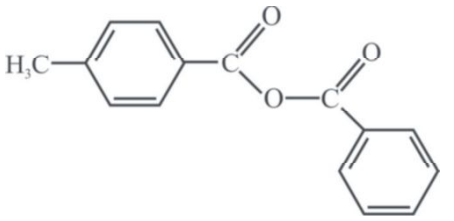


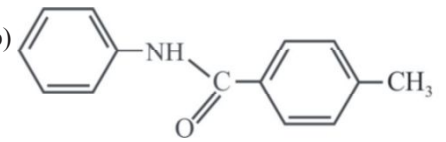
(a) $Br_2 + NaOH, CH_3OH$
(b) $CH_3COCl, Br_2 + NaOH$
(c) $Br_2 + NaOH, CH_3COCl$
(d) $Br_2 + NaOH$

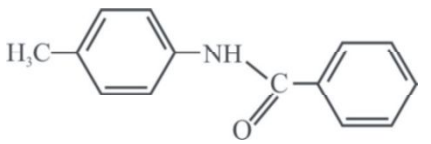
9. In the reaction

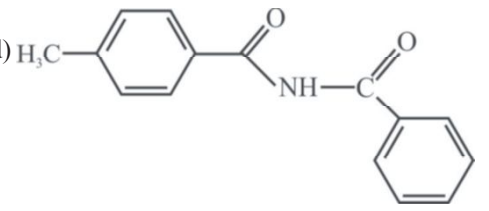


The structure of the product T is

(a) 

(b) 

(c) 

(d) 

10. $PhCH_2COOH \xrightarrow{C_2H_5OH,H^+} A \xrightarrow[2.HNO_2]{1.NH_2NH_2} B \xrightarrow{1.\Delta,C_6H_6,2.H_2O} C \xrightarrow{HNO_2} D \xrightarrow{PCC}$

Compound "E" is

(a) $PhCON_3$ (b) PhCOOH

(c) PhNCO (d) PhCHO

(MULTIPLE ANSWER TYPE)

11. In which of the following reaction(s) nitrene formation takes place?

(a) Hofmann rearrangement

(b) Baeyer Villiger rearrangement

(c) Beckmann rearrangement

(d) Dakin reaction

12. Amino acids can be prepared by using

(a) Lossen rearrangement

(b) Curtius rearrangement

(c) Hofmann rearrangement

(d) Riemer Tieman reaction

13. Primary amines can be prepared by using which of the following reactions?

(a) Beckmann rearrangement

(b) Lossen rearrangement

(c) Reduction of Cyanides

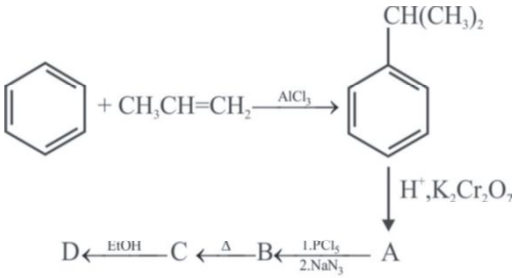
(d) Schmidt rearrangement

14. Reaction of $RCONH_2$ with a mixture of Br_2 and KOH gives RNH_2 as the main product. The intermediates involved in this reactions are

(a) RCONHBr (b) RNHBr

(c) RNCO (d) $RCONBr_2$

Comprehension Type questions(For Q. No. 15 to 17)



15. The compound C is

(a) $PhCON_3$ (b) PhNCO

(c) PhCOOH (d) PhNHCOOEt

16. The conversion of A to C is known as

(a) Hofmann rearrangement

(b) Schmidt reaction

(c) Curtius rearrangement

(d) Baeyer Villiger rearrangement

17. Cumene is oxidised with oxygen and on acidification gives an aromatic compound (P) and aliphatic compound (Q). "P" on reaction with $CHCl_3$ and KOH gives a compound "R". Compound "R" on reaction with alkaline hydrogen peroxide gives which of the following compound?

(a) Phenol (b) Catechol

(c) Resorcinol (d) Pyrogallol

Assertion and Reason Type

(a) Statement-I and Statement-II are true and Statement - II is the correct explanation of Statement - II

(b) Statement - I and Statement - II are true, but Statement - II is not the correct explanation of Statement - I

(c) Statement - I is true, but Statement - II is false

(d) Statement - I is false, but Statement - II is true

18. Statement I: 1^o amides react with $NaOH + Br_2$ to give 1^o amines with one carbon atom less than the parent amide
Statement II: The reaction occurs through intermediate formation of acylnitrene.

19. Statement I: Ester of hydroxamic acid reacts with base to give isocyanate that could be converted into amine upon hydrolysis.
Statement II: Amines can only prepared by using Lossen rearranment.

20. Statement I: Arylazides can yield ring expansion on heating in presence of Aniline.
Statement II: Due to the ring expansion, heterocyclic compound will be formed.

ANSWER KEY

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

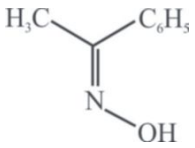
HINTS & SOLUTIONS

1.Sol:  group in amide is converted to CO_2 which later combine with NaOH forms Na_2CO_3.

2.Sol: It is an applicaiton of Beckmann rearrangement

3.Sol: The product is Lactone which is Baeyer Villiger oxidation product

4.Sol: The migratory aptitudes of various electron donating groups are t - alkyl >Cyclohexyl = 2^o alkyl = benzyl = phenyl > vinylic > 1^o alkyl > cyclopropyl > methyl

5.Sol: 

$$\xrightarrow{PCl_5} C_6H_5CONHCH_3$$

$$\xrightarrow{H_2O/H^+,\Delta} C_6H_5COOH + CH_3NH_2$$

The above reaction follows Beckmann's rearrangement mechanism.

6.Sol: $RCH_2COOH \xrightarrow{C_2H_5OH.H^+} RCH_2COOC_2H_5$

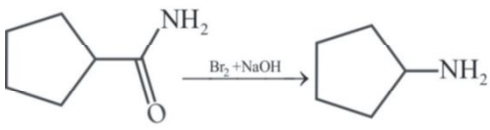
$$\xrightarrow[2.HNO_2]{1.NH_2NH_2} RCH_2CON_3$$

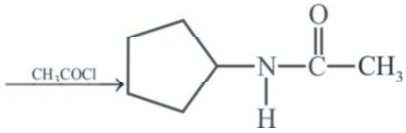
$$\xrightarrow{1.\Delta, C_6H_6, 2.H_2O} RCH_2NH_2 \xrightarrow{HNO_2} RCH_2OH$$

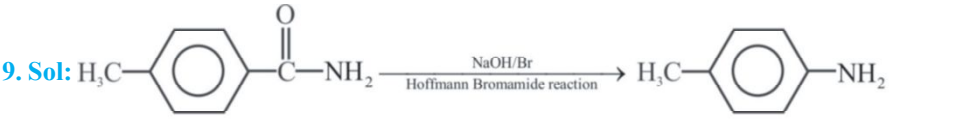
$$\xrightarrow{Oxidation} RCOOH$$

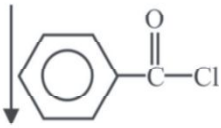
7.Sol: When an alkene and carbonyl are present in the same molecule, an increase in the acidity of the medium favors attack at the carbonyl. Acid catalyzed side reactions can be suppressed by a phosphate buffer.

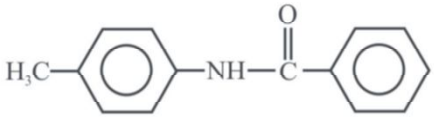
8. Sol:





9. Sol: 





(T)

10. Sol: $PhCH_2COOH \xrightarrow{C_2H_5OH,H^+} PhCH_2COOC_2H_5 \xrightarrow[2.HNO_2]{1.NH_2NH_2} PhCH_2CON_3 \xrightarrow{1.\Delta,C_6H_6,2.H_2O}$

$PhCH_2NH_2 \xrightarrow{HNO_2} PhCH_2OH \xrightarrow{PCC} PhCHO$

11.Sol: Nitrene formed in Hofmann rearrangement.

12.Sol: Conceptual

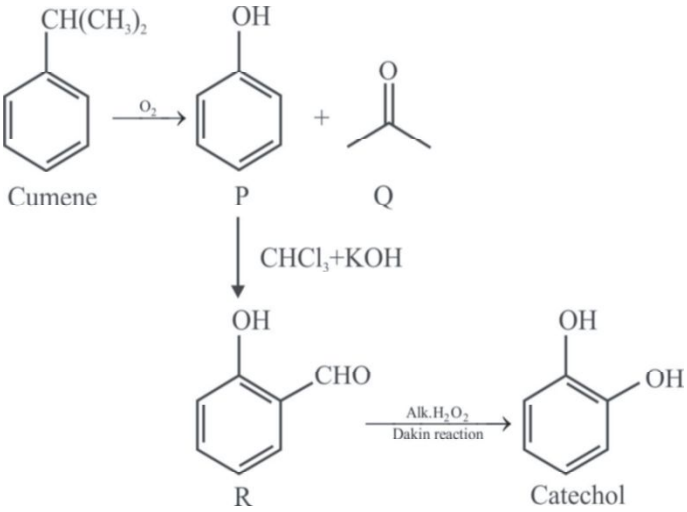
13.Sol: Conceptual

14.Sol: This is an example of Hofmann rearrangement.

15.Sol: A: PhCOOH, B: $PhCON_3$, C: PhNCO, D: PhNHCOEt

16.Sol: The conversion of carboxylic acid to isocyanate is an exmple of Schmidt reaction.

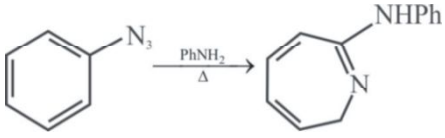
17. Sol:



18.Sol: Statement II is the correct explanation of Statement I.

19.Sol: Statement I is true and is an example of Lossen rearranment, Ester of hydroxamic acid reacts with base to give isocyanate that could be converted into amine upon hydrolysis.
Statement II is false, amines can be prepared by using Hofmann, Curtius reactions also.

20.Sol: Statement II is the correct explanation of Statement I



CHEMISTRY EXCEL

A Competitve Edge for NEET & IIT-JEE

EQUIVALENT CONCEPT

1. In the reaction

$Br_2 + Na_2CO_3 \longrightarrow NaBr + NaBrO_3 + CO_2$

The equivalent weight of $NaBrO_3$ is

(a) $\frac{Mol.wt}{1}$ (b) $\frac{Mol.wt}{10}$

(c) $\frac{Mol.wt}{5}$ (d) $\frac{Mol.wt}{4}$

2. Equivalent wt. of H_3PO_4 in each of the reaction will be respectively-

$H_3PO_4 + OH^- \rightarrow H_2PO_4^- + H_2O$

$H_3PO_4 + 2OH^- \rightarrow HPO_4^{2-} + 2H_2O$

$H_3PO_4 + 3OH^- \rightarrow PO_4^{3-} + 3H_2O$

(a) 98, 49, 32.67 (b) 49, 98, 32.67

(c) 98, 32.67, 49 (d) 32.67, 49, 98

3. The number of milli equivalents of acid in 100ml of 0.5 N HCl solution is -

(a) 50 (b) 100 (c) 25 (d) 200

4. For the reaction, $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$, if molecular masses of NH_3 and N_2 are M_1 and M_2, their equivalent weights are E_1 and E_2, then $E_1 - E_2$ is

(a) $\frac{2M_1 - M_2}{6}$ (b) $M_1 - M_2$

(c) $3M_1 - M_2$ (d) $M_1 - 3M_2$

5. In acting as a reducing agent, a piece of metal M weighing 16 grams gives up 2.25×10^{23} electrons. What is the equivalent weight of the metal?

(a) 42.83 (b) 21.33 (c) 83.32 (d) 32

6. What weight of HNO_3 is needed to convert 62 gm of P_4 in H_3PO_4 in the reaction ?

$P_4 + HNO_3 \rightarrow H_3PO_4 + NO_2 + H_2O$

(a) 63 gm (b) 630 gm (c) 315 gm (d) 126 gm

7. An element forms an oxide in which the oxygen is 20% of the oxide by weight, the equivalent weight of the given element will be -

(a) 32 (b) 40 (c) 60 (d) 128

8. If 0.20 g chloride of a certain metal, when dissolved in water and treated with excess of $AgNO_3$, yields 0.50 g of AgCl, the equivalent mass of the metal is

(a) 20.04 (b) 43.80 (c) 40.08 (d) 21.90

9. On heating 5×10^{-3} equivalents of $CaCl_2.xH_2O$, 0.18 g of water is obtained. What is the value of "x"?

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

10. 6.90 gm of a metal carbonate were dissolved in 60 ml of 2(N) HCl. The excess acid was neutralised by 20 ml of 1(N) NaOH. What is the equivalent wt. of metal ?

(a) 40 (b) 20 (c) 19 (d) 39

11. One gram of a chloride was found to contain 0.835 g of chlorine. Its vapour density is 85. The molecular formula of metal chloride is

(a) MCl (b) MCl_2 (c) MCl_3 (d) MCl_4

12. If m_1 gram of a metal A displaces m_2 gram of another metal B from its salt solution and if the equivalent weights are E_1 and E_2 respectively then the equivalent weight of A can be expressed by

(a) $E_1 = \frac{m_2 \times E_2}{m_1}$ (b) $E_1 = \frac{m_1}{m_2} \times E_2$

(c) $E_1 = \frac{m_1 \times m_2}{E_2}$ (d) $E_1 = \sqrt{\frac{m_1 \times m_2}{E_2}}$

13. 5.47 g of Mg metal reacted completely with 14.31 g of a non metal. The compound of this non metal with hydrogen contains 3.1% H. The equivalent weight of Mg is

(a) 24 (b) 11.95 (c) 13.5 (d) 48

14. When a titanium chloride solution is electrolysed for 500 sec with a 120mA current, 15 mg of titanium is produced. What is the oxidation number of titanium in titanium chloride?

(a) 2 (b) 3 (c) 4 (d) 5

15. 0.789 g of crystalline barium hydroxide is dissolved in water. For the neutralisation of this solution 20 mL of $\frac{N}{4} HNO_3$ is required. How many moles of water are present in one mole of this base?

(Ba = 137.4, O = 16, N = 14, H = 1)

(a) 6 (b) 8 (c) 10 (d) 12

16. BrO_3^- ion reacts with Br^- to form Br_2 in acid medium. The equivalent mass of Br_2 in this reaction is (M = molecular weight of Br_2)

(a) 4M/6 (b) 5M/8

(c) 3M/5 (d) 5M/3

17. An aqueous solution of 6.3 g of a hydrated oxalic acid $(H_2C_2O_4.xH_2O)$ is made upto 250 mL. The 40 mL of 0.1N NaOH was required to completely neutralise 10 mL of the above prepared stock solution. Which of the following statement is incorrect?

(a) The acid is dihydrate.

(b) Equivalent weight of the hydrated acid is 45.

(c) Equivalent weight of the anhydrous acid is 45.

(d) 20 mL of the stock would require 40 mL of 0.1 M $Ca(OH)_2$ solution for complete neutralisation.

18. An organic compound gave the following data: 0.236 g yielded 0.528 g of CO_2 and 0.324 g H_2O on combustion. 0.295 g of the compound gave 56 mL N_2 at STP. The compound is a monoacidic base. Its platinic chloride salt contains 36.53% Pt. The equivalent weight of base and molecular formula of the compound are, respectively

(a) $59, C_3H_9N$ (b) $59, C_6H_{18}N_2$

(c) $118, C_3H_9N$ (d) $118, C_6H_{18}N_2$

19. 100 g of a mixture of nitrates of two metals A and B are heated to constant weight of 50g, containing corresponding oxides of the metals. The equivalent weights of A and B are 103 and 31, respectively. What is the percentage composition of A and B in the mixture?

(a) 32% A and 68% B (b) 68% A and 32% B

(c) 50% A and 50% B (d) 40% A and 60% B

20. When 4.125 g of a metallic carbonate was heated in a hard glass tube, the CO_2 evolved was found to measure 1336 mL at $27°C$ and 700 mm pressure. What is the equivalent weight of the metal?

(a) 2.198 g (b) 12.188 g (c) 4.215 g (d) 24.12 g

ANSWER KEY

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

HINTS & SOLUTIONS

1.Sol.

Valency factor for formation of $NaBrO_3 = 5$

$\therefore$ Equivalent weight of $NaBrO_3 = \frac{Mol.wt}{5}$

2.Sol:

$H_3PO_4 + OH^- \rightarrow H_2PO_4^- + H_2O; \quad EW = MW/1 = 98$

$H_3PO_4 + 2OH^- \rightarrow HPO_4^{2-} + 2H_2O; EW = MW/2 = 49$

$H_3PO_4 + 3OH^- \rightarrow PO_4^{3-} + 3H_2O; EW = MW/3 = 32.67$

3.Sol:

Number of milli equivalents = NV(mL)

$= 0.5 \times 100 = 50$

4.Sol:

$$E_1 = \frac{M_1}{3} \qquad E_2 = \frac{M_2}{6}$$

$$E_1 - E_2 = \frac{M_1}{3} - \frac{M_2}{6} = \frac{2M_1 - M_2}{6}$$

5.Sol.

N_A electron will be removed by

$\frac{6.023 \times 10^{23}}{2.25 \times 10^{23}} \times 16$ gm of metal M = 42.83 gm of metal M

$\therefore$ Equivalent weight of metal is 42.83

6.Sol.

The equivalent weight of $P_4 = \frac{31 \times 4}{5 \times 4} = \frac{31}{5}$

$\therefore$ 62 gm $P_4 = \frac{62 \times 5}{31}$ equivalents of P_4

$= 10$ equivalents of P_4

The equivalent weight of $HNO_3 = \frac{Mol.wt}{1} = \frac{63}{1}$

$\therefore$ The weight of HNO_3 required $= 10 \times 63 = 630 gm$

7. Sol:

a_1 gm of the metal gave a_2 gm of its oxide. Hence equivalent weight of the metal is $\frac{a_1}{a_2 - a_1} \times 8$

According to the given data, equivalent weight of metal is $\frac{80}{100 - 80} \times 8 = 32$

8.Sol:

$$\frac{\text{Equivalent mass of Metal + Equivalent mass of } Cl^-}{\text{Equivalent mass of Ag + Equivalent mass of } Cl^-}$$

$$= \frac{0.2}{0.5} \Rightarrow \frac{E + 35.5}{108 + 35.5}$$

$$= \frac{0.2}{0.5} \Rightarrow E = 21.90$$

9.Sol:

No. of moles of

$$CaCl_2.xH_2O = \frac{\text{No. of equivalents}}{\text{Valency factor}}$$

$$= \frac{5 \times 10^{-3}}{2} = 2.5 \times 10^{-3}$$

On heating 2.5×10^{-3} moles

$CaCl_2.xH_2O, (2.5 \times 10^{-3} \times 18x) g$ of water is obtained

Given that, $(2.5 \times 10^{-3} \times 18x) = 0.18 \qquad (x = 4)$

10.Sol.

Equivalents of HCl taken $= 60 \times 2 \times 10^{-3}$

Equivalents of HCl present after the reaction

$= 20 \times 1 \times 10^{-3}$

$\therefore$ Equivalents of HCl utilised $= 100 \times 10^{-3}$

$\therefore 100 \times 10^{-3}$ equivalents of metal carbonate $= 6.90$gm

$\therefore$ 1 equivalent of metal carbonate

$$= \frac{6.90}{10^{-1}} = 69 gm$$

$\therefore$ Equivalent weight of metal = 69 – 30 = 39

[because equivalent weight of carbonate = 30]

11.Sol.

Mass of metal chloride = 1g

Mass of chlorine = 0.835 g

Mass of metal = (1 – 0.835) = 0.165 g

Equivalent mass of metal $= \frac{0.165 \times 35.5}{0.835}$

$= 7.01$

Valency of the metal $= \frac{2V.D}{E + 35.5}$

$= \frac{2 \times 85}{7.01 + 35.5} = 4$

Formula of the chloride = MCl_4

12.Sol:

For displacement reactions, $\frac{E_1}{E_2} = \frac{m_1}{m_2}$

13.Sol:

Weight of Mg = 5.47 g

Weight of non metal = 14.31 g

Weight of non metal in hydrogen compound
$= 100 - 3.1 = 96.9$

14.31 g of non metal contains

$$\frac{3.1}{96.9} \times 14.31 = 0.4578 \text{ g of } H_2$$

$$\text{Equivalent of Mg} = \frac{5.47}{0.4578} \times 1 = 11.95$$

14.Sol:

$$\text{Number of Faradays passed} = \frac{120 \times 10^{-3} \times 500}{96500}$$

$$= 6.22 \times 10^{-4}$$

$$\text{Equivalent weight} = \frac{\text{Weight of element}}{\text{Number of Faradays passed}}$$

$$= \frac{15 \times 10^{-3}}{6.22 \times 10^{-4}} = 24.116$$

$$\text{Valency} = \frac{\text{Molar mass}}{\text{Equivalent weight}} = \frac{48}{24.116} = 2$$

15.Sol.

Let the molecular formula be $Ba(OH)_2.xH_2O$

Mol. mass of $Ba(OH)_2.xH_2O$

$$= 137.4 + (2 \times 16) + 2 \times 1 + 18x$$
$$= 171.4 + 18x$$

Eq. mass of $Ba(OH)_2.xH_2O = \frac{171.4 + 18x}{2}$

$$20mL \frac{N}{4} HNO_3 \equiv 20mL \frac{N}{4} Ba(OH)_2.xH_2O$$

Amount of $Ba(OH)_2.xH_2O$

$$= \frac{(171.4 + 18x)}{2 \times 4} \times \frac{20}{1000} = \frac{171.4 + 18x}{400} g$$

Amount of $Ba(OH)_2.xH_2O = 0.789g$

Hence, $\frac{171.4 + 18x}{400} = 0.789$

or $171.4 + 18x = 0.789 \times 400$

$$x = \frac{144.2}{18} = 8.01 \approx 8$$

Thus, 8 moles of water molecules are present in one mole of the base.

