

# HINTS TO MULTIPLE CHOICE QUESTIONS & EVALUATION TESTS



MHT-CET

TRIUMPH

# CHEMISTRY

# MULTIPLE CHOICE QUESTIONS

BASED ON STD. XI & XII SYLLABUS OF MHT-CET

A chameleon basks in the sun. As its body temperature increases, the chemical reactions of its metabolism speed up!



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**MHT-CET TRIUMPH**  
**CHEMISTRY**

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&  
EVALUATION TESTS**

# CONTENT

Sr. No.	Textbook Chapter No.	Chapter Name	Page No.
<b>Std. XI</b>			
1	1	Some Basic Concepts of Chemistry	1
2	2	States of Matter (Gases and Liquids)	8
3	5	Redox Reactions	17
4	7	Surface Chemistry	23
5	8	Nature of Chemical Bond	29
6	9	Hydrogen	42
7	10	s-Block Elements	47
8	12	Basic Principles and Techniques in Organic Chemistry	55
9	13	Alkanes	71
<b>Std. XII</b>			
10	1	Solid State	80
11	2	Solutions and Colligative Properties	87
12	3	Chemical Thermodynamics and Energetics	106
13	4	Electrochemistry	121
14	5	Chemical Kinetics	139
15	6	General Principles and Processes of Isolation of Elements	165
16	7	p-Block Elements	171
17	8	d and f-Block Elements	181
18	9	Coordination Compounds	191
19	10	Halogen Derivatives of Alkanes and Arenes	206
20	11	Alcohols, Phenols and Ethers	227
21	12	Aldehydes, Ketones and Carboxylic Acids	251
22	13	Compounds Containing Nitrogen	276
23	14	Biomolecules	289
24	15	Polymers	299
25	16	Chemistry in Everyday Life	308
		Organic Reactions	311



## Hints



### Classical Thinking

16.  $\text{BaCl}_2 + \text{H}_2\text{SO}_4 \longrightarrow \text{HCl} + \text{BaSO}_4$   
 $\therefore 20.8 + 9.8 = 7.3 + x$   
 $x = 23.3$
21.  $\text{CH}_4 + 2\text{O}_2 \longrightarrow \text{CO}_2 + 2\text{H}_2\text{O}$   
 (1 vol.) (2 vol.) (1 vol.) (2 vol.)  
 $\therefore 1 \text{ cm}^3$  of  $\text{CH}_4$  requires  $2 \text{ cm}^3$  of  $\text{O}_2$  for its complete combustion  
 $\therefore 0.25 \text{ cm}^3$  of  $\text{CH}_4$  gives  $0.5 \text{ cm}^3$  of  $\text{O}_2$ .
26. u means unified mass.
36. Molecular mass of  $\text{H}_2 = 2 \text{ g}$   
 $2 \text{ g}$  will contain  $6.022 \times 10^{23}$  molecules of  $\text{H}_2$ .  
 $\therefore 1 \text{ g}$  of  $\text{H}_2$  will contain  $\frac{6.022 \times 10^{23}}{2}$  molecules  
 $= 3.011 \times 10^{23}$  molecules  
 $\approx 3 \times 10^{23}$  molecules
39. Molecular formula of benzene is  $\text{C}_6\text{H}_6$ .  
 $\therefore$  Molecular mass = sum of atomic weight of all the atoms  
 $\therefore$  Molecular mass =  $12 \times 6 + 6 \times 1 = 72 + 6 = 78$   
 $\therefore$  According to Avogadro's law, the gram molecule of benzene is equal to  $78 \text{ g}$  of  $\text{C}_6\text{H}_6$ .
40. Atomic mass of the element  
 $= 1.792 \times 10^{-22} \times 6.022 \times 10^{23} = 108$
41. 1 mole of ozone ( $\text{O}_3$ ) =  $48 \text{ g}$   
 $\therefore 0.5$  mole of ozone ( $\text{O}_3$ ) =  $\frac{0.5 \times 48}{1} = 24 \text{ g}$ .
42. Number of molecules =  $n \times 6.022 \times 10^{23}$   
 Now,  $n = \frac{\text{mass of oxygen}}{\text{molar mass of oxygen}} = \frac{16}{32} = 0.5$   
 $\therefore$  Number of molecules =  $0.5 \times 6.022 \times 10^{23} = 3.011 \times 10^{23}$
43. 2 gram mole of  $\text{CO}_2 \equiv 88 \text{ g}$  of  $\text{CO}_2$   
 $0.1$  mole of sucrose ( $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ ) =  $34.2 \text{ g}$  of sucrose  
 $1$  gram atom of calcium  $\equiv 40 \text{ g}$  of calcium  
 $1.5$  mole of water  $\equiv 27 \text{ g}$  of water  
 $\therefore 1.5$  mole of water weighs the least amongst the given options.

44.  $16 \text{ g O}_2$  has number of moles =  $\frac{16}{32} = \frac{1}{2}$

$14 \text{ g N}_2$  has number of moles =  $\frac{14}{28} = \frac{1}{2}$

Number of moles is same, so number of molecules is same.

46.  $V \propto n$   
 Number of moles (n)  
 $= \frac{\text{Mass of the substance}}{\text{Molar mass of the substance}}$

$\therefore n = \frac{\text{mass}}{\text{atomic mass}(M)} \quad \therefore V \propto n \propto \frac{1}{M}$

Atomic Mass of O = 16  
 Atomic Mass of N = 14

$\therefore \frac{V_{(\text{O})}}{V_{(\text{N})}} = \frac{n_{(\text{O})}}{n_{(\text{N})}} = \frac{M_{(\text{N})}}{M_{(\text{O})}}$

$\frac{V_{(\text{O})}}{V_{(\text{N})}} = \frac{14}{16} = \frac{7}{8}$

$\therefore$  The ratio is 7 : 8

49. Urea [ $\text{H}_2\text{N} - \text{CO} - \text{NH}_2$ ]

$\therefore 60 \text{ gm}$  of urea contains  $12 \text{ g}$  of carbon.

$\therefore 100 \text{ gm}$  of urea contains  $\frac{12}{60} \times 100 = 20\%$

50. In  $\text{Fe}(\text{CNS})_3 \cdot 3\text{H}_2\text{O}$

% of  $\text{H}_2\text{O} = \frac{3 \times 18}{284} \times 100 = 19\%$

51.  $\therefore 40 \text{ gm NaOH}$  contains  $16 \text{ gm}$  of oxygen

$\therefore 100 \text{ gm}$  of  $\text{NaOH}$  contains  $\frac{16}{40} \times 100 = 40\%$  oxygen.

52.

Elements	% Composition	Atomic Mass	Moles	Ratio
A	25	12.5	$\frac{25}{12.5} = 2$	$\frac{2}{2} = 1$
B	75	37.5	$\frac{75}{37.5} = 2$	$\frac{2}{2} = 1$

Hence, the simplest formula of the compound is AB.

59.  $1\text{L} = 10^{-3}\text{m}^3 = 10^3\text{cm}^3 = 1\text{dm}^3 = 10^3\text{mL}$ .



### Critical Thinking

2. Mixture of liquids may be homogeneous or heterogeneous mixtures.

4.	Physical quantity	Unit
(A)	Density	$\text{kg m}^{-3}$
(B)	Acceleration	$\text{m s}^{-2}$
(C)	Pressure	$\text{kg m}^{-1} \text{s}^{-2}$
(D)	Force	$\text{kg m s}^{-2}$

5. The magnitude of 'mega-' is  $10^6$ .

10.  $\text{N}_2 + 3\text{H}_2 \longrightarrow 2\text{NH}_3$   
 (1 vol.) (3 vol.) (2 vol.)  
 3 volumes of  $\text{H}_2$  gives 2 volumes of ammonia

$\therefore$  2 L of  $\text{H}_2$  will give =  $\frac{2 \times 2}{3}$  L of ammonia  
 = 1.33 L of ammonia

12. A molecule cannot be divided into its constituent atoms by simple methods. However, under drastic conditions, it can be decomposed into constituent atoms.

13. Isotopes are the atoms of the same element having same atomic number (i.e., containing same number of protons and electrons) but different mass number (i.e., different number of neutrons).

14. The natural abundance means percentage occurrence.

16. Molecular weight of sodium oxide ( $\text{Na}_2\text{O}$ )  
 =  $46 + 16 = 62$   
 62 gm of  $\text{Na}_2\text{O} = 1$  mole  
 620 gm of  $\text{Na}_2\text{O} = 10$  moles.

17.  $d = \frac{M}{V}$  (d = density, M = mass, V = volume)

Since  $d = 1$

So,  $M = V$

18 gm = 18 mL

18 mL =  $N_A$  molecules ( $N_A$  = Avogadro's number)

1000 mL =  $\frac{N_A}{18} \times 1000 = 55.555 N_A$ .

19.  $6.022 \times 10^{23}$  atoms of H weighs 1 g.

$\therefore$  Mass of 1 atom of hydrogen =  $\frac{1}{6.022 \times 10^{23}}$   
 =  $1.6 \times 10^{-24}$  g

20. 1 gram atom of nitrogen  $\equiv$  22.4 L of N  
 (molar volume at N.T.P.)  
 $\equiv$  11.2 L of  $\text{N}_2$

21. At S.T.P,  
 22.4 dm<sup>3</sup> of any gas  $\equiv$   $6.022 \times 10^{23}$  molecules

22. 1 mole  $\equiv$   $6.022 \times 10^{23}$  electrons  
 One electron weighs  $9.108 \times 10^{-31}$  kg

$\therefore$  1 mole of electrons weighs  
 $6.022 \times 10^{23} \times 9.108 \times 10^{-31}$  kg  
 $\therefore$  Number of moles that will weigh 1 kg  
 =  $\frac{1}{6.022 \times 10^{23} \times 9.108 \times 10^{-31}}$  moles

$\therefore$   $\frac{1}{9.108 \times 6.022} \times 10^8$  moles of electrons will weigh one kilogram.

23. 18 g of  $\text{H}_2\text{O} \equiv$  1 mole =  $3 \times N_A$  atoms  
 ( $\therefore$  Number of atoms =  $n \times N_A \times$  Atomicity)

16 g of  $\text{O}_2 \equiv \frac{1}{2}$  mole =  $2 \times \frac{1}{2} N_A$  atoms

4.4 g of  $\text{CO}_2 \equiv \frac{1}{10}$  mole  $\equiv 3 \times \frac{1}{10} \times N_A$  atoms

16 g of  $\text{CH}_4 \equiv$  1 mole =  $5 \times N_A$  atoms

$\therefore$  maximum number of atoms is present in 16 g of  $\text{CH}_4$ .

24. Number of atoms =  $n \times N_A \times$  Atomicity  
 Number of S atoms  
 =  $6.022 \times 10^{23} \times 0.2 \times 8$   
 $\approx 9.63 \times 10^{23}$

25.  $\text{CaCO}_3 \longrightarrow \text{CaO} + \text{CO}_2$   
 10 g

10 g of 90% pure  $\text{CaCO}_3 \equiv$  9 gm of  $\text{CaCO}_3$

$\therefore$  Number of moles of  $\text{CaCO}_3$   
 =  $\frac{\text{Mass of CaCO}_3 \text{ in gm}}{\text{Molecular weight of CaCO}_3 \text{ in gm}}$

$\therefore$  Number of moles of  $\text{CaCO}_3 = \frac{9}{100}$   
 = 0.09 mole

$\text{CaCO}_3 \equiv \text{CO}_2 = 0.09$  mole

At NTP Vol.  $\text{CO}_2 = 0.09 \times 22.4$   
 = 2.016 L.

27. Molecular mass of  $\text{CH}_3\text{COOH} = 60$

$\therefore$  % of C in  $\text{CH}_3\text{COOH} = \frac{24}{60} \times 100 = 40\%$

Similarly,

Molecular weight of  $\text{C}_6\text{H}_{12}\text{O}_6 = 180$

$\therefore$  % of C in  $\text{C}_6\text{H}_{12}\text{O}_6 = \frac{72}{180} \times 100 = 40\%$



28. Molecular mass of Urea i.e.,  $\text{H}_2\text{N}-\overset{\text{O}}{\parallel}{\text{C}}-\text{NH}_2$  is 60.

urea has 2 N atoms.

$$\therefore \text{mass of N} = 2 \times 14 = 28$$

$$\therefore \% \text{ of N in urea} = \frac{28}{60} \times 100 = 46.6 \%$$

29. % of X = 75.8

$$\therefore \% \text{ of Y} = 100 - 75.8 = 24.2$$

Element	% Composition	Atomic ratio	Simplest ratio
X	75.8	$\frac{75.8}{75} = 1.011$	$\frac{1.011}{1.011} = 1$
Y	24.2	$\frac{24.2}{12} = 2.02$	$\frac{2.02}{1.011} = 1.99 \approx 2$

Thus, empirical formula of the compound is  $\text{XY}_2$ .

30. Empirical formula mass = CH = 12 + 1 = 13  
Molecular mass = 78

$$r = \frac{\text{Molecular mass}}{\text{Empirical mass}} = \frac{78}{13} = 6$$

$$\begin{aligned} \text{Molecular formula} &= r \times \text{Empirical formula} \\ &= 6 \times \text{CH} \\ &= \text{C}_6\text{H}_6 \end{aligned}$$

31. Since, 0.0835 mole of compound contains 1 gm of hydrogen

$$\therefore 1 \text{ g mole of compound contain} = \frac{1}{0.0835} = 11.97 \approx 12 \text{ g of hydrogen.}$$

12 g of H is present in  $\text{C}_2\text{H}_{12}\text{O}_6$

32.  $\text{CH}_4 + 2\text{O}_2 \longrightarrow \text{CO}_2 + 2\text{H}_2\text{O}$   
(12+4) (2×32) (12+32) (2×18)  
16 g 62 g 44 g 36 g

16 g  $\text{CH}_4 \equiv 44$  g of  $\text{CO}_2$

$$33 \text{ g of } \text{CO}_2 \equiv \frac{33 \times 16}{44}$$

$$= 12 \text{ g of } \text{CH}_4$$

$$\text{Number of moles} = \frac{12}{16}$$

$$= 0.75 \text{ moles of methane}$$

33.  $4\text{Al} + 3\text{O}_2 \longrightarrow 2\text{Al}_2\text{O}_3$   
(108 g) (96 g) (204 g)

108 g Al combines with 96 g of  $\text{O}_2$

$$27 \text{ g Al combines with } \frac{96 \times 27}{108} = 24 \text{ g}$$

34.  $\text{N}_2 + 3\text{H}_2 \rightleftharpoons 2\text{NH}_3$   
10 mL 30 mL 20 mL

Thus, ammonia obtained in the reversible reaction of  $\text{NH}_3$  is 20 mL.

35.  $3\text{CaCO}_3 \xrightarrow{\Delta} 3\text{CaO} + 3\text{CO}_2$

$\therefore$  Molecular mass of CaO is = 40 + 16 = 56

$\therefore$  3 moles of CaO is formed in the reaction.

$\therefore$   $3 \times 56 = 168$  g of CaO is formed.

36.  $2\text{H}_2 + \text{O}_2 \longrightarrow 2\text{H}_2\text{O}$

Ratio of mole of reactant,  $\text{H}_2 : \text{O}_2 = 2 : 1$

Actual amount 3 g of  $\text{H}_2$  and 29 g of  $\text{O}_2$ .

$$\frac{3}{2} = 1.5 \text{ mol of } \text{H}_2 \text{ and } \frac{29}{32} = 0.91 \text{ mol of } \text{O}_2.$$

$$\text{Ratio of actual moles of } \text{H}_2 : \text{O}_2 = \frac{1.5}{0.91} = 1.66 : 1$$

Theoretical ratio of moles of  $\text{H}_2 : \text{O}_2 = 2 : 1$

Actual ratio of moles of  $\text{H}_2 : \text{O}_2 = 1.66 : 1$

Hence,  $\text{H}_2$  is limiting reactant and  $\text{O}_2$  is excess reactant.

Now, 2 mol  $\text{H}_2$  give 2 mol  $\text{H}_2\text{O}$ .

$\therefore$  1.5 mol  $\text{H}_2$  will give 1.5 mol  $\text{H}_2\text{O}$ .

37. Baking soda or sodium hydrogen carbonate ( $\text{NaHCO}_3$ ) is a compound. Diamond and charcoal are different forms of the element carbon. 22 carat gold is an alloy of gold with other metals (mainly copper). Hence, it is a mixture.

38. In compound B, 32 parts of X react with 84 parts of Y.

$\therefore$  In compound B, 16 parts of X react with 42 parts of Y.

In compound C, 16 parts of X react with  $x$  parts of Y.

The ratio of masses of Y, which combine with fixed mass of X in compounds B and C, is 3:5.

B	42	3
C	$x$	5

$$\therefore x = \frac{42 \times 5}{3} = 70$$



### Competitive Thinking

4. Molecular weight of  $\text{C}_{60}\text{H}_{122}$

$$= 12 \times 60 + 122 \times 1$$

$$= 720 + 122 = 842$$

$\therefore$   $6 \times 10^{23}$  molecules = 842 g



- 1 molecule =  $\frac{842}{6 \times 10^{23}}$   
 $= 140.33 \times 10^{-23}$   
 $= 1.4 \times 10^{-21}$  g
5. Atomic mass =  $\frac{10 \times 19 + 81 \times 11}{100}$   
 $= \frac{1081}{100} = 10.81$
6. Average atomic mass  
 $= \frac{200 \times 90 + 199 \times 8 + 202 \times 2}{100} = 199.96 \approx 200$
7. Molecular mass of  $\text{NH}_3 = 14 + (3 \times 1) = 17$   
 Number of moles =  $\frac{4.25}{17} = 0.25$   
 Number of molecules of  $\text{NH}_3 = 0.25 \times N_A$   
 $= 1.506 \times 10^{23}$  molecules  
 One molecule of  $\text{NH}_3$  contains 4 atoms.  
 $\therefore 1.506 \times 10^{23}$  molecules will contain  
 $= 1.506 \times 10^{23} \times 4$   
 $= 6.024 \times 10^{23}$  atoms  $\approx 6 \times 10^{23}$  atoms.
8.  $6.022 \times 10^{23}$  dioxygen molecules are present in 1 mole i.e., 32 g of dioxygen.  
 $\therefore 1.8 \times 10^{22}$  dioxygen molecules will be present in  $\frac{1.8 \times 10^{22} \times 32}{6.022 \times 10^{23}} = 0.96$  g of dioxygen.
9. Number of moles in 4.4 g of  $\text{CO}_2$   
 $= \frac{4.4}{44} = 0.1$   
 Number of oxygen atoms in 1 mole of  $\text{CO}_2 = 2 \times N_A$   
 $\therefore$  Number of oxygen atoms in 0.1 mole of  $\text{CO}_2$   
 $= 0.1 \times 2 \times N_A$   
 $= 0.2 \times 6.022 \times 10^{23}$   
 $= 1.20 \times 10^{23}$
10. Volume occupied by 1 mole of any gas at STP  
 $= 22.4 \text{ dm}^3$   
 $\therefore$  Volume occupied by 4.4 g of  $\text{CO}_2$  i.e., 0.1 mole of  $\text{CO}_2$  at STP  $= 2.24 \text{ dm}^3 = 2.24 \text{ L}$
11. Number of atoms  
 $= n \times N_A \times \text{Atomicity}$   
 $= 0.1 \times N_A \times 3$  ( $\because$  It's a triatomic gas)  
 $= 6.02 \times 10^{22} \times 3$   
 $= 18.06 \times 10^{22}$   
 $= 1.806 \times 10^{23}$
12. Total number of atoms in molecule  
 $= n \times N_A \times \text{Atomicity}$   
 Atomicity of  $\text{NH}_3$ ,  $\text{O}_2$ ,  $\text{H}_2$  and He molecules are 4, 2, 2 and 1 respectively.  
 17 g of  $\text{NH}_3 = 4 \times N_A$  atoms  
 $\therefore 4.25$  g of  $\text{NH}_3 = \left(\frac{4.25}{17}\right) \times 4 \times N_A = N_A$  atoms  
 32 g of  $\text{O}_2 = 2 \times N_A$  atoms  
 $\therefore 8$  g of  $\text{O}_2 = \frac{2 \times 8}{32} \times N_A = \frac{N_A}{2}$  atoms  
 2 g of  $\text{H}_2 = 2 \times N_A$  atoms  $= 2N_A$  atoms  
 4 g of He  $= N_A$  atoms  
 Thus, the system that contains 2 g of  $\text{H}_2$  has maximum numbers of atoms.
13. 1 mole of water = 18 g of water  
 $= 6.022 \times 10^{23}$  molecules of water  
 $\therefore 18$  moles of water =  $18 \times 6.022 \times 10^{23}$  molecules of water  
 $= 1.08396 \times 10^{25}$  molecules of water
14. Since, 1 mole of  $\text{BaCO}_3$  contains 3 moles of oxygen  
 $\therefore 1.5$  moles of oxygen  $= \frac{1}{3} \times 1.5 = \frac{1}{2} = 0.5$  moles of  $\text{BaCO}_3$
15. 1 L of air = 1000 mL = 1000 cc.  
 1000 cc of air contains 210 cc of  $\text{O}_2$   
 1 mole = 22.4 L = 22400 cc.  
 $\therefore$  number of moles of  $\text{O}_2 = \frac{210}{22400} = 0.0093$  moles.
16. 22.4 L of water contains  $N_A$  molecules  
 22400 mL of water contains  $N_A$  molecules  
 1 mL of water i.e., 20 drops contains  $\frac{N_A}{22400}$  molecules  
 $\therefore 1$  drop contains  $\frac{N_A}{22400 \times 20} = \frac{6.022 \times 10^{23}}{448 \times 10^3}$   
 $= 1.344 \times 10^{18}$
17. Molecular weight of  $\text{PbO} = 207.2 + 16 = 223.2$   
 Molecular weight of  $\text{PbCl}_2 = 207.2 + 2(35.5) = 278.2$   
 223.2 g of  $\text{PbO}$  gives 278.2 g of  $\text{PbCl}_2$   
 $\therefore 6.5$  g of  $\text{PbO}$  will give  $= \frac{6.5 \times 278.2}{223.2}$   
 $= 8.102$  g of  $\text{PbCl}_2$   
 $\therefore$  moles of  $\text{PbCl}_2$  obtained  $= \frac{8.102}{278.2} = 0.029$  moles.



18. Since, 0.5 g Se  $\equiv$  100 gm peroxidase anhydrous enzyme  
 $\therefore 78.4 \text{ g Se} = \frac{100 \times 78.4}{0.5} = 1.568 \times 10^4$   
 Minimum molecular mass of peroxidase anhydrous enzyme means molecule atleast contains one selenium atom.
19. Empirical formula of an acid is  $\text{CH}_2\text{O}_2$   
 (Empirical formula)  $\times n =$  Molecular formula  
 $n =$  whole number multiple i.e., 1,2,3,4.....  
 If  $n = 1$  molecular formula  $\text{CH}_2\text{O}_2$ .
20. C = 24 g, H = 4 g, O = 32 g  
 So, Molecular formula =  $\text{C}_2\text{H}_4\text{O}_2$   
 So, Empirical formula =  $\text{CH}_2\text{O}$   
 (Simplest formula).
21. Relative number of atoms of  
 $\text{C} = \frac{38.71}{12} = 3.22$   
 $\text{H} = \frac{9.67}{1} = 9.67$   
 $\text{O} = \frac{51.62}{16} = 3.22$   
 Simplest ratio : C : H : O  
 $\frac{3.22}{3.22} : \frac{9.67}{3.22} : \frac{3.22}{3.22}$   
 $1 : 3 : 1$   
 $\therefore$  Empirical formula =  $\text{CH}_3\text{O}$
22.  $\text{H}_2\text{O} \longrightarrow \text{H}_2 + \frac{1}{2} \text{O}_2$   
 $\text{H}_2 : \text{O}_2 = 2 : 1$   
 $\therefore$  for 2.24  $\text{dm}^3$  of  $\text{O}_2$ ,  $\text{H}_2$  liberated will be 4.48  $\text{dm}^3$
23.  $\text{BaCO}_3 \longrightarrow \text{BaO} + \text{CO}_2 \uparrow$   
 Molecular weight of  $\text{BaCO}_3$   
 $= 137 + 12 + (3 \times 16)$   
 $= 197$   
 22.4 L of  $\text{CO}_2$  is released by 197 g of  $\text{BaCO}_3$   
 $\therefore$  x L of  $\text{CO}_2$  is released by 9.85 g of  $\text{BaCO}_3$   
 $x = \frac{22.4 \times 9.85}{197} = 1.12 \text{ L}$
24.  $\text{BCl}_3 + \frac{3}{2} \text{H}_2 \longrightarrow \text{B} + 3\text{HCl}$   
 $\frac{3}{2}$  moles of  $\text{H}_2 \equiv$  1 mole of B  
 number of moles of B =  $\frac{21.6}{10.8} = 2$   
 $\therefore$  x moles of  $\text{H}_2 \equiv$  2 moles of B  
 moles of  $\text{H}_2 = 3$   
 volume =  $3 \times 22.4 = 67.2 \text{ L}$
25.  $\text{C}_3\text{H}_8 + 5\text{O}_2 \longrightarrow 3\text{CO}_2 + 4\text{H}_2\text{O}$   
 (1 vol) (5 vol)  
 $\therefore$  1 L of propane gas will require 5 L of  $\text{O}_2$
26.  $2\text{Al}_{(s)} + 6\text{HCl}_{(aq)} \longrightarrow 2\text{Al}_{(aq)}^{3+} + 6\text{Cl}_{(aq)}^- + 3\text{H}_{2(g)}$   
 For each mole of HCl reacted  $\frac{1}{2}$  mole of  $\text{H}_2$  is formed.  
 $\therefore$  volume of  $\text{H}_2$  gas formed at STP per mole of HCl is  $= \frac{1}{2} \times 22.4 = 11.2 \text{ L}$ .
27. 1 mole of  $\text{Mg}_3(\text{PO}_4)_2$  gives 8 moles of  $\text{O}_2$   
 x moles will give 0.25 moles of  $\text{O}_2$   
 $x = \frac{0.25}{8} = 3.125 \times 10^{-2}$  moles.
28.  $\text{M}_2\text{CO}_3 + 2\text{HCl} \longrightarrow 2\text{MCl} + \text{H}_2\text{O} + \text{CO}_2$   
 From balanced chemical equation,  
 1 mol  $\text{M}_2\text{CO}_3 \equiv$  1 mol  $\text{CO}_2$   
 From the data given in the problem,  
 1 g  $\text{M}_2\text{CO}_3 \equiv$  0.01186 mol  $\text{CO}_2$   
 Now,  $\frac{1 \text{ g } \text{M}_2\text{CO}_3}{0.01186 \text{ mol } \text{CO}_2} \times \frac{1 \text{ mol } \text{CO}_2}{1 \text{ mol } \text{M}_2\text{CO}_3}$   
 $= 84.3 \text{ g mol}^{-1} \text{ M}_2\text{CO}_3$   
 Thus, molar mass of  $\text{M}_2\text{CO}_3 = 84.3 \text{ g mol}^{-1}$ .
29.  $2\text{H}_{2(g)} + \text{O}_{2(g)} \longrightarrow 2\text{H}_2\text{O}_{(g)}$   
 Ratio of moles of reactants,  $\text{H}_2 : \text{O}_2 = 2 : 1$   
 Actual amount of reactants: 10 g  $\text{H}_2$  and 64 g  $\text{O}_2$   
 Actual moles of reactants: 5 mol  $\text{H}_2$  and 2 mol  $\text{O}_2$   
 Ratio of actual moles of reactants,  
 $\text{H}_2 : \text{O}_2 = 5 : 2 = 2.5 : 1$   
 $\therefore$  The limiting reactant is  $\text{O}_2$ .  
 Now, 1 mole of oxygen gives 2 moles of water. Hence, 2 moles of oxygen will give 4 moles of water.
30.  $2\text{Mg} + \text{O}_2 \longrightarrow \text{MgO}$   
 (2 $\times$ 24) (32)  
 48 g of Mg requires 32 g of  $\text{O}_2$   
 $\therefore$  0.56 g of  $\text{O}_2$  requires  $= \frac{0.56 \times 48}{32}$   
 $= 0.84 \text{ g of Mg}$   
 $\therefore$  Mg left =  $1 - 0.84 = 0.16 \text{ g}$





31. Both  $O_2$  and  $N_2$  are diatomic.  
 $\therefore$  ratio of their number of molecules will be equal to ratio of their number of moles.

$$\text{number of moles of } O_2 = \frac{\text{weight of } O_2}{32}$$

$$\text{number of moles of } N_2 = \frac{\text{weight of } N_2}{28}$$

number of moles of  $O_2$  = number of moles of  $N_2$

$$\frac{\text{weight of } O_2}{32} = \frac{\text{weight of } N_2}{28}$$

$$\frac{1}{32} : \frac{4}{28}$$

$$\frac{1}{32} : \frac{1}{7}$$

$\therefore$  ratio is 7 : 32

32. Total weight of person = 75 kg

$$\text{Mass due to } ^1\text{H atoms} = 75 \times \frac{10}{100} = 7.5 \text{ kg}$$

Mass of  $^2\text{H}$  atom is twice that of  $^1\text{H}$  atom.

All  $^1\text{H}$  atoms are replaced by  $^2\text{H}$  atoms.

Hence, mass increase is twice i.e., by 7.5 kg.

33.  $\text{MgCO}_{3(s)} \rightarrow \text{MgO}_{(s)} + \text{CO}_{2(g)}$

Molar mass of  $\text{MgCO}_3 = 84 \text{ g mol}^{-1}$

- $\therefore$  Number of moles of  $\text{MgCO}_3 = \frac{20}{84} = 0.238 \text{ mol}$

$\therefore$  1 mole  $\text{MgCO}_3$  gives 1 mole  $\text{MgO}$

$\therefore$  0.238 mole  $\text{MgCO}_3$  will give 0.238 mole  $\text{MgO}$ .

Molar mass of  $\text{MgO} = 40 \text{ g mol}^{-1}$

$\therefore$  0.238 mole  $\text{MgO} = 40 \times 0.238 = 9.52 \text{ g MgO}$

$\therefore$  Theoretical yield of  $\text{MgO} = 9.52 \text{ g}$

Practical yield of  $\text{MgO}$  is 8.0 g

$\therefore$  Percentage purity =  $\frac{8}{9.52} \times 100 = 84\%$

34. 100 g of haemoglobin contains 0.33 g of Fe

$\therefore$  67200 g of haemoglobin contains

$$= \frac{67200 \times 0.33}{100}$$

$$= 221.76 \text{ g of Fe.}$$

$$\text{Number of atoms of Fe} = \frac{221.76}{56} = 3.96 \approx 4$$

35. When Avogadro number is  $6.022 \times 10^{23} \text{ mol}^{-1}$ , the mass of 1 mol of carbon = 12 g

$\therefore$  Mass of 1 mol of carbon when Avogadro number is  $6.022 \times 10^{20} \text{ mol}^{-1}$

$$= \frac{12 \times 6.022 \times 10^{20}}{6.022 \times 10^{23}} = 12 \times 10^{-3} \text{ g}$$

Thus, the mass of 1 mol of carbon is changed.

36. 0.1 mol of  $\text{XY}_2 = 10 \text{ g}$

$\therefore$  1 mol of  $\text{XY}_2 = 100 \text{ g}$

i.e., Molecular weight of  $\text{XY}_2 = 100$

0.05 mol of  $\text{X}_3\text{Y}_2 = 9 \text{ g}$

$\therefore$  1 mol of  $\text{X}_3\text{Y}_2 = 180 \text{ g}$

i.e., Molecular weight of  $\text{X}_3\text{Y}_2 = 180$

Let atomic weights of X and Y be x and y respectively.

$$\therefore x + 2y = 100 \quad \dots(1)$$

$$3x + 2y = 180 \quad \dots(2)$$

Subtracting (1) from (2),

$$2x = 180 - 100$$

$$\therefore x = 40$$

Substituting  $x = 40$  in (1),

$$40 + 2y = 100$$

$$\therefore y = 30$$



### Evaluation Test

2. Molecular mass of  $\text{N}_2\text{O}_4 = 28 + 64 = 92 \text{ g}$

$\therefore$  number of moles =  $\frac{54}{92} = 0.59 \text{ moles}$

Molecular mass of  $\text{CO}_2 = 12 + 32 = 44 \text{ g}$

$\therefore$  number of moles =  $\frac{28}{44} = 0.64 \text{ moles}$

Molecular mass of  $\text{H}_2\text{O} = 2 + 16 = 18 \text{ g}$

$\therefore$  number of moles =  $\frac{36}{18} = 2 \text{ moles}$

Molecular mass of  $\text{C}_2\text{H}_5\text{OH} = 24 + 6 + 16 = 46$

$\therefore$  number of moles =  $\frac{46}{46} = 1 \text{ mole}$

$\therefore$  Water has more moles.

$\therefore$  Largest number of molecules is present in 36 g of water.

3. Mass of  $6 \times 10^{23}$  molecules of water = 18 g

$$\begin{aligned} \text{Mass of 1 molecule of water} &= \frac{18}{6 \times 10^{23}} \\ &= 3 \times 10^{-23} \text{ g} \\ &= 3 \times 10^{-26} \text{ kg.} \end{aligned}$$



5. I. Mass of 1 molecule of O =  $\frac{32}{N_A}$   
 $= \frac{32}{6.023} \times 10^{-23}$
- II. Mass of 1 atom of N =  $\frac{14}{N_A} = \frac{14}{6.023} \times 10^{-23}$
- III. Mass of  $1 \times 10^{-10}$  mole of O<sub>2</sub> =  $32 \times 10^{-10}$
- IV. Mass of  $1 \times 10^{-10}$  mole of Cu =  $63 \times 10^{-10}$
- $\therefore \frac{14}{6.023} \times 10^{-23} < \frac{32}{6.023} \times 10^{-23} < 32 \times 10^{-10} < 63 \times 10^{-10}$
- Therefore, the correct order of increasing masses for given species is II < I < III < IV.
6. 
$$\begin{array}{ccccccc} \text{C}_2\text{H}_4 & + & 2\text{O}_2 & \longrightarrow & 2\text{CO}_2 & + & 2\text{H}_2\text{O} \\ (2 \times 12) + 4 & & 2 \times 32 & & & & \\ 28 \text{ g} & & 64 \text{ g} & & & & \end{array}$$
- 28 g of ethylene requires 64 g of O<sub>2</sub>
- $\therefore$  2.8 kg of ethylene will require  
 $= \frac{2.8 \text{ kg} \times 64 \text{ g}}{28 \text{ g}} = 6.4 \text{ kg of O}_2$
7. 
$$\begin{array}{ccccccc} 2\text{PH}_{3(\text{g})} & \longrightarrow & 2\text{P}_{(\text{s})} & + & 3\text{H}_{2(\text{g})} \\ 2\text{vol} & & 0 & & 3\text{vol} \\ 100 \text{ mL} & & & & x \end{array}$$
- 2 vol. of PH<sub>3</sub> gives 3 vol. of H<sub>2</sub>
- $\therefore$  100 mL of PH<sub>3</sub> gives x mL of H<sub>2</sub>
- $x = \frac{100 \times 3}{2} = 150 \text{ mL of H}_2$
- change in volume = 150 – 100 = 50 mL increase
8. Density =  $\frac{\text{mass}}{\text{volume}}$
- At STP, 1 mole of any gas will occupy 22.4 L of volume.
- mass of 1 mole of gas = molecular mass
- $\therefore$  density =  $\frac{45}{22.4} = 2.008 \approx 2 \text{ g/L}$ .
9. 1 molecule of PCl<sub>3</sub>  $\equiv$  4 atoms
- $\therefore$  1 mole i.e., Avogadro number (N<sub>A</sub>) of PCl<sub>3</sub> molecules will contain 4  $\times$  N<sub>A</sub> atoms.
- $\therefore$  1.4 moles of PCl<sub>3</sub> = 4  $\times$  1.4  $\times$  N<sub>A</sub> atoms  
 $= 3.372 \times 10^{24}$  atoms
10.  $4\text{NH}_{3(\text{g})} + 5\text{O}_{2(\text{g})} \longrightarrow 4\text{NO}_{(\text{g})} + 6\text{H}_2\text{O}_{(\text{g})}$
- 4 moles of NH<sub>3</sub> reacts with 5 moles of O<sub>2</sub>
- $\therefore$  1 mole of NH<sub>3</sub> will react with  $\frac{5}{4}$  moles of O<sub>2</sub>  
 i.e., 1.25 moles of O<sub>2</sub>.
- $\therefore$  only 1 mole of O<sub>2</sub> is available, all the O<sub>2</sub> will be consumed.