16.Sol:

$2BrO_3^- + 12H^+ + 10e \rightarrow Br_2 + 6H_2O \quad n_1 = 10$

$2Br^- \rightarrow Br_2 + 2e \quad n_2 = 2$

$$\text{Valency factor} = \frac{n_1 \times n_2}{n_1 + n_2} = \frac{10 \times 2}{10 + 2} = \frac{5}{3}$$

$$\text{Equivalent weight} = \frac{M}{\frac{5}{3}} = \frac{3M}{5}$$

17.Sol:

Condition for complete neutralisation is,

$N_a V_a = N_b V_b$

$$\left[\frac{6.3}{\left(\frac{90 + 18x}{2} \right)} \frac{1000}{25} \right] 10 = 0.1 \times 40$$

$x = 2$

Equivalent weight of anhydrous acid $= 90 / 2 = 45$

Also 20 ml of stock solution

$= 2 \times 40 \times 0.10 = 8$ meq of acid

8 meq $Ca(OH)_2$ will be present in $8/0.2 = 40$ mL

18.Sol:

% of Carbon

$$= \frac{12}{44} \times \frac{\text{Wt. of } CO_2}{\text{Wt. of organic compound}} \times 100$$

$$= \frac{12}{44} \times \frac{0.528}{0.236} \times 100 = 61.07\%$$

% of hydrogen

$$= \frac{2}{18} \times \frac{\text{Wt. of } H_2O}{\text{Wt. of organic compound}} \times 100$$

$$= \frac{2}{18} \times \frac{0.324}{0.236} \times 100 = 15.25\%$$

$$\% \text{ of nitrogen} = \frac{1}{8} \times \frac{V_{N_2} \text{ at STP}}{\text{Wt. of organic compound}}$$

$$= \frac{1}{8} \times \frac{56}{0.295} = 23.73\%$$

Element	%	Relative number of atoms	Simplest ratio
C	61.07	5.08	3
H	15.25	15.25	9
N	23.73	1.695	1

Empirical formula $= C_3H_9N$

Empirical formula weight = 59

Equivalent weight of base

$$= \frac{1}{2}\left[\frac{\text{Wt. of Pt salt}}{\text{Wt. of Pt}} \times 195 - 410\right]$$

$$= \frac{1}{2}\left[\frac{100}{36.93} \times 195 - 410\right] = 59$$

Molecular weight of base = Equivalent weight of base × Valency factor = 59

n = Molecular weight/Empirical weight = 59/59 = 1

Molecular formula $= C_3H_9N$

19.Sol:

Equivalent weight of metal nitrate = Equivalent weight of metal + Equivalent weight of nitrate - Radical

Equivalent weight of nitrate of A = 103 + 62 = 165

Equivalent weight of oxide of A = 103 + 8 = 111

Equivalent weight of nitrate of B = 31 + 62 = 93

Equivalent weight of oxide of B = 31 + 8 = 39

Let the mass of A in the mixture be x gm. Then mass of B is (100 - x)gm. Applying concept of equivalent weight concept to chemical reaction, 165 g of nitrate of A yields 111 g of A's oxide.

Therefore, x g of A's nitrate yields:

Mass of A's oxide $= 111x/165 = 0.67x$

Similarly, Mass of B's oxide $= 39(100-x)/93$

$= 42 - 0.42x$

According to question,

$0.67x + 42 - 0.42x = 50$

$x = 32g$

Mass of A $= x = 32g$

Mass of B = $= 100 - x = 68g$

Mixture contains 32% A and 68% B

20.Sol:

$$PV = \frac{w}{MW}RT \Rightarrow \frac{700}{760} \times \frac{1336}{1000}$$

$$= \frac{w}{44} \times 0.0821 \times 300 \Rightarrow w = 2.198gCO_2$$

The molecular mass of any metal carbonate is 2E+60

Where, E is the equivalent mass of the metal.

$$\frac{2E+60}{4.215} = \frac{44}{2.198} \Rightarrow E = 12.188g$$

NEET EVA-AITS - 11

"A Colossal juncture to get introduced to the national standard mock tests of NEET"

1. Silver metal crystallises in a cubic close packed arrangement with edge length 404 pm. Thus, radius of the silver atom is
(a) 203.5 pm (b) 120.5 pm
(c) 142.8 pm (d) 407.0 pm

2. An X molal solution of a compound in benzene has mole fraction of solute = 0.2. The value of X is
(a) 14.0 (b) 3.2
(c) 1.4 (d) 2.0

3. Normal aluminium electrode coupled with normal hydrogen electrode gives an emf of 1.66 V. So the standard electrode potential of aluminium is,
(a) - 1.66 V (b) + 1.66 V
(c) - 0.83 V (d) + 0.83 V

4. The rate of disappearance of SO_2 in the reaction $2SO_2 + O_2 \rightarrow 2SO_3$ is $1.28\times10^{-3}\ g/\text{sec}$ then the rate of formation of SO_3 is
(a) $0.64\times10^{-3}\ g/\text{sec}$ (b) $0.80\times10^{-3}\ g/\text{sec}$
(c) $1.28\times10^{-3}\ g/\text{sec}$ (d) $1.60\times10^{-3}\ g/\text{sec}$

5. For adsorption of gas on solid surface, the plots of log *x/m* versus log *P* is linear with a slope equal to
(a) k (b) $\log k$
(c) log C (d) $\frac{1}{n}$ (n being integer)

6. The process of the isolation of a metal by dissolving the ore in a suitable chemical reagent followed by precipitation of the metal by a more electropositive metal is called:
(a) Hydrometallurgy (b) Electrometallurgy
(c) Zone refining (d) Electro - refining

7. Which is a set of acid salts and can react with base?
(a) $NaH_2PO_2, Na_2HPO_3, NaH_2PO_4$
(b) $Na_2HPO_3, NaH_2PO_3, Na_2HPO_4$
(c) $NaH_2PO_4, NaH_2PO_3, Na_2HPO_4$
(d) All of these

8. Which of the following gases is responsible for global warming as well as ozone layer depletion?
(a) $CFCs$ (b) O_2
(c) CO_2 (d) N_2

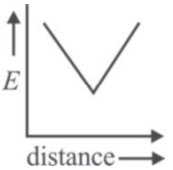
9. 7.5 grams of a gas occupy 5.6 litres of volume at STP. The formula of gas is
(a) CO_2 (b) N_2O
(c) CO (d) NO

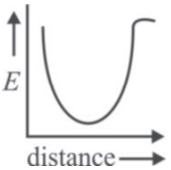
10. What is the ratio of mass of an electron to the mass of a proton?
(a) 1 : 2 (b) 1 : 1
(c) 1 : 1837 (d) 1 : 3

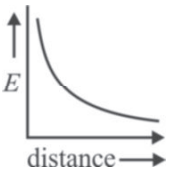
11. The energy of electron in first Bohr's orbit of H-atom is -13.6 eV. What will be its potential energy in $n = 4^{th}$ orbit?
(a) - 13.6 eV (b) - 3.4 eV
(c) - 0.85 eV (d) - 1.70 eV

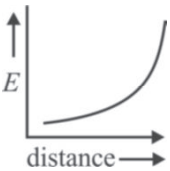
12. Adiabatic reversible expansion of a gas is represented by
(a) $\left(\frac{T_1}{T_2}\right)^{\gamma} = \left(\frac{P_2}{P_1}\right)^{(\gamma-1)}$ (b) $\left(\frac{T_1}{T_2}\right)^{\gamma} = \left(\frac{P_1}{P_2}\right)^{(1-\gamma)}$
(c) $\left(\frac{T_1}{T_2}\right)^{\gamma} = \left(\frac{P_2}{P_1}\right)^{(1-\gamma)}$ (d) All of the above

13. Which plot best represents the potential energy (E) of two hydrogen atoms as they approach one another to form a hydrogen molecule?

(a) 

(b) 

(c) 

(d) 

14. From B_2H_6, all the following can be prepared except

(a) B_2O_3 (b) H_3BO_3

(c) $B_2(CH_3)_6$ (d) $NaBH_4$

15. The inductive effects of the group $-CH_3, -COO^-$, $-Br, -NH_3^+$ respectively are

(a) -I, +I, -I, +I (b) +I, -I, +I, +I

(c) +I, +I, -I, -I (d) -I, -I, +I, +I

16. Which of the following statements is true about photochemical smog?

(a) It is reducing in nature.

(b) It is formed in winter.

(c) It is a sulphurous smog.

(d) Components of the smog, NO and O_3, irritate the nose and throat and their high concentration causes headache, chest pain, dryness of the throat, cough and difficulty in breathing.

17. The number of nodal planes in a p_x orbital is

(a) One (b) Two

(c) Three (d) Zero

18. Find the work done when 2 moles of hydrogen expand isothermally from 15 to 50 litres against a constant pressure of 1 atm at 25^o C.

(a) 847.0 cal (b) 847 kcal

(c) 84.7 cal (d) 84.7 kcal

19. For a reaction $H_2 + I_2 \rightleftharpoons 2HI$ at 721 K, the value of equilibrium constant is 50. If 0.5 mol each of H_2 and I_2 is added to the system the value of equilibrium constant will be

(a) 40 (b) 60 (c) 50 (d) 30

20. Which of the following substance is an electrolyte?

(a) Chloroform (b) Benzene

(c) Toluene (d) Magnesium chloride

21. What is the oxidation number of Co in $[Co(NH_3)_4ClNO_2]$?

(a) +5 (b) +3 (c) +4 (d) +2

22. By adding which of the following compound, both temporary and permanent hardness of water can be removed?

(a) Sodalime (b) Sodium bicarbonate

(c) Washing soda (d) Sodium chloride.

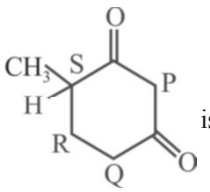
23. The main factor responsible for weak acidic nature of B - F bonds in BF_3 is:

(a) Large electronegativity of F

(b) $p\pi - p\pi$ back bonding

(c) $p\pi - d\pi$ back bonding

(d) Three centred two electron bonds in BF_3

24. If 

is mixed with NaOH solution, acid-base reaction occurs and snatches from organic molecule. Which carbon will lose easily?

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

25. Gasoline has composition

(a) $C_8 - C_{12}$ (b) $C_6 - C_{11}$

(c) $C_2 - C_5$ (d) None of these

26. Purity of butter is determined in terms of:

(a) Saponification value

(b) Iodine value

(c) Acetyl value

(d) Reichert-Meissl value

27. If $N_1, N_2, N_3....$ are the number of molecules with molecular masses $M_1, M_2, M_3....$ respectively, then average molecular mass is expressed as

(a) $\frac{\sum N_i M_i^2}{\sum N_i M_i}$ (b) $\frac{\sum N_i M_i}{\sum N_i}$

(c) Both of these (d) None of these

28. 20% aqueous solution of sodium chloride containing ethyl alcohol on electrolysis gives:
(a) Ethyl chloride (b) Chloral
(c) Acetaldehyde (d) Chloroform

29. The reaction $2NO(g)+O_2(g) \rightleftharpoons 2NO_2(g)$ is of first order. If volume of reaction vessel is reduced to 1/3, the rate of reaction would be
(a) 1/3 times (b) 2/3 times
(c) 3 times (d) 6 times

30. When the temperature is raised, the viscosity of liquid decreases, this is because
(a) Decreased volume of the solution
(b) Increase in temperature increases the average kinetic energy of molecules, which overcomes the attractive force between them
(c) Decreased covalent and hydrogen bond forces
(d) Increased attraction between molecules

31. When HNO_3 is dropped into the palm and washed with water, it turns into yellow. It shows the presence of
(a) NO_2 (b) N_2O
(c) NO (d) N_2O_5

32. Some salts although containing two different metallic elements give test for one of them in solution. Such salts are:
(a) Double salts (b) Complex salts
(c) Normal salts (d) None of these

33. Which of the following is not correct?
(a) The metallic conduction is due to the movement of electrons in the metal.
(b) The electrolytic conduction is due to the movement of ions in the solution.
(c) The current carrying ions are not necessarily discharged at the electrodes.
(d) The metallic conduction increases with the increase in temperature, whereas that of electrolytic conduction decreases with temperature.

34. Some of the properties given below are for colloidal sols.
(I) Viscosity is same as that of the medium.
(II) Extensive hydration takes place.
(III) Migration of the particles under electric field.
(IV) Particles cannot be detected even under ultra-microscope.
Properties applicable for lyophilic and lyophobic colloidal sols are

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

35. Which of the following is least reactive?
(a) White phosphorus (b) Yellow phosphorus
(c) Red phosphorus (d) Black phosphorus

36. Acetaldehyde and acetone differ in their reaction with
(a) Sodium bisulphite
(b) Ammonia
(c) Phosphorus pentachloride
(d) Phenyl hydrazine

37. The actinoids exhibit more member of oxidation states in general than the lanthanids. This is because
(a) the actinides are more reactive than the lanthanides
(b) the 5*f*-orbitals are more buried than the 4*f*-orbitals
(c) there is a similarity between 4*f* and 5*f*-orbitals in their angular part of the wave function
(d) the 5*f*-orbitals extend farther from the nucleus than the 4*f*-orbitals

38. An unknown alcohol is treated with the 'Lucas reagent' to determine whether the alcohol is primary, secondary or tertiary. Which alcohol reacts fastest and by what mechanism?
(a) Secondary alcohol by S_N1
(b) Tertiary alcohol by S_N1
(c) Secondary alcohol by S_N2
(d) Tertiary alcohol by S_N2

39. Which of the following reactions does not yield an amine?
(a) $RX + NH_3 \longrightarrow$
(b) $RCH = NOH + [H] \xrightarrow[C_2H_5OH]{Na}$
(c) $RCN + H_2O \xrightarrow{H^+}$
(d) $RCONH_2 + 4H \xrightarrow{H_2O/H^+}$

40. The number of atoms in 100 g of an fcc crystal with density $d = 10\ g/cm^3$ and cell edge equal to 100 pm is equal to
(a) 3×10^{25} (b) 2×10^{25}
(c) 1×10^{25} (d) 4×10^{25}

41. Equilibrium constants K_1 and K_2 for the following equilibria

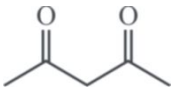
$$NO(g)+\frac{1}{2}O_2 \overset{K_1}{\rightleftharpoons} NO_2(g)$$

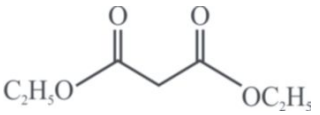
$$2NO_2(g) \overset{K_2}{\rightleftharpoons} 2NO(g)+O_2(g)$$ are related as

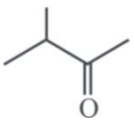
(a) $K_2=\frac{1}{K_1}$ (b) $K_2=\frac{1}{K_1^2}$

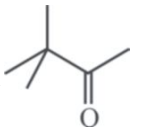
(c) $K_2=\frac{K_1}{2}$ (d) $K_2=K_1^2$

42. Arrange the following in the increasing order of stability of their most stable enol.

I. 

II. 

III. 

IV. 

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

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

43. Sulphur forms the chlorides S_2Cl_2 and SCl_2. The equivalent mass of sulphur in SCl_2 is

(a) 8 g/mol (b) 16 g/mol

(c) 64.8 g/mol (d) 32 g/mol

44. The dissociation constant of weak acid HA is 4.9×10^{-8}. After making the necessary approximations, calculate pH in 0.1 M acid.

(a) 4.155 (b) 2.155

(c) 3.155 (d) 1.155

45. Which is the wrong IUPAC name of chlorocyclohexanedione?

(a) 3-chloro-1, 4-cyclohexanedione

(b) 2-chloro-1, 3-cyclohexanedione

(c) 4-chloro-1, 3-cyclohexanedione

(d) 5-chloro-1, 3-cyclohexanedione

Student Name: ..... **School/ College Name:** .....

OMR SHEET **NEET-11** **Chemistry**

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

Total Marks: Marks Obtained:

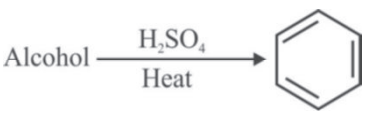
JEE-ADVANCED EVA-AITS - 2

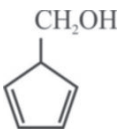
"A Colossal juncture to get introduced to the national standard mock tests of JEE ADVANCED"

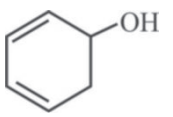
Section - A

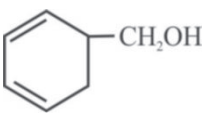
This section contains 10 multiple choice questions. Each question has 4 choices (a), (b), (c) and (d) for its answer, out of which only one or more than one is/are correct.

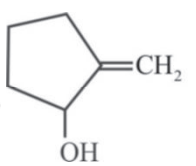
1. The possible structure of the alcohol in the following reaction is



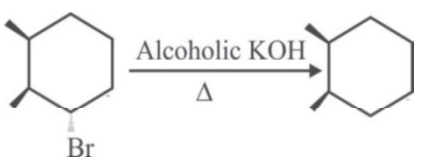
(a) 

(b) 

(c) 

(d) 

2. Identify reactions that correctly match with their products:

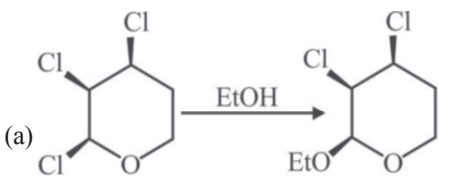
(a) 

(b) 

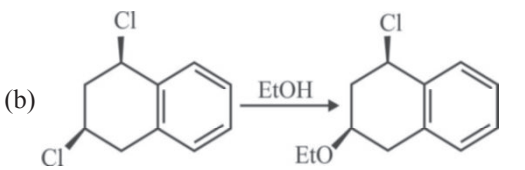
(c) 

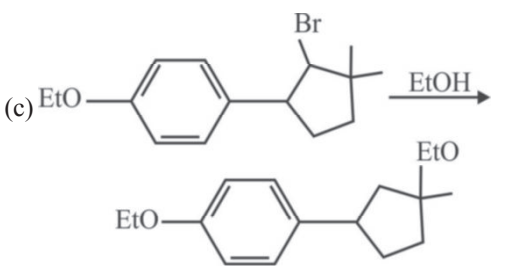
(d) 

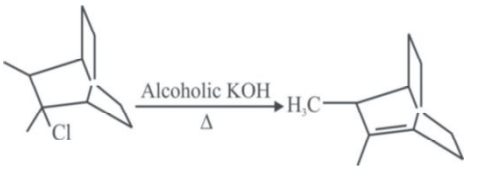
3. Identify reactions that correctly match with their products?

(a) 

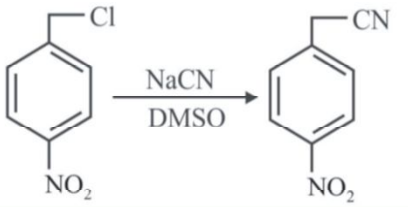
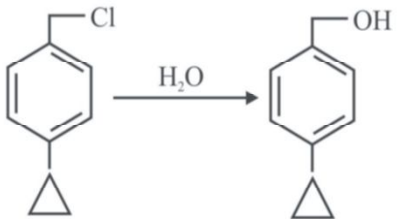
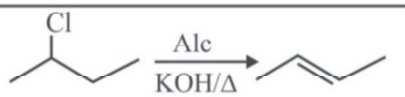
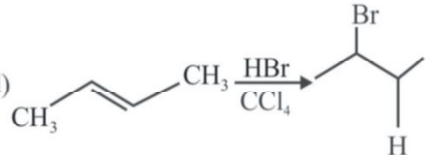
Mono substituted product

(b) 

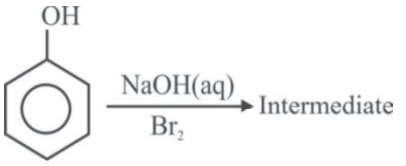
(c) 

(d) 

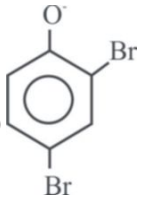
4. Which of the following is/are correctly matched?

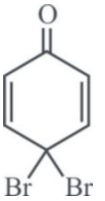
Column I	Column II
(a) 	(P) Carbocation intermediate is formed
(b) 	(Q) S_N1
(c) 	(R) S_N2
(d) 	(S) Addition reaction

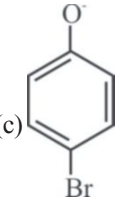
5. In the reaction

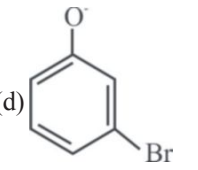


the intermediate are

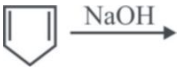
(a) 

(b) 

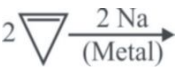
(c) 

(d) 

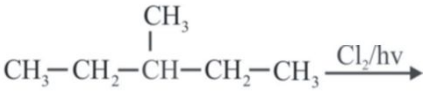
6. In which of the following reactions H_2 gas is liberated?

(a) 

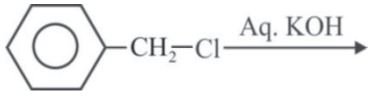
(b) 

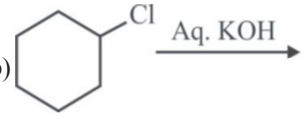
(c) 

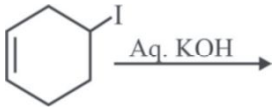
(d) 

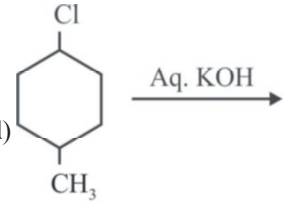
7.  Select the correct statement about products.
(a) total four products are formed including stereoisomer
(b) 4 Enantiomeric pair are formed stereoisomer
(c) major product is 3° halide
(d) total 8 product are formed including stereo isomers.

8. Which of the following gives same product with S_N^1 & S_N^2 reaction (including stereo product)?

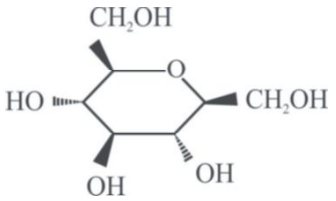
(a) 

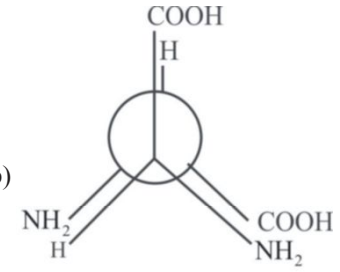
(b) 

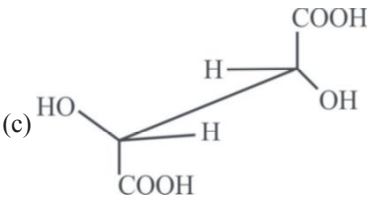
(c) 

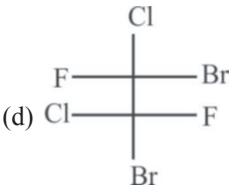
(d) 

9. Which of the following is/are a meso compound?

(a) 

(b) 

(c) 

(d) 

10. Two liquids A and B form an ideal solution. The solution has a vapour pressure of 700 Torr at 80°C. It is distilled till 2/3rd of the solution which is collected as condensate. The composition of the condensate is $x'_A = 0.75$ and that of the residue is $x''_A = 0.6$. If the vapour pressure of the residue at 80°C is 600 Torr, which of the following is/ are true?
(a) The composition of the original liquid was $x_A = 0.4$
(b) The composition of the original liquid was $x_A = 0.6$
(c) $P_A^o = \frac{2500}{3} Torr$
(d) $P_B^o = 500 Torr$

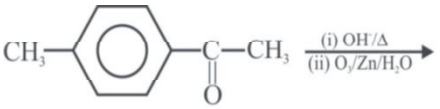
Section - B

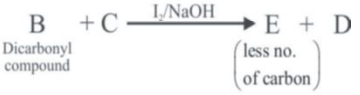
(One integer value Correct type)
This section contains 10 questions. Each question, when worked out will result is one integer from 0 to 9 (both inclusive)

11. In diamond, effective number of carbon atoms along any body diagonal of unit cell is n/4. What is the value of n?
12. Brown coloured ring formed in nitrate test has formula $[Fe(H_2O)_5 NO]SO_4$. Unpaired electron in Fe is:
13. Taking one mole of $N_{2(g)}$ and excess of $H_{2(g)}$, under suitable conditions, formation of NH_3 is completed when $NH_3(g)$ has mole fraction of 0.5. The initial moles of H_2 are

14. The mole fraction of solute in some solution is 1/n. If 50% of the solute molecules dissociates into two parts and remaining 50% get dimerised now mole fractions of solvent becomes 4/5. Find value of n.

15.





How many statements are correct for this sequence?

(i) Reactant can give bisulphite adduct.

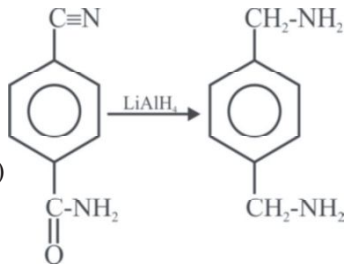
(ii) D is also one of the product of cannizaro reaction of Benzaldehyde.

(iii) B gives Tollen's reagent Test.

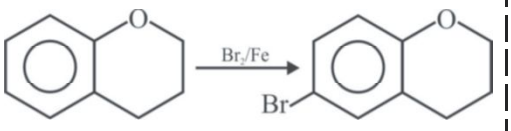
(iv) C gives iodoform test.

16. How many reactions are correctly matched for major product?

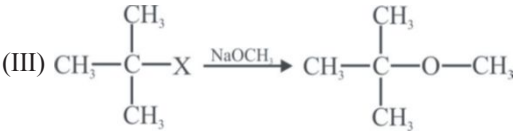
(I)



(II)

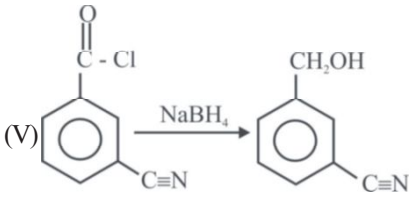


(III)



(IV)

(V)



(VI)

17. The electrolysis of cold sodium chloride solution produces NaOH and Cl_2. The Cl_2 produced, disproportionates into NaOH solution to give sodium hypochlorite (NaOCl) and sodium chloride. The time required for a cell to operate to produce $1.00\times10^3\,L$ of 7.45 % (w/w) solution of NaOCl if the cell current is 9.65 A is y x 10^7. The value of y is Assume that the density of solution is 1.00 gm/ml.

18. Given :

$$Zn(OH)_2(s) \rightleftharpoons Zn(OH)_2(aq) \quad ; K_1 = 10^{-6}$$

$$Zn(OH)_2(aq) \rightleftharpoons [Zn(OH)]^+ + OH^- \quad ; K_2 = 10^{-7}$$

$$[Zn(OH)]^+(aq) \rightleftharpoons Zn^{+2} + OH^- \quad ; K_3 = 10^{-4}$$

$$[Zn(OH)_3]^-(aq) + OH^- \rightleftharpoons [Zn(OH)_4]^{2-}; K_5 = 10$$

Find out the negative of logarithm of the solubility of solid $Zn(OH)_2$ at 25°C at pH = 6. Consider $Zn(OH)_2$ makes saturated solution at 25°C.

19. 0.0125 mole of sucrose is dissolved in 100 gm of water and it undergoes inversion according to following equation

$$C_{12}H_{22}O_{11} + H_2O \longrightarrow C_6H_{12}O_6 + C_6H_{12}O_6$$

If elevation in boiling point of solution is 0.104°C.

Calculate $\left(\frac{1}{10}\right)^{th}$ of mole percentage of sugar inverted (K_b for $H_2O = 0.52$).

20. Polychlorinated biphenyls, PCBs, known to be dangerous enviromental pollutants, are a group of compounds with the general empirical formula $C_{12}H_mCl_{10-m}$ where m is an integer. What is the value of m, if percentage of carbon atom in the compound is 40 ?

Synopticglance

p-BLOCK ELEMENTS - I

Group 15 Elements: (Introduction)

- Nitrogen, Phosphorus, Arsenic, Antimony, Bismuth and Moscovium (Mc) belong to VA group or 15th group of the periodic table.
- Group 15 elements or elements of nitrogen family are called pnictogens and their compounds are called pnictides as these elements forms pungent smelling compounds.

Occurrence

- Molecular nitrogen comprises 78% by volume of the atmosphere. In earth's crust, it occurs as $NaNO_3$ called Chile saltpeter and KNO_3 called Indian saltpeter. It is found in the form of proteins in plants and animals.
- Phosphorus occurs in minerals of the apatite family $Ca_9(PO_4)_6.CaX_2$ (X = F, Cl or OH) which are the components of phosphate rocks. It is present in bones as well as in living cells.
- Arsenic, antimony and bismuth are found mainly as sulphide minerals.

Electronic configuration

Electronic configuration of Group 15 Elements

Element	Symbol	Atomic number	Configuration
Nitrogen	N	7	$[He]2s^2 2p^3$
Phosphorus	P	15	$[Ne]3s^2 3p^3$
Arsenic	As	33	$[Ar]3d^{10}4s^2 4p^3$
Antimony	Sb	51	$[Kr]4d^{10}5s^2 5p^3$
Bismuth	Bi	83	$[Xe]4f^{14}5d^{10}6s^2 6p^3$

The general electronic configuration of group 15 elements is ns^2np^3. The s - orbital in these elements is completely filled and p-orbitals are half filled, making their electronic configuration extra stable.

Physical Properties

(1) Atomic and Ionic Radii

Covalent and ionic radii (in a particular state) increases down the group. From N to P considerable increase in covalent radius is observed, but from As to Bi small increase occurs due to presence of completely- filled d- and /or f- orbitals that offer poor shielding to the outermost shell electrons and thus the increase in atomic radius is less than expected.

(2) Ionisation Enthalpy

Down the group, ionisation enthalpy decreases due to gradual increase in atomic size. Successive ionisation enthalpies:

$\Delta_i H_1 < \Delta_i H_2 < \Delta_i H_3$ also ionisation enthalpy of Group 15 elements much higher than that Group 14 element in a particular period, because of smaller size and stable half-filled p orbital electronic configuration of Group 15 elements.

IMPORTANT POINTS

- The ionisation energy of nitrogen is very high due to its small size.
- The difference between N and P is comparatively high but the difference afterwards between two consecutive members is small. This is due to less shielding effect of d - electrons in As and Sb, d- and f- electrons in Bi.

(3) Electronegativity

Down the group electronegativity value decreases, but difference in value is not much in heavier elements.

IMPORTANT POINTS

Nitrogen is most electronegative element, i.e., typical non - metal.

(4) Atomicity

- Nitrogen is a diatomic gaseous molecule at ordinary temperature and the existence is due to its ability to form triple bond.
- Phosphorus, arsenic and antimony all exist as discrete tetratomic molecules (tetrahedral structures) *i.e.,* P_4, As_4 and Sb_4 as these are not capable of forming multiple bonds due to repulsion between non-bonding electrons in inner core.
- Bismuth possess purely metallic bonding.

(5) Boiling point

Increases down the group, but that of Sb is greater than Bi.

(6) Melting Point

Increases upto arsenic and then decreases upto bismuth.

(7) Allotropy

All elements of group 15 show allotropy except nitrogen.

(8) Oxidation State

- Common oxidation state of Group 15 elements are -3, +3 and +5.
- Tendency to show -3 oxidation state decreases down the group due to increase in size and metallic character.
- The stability of +5 oxidation state decreases and that of +3 oxidation state increases down the group due to inert pair effect. The only well charcterised Bi (V) compound is BiF_5.
- Nitrogen besides -3, +3 and +5 oxidation states, exhibits a large number of oxidation states from -3 to +5 and also -1/3 (in N_3H). All oxidation state from +1 to +4 disproportionate in acid solution in case of nitrogen, e.g.,

$$3HNO_2 \longrightarrow HNO_3 + H_2O + 2NO$$

- Phosphorus also shows +1 and +5 oxidation states in some oxoacids.
- All intermediate oxidation state disproportionate in both acid and alkali from -3 and +5.

$$2H_3PO_2 \rightarrow H_3PO_4 + PH_3$$

- However +3 oxidation state for As, Sb, Bi become increasingly stable with respect to disproportionation due to inert pair effect.

(9) Covalency

Nitrogen shows maximum covalency of four, as only four orbitals (one *s* and three *p*) are available for bonding. The heavier element with vacant *d* orbital can show covalency more than four e.g., in PF_6^-, P has covalency of six.

(10) Metallic and non - metallic character

- Metallic character increases as the atomic number increases.

  N and P $\rightarrow$ purely non - metals
  Arsenic $\rightarrow$ metalloid
  Sb and Bi $\rightarrow$ metals

Chemical Properties

(1) Reactivity towards hydrogen (Hydrides)

- VA group elements form hydrides of type MH_3

  NH_3 - Ammonia PH_3 - Phosphine
  AsH_3 - Arsine SbH_3 - Stibine
  BiH_3 - Bismuthine

- All the hydrides are prepared by the action of water or dilute acids on their metal compounds like Mg_3N_2, Ca_3P_2, Zn_3As_2, Mg_3Sb_2 and Mg_3Bi_2.

$$Mg_3N_2 + 6H_2O \rightarrow 3Mg(OH)_2 + 2NH_3$$
$$Ca_3P_2 + 6H_2O \rightarrow 3Ca(OH)_2 + 2PH_3$$
$$Zn_3As_2 + 6HCl \rightarrow 3ZnCl_2 + 2AsH_3$$
$$Mg_3E_2 + 6HCl \rightarrow 3MgCl_2 + 2XH_3$$

(E= Sb or Bi)

IMPORTANT POINTS

BiH_3 is very difficult to prepare because, it dissociates even at 25^0C.

- The ease of formation of hydrides decreases from NH_3 to BiH_3.
- Except NH_3, the remaining hydrides are poisonous gases.
- These hydrides are trigonal pyramidal shape and hybridisation is sp^3. The bond angle decreases

from NH_3 to BiH_3 due to increase in the size of atom M and decrease in the E.N. As pure 'p' orbitals of As and Sb are involved, the HMH bond angle in AsH_3 and SbH_3 are expected to be 90^0. But due to repulsions between M-H bonds, the angle increases to $91^0.48^1$

❍ Trends in some properties of hydrides of VA group elements:

- **Melting Point** $PH_3 < AsH_3 < SbH_3 < NH_3$
- **Boiling Point** $PH_3 < AsH_3 < NH_3 < SbH_3$
- **Bond Length(M-H)** $NH_3 < PH_3 < AsH_3 < SbH_3$
- **Reducing power** $NH_3 < PH_3 < AsH_3 < SbH_3 < BiH_3$.
- **Bond Enthalpy** $NH_3 > PH_3 > SbH_3 > AsH_3$
- **Bond Angle** $NH_3 > PH_3 > AsH_3 > SbH_3$
- **Basic Nature** $NH_3 > PH_3 > AsH_3 > SbH_3 > BiH_3$.
- **Stability** $NH_3 >> PH_3 > AsH_3 > SbH_3 > > BiH_3$.

IMPORTANT POINTS

❑ In NH_3, molecules are associated by hydrogen bonding and thus its bonding is comparatively high in comparison to PH_3 and AsH_3 where no hydrogen bond is present.

❑ In moving from PH_3 to BiH_3, boiling points increase in the magnitude of van der Waal's forces due to increase in molecular size.

(2) Reactivity towards oxygen (Oxides)

❍ Group 15 elements form two types of oxides - Trioxides (M_2O_3) and Pentoxides (M_2O_5).

❍ Trioxides and pentoxides of P, As and Sb are dimers with general M_4O_6 and M_4O_{10}.

❍ Trioxides are more stable than pentoxides because in pentoxides elements are in excited state.

❍ Order of Stability and Acidic strength:
Acidic nature increases with Oxidation number and decreases with Atomic size of the element.

Trioxides :

$N_2O_3 > P_4O_6 > As_4O_6 > Sb_4O_6 > Bi_2O_3$

Pentoxides :

$N_2O_5 > P_4O_{10} > As_4O_{10} > Sb_4O_{10} > Bi_2O_5$

❍ Nitrogen forms number of oxides due to $p\pi - p\pi$ multiple bonding between N and O atoms. They are N_2O, NO, N_2O_3, NO_2, N_2O_5.

❍ Trioxides and Pentoxides dissolve in water giving - **Ous acids and -Ic acids** respectively.

$$P_4O_6 + 6H_2O \rightarrow \underset{(Orthophosphorus\ acid)}{4H_3PO_3}$$

$$P_4O_{10} + 6H_2O \rightarrow \underset{(Orthophosphoric\ acid)}{4H_3PO_4}$$

(3) Reactivity towards halogens(Halides)

❍ Group 15 elements form Trihalides(MX_3) and Pentahalides (MX_5 - **Except N**).

❍ Trihalides are covalent (except **BiF_3**), **sp^3** hybridised and have trigonal pyramid structure.

❍ All the trihalides except those of nitrogen are stable except NF_3 which is stable.

❍ The extent of hydrolysis decreases from NX_3 to BiX_3.

❍ Trihalides are prepared by the reaction of VA group element or its compound with halogen. NCl_3 on hydrolysis gives NH_3 and Hypochlorous acid.

$$NCl_3 + 3H_2O \rightarrow NH_3 + 3HOCl$$

❍ Aqueous solution of NCl_3 used as a bleaching agent due to formation of HOCl.

❍ Pentahalides are more covalent than trihalides, **sp^3d** hybridised and have trigonal bipyramidal structure.

IMPORTANT POINTS

❑ Decreasing order of basic character of halides of nitrogen as follows:
$NI_3 > NBr_3 > NCl_3 > NF_3$

❑ NF_3 is least basic due to more electronegativity of "F".

❑ Solid PCl_5 is an ionic compound consisting of $[PCl_4]^+[PCl_6]^-$.$[PCl_4]^+$ has a tetrahedral structure, while $[PCl_6]^-$ has an octahedral structure.

❑ Bi cannot form stable BiX_5 due to inert pair effect.

❍ Nitrogen does not form pentahalides due to non-availibility of vacant d-orbitals.
The pentachloride of phosphorus is not very stable because axial bonds are longer (and hence weaker) than equitorial bonds.

Hence, PCl_5 decomposes to give PCl_3 and Cl_2.

Anomalous properties of nitrogen

- Nitrogen differs from the rest of the members of this group due to its
  (i) Small size
  (ii) High E.N.
  (iii) High I.E.
  (iv) Non-availiability of vacant d - orbitals.
- Nitrogen exhibits unique ability to form $p\pi - p\pi$ multiple bonds with itself and other elements having small size and high EN like C, O.
- Due to absence of vacant d-orbitals nitrogen covalency is restricted to four and cannot form $d\pi - p\pi$ similar to the heavier elements

  $Eg: R_3P=O\,(or)\,R_3P=CH_2$
- Hydride of nitrogen (NH_3) is stable while the hydrides of other elements are not stable. Hydrogen bonding is present in ammonia but not present in other hydrides.
- Nitrogen can form trinegative ion N^{3-}. This tendency is less in P but absent on other elements.

Dinitrogen (N_2)

(1) Preparations

(I) Laboratory method :

$$NH_4Cl_{(aq)} + NaNO_{2(aq)} \rightarrow N_{2(g)} + 2H_2O_{(l)} + NaCl_{(aq)}$$

$$NH_4NO_2 \xrightarrow{\Delta} N_2 + 2H_2O$$

(II) Commercial methods: Liquefaction and Fractional Distillation of air. Liquid N_2 (b.p. 77.2K) distils out first leaving behind liquid oxygen (b.p.90K).

(III) Preparation of Pure N_2

$$(NH_4)_2Cr_2O_7 \xrightarrow{Heat} N_2 + 4H_2O + Cr_2O_3$$

Ultra Pure N_2 : $Ba(N_3)_2 \xrightarrow{\Delta} Ba + 3N_2$

$$2NaN_3 \xrightarrow{\Delta} 2Na + 3N_2$$

(2) Properties

- Dinitrogen is colourless, odorless, and non - toxic diatomic gas.
- Nitrogen has very low solubility in water and low melting and freezing points.
- Nitrogen has two stable isotopes: ^{14}N and ^{15}N.
- N_2 is inert at room temperature. Reactivity increases rapidly with rise in temperature.
- Form ionic nitrides with metals and covalent nitrides with non-metals at high temperatures.

$$6Li + N_2 \xrightarrow{Heat} 2Li_3N$$

$$3Mg + N_2 \xrightarrow{Heat} Mg_3N_2$$

- Boron nitride (BN), Cyanogen, $(CN)_2$ are covalent nitrides.

$$B_2O_3 + 3CaB_6 + 10N_2 \xrightarrow{>1500^0C} 20BN + 3CaO$$

- Haber Process:
  Nitrogen combines with hydrogen at 773K, 200 atm in presence of Fe catalyst and Mo promoter to give ammonia. This reaction is an example of exothermic reaction.

$$N_{2(g)} + 3H_{2(g)} \underset{Fe\ catalyst}{\overset{773K,200atm}{\rightleftharpoons}} 2NH_{3(g)}; \Delta_f H° = -46.1 kJmol^{-1}$$

- Nitrogen combines with oxygen at only about 2000°C.

$$N_{2(g)} + O_{2(g)} \underset{Pt}{\overset{2000^0C}{\rightleftharpoons}} 2NO_{(g)}$$

- When nitrogen is passed over heated mixture of alumina and carbon, aluminum nitride is formed

  $Al_2O_3 + 3C + N_2 \rightarrow 2AlN + 3CO$
- This reaction is used for the purification of alumina ore (Serpeck's process).

(3) Uses

- In the manufacture of NH_3 & industrial chemical having N_2
  Eg: Calcium Cyanamide
- Provide an inert atmoshpere in reactions
  Eg: Inert diluent for reactive chemical in iron and steel industry.
- Liquid dinitrogen is used as a refrigerant to preserve biological materials, food items and in Cryosurgery.

Compounds of Nitrogen

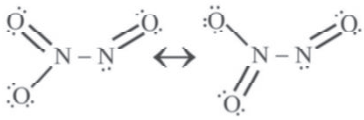
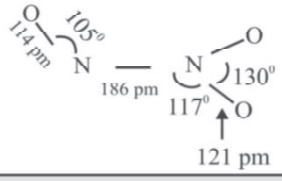
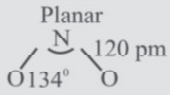
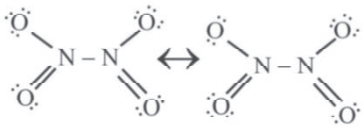
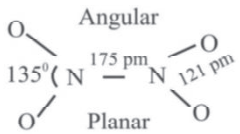
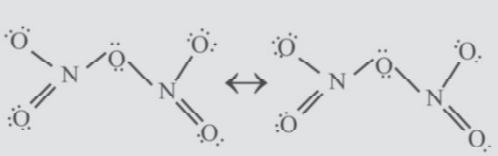
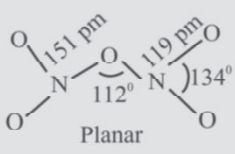
(1)Oxides of Nitrogen

Nitrogen forms a number of oxides in different oxidation states. The detail is given below:

Table: Oxides of Nitrogen

Name	Formula	Oxidation state of nitrogen	Common methods of preparation	Physical appearance and chemical nature
Dinitrogen oxide [Nitrogen(I) oxide]	N_2O	+ 1	$NH_4NO_3 \xrightarrow{Heat} N_2O + 2H_2O$	Colourless gas, Neutral
Nitrogen monoxide [Nitrogen(II) oxide]	NO	+ 2	$2NaNO_2 + 2FeSO_4 + 3H_2SO_4 \longrightarrow Fe_2(SO_4)_3 + 2NaHSO_4 + 2H_2O + 2NO$	Colourless gas, Neutral
Dinitrogen trioxide [Nitrogen(III) oxide]	N_2O_3	+ 3	$2NO + N_2O_4 \xrightarrow{250K} 2N_2O_3$	Blue solid, Acidic
Nitrogen dioxide [Nitrogen(IV) oxide]	NO_2	+ 4	$2\,Pb(NO_3)_2 \xrightarrow{673K} 4NO_2 + 2PbO + O_2$	Blue gas, Acidic
Dinitrogen tetroxide [Nitrogen(IV) oxide]	N_2O_4	+ 4	$2NO_2 \underset{Heat}{\overset{Cool}{\rightleftharpoons}} N_2O_4$	Colourless solid/ liquid, Acidic
Dinitrogen pentoxide [Nitrogen(V) oxide]	N_2O_5	+ 5	$4HNO_3 + P_4O_{10} \longrightarrow 4HPO_3 + 2N_2O_5$	Colourless solid, Acidic

Table: Lewis dot main resonance structure and bond parameters of oxides of nitrogen

Formula	Resonance Structures	Bond Parameters
N_2O	$\ddot{N} = N = \ddot{O} \leftrightarrow :N \equiv N - \ddot{O}:$	N – N – O 113 pm 119 pm
NO	$:N = \ddot{O}: \leftrightarrow :\dot{N} = \ddot{O}$	Linear N – O 115 pm
N_2O_3		
NO_2		
N_2O_4		
N_2O_5		

(2) Oxoacids of Nitrogen

Nitogen forms oxoacids such as: $H_2N_2O_2$ (Hyponitrous acid), HNO_2 (Nitrous acid) and HNO_3 (Nitric acid). HNO_3 is the most important.

Oxyacids of nitrogen

Name of oxoacid	M.F.	Structure	Oxidation State of N	Basicity	pK_a	Nature
Hyponitrous acid	$H_2N_2O_2$	$HO-\overset{\cdot\cdot}{N}=\overset{\cdot\cdot}{N}-OH$	+1	2(dibasic)	Very weak	Highly explosive
Nitrous acid	HNO_2	$H-N(\rightarrow O)=O$	+3	1 (monobasic)	3.3	Unstable, Weak acid
Nitric acid	HNO_3	$H-O-N(\rightarrow O)=O$	+5	1 (monobasic)	-3.0	Stable, Strong acid
Pernitric acid	HNO_4	$O=N-O-O-H$ $\downarrow$ O	+5	1 (monobasic)		Unstable and explosive

Nitric acid

(1) Preparation

(I) In laboratory HNO_3 is prepared by heating KNO_3 or $NaNO_3$ and conc. H_2SO_4 in glass retort.

$$NaNO_3 + H_2SO_4 \longrightarrow NaHSO_4 + HNO_3$$

(II) Large Scale (by Ostwald's process)

- It is based on catalytic oxidation of NH_3 by atmospheric oxygen.

$$4NH_3(g) + \underset{\text{(from air)}}{5O_2} \xrightarrow[500K,\ 9\ bar]{\text{Pt/Rh gauge catalyst}} 4NO(g) + 6H_2O(g)$$

$$(\Delta H = -905.2 kJ/mol)$$

- Nitic oxide combines with O_2 giving NO_2.

$$2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)$$

- Nitrogen dioxide so formed dissolves in water to give HNO_3.

$$3NO_2(g) + H_2O(l) \longrightarrow 2HNO_3(aq.) + NO(g)$$

- Aqueous HNO_3 can be concentrated by distillation upto ~ 68% by mass. Further concentration upto 98% achieved by dehydration with conc. H_2SO_4.