11.  $\text{S} + \text{O}_2 \longrightarrow \text{SO}_2$   
 1 mole of O<sub>2</sub> gives 1 mole of SO<sub>2</sub>  
 5 moles of O<sub>2</sub> will give 5 moles of SO<sub>2</sub>  
 Molecular mass of SO<sub>2</sub> = 32 + 2  $\times$  16 = 64  
 $\therefore$  mass of SO<sub>2</sub> formed = 64  $\times$  5 = 320 g
12. 14 g of CO =  $\frac{14}{28} = 0.5$  mole.  
 1 mole of CO occupies 22.4 L at NTP  
 $\therefore$  0.5 mole will occupy 11.2 L
13. 1 molecule of CO contains 1 oxygen atom  
 $\therefore$   $6.02 \times 10^{24}$  CO molecules contain  
 $6.02 \times 10^{24}$  oxygen atoms.  
 1 gram atom =  $6.02 \times 10^{23}$  atoms  
 $\therefore$   $6.02 \times 10^{24}$  oxygen atoms = 10 gram atom  
 of oxygen.
14. A hydrocarbon contains H and C only.  
 % of carbon = 80%  
 $\therefore$  % of hydrogen = 20%
- Relative number of carbon atoms =  $\frac{80}{12} = 6.66$
- Relative number of hydrogen atoms =  $\frac{20}{1} = 20$
- Simplest ratio =  $\frac{6.66}{6.66} : \frac{20}{6.66} = 1 : 3$ .
- $\therefore$  Empirical formula = CH<sub>3</sub>
18. The SI unit of mass is 'kilogram' and not 'gram'.
19. According to the given data, reactant B is the limiting reagent. Hence, the amount of C formed will be 3 moles.
20. In first experiment:  
 2.70 g of copper oxide contain 2.16 g of copper.  
 % of copper =  $2.16 / 2.70 \times 100 = 80 \%$   
 In second experiment:  
 1.83 g of copper oxide contain 1.46 g of copper.  
 % of copper =  $1.46 / 1.83 \times 100 = 79.8 \%$   
 Therefore, percentage of copper in copper oxide is approximately 80 %.  
 Since the percentage of copper in both the sample of copper oxide is nearly same, the above data illustrates the law of definite proportion.



## Hints



### Classical Thinking

7. Gases do not have definite shape and volume. Their volume is equal to the volume of the container.
20. Krypton, an inert gas, exists as a monoatomic gas. Ozone is a triatomic gas whereas fluorine and hydrogen are diatomic gases.
23.  $^{\circ}\text{F} = \frac{9}{5}^{\circ}\text{C} + 32 = \frac{9}{5}(0) + 32 = 32$
25. The SI unit of pressure is Newton per square meter ( $\text{Nm}^{-2}$ ). It is called Pascal (Pa).
33. According to Boyle's law, at a constant temperature for a given mass of an ideal gas, pressure is inversely proportional to the volume.
- $$P \propto \frac{1}{V}$$
- $$\therefore P \propto \frac{1}{(m/d)} \qquad \therefore P \propto \frac{d}{m}$$
- $$\therefore P \propto d (\because m = \text{constant})$$
37. Temperature in K =  $-10 + 273 = 263$  K
38. initial volume =  $V_1$   
final volume =  $V_2 = 2V_1$   
initial temperature =  $T_1 = 0^{\circ}\text{C} = 273.15$  K  
final temperature =  $T_2$
- $$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$
- $$T_2 = \frac{T_1 \times V_2}{V_1} = \frac{273.15 \times 2V_1}{V_1} = 546.30 \text{ K}$$
- $$T_2 = 546.30 \text{ K} = 546.30 - 273.15 = 273.15^{\circ}\text{C}$$
39.  $V_1 = V_0$   
 $T_1 = 273$  K  
 $T_2 = 10^{\circ}\text{C} = 10 + 273 = 283$  K
- $$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$
- $$V_2 = \frac{T_2 \times V_1}{T_1} = \left(\frac{283}{273}\right)V_0$$

$$42. \frac{T_1}{T_2} = \frac{300}{600} = \frac{1}{2} \text{ and } P_2 = 2P_1 \text{ i.e., } \frac{P_1}{P_2} = \frac{1}{2}$$

$$\therefore \frac{P_1}{P_2} = \frac{T_1}{T_2}$$

According to Gay Lussac's law this happens when  $V$  is constant.

$$\therefore V \text{ will remain same i.e., } 5 \text{ L}$$

44. One mole of a pure gas always occupies  $22.4 \text{ dm}^3$  at STP.

$$50. T = \frac{P \times V}{n \times R} = \frac{2.46 \text{ atm} \times 10 \text{ L}}{1 \text{ mol} \times 0.0821 \text{ L atm mol}^{-1} \text{ K}^{-1}} = 299.63 \text{ K}$$

51. Dispersion forces increase with the mass of the molecule. Among  $\text{H}_2$ ,  $\text{Cl}_2$ ,  $\text{O}_2$  and  $\text{N}_2$ ,  $\text{Cl}_2$  has high molecular mass. So  $\text{Cl}_2$  is easy to liquefy.

59. The pressure exerted by a gas is due to collisions of gas molecules with the walls of the container.

72. According to Charles' law,  $V \propto T$ .



### Critical Thinking

3. Solids are also non-crystalline in nature.
6. Intermolecular forces of attraction keep the molecules together. Intramolecular forces of attraction hold the constituent atoms of the molecule intact in the molecule. This is due to formation of chemical bonds between the atoms of the molecule. So, intermolecular force of attraction are much smaller than the intramolecular force of attraction.
7. Molecular attraction keeps the molecules together while the thermal energy provides motions to the molecules and increases the tendency to escape from attractive forces of neighbouring molecules. In gaseous state, the molecules have least intermolecular attraction and highest kinetic energy as compared to that in solid and liquid state. So in gaseous state thermal energy is far greater than the molecular attraction.
11. Strength of ion-dipole interaction depends on charge and size of the ion. Smaller the size of the ion, stronger is the interaction. Cations being smaller in size than anions,  $\text{Na}^+ - \text{H}_2\text{O}$  interaction will be stronger than  $\text{Cl}^- - \text{H}_2\text{O}$  interaction.



12. On dissolution of NaCl in water, almost complete dissociation of NaCl and formation of  $\text{Na}^+$  (cation) and  $\text{Cl}^-$  (anion) takes place.  $\text{Na}^+$  and  $\text{Cl}^-$  ions are separated from each other and both undergo process of hydration.
13. Higher magnitude of charge along with smaller size of the ion leads to concentration of charge. Hence, such a hydrated ion will show strong ion-dipole interaction. Among  $\text{Na}^+$  and  $\text{K}^+$ ,  $\text{Na}^+$  is smaller as it has one orbit less as compared to  $\text{K}^+$ .  $\text{Na}^+$ ,  $\text{Mg}^{2+}$  and  $\text{Al}^{3+}$  belong to the same period. As we move from left to right in a period, the atomic/ionic size decreases. Al has the smaller size and has +3 charge on it. So,  $\text{Al}^{3+}$  will show strong ion-dipole interaction on hydration.
14. In a collection of atoms, the instantaneous dipoles may induce temporary dipoles in the atoms or molecules in the vicinity and then interact with these induced dipoles. This interaction produces dispersion forces.
16. Intermolecular hydrogen bonding is seen in only those compounds, which have H-atom bonded to strong electronegative atoms like O, N, F and Cl. Hence,  $\text{H}_2\text{O}$  has strong intermolecular interactions (hydrogen bonding) among other compounds given in the options.
17. Greater the electronegativity difference between the bonding molecules, stronger will be the hydrogen bonding. Among the given molecules, HF has the greatest electronegativity difference. So, two HF molecules will have strongest hydrogen bonding than the other given options.
20.  $^{\circ}\text{F} = \frac{9}{5} ^{\circ}\text{C} + 32 = \frac{9}{5} (-40) + 32 = -40$
21. Lighter gas diffuses faster than the heavier gas. The increasing order of molar mass of the given gases is  $\text{H}_2 < \text{NH}_3 < \text{N}_2 < \text{O}_2$   
 $\therefore$  Order of diffusion is  $\text{H}_2 > \text{NH}_3 > \text{N}_2 > \text{O}_2$
23. According to Boyle's law  $PV = \text{constant}$  i.e., at constant temperature product of pressure and volume is constant.
24. From ideal gas equation,  
 $PV = nRT$   
Therefore,  
 $PV \propto T$  ( $\because n, R = \text{constant}$ )  
As temperature increases, the product of pressure and volume increases, Therefore,  
 $(PV)_3 > (PV)_2 > (PV)_1$ .
25. Given :  
 $V_1 = 100 \text{ mL}, P_1 = 720 \text{ mm}, V_2 = 84 \text{ mL}$ ,  
According to the Boyle's law  
 $P_1V_1 = P_2V_2$   
 $\therefore P_2 = \frac{P_1V_1}{V_2} = \frac{720 \times 100}{84} = 857.142$   
Hence,  $P_2 = 857.14 \text{ mm}$ .
26.  $P_1V_1 = P_2V_2$   
 $\therefore V_2 = \frac{P_1V_1}{P_2} = \frac{500 \times 50}{250} = 100 \text{ mL}$
27.  $T_1 = 12 ^{\circ}\text{C} = 12 + 273 = 285 \text{ K}$   
 $V \propto T$   
 $\therefore \frac{V_1}{T_1} = \frac{V_2}{T_2} \quad \therefore \frac{2}{285} = \frac{3.4}{T_2}$   
 $\therefore T_2 = \frac{285 \times 3.4}{2} = 484.5 \text{ K}$   
 $= 484.5 - 273 = 211.5 ^{\circ}\text{C}$
28.  $V_1 = 283 \text{ mL}, T_1 = 283 \text{ K}, T_2 = 293 \text{ K}$   
 $\frac{V_1}{V_2} = \frac{T_1}{T_2}$   
 $\therefore \frac{283}{V_2} = \frac{283}{293}$   
 $\therefore V_2 = 293 \text{ mL}$
29.  $V \propto T$   
 $\therefore \frac{V_1}{T_1} = \frac{V_2}{T_2}$   
 $\therefore \frac{1 \times 10^{-4}}{300} = \frac{V_2}{450}$   
 $\therefore V_2 = \frac{450 \times 1 \times 10^{-4}}{300} = 1.5 \times 10^{-4} \text{ dm}^3$
30.  $0 ^{\circ}\text{C} = 273 \text{ K}$   
 $273 ^{\circ}\text{C} = 546 \text{ K}$   
 $V \propto T$   
 $\therefore \frac{V_1}{T_1} = \frac{V_2}{T_2}$   
 $\therefore \frac{0.2}{273} = \frac{V_2}{546}$   
 $\therefore V_2 = \frac{546 \times 0.2}{273} = 0.4 \text{ L}$
31.  $V_2 = \frac{T_1}{T_2} \times V_1 = \frac{270 \text{ K}}{300 \text{ K}} \times 400 \text{ cm}^3 = 360 \text{ cm}^3$   
 $\therefore$  Contraction in volume  $= V_1 - V_2 = 400 - 360 = 40 \text{ cm}^3$



32.  $\frac{V_1}{T_1} = \frac{V_2}{T_2}$   
 $\therefore T_2 = \frac{T_1 V_2}{V_1} = 300 \text{ K} \times \frac{2V}{V} = 600 \text{ K}$   
 $\therefore T_2 = 600 \text{ K} = (600 - 273)^\circ\text{C} = 327^\circ\text{C}$
33. At constant pressure, according to Charles' law  
 $\frac{V_1}{T_1} = \frac{V_2}{T_2}$   
 Let,  $V_1 = x$   
 $\therefore V_2 = x + 0.1x = 1.1x$   
 Now,  $\frac{x}{T_1} = \frac{1.1x}{T_2}$   
 $\therefore T_2 = 1.1 T_1$   
 Percentage increase =  $\frac{1.1 T_1 - T_1}{T_1} \times 100$   
 $= 10\%$   
 Hence, at constant pressure, 10% increase in volume results into 10% increase in temperature.
34.  $T_1 = 273^\circ\text{C} = 273 + 273 \text{ K} = 546 \text{ K}$   
 $T_2 = 0^\circ\text{C} = 273 + 0^\circ\text{C} = 273 \text{ K}$   
 $P_1 = 1 \text{ atm}$   
 According to Gay-Lussac's law  
 $\frac{P_1}{T_1} = \frac{P_2}{T_2}$   
 $\therefore P_2 = \frac{P_1 T_2}{T_1} = \frac{1 \times 273 \text{ K}}{546 \text{ K}} \text{ atm} = \frac{1}{2} \text{ atm}.$
35. Volume and number of moles being constant,  
 Gay-Lussac's law can be given as,  $\frac{P}{T} = \frac{P_1}{T_1}$   
 $\therefore \frac{P}{T} = \frac{P_1}{2T}$   
 $\therefore P_1 = 2P$
36. The given graph represents Gay Lussac's law, which holds good at constant volume and constant number of moles. Different graphs plotted at constant volumes are called isochors.
38. In the identical vessels at constant temperature and pressure, the volume and hence, their number of moles will be same.  
 $\therefore$  The number of moles of hydrogen gas will be equal to the number of moles of argon. Hydrogen being diatomic and argon being monoatomic, the number of atoms of argon is half that of hydrogen.
39. Pressure and temperature being constant,  
 Volume  $\propto$  number of moles  
 Also, Volume  $\propto \frac{1}{\text{molecular mass}}$   
 Molecular mass of  
 HF = 1 + 19 = 20  
 HCl = 1 + 35.5 = 36.5  
 HBr = 1 + 80 = 81  
 HI = 1 + 127 = 128  
 $\therefore$  HI has the greatest molecular mass and least volume.
40. Density of a gas increases with decrease in temperature and increase in pressure.
42. The value of gas constant in calories is  $1.987 \text{ Cal K}^{-1} \text{ mol}^{-1}$ .
44.  $V = 44.8 \text{ L}$ ,  $n = 2 \text{ mol}$ ,  $T = 540 \text{ K}$ ,  
 $R = 0.0821 \text{ L atm mol}^{-1} \text{ K}^{-1}$   
 $PV = nRT$   
 $\therefore P = \frac{2 \times 0.0821 \times 540}{44.8} = 1.98 \text{ atm} \approx 2 \text{ atm}$
45.  $n = 2 \text{ mol}$ ,  $P = 3 \times 10^5 \text{ Nm}^{-2}$ ,  
 $T = 300 \text{ K}$ ,  $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$   
 $PV = nRT$   
 $\therefore V = \frac{2 \times 8.314 \times 300}{3 \times 10^5} = 0.0166 \text{ m}^3 = 16.6 \text{ dm}^3$
46.  $P = 760 \text{ mm of Hg} = 1 \text{ atm}$   
 $T = 27^\circ\text{C} = 273 + 27 = 300 \text{ K}$   
 $n = \frac{2}{32} = \frac{1}{16}$   
 $PV = nRT$   
 $V = \frac{1 \times 0.0821 \times 300}{16 \times 1} = 1.54 \approx 1.5 \text{ L}$
47. Molecular weight of  $\text{C}_4\text{H}_{10} = (4 \times 12) + (10 \times 1)$   
 $= 48 + 10 = 58$   
 $n = \frac{1}{58}$   
 $P = 1 \text{ atm}$   
 $T = 350 \text{ K}$   
 $V = \frac{nRT}{P} = \frac{\left(\frac{1}{58}\right) \times 0.082 \times 350}{1}$   
 $= 0.495 \text{ L} = 495 \text{ cm}^3$   
 $(\because 1 \text{ L} = 1 \text{ dm}^3 = 1000 \text{ cm}^3)$



$$48. \text{ Number of moles of O}_2 = \frac{16}{32} = \frac{1}{2}$$

$$\text{Number of moles of H}_2 = \frac{3}{2}$$

$$\text{Total number of moles} = \frac{3}{2} + \frac{1}{2} = 2$$

$$V = \frac{nRT}{P} = \frac{2 \times 0.082 \times 273}{1} \\ = 44.8 \text{ litres} = 44800 \text{ mL}$$

$$49. T_2 = 2T_1$$

$$P_2 = \frac{1}{2} P_1$$

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

$$\frac{V_2}{V_1} = \frac{P_1 T_2}{P_2 T_1} = \frac{2}{1} \times 2 = 4$$

$\therefore$  There will be four-fold increase in the volume of the gas.

$$50. PV = nRT, n = \frac{PV}{RT} = \frac{1 \times 145}{0.082 \times 300} = 5.8 \approx 6 \text{ mole}$$

1 mole of H<sub>2</sub> gas weighs 2 g

$\therefore$  6 moles of H<sub>2</sub> gas weighs  $6 \times 2 = 12$  g

$$51. \frac{\rho_1}{\rho_2} = \frac{1}{2}$$

$$\therefore \frac{V_2}{V_1} = \frac{1}{2} \quad (\because \rho \propto \frac{1}{V})$$

$$\frac{T_1}{T_2} = \frac{2}{1}$$

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

$$\therefore \frac{P_1}{P_2} = \frac{V_2}{V_1} \times \frac{T_1}{T_2} = \frac{1}{2} \times \frac{2}{1}$$

$$\frac{P_1}{P_2} = \frac{1}{1}$$

$\therefore$  Ratio of pressure = 1 : 1

52. According to ideal gas equation,

$$PV = nRT, n = \frac{PV}{RT}$$

$$\frac{n_A}{n_B} = \frac{\frac{P_1 V_1}{RT_1}}{\frac{P_2 V_2}{RT_2}}; \frac{n_A}{n_B} = \frac{P_1 V_1}{T_1} \times \frac{T_2}{P_2 V_2}$$

$$\frac{n_A}{n_B} = \frac{2P \times 2V}{2T} \times \frac{T}{PV}; \frac{n_A}{n_B} = \frac{2}{1}$$

Since, number of molecules is directly proportional to number of moles

$$\frac{n_A}{n_B} = \frac{\text{number of molecules of A}}{\text{number of molecules of B}} = \frac{2}{1}$$

53. Ideal gas equation,

$$PV = nRT$$

$$V = \frac{\text{mass}}{\text{density}(\rho)} = \frac{\text{given mass of ideal gas}}{\rho}$$

$$\text{Number of moles, 'n'} = \frac{\text{given mass}}{M}$$

$$P \times \frac{\text{given mass}}{\rho} = \frac{\text{given mass}}{M} RT$$

$$\frac{P}{\rho} = \frac{RT}{M} \quad \therefore \rho = \frac{PM}{RT}$$

54.  $P_1 = P, V_1 = V, T_1 = 273 + 75 = 348$  K

$$P_2 = 2P, V_2 = \frac{85}{100}$$

$$\therefore \frac{P \times V}{348} = \frac{2P \times 85V}{T_2 \times 100}$$

$$T_2 = \frac{348 \times 2 \times 85}{100}$$

$\therefore T_2 = 591.6$  K = 318.6 °C  $\approx$  319 °C

56.  $PV = znRT$

For an ideal gas  $z = 1$

$$58. z = \frac{V_{\text{real}}}{V_{\text{ideal}}} = \frac{V_0}{V_i}$$

65. Kinetic energy will also remain constant if temperature is constant.

68. root mean square speed  $u = \sqrt{\frac{3RT}{M}}$

$$\text{average speed} = v = \sqrt{\frac{8RT}{\pi M}}$$

$$u : v = \sqrt{\frac{3RT}{M}} : \sqrt{\frac{8RT}{\pi M}} \\ = \sqrt{3} : \sqrt{\frac{8}{\pi}} = 1.0861 : 1$$

$$70. u_{\text{rms}} = \sqrt{\frac{3RT}{M}}$$

$$30\sqrt{R} = \sqrt{\frac{3RT}{M}}$$

Squaring on both the sides

$$30 \times 30 \times R = \frac{3 \times R \times 300}{M}$$

( $\because T = 27 + 273 = 300$  K)

$$M = 1 \text{ g} = 0.001 \text{ kg}$$



71.  $T_1 = 10^\circ\text{C} = 283\text{ K}$   
 $T_2 = 20^\circ\text{C} = 293\text{ K}$   
 $\text{K.E}_1 = \frac{3RT_1}{2}$ ;  $\text{K.E}_2 = \frac{3RT_2}{2}$   
 $\frac{\text{K.E}_2}{\text{K.E}_1} = \frac{T_2}{T_1} = \frac{293}{283} = 1.03$   
 $u_1 = \sqrt{\frac{3RT_1}{M}}$ ;  $u_2 = \sqrt{\frac{3RT_2}{M}}$   
 $\frac{u_2}{u_1} = \sqrt{\frac{T_2}{T_1}} = 1.02$   
 $\therefore$  both the average kinetic energy and r.m.s velocity increases, but not significantly.
72.  $T_1 = 27^\circ\text{C} = 300\text{ K}$   
 $T_2 = 127^\circ\text{C} = 400\text{ K}$   
 $u_1 = \sqrt{\frac{3RT_1}{M}} = \sqrt{3 \times 300 \times \frac{R}{M}} = 30\sqrt{\frac{R}{M}}$   
 $u_2 = \sqrt{\frac{3RT_2}{M}} = \sqrt{3 \times 400 \times \frac{R}{M}} = 20\sqrt{\frac{3R}{M}}$   
 Relative change =  $\frac{u_2 - u_1}{u_1}$ ;  
 Relative percentage change =  $\frac{u_2 - u_1}{u_1} \times 100$   

$$\frac{u_2 - u_1}{u_1} \times 100 = \frac{20\sqrt{\frac{3R}{M}} - 30\sqrt{\frac{R}{M}}}{30\sqrt{\frac{R}{M}}} \times 100$$

$$= \frac{20\sqrt{3}\sqrt{\frac{R}{M}} - 30\sqrt{\frac{R}{M}}}{30\sqrt{\frac{R}{M}}} \times 100$$

$$= \frac{20\sqrt{3} - 30}{30} \times 100$$

$$= \frac{20 \times 1.732 - 30}{30} \times 100$$

$$= 15.5\%$$
73.  $\text{K.E.} = \frac{3}{2} nRT$   
 $= \frac{3}{2} \times \frac{1}{32} \times 8.314 \times 320$   
 $= 1.24 \times 10^2\text{ J}$
77. Molecules on the surface of liquid experience attractive forces in the downward direction.
79.  $1\text{ atm} = 10^6\text{ dynes cm}^{-2}$

80.  $P.V = \text{constant}$  at constant temperature. As temperature changes, the value of constant also changes.
81. At a particular temperature, there are always elastic collisions taking place between the gas molecules. During collisions, redistribution of kinetic energy and velocity of molecules takes place. Thus, all gas molecules do not possess same velocity.
82.  $1\text{ atmosphere} = 760\text{ torr}$



### Competitive Thinking

- The mass of a gas can be determined by weighing the container, filled with the gas and again weighing this container after removing the gas. The difference between the two weights gives the mass of the gas.
- Greater the electronegativity difference between the atoms in a molecule, stronger is the hydrogen bonding.  
Thus, the strength of hydrogen bonding among hydrogen halides can be given as-  
 $\text{HF} > \text{HCl} > \text{HBr} > \text{HI}$   
 Stronger the hydrogen bonding greater will be the boiling point. So, HF has the highest boiling point.
- At constant T,  $P_1V_1 = P_2V_2$   
 $1 \times 20 = P_2 \times 50$ ;  $P_2 = 20 \times \frac{1}{50}$
- $\frac{P_1}{P_2} = \frac{1}{2}$ ,  $\frac{V_1}{V_2} = \frac{P_2}{P_1} = \frac{2}{1}$   
 $\frac{2L}{V_2} = \frac{2}{1}$ ;  $V_2 = 1L$
- For every  $1^\circ\text{C}$  increase in temperature, the volume of a given mass of an ideal gas increases by a definite fraction  $\frac{1}{273.15}$  of  $V_0$  at constant pressure.  
 Here,  $V_0$  is volume at  $0^\circ\text{C}$  temperature.
- $PV = nRT$   
 $\therefore \frac{n}{V} = \frac{P}{RT}$
- $PV = nRT$   
 $\therefore V \propto nT \propto \frac{m}{M}T$   
 $(\because P \text{ and } R \text{ are constant and } n = \frac{m}{M})$



$$\frac{V_1}{V_2} = \frac{m_1 T_1}{m_2 T_2}$$

$$\therefore \frac{T_1}{T_2} = \frac{V_1}{m_1} \times \frac{m_2}{V_2} = \frac{d_2}{d_1}$$

$$\frac{300 \text{ K}}{T_2} = \frac{0.75 \text{ d}}{d}$$

$$T_2 = \frac{300}{0.75} = 400 \text{ K}$$

11.  $PV = nRT$

$$P = \frac{n}{V} RT \quad (\because \text{concentration, } C = \frac{n}{V})$$

$$P = CRT$$

$$P = 1 \text{ atm}$$

$$C = 1 \text{ mole litre}^{-1}$$

$$R = 0.082 \text{ L atm mol}^{-1} \text{ K}^{-1}$$

$$T = \frac{P}{CR} = \frac{1}{1 \times 0.082} = 12.1 \approx 12 \text{ K}$$

12.  $PV = nRT$

$$P = \frac{nRT}{V} = \left( \frac{m}{M} \right) \frac{R \times T}{V}$$

$$= \left( \frac{6}{16.05} \right) \times \frac{8.314 \times (129 + 273)}{0.03}$$

$$= 41647.7 \text{ Pa} = 41648 \text{ Pa}$$

13.  $V_1 = 300 \text{ c.c.}$   
 $T_1 = 27^\circ \text{C} = 300 \text{ K}$   
 $P_1 = 620 \text{ mm} = 62 \text{ cm}$   
 $P_2 = 640 \text{ mm} = 64 \text{ cm}$   
 $T_2 = 47^\circ \text{C} = 320 \text{ K}$

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

$$V_2 = \frac{P_1}{P_2} \times \frac{T_2}{T_1} \times V_1$$

$$= \frac{62}{64} \times \frac{320}{300} \times 300$$

$$V_2 = 310 \text{ c.c.}$$

14.  $\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$

$$P_1 = 1 \text{ atm} \quad P_2 = 0.5 \text{ atm}$$

$$T_1 = 27^\circ \text{C} = 300 \text{ K} \quad T_2 = -23^\circ \text{C} = 250 \text{ K}$$

$$V_1 = 12000 \text{ L}$$

$$\therefore V_2 = \frac{P_1}{P_2} \times \frac{T_2}{T_1} \times V_1 = \frac{1}{0.5} \times \frac{250}{300} \times 12000$$

$$= 20,000 \text{ L}$$

15.  $\frac{P_1 V_1}{n_1 T_1} = \frac{P_2 V_2}{n_2 T_2}$

$$T_1 = 300 \text{ K} \quad m_1 = 2 \text{ g}$$

$$P_1 = 1 \text{ atm} \quad m_2 = 1 \text{ g}$$

$$P_2 = 0.75 \text{ atm} \quad V_1 = V_2 = 1 \text{ L}$$

$$n = \frac{m}{M}$$

$\therefore$  gas is same, molecular mass =  $M$

$$\frac{n_1}{n_2} = \frac{m_1}{m_2}$$

$$T_2 = \frac{P_2}{P_1} \times \frac{V_2}{V_1} \times \frac{n_1}{n_2} \times T_1 = \frac{P_2}{P_1} \times \frac{V_2}{V_1} \times \frac{m_1}{m_2} \times T_1$$

$$= \frac{0.75}{1} \times \frac{1}{1} \times \frac{2}{1} \times 300 = 450 \text{ K}$$

16.  $V_2 = \frac{P_1 V_1}{T_1} \cdot \frac{T_2}{P_2} = \frac{P}{2P} \times 2 \text{ litres} \times \frac{2T}{T} = 2 \text{ litres}$

17.  $\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$

$$T_1 = 15^\circ \text{C} = 288 \text{ K}$$

$$P_1 = 1.5 \text{ bar}$$

$$T_2 = 25^\circ \text{C} = 298 \text{ K}$$

$$P_2 = 1.0 \text{ bar}$$

$$\frac{V_2}{V_1} = \frac{P_1 T_2}{T_1 P_2} = \frac{1.5 \times 298}{288 \times 1.0} = 1.55$$

$$V_2 = 1.55 V_1 \approx 1.6 V_1$$

18.  $PV = nRT$

$$d = \frac{M}{V} \quad \therefore P \frac{M}{d} = nRT$$

For 1 mole,

$$\therefore d = \frac{PM}{RT}$$

As  $M$  and  $R$  are constant,  $d \propto \frac{P}{T}$

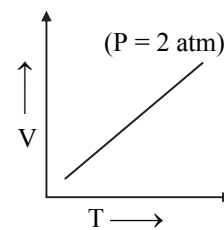
$\frac{P}{T}$  ratio is highest for 4 atm and 500 K.

$\therefore$  Density of carbon monoxide is maximum at 4 atm and 500 K.

19. For given conditions,  
 $PV = RT \quad (\because n = 1)$

$$\therefore V = \frac{RT}{P}$$

When pressure is constant, the slope is  $\frac{R}{P}$







- $\therefore \text{slope} = X = \frac{R}{P}$   
 $\therefore R = X(\text{lit mol}^{-1} \text{K}^{-1}) \times P(\text{atm}) \quad (\because P = 2 \text{ atm})$   
 $\therefore R = 2X \text{ lit atm mol}^{-1} \text{K}^{-1}$
21.  $z = \frac{PV}{nRT}$   
 $z < 1 \quad \therefore \frac{PV}{nRT} < 1$   
 $V < \frac{nRT}{P}$   
 $V_m < \frac{RT}{P} \quad (V = V_m \text{ when } n = 1 \text{ mole})$   
 $V_m < \frac{0.0821 \times 273}{1}$   
 $V_m < 22.4 \text{ litres.}$
23. At Boyle temperature, the gas behaviour is ideal over considerable range of pressure and hence,  $z = 1$ .
24. A gas can be liquefied by successive cooling to temperature lower than its critical temperature and by applying pressure higher than its critical pressure i.e.,  $T < T_c$  and  $P > P_c$ .
27. Increase in temperature, increases the kinetic energy of the molecules thus increasing the collisions against the walls of the container. Thus, the force exerted on the container per unit area i.e., pressure of the gas increases.
28.  $\text{K.E} = \frac{3}{2} RT$  it means that K.E depends upon  $T$  (absolute temperature) only.
29.  $\text{K.E.} = \frac{3}{2} RT$ .  
 So, average molar kinetic energy is independent of molecule/molar mass of the gas. So, the average molar kinetic energy is same for both the gases at the same temperature.
30. i. Most probable velocity  $= \alpha = \sqrt{\frac{2RT}{M}}$   
 ii. Average (or mean) velocity  $= v = \sqrt{\frac{8RT}{\pi M}}$   
 iii. Root mean square velocity  $= u = \sqrt{\frac{3RT}{M}}$   
 most probable velocity : mean velocity : root mean square velocity  
 $= \sqrt{\frac{2RT}{M}} : \sqrt{\frac{8RT}{\pi M}} : \sqrt{\frac{3RT}{M}} = \sqrt{2} : \sqrt{\frac{8}{\pi}} : \sqrt{3}$

33. average velocity  $(v) \propto \sqrt{T}$   
 $\frac{(\text{average velocity})_2}{(\text{average velocity})_1} = \sqrt{\frac{T_2}{T_1}} = \sqrt{2}$   
 $\frac{v_2}{v_1} = 1.4$   
 $\therefore v_2 = 1.4 \times v_1$
34. average velocity = root mean square velocity at  $27^\circ\text{C}$  (300 K)  
 $\sqrt{\frac{8RT}{\pi M}} = \sqrt{\frac{3R(300)}{M}}$   
 $\frac{8T}{\pi} = 900$   
 $T = \frac{900}{8} \times 3.142 = 353.47$   
 $T = 353.47 - 273 = 80.47^\circ\text{C}$
35.  $u = \sqrt{\frac{3RT}{M}} \quad u_1 = \sqrt{\frac{3R \times 300}{M}}$   
 $u_2 = \sqrt{\frac{3R \times 1200}{M}} \quad \frac{u_2}{u_1} = \sqrt{\frac{1200}{300}} = \sqrt{4} = 2$   
 $\therefore u_2 = 2u_1$
36. rms velocity,  $u = \sqrt{\frac{3RT}{M}}$   
 $\therefore u_{\text{CO}} = \sqrt{\frac{3RT_{\text{CO}}}{M_{\text{CO}}}}$  and  $u_{\text{N}_2} = \sqrt{\frac{3RT_{\text{N}_2}}{M_{\text{N}_2}}}$   
 $\therefore \frac{u_{\text{CO}}}{u_{\text{N}_2}} = \sqrt{\frac{T_{\text{CO}}}{T_{\text{N}_2}} \times \frac{M_{\text{N}_2}}{M_{\text{CO}}}}$   
 $\therefore \frac{1000}{u_{\text{N}_2}} = \sqrt{\frac{300}{28} \times \frac{28}{600}} = \frac{1}{\sqrt{2}} = \frac{1}{1.414}$   
 $\therefore u_{\text{N}_2} = 1000 \times 1.414 = 1414 \text{ m/s}$
37.  $u_{(\text{O}_2)} = \sqrt{3R \times \frac{800}{32}} \quad u_{(\text{H}_2)} = \sqrt{3R \times \frac{50}{2}}$   
 $\frac{u_{(\text{H}_2)}}{u_{(\text{O}_2)}} = \frac{\sqrt{3R \times \frac{50}{2}}}{\sqrt{3R \times \frac{800}{32}}} = \sqrt{\frac{50}{2} \times \frac{32}{800}} = 1$   
 $u_{(\text{H}_2)} = u_{(\text{O}_2)}$
38.  $\text{K.E. (E)} = \frac{1}{2} \times M \times U_{\text{rms}}^2$   
 $U_{\text{rms}}^2 = \frac{2E}{M}$   
 $\therefore U_{\text{rms}} = \sqrt{\frac{2E}{M}}$



$$39. \quad u = \sqrt{\frac{3RT}{M}}$$

$$\therefore u \propto \frac{1}{\sqrt{m}}$$

$$\therefore \frac{u_1}{u_2} = \frac{m_2^{1/2}}{m_1^{1/2}}$$

$$\therefore \frac{u_1^2}{u_2^2} = \frac{m_2}{m_1}$$

$$\therefore m_1 u_1^2 = m_2 u_2^2$$

$$40. \quad T = 25^\circ\text{C} = 25 + 273 = 298 \text{ K}$$

Average kinetic energy per molecule

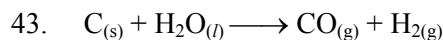
$$= \frac{3RT}{2N_A} = \frac{3}{2} \times \frac{8.314}{6.02 \times 10^{23}} \times 298 = 6.17 \times 10^{-21} \text{ J}$$

41. average kinetic energy i.e., K.E.  $\propto T$

$$T_1 = 20^\circ\text{C} = 293 \text{ K}, T_2 = 40^\circ\text{C} = 313 \text{ K}$$

$$\frac{(\text{average kinetic energy})_2}{(\text{average kinetic energy})_1} = \frac{T_2}{T_1} = \frac{313}{293}$$

42. Helium (He) has weak dispersion forces among given options while others have strong intermolecular hydrogen bonding along with dispersion forces.