(2) Properties

- It is colourless liquid and freezing point is 231.4 K and boiling point 355.6 K
- Lab. HNO_3 contains ~ 68% of HNO_3 by mass and has specific gravity 1.504.
- In aqueous solution, HNO_3 behaves as strong acid giving hydronium and nitrate ions.

$$HNO_3(aq) + H_2O(l) \longrightarrow H_3O^+(aq) + NO_3^-(aq)$$

- Concentrated nitric acid is strong oxidising agent and attacks most except noble metals such as gold and platinum.
  The products of oxidation depends upon the concentration of the acid, temperature and the nature of material undergoing oxidation.

$$3Cu + 8HNO_3(dilute) \longrightarrow 3Cu(NO_3)_2 + 2NO + 4H_2O$$

$$Cu + 4HNO_3(conc.) \longrightarrow Cu(NO_3)_2 + 2NO_2 + 2H_2O$$

$$4Zn + 10HNO_3(dilute) \longrightarrow 4Zn(NO_3)_2 + 5H_2O + N_2O$$

$$Zn + 4HNO_3(dilute) \longrightarrow Zn(NO_3)_2 + 2H_2O + 2N_2O$$

  Due to formation of passive film of oxide on the surface of some metals like Cr, Al do not dissolve in concentrated nitric acid.

- Conc. HNO_3 also oxidises non-metals and their compounds

$$I_2 + 10HNO_3 \longrightarrow 2HIO_3 + 10NO_2 + 4H_2O$$

$$C + 4HNO_3 \longrightarrow CO_2 + 2H_2O + 4NO_2$$

$$S_8 + 48\underset{(conc.)}{HNO_3} \longrightarrow 8H_2SO_4 + 48NO_2 + 16H_2O$$

$$P_4 + 20\underset{(conc.)}{HNO_3} \longrightarrow 4H_3PO_4 + 20NO_2 + 4H_2O$$

❍ Brown Ring Test for Nitrates

This depends on the ability of Fe^{2+} to reduce nitrates to nitric oxide, which reacts with Fe^{2+} to form brown coloured complex.

This test is done by adding dil. $FeSO_4$ to an aqueous solution containing NO_3^-, and then adding conc. H_2SO_4 along the sides of that tube. Brown ring at interface between solution and H_2SO_4 layer indicates the presence of NO_3^- in solution.

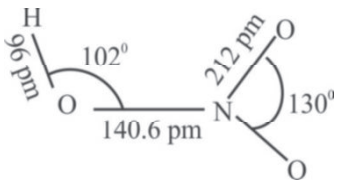
$$NO_3^- + 3Fe^{2+} + 4H^+ \longrightarrow NO + 3Fe^{3+} + 2H_2O$$

$$[Fe(H_2O)_6]^{2+} + NO \longrightarrow \underset{\text{brown ring}}{[Fe(H_2O)_5(NO)]^{2+}} + H_2O$$

IMPORTANT POINTS

Xanthoproteic reaction is a method that can be used to determine the amount of protein soluble in solution using concentrated nitric acid. It gives positive test with proteins having amino acids with aromatic ring.

(3) Structure: In the gaseous state HNO_3 has planar structure.



(4) Uses of HNO_3

❍ In the manufacture of ammonium nitrate for fertilisers and other nitrates for use in explosives and pyrotechnics.

❍ Also used for the preparation of nitroglycerin, trinitrotoluene (TNT) and other organic nitro compounds.

❍ Other uses are in picking of stainless steel, ethching of metals and as an oxidiser in rocket fuels.

Knowledge POOL

Element	Nature of HNO_3	Changes to	Reactions
(A) Metals placed above H in electrochemical series (ECS) 1. Mg, Mn	cold and dilute	$M(NO_3)_2$	$M + 2HNO_3 \rightarrow M(NO_3)_2 + H_2$
2. Zn, Fe	(a) very dilute (b) dilute (c) concentrated	NH_4NO_3 N_2O NO_2	$4Zn+10HNO_3 \rightarrow 4Zn(NO_3)_2+NH_4NO_3+3H_2O$ $4Zn+10HNO_3 \rightarrow 4Zn(NO_3)_2+N_2O+5H_2O$ $Zn+4HNO_3 \rightarrow Zn(NO_3)_2+2NO_2+2H_2O$
3. Sn	(a) dilute (b) concentrated	NH_4NO_3 NO_2	$4Zn+10HNO_3 \rightarrow 4Zn(NO_3)_2+NH_4NO_3+3H_2O$ $Sn+4HNO_3 \rightarrow \underset{\text{meta stannic acid}}{H_2SnO_3}+4NO_2+H_2O$
4. Pb	(a) dilute (b) concentrated	NO NO_2	$3Pb+8HNO_3 \rightarrow 3Pb(NO_3)_2+2NO+4H_2O$ $Zn+4HNO_3 \rightarrow Zn(NO_3)_2+2NO_2+2H_2O$
(B) Metals below H in ECS 5. Cu, Ag Hg	(a) dilute (b) concentrated	NO NO_2	$3Pb+8HNO_3 \rightarrow 3Pb(NO_3)_2+2NO+4H_2O$ Hg forms $Hg_2(NO_3)_2$ $Zn+4HNO_3 \rightarrow Zn(NO_3)_2+2NO_2+2H_2O$
(C) Metalloids Sb, As	concentrated	NO_2	$Sb+5HNO_3 \rightarrow \underset{\text{antimonic acid}}{H_3SbO_4}+5NO_2+H_2O$

BIT SAT EVA-AITS - 1

"A Colossal juncture to get introduced to the national standard mock tests of BITSAT"

1. The value of enthalpy change (ΔH) for the reaction

$C_2H_5OH(l)+3O_2(g)\rightarrow 2CO_2(g)+3H_2O(l)$

at 27^0C is $-1366.5\ kJ\ mol^{-1}$. The value of internal energy change for the above reaction at this temperature will be

(a) $-1366.5\ kJ$ (b) $-1369.0\ kJ$

(c) $-1364.0\ kJ$ (d) $-1361.5\ kJ$

2. The first ionisation potential is maximum for

(a) B (b) N (c) O (d) Be

3. In an ionic compound moles ratio of cation to anion is 1:2. If atomic masses of metal and non-metal respectively are 138 and 19, then correct statement is

(a) molecular mass of compound is 176

(b) formula mass of compound is 176

(c) formula mass of compound is 157

(d) molecular mass of compound is 157

4. What molar concentration of ammonia will provide a hydroxyl ion concentration of 1.5×10^{-3} ?

$\left(K_b=1.8\times10^{-5}\right)$

(a) 0.125 M (b) 0.12 M

(c) 0.13 M (d) 0.14 M

5. In context with the industrial preparation of hydrogen from water gas $(CO+H_2)$, which of the following is the correct statement?

(a) CO is oxidised to CO_2 with steam in the presence of a catalyst followed by absorption of CO_2 in alkali.

(b) CO and H_2 are fractionally separated using difference in their densities.

(c) CO is removed by absorption in aqueous Cu_2Cl_2.

(d) H_2 is not a metal.

6. The ratio of rates of discussion of CO_2 and SO_2 at the same pressure and temperature is:

(a) $4:\sqrt{11}$ (b) 11 : 4

(c) 1 : 4 (d) 1 : 6

7. Which one of the following has intramolecular H-bonding?

(a) H_2O (b) o-Nitrophenol

(c) HF (d) CH_3OH

8. When beryllium is bombarded with α – particles, extremely penetrating radiations which cannot be deflected by electrical or magnetic field are given out. These are

(a) A beam of protons (b) α – rays

(c) A beam of neutrons (d) X – rays

9. When alumina is heated with carbon in the atmosphere of nitrogen then products formed are

(a) $Al+CO$ (b) $ALN+CO$

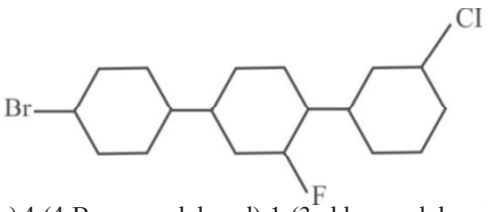
(c) $Al+CO_2$ (d) $Al+CO+N_2$

10. The heat of neutralisation of a strong acid and a strong alkali is $57.0\ kJ\ mol^{-1}$. The heat released when 0.5 mole of HNO_3 solution is mixed with 0.2 mole of KOH is

(a) 57.0 kJ (b) 11.4 kJ

(c) 28.5 kJ (d) 34.9 kJ

11. According to IUPAC convention, the systematic name of the compound given below is



(a) 4-(4-Bromocyclohexyl)-1-(3-chlorocyclohexyl) - 2- fluorocyclohexane
(b) 5-(4-Bromocyclohexyl)-2-(3-chlorocyclohexyl)- 1- fluorocyclohexane
(c) 1-(3-Chlorocyclohexyl)-4-(4-bromocyclohexyl) -2- fluorocyclohexane
(d) 1-(4-Bromocyclohexyl)-4-(3-chlorocyclohexyl) -3- fluorocyclohexane

12. In which of the following compounds transition metal is in oxidation state zero?

(a) $[Co(NH_3)_6]CI_2$ (b) $[Fe(H_2O)_6SO_4]$

(c) $[Ni(CO)_4]$ (d) $[Fe(H_2O)_3](OH)_2$

13. The metallic luster exhibited by sodium is explained by
(a) Diffusion of sodium ions
(b) Oscillations of lose electrons
(c) Excitation of free protons
(d) Existence of body centered cubic lattice

14. Which of the following causes lung cancer?
(a) Paper (b) Asbestos
(c) Silica (d) Textiles

15. Among the following compounds, the strongest acid is:

(a) $HC \equiv CH$ (b) C_6H_6

(c) C_2H_6 (d) CH_3OH

16. The rate of forward reaction is two times that of reverse reaction at a given temperature and identical concentration. $K_{equilibrium}$ is
(a) 2.5 (b) 2.0
(c) 0.5 (d) 1.5

17. The reagent used for catalytic hydrogenation of an alkene as well as bring about homogeneous catalysis is
(a) Raney nickle
(b) $(Ph_3P)_3RhCI$ "Wilkinson's reagent"
(c) Pd/C (d) PtO_2

18. How many structural isomers are possible for compounds containing C, H and O atoms only with their molar masses 100 as well as the isomers are simultaneously ketones?
(a) 3 (b) 4 (c) 5 (d) 6

19. A 400 mg iron capsule contains 100 mg of ferrous furmate, $(CHCOO)_2Fe$. The percentage of iron present in it is approximately
(a) 33% (b) 25% (c) 14% (d) 8%

20. The first ionisation energies of alkaline earth metal are higher than those of the alkali metals. This is because:
(a) There is an increase in the nuclear charge of the alkaline earth metal
(b) There is a decrease in the nuclear charge of the alkaline earth metal
(c) There is no change in the nuclear charge
(d) None of these

21. Which of the following does not react with AgCl?

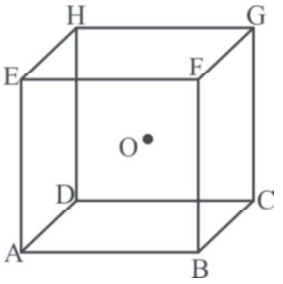
(a) NH_4OH (b) Na_2CO_3

(c) $Na_2S_2O_3$ (d) $NaNO_3$

22. The reaction is spontaneous if the cell potential is
(a) Negative (b) Positive
(c) Zero (d) Infinite

23. The internal energy of one mole of a gas is
(a) 3/2 RT (b) 1/2 kT (c) 1/2 RT (d) 3/2 kT

24. A body centred cubic arrangement is shown: O is the body centre; A,B,C,D, ..., H are the corners. What is the magnitude of the angle AOB?



(a) 120^0 (b) $109^028'$ (c) $104^031'$ (d) $70^032'$

25. Which one of the following is not a colloidal solution?
(a) Smoke (b) Ink
(c) Peptisation (d) Blood

26. Hydrogen is not obtained when zinc reacts with
(a) Cold water (b) Hot NaOH solution
(c) Conc. sulphuric acid (d) Dilute HCl

27. Which of the following is known as inorganic benzene?
(a) Borazine (b) Boron nitride
(c) p-dichlorobenzene (d) Phosphonitrilic acid

28. How many grams of a dibasic acid (mol. wt. = 200) should be present in 100 ml of its aqueous solution to give decinormal strength?

(a) 20g (b) 2g (c) 10g (d) 1g

29. If The rate constant for the disintegration of a radioactive nucleus is λ. Therefore, the probability P of survival of a radioactive nucleus for one mean life is

(a) e (b) e^2 (c) e^{-1} (d) e^{-2}

30. Which one of the following oxides is neutral?

(a) SiO_2 (b) SnO_2 (c) ZnO (d) CO

31. The K_{sp} of $Mg(OH)_2$ is 1×10^{-12}. $0.01M$ $Mg(OH)_2$ will precipitate at the limiting pH is

(a) 3 (b) 9 (c) 5 (d) 8

32. According to Graham's law, at a given temperature the ratio of the rates of diffusion $\frac{r_1}{r_2}$ of gases A and B is given by

(a) $\frac{P_1}{P_2}\times\sqrt{\frac{M_2}{M_1}}$ (b) $\frac{M_1}{M_2}\times\sqrt{\frac{P_1}{P_2}}$

(c) $\frac{P_1}{P_2}\times\sqrt{\frac{M_1}{M_2}}$ (d) $\frac{M_2}{M_1}\times\sqrt{\frac{P_1}{P_2}}$

33. Lithum shows similarities to magnesium in its chemical behaviour because

(a) Similar size, greater electronegativity, and similar polarising power.
(b) Similar size, same electronegativity, and lower polarising power
(c) Similar size, same electronegativity, and similar high polarising power
(d) None of these

34. The latest technique for the purification of organic compounds is

(a) Fractional distillation
(b) Chromatography
(c) Vaccum distillation
(d) Crystallisation

35. The complex shown below can exhibit

(a) Optical isomerism only
(b) Both optical and geometrical isomerism
(c) Geometrical isomerism only
(d) None of the above

36. Diethyl ether and methyl *n*-propyl ether are

(a) Position isomers (b) Functional isomers
(c) Metamers (d) Chain isomers

37. Mercury is transported in metal containers made of

(a) Silver (b) Iron
(c) Lead (d) Aluminium

38. Identify the incorrect statement from the following

(a) Oxides of nitrogen in the atmosphere can cause the depletion of ozone layer
(b) Ozone absorbs infrared radiation
(c) Depletion of ozone layer is because of its chemical reactions with chlorofluroalkanes.
(d) Ozone absorbs the intense ultraviolet radiation of the sun.

39. Styrene at room temperature is

(a) Solid (b) Liquid
(c) Gas (d) Colloidal solution

40. Ethyl bromide can be converted into ethyl alcohol by

(a) The action of moist silver oxide
(b) Boiling with an alcoholic solution of KOH
(c) Heating with dilute hydrochloric acid and zinc
(d) Refluxing methanol

41. Which of the following does not show geometrical isomerism?

(a) 1, 2 dichloro-1-pentene
(b) 1,3-dichloro-2-pentene
(c) 1,1-dichloro-1-pentene
(d) 1,4-dichloro-2-pentene

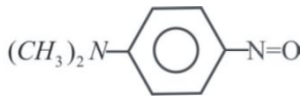
42. $(CH_3)_2C=CHCOCH_3$ can be oxidised to $(CH_3)_2C=CHCOOH$ by

(a) Chromic acid (b) $NaOH$
(c) Cu at 300^0c (d) $KMnO_4$

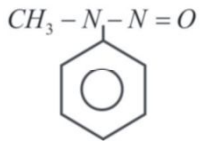
43. Which among the following compounds will not give effervescence with sodium bicarbonate?

(a) $C_6H_5CO_2H$ (b) $C_6H_5SO_3H$
(c) C_6H_5OH (d) Picric acid

44. N,N – Dimethyl aniline reacts with nitrous acid to yield

(a) 

(b) $(CH_3)_2N-N=O$

(c) 

(d) Does not react

45. The total number of possible isomers of the complex compound $\left[Cu^{11}(NH_3)_4\right]\left[Pt^{11}CI_4\right]$ is

(a) 3 (b) 6 (c) 5 (d) 4

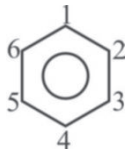
CHEMIS TRICKS

By: A.N.S. SANKARA RAO (Hyderabad)

Directive Influence

Questions on directive influence are coming in most of the competitive exams

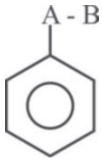
Electrophilic aromatic substitution reactions could be remembered easily once we know the directional nature of mono substituent in benzene ring. Already substituent present in benzene ring is called **"host"** and newly coming substituent is called **"guest"**. So always we must think of directional nature of host to substitute the guest at ortho & para or meta positions

In benzene ring  let us suppose C_1, is reference point, C_2 & C_6 ortho, C_3 & C_5 are meta and C_4 is para positions

Host may **activate** (highly reactive than C_6H_6 & increase the rate of reaction) i.e., donate e^- (**eDG** = e^- donating substituent) or may **deactivate** (less reactive than C_6H_6 & decrease the rate of reaction) i.e., withdraw e^- ($eWG = e^-$ withdrawing substituent).

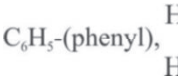
CHEMISTRICK : AVOPa gives **Dem**o on organic chemistry.
Where **AV** = Activating substituent, **O** = ortho, **Pa** = Para, **De** = Deactivating substituent, **m** = meta. Hence activating substituent is ortho & para directing and deactivating substituent is meta directing. Among ortho & para compounds, **para** is formed as **major** (as eWG is less hindered) and **ortho** is formed as **minor** (as eDG is more hindered).

Ortho & para directing groups:

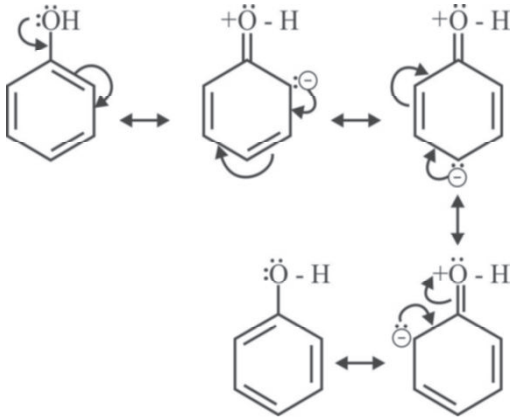
This type of substituents involve +E (electromeric), +R(resonance), $\pm I$ (Inductive and hyper-conjugation effects if A in  is more electronegative (than B), then AB becomes **eDG** with respect to H, **activating groups** are classified as

I. Very strongly activating groups:
$\ddot{O}$,-OH, -NH_2, - NHR, -NR_2

II. Strongly activating : -OR, -COOR, -NHCOR

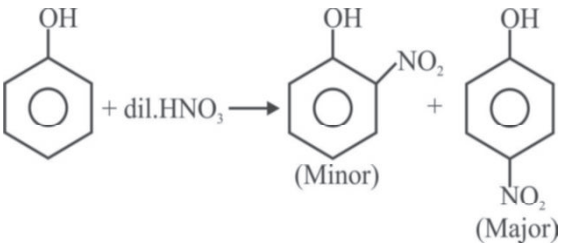
III. Weakly activating: -R(alkyl), -Ar(Aryl), C_6H_5-(phenyl),  (vinyl)

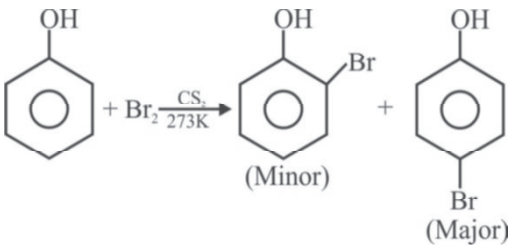
When we look at resonating structures of phenols, substitution takes place at O- & P- positions where e^- density is more, hence electrophile can attack.

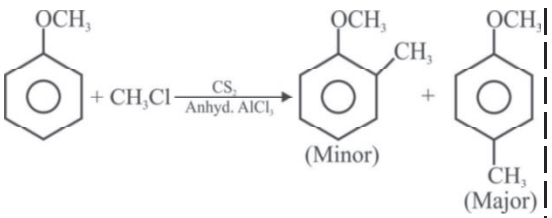


-Cl: Chlorine withdraws e^- through -I and releases e^- through resonance. As the resonance effect oppose the inductive effect to attack at ortho & para positions. Hence -Cl is O & P director.

Eg:







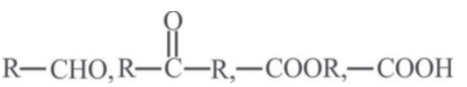
Meta Directing groups

This type of substituents involve -I, -R, -E effects to cause meta orientation. If B in  is more electronegative (than A) AB becomes **eWD** with respect to H, **deactivating groups** are classified as

I. Very strongly deactivating:

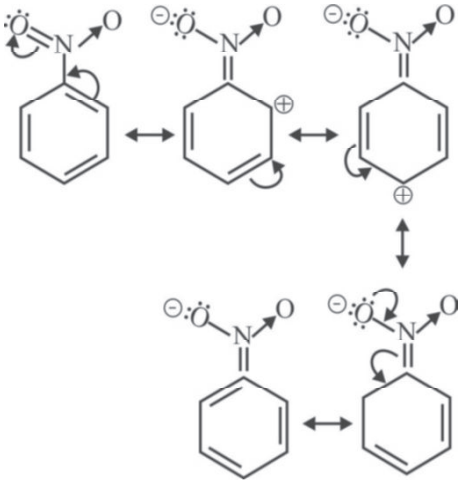
$-NO_2, -CF_3, -CN, -SO_3H$

II. Strongly deactivating:

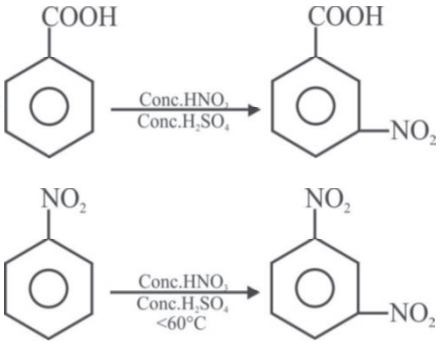


III. Weakly deactivating: $-\overset{+}{N}H_3$, $-\overset{+}{N}R_3$, halogens

We conclude from resonating structures of nitrobenzene, substitution takes place at meta position where e^- density is more, hence electrophile can attack.



Eg:



In nitration of aniline, in addition to para (51%) & ortho (2%) good amount of meta (47%) nitro aniline are formed. In strongly acidic medium aniline is protonated to form $C_6H_5\overset{+}{N}H_3$ ion, which is meta director.

BIT SAT EVA-AITS - 2

"A Colossal juncture to get introduced to the national standard mock tests of BITSAT"

1. The reduction potential of hydrogen electrode when placed in a buffer solution is found to be -0.413 V. The pH of the buffer is
(a) 10 (b) 4 (c) 7 (d) 12

2. Roasting is carried out in case of:
(a) Galena (b) Iron pyrites
(c) Copper glance (d) All of these

3. $AgNO_3$ does not give precipitate with $CHCl_3$ because
(a) $CHCl_3$ does not ionise in water
(b) $AgNO_3$ does not react with $CHCl_3$
(c) $CHCl_3$ is chemically inert
(d) None of these

4. Units of rate constant of first and zero order reactions in terms of molarity, M are respectively:
(a) s^{-1}, s^{-1} (b) s^{-1}, M
(c) Ms^{-1}, s^{-1} (d) M, s^{-1}

5. The molarity of a urea solution in which 0.0100 g of urea, $[(NH_2)_2CO]$ is added to $0.3000\,dm^3$ of water at STP is
(a) 0.555 M
(b) $5.55\times10^{-4}\,M$
(c) $33.3M$
(d) $3.33\times10^{-2}\,M$

6. Which of the following have maximum number of unpaired electrons?
(a) Co^{3+} (b) Fe^{2+} (c) Co^{2+} (d) Fe^{3+}

7. The composition of a sample of wustite is $Fe_{0.93}O_{1.00}$. What percentage of the iron is present in the form of Fe(III)?
(a) 15.05 (b) 84.95 (c) 60.25 (d) 40.45

8. Identify the correct order of boiling points of the following compounds:
(1) $CH_3CH_2CH_2OH$
(2) CH_3CH_2CHO
(3) $CH_3CH_2CH_2COOH$
(a) 1 > 2 > 3 (b) 3 > 1 > 2
(c) 1 > 3 > 2 (d) 3 > 2 > 1

9. Pick out from the following complex compounds, a poor electrolytic conductor in solution?
(a) $K_2[PtCl_6]$
(b) $[Co(NH_3)_3(NO_2)_3]$
(c) $K_4[Fe(CN)_6]$
(d) $[Co(NH_3)_4]SO_4$

10. Azo dye is prepared by the coupling of phenol and
(a) Diazonium chloride
(b) o-nitro aniline
(c) Benzoic acid
(d) Chlorobenzene

11. As_2S_3 sol has a negative charge. Capacity to precipitate it is highest in
(a) $AlCl_3$ (b) Na_3PO_4
(c) $CaCl_2$ (d) K_2SO_4

12. 1-Propanol and 2-propanol can be best distinguished by

(a) Oxidation with alkaline $KMnO_4$ followed by reaction with Fehling solution
(b) Oxidation with acidic dichromate followed by reaction with Fehling solution
(c) Oxidation by heating with copper followed by reaction with Fehling solution
(d) Oxidation with concentrated H_2SO_4 followed by reaction with Fehling solution.

13. 10^{-2} mol of Fe_3O_4 is treated with excess of KI solution in the presence of dilute H_2SO_4, the products are Fe^{2+} and $I_2(g)$. What volume of 0.1(M) $Na_2S_2O_3$ will be needed to reduce the liberated $I_2(g)$?
(a) 200 ml (b) 100 ml
(c) 50 ml (d) 400 ml

14. The density of gold is 19 g/cm^3. If 1.9×10^{-4} g of gold is dispersed in one litre of water to give a sol having spherical gold particles of radius 10 nm, then the number of gold particles per mm^3 of the sol will be
(a) 1.9×10^{12} (b) 6.3×10^{14}
(c) 6.3×10^{10} (d) 2.4×10^{6}

15. A sample of copper sulphate pentahydrate, $CuSO_4.5H_2O$ contains 3.782 g of Cu. How many grams of oxygen are in this sample?
(a) 8.570 g (b) 3.809 g
(c) 0.952 g (d) 4.761 g

16. Two liquids X and Y form an ideal solution. At 300 K, vapour pressure of the solution containing 1 mol of X and 3 mol of Y is 550 mm Hg. At the same temperature, if 1 mol of Y is further added to this solution, vapour pressure of the solution increases by 10 mm Hg. Vapour pressure (in mm Hg) of X and Y in their pure states will be, respectively.
(a) 200 and 300
(b) 300 and 400
(c) 400 and 600
(d) 500 and 600

17. Dissociation of H_3PO_4 occurs in how many equilibrium steps?
(a) 3 (b) 4 (c) 1 (d) 2

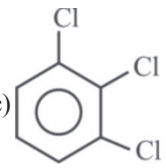
18. Acidified solution of chromic acid on treatment with hydrogen peroxide yields
(a) $CrO_3 + H_2O + O_2$
(b) $CrO_5 + H_2O$
(c) $Cr_2O_3 + H_2O + O_2$
(d) $H_2Cr_2O_3 + H_2O + O_2$

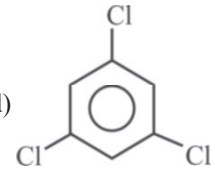
19. The cost of electricity required to deposit 1 g of Mg is Rs. 5.00. How much would it cost to deposit 10.0 g of Al?
(a) Rs. 44.44 (b) Rs. 27.0
(c) Rs. 10.0 (d) Rs. 66.67

20. When the all-cis isomer of $C_6H_6Cl_6$ (1, 2, 3, 4, 5, 6-Hexachlorocyclohexane) is heated with alc. KOH, the most probable product is:

(a) 

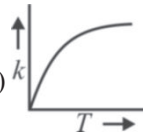
(b) 

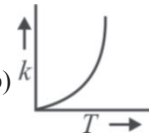
(c) 

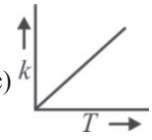
(d) 

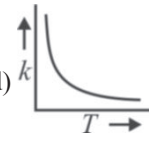
21. 100 mL of a buffer solution contains 0.1 M each of weak acid HA and salt NaA. How many gram of NaOH should be added to the buffer so that its pH will be 6? (K_a of $HA = 10^{-5}$)
(a) 0.328 (b) 4.19
(c) 0.458 (d) None

22. The rate constant of most of the reactions increases with increase in temperature. According to the Arrhenius equation, $k = Ae^{-E_a/RT}$. The curve of rate constant 'k' against temperature 'T' will be.

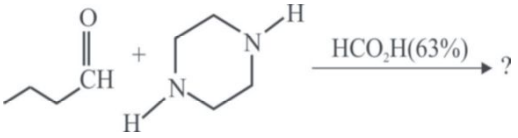
(a) 

(b) 

(c) 

(d) 

23. The product expected in the following reaction is



(a) N, N'-di-n-butyl piperidine
(b) N, N'-dibutoxy piperidine
(c) 2 moles of pentanamide
(d) pentanamine

24. The rusting of iron takes place as follows:

$2H^+ + 2e^- + \frac{1}{2}O_2 \longrightarrow H_2O(l);$

$E^o = +1.23V$

$Fe^{2+} + 2e^- \longrightarrow Fe(s); E^o = -0.44\,V$

Calculate ΔG^o for the net process

(a) -152 kJ mol^{-1} (b) -161 kJ mol^{-1}

(c) -322 kJ mol^{-1} (d) -76 kJ mol^{-1}

25. The process of calcination and roasting is carried out to
(a) Remove the siliceous materials
(b) Add flux to the mineral
(c) Convert the ore to oxide
(d) Remove the poisonous impurities

26. Calculate the molarity of pure water ($d = 1$ g/L)
(a) 555 M (b) 5.55 M
(c) 55.5 M (d) 0.555 M

27. The Balmer series occurs between the wavelength of $[R = 1.0968 \times 10^7\, m^{-1}]$:

(a) 4623 Å and 6563 Å

(b) 1243 Å and 6563 Å

(c) 3647 Å and 6563 Å

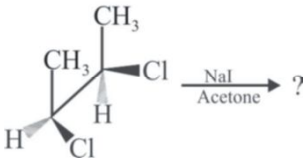
(d) 3647 Å and 7210 Å

28. For the reaction, $aA \longrightarrow bB$;

$$\log\left[\frac{-dA}{dt}\right] = \log\left[\frac{dB}{dt}\right] + 0.6020, \text{ then } a : b \text{ is}$$

(a) 2 (b) 4 (c) 1.5 (d) 0

29. What is the major product of the reaction given below?



(a) cis-2-butene (b) 1, 3-butadiene
(c) trans-2-butene (d) 1-butene

30. The process of evaporation of a liquid is accompanied by
(a) an increase in entropy
(b) a decrease in entropy
(c) no change in entropy
(d) no change in free energy

31. Which of the following statements about polar stratosphere clouds (PSCs) is not correct?
(a) PSCs do not react with chlorine nitrate and HCl.
(b) Type I clouds are formed at about - 77^oC and contain solid $HNO_3 \cdot 3H_2O$.
(c) Type II clouds are formed at about - 85^oC and contain some ice.
(d) A tight whirlpool of wind called polar vortex is formed which surrounds Antarctica.

32. In ethane and cyclohexane which one of the following pairs of conformations are more stable?
(a) Eclipsed and chair conformations
(b) Staggered and chair conformations
(c) Staggered and boat conformations
(d) Eclipsed and boat conformations

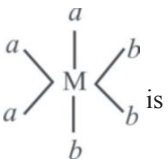
33. Which of the following is not a characteristic of alcohols?
(a) They are lighter than water
(b) Their boiling points rise fairly uniformly with increasing molecular weight
(c) Lower members have pleasent smell and burning taste, while higher members are odourless and tasteless
(d) Lower members are insoluble in water and organic solvents but solubility regularly increases with molecular weight

34. Which of the following ion is expected to have highest value of molar conductivity at infinite dilution in the aqueous solution?

(a) Na^+ (b) K^+

(c) $\frac{1}{2}Ca^{2+}$ (d) H^+

35. Octahedral complex



is

(a) cis (b) trans
(c) mer (d) fac

36. According to Ellingham diagram the oxidation reaction of carbon and carbon monoxide may be used to reduce which one of the following oxides at the lowest temperature?

(a) Al_2O_3 (b) Cu_2O
(c) MgO (d) ZnO

37. Pressure remaining the same, the volume of a given mass of an ideal gas increases for every degree centigrade rise in temperature by definite fraction of its volume at

(a) 0^oC
(b) Its critical temperature
(c) Absolute zero
(d) Its Boyle temperature

38. Which one is not a state function?
(a) Internal energy *(E)*
(b) Volume
(c) Heat *(q)*
(d) Enthalpy

39. pH of water is 7.0 at 25^oC. If water is heated to 70^oC, the:
(a) pH will decrease and solution becomes acidic
(b) pH will increase
(c) pH will remain constant as 7
(d) pH will decrease but solution will be neutral

40. Electronic configuration of M^{3+} is $[Ar]3d^{10}4s^2$, it belongs to
(a) *s*-block
(b) *p*-block
(c) *d*-block
(d) *f*-block

41. At higher temperature sodium metal reacts with alumina to give a sodium compound '*X*'. '*X*' is dissolved in water and then carbon dioxide gas is passed through it, a compound '*Y*' is formed. The compound '*X*' and '*Y*' are respectively:

(a) Na_2O_2 and Na_2CO_3
(b) Na_2O and Na_2CO_3
(c) Na_2O_2 and $NaAlO_2$
(d) $NaAlO_2$ and Na_2CO_3

42. Arrange the following amines in order of increasing basicity.
(1) p-chloroaniline
(2) 4-chlorohexanamine
(3) aniline
(a) 1 < 3 < 2
(b) 3 < 2 < 1
(c) 1 < 2 < 3
(d) 2 < 3 < 1

43. Which of the following statements regarding ethanoic acid and methyl methanoate are correct?
(I) They are functional isomers with molecular formula $C_2H_4O_2$.
(II) They belong to different homologous series.
(III) They have different chemical properties.
(a) I and II
(b) I, II and III
(b) II and III
(d) I and III

44. Which of the following is the correct sequence of atomic weights of given elements?
(a) Fe > Co > Ni
(b) Co > Ni > Fe
(c) Ni > Co > Fe
(d) Fe > Ni > Co

45. Empirical formula of a compound is CH_2O and its vapour density is 30. Molecular formula of the compound is

(a) $C_3H_6O_3$
(b) $C_2H_4O_2$
(c) C_2H_4O
(d) CH_2O

SOLVED PAPER

★ Chemistry ★

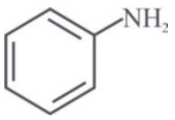
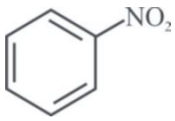
JEE MAIN 2018

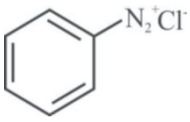
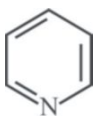
1. Which of the following salts is the basic in aqueous solution ?

(a) CH_3COOK (b) $FeCl_3$

(c) $Pb(CH_3COO)_2$ (d) $Al(CN)_3$

2. Which of the following compounds will be suitable for kjeldahl's method for nitrogen estimation ?

(a)  (b) 

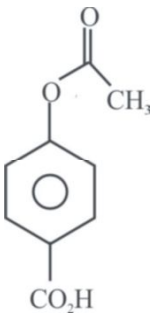
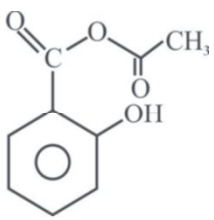
(c)  (d) 

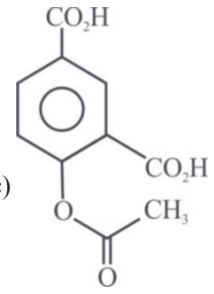
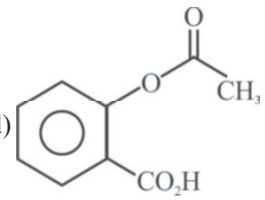
3. Which of the following are Lewis acids ?

(a) $AlCl_3$ and $SiCl_4$ (b) PH_3 and $SiCl_4$

(c) BCl_3 and $AlCl_3$ (d) PH_3 and BCl_3

4. Phenol on treatment with CO_2 in the presence of $NaOH$ followed by acidification produces compound X as the major product. X on treatment with $(CH_3CO)_2O$ in the presence of catalytic amount of H_2SO_4 produces:

(a)  (b) 

(c)  (d) 

5. An alkali is titrated against an acid with methy1 orange as indicator , which of the following is a correct combination ?

	Base	Acid	End point
(a)	Strong	Strong	Pinkish red to yellow
(b)	Weak	Strong	Yellow to pinkish red
(c)	Strong	Strong	Pink to colourless
(d)	Weak	Strong	Colourless to pink

6. An aqueous solution contains 0.10 M H_2S and 0.20 M HCl. If the equilibrium constants for the formation of HS^- ions is 1.0×10^{-7} and that of S^2 from HS^- ions is 1.2×10^{-13} then the concentration of S^{2-} ions in aqueous solution is :

(a) 3×10^{-20} (b) 6×10^{-21}

(c) 5×10^{-19} (d) 5×10^{-8}

7. The combustion of benzene (1) gives CO_2 (g) and H_2O (I). Given that heat of combustion of benzene at constant volume is $-3263.9\,kJ\,mol^{-1}$ at $25°C$; heat of combustion (in kJ mol^{-1}) of benzene at constant pressure will be - $(R = 8.134\,kJ^{-1}\,mol^{-1})$

(a) -452.46 (b) 3260
(c) -3267.6 (d) 4152.6

8. The compound that does not produce nitrogen gas by the thermal decomposition is

(a) $(NH_4)_2 Cr_2O_7$ (b) NH_4NO_2

(c) $(NH_4)_2 SO_4$ (d) $Ba(N_3)_2$

9. How long (approximate) should water be electrolysed by passing through 100 amperes current so that the oxygen released can completely burn 27.66 g of diborane ?
(Atomic weight of B=10.8 u)
(a) 0.8 hours (b) 3.2 hours
(c) 1.6 hours (d) 6.4 hours

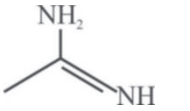
10. Total number of lone pair of electrons in I_3^- ion is
(a) 6 (b) 9 (c) 12 (d) 3

11. When metal 'M' is treated with NaOH, a white gelatinuos precipitate 'X' is obtained, which is soluble in excess of NaOH. Compound 'X' when heated strongly given an oxide which is used in chromatography as an adsorbent. The metal 'M' is
(a) Ca (b) Al (c) Fe (d) Zn

12. According to molecular orbital theory, which of the following will not be a viable molecule?
(a) He_2^+ (b) H_2^- (c) H_2^{2-} (d) He_2^{2+}

13. The increasing order of basicity of the following compounds is :

(1)  (2) 

(3)  (4) 

(a) (2) < (1) < (3) < (4)
(b) (2) < (1) < (4) < (3)
(c) (4) < (2) < (1) < (3)
(d) (1) < (2) < (3) < (4)

14. Which type of 'defect' has the present of cations in the interstitical sites ?
(a) Vacancy defect
(b) Frenkel defect
(c) metal deficiency defect
(d) Schottky defect

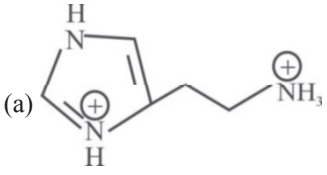
15. Which of the following compounds contain(s) no covalent bomds (s) ?
$KCl, PH_3, O_2, B_2H_6, H_2SO_4$
(a) KCl, H_2SO_4 (b) KCl
(c) KCl, B_2H_6 (d) KCl, B_2H_6, PH_3

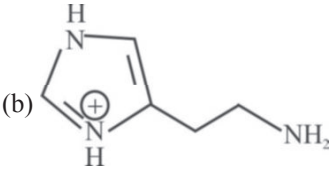
16. The oxidation state of Cr in and $K_2[Cr(CN)_2(O)_2(O_2)(NH_3)]$ respectively are:
(a) +3, +2 and +4 (b) +3, 0, and +6
(c) +3, 0, and +4 (d) +3, +4, and +6

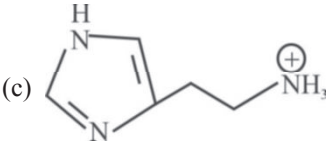
17. Hydrogen peroxide oxidises $[Fe(CN)_6]^{4-}$ to $[Fe(CN)_6]^{3-}$ in acidic medium but reduces $[Fe(CN)_6]^{3-}$ to $[Fe(CN)_6]^{4-}$ in alkaline medium. The other products formed are, respectively:
(a) $(H_2O + O_2)$ and $(H_2O + OH^-)$
(b) H_2O and $(H_2O + O_2)$
(c) H_2O and $(H_2O + OH^-)$
(d) $(H_2O + O_2)$ and H_2O

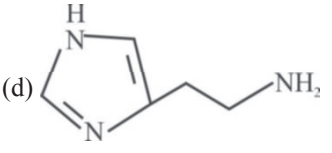
18. Glucose on prolonged heating with HI gives
(a) 1-hexene (b) Hexanoic acid
(c) 6-iodohexanal (d) n-Hexane

19. The predominant from of histamine present in human blood is $(PK_a$, Histidine=6.0)

(a) 

(b) 

(c) 

(d) 

20. The recommended concentration of fluoride ion in drinking water is up to 1 ppm as fluoride ion is required to make teeth enamel harted by converting $\left[3Ca_3(PO_4)_2.Ca(OH)_2\right]$ to :

(a) $\left[3(CaF_2).Ca(OH)_2\right]$

(b) $\left[3(Ca_3(PO_4)_2.CaF_2\right]$

(c) $\left[3(Ca(OH)_2\right].CaF_2\right]$

(d) $\left[CaF_2\right]$

21. Consider the following reaction and statement :

$$\left[Co(NH_3)_4\,Br_2\right]^+ + Br^-$$

$$\rightarrow \left[Co(NH_3)_3\,Br_3\right] + NH_3$$

(I) Two isomers are produced if the reactant complex ion is a cis-isomer.

(II) Two isomers are produced if the reactant complex ion as a trans-isomer.

(III) Only one isomer is produced if the reactant complex ion is a trans-isomer.

(IV) Only one isomer is produced if the reactant complex ion is a cis-isomer.

The correct statements are:

(a) (I) and (III) (b) (III) and (IV)

(c) (II) and (IV) (d) (I) and (II)

22. The trans-alkenes are formed by the reduction of alkynes with :

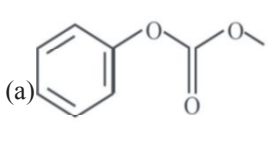
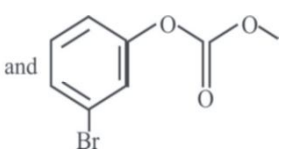
(a) $NaBH_4$ (b) $Na/liq.NH_3$

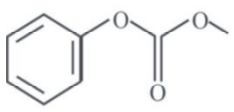
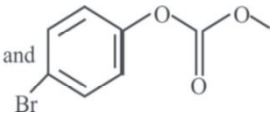
(c) $Sn-HCl$ (d) $H_2-Pd/C, BaSO_4$

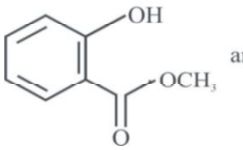
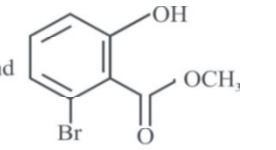
23. The ratio of mass percent of C and H of an origin compound $\left(C_xH_yO_z\right)$ is 6:1. If one molecule of the above compound $\left(C_xH_yO_z\right)$ contains half as much oxygen as required to burn one molecule of compound C_xH_y completely to CO_2 and H_2O. The empirical formula of compound $C_xH_yO_z$ is :

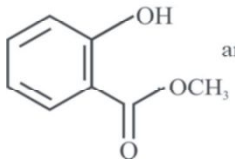
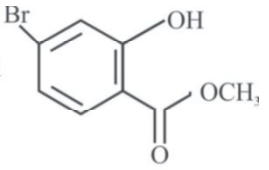
(a) C_2SO_4 (b) $C_3H_4O_2$ (c) $C_2H_4O_3$ (d) $C_3H_6O_3$

24. Phenol reacts with methyl chloroformate in the presence of NaOH to from product A. A reacts with Br_2 to form product B. A and B are respectively

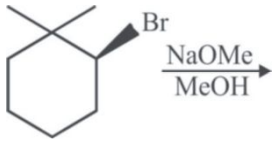
(a)  and 

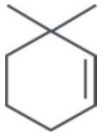
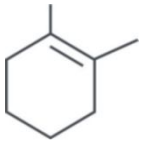
(b)  and 

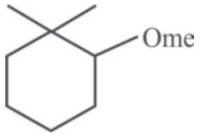
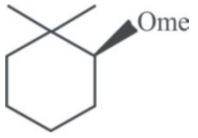
(c)  and 

(d)  and 

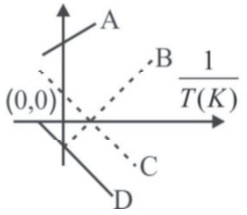
25. The major product of the following reaction is :



(a)  (b) 

(c)  (d) 

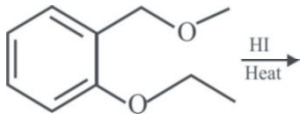
26. Which of the following lines correctly show the temperature dependence of equilibrium constant, K, for an exothermic reaction ?