1 mole of C gives 1 mole of CO and 1 mole of H<sub>2</sub> i.e., 12 g of C gives 2 moles of product gases

$\therefore$  48 g of C will give 8 moles of product gases

At STP, 1 mole of gas occupies 22.4 L of volume

$\therefore$  At STP, 8 mole of gas will have volume =  $22.4 \times 8 = 179.2 \text{ L}$ .

45. Ideal gas cannot be liquefied at any value of P and T, because of absence of intermolecular attraction.

46. The gas with highest critical temperature will liquefy first.

51. Unit of surface tension =  $\text{N m}^{-1} = \text{kg s}^{-2}$

Viscosity is measured in terms of viscosity coefficient.

$$\text{Unit of viscosity coefficient} = \text{N s m}^{-2} = \text{kg m}^{-1} \text{ s}^{-1}$$



### Evaluation Test

$$1. \quad \text{Rate of diffusion} \propto \frac{1}{\text{molecular mass}}$$

$\therefore$  H<sub>2</sub> gas diffuses first.

$$2. \quad \text{Density} = \frac{\text{mass}}{\text{volume}}$$

Volume of 1 mole at NTP = 22.4 dm<sup>3</sup>

$$\therefore \text{density} = \frac{45}{22.4} \approx 2 \text{ g/L}$$

3. Pressure depends upon the number of moles in the system. In the reaction, from one mole of N<sub>2</sub>O<sub>4</sub> two moles of NO<sub>2</sub> is formed.

So, the number of mole increase and hence, the pressure increases.

5. The density of an ideal gas is given as

$$d = \frac{PM}{RT}$$

$$\therefore d \propto \frac{1}{T} \quad (\because P, M, R = \text{constant})$$

$$6. \quad PV = nRT \quad \therefore PV = \frac{m}{M} RT$$

$$\therefore m = \frac{PVM}{RT} = \frac{1 \times 8.21 \times 32}{0.0821 \times 200} = 16 \text{ g}$$

$$7. \quad u_2 = 2u_1$$

$$\sqrt{\frac{3RT_2}{M}} = 2\sqrt{\frac{3RT_1}{M}}$$

$$T_2 = 4 \times 323$$

$$= 1292 \text{ K}$$

$$= 1292 - 273$$

$$= 1019^\circ\text{C}$$

$$8. \quad P_1 V_1 = P_2 V_2$$

$$P_2 = \frac{P_1 V_1}{V_2} = \frac{1 \times 20}{40} = 0.5 \text{ atm}$$

$$10. \quad \frac{V_1}{T_1} = \frac{V_2}{T_2}$$

$$V_2 = \frac{V_1 \times T_2}{T_1} = \frac{300 \times 310}{300} = 310 \text{ cm}^3$$

$$\therefore \text{Volume of air expelled} = V_2 - V_1 = 310 - 300 = 10 \text{ cm}^3$$

$$11. \quad \text{Average speed} = \sqrt{\frac{8RT}{\pi M}}$$

$$\text{Average speed} \propto \sqrt{\frac{T}{M}}$$



$$\frac{v_{\text{CH}_4}}{v_{\text{O}_2}} = \sqrt{\frac{T_{\text{CH}_4}}{T_{\text{O}_2}} \times \frac{M_{\text{O}_2}}{M_{\text{CH}_4}}}$$

$$1 = \sqrt{\frac{T_{\text{CH}_4}}{300} \times \frac{32}{16}}$$

$$T_{\text{CH}_4} = 150 \text{ K}$$

12.  $\frac{P_{\text{bottom}}}{P_{\text{top}}} = \frac{V_{\text{top}}}{V_{\text{bottom}}}$  (at constant T)

$$\frac{P_{\text{bottom}}}{P_{\text{top}}} = \frac{8V_{\text{bottom}}}{V_{\text{bottom}}}$$

$$P_{\text{bottom}} = 8P_{\text{top}}$$

Pressure at the bottom (in terms of height of water column) =  $8 \times 10 = 80 \text{ m}$

$\therefore$  Depth of lake =  $80 - 10 = 70 \text{ m}$ .

13. At constant volume

$$\frac{P_1}{P_2} = \frac{T_1}{T_2}$$

$$\therefore P_2 = \frac{P_1 T_2}{T_1}$$

$$= \frac{800 \times 300/2}{300}$$

$$= 400 \text{ mmHg}$$

14. Surface tension at critical point is zero.

19. The temperature  $0^\circ\text{C} = 273.15 \text{ K}$  and pressure  $1 \text{ atm}$  is called as standard temperature and pressure (STP). Many real gases behave as ideal gases at  $0^\circ\text{C}$  and  $1 \text{ atm}$ .

20.  $V_{\text{av}} : V_{\text{rms}} : V_{\text{most probable}} = v : u : \alpha$

$$\sqrt{\frac{8RT}{\pi M}} : \sqrt{\frac{3RT}{M}} : \sqrt{\frac{2RT}{M}}$$

$$\alpha : v : u = \sqrt{2} : \sqrt{\frac{8}{\pi}} : \sqrt{3} = 1 : 1.128 : 1.224$$

# 05 Redox Reactions



## Hints



### Classical Thinking

1. Chemical reactions are generally classified into three types viz., precipitation reactions, acid-base neutralization reactions and oxidation-reduction or redox reactions.

3.  $M^{+2} \longrightarrow M^{+5} + 3e^{-}$   
A metal ion  $M^{+2}$  loses 3 electrons, its oxidation number will become +5.

4. A substance that causes oxidation is an oxidizing agent or oxidant. It accepts electron(s) and itself gets reduced. Thus, in the course of a chemical reaction, an oxidant gains electron(s).

6. A reducing agent or reductant causes reduction of the other chemical species involved in the reaction. While doing so it itself undergoes oxidation by donating its electron(s). Thus, there is an increase in its oxidation number.

7.  $Zn + Cu^{2+} \longrightarrow Zn^{2+} + Cu$   
Oxidation is increase in oxidation number. For the given reaction, the oxidation number of Zn increases from 0 to +2.  
Hence, Zn is oxidized to  $Zn^{2+}$ .

10. Hydrogen has oxidation number of -1 in metal hydrides, zero in  $H_2$  and +1 in halogen acids.

11. The oxidation number of F is always -1 in all of its compounds i.e., it never has a positive oxidation number in any of its compounds.

12. Nitrogen shows the oxidation number of -3, -2, -1, 0, +1, +2, +3, +4, +5 i.e., -3 to +5.

13.  $C_{12}H_{22}O_{11}$   
Let  $x$  be the oxidation number of C.  
 $\therefore 12x + 22 \times (+1) + 11 \times (-2) = 0$   
 $\therefore 12x + 22 - 22 = 0$   
 $\therefore x = 0.$

14.  $HClO_4$   
Let  $x$  be the oxidation number of Cl.

$\therefore (+1) + (x) + 4(-2) = 0$   
 $\therefore +1 + x - 8 = 0$   
 $\therefore x - 7 = 0$   
 $\therefore x = +7$

15.  $S_2O_7^{2-}$   
Let  $x$  be the oxidation number of S.

$\therefore 2(x) + 7(-2) = -2$   
 $2x - 14 = -2$   
 $2x = +12$   
 $\therefore x = +6$

16. (A)  $CH_4$   $\therefore x + 4(+1) = 0 \therefore x = -4$

(B)  $CF_4$   $\therefore x + 4(-1) = 0 \therefore x = +4$

(C)  $CO_2$   $\therefore x + 2(-2) = 0 \therefore x = +4$

(D)  $CCl_4$   $\therefore x + 4(-1) = 0 \therefore x = +4$

Thus, among the given options, carbon has lowest oxidation state in  $CH_4$ .

17. The oxidation number of Cl in the given compounds is as follows:

$KCl \longrightarrow +1 + x = 0$

$\therefore x = -1$

$HClO \longrightarrow +1 + x + (-2) = 0$

$\therefore x = +1$

$HClO_2 \longrightarrow +1 + x + (-2 \times 2) = 0$

$\therefore x = +3$

$HClO_4 \longrightarrow +1 + x + (-2 \times 4) = 0$

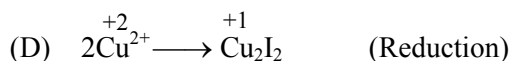
$\therefore x = +7$

$\therefore$  In  $HClO_4$ , Cl has highest oxidation number of +7.

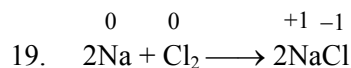
18. (A)  $Br_2 \longrightarrow HBr$  (Reduction)

(B)  $2HgCl_2 \longrightarrow Hg_2Cl_2$  (Reduction)

(C)  $2KI \longrightarrow I_2$  (Oxidation)

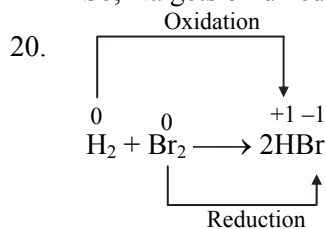


Only in option (C) the oxidation number of I increases from  $-1$  to  $0$  and hence KI gets oxidised to  $\text{I}_2$ .

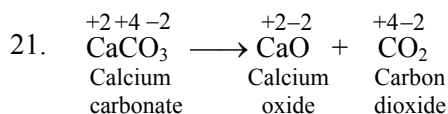


The oxidation number of Na increases from  $0$  to  $+1$  while the oxidation number of  $\text{Cl}_2$  decreases from  $0$  to  $-1$ .

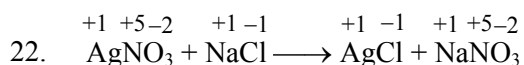
So, Na gets oxidized while  $\text{Cl}_2$  gets reduced.



Hydrogen undergoes oxidation and bromine undergoes reduction. Thus, the reaction involves both, oxidation and reduction and is a redox reaction.



This is not a redox reaction since no element undergoes a change in oxidation number.



None of the elements in reaction (C) undergoes a change in oxidation number, therefore, (C) is not a redox reaction.

23. In reaction (D),  $\text{Ag}_2\text{O}$  gets reduced to Ag by  $\text{H}_2\text{O}_2$  hence it acts as a reducing agent.

25. In balancing of equations by oxidation number method, the first step involves writing the unbalanced net equation and balancing it for all atoms (except H and O).

28. NaOCl (sodium hypochlorite) is used as an oxidising agent in bleaching of clothes to remove stains.



### Critical Thinking

2.  $\text{Sn}^{2+} \longrightarrow \text{Sn}^{4+} + 2\text{e}^-$ . In this reaction  $\text{Sn}^{2+}$  changes to  $\text{Sn}^{4+}$ , it is called an oxidation reaction, because of loss of two electrons from  $\text{Sn}^{2+}$ .

4. Reactions given in option (A) and (B) are neutralization reactions whereas reaction in option (C) is a precipitation reaction. Reaction given in option (D) represents redox reaction as there is a net transfer of electrons from Fe atoms to  $\text{Cu}^{+2}$  ions.

5. Let  $x$  be the oxidation number of C in  $\text{C}_3\text{O}_2$

$$\therefore 3x + 2 \times (-2) = 0$$

$$\therefore x = +4/3.$$

6. (A) oxidation number of N in  $\overset{x}{\text{HNO}}_3$

$$\therefore +1 + x + 3(-2) = 0$$

$$\therefore x = +5$$

(B) oxidation number of N in  $\overset{x}{\text{NH}}_2\text{OH}$

$$\therefore x + (2 \times 1) - 2 + 1 = 0$$

$$\therefore x = -1$$

(C) oxidation number of N in  $(\overset{x}{\text{N}}_2\text{H}_5)_2^{2+}$

$$\therefore 2[(2 \times x) + (5 \times 1)] = +2$$

$$\therefore x = -2$$

(D) oxidation number of N in  $\overset{x}{\text{Mg}}_3\text{N}_2$

$$\therefore 3 \times (+2) + 2x = 0$$

$$\therefore x = -3$$

Thus, option (D) is correct.

7. In  $\text{I}_3^-$ , let the oxidation number of I be  $x$

$$\therefore 3x = -1$$

$$\therefore x = -1/3.$$

8.  $\overset{0}{\text{S}}_8, \overset{+1}{\text{S}}_2\overset{-1}{\text{F}}_2, \overset{+1}{\text{H}}\overset{-2}{\text{S}}$

$\therefore$  oxidation number of S in  $\text{S}_8, \text{S}_2\text{F}_2$  and  $\text{H}_2\text{S}$  respectively are  $0, +1$  and  $-2$ .

9.  $\overset{+1}{\text{K}}_4\overset{x}{\text{P}}\overset{-2}{\text{O}}_7$

$$4(+1) + 2x + 7(-2) = 0$$

$$2x - 10 = 0$$

$$2x = +10$$

$$\therefore x = +5$$

10. Let  $x$  be the oxidation state of Cu in  $\text{YBa}_2\text{Cu}_3\text{O}_7$

$$(+3) + 2(+2) + 3x + 7(-2) = 0$$

$$(+3) + 4 + 3x - 14 = 0$$

$$3x - 7 = 0$$

$$\therefore x = +\frac{7}{3}$$



Compound	Oxidation state of metal
MnO <sub>2</sub>	Mn(+4)
FeCl <sub>3</sub>	Fe(+3)
V <sub>2</sub> O <sub>5</sub>	V(+5)
CrO <sub>3</sub>	Cr(+6)
Mn <sub>2</sub> O <sub>3</sub>	Mn(+3)
V <sub>2</sub> O <sub>3</sub>	V(+3)
SnCl <sub>2</sub>	Sn(+2)

Thus, among the given pairs of compounds, V<sub>2</sub>O<sub>5</sub> and CrO<sub>3</sub> is the pair, which has metals in their highest oxidation state.

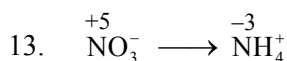
12. Potassium permanganate is KMnO<sub>4</sub>.  
Let  $x$  be the oxidation number of Mn in KMnO<sub>4</sub>.



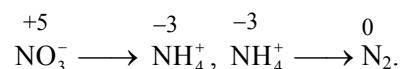
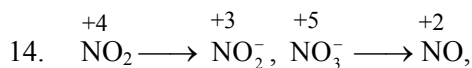
$$\therefore 1 + x + (-2 \times 4) = 0$$

$$\therefore x = +7.$$

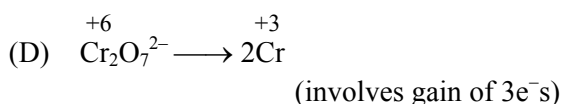
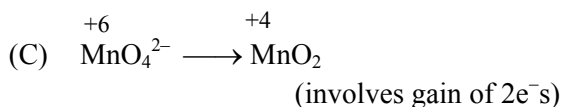
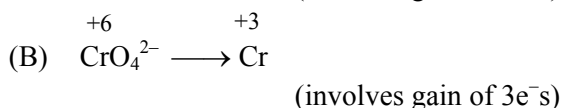
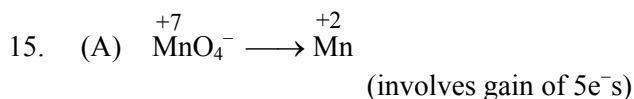
Whereas oxidation number of Mn in manganese dioxide (MnO<sub>2</sub>), manganese chloride (MnCl<sub>2</sub>) and manganese sulphate (MnSO<sub>4</sub>) is +4, +2 and +2 respectively.



Here, oxidation number of N decreases from +5 in NO<sub>3</sub><sup>-</sup> to -3 in NH<sub>4</sub><sup>+</sup> and hence NO<sub>3</sub><sup>-</sup> gets reduced to NH<sub>4</sub><sup>+</sup>

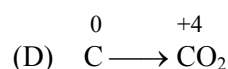
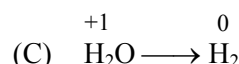
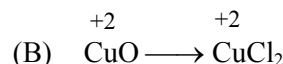
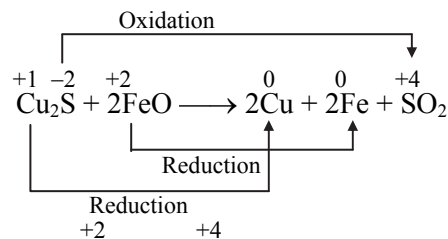


Thus in option (D) the oxidation number of N increases from -3 to 0 i.e., N gets oxidised.



Hence, option (A) is correct.

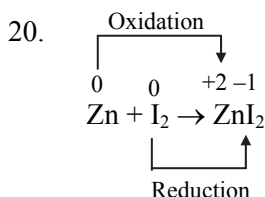
16. Only in reaction (D), the oxidation number of the elements undergo a change.



Only in option (C), oxidation number of hydrogen decreases from +1 to 0 and hence H<sub>2</sub>O gets reduced to H<sub>2</sub>.

18. In the given reaction, nickel (Ni) itself gets oxidized (i.e., its oxidation number increases from 0 to +2) and thus serves as a reducing agent.

19. Here, NO acts as a reducing agent and reduces I<sub>2</sub> to I<sup>-</sup>. Also, NO itself undergoes oxidation since the oxidation number of nitrogen changes from +2 in NO to +5 in NO<sub>3</sub><sup>-</sup>.



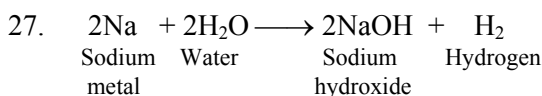
In this reaction Zn atom gets oxidised to Zn<sup>2+</sup> ion and iodine gets reduced to I<sup>-</sup>.

21. Al is the reductant as it gets oxidised to Al<sub>2</sub>O<sub>3</sub>.  
 $\text{Al} \longrightarrow \text{Al}^{+3}$   
Thus, in oxidising one Al atom 3 electrons are transferred.

∴ For oxidising 8 Al atoms, the electrons transferred = 8 × 3 = 24

22. For the given reaction, oxidation number of Cr changes from +6 to +3. Thus, it gets reduced.

23. The balanced equation is  
 $2\text{C}_2\text{H}_6 + 7\text{O}_2 \longrightarrow 4\text{CO}_2 + 6\text{H}_2\text{O}$ . Ratio of the coefficients of CO<sub>2</sub> and H<sub>2</sub>O is 4 : 6 or 2 : 3.



It is a redox reaction since sodium gets oxidised to NaOH while water gets reduced to H<sub>2</sub>.



28.  $2\overset{0}{\text{Li}} + \overset{0}{\text{H}_2} \longrightarrow 2\overset{+1-1}{\text{LiH}}$   
Here,  $\text{H}_2$  acts as an oxidizing agent since the oxidation number of Li increases from 0 to +1 and that of H decreases from 0 to -1.

29. (A)  $\text{H}_2\text{SO}_4 + 2\text{NaOH} \longrightarrow \text{Na}_2\text{SO}_4 + 2\text{H}_2\text{O}$   
This is a neutralization reaction.

(B)  $2\overset{0}{\text{O}_3} \longrightarrow 3\overset{0}{\text{O}_2}$   
Oxidation number of O in both  $\text{O}_3$  and  $\text{O}_2$  is zero, therefore, it is not a redox reaction.

(C)  $2\overset{0}{\text{N}_2} + \overset{0}{\text{O}_2} \longrightarrow 2\overset{+2-2}{\text{NO}}$   
Here oxidation number of N increases from 0 in  $\text{N}_2$  to +2 in NO and that of O decreases from 0 in  $\text{O}_2$  to -2 in NO therefore, it is a redox reaction.

(D)  $\text{H}_2\text{O}_{(l)} \longrightarrow \text{H}_2\text{O}_{(g)}$   
Only state of matter changes and hence there is no change in oxidation number. Thus, among given options only option(C) represents redox reaction.



### Competitive Thinking

1. The oxidation numbers of the elements in their compounds are as follows:

N : -3, -2, +1 to +5

O : -1, -1/2, +2

C : -4, +2, +4

Cl : -1, +1, +3, +4, +5, +6, +7

Thus Cl exhibit highest oxidation number of +7 among the given options.

2.  $\text{Fe}_3\text{O}_8$   
 $3x + 8(-2) = 0$  or  $3x - 16 = 0$  or  $x = \frac{+16}{3}$

3.  $\text{F}_2\text{O}$   
 $\therefore 2(-1) + x = 0$   
 $\therefore x = +2$

4.  $\text{CH}_2\text{Cl}_2$   
 $x + 2(+1) + 2(-1) = 0$   
 $\therefore x = 0$

5.  $\text{HIO}_4$   
 $+1 + x + 4(-2) = 0$   
 $\therefore x = +7$

$\text{H}_3\text{IO}_5$   
 $3(+1) + x + 5(-2) = 0$   
 $\therefore x = +7$

$\text{H}_5\text{IO}_6$   
 $5(+1) + x + 6(-2) = 0$   
 $\therefore x = +7$

6.  $\text{NaNO}_2$   
The oxidation state of N is  
 $+1 + x + 2(-2) = 0$   
 $\therefore +1 + x - 4 = 0$   
 $\therefore x = +3$

7.  $\text{H}_4\text{IO}_6^-$   
The oxidation state of I is  
 $4(+1) + x + 6(-2) = -1$   
 $\therefore 4 + x - 12 = -1$   
 $\therefore x = +7$

8. Let the oxidation state of N be x.

$\overset{x+1}{\text{N}_2}\text{H}_4$   $\therefore 2x + 4(+1) = 0$   
 $\therefore 2x = -4$   
 $\therefore x = -2$

$\overset{x+1}{\text{NH}_3}$   $\therefore x + 3(+1) = 0$   
 $\therefore x = -3$

$\overset{x+1}{\text{N}_3}\text{H}$   $\therefore 3x + 1 = 0$   
 $\therefore x = -1/3$

$\overset{x+1-2+1}{\text{NH}_2}\text{OH}$   $\therefore x + 2(+1) - 2 + 1$   
 $\therefore x = -1$

$\therefore$  Nitrogen in  $\text{N}_3\text{H}$  exhibits highest oxidation state.

9. Ferrous ions ( $\text{Fe}^{+2}$ ) and ferric ions ( $\text{Fe}^{+3}$ ) have net charge of +2 and +3 respectively.

10.  $\text{Fe}_3\text{O}_4$   
The oxidation state of Fe is  
 $3x + 4(-2) = 0$   
 $\therefore 3x - 8 = 0$   
 $\therefore x = +\frac{8}{3}$

11. The oxidation state of N in the following compounds can be given as,

$\text{HNO}_3$  :  $+1 + x + 3(-2) = 0$   
 $\therefore x = +5$   
 $\text{NO}$  :  $x - 2 = 0$   
 $\therefore x = +2$

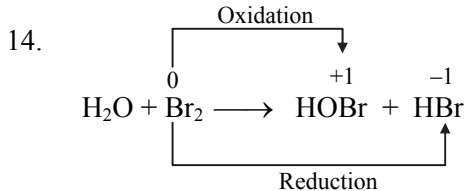


- $\text{NH}_4\text{Cl} : x + 4(+1) - 1 = 0$   
 $\therefore x = -3$   
 $\text{N}_2 : x = 0$   
 $\therefore$  The ordering of compounds according to the decreasing order of the oxidation state of nitrogen will be  $\text{HNO}_3$ ,  $\text{NO}$ ,  $\text{N}_2$ ,  $\text{NH}_4\text{Cl}$ .

12.  $\text{HNO}_3 \xrightarrow{+5} \text{N}_2\text{O} \xrightarrow{+1}$   
 When  $\text{HNO}_3$  changes to  $\text{N}_2\text{O}$ , the oxidation number of N changes from +5 to +1 i.e., the oxidation number is changed by

$$(+5) - (+1) = +4$$

13. (A)  $\text{XeF}_4 + \text{O}_2\text{F}_2 \xrightarrow{+4 \ -1 \ +1 \ -1} \text{XeF}_6 + \text{O}_2 \xrightarrow{+6 \ -1 \ 0}$   
 (B)  $\text{XeF}_2 + \text{PF}_5 \xrightarrow{+2 \ +5} [\text{XeF}]^+ \text{PF}_6^- \xrightarrow{+2 \ +5}$   
 (C)  $\text{XeF}_6 + \text{H}_2\text{O} \xrightarrow{+6 \ -1 \ +1 \ -2} \text{XeOF}_4 + 2\text{HF} \xrightarrow{+6 \ -2 \ -1 \ +1 \ -1}$   
 (D)  $\text{XeF}_6 + 2\text{H}_2\text{O} \xrightarrow{+6 \ -1 \ +1 \ -2} \text{XeO}_2\text{F}_2 + 4\text{HF} \xrightarrow{+6 \ -2 \ -1 \ +1 \ -1}$   
 The reaction in option (A) is an example of a redox reaction since xenon undergoes oxidation and oxygen undergoes reduction.

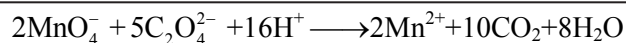
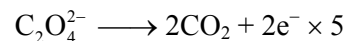
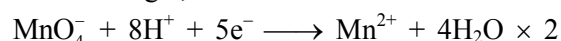


Thus, in given reaction,  $\text{Br}_2$  is oxidised as well as reduced.

15. In the equation, (A), iodine in HI gets oxidised to  $\text{I}_2$ . Hence, in this equation  $\text{H}_2\text{SO}_4$  acts as an oxidising agent.

16.  $\text{CaF}_2 + \text{H}_2\text{SO}_4 \xrightarrow{+6} \text{CaSO}_4 + 2\text{HF} \xrightarrow{+6}$   
 The oxidation number of S remains unchanged. Hence, reaction given in option (A) is the one that does not show oxidizing behaviour of  $\text{H}_2\text{SO}_4$ .

18. After balancing the equations by ion-electron method we get,



Thus, the coefficient of  $\text{MnO}_4^-$ ,  $\text{C}_2\text{O}_4^{2-}$  and  $\text{H}^+$  in the above balanced equation are 2, 5, 16 respectively.

19. The metallic iron is oxidised to  $\text{Fe}^{3+}$ .  
 20. Oxidising agent itself undergoes reduction by accepting electrons. Among the given options, F being highly electronegative easily accepts electron. Hence,  $\text{F}_2$  is most powerful oxidising agent.  
 21.  $\text{Cl}^-$  has eight valence electrons (i.e., complete octet). Hence, it cannot accept electrons i.e., it cannot function as an oxidising agent.  
 In  $\text{ClO}_4^-$  and  $\text{MnO}_4^-$ , the central atoms Cl and Mn are in their highest oxidation states (i.e., +7). Hence, these species cannot donate electrons i.e., these species cannot function as reducing agents.  
 In  $\text{ClO}^-$ , the oxidation number of Cl is +1. The highest oxidation number of Cl is +7 and the lowest is -1. Hence,  $\text{ClO}^-$  can accept or donate electrons and can function both as oxidising as well as reducing agent.



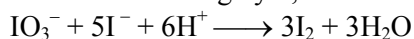
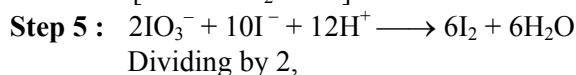
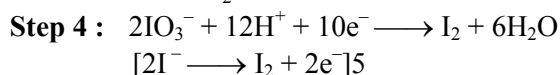
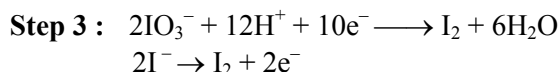
### Evaluation Test

1. When an elemental sulphur atom becomes a sulphide ion, the oxidation number of S changes from 0 to -2 by the gain of two electrons.  
 2.  $\text{KO}_3 : +1 + 3(x) = 0$   
 $\therefore 3x = -1$   
 $\therefore x = \frac{-1}{3}$  or -0.33  
 $\text{Na}_2\text{O}_2 : 2(+1) + 2x = 0$   
 $\therefore 2x = -2$   
 $\therefore x = -1$

3. In the reaction,  

$$3\text{Br}_2 \xrightarrow{0 \quad -1 \quad +5} 5\text{Br}^- + \text{BrO}_3^-$$
  
 The oxidation number of Br changes from 0 to -1 and also from 0 to +5. Thus, Br undergoes both reduction and oxidation.  
 4.  $\text{IO}_3^- + \text{aI}^- + \text{bH}^+ \longrightarrow \text{cI}_2 + \text{dH}_2\text{O}$   
**Step 1 :**  $\text{I}^- \longrightarrow \text{I}_2$  (oxidation)  
 $\text{IO}_3^- \longrightarrow \text{I}_2$  (reduction)  
**Step 2 :**  $2\text{IO}_3^- + 12\text{H}^+ \longrightarrow \text{I}_2 + 6\text{H}_2\text{O}$





On comparing,  $a = 5$ ,  $b = 6$ ,  $c = 3$ ,  $d = 3$

5. Ionization enthalpy (I.E.)  $\propto \frac{1}{\text{Ionic size}}$

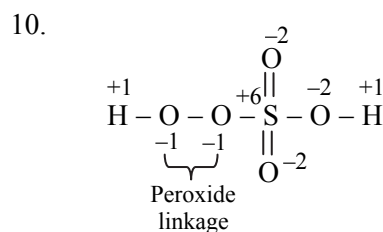
The ionic size increases from  $\text{F}^-$  to  $\text{I}^-$  and the I.E. decreases. Thus, among given options,  $\text{I}^-$  is the strongest reducing agent as it can donate electrons easily compared to others.

6.  $\text{Mo}_2\text{Cl}_8^{4-}$   
 $2x + 8(-2) = -4$   
 $2x - 16 = -4$   
 $2x = +12$   
 $\therefore x = +6$

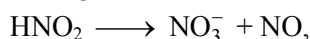
7.  $\text{I}^-$  (-1),  $\text{Na}$  (0) and  $\text{Fe}^{2+}$  (+2) all are in their lowest oxidation state. They cannot be reduced further but can only be oxidised. So these can act as reducing agents.

8.  $\text{Ba}(\text{H}_2\text{PO}_2)_2$   
 $\therefore 2 + 2 [2 \times (+1) + x + 2 \times (-2)] = 0$  or  
 $\therefore 2 + 4 + 2x - 8 = 0$   
 $\therefore x = +1$

9. Diamond is an allotropic form of elemental carbon. Thus, the oxidation state of C is 0.



11. In disproportion reaction, a substance undergoes oxidation and reduction. In



$\text{HNO}_2$  is oxidized to  $\text{NO}_3^-$  and is reduced to  $\text{NO}$ . Hence, it is a disproportion reaction.

13.  $\text{C}_4\text{H}_4\text{O}_6^{2-}$   
 Oxidation number of H = +1  
 Oxidation number of O = -2

Sum of the oxidation states of all atoms = -2

$\therefore 4 \times (\text{Oxidation number of C}) + 4 \times (\text{Oxidation number of H}) + 6 \times (\text{Oxidation number of O}) = -2$

$\therefore 4 \times (\text{Oxidation number of C}) + 4 \times (+1) + 6 \times (-2) = -2$

$\therefore 4 \times (\text{Oxidation number of C}) + 4 - 12 = -2$

$\therefore 4 \times (\text{Oxidation number of C}) = -2 + 8 = +6$

Oxidation number of C = +1.5

15. Oxidation number of oxygen = -2; Oxidation number of hydrogen = +1

Oxidation number of nitrogen = -3; Oxidation number of zinc = +2

Sum of the oxidation states of all atoms = 0

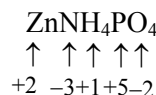
$\therefore (\text{Oxidation number of Zn}) + (\text{Oxidation number of N}) + 4 \times (\text{Oxidation number of H}) + (\text{Oxidation number of P}) + 4 \times (\text{Oxidation number of O}) = 0$

$\therefore (+2) + (-3) + 4 \times (+1) + (\text{Oxidation number of P}) + 4 \times (-2) = 0$

$\therefore (\text{Oxidation number of P}) + (+2) + (-3) + (+4) + (-8) = 0$

$\therefore (\text{Oxidation number of P}) - 5 = 0$

$\therefore \text{Oxidation number of P} = +5$



# 07 Surface Chemistry



## Hints



### Classical Thinking

- Surface or interface represents the boundary which separates two bulk phases.
- Rate of adsorption is rapid in the beginning and falls as the time passes.
- The extent of adsorption is large at low temperature and decreases as the temperature is raised.
- Adsorption of hydrogen on glass is endothermic because hydrogen dissociates.
- Adsorption of  $H_2$  on Ni is physical adsorption at low temperature and becomes chemisorption at higher temperature.
- Freundlich's adsorption isotherm is given by  $\frac{x}{m} = kP^{1/n}$  or  $\frac{m}{x} = \frac{1}{kP^{1/n}}$   
 where  $x$  = mass of gas adsorbed  
 $m$  = mass of adsorbent  
 $P$  = equilibrium pressure  
 $k$  and  $n$  are constants that depend on the nature of adsorbate and adsorbent and temperature.
- Activation energy changes when catalyst is used in a reaction.
- Ethanol acts as an inhibitor by suppressing the formation of carbonyl chloride from chloroform due to oxidation with air.  
 $4CHCl_3 + 3O_2 \longrightarrow 4COCl_2 + 2H_2O + 2Cl_2$   
 Chloroform                      Carbonyl chloride
- Catalyst and reactants exist in the same phase in homogeneous catalysis.
- $SO_2$  and  $O_2$  are gases whereas  $V_2O_5$  is a solid, hence the reaction in option D is a heterogeneous catalysis.
- Finely divided metals like Ni, Pd or Pt are used as catalyst during hydrogenation of unsaturated vegetable oils.
- Finely divided matter provides a much larger surface area, compared to its solid state. Thus, a catalyst in the finely divided state is more efficient.
- The product in presence of  $Pd/Al_2O_3$  catalyst is acetaldehyde while in the presence of  $Ag/Al_2O_3$  catalyst, the product is ethylene oxide.  
 $2C_2H_{4(g)} + O_{2(g)} \xrightarrow{Pd/Al_2O_3} 2CH_3CHO_{(g)}$   
 $2C_2H_{4(g)} + O_{2(g)} \xrightarrow{Ag/Al_2O_3} 2C_2H_4O_{(g)}$
- Except ribozymes (ribonucleic acid enzymes), enzymes are proteins.
- Enzyme catalase catalyses decomposition of hydrogen peroxide ( $H_2O_2$ ).  
 $H_2O_{2(aq)} \xrightarrow{\text{catalase}} H_2O_{(l)} + \frac{1}{2} O_{2(g)}$   
 Hydrogen peroxide                      Water                      Oxygen
- Particle size in colloidal dispersion is between 1 nm to  $10^3$  nm i.e.,  $10^{-9}$  m to  $10^{-6}$  m.



30. Colloidal dispersion is heterogeneous and is a two phase system, with dispersion medium as one phase and the dispersed substance as the other because there is a definite surface of separation between each particle and the medium.
31. Dilute sulphuric acid is a true solution while milk of magnesia, milk and fog are colloids.

35.

Substance	Name of colloidal system
Rubber	Solid foam
Milk	Emulsion
Paint	Sol
Cheese	Gel

36. Mist is a colloidal dispersion of liquid in gas.

37.

Dispersion medium	Disperse phase	Colloidal system	Example
Solid	Gas	Solid foam	Cake
Solid	Gas	Solid foam	Pumice stone
Solid	Solid	Solid sol	Gold in glass
Gas	Solid	Aerosol	Smoke

39. Metal sols are lyophobic sols, hence gold sol is an example of lyophobic sol. Rubber in benzene, cellulose acetate or cellulose nitrate in acetone are examples of lyophilic sols.
43. When light passes through true solution containing solute particles not larger than 1 nm, the path of the light through the solution cannot be detected. However, if the light passes through colloidal dispersion, because of the scattering of light by the colloidal particles, the path of the light through the colloidal dispersion becomes visible. This phenomenon of scattering of light by colloidal particles and making the path of the light visible through the dispersion is referred to as Tyndall effect.
44. The colloidal particles undergo ceaseless, random motion in all directions over a large area. This motion of disperse phase particles is called Brownian motion.
47. Coagulation of colloids is achieved by removal of the charge associated with the colloidal particles. The most common method to do so is by adding electrolytes.
51. When a quantum dot is irradiated with UV light, it emits visible light, the wavelength of which depends on the size of nanoparticle. For example, a 3 nm cadmium selenide particle emits green light of wavelength 520 nm whereas 5.5 nm particle of the same substance emit red light at the wavelength of 620 nm.



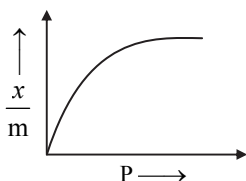
### Critical Thinking

- The surface that is capable for adsorption of molecules on it is called adsorbent and the adsorbed molecules are known as adsorbate. Thus, during the adsorption of oxalic acid by activated charcoal, molecules of oxalic acid are adsorbate while adsorbent is activated charcoal.
- The physical adsorption may be easily reversed by lowering the pressure of the gas or by raising the temperature of the surface.
- Chemisorption occurs at all temperatures but extent of adsorption increases with rise in temperature.
- Critical temperature  $\propto$  Ease of liquefaction of a gas  $\propto$  Extent of adsorption of the gas. Nitrogen gas has the lowest critical temperature (126 K) among the given gases and thus is difficult to liquefy. Hence, it is adsorbed in minimum amount by activated charcoal.

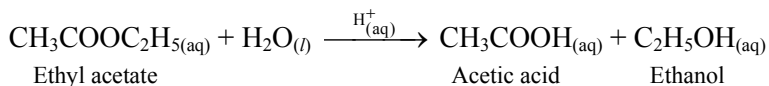


7. The substances, which provide large surface area for a given mass, are much effective as adsorbents and adsorb appreciable volumes of gases. Finely divided substances, rough surfaces, colloidal substances, etc. are good adsorbents because they provide large surface area for a given mass. Therefore, nickel metal sheet having smooth surface is a less effective adsorbent compared to nickel metal sheet having rough surface.

8. In the low pressure range at constant temperature, the extent of adsorption is directly proportional to the pressure of the gas. However, as the pressure increases and becomes higher, the extent of adsorption becomes independent of pressure because the surface of adsorbent is almost fully covered by the adsorbed gaseous molecules. This relation is correctly shown by graph of Freundlich equation, which is as follows:



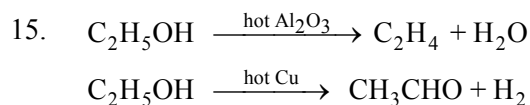
9. In few cases, the catalyst initiates the chemical reaction.
10. Inhibitors slow down the rate of reaction.
11. Acid catalyzed hydrolysis of an ester such as ethyl acetate by water to form an organic acid and alcohol is an example of homogeneous catalysis.



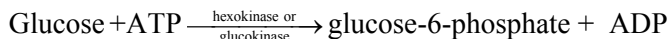
In this reaction, acids like HCl acts as catalyst which are in same phase (i.e., in liquid state) as that of reactants.

12. In synthesis of  $\text{NH}_3$  by Haber's process from  $\text{N}_2$  and  $\text{H}_2$  using finely divided Fe, the reactants are in gaseous state while the catalyst is in the solid state. Hence, the process is an example of heterogeneous catalysis.
13. The rate of heterogeneous catalysis is proportional to the surface area of catalyst.
14. Heterogeneous catalysts are used in catalytic converters in automobiles to reduce toxic emissions and pollution by automobiles.

The typical catalysts are metals such as Pt, Pd and Rh and transition metal oxides  $\text{V}_2\text{O}_5$ ,  $\text{Cr}_2\text{O}_3$  and  $\text{CuO}$ . These catalysts are poisoned by the adsorption of Pb. For this reason, automobiles with catalytic converters require unleaded petrol.



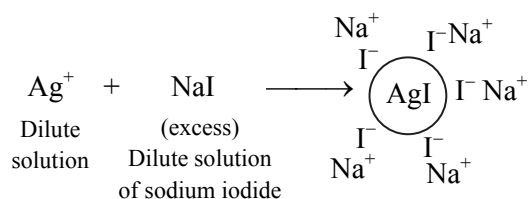
16. According to the lock and key concept of enzyme catalysis, the active site acts like a lock into which fits only a specific key (substrate or reactant).
17. Enzyme hexokinase catalyzes the conversion of glucose to glucose-6-phosphate in the heart and brain. The same reaction is catalysed by an enzyme glucokinase present in liver.



18. Starch forms a hydrophilic sol in water. All others form true aqueous solutions.



19. Lyophobic sols are readily precipitated by the addition of small amounts of electrolytes. Once they are precipitated, the precipitate cannot be reconverted into sols by simple addition of dispersion medium. Hence, the lyophobic sols are called irreversible sols.
21. Sulphur sol is a multimolecular colloid. The aqueous solutions of proteins, polyvinyl alcohol, solutions of rubber and high polymeric material in organic solvents are macromolecular colloids.
23. The charge on colloidal particles is due to the adsorption of the ions of the electrolyte (present in colloidal solution in minute amount) on the surface of colloidal particles. Electrical neutrality is maintained as the dispersion medium carries an equal and opposite charge.
24. When  $\text{AgNO}_3$  solution is added to an excess of dilute solution of  $\text{NaI}$ ,  $\text{AgI}$  sol is formed which selectively adsorbs  $\text{I}^-$  ions and carries negative charge.



26. According to Schulze-Hardy rules, the ions having opposite charge to sol particles cause coagulation and greater the valency of oppositely charged ion, more is the coagulating power, i.e.,  $\text{PO}_4^{3-} > \text{SO}_4^{2-} > \text{NO}_3^-$ .
27. The positive particles of one sol are attracted by the negative particles of the second sol. This is followed by mutual coagulation of both the sols.
28. In oil in water emulsion, the continuous phase is water.
30. The surface of a quantum dot can be chemically modified by attaching on organic molecule. Such a modified quantum dot targets and forms a chemical bond with specific biomolecule such as DNA or protein.



### Competitive Thinking

- Particle size of adsorbent will affect the amount of adsorption, as adsorption is a surface phenomenon. Finely divided substances are good adsorbents as they provide large surface area.
- Multilayer of adsorbate is formed on the adsorbent during physical adsorption.
- 

Gas	$\text{NH}_3$	$\text{O}_2$	$\text{N}_2$	$\text{H}_2$
<b>Critical Temperature (K)</b>	406	154	126	33

On the basis of critical temperatures of these gases,  $\text{NH}_3$ , having highest critical temperature, will undergo maximum adsorption.

- The general form of Freundlich adsorption isotherm may be also represented as:

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

This will give a straight line on plotting  $\log \frac{x}{m}$  versus  $\log P$  with intercept as  $\log k$ .



5. Freundlich adsorption isotherm is

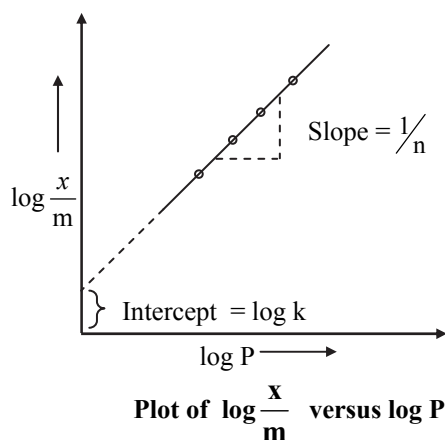
$$\frac{x}{m} = kP^{1/n} \dots\dots (k, n \text{ are constants.})$$

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

Comparing with general form :  $y = mx + c$

$$\therefore \frac{1}{n} = \text{slope}$$

6. The slope of the line is equal to  $\frac{1}{n}$  and the intercept is equal to  $\log k$ .



7. Catalyst does not affect the value of equilibrium constant.

9. An increase in rate of reaction in forward direction by a catalyst brings in an increase in concentration of products and thus rate of backward reaction also increase to same magnitude. Thus, the equilibrium is achieved quickly.

12. Enzymes are biological catalysts, which decrease the activation energy of the reaction.

17. Gold sol is a lyophobic sol. Gold particles have very less affinity towards dispersion medium, hence its sol can be easily coagulated.

18. Lyophilic colloids possess solvent-loving nature and thus a thin layer of dispersion medium is formed around sol particles.

19. Gold sol consists of particles which are formed by the aggregation of many gold atoms. Hence, gold sol is an example of multimolecular colloid.

20. Sulphur sol is formed by the aggregation of S molecules within colloidal dimensions.

21. Macromolecular colloids behave like lyophilic colloids hence cannot be easily coagulated.

22. The colour of colloidal solutions depends on the wavelength of the light scattered by the dispersed particles, which in turn depends on the size and nature of the particles.

23. Dispersion medium and disperse phase are two phases of colloid. These phases can be solid, liquid or gas (except gas in gas, which is not a colloid). Colloids can be electrolysed by using electrophoresis method and colloids can be hydrophobic and hydrophilic in nature.

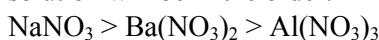
25. According to Schulze-Hardy rule, higher the charge (greater the valency) of the coagulating ion, more is its coagulating power ( $\text{PO}_4^{3-} > \text{SO}_4^{2-} > \text{Cl}^-$ ).



26. According to Schulze-Hardy rule, for the coagulation of a negatively charged colloid, greater the charge on the cation, greater will be its coagulating power and less will be the amount of electrolyte required.

Electrolyte	Cation	Charge on cation
NaNO <sub>3</sub>	Na <sup>+</sup>	+1
Ba(NO <sub>3</sub> ) <sub>2</sub>	Ba <sup>2+</sup>	+2
Al(NO <sub>3</sub> ) <sub>3</sub>	Al <sup>3+</sup>	+3

Thus, the amount of electrolytes required to coagulate a given amount of negatively charged AgI colloidal solution will be in the order:



27. Milk consists of particles of liquid fat dispersed in water.



### Evaluation Test

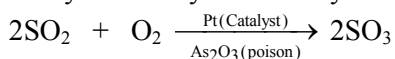
1. Coagulation is brought about by the oppositely charged ions. According to Schulze-Hardy rule, coagulating power is directly proportional to charge on the ion. Hence, minimum amount of AlCl<sub>3</sub> will be needed for the coagulation of negatively charged suspension of clay in water.

2. Freundlich adsorption isotherm is  $\frac{x}{m} = kP^{1/n}$

Taking the logarithm of both sides of the equation,  $\log \frac{x}{m} = \log k + \frac{1}{n} \log P$

The equation is the straight line equation of the form  $y = mx + c$ . Hence, Freundlich adsorption isotherm gives a straight line on plotting  $\log \frac{x}{m}$  vs  $\log P$ .

3. In the conversion of SO<sub>2</sub> to SO<sub>3</sub>, presence of a trace amount of arsenic compound completely destroys the catalytic activity of Pt catalyst forming platinum arsenide at the surface.



Sulphur  
dioxide

Sulphur  
trioxide

5. In an electrophoresis experiment, if the boundary between sol and water falls on the cathode side, then the particles migrate towards negative electrode and they carry positive charge. Among the given options, only Fe(OH)<sub>3</sub> sol is positively charged sol.
6. Lyophilic sol requires large amount of electrolyte to effect coagulation because lyophilic particles are surrounded by layer of dispersion medium through which penetration of ions is difficult.
9. Coagulation power  $\propto$  charge on ion. Hence, Sn<sup>4+</sup> has the maximum coagulation power among the given options.
10. In lyophilic colloids, the lyophilic particles first attract the molecules of dispersion medium to form a layer of dispersion medium surrounding the particles. This layer should also be removed along with charge to cause coagulation. Thus, hydration (or solvation) contributes towards the extra stability of lyophilic colloids.



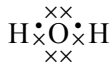
## Hints



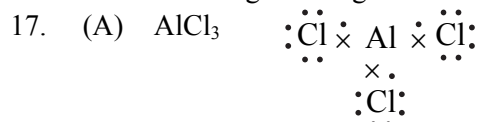
### Classical Thinking

- A chemical bond may be ionic, covalent, metallic or molecular in nature.
- The correct Lewis symbol for oxygen atom is  $\overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{O}}}$
- Electropositive elements have a tendency to form positive ions by losing or donating electrons.
- According to octet rule, atoms try to achieve a complete octet in the valence shell. Since the given element 'X' already has six electrons in the valence shell, it accepts two more electrons and thus completes its octet. Therefore, its ions will have two negative charges (2-).
- Charge on the given cation M is +2 while that on the given anion A is -3. Thus, the electrovalence of M is 2 while that of A is 3. Hence, the compound formed will have the formula  $M_3A_2$ .
- The covalent bond may be directional depending upon the spatial arrangement of overlapping orbitals.
- Bond between two atoms of same element is always covalent in nature.
- Two electrons from each atom are shared, thereby four shared electrons form a double bond.
- Oxygen  ${}_8\text{O}$  ( $1s^2, 2s^2, 2p^4$ ) contains two lone pairs of electrons, in water molecule. Water molecule is formed by oxygen sharing one electron each with two hydrogen atoms.

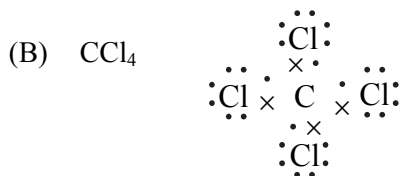
$\therefore$  The correct Lewis structure of  $\text{H}_2\text{O}$  molecule is



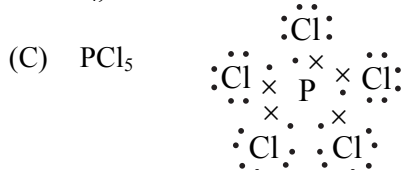
- Be contains 2 electrons in its outer shell. So, it will donate 2 electrons to Cl atoms in order to acquire nearest noble gas configuration and thereby form  $\text{BeCl}_2$ .



In  $\text{AlCl}_3$ , Al contains 6 electrons in the outermost orbit while Cl contains 8 electrons in the outermost orbit.



In  $\text{CCl}_4$ , both C and Cl contain 8 electrons in their respective outermost orbits.



In  $\text{PCl}_5$ , P contains 10 electrons in the outermost orbit while Cl contains 8 electrons in the outermost orbit.



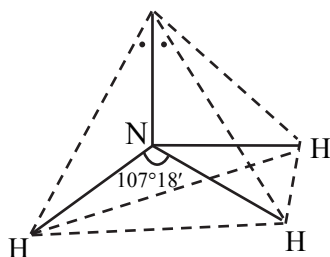
In  $\text{BF}_3$ , B contains 6 electrons in the outermost orbit while F contains 8 electrons in the outermost orbit. Thus, among given options,  $\text{PCl}_5$  is having an expanded octet.



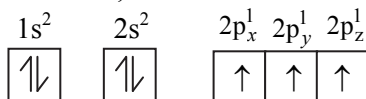


18. Six covalent bonds with six fluorine atoms will result in twelve electrons around S, which is the central element in  $\text{SF}_6$  molecule.
22. Bond enthalpy  $\propto \frac{1}{\text{size of atoms}}$   
 Bond length  $\propto \text{size of atoms}$   
 Thus, smaller the size of bond forming atoms, smaller is the bond length and stronger is the bond formed (i.e., more bond enthalpy). Atomic size of hydrogen is smaller than that of iodine and thus, the bond energy of  $\text{H}_2$  is greater than that of  $\text{I}_2$  because of smaller bond length.
24. Resonating structures of a compound are structures exhibiting different positions of electrons i.e., different electronic arrangements.
25. Resonance structure can be written for only those molecules, which contain multiple bonds such as  $\text{O}_3$  and not for molecules such as  $\text{CH}_4$ ,  $\text{NH}_3$ ,  $\text{H}_2\text{O}$ , etc., which contain only single bonds.
26. As compared to resonating structures, resonance hybrid has the least energy and hence it is most stable.
27. A difference of 1.7 in the electronegativities of the combining atoms produces an ionic character of about 50% in the covalent bond.
28. In  $\text{NH}_3$ , lone pair on nitrogen is in same direction as the resultant dipole moment of N–H bonds. Therefore, it has a net dipole moment, while in  $\text{BF}_3$ ,  $\text{CCl}_4$  and  $\text{CH}_4$  the net dipole moment is zero.
32. The attractive and repulsive forces between the atoms are balanced at an equilibrium inter-nuclear distance, which is 74.0 pm for  $\text{H}_2$ .
36. Hydrogen has its valence electron in the 1s-orbital, whereas halogens have their valence electrons in the respective p-orbital. Therefore, covalent bond between  $\text{HX}$  ( $\text{X} = \text{halogen}$ ) is formed by s-p overlap.
37. Co-axial or head-on overlapping of orbitals result in formation of  $\sigma$ -bonds.
38. Hybridisation is the process of mixing and recasting of atomic orbitals of the same atom with slightly different energies to form equal number of new orbitals with equivalent energy, maximum symmetry and definite orientation in space.
41. In  $\text{PCl}_5$ , the two axial bonds are longer than the three equatorial bonds.

43.

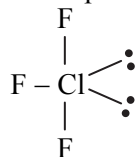


46. The % distribution indicates 2 p-orbitals and one s-orbital to be the components, thereby  $sp^2$  – hybridisation.
47. Carbon does not have d-orbital in the valence shell. Therefore, carbon does not undergo  $sp^3d$  hybridisation.
49. The valence shell electron pairs include the lone pairs and the bond pairs of electrons on the central atom.
50. During formation of  $\text{PF}_5$ , P undergoes  $sp^3d$  hybridisation using all its 5 valence electrons, Hence, it does not have any lone pair.
52. In  $\text{OF}_2$  molecule, oxygen undergoes  $sp^3$  hybridisation.  $\text{OF}_2$  molecule contains 2 lone pairs and 2 bond pairs of electrons. Hence, its shape is bent.
53. The valency of nitrogen in  $\text{NH}_3$  is three, which can be explained by ground state electronic configuration. Therefore, formation of an excited state is not observed for the formation of  $\text{NH}_3$ .

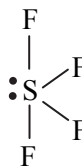




54.  $\text{ClF}_3$  is a T-shaped molecule.



55.  $\text{SF}_4$  molecule contains 1 lone pair and 4 bond pair of electrons. Hence, the geometry of the molecule  $\text{SF}_4$ , according to VSEPR theory, is see saw.



See saw shape

56.  $\text{SF}_6$  has octahedral geometry. Hence,  $\text{F-S-F}$  bond angles are  $180^\circ$  and  $90^\circ$ .
57.  $\text{sp}^3\text{d}$  hybrid orbitals have a trigonal bipyramidal geometry, where 3 hybridised orbitals lie in one plane making angle of  $120^\circ$  between them, and the other two lie opposite to each other and perpendicular to the equatorial plane.
59. Bonding molecular orbitals (MO's) have high electron density between the two nuclei.
62. H, O and C form diatomic molecules i.e.,  $\text{H}_2$ ,  $\text{O}_2$  and  $\text{C}_2$  respectively. Whereas helium (He) owing to its completed duplet do not form diatomic molecules.
64. Hydrogen bond is formed when hydrogen is attached with the atom which is highly electronegative and having small radius. F is the highest electronegative element and hence HF will show strongest hydrogen bond among the given options.
65.  $\text{CH}_3 - \text{CH} \overset{\pi}{=} \text{CH} - \text{CH}_2 - \text{C} \overset{\pi}{\equiv} \text{CH}$   
Carbon – carbon triple bond contains  $2\pi$  bonds and the carbon – carbon double bond contains one  $\pi$  bond, thereby a total of three  $\pi$  bonds in all.



### Critical Thinking

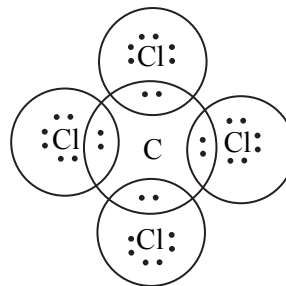
2. Neon is a noble gas and has a completed octet. Thus, its valence is zero.

Element	Lewis symbol	Number or dots in Lewis symbol	Valence
Neon	$\text{:}\ddot{\text{Ne}}\text{:}$	8	$8 - 8 = 0$

4. Electronic configuration of X ( $Z = 12$ ) = 2, 8, 2  
Electronic configuration of Y ( $Z = 17$ ) = 2, 8, 7  
Thus, the X atom will form the corresponding dipositive ion and attain the noble gas configuration of neon.  $\text{X}^{+2} = 2, 8$  (electrovalence = 2 and electronic configuration similar to neon).  
Similarly, the Y atom will form the corresponding univalent anion and attain the noble gas configuration of argon.  
 $\text{Y}^- = 2, 8, 8$  (electrovalence = 1 and electronic configuration similar to argon).
5. Li, Na and K are alkali metals, which are highly electropositive, with low ionization energy and one electron in their outermost shell. So, they form cations easily.
6. The energy required for combination of  $\text{Na}^+$  and  $\text{Cl}^-$  ions (in gaseous state) to form one mole of solid NaCl crystal is called Lattice energy (L). However, the enthalpy of formation of one mole of sodium chloride crystal from sodium and chlorine is the sum of all energies i.e.,  
 $\Delta_f\text{H of NaCl} = \Delta_{\text{sub}}\text{H} + \Delta_{\text{d}}\text{H} + \Delta_{\text{ion}}\text{H} + \Delta_{\text{eg}}\text{H} + \text{L}$

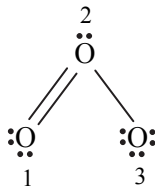


7. When the covalent bond is formed between two atoms, each combining atom contributes one electron to the shared pair. Thus, during the formation of  $\text{CCl}_4$  molecule, each chlorine atom contributes one electron to the shared pair.



9. The formal charge is based on a pure covalent bonding in which electron pairs are shared equally by adjacent atoms. The formal charge is assigned to each atom of the polyatomic molecule or ion.

10.



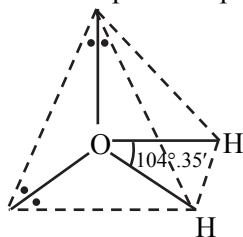
Formal charges on oxygen atoms labelled as 1, 2, 3 in an ozone molecule are calculated as follows:

Number of oxygen atom	Total number of electrons in free atom (A)	Total number of non-bonding electrons (B)	Total number of shared electrons in bond (C)	Formal charge (F.C.) = (A) - (B) - $\frac{1}{2}$ (C)
1	6	4	4	F.C. = $6 - 4 - \frac{1}{2}(4) = 0$
2	6	2	6	F.C. = $6 - 2 - \frac{1}{2}(6) = +1$
3	6	6	2	F.C. = $6 - 6 - \frac{1}{2}(2) = -1$

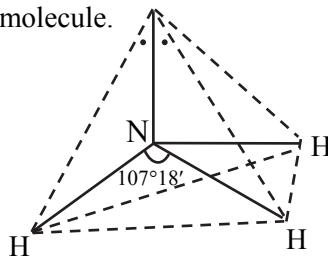
11. In  $\text{BF}_3$ , octet of boron is not complete. B has only six electrons in the outermost shell after forming  $\text{BF}_3$ . Hence, among given options boron trifluoride ( $\text{BF}_3$ ) does not obey octet rule.
13. The bond energy increases with the multiplicity of bonds. Thus, the increasing order of bond energy between carbon-carbon atoms is given as single bond < double bond < triple bond i.e., carbon-carbon triple bond of  $\text{C}_2\text{H}_2$  has the highest energy.
14. Bond energy is defined as the average amount of energy required to break a bond in one mole of a substance in gaseous state. Total energy required to break all the bonds in the gaseous state molecule of  $\text{AB}_2$  is  $x \text{ kJ mol}^{-1}$ . There are two A - B bonds in  $\text{AB}_2$
- $\therefore$  Bond energy of bond A - B =  $\frac{x}{2} \text{ kJ mol}^{-1}$ .
15. Isolectronic molecules and ions have identical bond order.  
 $\text{N}_2$  and  $\text{CO}$  are isoelectronic species with each molecule containing 14 electrons and having three shared pairs of electrons. Hence, their bond order is same (i.e., B.O. = 3)
16. As we move across a period from left to right, the electronegativity increases. Therefore correct order of increasing electronegativity is  $\text{C} < \text{N} < \text{O} < \text{F}$ .  
 Greater the difference in electronegativity of the two atoms forming covalent bonds more is its polar nature. The electronegativity difference between carbon and fluorine is maximum. Hence, among the given options, C-F bond is most polar.
17. The bonds formed between P and Cl in  $\text{PCl}_5$  are covalent bonds, but some ionic character (polarity) arises due to difference in their electronegativity.



19. Larger the charge on cation, greater is extent of polarisation in an ionic compound. So, among given options,  $\text{Al}^{3+}$  has high polarising power than  $\text{Na}^+$  and  $\text{Mg}^{2+}$ . Greater the size of anion greater is the extent of polarisation. Among  $\text{I}^-$  and  $\text{Cl}^-$ ,  $\text{I}^-$  has larger atomic size than  $\text{Cl}^-$ . Thus, among the given options,  $\text{AlI}_3$  has maximum covalent character.
20. Except s-orbital, each atomic orbital has a particular orientation in space.
21. Since s-orbitals do not have a particular direction in space, it provides the most efficient overlap.
22. Energy of atomic orbitals is determined by their respective principal quantum numbers (n). As during hybridisation, atomic orbitals of the atom with same or comparable energies get mixed to form equivalent hybrid orbitals, they necessarily needs to have the same principal quantum number. However, the orbitals taking part in hybridisation can be ns, np or nd; depending on requirement for molecule formation. So, the orbitals of different azimuthal quantum number can participate in the formation of hybrid orbitals.
23. (A) The covalent bonds formed by hybrid orbitals are stronger than those formed by pure atomic orbitals.  
(C) The number of hybrid orbitals formed is same as the number of orbitals taking part in hybridisation.  
(D) Atomic orbitals of same atom can take part in hybridisation.  
Thus, among given options only option (B) is correct.
24. In methane, carbon undergoes  $sp^3$  hybridisation forming four  $sp^3$  hybrid orbitals, which overlaps co-axially with each of the four hydrogen atoms. Thus, there are four bond pairs and no lone pairs.
26. Be has 4 electrons and a valency of two. So it undergoes  $sp$ -hybridisation to form  $\text{BeCl}_2$ .  $sp$ -hybridisation gives the molecule a linear shape.
27. pi bonds are not formed between hybrid orbitals whereas sigma bonds are formed between hybridised orbitals.
28. All the bond angles in trigonal bipyramidal geometry of  $\text{PCl}_5$  molecule are not equivalent. Also, as the bonds in  $\text{PCl}_5$  molecule are slightly longer than the equatorial bonds, they are slightly weaker.
29.  $\text{NH}_3$ ,  $\text{PH}_3$  and  $\text{PCl}_3$  have one lone pair in valence shell of their corresponding central atoms while  $\text{BF}_3$  has none.
30. In water molecule and ammonia molecule, the central atom has  $sp^3$  hybridisation and so the expected bond angle is  $109^\circ 28'$ . Two lone pairs and two bond pairs are present in water molecule whereas one lone pair and three bond pairs are present in ammonia molecule.



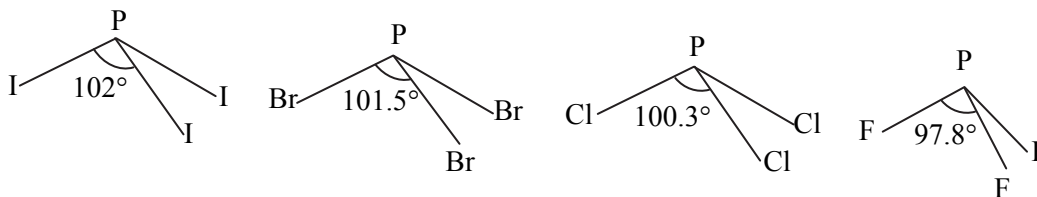
Geometry of water molecule



Geometry of ammonia molecule

The decreasing order of the repulsion between electron pairs is Lone pair–Lone pair > Lone pair–Bond pair > Bond pair–Bond pair. Due to the lone pair–lone pair repulsions, there is decrease in bond angle ( $\sim 5^\circ$ ) of water molecule. Thus, the bond angle in water is less than that of ammonia.

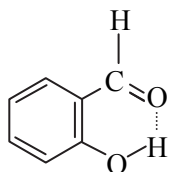
32. As the electronegativity increases from I to F, the bonding electron pairs are attracted more towards the halogen i.e., they move away from nucleus of phosphorus atom thus allowing maximum expansion of the lone pair. So, the bond angle decreases from  $\text{PI}_3$  to  $\text{PF}_3$ .





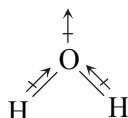
34. Valence bond theory could explain the directional nature of covalent bond. However, it failed to explain:
- the observed valencies of the elements like Be, B, C, etc.
  - geometries of molecules like water and ammonia
  - formation of a co-ordinate covalent bond
  - paramagnetism of oxygen molecule
  - the bonding in electron deficient molecules like  $B_2H_6$ .
35. Atomic orbitals having same or nearly same energy will not combine if they do not have same symmetry.
36. (B) A pi bonding molecular orbital has large electron density above and below the internuclear axis.  
(C) A  $\pi$  antibonding molecular orbital has node between the nuclei.  
(D) In delta orbitals, the internuclear axis lies in two mutually perpendicular planes.
37. A positive bond order means stable molecule. Negative bond or zero bond order indicates an unstable molecule.
39. Bond order (B.O.) =  $\frac{N_b - N_a}{2} = \frac{8-2}{2} = 3$
40. Nitrogen molecule has highest bond energy due to presence of triple bond.
41. Helium molecule does not exist as the bond order of  $He_2 = 0$ .
42. Bond order  $N_2 = \frac{8-2}{2} = 3$  ; Bond order  $C_2 = \frac{6-2}{2} = 2$   
Bond order  $B_2 = \frac{4-2}{2} = 1$  ; Bond order  $Be_2 = \frac{2-2}{2} = 0$
43. The electronic configuration of  $O_2$  molecule is  $KK \sigma 2s^2 \sigma^* 2s^2 \sigma 2p_z^2 \pi 2p_x^2 \pi 2p_y^2 \pi^* 2p_x^1 \pi^* 2p_y^1$  where KK is the closed K shell structure  $(\sigma 1s)^2 (\sigma^* 1s)^2$ . The molecular orbitals  $\pi^* 2p_y$  and  $\pi^* 2p_x$  have one electron each and are degenerate.  
Bond order of  $O_2$  molecule =  $\frac{N_b - N_a}{2} = \frac{8-4}{2} = 2$ .  
The electronic configuration of  $O_2^+$  molecule is  $KK \sigma 2s^2 \sigma^* 2s^2 \sigma 2p_z^2 \pi 2p_x^2 \pi 2p_y^2 \pi^* 2p_x^1 \pi^* 2p_y^0$   
Bond order of  $O_2^+$  molecule =  $\frac{N_b - N_a}{2} = \frac{8-3}{2} = 2\frac{1}{2}$ .
44. (A) The magnitude of hydrogen bonding is dependent of physical state of compound. It is maximum in solid state and minimum in gaseous state.  
(B) The magnitude of hydrogen bonding is minimum in gaseous HF than in liquid HF.  
(D) Intramolecular hydrogen bonding decreases melting point and boiling point of a substance.  
Thus, the only correct option is (C).

45.



**Intramolecular hydrogen bonding in salicylaldehyde**

46. When two helium atoms approach each other, forces of repulsion are greater than the forces of attraction and the potential energy of the system increases and no bond is formed.
47.  $:\ddot{Cl} \times Be \times \ddot{Cl}:$  — Only 4-electrons around central  $Be^-$  atom (incomplete octet)



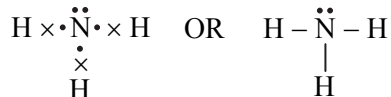
Hence,  $H_2O$  is dipolar whereas  $BeF_2$  is not.

**Competitive Thinking**

- Element 'X' has atomic number 7. So its electronic configuration is 2, 5. Thus, its electron dot symbol would be  $\cdot\overset{\cdot}{\underset{\cdot}{\text{X}}}\cdot$  (as it has 5 valence electrons).
- Lesser the ionization energy/ionization potential of an atom, greater is the ease of losing the valence electron(s) to form the corresponding cations. Higher the value of electron affinity, greater is the ease of formation of corresponding anion. Thus, when an element with very low ionization potential combines with an element having high electron affinity, a strong ionic bond is formed.
- As electronegativity increases, difference between the electronegativities an anion and cation increases. Hence, the ionic bond strength increases.
- Given element X is a second group element. Thus, it can lose two electrons from its outermost shell and so its chloride will have the formula  $\text{XCl}_2$ .
- Two identical atoms are joined with covalent bond, so  $\text{H}_2$  will be covalent. All the other given compounds are made up of elements with high difference in electronegativity. Thus, they will form ionic bonds.
- In  $\text{N}_2$  molecule, each nitrogen atom contributes 3 electrons, so a total number of 6 electrons are shared.

**Triple bond in  $\text{N}_2$  molecule**

- The electronic configuration of nitrogen is  ${}_{7}\text{N} = 1s^2, 2s^2, 2p^3$ . It has 5 electrons in valence shell, hence in ammonia molecule it completes its octet by sharing of three electrons with three H atom. Therefore, it has 8 electrons in its valence shell in ammonia molecule.



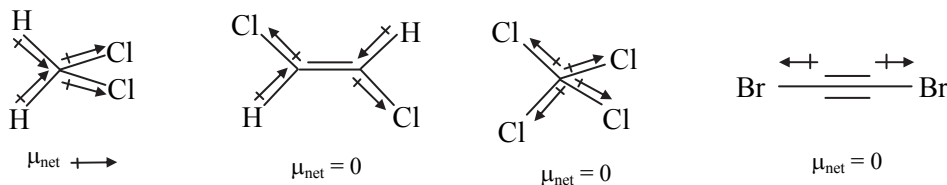
- NO has one unpaired electron with nitrogen.  
 $\cdot\text{N} \cdot \cdot \ddot{\text{O}} \cdot$
- The magnitude of bond energy increases with the multiplicity of bonds. The largest amount of bond energy is required by  $\text{N}_2$  due to triple bonding in  $\text{N}_2$  molecule.
- Lower the bond order, greater will be the bond length. Thus, bond length in NO (bond order 2.5) is greater than in  $\text{NO}^+$  (bond order 3).
- Due to unequal sharing of the bonded pair, the element that is slightly more electronegative develops a partial negative charge and its counterpart develops a partial positive charge. This creates a dipole moment in the molecule.
- Given ionic charge =  $4.8 \times 10^{-10}$  e.s.u. and ionic distance =  $1 \text{ \AA} = 10^{-8}$  cm  
 $\therefore$  Dipole moment = ionic charge  $\times$  ionic distance  
 $\therefore$  Dipole moment of given polar molecule =  $4.8 \times 10^{-10} \times 10^{-8}$   
 $= 4.8 \times 10^{-18}$  e.s.u. cm = 4.8 Debye. (Since 1 Debye unit =  $10^{-18}$  e.s.u. cm)
- Polarity is created due to the difference in electronegativity of atoms in a molecule. As in  $\text{H}_2$  molecule the atoms are same, there is no difference in electronegativity. Hence,  $\text{H}_2$  is non-polar molecule.
- HF has largest dipole moment because electronegativity difference between H and F is highest among other given options, so it is highly polar.
- $\text{CO}_2$  is a symmetrical molecule so its dipole moment is zero.