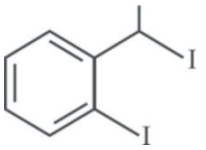
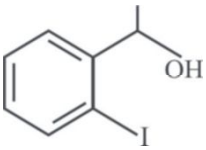


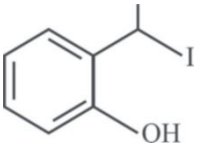
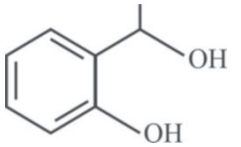
(a) B and C (b) C and D

(c) A and D (d) A and B

27. The major product formed in the following reaction is :



(a)  (b) 

(c)  (d) 

28. A aqueous solution contains an unknown concentration of Ba^{2+}. When 50 ml of a 1M solution of Na_2SO_4 is added, $BaSO_4$ just begins to precipitate. The final volume is 500 mL. The solubility product of $BaSO_4$ is 1×10^{-10}. What is the original concentration of Ba^{2+} ?

(a) 2×10^{-9} M (b) 1.1×10^{-9} M

(c) 1.0×10^{-10} M (d) 5×10^{-9} M

29. At 518° C, the rate of decomposition of a sample of gaseous acetaldehyde, initially at a pressure of 363 Torr, was 1.00 Torr s^{-1} when 5% had reacted and 0.5 torr s^{-1} when 33% had reacted. The order of the reaction is :

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

30. For 1 molal aqueous solution of the following compounds, which one will show the highest freezing point ?

(a) $\left[Co(H_2O)_5Cl\right]Cl_2.H_2O$

(b) $\left[Co(H_2O)_4Cl_2\right]Cl.2H_2O$

(c) $\left[Co(H_2O)_3Cl_3\right].3H_2O$

(d) $\left[Co(H_2O)_6\right]Cl_3$

ANSWER KEY

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

HINTS & SOLUTIONS

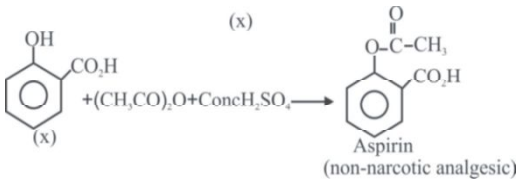
1.Sol: $CH_3COOK + H_2O \rightarrow CH_3COOH + KOH$

Hence nature of solution is basic

2.Sol: Kjeldahl is suitable for aniline . This method is used for quantative analysis of N compound in organic substance $\left(NH_3 / NH_4^+\right)$.

3.Sol: BCl_3 & $AlCl_3$ both have vacant p-orbital & incomplete octet. So they act as Lewis acid.

4.Sol: Formation of X is called Kolbe reactions. Reaction of X with $(CH_3CO)_2O$ step is called acylation.



5.Sol: Methyl orange shows red (pinkish) color in Acidic medium & yellow color in basic medium since original solution is basic so

initial color $\Rightarrow$ yellow & Titrated with acid so

Final color $\Rightarrow$ pinkish (red)

6.Sol: $\left[H_2S\right] = 0.10$ M

$\left[HCl\right] = 0.20\ \text{M} \Rightarrow \left[H^+\right] = 0.2\ \text{M}$

(1) $H_2S \rightleftharpoons HS^- + H^+ \quad K_1 = 1.0\times10^{-7}$

(2) $HS \rightleftharpoons S^{2-} + H^+ \quad K_2 = 1.2\times10^{-13}$ So,

$$= \frac{1.2\times10^{-20}\times10^{-1}}{4\times10^{-2}} = 3\times10^{-20}\ \text{M}$$

All the $\left[H^+\right]$ will come from strong acid $\left[HCl\right]$ only.

7.Sol: $C_6H_6(l) + \frac{15}{2}O_2(g) \rightarrow 6CO_2(g) + 3H_2O(l)$

$\Delta n_g = 6 - 7.5 = -1.5$ (change in gaseous mole)

ΔU or $\Delta E = -3263.9kJ$

$\Delta H = \Delta U + \Delta n_g RT$

$\Delta n_g = -1.5$

$R = 8.134\,JK^{-1}\,mol^{-1}$

$T = 298K$ So

$\Delta H = -3263.9 + (-1.5)8.314 \times 10^{-3} \times 298$

$= -3267.6KJ$

$\Delta H =$ Heat at constant pressure, $\Delta U =$ Heat at constant volume, R=gas constant

8.Sol: a. $(NH_4)_2 Cr_2O_7 \xrightarrow{\Delta} Cr_2O_3 + N_2 + 4H_2O$

b. $NH_4NO_2 \xrightarrow{\Delta} N_2 + 2H_2O$

c. $(NH_4)_2 SO_4 \xrightarrow{\Delta} 2NH_3 + H_2SO_4$

d. $Ba(N_3)_2 \xrightarrow{\Delta} Ba + 3N_2$

In reaction (c) NH_3 is evolved where as in reaction a, b and d N_2 is evolved

9.Sol: $B_2H_6 + 3O_2 \rightarrow B_2O_3 + 3H_2O$

moles of O_2 required=3x moles of B_2H_6

$= 3 \times \frac{27.6}{27.6} = 3$

$\frac{1 \times t}{96500} =$ moles of $O_2 \times 4$

$\frac{100 \times t}{96500} = 3 \times 4$

$t = \frac{3 \times 4 \times 96500}{100}$ sec $= 3.2$ hours.

10.Sol:

Total number of lone pair in I_3^- is 9

11.Sol: $Al + 3H_2O \xrightarrow{NaOH} Al(OH)_3 \downarrow +3/2H_{2(g)}$

(x)

White gelatinous ppt.

$\downarrow$

Soluble in excess of NaOH and form

$Na[Al(OH_4)]$

$2A(OH)_3 \xrightarrow{\Delta} Al_2O_3 + 3H_2O$

Used as adsorbent in chromatography so metal is Al.

12.Sol: The electronic configuration of H_2^{2-} is

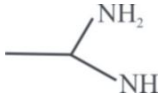
$\Rightarrow (\sigma 1s^2), (\sigma^* 1s)^2$

Bond order of $H_2^{\,2} = \frac{N_b - N_a}{2} = \frac{2-2}{2} = 0$

Hence $H_2^{\,2}$ does not exist, due to zero bond order

13.Sol: Order of base natute depends on electron donation tendency.

In compound  nitrogen is sp^2 hybridized so least basic among all given compound.

compound  is very strong nitrogenous organic base as lone pair of one nitrogen delocalize in resonance and make another nitrogen negatively charged and conjugate acid have two equivalent resonating structure.

Thus it is most basic in given compounds

 (Secondary amine) more basic than  (Primary amine).

14.Sol: In Frenkel defect, some of ion (usually cation due to their small size) missing from their correct position and occupies position in interstitial.

15.Sol:

PH_3
O_2
B_2H_6
H_2SO_4

} All are covalent compounds

KCl is ionic compound.

16.Sol: $K_2[Cr(CN)_2(O)_2(O_2)(NH_3)]$:

Potassium amine dicyanido dioxido peroxidochromate (VI)

$2 \times 1 + z + 2 \times (-1) + 2 \times (-2) + (-2) + 0 = 0$

$z = +6$

The oxidation states of Cr in and $K_2[Cr(CN)_2(O)_2(O_2)(NH_3)]$ respectively are +3, 0 and +6

17.Sol: (i) $[Fe^{+2}(CN)_6]^{4-} + H_2O_2^{-1} + 2H^+$

$\downarrow$

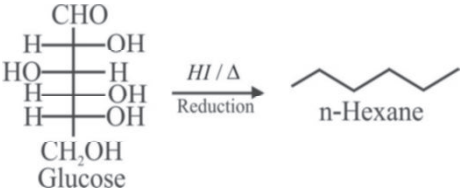
$[Fe^{+3}(CN)_6]^{3-} + 2H_2O^{-2}$

(ii) $\left[Fe^{+3}(CN)_6\right]\downarrow^{3-} + H_2O_2^{-1} + 2OH^-$

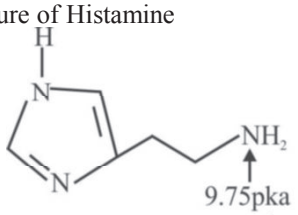
$\downarrow$

$\left[Fe^{+2}(CN)_6\right]^{4-} + O_2^{0} + 2H_2O$

18.Sol:



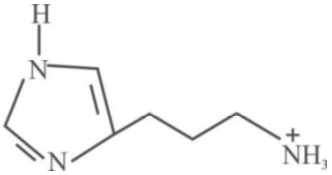
19.Sol: Structure of Histamine



Blood is slightly basic in nature (7, 35 PH) approx.

At this pH terminal NH_2 will get protonated due to more basic nature.

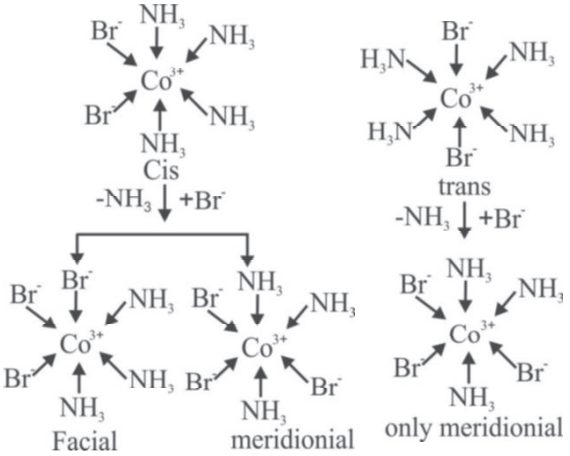
$\therefore$ Predominant structure of histamine is



20.Sol: $\left[3Ca_3(PO_4)_2.Ca(OH_2)\right] + 2F \rightarrow$

$\left[3Ca_3(PO_4)_2.CaF_2.\right] + 2OH^-$

21.Sol:



22.Sol : Birch reduction is addition. So trans alkene will be produced.

23.Sol: $\frac{12x}{y} = \frac{1}{6}$

$2x = y$ for $C_xH_yO_z$

$C_xH_y(g) + \left(x + \frac{y}{4}\right)O_{2(g)} \rightarrow xCO_{2(g)} + \frac{y}{2}H_2O(l)$

No. of oxygen atoms in $C_xH_yO_z = Z$

No.of oxygen atoms required for C_xH_y combustion is $\left(x + \frac{y}{4}\right) \times 2 = \left(2x + \frac{y}{2}\right)$.

So $z = \frac{1}{2}\left(2x + \frac{y}{2}\right)$

$z = x + \frac{y}{4}$

$z = x + \frac{2x}{4} = \frac{3x}{2}$

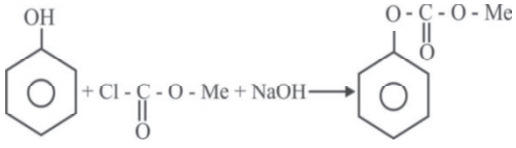
$x : 2x : \frac{3x}{2}$

$2x : 4x : 3x$

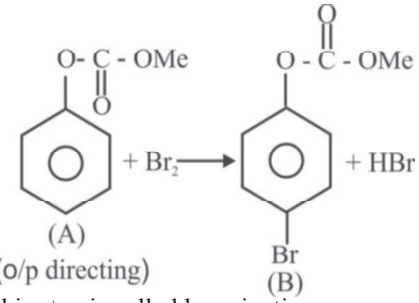
$2 : 4 : 3$

Hence $C_2H_4O_3$

24.Sol:

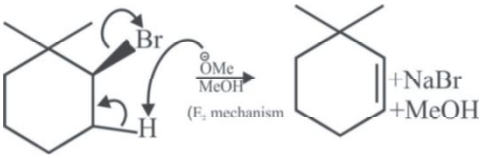


This step involves acid base reaction at first followed by S_NAE reactions.



this step is called bromination.

25.Sol:



Reaction is dehydrohalogenation E_2 -elimination reaction. Elimination takes place in single step and proceed by formation of transition state from anti position.

26.Sol: From thermodynamics

$$\ln k = \frac{-\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R}$$

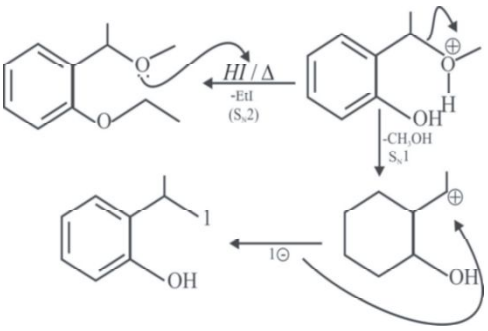
for exothermic reaction,

$$\Delta H = -VE$$

$$\text{Slope} = \frac{-\Delta H^\circ}{R} = +ve$$

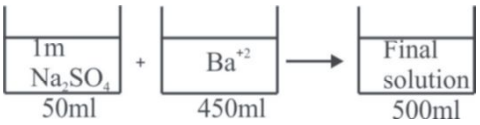
So from graph, line should be A & B.

27.Sol:



It is nucleophilic substitution reaction.

28.Sol:



Concentration of SO_4^{-2} in Ba^{+2} solution

$$M_1V_1 = M_2V_2$$

$$1 \times 50 = M_2 \times 500$$

$$M_2 = \frac{1}{10}$$

for just precipitation

$$I.P. = K_{SP}$$

$$\left[Ba^{+2}\right]\left[SO_4^{-2}\right] = K_{SP}\left(BaSO_4\right)$$

$$\left[Ba^{+2}\right] \times \frac{1}{10} = 10^{-10}$$

$$\left[Ba^{+2}\right] = 10^{-9}\ \text{M in 500 ml solution}$$

for calculation of $\left[Ba^{+2}\right]$ in original solution(450ml)

$$M_1 \times 450 = 10^{-9} \times 500$$

$$M_1 = \frac{500}{450} \times 10^{-9} = 1.11 \times 10^{-9} M$$

$[M_1 = \text{molarity of } Ba^{+2} \text{ in original solution (450 ml)}]$

29.Sol: $CH_3CHO \rightarrow CH_4 + CO$

$r_1 = 1\,\text{torr sec}^{-1}$, when 5% reacted (95% unreacts)

$r_2 = 0.5$ torr sec^{-1}, when 33% reacted (67% unreacted)

$r \propto (a-x)^m$ m=order of reaction

a-x=unreacted

$$\frac{r_1}{r_2} = \left[\frac{(a-x_1)}{(a-x_2)}\right]^m$$

$$\frac{1}{0.5} = \left(\frac{0.95}{0.67}\right)^m$$

$$2 = (1.41)^m \Rightarrow 2 = \left(\sqrt{2}\right)^m$$

$$\Rightarrow m = 2$$

30.Sol: $\left[Co\left(H_2O\right)_5 Cl\right]Cl_2.H_2O$ i=3

$\left[Co\left(H_2O\right)_6 Cl_2\right]Cl.2H_2O$ i=2

$\left[Co\left(H_2O\right)_3 Cl_3\right].3H_2O$ i=1

$\left[Co\left(H_2O\right)_6\right]Cl_3$ i=4

$\Delta T_f \propto i$

where $\Delta T_f = \left(T_f - T_f'\right)$; T_f' = F.P. of solution

Freezing point of solution ↑ as i ↓.

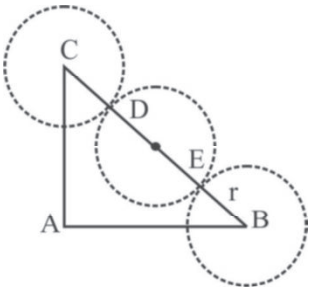
EVAAITS (NEET - 11) SOLUTIONS

ANSWER KEY

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

HINTS & SOLUTIONS

1. Sol: $AB = a, AC = a$



$BC^2 = AB^2 + AC^2 = 2a^2$

Radius = r,

then $BC = CD + DE + EB$

$= r + 2r + r = 4r$

$\therefore \quad 16r^2 = 2a^2$

$r^2 = \frac{a^2}{8}$

$\therefore \quad r = \frac{a}{2\sqrt{2}} = \frac{404}{2\sqrt{2}} = \frac{404}{2.828} = 142.8\,pm$

Note: Detailed calculations to relate radius with edge length have been given. Examinee can use direct relation.

Simple cubic, $r = \frac{a}{2}; hcp / ccp, r = \frac{a}{2\sqrt{2}}; bcc,$

$r = \frac{\sqrt{3}}{4}a$

2. Sol: Mole fraction of solute $X_2 = 0.2$.

Therefore, mole fraction of solvent $X_1 = 0.8$

Or $\quad \frac{n_2}{n_1 + n_2} = 0.2$ and $\frac{n_1}{n_1 + n_2} = 0.8$

Or $\quad \frac{n_2}{n_1} = \frac{0.2}{0.8} = \frac{1}{4}$

Now, if n_1 (solvent moles) = 1000/78 = 12.8 moles.

$n_2 = 12.8 / 4 = 3.2$ moles. Therefore, 3.2 moles of the compound are present in one kg of solvent benzene and so molality = 3.2.

3. Sol: Al is above hydrogen in the electrochemical series, therefore Al^{3+} has lesser reduction tendency as compared with H^+. Hence, hydrogen electrode acts as anode when coupled with aluminium electrode.

$E^o_{cell} = E^o_{H^+/H_2} - E^o_{Al^{3+}/Al}$

$\therefore \quad 1.66V = 0.0V - E^o_{Al^{3+}/Al}$

$E^o_{Al^{3+}/Al} = -1.66V.$

4. Sol:

$\frac{-d[SO_2]}{dt} = 1.28 \times 10^{-3}$ g/sec $= 0.02 \times 10^{-3}$ mole/sec

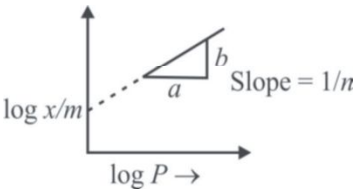
$r = -\frac{1}{2}\frac{d[SO_2]}{dt} = \frac{1}{2}\frac{d[SO_3]}{dt} = -\frac{d[O_2]}{dt}$

$\Rightarrow -\frac{1}{2}\frac{d[SO_2]}{dt} = \frac{1}{2}\frac{d[SO_3]}{dt}$

$\Rightarrow \frac{d[SO_3]}{dt} = 0.02\text{x}10^{-3}$ mole/sec $= 1.6\text{x}10^3$ g/sec

5. Sol: $x / m = k.P^{\frac{1}{n}}$

$\log x / m = \log k + \frac{1}{n}\log P$



$Slope = \frac{1}{n}$ where n being integer

6.Sol: Conceptual

7.Sol: Acid salts react with bases forming salts and water as per the reaction, given below.

$NaH_2PO_4 + NaOH \longrightarrow Na_2HPO_4 + H_2O$;

$NaH_2PO_3 + NaOH \longrightarrow Na_2HPO_4 + H_2O$

$Na_2HPO_4 + NaOH \longrightarrow Na_3PO_4 + H_2O$

8. Sol: CFCs is IR absorber and thus causes global warming.

CFCs is the major source of O_3 layer depletion.

$CCl_2F_2 \longrightarrow Cl + CClF_2$

$Cl + O_3 \longrightarrow ClO + O_2$

$ClO + O_2 \longrightarrow 2O_2 + Cl$

9. Sol: 5.6 L of gas has mass $= 7.5$ g

$\therefore$ 22.4 L of gas mass $= \frac{7.5}{5.6} \times 22.4 = 30$

So molecular weight = 30

So, molecular formula of compound is NO.

10. Sol: Electron is $\frac{1}{1837}$ times lighter than proton so their mass ratio will be 1 : 1837.

ratio $= \frac{1.67 \times 10^{-27}}{9.1 \times 10^{-31}} = 1837$

11. Sol: Energy of nth orbit of H-atom

$= \frac{2\pi^2 me^4 k^2}{h^2} \times \frac{1}{n^2}$

Energy of Bohr's orbit of H-atom

$= \frac{2\pi^2 me^4 k^2}{h^2}$

= - 13.6 eV (given)

Energy of fourth Bohr's orbit of H-atom

$= \frac{2\pi^2 me^4 k^2}{h^2} \times \frac{1}{4^2}$

$= 13.6 \times \frac{1}{16} eV = -0.85\ eV$

PE of electron in nth orbit $= 2 \times E_n$

So, P.E. of electron in 4^{th} orbit

$= 2 \times (-0.85) = -1.70\ eV$

12. Sol: $T_1V_1^{(\gamma-1)} = T_2V_2^{(\gamma-1)}$

or $\frac{T_1}{T_2} = \left(\frac{V_2}{V_1}\right)^{(\gamma-1)}$

According to ideal gas equation for 1 mole

PV = RT

$\frac{V_2}{V_1} = \left(\frac{T_2}{T_1}\right)\left(\frac{P_1}{P_2}\right)$

From equations (1) and (2), we get

$\frac{T_1}{T_2} = \left(\frac{T_2}{T_1}\right)^{\gamma-1}\left(\frac{P_1}{P_2}\right)$

$\left(\frac{T_1}{T_2}\right)^{\gamma} = \left(\frac{P_2}{P_1}\right)^{(1-\gamma)}$

13. Sol: As two H atoms approach each other, there is stable bond formation where P.E. is minimum as shown in (b)

14. Sol: $B_2H_6 + 3O_2 \longrightarrow B_2O_3 + 3H_2O + Heat$

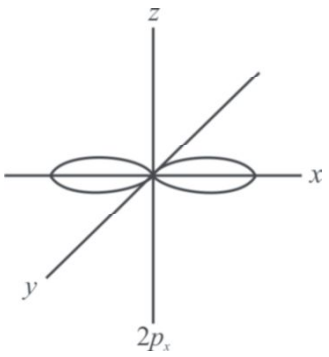
$B_2H_6 + 6H_2O \longrightarrow H_3BO_3 + 6H_2$

$2NaH + B_2H_6 \xrightarrow{ether} NaBH_4$

15. Sol: Methyl group and carboxylate group $(-COO^-)$ both give electron donating +I-effect while -Br and $-NH_3^+$ give electron withdrawing -I-effect.