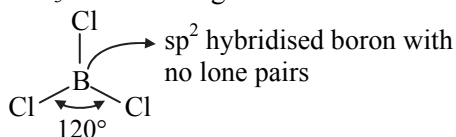
23.

Molecule	Nature of bonds	Dipole moment of the molecule, $\mu$ (D)
NH <sub>3</sub>	N – H, Polar	1.47 (Polar)
CH <sub>4</sub>	C – H, Non-polar	0 (Non-polar)
CHCl <sub>3</sub>	C – Cl, Polar	1.04 (Polar)
H <sub>2</sub> S	H – S, Polar	0.95 (Polar)

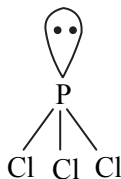
24.



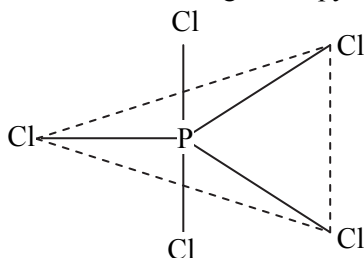
25. As the size of anion increases, polarisability increases. For halide ions the anionic size increases in the order  $F^- < Cl^- < Br^- < I^-$ . Hence, polarisability of halide ions increases in the order  $F^-, Cl^-, Br^-, I^-$ .
26. According to Fajan's rule, greater charge and smaller size of cation increases the extent of polarisation (i.e., increase in covalent character in ionic bond). Among the  $Li^+, Rb^+, Be^{2+}$  and  $Mg^{2+}$ ,  $Be^{2+}$  has greater charge and smaller ionic radius. So,  $BeCl_2$  is having least ionic character. Similarly, compound with lesser charge and greater size of cation will have greatest ionic character. So,  $RbCl$  is having greatest ionic character.
27. Order of polarising power  $Be^{++} > Li^+ > Na^+$   
Hence order of covalent character  $BeCl_2 > LiCl > NaCl$ .
28. Geometry in  $sp^2$ - hybridisation is trigonal.
29. In  $BF_3$  molecule, boron is  $sp^2$  hybridised. Hence, it will have planar trigonal geometry. So, all its atoms are co-planar.
30.  $BCl_3$  has bond angles of  $120^\circ$ .



31. Hybridization of phosphorus atom in  $PCl_3$  is  $sp^3$ .



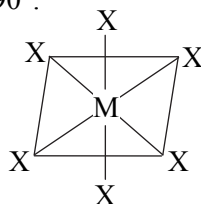
32. The combining atomic orbitals must have same symmetry about the molecular axis. Since the z axis is considered as the molecular axis,  $p_z$  orbital of one atom combines with  $p_z$  orbital of the other atom to form two sigma molecular orbitals. However,  $p_x$  orbital of one atom cannot combine with  $p_y$  orbital of the other atom because of their different symmetries.
33.  $\pi$ -bond is formed by lateral overlapping of unhybridised p-p orbitals.
34.  $PF_5$  involves  $sp^3d$  hybridisation and hence has trigonal bipyramidal structure.
35.  $dsp^3$  or  $sp^3d$  hybridisation exhibits trigonal bipyramidal geometry eg.  $PCl_5$



**Trigonal bipyramidal geometry of  $PCl_5$  molecule**

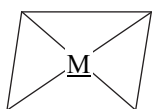


37.  $\text{IF}_7$  molecule shows  $\text{sp}^3\text{d}^3$  hybridisation and hence has pentagonal bipyramidal shape.
38. In octahedral molecule, six hybrid orbitals are directed towards the corner of a regular octahedron with a bond angle of  $90^\circ$ .

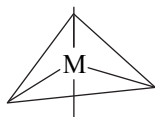


According to this geometry, the number of X–M–X bond at  $180^\circ$  is three.

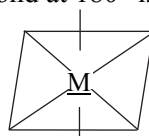
39.



$\text{dsp}^2$  hybridisation  
(Four  $90^\circ$  angles between  
bond pair and bond pair)



$\text{sp}^3\text{d}$  hybridisation  
(Six  $90^\circ$  angle between  
bond pair and bond pair)



$\text{sp}^3\text{d}^2$  hybridisation  
(Twelve  $90^\circ$  angle between  
bond pair and bond pair)

In  $\text{sp}^3$  hybridisation, the molecule has tetrahedral geometry in which the angle between bond pairs is  $\sim 109^\circ$ . In  $\text{dsp}^2$  hybridisation, the molecule has square planar geometry in which the hybridised orbitals are perpendicular to each other. In  $\text{sp}^3\text{d}$  hybridisation, the molecule has trigonal bipyramid structure. The axial orbitals are perpendicular to the three equatorial orbitals present in the triangular plane. So, two axial orbitals together will give six  $90^\circ$  angle between bond pairs.

In  $\text{sp}^3\text{d}^2$  hybridisation, the molecule has octahedral geometry in which all the six orbitals are perpendicular to each other and hence give twelve  $90^\circ$  angles. Thus, the maximum number of  $90^\circ$  angles between bond pair-bond pair of electrons is observed in  $\text{sp}^3\text{d}^2$  hybridisation.

40. The forces of repulsion between electron pairs decrease in the following order:  
lone pair – lone pair > lone pair – bond pair > bond pair – bond pair
41. Compound is carbon tetrachloride because carbon in  $\text{CCl}_4$  has  $\text{sp}^3$  hybridisation, 4 orbitals giving regular tetrahedral structure. In other given options, the geometry is little distorted in spite of  $\text{sp}^3$  hybridisation due to different atoms on the vertices of tetrahedron, which results in dipole and thereby distortion.
42. In  $\text{NH}_3$ , although the central atom N is  $\text{sp}^3$  hybridised, the bond angle is  $107^\circ 18'$  (instead of  $109^\circ 28'$ ). The decrease in bond angle is due to repulsion between the lone pair of electrons on N-atom and bond pairs of electrons between N and H atoms.

44.

Molecule	Bond angle
$\text{CH}_4$	H – C – H: $109^\circ 28'$
$\text{NH}_3$	H – N – H: $107^\circ 18'$
$\text{H}_2\text{O}$	H – O – H: $104^\circ 35'$

45.

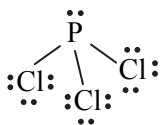
Molecule	$\text{H}_2\text{O}$	$\text{NH}_3$	$\text{CH}_4$	$\text{CO}_2$
Bond angle	$104^\circ 35'$	$107^\circ 18'$	$109^\circ 28'$	$180^\circ$

Hence, among given options, the bond angle between two covalent bonds is greatest in  $\text{CO}_2$ .





46.



Each bond represents one bond pair. Thus in  $\text{PCl}_3$ , the molecule contains three bond pairs and a lone pair around the central phosphorus atom.

48. The bonding molecular orbitals have lower energy than the combining atomic orbitals and hence, are much more stable than corresponding antibonding molecular orbitals.

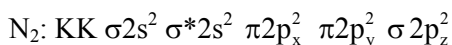
50. With increase in bond order, bond enthalpy or bond energy increases and bond length decreases.

51.

Species	EC	BO	Magnetic nature
$\text{He}_2^+$	$\sigma 1s^2 \sigma^* 1s^1$	$\frac{1}{2}$	P
$\text{H}_2$	$\sigma 1s^2$	1	D
$\text{H}_2^+$	$\sigma 1s^1$	$\frac{1}{2}$	P
$\text{H}_2^-$	$\sigma 1s^2 \sigma^* 1s^1$	$\frac{1}{2}$	P

(P = Paramagnetic, D = Diamagnetic)

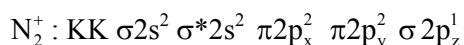
52. Electronic configuration of  $\text{N}_2$  molecule is



KK represents closed K shell structure  $(\sigma 1s)^2 (\sigma^* 1s)^2$ .

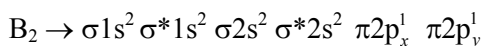
$$\text{Bond order of } \text{N}_2 \text{ molecule} = \frac{N_b - N_a}{2} = \frac{8 - 2}{2} = 3$$

53. Electronic configuration of  $\text{N}_2^+$  molecule is

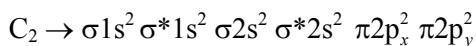


$$\text{Bond order of } \text{N}_2^+ \text{ molecule} = \frac{N_b - N_a}{2} = \frac{7 - 2}{2} = \frac{5}{2} = 2.5$$

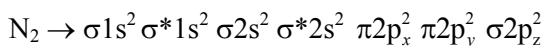
54. Paramagnetic property arises through unpaired electron in one or more molecular orbitals.



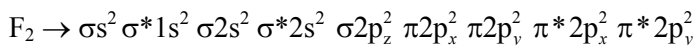
(2 unpaired electrons)



(No unpaired electron)



(No unpaired electron)

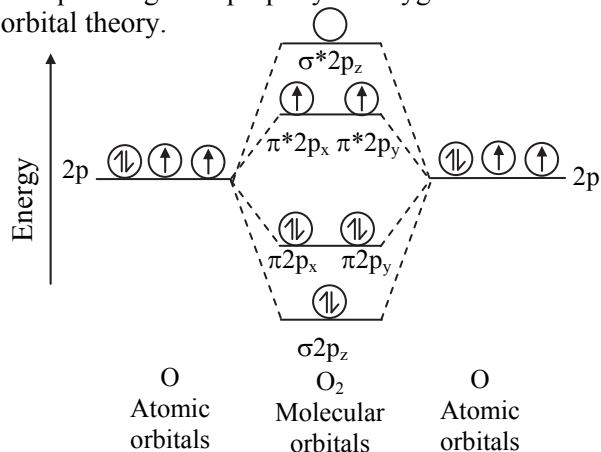


(No unpaired electron)

So, only  $\text{B}_2$  has unpaired electrons and show the paramagnetism.



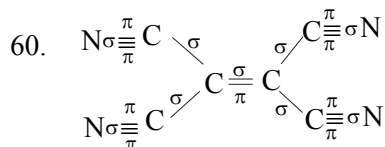
55. The paramagnetic property in oxygen is due to unpaired electron, which can be explained by molecular orbital theory.



### Molecular orbital diagram for O<sub>2</sub> molecule

So, 2 unpaired of electrons are present in  $\pi^*2p_x$  and  $\pi^*2p_y$ .

56.  $O_2^-$  : B.O. =  $\frac{8-6}{2} = 1$ ,                       $O_2^-$  : B.O. =  $\frac{8-5}{2} = 1.5$ ,  
 $O_2$  : B.O. =  $\frac{8-4}{2} = 2$ ,                       $O_2^+$  : B.O. =  $\frac{8-3}{2} = 2.5$
59. NH<sub>3</sub>, H<sub>2</sub>O and HF form extensive intermolecular hydrogen bonding due to high electronegativity of N, O and F. Thus, NH<sub>3</sub>, H<sub>2</sub>O and HF show abnormally high values for melting and boiling points.



9 $\pi$  and 9 $\sigma$  bonds.

61. Diamond consists of only carbon atoms joined together to form a crystal lattice. Two identical atoms are joined by covalent bond. So, the nature of bonding in diamond is covalent.
63. Bond angle of H<sub>2</sub>O is 104.5° due to lp-lp repulsion. Also, water has dipole moment of 1.84 Debye.
64. CO  $\Rightarrow$  Bond order = 3  
 CN<sup>-</sup>  $\Rightarrow$  Bond order = 3



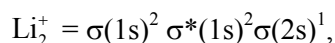
### Evaluation Test

- In a homologous series, hybridisation involved does not alter.  
 $\therefore$  the % of 's' - character remains the same.
- Beryllium undergoes sp hybridisation. One 2s and 2p<sub>x</sub> gets hybridised to form two 'sp' hybrid orbitals. The 2p<sub>y</sub> and 2p<sub>z</sub> orbitals are not used.  
 BF<sub>3</sub> undergoes sp<sup>2</sup>-hybridisation. Only one p-orbital remains unused. NH<sub>3</sub> undergoes sp<sup>3</sup>-hybridisation hence all p orbitals are used. Acetylene (C<sub>2</sub>H<sub>2</sub>) undergoes sp-hybridisation. The remaining p<sub>y</sub> and p<sub>z</sub> orbitals of each carbon atom overlap laterally with that of the other C atom to form two pi bonds.
- Bond energy is the energy required to dissociate one mole of the molecule into its constituent gaseous atoms.  
 For H<sub>2</sub>, 1 mole  $\equiv$  2 g  
 $\therefore$  4 g = 2 moles  
 $\therefore$  energy required =  $\frac{208}{2} = 104$  kcal

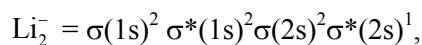


$$6. \quad \text{Li}_2 = \sigma(1s)^2 \sigma^*(1s)^2 \sigma(2s)^2,$$

$$\text{Bond order} = \frac{1}{2}(4 - 2) = 1$$



$$\text{Bond order} = \frac{1}{2}(3 - 2) = \frac{1}{2}$$

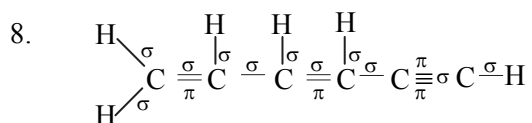


$$\text{Bond order} = \frac{1}{2}(4 - 3) = \frac{1}{2}$$

$\text{Li}_2^-$  is less stable than  $\text{Li}_2^+$  because  $\text{Li}_2^-$  has more number of electrons in the antibonding molecular orbitals. Otherwise greater the bond order, greater is the stability. Hence, the correct order is



7. Bond angle is expressed in degree ( $^\circ$ ), minutes ( $'$ ) and seconds ( $''$ ).



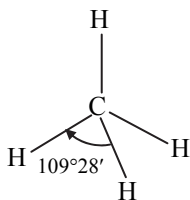
Thus, the given molecule contains 11 sigma bonds.

9. Higher the lattice energy, greater will be the ease of formation of the crystal and more stable will be the ionic crystal.

10. In  $\text{BeCl}_2$ , there are only 4 electrons around Be. Hence,  $\text{BeCl}_2$  is electron deficient, as octet of Be is incomplete.

11.  $sp^3d^2$  hybridisation results in octahedral geometry. e.g.  $\text{SF}_6$

12.  $\text{CH}_4$  has bond angles of  $109^\circ 28'$ .



14. A bond order can be negative, zero or positive. A positive bond order means stable molecule while negative bond or zero bond order indicate an unstable molecule.

Bond order can be given as:

$$= \frac{1}{2}(N_b - N_a)$$

Where,  $N_b$  = number of bonding orbitals

$N_a$  = number of antibonding orbitals

So, for molecule to be stable i.e., for positive bond order, the number of bonding orbitals should be greater than the number of antibonding orbitals.

15. Bond order in  $\text{Be}_2$  is zero. Therefore, it does not exist under normal conditions.

16. Polar nature increases as the electronegativity difference increases. In  $\text{O} - \text{H} = 3.5 - 2.1 = 1.4$ , electronegativity difference is maximum.

Hence, the  $\text{O} - \text{H}$  bond is the most polar.



17.  $\text{BF}_3$ ,  $\text{sp}^2$ , trigonal planar  
 $\text{CO}_2$ , sp, linear
18. Ionic distance =  $0.8 \text{ \AA} = 0.8 \times 10^{-8} \text{ cm}$   
 $= 8 \times 10^{-9} \text{ cm}$   
Dipole moment = ionic charge  $\times$  ionic distance  
 $= 2.6 \times 10^{-10} \times 8 \times 10^{-9} = 2.08 \times 10^{-18} \text{ e.s.u. cm}$   
 $= 2.08 \text{ Debye}$  ( $\because 1 \text{ Debye} = 10^{-18} \text{ e.s.u. cm}$ )
19.  $\text{NH}_3$ ,  $\text{H}_2\text{O}$  and  $\text{HF}$  form extensive intermolecular hydrogen bonding due to high electronegativity of N, O and F.

# 09 Hydrogen



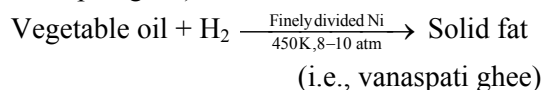
## Hints



### Classical Thinking

5. Hydrogen has three isotopes viz.,  
Hydrogen or Protium ( ${}^1_1\text{H}$  or H),  
Deuterium ( ${}^2_1\text{H}$  or D),  
Tritium ( ${}^3_1\text{H}$  or T)
6. Tritium is a  $\beta$ -particle emitter.
7. Number of neutrons  
= Mass number – Atomic number  
= 3 – 1  
= 2
10.  $\text{Zn} + 2\text{NaOH} \longrightarrow \text{Na}_2\text{ZnO}_2 + \text{H}_2\uparrow$   
Zinc      Sodium      Sodium  
            hydroxide      zincate  
            (Alkali)
- $\text{Zn} + 2\text{HCl} \longrightarrow \text{ZnCl}_2 + \text{H}_2\uparrow$   
Zinc      Hydrochloric      Zinc  
            acid                      chloride  
            (Acid)
11.  $\text{Mg} + \text{H}_2\text{SO}_4 \longrightarrow \text{MgSO}_4 + \text{H}_2\uparrow$   
Magnesium      (dil.)      Magnesium      Hydrogen gas  
ribbon                      sulphate      (very pure)
14. In Lane's process, hydrogen is formed by passing superheated steam over iron fillings.  
 $3\text{Fe} + 4\text{H}_2\text{O} \xrightarrow[\text{Fe}]{1023-1073 \text{ K}} \text{Fe}_3\text{O}_4 + 4\text{H}_2$   
Iron (Steam)                      Ferric  
fillings                                      oxide
17. Production of atomic hydrogen is carried out at a high temperature in an electric arc or under ultraviolet radiations. Methods given in other options produce molecular hydrogen.
18. Among the halogens, fluorine has great affinity for hydrogen and combines even at very low temperature (63 K) forming hydrogen fluoride.
19. In Haber process for the manufacture of ammonia, dinitrogen and dihydrogen react in presence of catalyst to form ammonia.  
 $3\text{H}_{2(g)} + \text{N}_{2(g)} \xrightarrow[200 \text{ atm}]{673 \text{ K, Fe catalyst}} 2\text{NH}_{3(g)}$   
Dihydrogen      Dinitrogen                      Ammonia

20. Hydrogenation of vegetable oils using nickel as catalyst gives edible fats (margarine and vanaspati ghee).



25. Ionic hydrides are generally crystalline, non-volatile and non-conducting in solid state. However, in the molten state, they conduct electricity.

26.

Compound	Type of hydride
$\text{CaH}_2$	Ionic hydride
$(\text{MgH}_2)_n$	Ionic hydride
$\text{CH}_4$	Molecular hydride
$\text{LiH}$	Ionic hydride

27. Covalent hydrides are formed by p-block elements like oxygen, nitrogen, etc. Nickel is a transition metal from d-block while potassium and sodium are s-block elements.

28.

Compound	Type of hydride
HF	Electron-rich hydride (3 lone pairs of $e^-$ )
$\text{CH}_4$	Electron-precise hydride
$\text{B}_2\text{H}_6$	Electron-deficient hydride
KH	Ionic hydride

30. Metallic hydrides are deficient in hydrogen as the quantity of hydrogen does not bear an exact stoichiometric ratio to the metal.

31. The estimated world water supply by oceans is around 97.33%.

32. Ice crystallizes in the hexagonal form at atmospheric pressure and condenses to cubic form at very low temperatures.

37.

Isotopic varieties of water	Molecular weight ( $\text{g mol}^{-1}$ )
$\text{H}_2^{16}\text{O}$	18
$\text{D}_2^{17}\text{O}$	21
$\text{H}_2^{18}\text{O}$	20
$\text{T}_2^{18}\text{O}$	24



39.  $3\text{BaO}_2 + 2\text{H}_3\text{PO}_4 \longrightarrow \text{Ba}_3(\text{PO}_4)_2\downarrow + 3\text{H}_2\text{O}_2$   
 Barium Peroxide      Phosphoric acid      Barium phosphate      Hydrogen peroxide
41. 30 volume  $\text{H}_2\text{O}_2$  means that 1L of this solution gives 30 L of oxygen at S.T.P.  
 $\therefore$  1  $\text{cm}^3$  of this solution will give 30  $\text{cm}^3$  of oxygen at S.T.P.
42. Volume strength of  $\text{H}_2\text{O}_2 = \text{Normality} \times 5.6$   
 $\therefore$  Normality =  $\frac{10}{5.6} = 1.79 \text{ N}$
49.  $\begin{array}{c} \text{CH}_2 \\ || \\ \text{CH}_2 \end{array} + \text{H}_2\text{O}_2 \longrightarrow \begin{array}{c} \text{CH}_2\text{OH} \\ | \\ \text{CH}_2\text{OH} \end{array}$   
 Ethene      Ethylene glycol
52. For fuel cells that use dihydrogen, the energy released per unit mass of fuel (dihydrogen) is greater in comparison to gasoline.

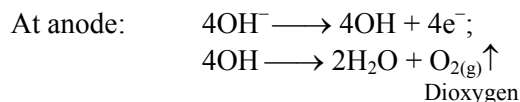
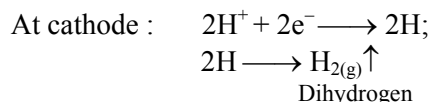
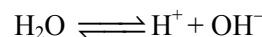
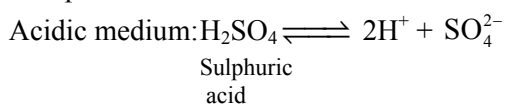
**Critical Thinking**

- ${}^2_1\text{H}$  or D has 2 nucleons (1 proton + 1 neutron) and one electron, so sum of these is  $2 + 1 = 3$ .
- Deuterium ( ${}^2_1\text{H}$ ) and hydrogen ( ${}^1_1\text{H}$ ) both have same atomic number but different mass numbers so they have similar chemical properties but different physical properties.
- The three isotopes of hydrogen exist in the following ratio.  
 Protium : Deuterium : Tritium  
 1 :  $1.56 \times 10^{-4}$  :  $1 \times 10^{-17}$

4.

Property	Hydrogen	Deuterium	Tritium
Relative atomic mass ( $\text{g mol}^{-1}$ )	1.008	2.014	3.016
Density ( $\text{g L}^{-1}$ )	0.09	0.18	0.27
Melting point (K)	13.96	18.73	20.62
Active abundance (%)	99.985	0.0156	$10^{-15}$

- During electrolysis, of acidified water using platinum electrodes, the following reactions take place:



Thus, dihydrogen is liberated at cathode and dioxygen is liberated at anode.

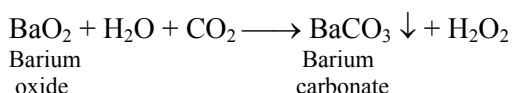
- The reactivity of hydrogen towards halogens decreases in the order  $\text{F} > \text{Cl} > \text{Br} > \text{I}$ . Fluorine has great affinity for hydrogen and reacts with it at low temperature or even in dark to form HF.
- Alkali metal hydrides react with water to give metal hydroxide and  $\text{H}_2$ .  
**eg.**  $\text{NaH} + \text{H}_2\text{O} \longrightarrow \text{NaOH} + \text{H}_2\uparrow$   
 Sodium hydride      Sodium hydroxide

Alkali metal hydroxides are strongly basic in nature.

- $8\text{LiH} + \text{Al}_2\text{Cl}_6 \longrightarrow 2\text{LiAlH}_4 + 6\text{LiCl}$   
 Lithium hydride      Lithium aluminium hydride      Lithium chloride
- $\text{CrH}$  and  $\text{TiH}_2$  are metallic hydrides.  $\text{CH}_4$  and  $\text{HF}$  are molecular hydrides.  $\text{NaH}$  and  $\text{CaH}_2$  are ionic hydrides.  $\text{BaH}_2$  is an ionic hydride while  $\text{SiH}_4$  is a molecular hydride.
- Al forms the polynuclear hydride having the general formula  $(\text{AlH}_3)_x$ .
- Water has high dielectric constant i.e., 78.39, a very strong solvating tendency and can dissolve maximum number of compounds through hydrogen bonding. Hence, it is called as universal solvent.
- $2\text{F}_{2(\text{g})} + 2\text{H}_2\text{O}_{(\text{l})} \rightarrow 4\text{H}_{(\text{aq})}^+ + 4\text{F}_{(\text{aq})}^- + \text{O}_{2(\text{g})}$   
 Fluorine      Dioxygen
- Tritium oxide ( $\text{T}_2^{16}\text{O}$ ) molecule has two tritium (T or  ${}^3_1\text{H}$ ) atoms and one oxygen ( ${}^{16}\text{O}$ ) atom.  
 Therefore, molecular weight of  $\text{T}_2^{16}\text{O}$   
 $= 2 \times 3 + 1 \times 16$   
 $= 22 \text{ amu}$



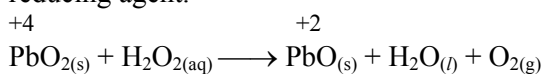
21.  $\text{H}_2\text{O}_2$  is prepared by bubbling  $\text{CO}_2$  through a paste of  $\text{BaO}_2$ .



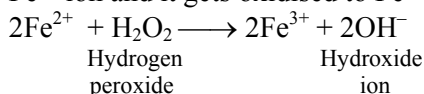
22. Volume strength of  $\text{H}_2\text{O}_2 = 11.2 \times \text{Molarity}$   
 $= 11.2 \times 3.0$   
 $= 33.6$

24. It has slightly different bond lengths and bond angles in liquid and solid phases due to hydrogen bonding.

26. In the following reaction,  $\text{H}_2\text{O}_2$  acts as a reducing agent.



27. When small amount of  $\text{H}_2\text{O}_2$  is added to ferrous sulphate solution, an electron is lost by  $\text{Fe}^{+2}$  ion and it gets oxidised to  $\text{Fe}^{+3}$  ion.



29. Generation of hydrogen is possible from sea water, thus it is limitless and renewable source of energy. However, it is an expensive form of energy, as production of  $\text{H}_2$  requires considerable energy.

30.  $\text{D}_2$  molecule has two atoms of deuterium (D or  ${}^2_1\text{H}$ ).

Each deuterium atom has 1 proton and 1 neutron.

- $\therefore$  Number of nucleons in  $\text{D}_2$  molecule  
 $= 2 \text{ protons} + 2 \text{ neutrons}$   
 $= 4 \text{ nucleons}$

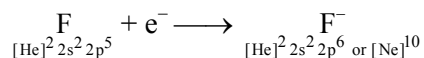
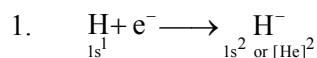
31.  $\text{CaH}_2$  i.e.,  $2 + 2x = 0$ ,

$$\therefore 2x = -2$$

$$x = \frac{-2}{2} = -1$$



### Competitive Thinking

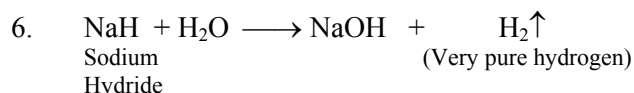


2. Unlike alkali metals, hydrogen does not exhibit metallic character.

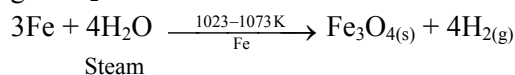
4. Hydrogen resembles halogens in some properties and therefore, hydrogen can be

placed in group 17 of periodic table. Hydrogen resembles alkali metals in some other properties and therefore, can also be placed in first group of periodic table.

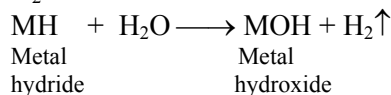
Since, hydrogen resembles both alkali metals and halogens, but also differs from them, it is placed separately in the periodic table.



7. Iron (Fe) does not react with cold water to give  $\text{H}_2$ . However, iron reacts with steam to give  $\text{H}_2$ .

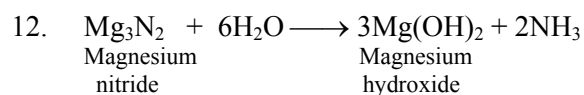
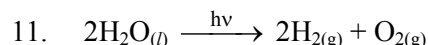


8. Metal hydride on treatment with water gives  $\text{H}_2$ .

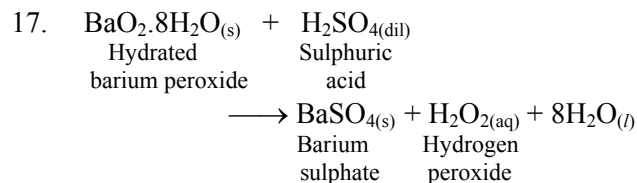
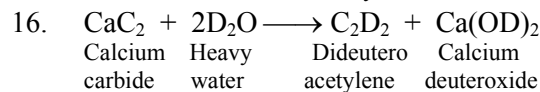
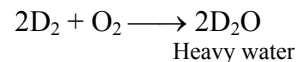


9. Water molecules associate due to intermolecular hydrogen bonding. Energy is required to break these bonds and so the boiling point of water is exceptionally high.

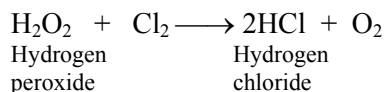
10. The H–O–H angle in water molecule is  $104^\circ 35'$   $\approx 105^\circ$  (due to two lone pair of electrons).



13. Heavy water is formed by the combination of heavier isotope ( ${}^2_1\text{H}$  or D) of hydrogen with oxygen.



18.  $\text{H}_2\text{O}_2$  reduces  $\text{Cl}_2$  to  $\text{HCl}$ , hence it is known as antichlor.





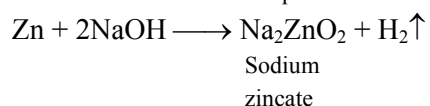
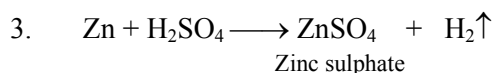
19. Volume strength of  $\text{H}_2\text{O}_2 = \text{Normality} \times 5.6$   
 $= 1.5 \times 5.6$   
 $= 8.4$
20.  $2\text{H}_2\text{O}_2 \longrightarrow 2\text{H}_2\text{O} + \text{O}_2$   
 $2 \times 34 \text{ g} \qquad\qquad 22400 \text{ mL}$   
 $\therefore 2 \times 34 \text{ g} = 68 \text{ g of } \text{H}_2\text{O}_2 \text{ liberates } 22400 \text{ mL}$   
 $\text{O}_2 \text{ at STP}$   
 $\therefore 0.68 \text{ g of } \text{H}_2\text{O}_2 \text{ liberates } = \frac{0.68 \times 22400}{68}$   
 $= 224 \text{ mL}$
21. 10 volume solution of  $\text{H}_2\text{O}_2$  means that 1 L of this  $\text{H}_2\text{O}_2$  will give 10 L of oxygen at STP.  
 $2\text{H}_2\text{O}_2 \longrightarrow \text{O}_{2(\text{g})} + 2\text{H}_2\text{O}_{(\text{l})}$   
 $2 \times 34 \text{ g} \equiv 22.4 \text{ L at STP}$   
 $68 \text{ g} \equiv 22.4 \text{ L at STP}$   
 $22.4 \text{ L of } \text{O}_2 \text{ at STP is produced from } 68 \text{ g of } \text{H}_2\text{O}_2.$   
 $\therefore 10 \text{ L of } \text{O}_2 \text{ at STP is produced from } \text{H}_2\text{O}_2$   
 $= \frac{68 \times 10 \text{ g}}{22.4}$   
 $= 30.35 \text{ g}$   
 $\therefore \text{Strength of } \text{H}_2\text{O}_2 \text{ in } 10 \text{ volume solution}$   
 $= 30.35 \text{ g/L}$
22. 10 volume solution of  $\text{H}_2\text{O}_2$  means that 1 L of  $\text{H}_2\text{O}_2$  will give 10 L of oxygen at STP.  
 $2\text{H}_2\text{O}_2 \longrightarrow \text{O}_{2(\text{g})} + 2\text{H}_2\text{O}_{(\text{l})}$   
 $2 \times 34 \text{ g} \equiv 22.4 \text{ L at STP}$   
 $\therefore 68 \text{ g} \equiv 22.4 \text{ L at STP}$   
 $\text{Thus, } 22.4 \text{ L of } \text{O}_2 \text{ at STP is produced from } \text{H}_2\text{O}_2 = 68 \text{ g}$   
 $\therefore 10 \text{ L of } \text{O}_2 \text{ at STP is produced from } \text{H}_2\text{O}_2$   
 $= \frac{68 \times 10}{22.4} \text{ g} = 30.35 \text{ g}$   
 $\text{Thus, strength of } \text{H}_2\text{O}_2 \text{ in } 10 \text{ volume } \text{H}_2\text{O}_2 =$   
 $30.35 \text{ g/L}$   
 $\therefore \text{Percentage strength of } \text{H}_2\text{O}_2 \text{ in } 10 \text{ volume}$   
 $\text{H}_2\text{O}_2 = 3.035 \%$
23. Quantity of 20 volume  $\text{H}_2\text{O}_2 = 15 \text{ mL}$   
 $20 \text{ volume of } \text{H}_2\text{O}_2 \text{ means } 1 \text{ litre of this}$   
 $\text{solution will give } 20 \text{ litres of oxygen at S.T.P.}$   
 $\text{Since, oxygen liberated from } 1000 \text{ mL (1 litre)}$   
 $\text{of } \text{H}_2\text{O}_2 = 20 \text{ litres, therefore oxygen liberated}$   
 $\text{from } 15 \text{ mL of } \text{H}_2\text{O}_2 = \frac{20}{1000} \times 15$   
 $= 0.3 \text{ litre} = 300 \text{ mL}$
24. 100 volume  $\text{H}_2\text{O}_2$  means that 1 L of this  $\text{H}_2\text{O}_2$  will give 100 L of oxygen at STP.  
 $\therefore 200 \text{ mL of this } \text{H}_2\text{O}_2 \text{ will give}$   
 $\frac{100 \times 200 \times 10^{-3}}{1} = 20 \text{ L of oxygen at STP}$   
 $2\text{H}_2\text{O}_2 \longrightarrow 2\text{H}_2\text{O} + \text{O}_2$   
 $(68 \text{ g}) \qquad\qquad\qquad (22.4 \text{ L})$   
 $\therefore 22.4 \text{ L of } \text{O}_2 \text{ at STP is produced from}$   
 $\text{H}_2\text{O}_2 = 68 \text{ g}$   
 $\therefore 20 \text{ L of } \text{O}_2 \text{ at STP is produced from}$   
 $\frac{68 \times 20}{22.4} = 60.71 \text{ g of } \text{H}_2\text{O}_2$
25. Equivalent weight of  $\text{H}_2\text{O}_2 = 17$   
 $N = \frac{30.36}{17} = 1.78 \text{ N}$   
 $\text{Volume strength} = 5.6 \times \text{Normality}$   
 $= 5.6 \times 1.78 = 10$
27.  $\overset{0}{\text{Cl}}_2 + \text{H}_2\overset{-1}{\text{O}}_2 \longrightarrow 2\overset{-1}{\text{H}}\overset{-1}{\text{Cl}} + \text{O}_2$   
 $\text{Hydrogen} \qquad \text{Hydrochloric}$   
 $\text{Peroxide} \qquad \text{acid}$   
 $\text{In the above reaction, } \text{H}_2\text{O}_2 \text{ acts as reducing}$   
 $\text{agent and reduces chlorine.}$   
 $\text{In this reaction, } \text{H}_2\text{O}_2 \text{ works as reducing agent.}$
28.  $\text{H}_2\text{O}_2$  can act as both oxidizing as well as reducing agent.
29. Hydrogen is the lightest gas. It is insoluble in water.
30.  $\text{D}_2\text{O}$  is heavy water, in which  $\text{D} = {}^2_1\text{H}$



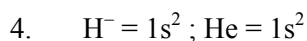
## Evaluation Test

1. Following six diatomic molecules are possible.  
 ${}^1\text{H} - {}^1\text{H}, {}^1\text{H} - {}^2\text{H}$   
 ${}^2\text{H} - {}^2\text{H}, {}^2\text{H} - {}^3\text{H}$   
 ${}^3\text{H} - {}^3\text{H}, {}^1\text{H} - {}^3\text{H}$
2. Gold is a noble metal.



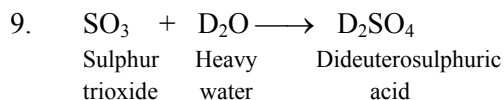
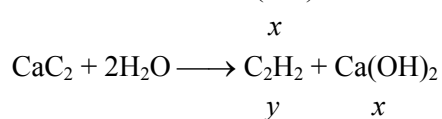
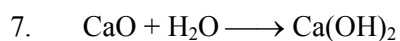


$\therefore$  Ratio of volumes of  $\text{H}_2$  evolved is 1 : 1.



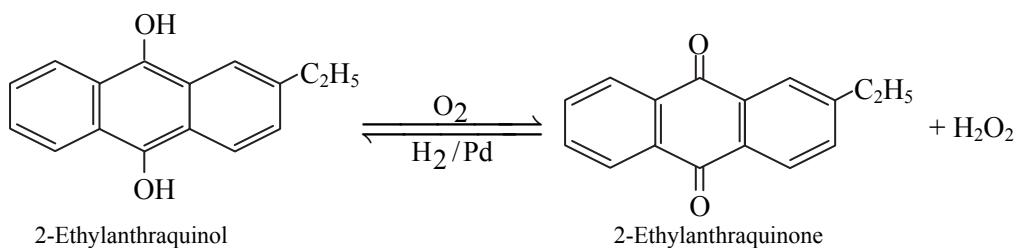
5.  $\text{CaH}_2$  is known as hydrolith.

6.  $\text{H}_2\text{O}_2$  is a better polar solvent than  $\text{H}_2\text{O}$ . However, it cannot be used as such because of the strong auto oxidation.



13. Elements of group 15 form electron-rich hydrides and act as Lewis bases.  
Electron-deficient hydrides act as Lewis acids.

14.  $\text{H}_2\text{O}_2$  is prepared industrially by the auto-oxidation of 2-ethylanthraquinol (10% solution in benzene and cyclohexane).



15.

	Compound	Molar mass
I	$\text{H}_2^{17}\text{O}$	$19 \text{ g mol}^{-1}$
II	$\text{D}_2^{18}\text{O}$	$22 \text{ g mol}^{-1}$
III	$\text{D}_2^{16}\text{O}$	$20 \text{ g mol}^{-1}$
IV	$\text{DT}^{16}\text{O}$	$21 \text{ g mol}^{-1}$

# 10 s-Block Elements

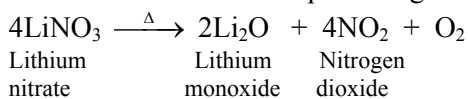


## Hints



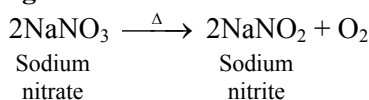
### Classical Thinking

- Caesium ( $Z = 55$ ), rubidium ( $Z = 37$ ) and potassium ( $Z = 19$ ) are alkali metals while strontium ( $Z = 38$ ) is an alkaline earth metal.
- Among alkaline earth metals, radium is the rarest element comprising of only  $10^{-10}\%$  of igneous rocks.
- Lithium nitrate on decomposition gives lithium monoxide, nitrogen dioxide and oxygen.

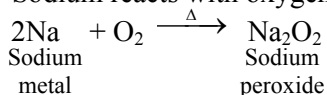


Other alkali metal nitrates on decomposition gives the corresponding nitrites and oxygen.

eg.

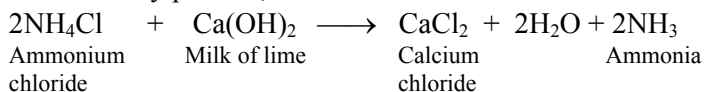


- Ionization enthalpies of alkali metals decreases down the group from Li to Cs.
- Sodium reacts with oxygen to form sodium peroxide.

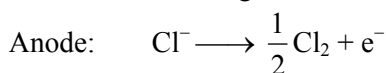
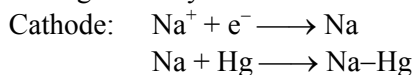


- $2\text{M} + 2\text{H}_2\text{O} \longrightarrow 2\text{M}^+ + 2\text{OH}^- + \text{H}_2\uparrow$   
Alkali metal Hydrogen gas

- In the Solvay process,  $\text{NH}_4\text{Cl}$  is treated with milk of lime to recover  $\text{NH}_3$ .



- During electrolysis of sodium chloride in Castner-Kellner cell, the following reactions take place:



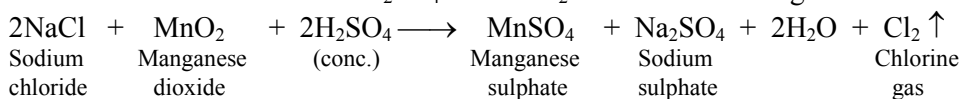
Thus, chlorine gas is evolved at anode.

- On passing HCl gas through saturated solution of crude NaCl, precipitate of pure NaCl is obtained due to common ion effect.



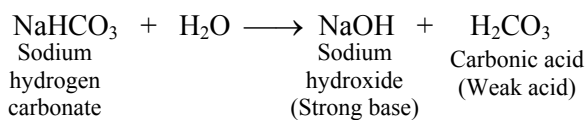
Therefore, X is HCl gas.

- NaCl when heated with conc.  $\text{H}_2\text{SO}_4$  and  $\text{MnO}_2$  liberates chlorine gas.



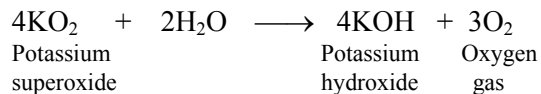


24. When dissolved in water, sodium hydrogen carbonate ( $\text{NaHCO}_3$ ) undergoes hydrolysis forming an alkaline solution.

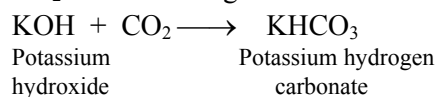


The presence of strong base i.e., NaOH makes the solution alkaline.

28. Potassium superoxide ( $\text{KO}_2$ ) reacts with moisture of breath ( $\text{H}_2\text{O}$ ) to liberate oxygen gas.



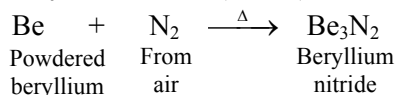
$\text{CO}_2$  formed during exhalation is removed by KOH and thus breathing apparatus works continuously.



30. Human blood plasma (outside the cell) has high concentration of sodium ion ( $\text{Na}^+$ ) and low concentration of potassium ion ( $\text{K}^+$ ).

35. When heated with oxygen, beryllium form oxide film on the surface as it is kinetically inert to the reaction with oxygen.

However, powdered beryllium burns brilliantly on ignition in air to produce beryllium oxide ( $\text{BeO}$ ) and beryllium nitride ( $\text{Be}_3\text{N}_2$ ).

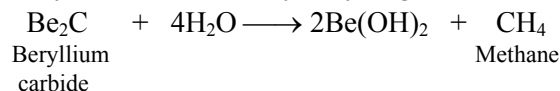


37.  $(\text{NH}_4)_2\text{BeF}_4 \longrightarrow \text{BeF}_2 + 2\text{NH}_4\text{F}$
- Ammonium
Beryllium
Ammonium  
fluoroberyllate
fluoride
fluoride

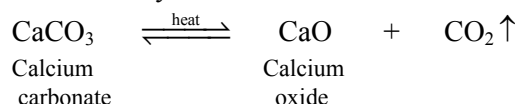
38. There is a presence of oxide film on the surface of beryllium and hence, it is not readily attacked by acids ( $\text{HCl}$ ,  $\text{H}_2\text{SO}_4$ ) while other alkaline earth metals are attacked easily. Thus, reaction given in option (A) does not occur under normal conditions.

40.  $\text{BaSO}_4$  being insoluble in  $\text{H}_2\text{O}$  and opaque to X-rays is used as 'barium meal' to scan the X-ray of human digestive system.

41. Beryllium carbide on hydrolysis gives methane.

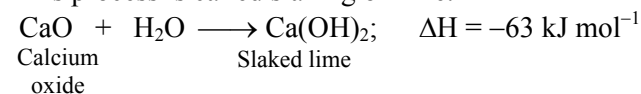


43. Quick lime or calcium oxide ( $\text{CaO}$ ) is prepared on commercial scale by heating limestone ( $\text{CaCO}_3$ ) in a reverberatory kiln at 1070–1270 K.



The reaction is made to proceed to completion by removing the carbon dioxide (i.e., the byproduct formed) as soon as it is produced.

44. The addition of limited quantity of water to  $\text{CaO}$  (quick lime) breaks the lumps of lime forming slaked lime. This process is called slaking of lime.

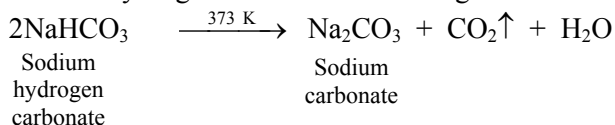




45.  $\text{CaCO}_3 + 2\text{HCl} \longrightarrow \text{CaCl}_2 + \text{H}_2\text{O} + \text{CO}_2\uparrow$   
 Calcium carbonate (dil.) Calcium chloride Carbon dioxide
46. Calcium carbonate ( $\text{CaCO}_3$ ) is insoluble in water.
50. Lithium forms monoxide ( $\text{Li}_2\text{O}$ ).
51. Cs form super oxide while Mg and Be forms monoxides MgO and BeO respectively.

**Critical Thinking**

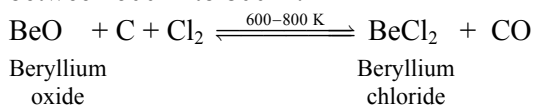
3. Alkaline earth metals are placed in group 2 in the periodic table. These metals have two valence electrons and hence, they form divalent  $\text{M}^{2+}$  ions. Thus, The common oxidation state for alkaline earth metals is +2.
5. Alkaline earth metals have two valence electrons which can be lost easily during a reaction. Hence, alkaline earth metals are highly reactive and do not occur in free state.
6. Chloride of lithium ( $\text{LiCl}$ ) is deliquescent and crystallizes as a hydrate ( $\text{LiCl}\cdot 2\text{H}_2\text{O}$ ) whereas chlorides of other alkali metals do not form hydrates.
9. The monoxide of magnesium (i.e., MgO) do not combine with excess of oxygen to give super oxide.
10. Alkali metals form monovalent  $\text{M}^+$  ions very easily by the loss of one valence electron. The  $\text{M}^+$  ion has noble gas electronic configuration and therefore, removing an outer electron from  $\text{M}^+$  ion requires high energy i.e., alkali metals have high second ionization enthalpy. Hence, alkali metals do not form dipositive ions.
11. In dry air, alkali metals react with oxygen to form corresponding oxides. This reaction tarnishes the alkali metals. When these oxides react with moisture, they form corresponding hydroxides.
15. Sodium hydrogen carbonate on heating forms sodium carbonate, liberating carbon dioxide.



20.  $\text{K}^+$  is especially an enzyme activator.
22. Retarded bone growth, reduction in fat deposit and low blood pressure are caused due to deficiency of sodium. Whereas, paralysis of muscles indicates deficiency of potassium in human body.
23. As we move down the group, the first ionization enthalpy decreases.

Element	Mg	Ca	Sr	Ba
<b>Ionization enthalpy (kJ/mol)</b>	737	590	549	503

26. Beryllium hydride ( $\text{BeH}_2$ ) is obtained by reduction of beryllium chloride ( $\text{BeCl}_2$ ) with lithium aluminium hydride ( $\text{LiAlH}_4$ ).
- $$2\text{BeCl}_2 + \text{LiAlH}_4 \longrightarrow 2\text{BeH}_2 + \text{LiCl} + \text{AlCl}_3$$
- Beryllium chloride    Lithium aluminium hydride                      Beryllium hydride    Lithium chloride    Aluminium chloride
27.  $\text{BeH}_2$  is covalent,  $\text{MgH}_2$  is partly ionic while  $\text{CaH}_2$ ,  $\text{SrH}_2$  and  $\text{BaH}_2$  are ionic solids. Thus, option (C) is incorrect.
28. Beryllium chloride ( $\text{BeCl}_2$ ) is prepared from beryllium oxide ( $\text{BeO}$ ) and carbon in the current of chlorine between 600 K to 800 K.





29. Beryllium has the highest melting point, boiling point and ionization enthalpy compared to all other alkaline earth metals.
30. BeO and Be(OH)<sub>2</sub> are amphoteric in nature while oxides and hydroxides of other alkaline earth metals are basic in nature.
34. The first member of the group-2 (i.e., Be) elements exhibits diagonal relationship with the second member of group-13 (i.e., Al) of the modern periodic table.
37. Calcium oxide or quick lime (CaO) is the cheapest form of alkali.
- $$\text{CaO} + \text{CO}_2 \longrightarrow \text{CaCO}_3 \xrightleftharpoons{1200\text{K}} \text{CaO} + \text{CO}_2 \uparrow$$
- Calcium Calcium  
oxide oxide  
(X) (X)
38. The lattice energy of alkali metal hydrides decreases from LiH to CsH, as the size of the metal cation increases.
39. Group 1 elements are highly electropositive. Hence they emit electrons even when exposed to light (photoelectric effect) and this character increases on moving down the group from lithium towards caesium.
40. Sodium metal on reaction with oxygen from air forms corresponding oxide which in turn reacts with moisture from air to form sodium hydroxide. On reacting with CO<sub>2</sub> from the atmosphere, sodium hydroxide forms sodium carbonate (Na<sub>2</sub>CO<sub>3</sub>).
- $$2\text{NaOH} + \text{CO}_2 \rightleftharpoons \text{Na}_2\text{CO}_3 + \text{H}_2\text{O}$$
- Sodium Sodium  
hydroxide carbonate
42. The element Rb ( $Z = 37$ ) is an alkali metal and is placed in the fifth period in the periodic table. Hence, the valence shell electronic configuration of Rb is  $5s^1$ .



### Competitive Thinking

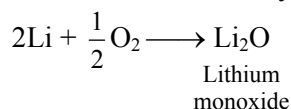
2. Li is harder than other alkali metals.
3. Lithium shows similarities to magnesium in its chemical behaviour because of:
- their similar size  
Atomic radii : Li = 152 pm, Mg = 160 pm  
Ionic radii : Li<sup>+</sup> = 76 pm, Mg<sup>2+</sup> = 72 pm
  - similar electronegativities: Li (1.00) and Mg (1.20) and nearly same polarizing power (charge/radius ratio).
4. In alkali metals, valence electrons are present in s-orbitals. They lose this loosely held valence electron to form monovalent M<sup>+</sup> ions.

5.

Element	Li	Na	K	Rb	Cs	Fr
Ionic radius (M <sup>+</sup> ) – (pm)	76	102	138	152	167	180

As the atomic number increases, the number of shells increases hence, atomic and ionic radius increases.

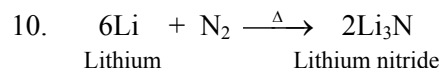
6. Alkali metals possess highest atomic volume and lowest atomic mass in their respective periods. Since, density is the ratio of mass by volume, alkali metals also possess lowest density in their respective periods.
7. Sodium reacts with oxygen in the air to form oxide, which in turn reacts with moisture to form hydroxide.
8. Lithium reacts with oxygen in the air to form lithium monoxide (Li<sub>2</sub>O).



Sodium reacts with oxygen in the air to form sodium peroxide (Na<sub>2</sub>O<sub>2</sub>) while potassium and rubidium reacts with oxygen in the air to form corresponding super oxides.



9. Alkali metals are highly reactive towards air and water and hence they are normally stored under kerosene oil.

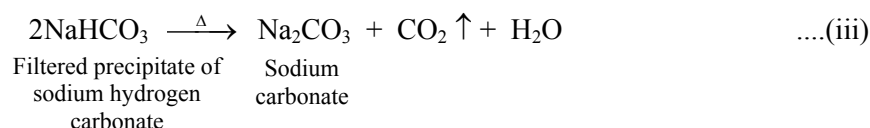
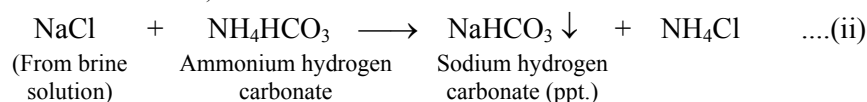
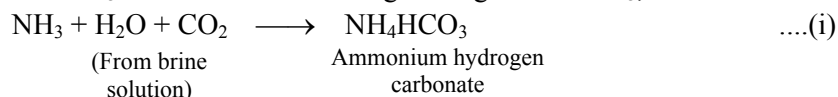


Other alkali metals cannot form such nitride compounds.

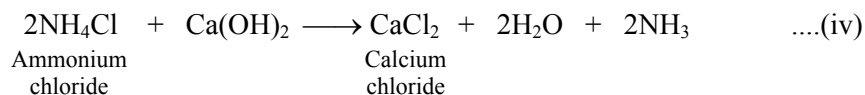
11. Chemical reactivity of alkali metals with water increases as the electropositive character increases down the group:  $\text{Li} < \text{Na} < \text{K} < \text{Rb} < \text{Cs}$ . Hence, among given options, Rb reacts with water at high rate.

12. The thermal stability of alkali metal hydrides decreases from LiH to CsH because the lattice energy decreases as the size of the metal cation increases.

14. In Solvay process,  $\text{CO}_2$  is bubbled through the solution of brine ( $\text{NaCl}$ ) saturated with  $\text{NH}_3$ . Precipitate of  $\text{NaHCO}_3$  is obtained which on ignition gives  $\text{Na}_2\text{CO}_3$ ,  $\text{H}_2\text{O}$  and  $\text{CO}_2$ .



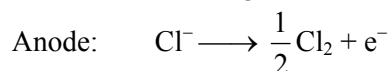
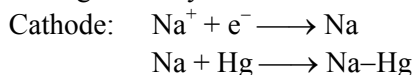
$\text{CO}_2$  obtained in reaction (iii) is again used in reaction (i).  $\text{NH}_4\text{Cl}$  obtained in reaction (ii) is treated with  $\text{Ca}(\text{OH})_2$  to recover  $\text{NH}_3$ .



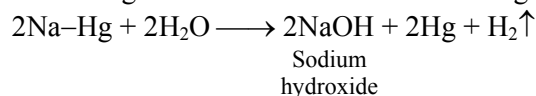
$\text{NH}_3$  obtained in reaction (iv) is used in reaction (i). Thus,  $\text{CO}_2$  and  $\text{NH}_3$  are recycled in the Solvay process.

15.  $\text{KHCO}_3$  being highly soluble in water (than  $\text{NaHCO}_3$ ) cannot be precipitated. Hence,  $\text{K}_2\text{CO}_3$  cannot be prepared using Solvay process.

17. During electrolysis of sodium chloride in Castner-Kellner cell, the following reactions take place:



The amalgam is then treated with water to give sodium hydroxide and hydrogen gas.



18. Molten sodium/liquid sodium metal is used as a coolant in fast breeder nuclear reactors.

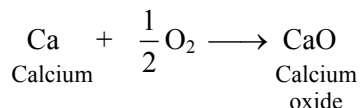
19. Excess of  $\text{Na}^+$  ions increase the blood pressure i.e., high B.P. or hypertension.

20.

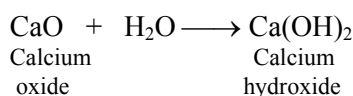
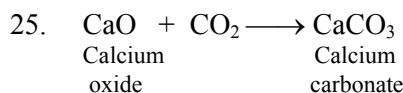
Element	Electronic configuration
Ca	$[\text{Ar}] 4s^2$
Sr	$[\text{Kr}] 5s^2$
Ba	$[\text{Xe}] 6s^2$
Ra	$[\text{Rn}] 7s^2$



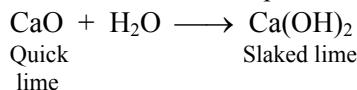
21. The electropositive character increases down the group from Be to Ba. Thus, the most electropositive amongst the given alkaline earth metals is barium.
22. Be has very small size, high enthalpy and high electronegativity due to which it can distort the electron cloud around the anion. Hence, Be mostly forms covalent compounds.
23. When calcium combines with oxygen, calcium oxide is formed.



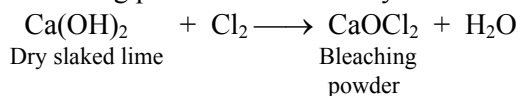
24. Be exhibits anomalous properties because it is the smallest and the most electronegative element in group 2.



26. Addition of water to quick lime i.e., calcium oxide gives slaked lime.

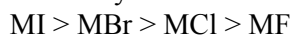


27. Bleaching powder is obtained by the interaction of chlorine and dry slaked lime.

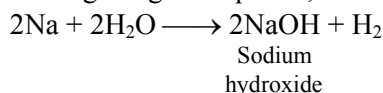


28. Magnesium is present in chlorophyll which is the main pigment for the absorption of light in plants.

30. As the size of the anion decreases, the electron cloud around the anion cannot be easily distorted and hence covalency decreases.



32. Among the given options, the metal which reacts with water at room temperature is sodium.



33. As the atomic size increases down the group, the attraction between the nucleus and the outermost electron decreases. Therefore, it is easier to remove the outermost electron from caesium compared to other alkali metals. Hence, among the alkali metals, caesium is the most reactive.

35. The first ionization enthalpy of alkaline earth metals are higher than those of corresponding alkali metals. Among alkaline earth metals, Be has highest ionization enthalpy.

Elements	Be	Mg	Na	K
1st I.E. (kJ/mol)	899	737	496	419

36. The ability to loose an electron (electropositive character) of alkali metals increases down the group from Li to Cs. Thus, among given options, Cs is most electropositive element.

37. Metallic character of alkali metals increases down the group as the electropositive character increases.



38. NaCl, CO<sub>2</sub>, milk of lime or slaked lime [Ca(OH)<sub>2</sub>] and ammonia are the raw materials used in the preparation of sodium carbonate by Solvay process.







## Evaluation Test

1. Beryllium does not show coordination number more than four, as in its valence shell there are only four orbitals (2s and 2p). Therefore,  $\text{BeF}_6^{3-}$  do not exist.
2.  $\text{Na}^+$  and  $\text{K}^+$  are stable because they have completely filled octet. So, Na and K are more electropositive compared to  $\text{Na}^+$  and  $\text{K}^+$ . Among Na and K, K is more electropositive because of its larger atomic radius. Thus, among the given species, K is most electropositive.
3. Lithium on reaction with ammonia forms lithium imide ( $\text{Li}_2\text{NH}$ ). Other alkali metals on reaction with ammonia form corresponding amides of the general formula  $\text{MNH}_2$ .
4. The element having electronic configuration  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$  is potassium, which forms basic oxide.
5. First element of a group shows diagonal relationship with the second element of the succeeding group. Na is the second element of group 1 and Mg is the second element of group 2.

Basic Principles and Techniques  
in Organic Chemistry

## Hints



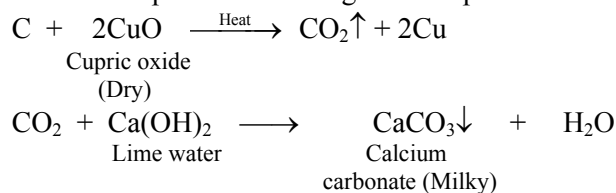
## Classical Thinking

4. Organic compounds can be synthesized in the laboratory.
5. Substances whose constituents (atoms, ions or molecules) are arranged in an orderly manner, leading to definite three dimensional geometrical shape are called crystalline substances. They are generally soluble in water and have sharp melting points.
7. The melting point is an important criterion for determining the purity of a solid. A pure solid melts at a definite temperature whereas impure solid does not melt at a definite temperature (it melts at a temperature lower than the melting point of pure solid or over a range of temperatures).
12. Crystallization techniques are used for separating solids. Acetone and benzene form a miscible solution. The difference in boiling points of acetone (329 K) and benzene (353 K) is only 24 K and hence, their mixture can be separated by fractional distillation.

13. The  $R_f$  (retardation factor) values describe the relative adsorption of each component of the mixture.

$$R_f = \frac{\text{Distance travelled by the substance from the base line (x)}}{\text{Distance travelled by the solvent from the base line (y)}}$$

16. The carbon present in the organic compound is oxidized to  $\text{CO}_2$  which turns the lime water milky.



19. On treating the sodium fusion extract of an organic compound with sodium nitroprusside, if violet colour is developed, it indicates the presence of sulphur.

23. Mass of 22400 mL of nitrogen at S.T.P. = 28 g

$$\therefore \text{Mass of 448 mL of nitrogen at S.T.P.} = \frac{28}{22400} \times 448 = 0.56 \text{ g}$$

$$\therefore \% \text{ of nitrogen} = \frac{0.56}{0.84} \times 100 = 66.7 \%$$

24.  $P_1 = 755.8 - 23.8 = 732 \text{ mm of Hg}$

$$V_1 = 31.7 \text{ mL}$$

$$T_1 = 25 + 273 = 298 \text{ K}$$

$$P_2 = 760 \text{ mm of Hg}$$

$$V_2 = ?$$

$$T_2 = 273 \text{ K}$$

$$\text{According to gas equation, } \frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

$$\therefore \frac{732 \times 31.7}{298} = \frac{760 \times V_2}{273}$$

$$\therefore V_2 = 28 \text{ mL}$$



22400 mL of nitrogen at S.T.P weighs 28 g.

$$\therefore 28 \text{ mL of nitrogen at S.T.P. will weigh} = \frac{28 \times 28}{22400} \text{ g} = 0.035 \text{ g}$$

0.2325 g of organic compound contains 0.035 g of nitrogen.

$$\therefore \% \text{ of nitrogen} = \frac{0.035}{0.2325} \times 100 = 15.1 \%$$

25. Mass of chlorine in 143.5 g AgCl = 35.5 g

$$\therefore \text{Mass of chlorine in 0.287 g of AgCl} = \left( \frac{35.5}{143.5} \times 0.287 \right) \text{ g} = 0.071 \text{ g}$$

$$\therefore \% \text{ of chlorine} = \frac{0.071}{0.099} \times 100 = 71.7\%$$

26. Molecular mass of  $\text{Mg}_2\text{P}_2\text{O}_7 = 222$

$\therefore$  222 g of  $\text{Mg}_2\text{P}_2\text{O}_7$  contains 62 g of phosphorus.

$$\therefore \text{Mass of phosphorus in 0.555 g of } \text{Mg}_2\text{P}_2\text{O}_7 = \left( \frac{62}{222} \times 0.555 \right) \text{ g} = 0.155 \text{ g}$$

$$\therefore \% \text{ of phosphorus} = \frac{0.155}{0.4} \times 100 = 38.75\%$$

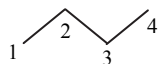
28. Empirical formula mass =  $12 + (2 \times 1) + 16$   
= 30

$$n = \frac{\text{Molecular mass}}{\text{Empirical formula mass}} = \frac{180}{30} = 6$$

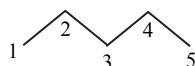
Molecular formula =  $n \times$  empirical formula =  $6 \times (\text{CH}_2\text{O}) = \text{C}_6\text{H}_{12}\text{O}_6$

30. In condensed formula, the arrangement of atoms is shown, but the bonds (dashes) between same or all atoms are omitted and the number of identical groups attached to an atom is indicated by a subscript.

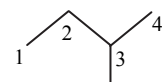
31. In bond-line formula, the terminals denote methyl groups and the line junctions denote carbon atoms bonded to appropriate number of hydrogen atoms required to satisfy the valency of carbon atoms.



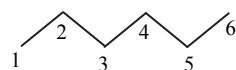
has four carbon atoms.



has five carbon atoms.



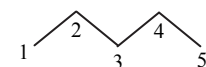
has a methyl side chain at carbon number 3.



has six carbon atoms.

The given compound  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$  has five carbons.

Therefore, its bond-line formula is





32.

Compound	Structure
Naphthalene	
Aniline	
Phenol	
Isobutane	$\begin{array}{c} \text{CH}_3 - \text{CH} - \text{CH}_3 \\   \\ \text{CH}_3 \end{array}$

33. Non-benzenoid compounds contain aromatic ring other than benzene and this aromatic ring may or may not contain hetero atoms.

38.  $\text{CH}_3\text{CH}_2\overset{\text{O}}{\parallel}{\text{C}}\text{NH}_2$  has the functional group  $-\overset{\text{O}}{\parallel}{\text{C}}-\text{NH}_2$  i.e., amido group. Hence, the class of compound to which this compound belongs is amides.

39.  $\begin{array}{c} \text{H} \quad \text{O} \quad \quad \text{H} \\ | \quad || \quad \quad | \\ \text{H} - \text{C} - \text{C} - \text{O} - \text{C} - \text{H} \\ | \quad \quad \quad | \\ \text{H} \quad \quad \quad \text{H} \end{array}$  has functional group  $-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-$  i.e., ester group. Hence, the compound is an ester.

41.  $\begin{array}{c} \text{CH}_3 \quad \text{CH}_3 \\ | \quad | \\ \text{CH}_3 - \text{CH} - \text{CH} - \text{CH}_3 \\ 1 \quad 2 \quad 3 \quad 4 \end{array}$

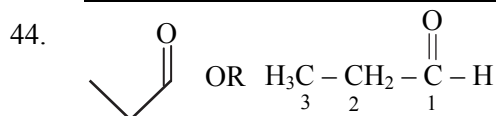
The IUPAC name of the compound is 2,3-dimethylbutane.

42.

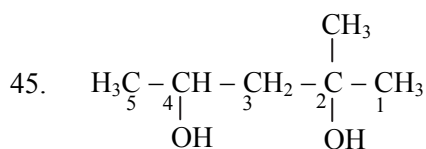
	Compound	IUPAC nomenclature
(A)		1,4-Dimethylcyclohexane
(B)		1,3-Dimethylcyclohexane
(C)		1,2-Dimethylcyclohexane
(D)		1,1-Dimethylcyclohexane



43.	Compound	IUPAC nomenclature
(A)		$\begin{array}{ccccccc} & \text{OH} & & \text{CH}_3 & & & \\ &   & &   & & & \\ \text{H}_3\text{C} & - \text{C} & - & \text{CH}_2 & - & \text{C} & - \text{CH}_3 \\ &   & & & &   & \\ & \text{H} & & & & \text{H} & \end{array}$ 4-Methylpentan-2-ol
(B)		$\begin{array}{ccccccc} & \text{OH} & \text{H} & & & & \\ &   &   & & & & \\ \text{H}_3\text{C} & - \text{C} & - & \text{C} & - & \text{CH}_2 & - \text{CH}_3 \\ &   &   & & & & \\ & \text{H} & \text{CH}_3 & & & & \end{array}$ 3-Methylpentan-2-ol
(C)		$\begin{array}{ccccccc} & & & \text{CH}_3 & & & \\ & & &   & & & \\ \text{H}_3\text{C} & - & \text{CH} & - & \text{CH}_2 & - & \text{CH}_2 & - & \text{CH}_2 & - & \text{OH} \\ & & & & & &   & & & & \\ & & & & & & \text{H} & & & & \end{array}$ 4-Methylpentan-1-ol
(D)		$\begin{array}{ccccccc} & & & & & \text{CH}_3 & \\ & & & & &   & \\ \text{H}_3\text{C} & - & \text{CH}_2 & - & \text{CH}_2 & - & \text{CH} & - & \text{CH}_2 & - & \text{OH} \\ & & & & & &   & & & & \\ & & & & & & \text{H} & & & & \end{array}$ 2-Methylpentan-1-ol

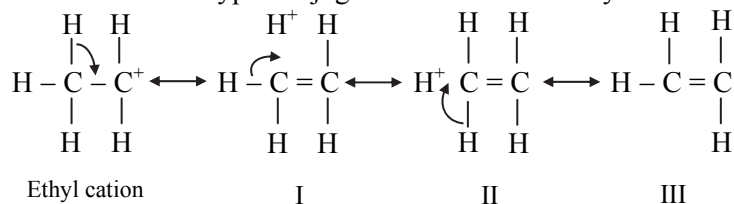


The functional group present is  $-\text{CHO}$ . So, the compound is an aldehyde. The parent alkane is propane. Aldehydes are named as alkanal. So, the name of the compound is propanal.



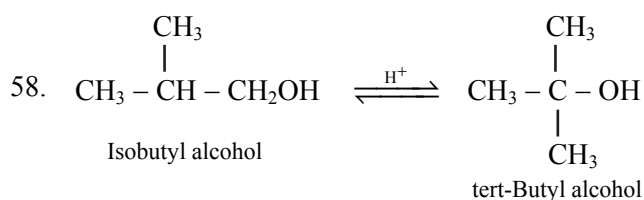
The IUPAC name of the compound is 2-methylpentane-2,4-diol.

47. Alkyl groups are electron-donating groups while  $-\text{SO}_3\text{H}$  is an electron-withdrawing group.
48. Resonance forms are shown with double-headed arrow between them.
49. The energy of the resonance hybrid is lower than that of any of the contributing resonance structures.
50. When the transfer of electrons is away from an atom or substituent group attached to the conjugated system, it is termed as positive resonance effect.  $-\text{NH}_2$  group shows positive resonance effect while  $-\text{COOH}$ ,  $-\text{CHO}$  and  $-\text{CN}$  groups show negative resonance effect.
51. There are three hyperconjugation structures in ethyl cation.





54. Carbon free radicals contain odd electrons i.e., unpaired electrons, hence paramagnetic in nature.
55.  $\text{BCl}_3$  is an electron-deficient species and hence, it is an electrophile.  $\text{CN}^-$ ,  $\text{ROH}$  and  $\text{NH}_3$  are electron-rich species and hence, these are nucleophiles.
56. A species that donates the electron-pair to a species other than  $\text{H}^+$  is termed as nucleophile while a species that donates the electron-pair to  $\text{H}^+$  is termed as a base.
57. Addition reaction takes place with unsaturated hydrocarbon compounds such as alkenes, alkynes and aromatic compounds. However, saturated hydrocarbons like alkanes do not undergo addition reactions.



In this rearrangement reaction, the carbon skeleton is modified while the functional group and molecular formula remains the same.