16. Sol: Photochemical smog occurs in warm, dry and sunny climate. It has high concentration of NO, NO_2 and O_3. Their low concentration causes irritation in nose and throat and their high concentration causes headache, chest pain, cough and difficulty in breathing.

17. Sol: p_x orbital being dumbbell shaped, have number of nodal planes = 1, in *yz* plane



18. Sol: $W = -P(V_2 - V_1)$

$= -1 \times 35 = -35$ L-atm

$= -35 \times 101.3$ J $= -3545.5$ J

$= -\dfrac{3545.5}{4.18} = 848.2$ cal

19. Sol: The equilibrium constant does not change when concentration of reactant is changed as the concentration of product also get changed accordingly.

20. Sol: $MgCl_2$ can dissociate into ions.

21. Sol: $[\dot{C}o(NH_3)_4ClNO_2]$

$x + 4(0) + 1(-1) + 1(-1) = 0$

$x + 0 - 1 - 1 = 0$

$x - 2 = 0;\ x = +2$

22. Sol: Washing soda removes both the temporary and permanent hardness by converting soluble calcium and magnesium compounds into insoluble carbonates.

$CaCl_2 + Na_2CO_3 \rightarrow CaCO_3 + 2NaCl$

$CaSO_4 + Na_2CO_3 \rightarrow CaCO_3 + Na_2SO_4$

$Ca(HCO_3)_2 + Na_2CO_3 \rightarrow CaCO_3 + 2NaHCO_3$

23. Sol: It is $p\pi - p\pi$ bonding involving B and F atoms responsible for the acidic nature of boron halides as $BF_3 < BCl_3 < BBr_3 < BI_3$. Smaller atom shows more back bonding.

24. Sol: Carbanion at position '*P*' will be stabilised by resonance with two >C=O groups.

25. Sol: The approximate composition of gasoline is $C_6 - C_{11}$ at boiling point $70 - 200^oC$ and is used in motor fuel, dry cleaning, petrol gas, etc.

26. Sol: It is defined as the number of milliliter of N/10 KOH solution required to neutralise the distillate acid of 5 g of hydrolysed fat.

27. Sol: Number average molecular mass

$$\overline{Mn} = \frac{\sum N_i M_i}{\sum N_i}$$

Mass average molecular mass $\overline{Mw} = \dfrac{\sum N_i M_i^2}{\sum N_i M_i}$

28. Sol: Cl_2 formed at anode reacts with C_2H_5OH in presence of NaOH (formed in reaction) to give haloform reaction.

29. Sol: For following reaction,

$2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)$ When the volume of vessel change into $\dfrac{1}{3}$, then concentration of reactant becomes three times $(\because c\ \alpha \dfrac{1}{v})$

The rate of reaction for first order reaction $\propto$ concentration. So rate of reaction will increase three times.

30. Sol: When the temperature is raised, the viscosity of liquid decreases, this is because increase in temperature increases the average kinetic energy of molecules which overcome the attractive force between them.

31. Sol: Nitric acid turns the skin yellow because it reacts with protein giving a yellow compound called xanthoprotein.

32. Sol: Complex compounds or complex salts containing two different metallic elements give test for only one element. For example, potassium hexacyanoferrate (II), $K_4[Fe(CN)_6]$ gives test only for K^+ ions and not for Fe^{2+} ions.

$K_4[Fe(CN)_6] \rightleftharpoons 4K^+ + [Fe(CN)_6]^{4-}$

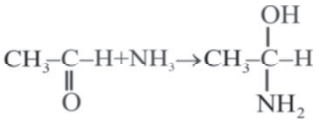
33. Sol: The metallic conduction decreases with increase in temperature, but electrolytic conduction increases with the increase in temperature.

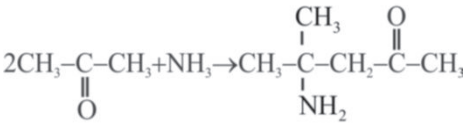
34. Sol: In lyophilic colloidal sol, extensive hydration takes place and their particles cannot be detected even under ultramicroscope.

In lyophobic colloidal sol, viscosity is same as that of the medium and particles migrate towards anode or cathode on passing electric current.

35. Sol: Black phosphorus is thermodynamically most stable form of phosphorus as it is a highly polymerised form of phosphorus. Hence it is least reactive.

36. Sol:





37. Sol: The wide range of oxidation state of actinoids is due to the fact that the 5*f*, 6*d* and 7*s* energy levels are of comparable energies and all these three subshells can participate in comparison to lanthanoid. The 5*f* orbitals extend farther from the nucleus than the 4*f* orbitals.

38. Sol: The reaction of alcohol with Lucas reagent is mostly S_N1 reaction and the rate of reaction is directly proportional to the stability of carbocation formed in the reaction.

Since 3^o R - OH forms 3^o carbocation (most stable) hence it will react fast by S_N1 reaction.

39. Sol: $R-CN+H_2O \xrightarrow{H_2O/H^+} RCOOH+NH_3$

It yields amine when reduced as -

$R-CN+H_2 \rightarrow R-CH_2-NH_2$

40. Sol: $M=\dfrac{\rho \times a^3 \times N_0 \times 10^{-30}}{z}$

$$=\frac{10\times(100)^3\times(6.02\times10^{23})\times10^{-30}}{4}$$

No. of atoms in 100 $g=\dfrac{6.02\times10^{23}}{15.05}\times100=4\times10^{25}$

41. Sol: $K_1=\dfrac{[NO_2]}{[NO][O_2]^{1/2}}; K_2=\dfrac{[NO]^2[O_2]}{[NO_2]^2}$

$$\Rightarrow \frac{[NO_2]^2}{[NO][O_2]}=\frac{1}{K_2}$$

$$\Rightarrow \frac{[NO_2]}{[NO][O_2]^{1/2}}=\frac{1}{\sqrt{K_2}}$$

$$\Rightarrow K_1=\frac{1}{\sqrt{K_2}}; K_2=\frac{1}{K_1^2}$$

42. Sol: Diketo (I) forms highest enol content due to stabilisation of enol by intermolecular H-bonding. Electron donating resonance effect by ester group slightly decreases enol content.

43. Sol: The atomic weight of sulphur = 32

In SCl_2 valency of sulphur = 2

So equivalent mass of sulphur $=\dfrac{32}{2}=16$

44. Sol: For weak acid $K_a=\alpha^2.C$

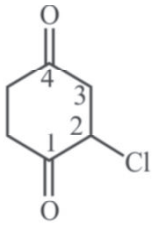
$$\therefore \quad \alpha=\sqrt{\frac{K_a}{C}}=\sqrt{\frac{4.9\times10^{-8}}{0.1}}=7\times10^{-4}$$

$$\text{pH}=-\log H^+=-\log \alpha C$$

$$=-\log 7\times10^{-4}\times10^{-1}$$

$$=4.1549=4.155$$

45. Sol: Position of chlorine is incorrectly mentioned. It is correctly written as:



2-chloro-1, 4-cyclohexanedione

EVAAITS (JEE ADVANCED-2) SOLUTIONS

ANSWER KEY

Section - A

1. a,b	**2.** b,c	**3.** a,d	**4.** b, d	**5.** a,c
6. d	**7.** c,d	**8.** a,b	**9.** a,b,d,c	**10.** b,c,d

Section - B

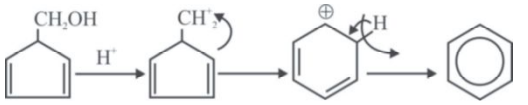
11. 5	**12.** 5	**13.** 5	**14.** 6	**15.** 3
16. 4	**17.** 2	**18.** 1	**19.** 6	**20.** 4

HINTS & SOLUTIONS

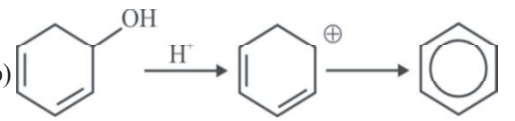
Section - A

1. Sol:

(a)



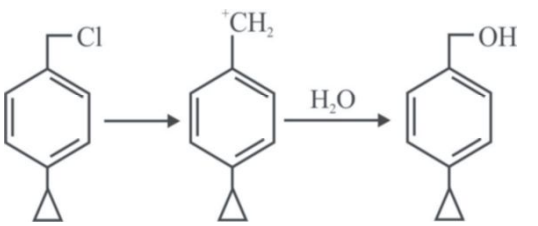
(b)



2. Sol: (a) Alkene should form
(b) More substituted product
(c) Less substituted product
(d) More substituted product

3. Sol: (a) Most stable cation
(d) More substituted alkene final product

4. Sol: (b)

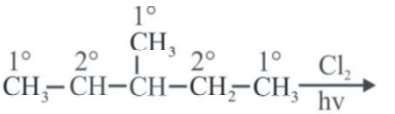


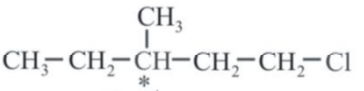
(d) Alkenes undergo addition reaction with HBr in presence of CCl_4

5. Sol: fact

6. Sol: Cyclopentadiene liberates when it combines with metal like Na or K and $NaNH_2$ due to aromaticity of cyclopentadienyl anion.

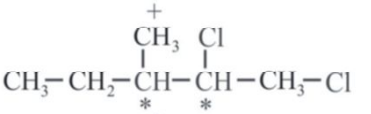
7. Sol:



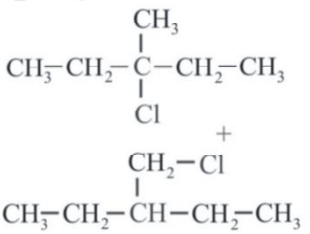


$2^n = 2^1 = 2$

+

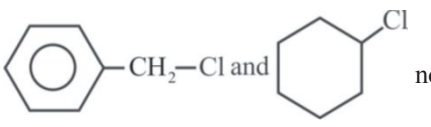


$2^n = 2^2 = 4$



Total (8) Product

8. Sol: Because



not have any chiral - C so that they gives same product by S_N^1, S_N^2.

9. Sol: All contains symmetry, with chiral centre

10. Sol: $x_A P_A^o + x_B P_B^o = 700 \quad ...(i)$

$x_A'' P_A^o + x_B'' P_B^o + 0.70 \; P_B^o = 600 \; ...(ii)$

if moles of A and B initially are x and y then

$$x = 0.75 \times \frac{2}{3}(x+y) + 0.30 \times \frac{1}{3}(x+y)$$

and $x_A = \frac{x}{x+y}$ or $x_B = \frac{x}{x+y}$

Solving gives

$x_A = 0.6, x_B = 0.4$,

$x_A = 0.6, x_B = 0.4, P_A^o = \frac{2500}{3} torr$

$P_B^o = 500\ torr$

Section - B

11.Sol: Unit cell is fcc with half of the tetrahedral voids are occupied by c- atoms hence effective no is

$= 1 + 2 \times \frac{1}{8} = \frac{5}{4}$

12.Sol: Present as Fe^+

13.Sol:

$N_2 + 3H_2 \longrightarrow 2NH_3$

1 a 0

0 $a-3$ 2

$\frac{2}{a-1} = \frac{1}{2}$

4 = a - 1

a = 5

14. Sol: i = 1.25

Original mole fraction $= \frac{1}{n} = \frac{i}{i+(n-1)}$

$= \frac{1.25}{1.25+(n-1)} = \frac{1}{5} \Rightarrow n = 6$

15. Sol: (B) is p-CH_3 C_6H_5 COCHO

(C) is O=C(CH_3)C-C_6H_5-CH_3-p

(E) CHI_3

(D) $^-$OOC-C_6H_5-CH_3-p

16. Sol: (I, II, V, VI are correct)

17. Sol: $2Cl^- \longrightarrow Cl_2 + 2e^-$

$Cl_2 + 2NaOH \longrightarrow NaOCl + NaCl + H_2O$

Mole of NaOCl required

$= \frac{10^6 \times 1 \times 7.45/100}{74.5} = 10^3$ moles of Cl_2

required 10^3 e.q of Cl_2 required $= 2 \times 10^3$

$2 \times 10^3 \times 96500 = 9.65 \times t$

$= 2 \times 10^7 = t$

18. Sol: Dissolved

$[Zn(OH)_2] = [OH^-]_{aq} + [Zn(OH^+)_2]_{aq}$

Now, $[Zn(OH)_2] = 10^{-6}$ M in saturated solution.

so, $[Zn(OH)]^+ = \frac{10^{-6} \times 10^{-7}}{[OH^-]} = \frac{10^{-13}}{[OH^-]}$

Similarly, $[Zn^{+2}] = \frac{10^{-17}}{[OH^-]^2}$

$[Zn(OH)_3] = 10^{-3}[OH^-]$

$[Zn(OH)_4^{2-}] = K_5[Zn(OH)_3^-]$

$[OH^-] = (10^{-2} M^{-1})[OH^-]^2$

Dissolved $Zn(OH)_2 = \frac{10^{-17}}{[OH^-]^2} + \frac{10^{-13}}{[OH^-]}$

$+10^{-6} + 10^{-3} \times [OH^-] + 10^{-2}[OH^-]^2$

$= \frac{10^{-17}}{10^{-16}} + \frac{10^{-13}}{10^{-8}} + 10^{-6} + 10^{-3} \times 10^{-8} + \cancel{10^{-18}}$

$= 10^{-1} + \cancel{10^{-5}} + \cancel{10^{-6}} + \cancel{10^{-11}} = 10^{-1}$

$= -\log Zn(OH)_2(aq) = 1$

19. Sol: $C_{12}H_{22}O_{11} + H_2O \longrightarrow C_6H_{12}O_6 + C_6H_{12}O_6$

mol 0.0125 0 0

$0.0125 - x$ x x

$\Delta T_b = m_1K_b + m_2K_b + m_3K_b$

$m_1 + m_2 + m_3 = \frac{0.104}{0.52} = 0.2$

$\frac{0.0125 - x + x + x}{10} \times 100 = 0.2$

$= (0.0125 + x)10 = 0.2$

$x = 0.0075$

$mol\% = \frac{0.0075}{0.0125} \times 100 = 60$

$\frac{1}{10}$th of mol% $= \frac{60}{10} = 6$

20. Sol: % of carbon

$= \frac{144}{144 + m + 35.5(10-m)} \times 100 = 40$

On solving m = 4.

EVAAITS (BIT SAT - 1) SOLUTIONS

ANSWER KEY

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

HINTS & SOLUTIONS

1.Sol: Relation between ΔH (enthalpy change) and ΔE (internal energy change) is

$$\Delta H = \Delta E + \Delta n_g RT$$

where Δn_g = (moles of gaseous products)-(mole of gaseous reactants)

For the given reaction,

$$\Delta n_g = 2 - 3 = -1$$

$$\Rightarrow -1366.5 = \Delta E - 1 \times 8.314 \times 10^{-3} \times 300$$

$$\therefore \quad \Delta E = -1364.0\ kJ\ mol^{-1}$$

2.Sol: Ionisation potential generally increases when we move in a period from left to right but IE_1 of nitrogen is greater than that of oxygen. It is due to the more stable (half-filled orbitals) configurations of N.

3.Sol: Metal $\Rightarrow$ Cation $\rightarrow A(138)$

Non-metal $\Rightarrow$ Anion $\Rightarrow B(19)$

Ionic compound $= AB_2$

$\therefore$ Formula mass (G.M.M. for ionic compound)

$$= 138 + 2 \times 19 = 176$$

4.Sol: The reaction is $NH_3 + H_2O \rightleftarrows NH_4^+ + OH^-$

$$K_b = 1.8 \times 10^{-5} = \frac{\left[NH_4^+\right]\left[OH^-\right]}{\left[NH_3\right]}$$

$$\frac{(1.5 \times 10^{-3})(1.5 \times 10^{-3})}{\left[NH_3\right]} = 1.8 \times 10^{-5}$$

Equilibrium conc. of ammonia $[NH_3] = 0.125\,M$

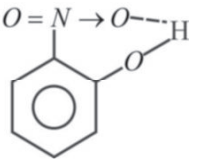
And, total $[NH_3] = 1.5 \times 10^{-3} + 0.125 = 0.13M$

5.Sol: The water gas is mixed with excess of steam and passed 450^0C over a heated catalyst $\left(Fe_2O_3 + Cr_2O_3\right)$. CO is mostly oxidised to CO_2 and more H_2 is set free. CO_2 is absorbed in alkali.

$$\underbrace{CO + H_2}_{\text{Water gas}} + \underset{\text{Steam}}{H_2O} \xrightarrow{\text{Catalyst}} CO_2 + 2H_2$$

6.Sol: $\frac{r_1}{r_2} = \sqrt{\frac{M_2}{M_1}} = \sqrt{\frac{64}{44}} = \frac{4}{\sqrt{11}}$

7.Sol: o-Nitrophenol has intramolecular H bonding as shown below



8.Sol: Neutron is a chargeless particle, so it is not deflected by electric or magnetic field.

9.Sol:

$$Al_2O_3.2H_2O + 3C + N_2 \xrightarrow{1800^0C} 2AlN + 3CO + 2H_2O$$

10.Sol: From the given data,

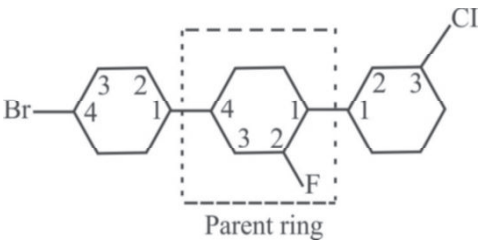
Only 0.2 moles of each of HNO_3 and KOH will be neutralised.

So 1 mol of strong acid and strong base releases 57.0 kJ

$\therefore$ 0.2 mol of HNO_3 and KOH releases 57.0 kJ

$$= 11.4\ kJ$$

11.Sol: Central ring has maximum of three locants, hence it is the parent ring. The lowest number series is 1,2 and 4 as



There is locant in the side rings, hence secondary numbering of side rings are also done.

12.Sol: Nickel shows zero oxidation state in carbonyl complex.

13.Sol: Electrons jump between different energy level and release photon.

14.Sol: Textile causes lung cancer.

15.Sol: Order of acidic strength is:

$$CH_3OH > HC \equiv CH > C_6H_6 > C_2H_6$$

16.Sol: The rate of forward reaction is two times that of reverse reaction at a given temperature and identical concentration $K_{equilibrium}$ is 2 because the reaction is reversible. So $K = \frac{k_f}{k_b} = \frac{2}{1} = 2$

17.Sol: Wilkinson's catalyst brings about homogeneous catalysis as it is soluble in reaction medium. All others bring about hetergeneous catalysis as catalysts and reactants remain in different phase.

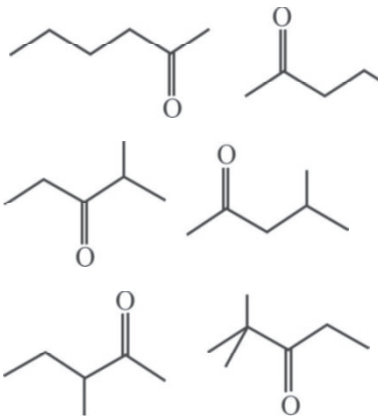
18.Sol: The general formula of ketone is $C_nH_{2n}O$ with molar mass

$$12n + 2n + 16$$

Hence, $14n + 16 = 100$

$n = 6$ and formula of compound is $C_6H_{12}O$

possible ketones are:



19.Sol: Molecular weight of $(CHCOO)_2Fe = 170$

Fe present in 100 mg of $(CHCOO)_2Fe$

$$= \frac{56}{170} \times 100\,mg = 32.9\,mg$$

This is present in 400 mg of capsule

$$\% \text{ of Fe in capsule } = \frac{32.9}{400} \times 100 = 8.2$$

20.Sol: Along the period from left to right, atomic number increases and, therefore, nuclear charge also increases. So first ionisation energies of alkaline earth metals are higher than those of the alkali metals of the same period because of higher nuclear charge.

21.Sol: $NaNO_3$ is purely ionic while AgCl is covalent; other compounds react with AgCl

$$2agCl + NaCO_3 \rightarrow 2Ag + 2NaCl + CO_2 + \frac{1}{2}O_2$$

$$AgCl + 2Na_2SO_3^2 \rightarrow Na_2\left[Ag(S_2O_3)_2\right] + NaCl$$

$$AgCl + 2NH_4OH \rightarrow \left[Ag(NH_3)_2Cl\right] + 2H_2O$$

22.Sol: EMF = [SRP of cathode - SRP of anode]
Where SRP = Standard reduction potential
If EMF is positive then the reaction is spontaneous
For e.g. in galvanic cell
(a) Cathode is made of copper
(b) EMF = 1.1 volt
(c) Anode is made of zinc
EMF = 0.34-(-0.76)=1.1 volt.

23.Sol: From kinetic energy gas equation

$$PV = \frac{1}{3}mnc^2$$

$$\therefore\ RT = \frac{1}{3}mnc^2 = \frac{1}{3}Mc^2 \text{ or } \frac{1}{2}\cdot\frac{2}{3}Mc^2$$

$$\text{or } = \frac{2}{3}K.E. \text{ or } K.E. = \frac{3}{2}RT$$

24.Sol: $AO = OB = \frac{\sqrt{3}}{2}a = l$

$$\therefore\ a^2 = 2l^2 - 2l^2\cos\theta$$

$$a^2 = 2l^2(1 - \cos\theta)$$

$$a^2 = \frac{3}{2}a^2(1 - \cos\theta)$$

$\therefore \quad 1-\cos\theta=\frac{2}{3}$

$\cos\theta=\frac{1}{3}, \quad \therefore \theta=70^{0}32'$

25.Sol: Air is not a colloidal solution because it is a homogeneous mixture.

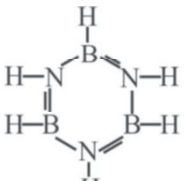
26.Sol: $Zn+H_2O\rightarrow ZnO+H_2$

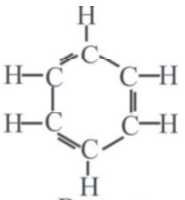
$Zn+2NaOH\rightarrow Na_2ZnO_2+H_2$

$Zn+2HCL\rightarrow ZnCI_2+H_2$

$Zn+2H_2SO_4\rightarrow ZnSO_4+SO_2+2H_2O$

27.Sol: Borazine $B_3N_3H_6$ is isoelectronic to benzene and, hence, is called inorganic benzene. Some physical properties of benzene and borazine are also similar.


Borazine


Benzene

28.Sol: For diabasic acid $E=\frac{M}{2}=\frac{200}{2}=100$

$N=\frac{W\times1000}{E\times V(in\ ml)}$

$\frac{1}{10}=\frac{W\times1000}{100\times100}=W=1g$

29.Sol: Probability for survival $=\frac{N}{N_0}=e^{-\lambda t}$

Now mean life period $=\frac{1}{\lambda}$

$\therefore$ Probability $=e^{-\lambda\times\frac{1}{\lambda}}=e^{-1}$

30.Sol: Examples of neutral oxides are CO, H_2O, N_2O. These oxides are neutral toward litmus paper.