60. The members of homologous series differ by  $-\text{CH}_2-$  units and they have same functional group. Among the given pairs, only the compounds in option (A) differ by  $-\text{CH}_2-$  unit and have same functional group. Hence, they represent a homologous series.
64. The saturated monocyclic hydrocarbons are known as cycloalkanes or cycloparaffins. Among the given structures, only the compound in option (B) is a saturated monocyclic hydrocarbon and hence, it is a cycloalkane.
65. The atom to which an electron-pair from  $\pi$ -bond shifts will have a negative charge.



66.

Method used for quantitative analysis	Amount of material required
Macro-methods	0.1–0.5 g
Semi-micro methods	20–50 mg
Micro-methods	3–5 mg

68. Silk is obtained from natural source and hence, it is a natural fibre. Terylene, rayon and nylon are synthetic fibres.



### Critical Thinking

6. When the triangular side arm of the Thiele's tube containing the paraffin oil is heated slowly and gently, convection current is set up which maintains uniform temperature throughout the liquid. Thus, for melting or boiling point determination, Thiele's tube is used which is designed in such a way that mechanical stirring of paraffin oil is not required while heating.
8. The solvent used for crystallization should not react chemically with the substance to be purified. If the solvent is a low boiling liquid, its removal becomes easy. Hence, low boiling liquid is preferred. Also, the solvent should have low viscosity.
11. Distillation involves both evaporation of a liquid and condensation of its vapour. Since, the distillation process is used for separation and purification of liquids, the processes such as crystallization, filtration, sublimation and melting are not involved.
13. Adsorption chromatography is based on the principle of differential adsorption and hence different compounds are adsorbed on an adsorbent to different degrees. The adsorbent or the stationary phase used may be a solid or a liquid. Paper chromatography is a type of partition chromatography.




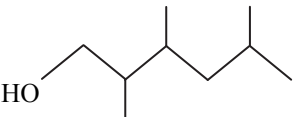
14.  $\text{Na} + \text{C} + \text{N} \xrightarrow{\Delta} \text{NaCN}$   
 Metallic sodium                      Sodium cyanide
15. When the sodium fusion extract is boiled with ferrous sulphate solution and then acidified with conc. sulphuric acid ( $\text{H}_2\text{SO}_4$ ), sodium cyanide (present in the sodium fusion extract) forms a complex of prussian blue colour indicating the presence of nitrogen in the given organic compound.
16. The black precipitate formed is of lead sulphide which confirms the presence of sulphur in the given organic compound.
17. Mass of iodine in 235 g of AgI = 127 g  
 $\therefore$  Mass of iodine in 0.3894 g of AgI =  $\frac{127}{235} \times 0.3894$   
 $\therefore$  % of iodine =  $\frac{127}{235} \times \frac{0.3894}{0.2585} \times 100 = 81.4\%$
19. % of carbon = 16.27  
 % of hydrogen = 0.68  
 % of chlorine = 72.20  
 Sum of percentages = 89.15  
 $\therefore$  % of oxygen =  $100 - 89.15 = 10.85$

Element	% composition	Atomic ratio	Simplest ratio
Carbon	16.27	$\frac{16.27}{12} = 1.36$	$\frac{1.36}{0.68} = 2$
Hydrogen	0.68	$\frac{0.68}{1} = 0.68$	$\frac{0.68}{0.68} = 1$
Chlorine	72.20	$\frac{72.20}{35.5} = 2.0$	$\frac{2.0}{0.68} = 3$
Oxygen	10.85	$\frac{10.85}{16} = 0.68$	$\frac{0.68}{0.68} = 1$

Thus, the empirical formula of the compound is  $\text{C}_2\text{HOC}_3$ .

22. In complete structural formula, all the bonds between the atoms are represented using a dash (-). A single bond is represented by a single dash (-), a double bond by double dash (=) and a triple bond by triple dash ( $\equiv$ ).

Thus, the complete structural formula of the compound  is  $\begin{array}{ccccccc} & \text{H} & \text{H} & \text{H} & \text{H} & \text{H} & \\ & | & | & | & | & | & \\ \text{H} & - \text{C} & - \text{C} & = \text{C} & - \text{C} & - \text{H} & \\ & | & | & & | & & \\ & \text{H} & \text{H} & & \text{H} & & \end{array}$

23.  OR  $\text{HO} - \text{CH}_2 - \overset{\text{H}}{\underset{\text{CH}_3}{\text{C}}} - \overset{\text{CH}_3}{\underset{\text{H}}{\text{C}}} - \text{CH}_2 - \overset{\text{CH}_3}{\underset{\text{H}}{\text{C}}} - \text{CH}_3$

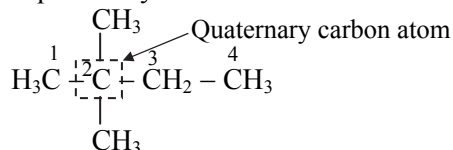
There are four methyl ( $-\text{CH}_3$ ) groups in the given structure.



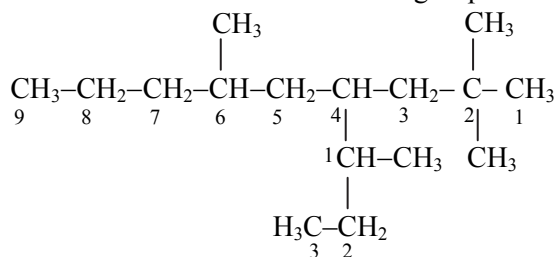
24.	Compound	Structure	Heterocyclic / Homocyclic
	Cyclobutane	$\begin{array}{c} \text{H}_2\text{C} - \text{CH}_2 \\   \qquad   \\ \text{H}_2\text{C} - \text{CH}_2 \end{array}$	Homocyclic
	Pyridine		Heterocyclic
	Tropone		Homocyclic
	Toluene		Homocyclic

25.	Class of the compound	General formula
	Ketones	$\begin{array}{c} \text{R} - \text{C} - \text{R}' \\    \\ \text{O} \end{array}$
	Acid anhydrides	$\begin{array}{c} \text{R} - \text{C} - \text{O} - \text{C} - \text{R}' \\    \qquad \qquad    \\ \text{O} \qquad \qquad \text{O} \end{array}$
	Esters	$\begin{array}{c} \text{R} - \text{C} - \text{OR}' \\    \\ \text{O} \end{array}$
	Ethers	$\text{R} - \text{O} - \text{R}'$

26. Homologues differ by  $-\text{CH}_2-$  unit. The molecular weight of  $-\text{CH}_2-$  is  $12 + (2 \times 1) = 14$ . Therefore, homologues differ in their molecular weights by 14 units.
27. Physical properties (like melting point, boiling point, density, solubility, etc.) of the members of homologous series show a gradual change with increase in the molecular weight of the members.
29. A quaternary carbon atom is bonded to four other carbon atoms.



30. If the substituent is further branched, it is named as substituted alkyl group, by numbering the carbon atom of this group attached to the parent chain as 1. The name of such a substituent is enclosed in brackets to avoid confusion with the numbering of parent chain.

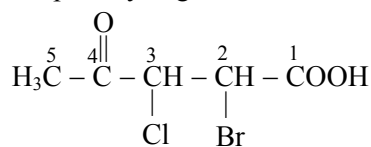


The IUPAC name is 2,2,6-trimethyl-4-(1-methylpropyl)nonane.

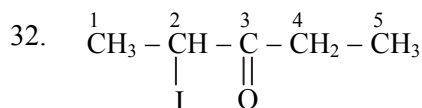




31. The priority is given to  $-\text{COOH}$  group and then to  $>\text{C}=\text{O}$  group.

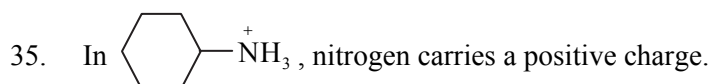


2-Bromo-3-chloro-4-oxopentanoic acid



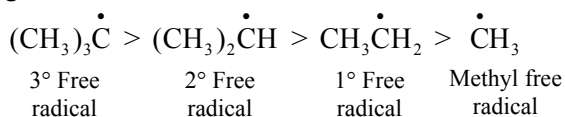
The name of the compound is 2-iodopentan-3-one.

34. The resonance structure with the lowest energy is a major resonance contributor.

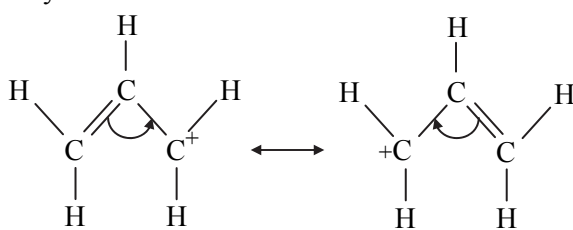


The structure does not have lone pair of electrons or  $\pi$  electrons that are required for resonance. Hence, resonance effect is not present in this structure.

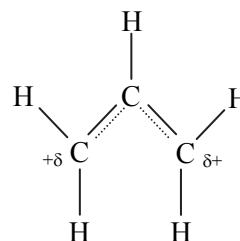
36. Free radicals are stabilized by electron-donating effect of alkyl groups. Higher the number of alkyl substituents, higher is the stability of the free radical. Hence, the stability of given free radicals decreases in the order.



38. Resonance is shown when a  $\pi$  bond is adjacent to a positively charged carbon atom. The filled p orbitals of  $\pi$  bond overlaps with the empty p orbitals of the carbocation. Delocalization of  $\pi$ -electrons takes place and the positive charge is shared by two atoms. Thus, the carbocation is stabilized by resonance and the cation is symmetrical about the central carbon atom.



Resonance forms of allyl cation



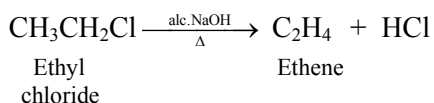
Resonance hybrid of allyl cation

39.

Nucleophiles	Electrophiles
$\text{H}_2\text{O}$ , $\text{NH}_3$ , $\text{R}-\text{OH}$ , $\text{CN}^-$ , $\text{OH}^-$	$\text{BF}_3$ , $\text{H}^+$ , $\text{AlCl}_3$ , $\text{NO}_2^+$

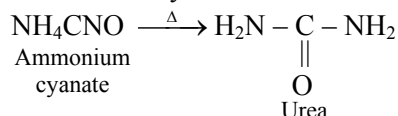
Thus, the series that contains only nucleophiles is  $\text{NH}_3$ ,  $\text{H}_2\text{O}$  and  $\text{R}-\text{OH}$ .

40. In substitution reaction, there is direct replacement of atom or group in the substrate by another atom or group. In the reaction,  $(\text{CH}_3)_3\text{C}-\text{Br} \xrightarrow[\text{-HBr}]{\text{H}_2\text{O}} (\text{CH}_3)_3\text{COH}$  the  $-\text{Br}$  group is replaced by  $-\text{OH}$  group and hence, it is an example of substitution reaction.
41. When one molecule is split into two fragment molecules, it is called an elimination reaction.





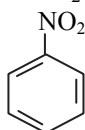
42. Urea can be synthesized in laboratory by heating  $\text{NH}_4\text{CNO}$ .



43. Benzenoid compounds contain at least one benzene ring.
44.  $\text{H}_3\text{C} - \text{C} - \text{CH}_3$  has a keto group and hence, it belongs to class of compounds called as ketones.

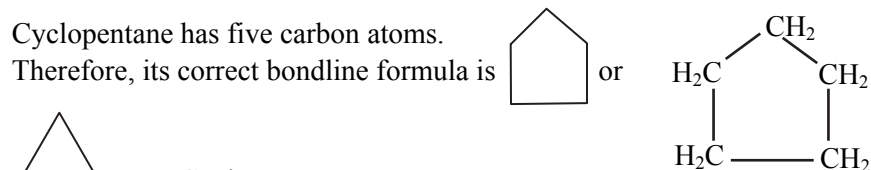
$\parallel$   
O  
The compounds in option (A), (C) and (D) have aldehydic group and hence, they belong to the same class of compounds i.e., aldehydes.

45. When an organic compound containing phosphorus is oxidised with fuming nitric acid, phosphorus is converted into phosphoric acid,  $\text{H}_3\text{PO}_4$ .
46. Organic solvents like benzene, chloroform and petroleum ether that are immiscible with water can be used to extract an organic compound present in aqueous solution by differential extraction. Organic solvents like methanol, ethanol and acetone are miscible with water and hence, these cannot be used for differential extraction.
47. The compound has molecular formula  $\text{C}_6\text{H}_5\text{O}_2\text{N}$ . It has six carbon atoms in a ring system with alternating single and double bonds. This indicates that the structure has an aromatic benzene ring. The compound also has an  $-\text{NO}_2$  group as a substituent. Hence, its structure will be



Thus, the given compound 'X' is homocyclic and aromatic.

48. Reactions given in option (B) and (C) are examples of addition reactions. While reactions given in option (A) and (D) are examples of rearrangement reactions. The reaction given in option (A) indicates modification of carbon skeleton whereas reaction in option (D) indicates modification of functional group i.e., the functional group of ether changes to functional group of phenols.
49. Cyclopentane has five carbon atoms.



Cyclopropane



Cyclobutane



Cyclohexane



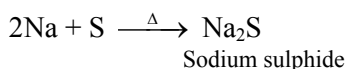
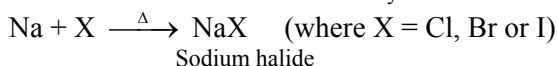
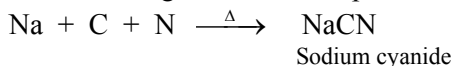
### Competitive Thinking

1. Sublimation, filtration and crystallisation are employed for separation and purification of solids. Distillation is used for separation and purification of liquids. Hence, a miscible solution of benzene and  $\text{CHCl}_3$  can be separated by distillation.
3. In paper chromatography, mobile phase is a suitable solvent or mixture of solvents (liquid) while the stationary phase is the water (liquid) which is trapped in the special quality paper i.e., a chromatography paper.



4.  $\text{Na} + \text{C} + \text{N} \xrightarrow{\Delta} \text{NaCN}$   
Sodium cyanide
5. In Lassaigne's test, if the given organic compound contains N, X or S then, nitrogen (N) is converted into sodium cyanide, halogen(X) into sodium halide and sulphur(S) into sodium sulphide.

The following reactions take place:



Thus, NaNC is not formed in Lassaigne's test.

6. Concentrated  $\text{HNO}_3$  is added to Lassaigne's extract to decompose  $\text{Na}_2\text{S}$  and  $\text{NaCN}$  otherwise these compounds would interfere with the tests of halogens.

7. 22,400 mL of nitrogen at STP weighs 28 g.

$$\therefore 45 \text{ mL nitrogen at STP will weigh } \frac{28 \times 45}{22,400} \text{ g} = 0.05625 \text{ g}$$

- $\therefore$  0.3 g of organic compound contains 0.05625 g of nitrogen.

$$\therefore \% \text{ of nitrogen} = \frac{0.05625 \times 100}{0.3} = 18.75\%$$

8. 188 g of AgBr contains of 80 g of bromine.

$$\therefore 0.141 \text{ g of AgBr will contain } \frac{80 \times 0.141}{188} \text{ g of bromine} = 0.06 \text{ g of bromine}$$

- $\therefore$  0.250 g of organic compound contains 0.06 g of bromine

$$\therefore \% \text{ of bromine} = \frac{0.06 \times 100}{0.250} = 24\%$$

9. Molecular mass of  $\text{BaSO}_4 = 137 + 32 + 4(16) = 137 + 32 + 64 = 233$

Mass of S in 233 g of  $\text{BaSO}_4 = 32 \text{ g}$

$$\therefore \text{Mass of S in } 0.35 \text{ g of } \text{BaSO}_4 = \frac{32}{233} \times 0.35 = 0.0480 \text{ g}$$

$$\% \text{ of S} = \frac{0.0480}{0.2595} \times 100 = 18.52\%$$

11. Empirical formula =  $\text{CH}_2\text{O}$

Empirical formula mass =  $12 + 2 + 16 = 30$

Molecular mass =  $2 \times \text{vapour density} = 2 \times 30 = 60$

$$n = \frac{\text{Molecular mass}}{\text{Empirical formula mass}} = \frac{60}{30} = 2$$

Molecular formula =  $n \times \text{empirical formula} = 2 \times (\text{CH}_2\text{O}) = \text{C}_2\text{H}_4\text{O}_2$ .

12. % of carbon = 40

% of hydrogen = 6.66

$$\therefore \% \text{ of oxygen} = 100 - 40 - 6.66 = 53.34$$

Element	Atomic Ratio	Simplest Ratio
C = 40%	$40/12 = 3.33$	$3.33/3.33 = 1$
H = 6.66%	$6.66/1 = 6.66$	$6.66/3.33 = 2$
O = 53.34%	$53.34/16 = 3.33$	$3.33/3.33 = 1$

The empirical formula of the compound is  $\text{CH}_2\text{O}$ .



13.

Element	Atomic ratio	Simplest ratio
C = 54.5 %	$54.5/12 = 4.54$	$4.54/2.27 = 2$
H = 9.1 %	$9.1/1 = 9.1$	$9.1/2.27 = 4$
O = 36.4 %	$36.4/16 = 2.27$	$2.27/2.27 = 1$

∴ The empirical formula is  $C_2H_4O$ .

14.

Element	Atomic ratio	Simplest ratio
C = 40%	$40/12 = 3.33$	$3.33/3.33 = 1$
H = 13.33%	$13.33/1 = 13.33$	$13.33/3.33 = 4$
N = 46.67%	$46.67/14 = 3.33$	$3.33/3.33 = 1$

Thus, the empirical formula is  $CH_4N$ .

15. Amount of oxygen =  $64 - (24 + 8) = 32$  g

Element	Atomic ratio	Simplest ratio
C (24 g)	$\frac{24}{12} = 2$	$\frac{2}{2} = 1$
H (8 g)	$\frac{8}{1} = 8$	$\frac{8}{2} = 4$
O (32 g)	$\frac{32}{16} = 2$	$\frac{2}{2} = 1$

∴ The empirical formula is  $CH_4O$ .

16. % of carbon = 52.14

% of hydrogen = 13.13

∴ % of oxygen =  $100 - 52.14 - 13.13$   
= 34.73%

Element	Atomic Ratio	Simplest Ratio
C = 52.14%	$52.14/12 = 4.345$	$4.345/2.170 = 2$
H = 13.13%	$13.13/1 = 13.13$	$13.13/2.170 = 6$
O = 34.73%	$34.73/16 = 2.170$	$2.170/2.170 = 1$

Thus, the empirical formula is  $C_2H_6O$ .

Empirical formula mass = 46

Molecular formula =  $n \times$  empirical formula

$$n = \frac{\text{molecular mass}}{\text{empirical formula mass}}$$

$$= \frac{46.068}{46} = 1$$

∴ Molecular formula =  $1 \times (C_2H_6O) = C_2H_6O$



17. 44 g of CO<sub>2</sub> contains 12 g of C.

$$\therefore 0.44 \text{ g of CO}_2 \text{ will contain } \frac{0.44 \times 12}{44} = 0.12 \text{ g of C.}$$

0.30 g of organic compound contains 0.12 g of C.

$$\therefore 100 \text{ g of organic compound will contain } \frac{0.12 \times 100}{0.30} = 40\% \text{ C}$$

18 g of H<sub>2</sub>O contains 2 g of H.

$$\therefore 0.18 \text{ g of H}_2\text{O will contain } \frac{2 \times 0.18}{18} = 0.02 \text{ g of H.}$$

0.30 g of organic compound contains 0.02 g of H.

$$\therefore 100 \text{ g of organic compound will contain } \frac{0.02 \times 100}{0.30} = 6.6667\% \text{ of H.}$$

$$\% \text{ of oxygen} = 100 - 40 - 6.6667 = 53.33\%$$

Element	Atomic Ratio	Simplest Ratio
C = 40%	40/12 = 3.33	3.33/3.33 = 1
H = 6.6667%	6.6667/1 = 6.6667	6.6667/3.33 = 2
O = 53.33%	53.33/16 = 3.33	3.33/3.33 = 1

Thus, empirical formula of compound is CH<sub>2</sub>O.

Empirical formula mass = 12 + 2 + 16 = 30

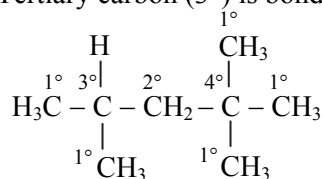
$\therefore$  Molecular formula = n  $\times$  empirical formula, where n is a whole integer and is given by,

$$n = \frac{\text{molecular mass}}{\text{empirical formula mass}}$$

$$n = \frac{60 \text{ g}}{30 \text{ g}} = 2$$

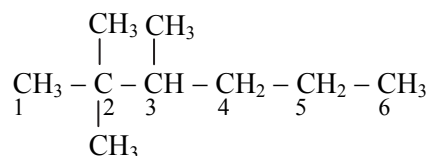
$\therefore$  Molecular formula = 2  $\times$  (CH<sub>2</sub>O) = C<sub>2</sub>H<sub>4</sub>O<sub>2</sub>

19. Tertiary carbon (3°) is bonded to three other carbon atoms.

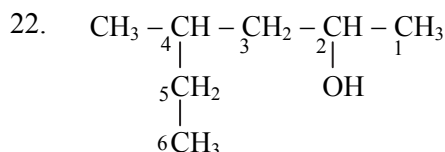


Thus, there is only one tertiary carbon atom in the given compound.

20. The longest continuous chain of carbon atoms in the structure is selected as the parent chain and the substituted carbon atoms should carry the lowest possible numbers.



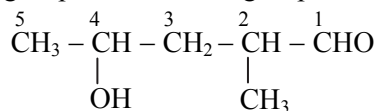
The compound given in option C is 2,2,3-trimethylhexane.



The IUPAC name of the compound is 4-methylhexan-2-ol.

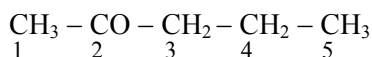


24. The priority is first given to  $-\text{CHO}$  group and then  $-\text{OH}$  group. So, the base name is derived from  $-\text{CHO}$  group and the  $-\text{OH}$  group is named as the substituent.



The IUPAC name of the compound is 4-hydroxy-2-methylpentanal.

25. The functional group in the molecule is keto group. In ketones, the final '-e' from the parent alkane name is dropped and the suffix '-one' is added to give the base name.

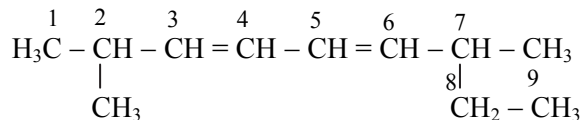


The IUPAC name of the compound is pentan-2-one.

26. 
$$\begin{array}{ccccccc} 1 & 2 & 3 & 4 & & & \\ \text{CH}_2 = \text{CH} & - \text{CH} & - \text{CH}_3 & & & & \\ & & | & & & & \\ & & \text{CH}_3 & & & & \end{array}$$

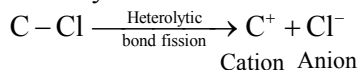
3-Methylbut-1-ene

27. The given molecule can also be written as follows:



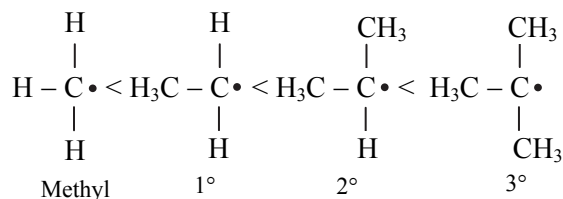
2,7-Dimethylnona-3,5-diene

28. The  $-\text{CH}_3$  group shows positive inductive (+I) effect and is an electron releasing group while  $-\text{COOH}$ ,  $-\text{CN}$  and  $-\text{NO}_2$  show negative inductive (-I) effect and are electron withdrawing groups.
29. Electromeric effect arises due to the mobility of electrons in double or triple bonds, i.e., it is possible only in a  $\pi$ -bonded compound. Among the given options, only ethyne has  $\pi$  bonds and can undergo electromeric effect.
30. Hyperconjugation involves the delocalization of electrons due to overlap between a  $\sigma$  bond and an empty p-orbital. However, it occurs only if  $\sigma$  bond and empty p-orbital have proper orientation.
34. Heterolysis of carbon-chlorine bond produces one cation and one anion.



In  $\text{C} - \text{Cl}$  bond, as chlorine atom is more electronegative than carbon atom, the electron pair is retained by chlorine atom on fission.

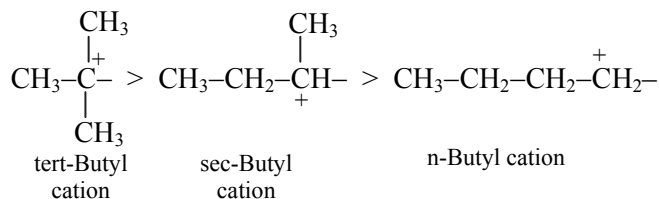
36. The positive inductive (+I) effect stabilises the free radical. Therefore, the free radicals containing more number of electron donating substituents like alkyl groups are more stable.



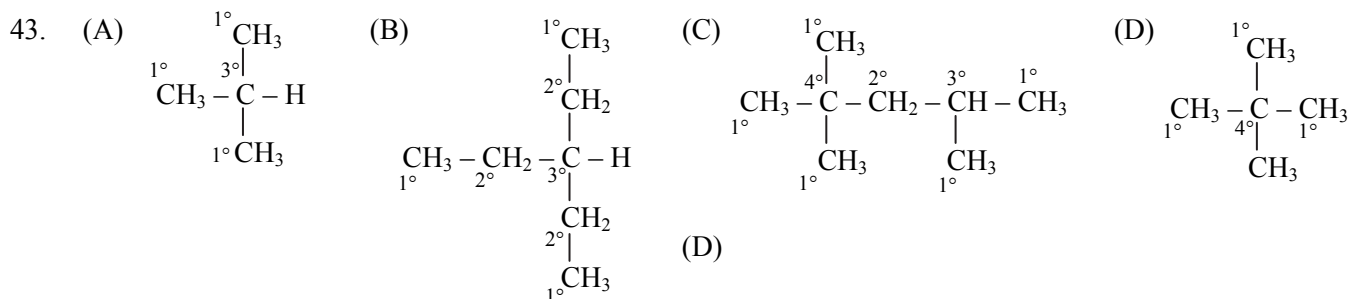
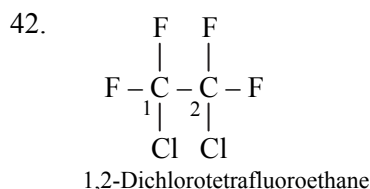
37. In a carbonium ion, the carbon atom is  $\text{sp}^2$  hybridized. Hence, carbonium ion is planar with  $\text{H} - \text{C} - \text{H}$  bond angle of  $120^\circ$ .



38. The stability of carbonium ion increases as the number of alkyl substituents bonded to the positively charged carbon atom increases.



39. Electrophiles are electron deficient species and hence they can accept a pair of electrons from nucleophiles. They are either neutral or positively charged.
40. Nucleophile is a Lewis base because it is electron rich species which can donate its electron-pair to another species.
41. Neutral molecules containing at least one lone pair of electrons such as  $\ddot{\text{N}}\text{H}_3$ ,  $\text{CH}_3\text{CH}_2\ddot{\text{N}}\text{H}_2$  and  $\text{H}_2\ddot{\text{O}}$  are nucleophiles. Neutral molecules with incomplete octet of electrons in outermost orbit such as  $\text{BF}_3$  are electrophiles. Thus, among the given options,  $\text{BF}_3$  is not a nucleophile.



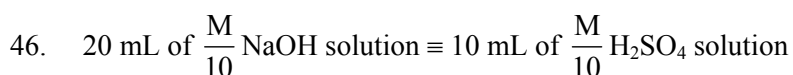
Thus, the structure given in option (C) contains primary, secondary, tertiary and quaternary carbon atoms together.

44.

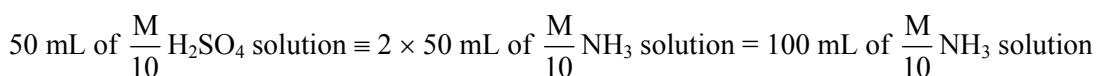
Compound	Hybridisation of carbon atom(s)
$\text{CO}_2$	$sp$
Ethane	$sp^3$
Ethyne	$sp$
Ethene	$sp^2$
Ethanol	$sp^3$

Thus, the compound having same hybridization as its combustion product ( $\text{CO}_2$ ) is ethyne.

45. Methane and isobutane are non-planar while acetylene is linear. Only benzene is planar molecule.



$\therefore$  Volume of  $\frac{M}{10} \text{ H}_2\text{SO}_4 \text{ solution used} = 60 - 10 \text{ mL} = 50 \text{ mL}$





1000 mL of 1 M  $\text{NH}_3$  solution contain 14 g of N.

$$\therefore 100 \text{ mL of } \frac{1}{10} \text{ M } \text{NH}_3 \text{ solution will contain } \frac{14 \times \frac{1}{10} \times 100}{1000} \text{ g N} = 0.14 \text{ g N}$$

$$\therefore \% \text{ of N} = \frac{0.14}{1.4} \times 100 = 10 \%$$

47. Kjeldahl's and Dumas methods are used for the quantitative estimation of nitrogen in an organic compound. In the Kjeldahl method, the nitrogen element of organic compound is changed to the ammonia.

48. Hydrazine ( $\text{NH}_2 - \text{NH}_2$ ) does not contain a carbon atom and so, it will not form sodium cyanide when fused with metallic sodium. Hence, the presence of nitrogen in hydrazine cannot be detected by Lassaigne method.

49. The hydrocarbon contains 75 % of C.

$\therefore$  100 g of hydrocarbon contains 75 g of carbon.

$$\therefore 0.8 \text{ g of hydrocarbon} \equiv \frac{75 \times 0.8}{100} \\ = 0.6 \text{ g of carbon}$$

Now, 12 g of carbon gives 44 g of  $\text{CO}_2$

$$\therefore 0.6 \text{ g of carbon} = \frac{44 \times 0.6}{12} \\ = 2.2 \text{ g of } \text{CO}_2$$

50. Given,  $m = 0.25 \text{ g}$ ,  $P = 725 \text{ mm}$ ,  $f = 25 \text{ mm}$ ,  $V_1 = 40 \text{ mL}$ ,  $T_1 = 300 \text{ K}$ ,  $P_0 = 760 \text{ mm}$ ,  $T_0 = 273 \text{ K}$   
Here  $P_0$  and  $T_0$  are the pressure and temperature of dry nitrogen at STP respectively.

$$\therefore P_1 = P - f = 725 - 25 = 700 \text{ mm}$$

$$\frac{P_0 V_0}{T_0} = \frac{P_1 V_1}{T_1}$$

$$\therefore V_0 = \frac{P_1 V_1}{T_1} \times \frac{T_0}{P_0} = \frac{700 \times 40}{300} \times \frac{273}{760} \\ = 33.53 \text{ mL}$$

22,400 mL of nitrogen at STP weighs 28 g.

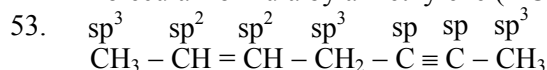
$\therefore$  33.53 mL of nitrogen at STP will weigh

$$= \frac{28 \times 33.53}{22,400} \text{ g} = 0.04191 \text{ g}$$

0.25 g of organic compound contains 0.04191 g of nitrogen.

$$\therefore 100 \text{ g of organic compound will contain} = \frac{0.04191 \times 100}{0.25} = 16.76 \% \text{ of nitrogen}$$

51.  $\text{C}_6\text{H}_{10}\text{O}_2\text{N}$  is the successive member of the homologous series of  $\text{C}_5\text{H}_8\text{O}_2\text{N}$  as they differ from each other in molecular formula by a methylene ( $-\text{CH}_2-$ ) group.



Number of  $\text{sp}^3$  hybridised carbon atoms = 3

$$\therefore \text{Number of } \text{sp}^3 \text{ hybrid orbitals} = 3 \times 4 = 12$$

Number of  $\text{sp}^2$  hybridised carbon atoms = 2

$$\therefore \text{Number of } \text{sp}^2 \text{ hybrid orbitals} = 2 \times 3 = 6$$

Number of  $\text{sp}$  hybridised carbon atoms = 2

$$\therefore \text{Number of } \text{sp} \text{ hybrid orbitals} = 2 \times 2 = 4$$

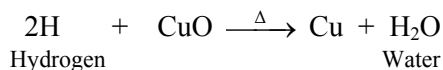
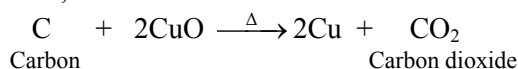
Thus, the ratio is 6 : 3 : 2.





## Evaluation Test

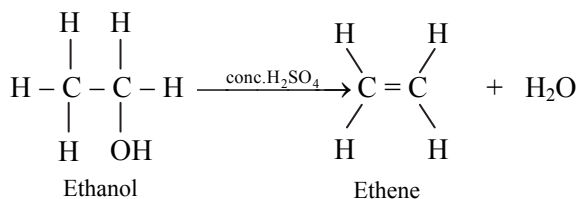
1. When organic compound 'A' containing carbon and hydrogen is heated with dry cupric oxide (CuO) in a tube, carbon is oxidised to carbon dioxide and hydrogen is oxidised to H<sub>2</sub>O.



When the organic compound 'A' is heated with Na<sub>2</sub>O<sub>2</sub>, followed by boiling with HNO<sub>3</sub> and ammonium molybdate gives yellow precipitate, this confirms the presence of phosphorus.

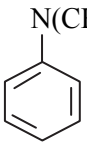
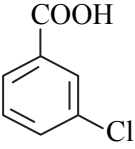
Thus, the elements present in compound 'A' are C, H and P.

2. When one molecule is split into two fragment molecules, the reaction is known as an elimination reaction.

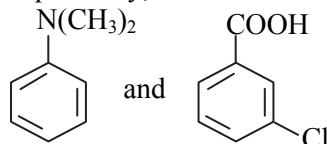


In dehydration of ethanol, ethene is formed along with the elimination of H<sub>2</sub>O. Hence, it is an example of elimination reaction.

3. Fractionating columns are used to separate the components of liquid mixture having small difference in their boiling points (less than 30 K) more efficiently. The difference in boiling points of liquid A and liquid C is less than 30 K and so, a fractionating column is required for their separation.
4. In Lassaigne's test, blue colouration/precipitate indicates presence of nitrogen and white precipitate indicates presence of chlorine.

Compound	Lassaigne's test result for nitrogen	Compound	Lassaigne's test result for chlorine
NH <sub>2</sub> CH <sub>2</sub> COOH	N and C present, so test is positive.	NH <sub>2</sub> CONH <sub>2</sub>	Cl is absent, so test is negative.
	N and C present, so test is positive.		Cl is present, so test is positive.
CH <sub>3</sub> COOH	N is absent, so test is negative.	ClCH <sub>2</sub> COOH	Cl is present, so test is positive.
CH <sub>3</sub> CH <sub>2</sub> NH <sub>2</sub>	N and C present, so test is positive.	CH <sub>3</sub> CH <sub>2</sub> I	Cl is absent, so test is negative.

Thus, the correct pair of compounds which gives blue colouration/precipitate and white precipitate, respectively, when their Lassaigne's tests are separately done is:



5. Molecular mass of AgBr = 108 + 80 = 188  
 Mass of Br in 188 g of AgBr = 80 g  
 $\therefore$  Mass of Br in 0.188 g of AgBr =  $\frac{80}{188} \times 0.188 = 0.08$  g  
 $\therefore$  % of Br =  $\frac{0.08}{0.4} \times 100 = 20\%$

# 13 Alkanes



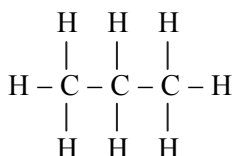
## Hints



### Classical Thinking

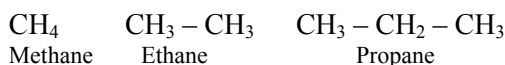
6. General molecular formula of alkanes is  $C_nH_{2n+2}$ .  
In butane, 4 carbon atoms are present therefore,  $n = 4$ . Substituting the value of  $n$  in the general formula of alkanes, we get the molecular formula of butane as  $C_4H_{10}$ .