31.Sol: $\left[Mg^{2+}\right]\left[OH^{-}\right]^2=10^{-12}$

$0.01\times\left[OH^{-}\right]^2=10^{-12}$

$\left[OH^{-}\right]=10^{-5}M$

$\therefore \quad \left[H^{+}\right]=10^{-9}M$ and $pH=-\log\left[10^{-9}\right]=9$

32.Sol: $\frac{r_1}{r_2}=\sqrt{\frac{M_2}{M_1}}$ (1)

$\frac{r_1}{r_2}=\frac{P_1}{P_2}$ (2)

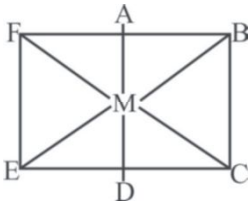
Combining (1) and (2), we get $\frac{r_1}{r_2}=\frac{P_1}{P_2}\sqrt{\frac{M_2}{M_1}}$

Rate of diffusion gases is directly proportional to pressure applied and inversely proportional to molecular weight.

33.Sol: Lithum shows diagonal relationships with Mg.

34.Sol: Chromatography is the latest technique for the purification of organic compounds.
Chromatography are of various types, viz., column chromatography, gas chromatography, and paper chromatography.

35.Sol: Show both optical and geometrical isomerism.



36.Sol: $C_2H_5-O-C_2H_5$ and $CH_3-O-C_3H_7$ are metamers.

37.Sol: Iron, because mercury does not form amalgum with iron.

38.Sol: Ozone does not absorb infrared radiation at all. It absorbs UV radiation coming from sun in the upper atmosphere and acts as an umbrella thus protecting human being living on earth.

39.Sol: Styrene at room temperature is liquid.

40.Sol: $Ag_2O+H_2O\rightarrow 2AgOH$

$C_2H_5Br+AgOH\rightarrow C_2H_5OH+AgBr$

41.Sol: $CI_2C=CH-CH_2-CH_2-CH_2$. It cannot show geometrical isomerism due to 2 Cl attached to double bonded carbon atom.

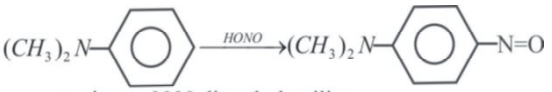
42.Sol: Both $KMnO_4$ and chromic acid will oxidise ketonic group as well as cleave the double bond.

Cu at 300^0C, on the other hand, cannot oxidise the ketonic group. $NaOI(NaOH + I_2)$ is the only reagent suitable for this conversion (iodoform test for methyl ketones).

$(CH_3)2C = CHCOCH_3 \xrightarrow{NaOI} (CH_3)_2C = CHCOOH + CHI_3$

43.Sol: Phenol does not react with $NaHCO_3$ or Na_2CO_3. Although picric acid is a phenolic compound (2,4,6-trinitrophenol), due to the presence of $3NO_2$ group (WWG), it is highly acidic and reacts with $NaHCO_3$ or Na_2CO_3.

44.Sol: Tertiary amines do not react with nitrous acid, and aromatic tertiary amines undergo electrophilic substitution with nitric acid.



p-nitroso-N,N-dimethyl aniline

45.Sol: The possible isomers of the complex are

$[Cu(NH_3)_3Cl][PtCl_3NH_3]$

$[Cu(NH_3)_2Cl_2][Pt(NH_3)_2Cl_2]$

$[Cu(NH_3)Cl_3][Pt(NH_3)Cl]$

$[CuCl_4][Pt(NH_3)_4]$

The total number of isomers is four.

EVAAITS (BIT SAT - 2) SOLUTIONS

ANSWER KEY

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

HINTS & SOLUTIONS

1. Sol: $-0.413 = 0 - 0.059 \log \frac{1}{[H^+]}$

or $\frac{0.414}{0.059} = -\log H^+ = pH$ or $pH = 7$

2. Sol: Generally the sulphides of Zn, Pb, Fe, Cu etc. are subjected to roasting to convert into their oxides prior to reduction by carbon.

3. Sol: $CHCl_3 + AgNO_3 \rightarrow$ No reaction

$CHCl_3$ is a covalent compound. It does not ionise in water.

4. Sol: Units of n^{th} order rate constant = $M^{1-n}s^{-1}$

For zero order, units of rate constant = Ms^{-1}

For first order, units of rate constant = s^{-1}

5. Sol: Molarity $= \frac{\text{Moles of urea}}{\text{Volume of solution(L)}}$

Moles of urea $= \frac{0.010}{60} mol$

Water at STP

$(d = 1g/cm^3 = 1kg/dm^3) = 0.3\,dm^3 = 0.3\,kg$

$\therefore$ Molarity $= \frac{0.010}{60 \times 0.3} = 5.55 \times 10^{-4} M$

6. Sol: $Co^{3+} \rightarrow [Ar]3d^6 4s^0$,

number of unpaired electrons $= 4$

$Fe^{2+} \rightarrow [Ar]3d^6 4s^0$,

number of unpaired electrons $= 4$

$Co^{2+} \rightarrow [Ar]3d^7 4s^0$,

number of unpaired electrons $= 3$

$Fe^{3+} \rightarrow [Ar]3d^5 4s^0$,

number of unpaired electrons $= 5$

7. Sol: According to electrical neutrality principle

$\Rightarrow (0.93x) - (2 \times 1) = 0$

$x = 2.15$

ON of Fe is an intermediate value of Fe^{+2} and Fe^{+3}

Let % of $Fe^{+3} = a$ and % of $Fe^{+2} = 100 - a$

$\therefore \quad \frac{3\times a + 2(100-a)}{100} = 2.15 \Rightarrow a = 15.05$

% of $Fe^{+3} = 15.05$ and % of $Fe^{+2} = 84.95$

8. Sol: $-COOH$ and $-OH$ group form the hydrogen bond by which they have high boiling point. $-COOH$ group shows strong hydrogen bonding so it forms dimer and have more boiling point than $-OH$ group while $-CHO$ group does not form hydrogen bond. Thus, the boiling point order is $3 > 1 > 2$.

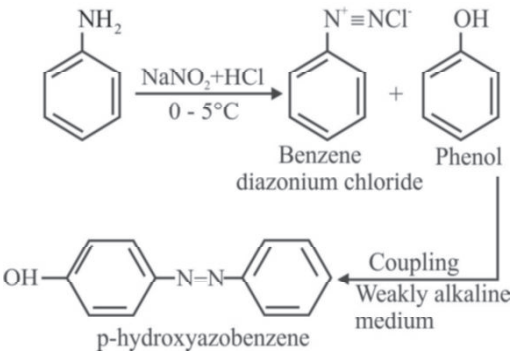
9. Sol: $[Co(NH_3)_3(NO_2)_3]$ There is no ions out of the coordination sphere thus it is poor conductor in electrolytic solution

$K_2[PtCl_6] = 3$ ions

$K_4[Fe(CN)_6] = 5$ ions

$[Co(NH_3)_4].SO_4 = 2$ ions

10. Sol: Azo dye is prepared by the coupling of phenol and diazonium chloride.



11. Sol: Negatively charged As_2S_3 sol coagulated most effectively by $AlCl_3$. This is because oppositely charged Al^{+3} ions have maximum charge.

$Al^{+3} > Ca^{2+} > Na^{+}$

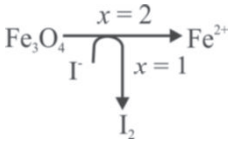
12. Sol: Fehling solution is a weak oxidsing agent which can oxidise aliphatic aldehyde but not ketone. Primary alcohols undergo oxidation with alkaline $KMnO_4$, acidic dichromate and conc. H_2SO_4 to give acids, whereas with Cu they give aldehydes.

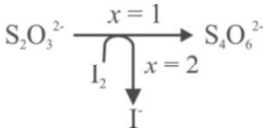
$$\underset{\text{Propaol-1}}{CH_3CH_2CH_2OH} \xrightarrow[heat]{Cu} \underset{\substack{\text{Propanal}\\ \text{(responds Fehling solution)}}}{CH_3CH_2CHO}$$

Secondary alcohols give ketones with Cu.

$$\underset{\text{Propaol-2}}{CH_3CHOHCH_3} \longrightarrow \underset{\substack{\text{Propanone}\\ \text{(negative to Fehling solution)}}}{CH_3COCH_3}$$

13. Sol:





$\therefore \quad Fe_3O_4 + 2I^- \rightarrow Fe^{2+} + I_2$

$\therefore$ No. of moles of I_2 produced $= 10^{-2}$ mol

Let v ml 0.1 (M) $Na_2S_2O_3$ solution is required

$\therefore \quad v \times 10^{-4} = 2 \times 10^{-2}$

$\therefore \quad v = 200$ ml

14. Sol: Volume of the gold dispersed in one litre water

$$= \frac{Mass}{Density} = \frac{1.9\times10^{-4}\,g}{19\,g\,cm^{-3}} = 1\times10^{-5}\,cm^3$$

Radius of gold sol particle

$= 10nm = 10\times10^{-9}\,m = 10\times10^{-7}\,cm = 10^{-6}\,cm$

Volume of the gold sol particle $= \frac{4}{3}\pi r^3$

$$= \frac{4}{3}\times\frac{22}{7}\times(10^{-6})^3 = 4.19\times10^{-18}\,cm^3$$

No. of gold sol particle in $1\times10^{-5}\,cm^3$

$$= \frac{1\times10^{-5}}{4.19\times10^{-18}} = 2.38\times10^{12}$$

No. of gold sol particle in one mm^3

$$= \frac{2.38\times10^{12}}{10^6} = 2.38\times10^6$$

15. Sol: Sample $CuSO_4.5H_2O$

$[Cu(H_2O)_5SO_4]$

63 g of Cu = 144 g (Oxygen)

$$3.782\text{ g Cu} = \frac{144\times3.782}{63} = 8.570\text{ g (Oxygen)}$$

16. Sol: Initially $p_m = p_X^o \cdot x_X + p_Y^o \cdot x_Y$

$$\text{or } 550 = p_X^o\left(\frac{1}{1+3}\right) + p_Y^o\left(\frac{3}{1+3}\right)$$

$$\therefore \quad p_X^o + 3p_Y^o = 2200$$

When 1 mole of Y is further added to it

$$p_m = p_X^o \cdot x_X + p_Y^o \cdot x_Y$$

$$560 = p_X^o\left(\frac{1}{1+4}\right) + p_Y^o\left(\frac{4}{1+4}\right)$$

$$\therefore \quad p_X^o + 4p_Y^o = 2800$$

By Eqs. (i) and (ii), we get

$p_X^o = 400$ mm and $p_Y^o = 600$ mm

17. Sol: $H_3PO_4 \rightleftharpoons H^+ + H_2PO_4^-$

$H_2PO_4^- \rightleftharpoons H^+ + H_2PO_4^{2-}$

$HPO_4^{2-} \rightleftharpoons H^+ + PO_4^{3-}$

18. Sol: CrO_5 and H_2O will be formed

19. Sol: $Mg^{2+} + 2e^- \rightarrow Mg$

Quantity of electricity required to deposit 1.0 g of

$$\text{Mg} = \frac{2\times96500}{24}$$

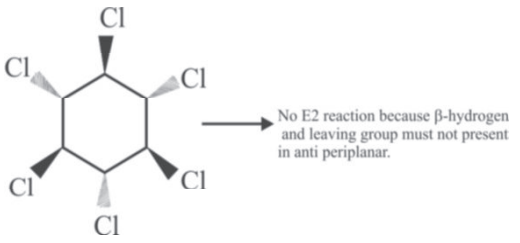
$Al^{3+} + 3e^- \rightarrow Al$

Quantity of electricity required to deposit 10.0 g of

$$\text{Al} = \frac{3\times96500}{27}\times10$$

$$\text{Cost} = \frac{3\times96500}{27}\times\frac{10\times5\times24}{2\times96500} = Rs.44.44.$$

20. Sol:



21. Sol: For acidic buffer, $pH = pK_a + \log\frac{0.1}{0.1}$

$pH = pK_a = -\log(10^{-5}) = 5$.

Rule: ABA (In acidic buffer (A), on addition of $S_B(B)$, the concentration of $W_A(A)$ decreases and that of salt increases).

Let x M of NaOH is added.

$$pH_{new} = 5 + \log\left(\frac{0.1+x}{0.1-x}\right)$$

$$6-5 = \log\left(\frac{0.1+x}{0.1-x}\right)$$

$$\left(\frac{0.1+x}{0.1-x}\right) = \text{Anti log}\,(1) = 10$$

Solve for x:

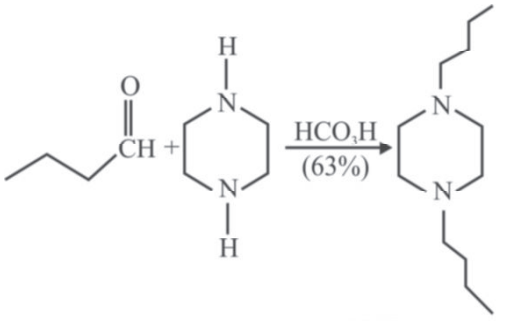
$$x = 0.082M = \frac{0.082}{1000}\times100$$

$$= 0.0082\text{ mol }(100mL)^{-1}$$

$$= 0.0082\times40g\ (100mL)^{-1} = 0.328g$$

22. Sol: According to Arrhenius equation, $k = Ae^{-E_a/RT}$ the rate constant increases exponentially with temperature.

23. Sol:



24. Sol:

$$Fe(s) \longrightarrow Fe^{2+} + 2e^-;\ \Delta G_1^o$$

$$2H^+ + 2e^- + \tfrac{1}{2}O_2 \longrightarrow H_2O(l);\ \Delta G_2^o$$

$$Fe(s) + 2H^+ + \tfrac{1}{2}O_2 \longrightarrow Fe^2 + H_2O;\ \Delta G_3^o$$

Applying, $\Delta G_1^o + \Delta G_2^o = \Delta G_3^o$

$$\Delta G_3^o = (-2F \times 0.44) + (-2F \times 1.23)$$

$$= -(2 \times 96500 \times 0.44 + 2 \times 96500 \times 1.23)$$

$$= -322310\ J$$

$$= -322\ kJ$$

25. Sol: During calcination and roasting, ore is converted to its oxide

26. Sol: Consider 1000 mL of water

Mass of 1000 mL of water $= 1000 \times 1 = 1000$ grams

$$\text{Number of moles of water} = \frac{1000}{18} = 55.5$$

$$\text{Molarity} = \frac{\text{No.of moles of water}}{\text{Volume in litre}}$$

$$= \frac{55.5}{1} = 55.5M$$

27. Sol: For Balmer series

$$\frac{1}{\lambda} = R\left[\frac{1}{2^2} - \frac{1}{n^2}\right]$$

Where $n = 3, 4, 5, ...\infty$

To obtain the limits for balmer series $n = 3$ and $n = \infty$ respectively.

$$\lambda_{max} = (n = 3) = \frac{1}{R\left[\frac{1}{2^2} - \frac{1}{3^2}\right]} = \frac{36}{5R}$$

$$= \frac{36}{5 \times 1.0968 \times 10^7} m = 6563\ \text{Å}$$

$$\lambda_{min} = (n = \infty) = \frac{1}{R\left[\frac{1}{2^2} - \frac{1}{\infty^2}\right]} = \frac{4}{R}$$

$$= \frac{4}{1.0968 \times 10^7} m = 3647\ \text{Å}$$

28. Sol: $aA \longrightarrow bB$

$$\frac{\left(\frac{-dA}{dt}\right)}{a} = \frac{\left(\frac{dB}{dt}\right)}{b} \text{ or } \frac{-dA}{dt} = \frac{a}{b} \times \frac{dB}{dt}$$

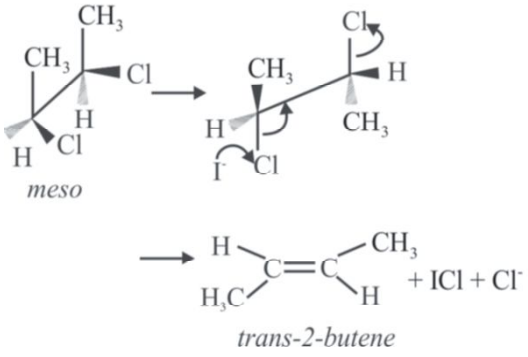
$$\log\left(\frac{-dA}{dt}\right) = \log\left(\frac{a}{b}\right) + \log\left(\frac{dB}{dt}\right)$$

Given $\log\left(\frac{-dA}{dt}\right) = \log\left(\frac{dB}{dt}\right) + 0.6020$

$$\therefore \quad \log\left(\frac{a}{b}\right) = 0.6020 = 2 \times 0.3010 = 2 \times \log 2 = \log 4$$

$\therefore \quad a : b = 4.$

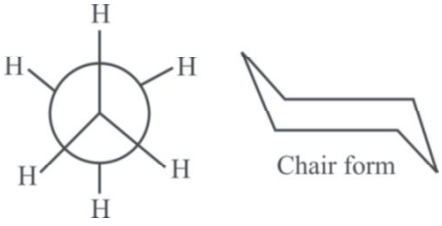
29. Sol: Iodide ion brings about dehalogenation from anti-vicinal dihalide.



30. Sol: When liquid changes into vapour, the molecules of vapour are less orderly, that is, the disorder increases or entropy increases.

31. Sol: PSCs react with chlorine nitrate and HCl to give HOCl and Cl_2.

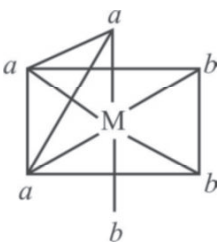
32. Sol: In ethane staggered form and in cyclohexane chair form is more stable.



33. Sol: Lower members are soluble in water and solubility decreases with increasing molecular mass because hydrophobic character increases.

34. Sol: Among the cations H^+ has the maximum conductivity due to Grotthus conduction.

35. Sol: When the three ligands (with same donor atoms) are on the same triangular face of the octahedron, the isomer is called facial or *fac* isomer.



In this complex the three ligands are on the same triangular face of the octahedron.

36. Sol: Because ΔG^o for reductions of rest three oxides $[Al_2O_3, ZnO$ and $MgO]$ are less negative than that of Cu_2O at lower temperature.

37. Sol: $V_t = V_0(1+\alpha_u t)$

$\because \quad (V_2 - V_1) = \Delta V = V_0\alpha(t_2 - t_1)$

if $t_2 - t_1 = 1^o$ then $\Delta V = \alpha V_0$

For every 1^oC increase in temperature, the volume of a given mass of an ideal gas increases by a definite fraction $\frac{1}{273.15}$ of V_0. Here V_0 is volume at 0^oC temperature.

38. Sol: State functions are those functions whose values depend only upon the initial and final states of the system and not on the path.

39. Sol: On heating water K_w increases and thus pH scale for neutrality changes from 7 to some lower value, i.e., 6.8 or 6.9 depending upon K_w values.

40. Sol: EC of $M^{3+} = [Ar]3d^{10}4s^2$

$\therefore \quad$ EC of $M = [Ar]3d^{10}4s^2, 4p^3$

The last electron enters in p-subshell hence it belongs to *p*-block.

41. Sol: $Al_2O_3 + 6Na \longrightarrow 3Na_2O(X) + 2Al;$

$Na_2O + H_2O \longrightarrow 2NaOH$

$NaOH + CO_2 \longrightarrow Na_2CO_3 + H_2O$

Note: Na_2O_2 is formed in presence of air.

42. Sol: EWG decreases basic character and EDG increases basic character

43. Sol: Ethanoic acid (CH_3COOH) and methyl methanoate $(HCOOCH_3)$ are isomers with different physical and chemical properties.

44. Sol: The atomic weight of Co, Ni and Fe are 58.933, 58.693 and 55 respectively. Therefore Co > Ni > Fe is the correct sequence of atomic weight.

45. Sol: Empirical Formula = CH_2O

Empirical formula mass = 12 + 2 + 16 = 30

mol. mass $= 2 \times V.D. = 2 \times 30 = 60$

$$n = \frac{\text{Mol. mass}}{\text{Empirical mass}} = \frac{60}{30} = 2$$

Molecular formula = (Empirical formula)$_n$

$= (CH_2O)_2 = C_2H_4O_2.$

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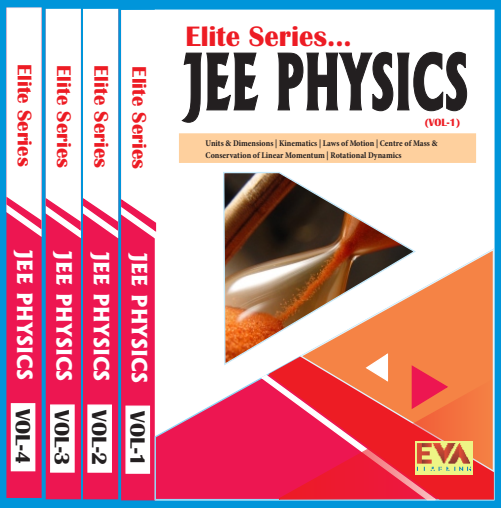

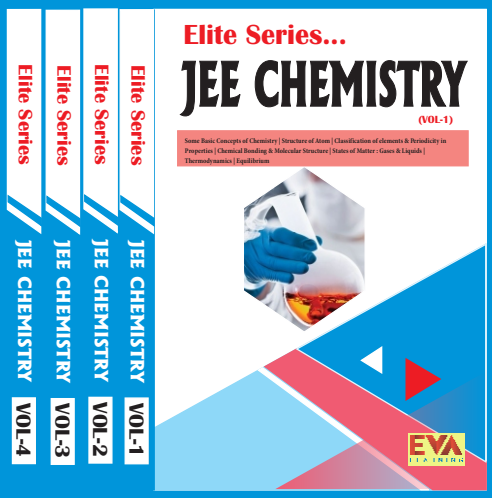

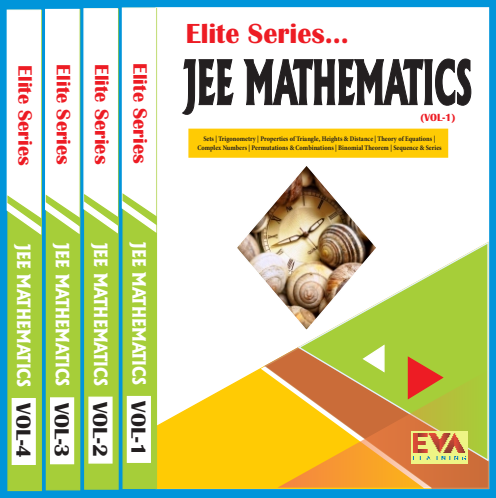

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