9. Each carbon atom retains tetrahedral geometry because in an alkane each carbon is  $sp^3$  hybridized.  
10. The structural formula for propane is given as



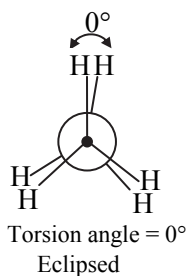
Thus, propane contains two carbon-carbon single bonds and eight C-H bonds.

13. The alkanes in which atleast one carbon atom is bonded to more than two other carbon atoms are known as branched chain alkanes.

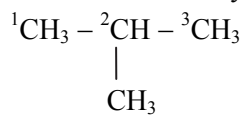


Methane, ethane and propane cannot form branched chain alkanes. Hence, the minimum number of carbon atoms necessary for a hydrocarbon to form a branched structure is 4 i.e., butane onwards alkanes can form branched chain alkanes.

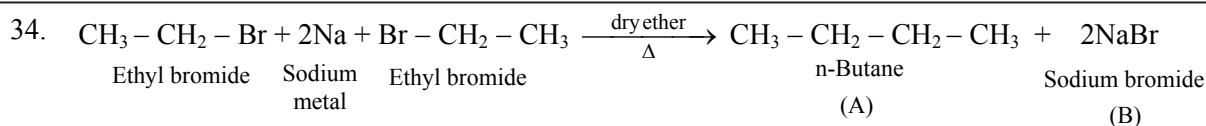
18. The isomers are different compounds having same molecular formula and therefore they exhibit different physical and chemical properties.  
19. Heptane has 9 isomers.  
23. In ethane, torsional angle is the angle between the  $H - C - C$  plane and the  $C - C - H$  plane. In eclipsed conformation, the torsional angle is  $0^\circ$ .



28. Isobutane is 2-Methylpropane



29.  $CH_3 - C \equiv CH + 2H_2 \xrightarrow[473-573\text{ K}]{\text{Raney Ni, } \Delta} CH_3 - CH_2 - CH_3$   
Propyne
Propane  
‘A’

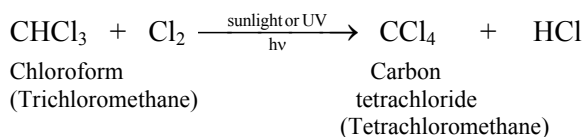
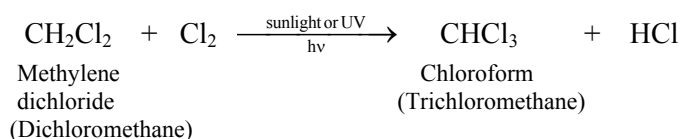
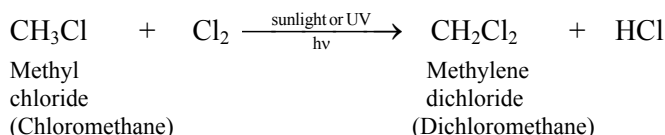
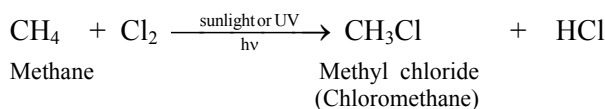


35. As the number of carbon atoms increases, melting and boiling points increases. Therefore the increasing order of the melting points of given compounds is  $\text{C}_3\text{H}_8 < \text{C}_4\text{H}_{10} < \text{C}_5\text{H}_{12} < \text{C}_6\text{H}_{14}$ .

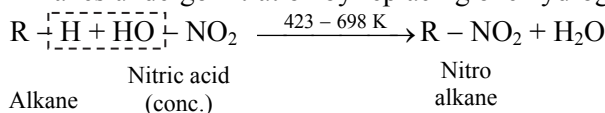
36. Alkanes having carbon atoms in the range from 5 to 17 are liquids.

38. Fluorine is highly reactive due to its highest electronegativity, hence fluorination is fast and explosive.

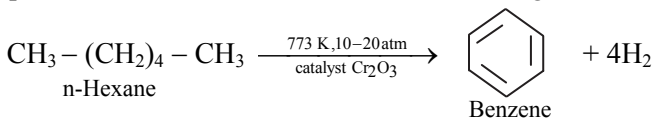
39. Chlorine reacts with methane in sunlight or U.V. light (or on heating) to give a mixture of four different alkyl halides. When all the four hydrogen atoms are substituted by chlorine atoms, the end product that gets formed is carbon tetrachloride.



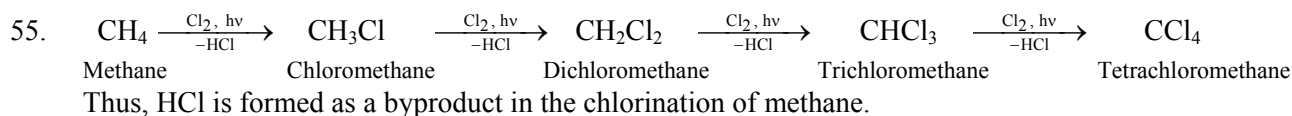
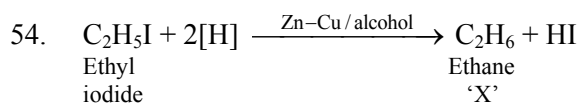
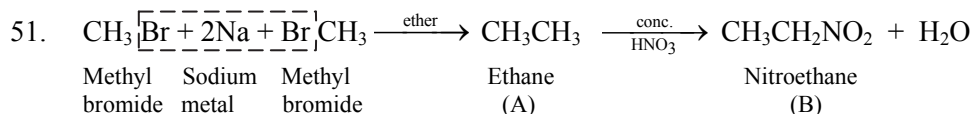
41. Alkanes undergo nitration by replacing one hydrogen atom by nitro ( $-\text{NO}_2$ ) group.



46. Higher alkanes with more than five carbon atoms get cyclised, on heating under 10 to 20 atm pressure at about 773 K in the presence of oxides of chromium, vanadium or molybdenum supported on alumina. The products formed are benzene and its homologues.



48. Alkanes ranging from  $\text{C}_{17}$  to  $\text{C}_{20}$  are viscous liquids and hence are used as lubricants.



**Critical Thinking**

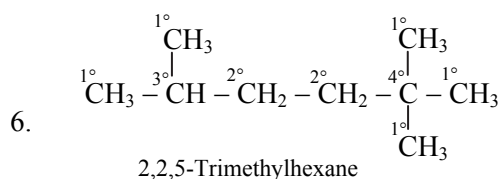
- General molecular formula of alkanes is  $C_nH_{2n+2}$ .  
In the alkane with 17 carbon atoms,  $n = 17$ . Substituting the value of  $n$  in the general formula of alkanes, we get the molecular formula as  $C_{17}H_{36}$ .
- Since, the given compound is saturated hydrocarbon therefore, comparing the formula with general molecular formula of alkanes  $C_nH_{2n+2}$  we get,  

$$2n + 2 = 14$$

$$2n = 12$$

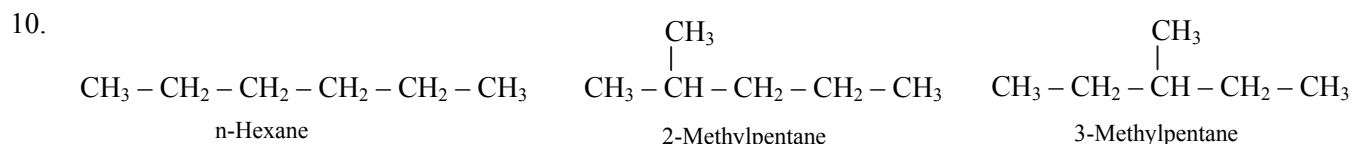
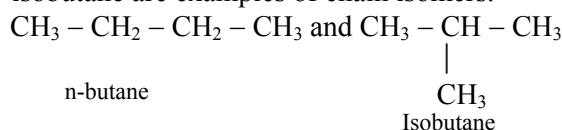
$$\therefore n = 6$$

- In alkanes, carbon undergoes  $sp^3$  hybridization. Hence, bond angle is  $109^\circ 28'$ .

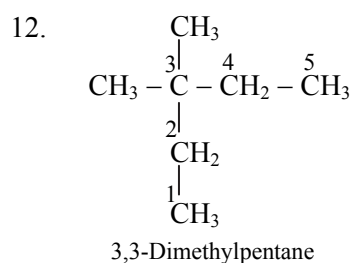


Thus, in 2,2,5-Trimethylhexane, there are five primary, two secondary, one tertiary and one quaternary carbon atoms present.

- n-Butane and isobutane have same molecular formula but different carbon skeleton. Hence n-Butane and isobutane are examples of chain isomers.



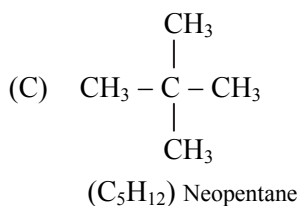
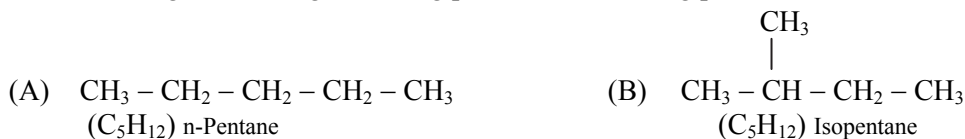
Except 2,2-Dimethylpentane which is an isomer of heptane (as it contains seven C-atoms), all others are isomers of hexane.





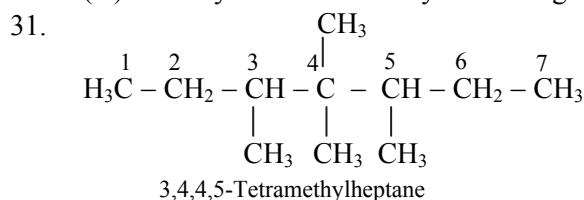


22. In alkanes, as the molecular mass increases the boiling point increases.  
 23. In isomeric alkanes, as branching increases, surface area decreases and hence intermolecular forces become weak resulting in lowering of boiling point. As the boiling point lowers, the alkanes become more volatile.



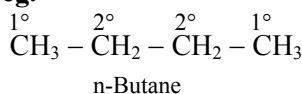
Among the given options, neopentane has the most number of branches (i.e., two methyl groups), hence it has the lowest boiling point and will be most volatile.

30. (A) The infinite number of intermediate conformations between staggered and eclipse conformations are called skew conformations.  
 (B) In neoalkanes, isobutyl group is present at one end of the normal chain of carbon atoms.  
 (D) Raney nickel is an alloy containing equal amount of nickel and aluminium.

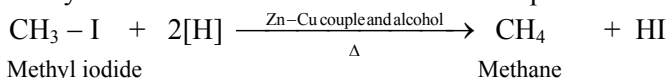


32. Normal hydrocarbon contains either only primary or both primary and secondary carbon atoms with no branching.

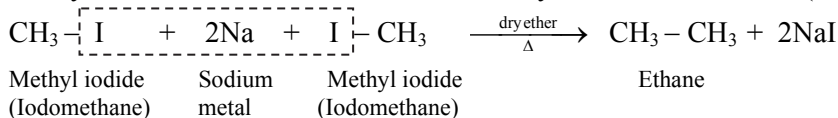
eg.



33. Methyl iodide on reduction with Zn - Cu couple and alcohol forms methane.



Methyl iodide reacts with sodium metal in dry ether to form ethane ( $\text{C}_2\text{H}_6$ ).

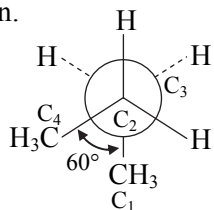


34.  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3 \xrightarrow{\text{Cracking}} \text{CH}_4 + \text{CH}_3 - \text{CH} = \text{CH}_2$   
 n-Butane  Methane  Propene



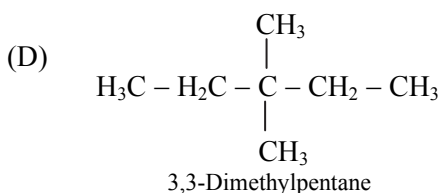
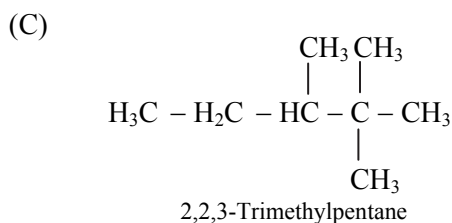
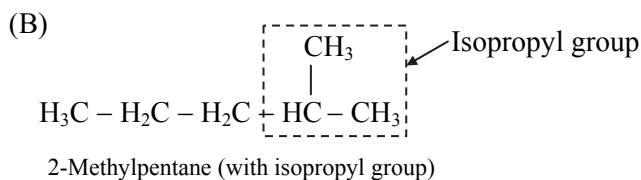
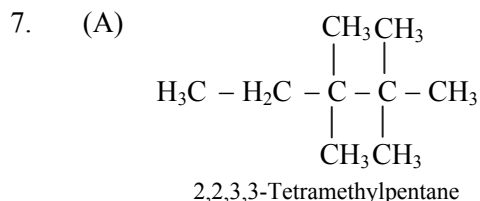
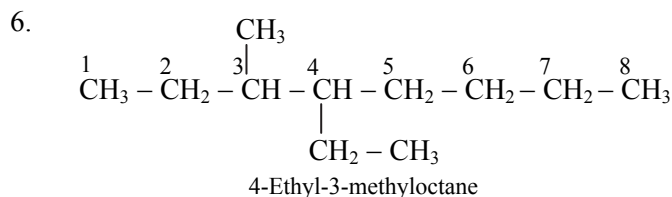
### Competitive Thinking

2.  $\text{C}_7\text{H}_{16}$  fits into the general formula of alkanes i.e., ( $\text{C}_n\text{H}_{2n+2}$ ) hence it represents an alkane.  
 4. After anticlockwise rotation of the  $\text{C}_2 - \text{C}_3$  bond by  $120^\circ$ , we get an angle of  $60^\circ$   $\text{C}_1 - \text{C}_4$  resulting in Gauche conformation.

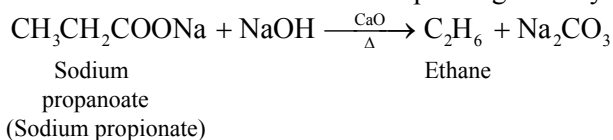




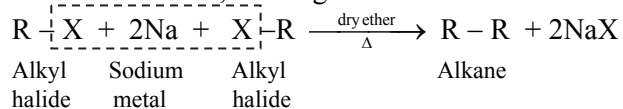
5. Conformers of ethane (eclipsed, staggered, gauche) have difference in dihedral angle, energy and stability but their bond lengths and bond angles do not change.



9. Anhydrous sodium salt of carboxylic acid when fused with soda lime (NaOH + CaO), gives alkane containing one carbon atom less than the corresponding carboxylic acid (i.e., decarboxylation reaction).



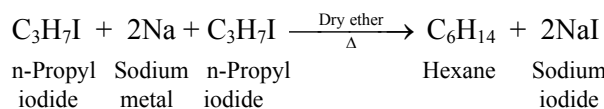
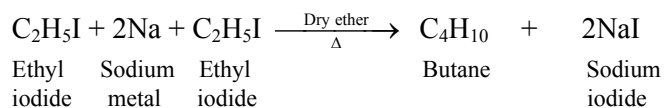
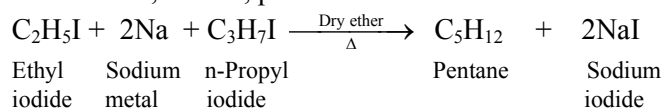
10. In Wurtz reaction, the reagent used is sodium metal in dry ether (Na/dry ether).



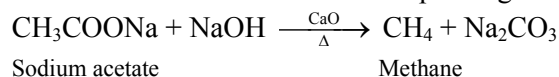
11. In Wurtz reaction, higher alkanes containing even number of carbon atoms are prepared by using only one type of alkyl halide. To prepare an alkane with odd number of carbon atoms an ethereal mixture of two different alkyl halides is heated with sodium metal. As a result, a mixture of different alkanes is obtained. Thus, in Wurtz reaction there is increase in the number of carbon atoms in the products formed as compared to the reactants. CH<sub>4</sub>, being an alkane that has only one carbon atom, cannot be prepared by Wurtz reaction.



12. When ethyl iodide and propyl iodide react with Na in the presence of ether they form mixture of three alkanes viz., butane, pentane and hexane.



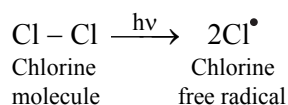
13. Anhydrous sodium salt of carboxylic acid when fused with soda lime (NaOH + CaO), gives alkane containing one carbon atom less than the corresponding carboxylic acid (i.e., decarboxylation reaction).



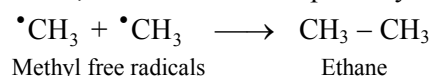
14. In alkanes, the boiling point depends on molecular mass. Greater the molecular mass, higher is the boiling point. Hence, among the given options, n-hexane has maximum boiling point.

15. For isomeric alkanes, straight chain isomers have higher boiling points than branched chain isomers.

16. Photochemical chlorination of alkane takes place by free radical mechanism which is initiated by homolysis of Cl – Cl bond. The Cl – Cl bond being weaker than C – H bond, is broken easily.



17.  $\text{CH}_4 \xrightarrow[-\text{HCl}]{\text{Cl}_2, h\nu} \text{CH}_3\text{Cl} \xrightarrow[-\text{HCl}]{\text{Cl}_2, h\nu} \text{CH}_2\text{Cl}_2 \xrightarrow[-\text{HCl}]{\text{Cl}_2, h\nu} \text{CHCl}_3 \xrightarrow[-\text{HCl}]{\text{Cl}_2, h\nu} \text{CCl}_4$
- Methane                      Chloromethane                      Dichloromethane                      Trichloromethane                      Tetrachloromethane
- Since, this reaction takes place by free radical mechanism, there is a possibility of formation of ethane.



However,  $\text{CH}_3\text{CH}_2\text{CH}_3$  is not formed by the reaction of  $\text{Cl}_2$  on  $\text{CH}_4$  in sunlight.

- 19.
- $$\text{CH}_3 - \text{CH}_2 - \text{CH}_3 \xrightarrow[\Delta]{\text{Conc. HO} - \text{NO}_2, 423 \text{ K} - 698 \text{ K}} \begin{cases} \text{CH}_3 - \text{NO}_2 + \text{CH}_3 - \text{CH}_2 - \text{NO}_2 \\ \text{Nitromethane} \quad \text{Nitroethane} \\ \text{CH}_3 - \text{CH}_2 - \text{CH}_2 - \text{NO}_2 \\ \text{1-Nitropropane} \\ \text{CH}_3 - \underset{\text{NO}_2}{\text{CH}} - \text{CH}_3 \\ \text{2-Nitropropane} \end{cases}$$
- Propane

- 21.
- $$\text{CH}_3(\text{CH}_2)_4\text{CH}_3 \xrightarrow[\text{Cr}_2\text{O}_3/\text{V}_2\text{O}_5/\text{Mo}_2\text{O}_3]{773 \text{ K}, 10-20 \text{ atm}} \text{C}_6\text{H}_6$$
- n-Hexane                      (Dehydrogenation)                      Benzene

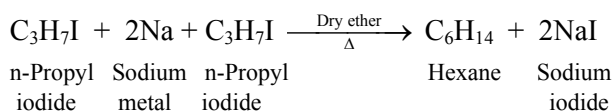
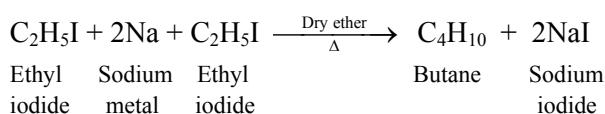
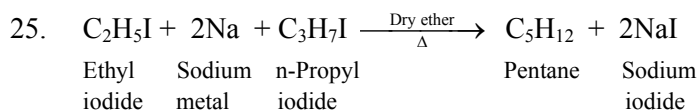
22.  $\text{CH}_4 + \text{O}_2 \xrightarrow[\text{Limited supply of air}]{\Delta} \text{C} + 2\text{H}_2\text{O}$
- Methane                      Carbon (in the form of carbon black)





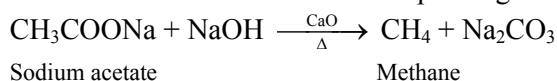
23. In alkanes, boiling point depends on molecular mass. Greater the molecular mass, higher will be the boiling point. For isomeric alkanes, boiling points of branched chain alkanes as compared to straight chain alkanes are lower. Hence, among given options n-octane has maximum boiling point.

24. Alkanes are insoluble in water.



Thus, n-propane is not formed when a mixture of ethyl iodide and n-propyl iodide is subjected to Wurtz reaction.

26. Anhydrous sodium salt of carboxylic acid when fused with soda lime (NaOH + CaO), gives alkane containing one carbon atom less than the corresponding carboxylic acid (i.e., decarboxylation reaction).



28. Homologues differ by  $\text{CH}_2$  unit. Hence, fourth higher homologue of ethane ( $\text{C}_2\text{H}_6$ ) will have additional four  $\text{CH}_2$  units i.e.,  $\text{C}_2\text{H}_6 + (\text{CH}_2)_4 = \text{C}_6\text{H}_{14}$ , which is the molecular formula of hexane. Thus, the fourth higher homologue of ethane is hexane.



### Evaluation Test

1. As the number of carbon atoms increases, melting and boiling points increases. CNG contains  $\text{C}_1$  to  $\text{C}_4$  members of alkanes. Gasoline contains  $\text{C}_6$  to  $\text{C}_8$  members of alkanes. Diesel contains  $\text{C}_{15}$  to  $\text{C}_{18}$  members of alkanes. Thus, the order of appearance with rising temperature, during the refining of crude oil, is CNG, gasoline and diesel.

2. Since, the given compound is an alkane ( $\text{C}_n\text{H}_{2n+2}$ ) with molecular weight 170.

$$\text{Therefore, } (12 \times n) + 1(2n + 2) = 170$$

Where n = integer indicating number of carbon atoms in a molecule

$$12 = \text{atomic weight of carbon}$$

$$1 = \text{atomic weight of hydrogen}$$

$$\therefore 12n + 2n + 2 = 170$$

$$\therefore 14n = 168$$

$$\therefore n = \frac{168}{14} = 12$$

$\therefore$  The molecular formula of the given alkane is  $\text{C}_{12}\text{H}_{26}$ .

3. One mole of any gas occupies 22.4 L at STP.

$\therefore$  x moles of the alkane occupies 5.6 L

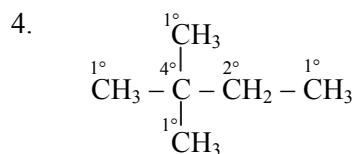
$$x = \frac{5.6}{22.4}$$



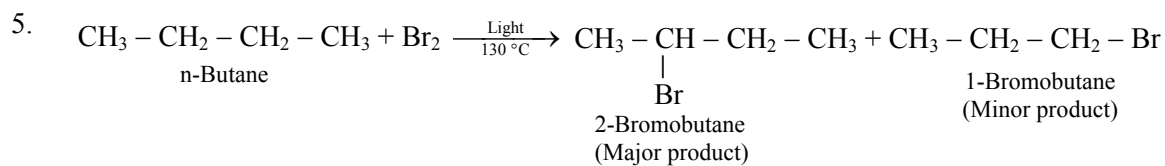
$$\text{Number of moles} = \frac{\text{weight}}{\text{molecular weight}}$$

$$\begin{aligned}\therefore \text{Molecular weight} &= \frac{\text{weight}}{\text{number of moles}} \\ &= 11 \times \frac{22.4}{5.6} \\ &= 44\end{aligned}$$

Among the given options, alkane having molecular weight of 44 is propane with molecular formula  $\text{C}_3\text{H}_8$ .



Thus, in neohexane, there is only one secondary carbon atom and there are two hydrogen atoms attached to it.



2-Bromobutane is the major product because  $2^\circ$  carbonium ion is more stable than  $1^\circ$ .

# 01 Solid State



## Hints



### Classical Thinking

34. Volume of unit cell =  $\frac{64r^3}{3\sqrt{3}}$   
 Volume occupied =  $\frac{8}{3}\pi r^3$   
 Volume occupied by two atoms in unit cell or packing =  $\frac{8}{3}\pi r^3 \times \frac{3\sqrt{3}}{64r^3} \times 100 = 68.04\%$ .

35. Total volume of unit cell =  $8\sqrt{8}r^3$   
 Volume occupied =  $\frac{16}{3}\pi r^3$   
 $\therefore$  Packing efficiency =  $\frac{16}{3}\pi r^3 \times \frac{1}{8\sqrt{8}r^3} \times 100 = 74.0\%$

42. Radius ratio =  $\frac{r_{\text{Na}^+}}{r_{\text{Cl}^-}} = \frac{0.95}{1.81} = 0.5248 \approx 0.52$

56. If a substance is diamagnetic, it weighs less in the magnetic field as the substance is repelled by the magnetic field.

58. Schottky defect is a type of point defect.



### Critical Thinking

14. The chemical formula of Buckminster fullerene is  $C_{60}$ .  
 Therefore, 1 mole of  $C_{60}$  contains 60 moles of carbon.

17. Orthorhombic unit cell has three unequal edges (sides) which are at right angles to each other.

23. Density of unit cell  

$$= \frac{z(\text{no. of atoms in unit cell}) \times M(\text{molecular weight})}{a^3(\text{volume of unit cell}) \times N_0(\text{Avogadro's number})} \text{ g cm}^{-3}$$

25. 
$$z = \frac{d \times N_0 \times a^3}{M}$$

$$= \frac{2.75 \times 6.022 \times 10^{23} \times (6.54 \times 10^{-8})^3}{119}$$

$$= \frac{2.75 \times 6.022 \times 27.97}{119}$$

$$= \frac{463.197}{119} = 3.89 \approx 4$$

26. For fcc lattice,  
 $4r = \sqrt{2}a$   
 $a = 620 \text{ pm}$ ;  
 $r = \frac{\sqrt{2} \times 620}{4} = \frac{1.414 \times 620}{4}$   
 $= 219.17 \approx 219.20 \text{ pm}$

27. 
$$N_0 = \frac{z \times M}{d \times a^3} = \frac{1 \times 108}{8 \times (3 \times 10^{-8})^3}$$

$$= \frac{108 \times 10^{+24}}{216} = 0.5 \times 10^{24} = 5 \times 10^{23}$$

28. NaCl forms face-centred cubic lattice with  $z = 4$ .  
 Edge length (a) of the unit cell  
 $= 2 \times \text{distance between Na}^+ \text{ and Cl}^-$   
 $= 2 \times 281 = 562 \text{ pm}$   

$$d = \frac{z \times M}{N_0 \times a^3}$$

$$\therefore N_0 = \frac{4 \times 58.5}{2.165 \times (5.62 \times 10^{-8})^3}$$

$$= 6.08 \times 10^{23} \text{ mol}^{-1}$$

29. In bcc lattice, the distance (D) between closest neighbours =  $\frac{\sqrt{3}}{2}a$

$$\therefore a = D \times \frac{2}{\sqrt{3}} = 1.73 \times \frac{2}{\sqrt{3}} = 2 \text{ \AA} = 200 \text{ pm}$$

30.  $d = 3.4 \text{ g cm}^{-3}$ ,  $z = 4$ ,  $M = 98.99 \text{ g mol}^{-1}$   

$$d = \frac{z \times M}{N_0 \times a^3}$$



$$a^3 = \frac{4 \times 98.99}{6.022 \times 10^{23} \times 3.4}$$

$$\therefore a^3 = \frac{395.96 \times 10^{-23}}{20.47}$$

$$\therefore a^3 = 19.34 \times 10^{-23}$$

$$\therefore a = \sqrt[3]{1.934 \times 10^{-22}} = 5.783 \times 10^{-8} \text{ cm}$$

$$= 5.783 \times 10^{-10} \text{ m} = 5.783 \text{ \AA}$$

31. Cell length,  $a = 4.24 \text{ \AA} = 4.24 \times 10^{-10} \text{ m}$   
 $= 4.24 \times 10^{-8} \text{ cm}$

In bcc lattice,  $z = 2$ ,  $M = 23 \text{ g mol}^{-1}$

$$d = \frac{z \times M}{N_0 \times a^3} = \frac{2 \times 23}{6.022 \times 10^{23} \times (4.24 \times 10^{-8})^3}$$

$$= \frac{46 \times 10^{24}}{6.022 \times 76.22 \times 10^{23}}$$

$$= 0.1002 \times 10^1 = 1.002 \text{ g cm}^{-3}$$

32.  $\text{Cu} = \text{ccp} = 4$

$$\text{Ag} = 12 (\text{edges}) \times \frac{1}{4} = 3$$

$$\text{Au} = 1 \quad \therefore \text{Cu}_4\text{Ag}_3\text{Au}$$

33. An atom at the corner of a cube is shared among 8 unit cells. As there are 8 corners in a cube, number of corner atom [A] per unit cell

$$= 8 \times \frac{1}{8} = 1$$

A face-centred atom in a cube is shared by two unit cells. As there are 6 faces in a cube, number of face-centred atoms [B] per unit cell

$$= 6 \times \frac{1}{2} = 3$$

Hence, the formula of the solid is  $\text{AB}_3$ .

34. One-eighth of each corner atom (Au) and one half of each face centered atom (Cu) are contained within the unit cell of the compound.

Thus, the number of Au atoms per unit cell

$$= 8 \times \frac{1}{8} = 1 \text{ and the number of Cu atoms per}$$

unit cell  $= 6 \times \frac{1}{2} = 3$ . The formula of the compound is  $\text{AuCu}_3$ .

35. There is one octahedral hole per oxide ion and only  $\left(\frac{2}{3}\right)^{\text{rd}}$  of these holes are occupied.

$$\therefore \text{the ratio should be } \frac{2}{3} : 1 = 2 : 3$$

37. In tetrahedral voids, four spheres are involved in its formation.

42.  $2r^+ + 2r^- = 552$ ;  $r^+ + r^- = \frac{552}{2} = 276$

$$r^- = 276 - 95 = 181 \text{ pm.}$$

43.  $\frac{r_{\text{Na}^+}}{r_{\text{Cl}^-}} = 0.55$ ,  $\frac{r_{\text{K}^+}}{r_{\text{Cl}^-}} = 0.74$

$$\frac{r_{\text{Na}^+}}{r_{\text{Cl}^-}} + 1 = 0.55 + 1$$

$$\frac{r_{\text{K}^+}}{r_{\text{Cl}^-}} + 1 = 0.74 + 1$$

$$\frac{r_{\text{Na}^+} + r_{\text{Cl}^-}}{r_{\text{Cl}^-}} = 1.55$$

$$\frac{r_{\text{K}^+} + r_{\text{Cl}^-}}{r_{\text{Cl}^-}} = 1.74$$

$$\frac{r_{\text{K}^+} + r_{\text{Cl}^-}}{r_{\text{Cl}^-}} \times \frac{r_{\text{Cl}^-}}{r_{\text{Na}^+} + r_{\text{Cl}^-}} = \frac{1.74}{1.55}$$

$$\therefore \frac{r_{\text{K}^+} + r_{\text{Cl}^-}}{r_{\text{Na}^+} + r_{\text{Cl}^-}} = 1.122$$

44.  $r_+ / r^- = \frac{180}{187} = 0.962$  which lies in the range of 0.732 – 1.000.

Hence, coordination number = 8 i.e., the structure is CsCl type.

53.  $d = \frac{z \times M}{V \times N_0}$

$$= \frac{4 \times 21.76}{6.8 \times 4.4 \times 7.2 \times 10^{-24} \times 6.023 \times 10^{23}}$$

$$= 0.6708 \text{ g/cm}^3$$

56. Quartz is a covalent crystal having a framework of silicates or silica, i.e., a three dimensional network when all the four oxygen atoms of each of  $\text{SiO}_4$  tetrahedron are shared.

57. Number of atoms of A  $= 6 \times \frac{1}{8} = \frac{3}{4}$

$$\text{Number of atoms of B} = 6 \times \frac{1}{2} = 3$$

$$\text{A} : \text{B} = \frac{3}{4} : 3 = 1 : 4$$

$$\therefore \text{Composition of alloy} = \text{AB}_4$$



59.

Type of unit cell	Packing efficiency	Example
Simple cubic lattice	52.4%	Po
Body centred cubic lattice	68%	Ti
Face centred cubic lattice	74%	Cu

60. For an ionic compound,  $A^+B^-$  having fcc structure like NaCl,  
Edge length (a) = 2 × Distance between  $A^+$  and  $B^-$  ions.



### Competitive Thinking

4. Pyrex glass contains 60–80%  $SiO_2$ , 10–25%  $B_2O_3$  and remaining amount of  $Al_2O_3$ .

6. Due to intermolecular hydrogen bonding between water molecules, almost half of the volume is vacant or unoccupied.

7. Ionic crystals exhibit non-directional properties of the bond.

11. In fullerene, sixty carbon atoms occupy sixty equidistant places. Each carbon is  $sp^2$  hybridized.

14. Unit cell dimension of hexagonal crystal is  $a = b \neq c$  and  $\alpha = \beta = 90^\circ, \gamma = 120^\circ$

16. Polonium – simple cubic crystal  
Iron – Body centred crystal  
Copper, gold – Face centred crystals

21. The bcc cell consists of 8 atoms at the corners and one atom at centre.

$$\therefore n = \left(8 \times \frac{1}{8}\right) + 1 = 2$$

The fcc cell consists of 8 atoms at the eight corners and one atom at each of the six faces. This atom at the face is shared by two unit cells.

$$\therefore n = 8 \times \frac{1}{8} + \left(6 \times \frac{1}{2}\right) = 4$$

22. Number of atoms per unit cell in fcc = 4  
Number of atoms per unit cell in bcc = 2

$$\therefore \text{Difference} = 4 - 2 = 2$$

25. There are two atoms in a bcc unit cell. So, number of atoms in  $12.08 \times 10^{23}$  unit cells  
 $= 2 \times 12.08 \times 10^{23}$   
 $= 24.16 \times 10^{23}$

$$29. \quad a\sqrt{2} = 4r \quad \Rightarrow a = 2\sqrt{2} r$$

$$\begin{aligned} \text{Packing fraction} &= \frac{\text{Occupied area}}{\text{Total area}} \\ &= \frac{2\pi r^2}{(2\sqrt{2}r)^2} \times 100 = 78.5\% \end{aligned}$$

31. Distance between two oppositely charged ions

$$(r^+ + r^-) = \frac{\sqrt{3}a}{2} = \frac{387 \times \sqrt{3}}{2} = 335.14 \text{ pm}$$

32. Closest approach in bcc lattice

$$= \frac{1}{2} \text{ of body diagonal}$$

$$= \frac{1}{2} \times \sqrt{3}a$$

$$= \frac{\sqrt{3}}{2} \times 4.3 = 3.72 \text{ \AA}$$

34. Closest distance in fcc = 2r

$$= \frac{2\sqrt{2} a}{4}$$

$$= \frac{\sqrt{2} a}{2}$$

$$= \frac{a}{\sqrt{2}}$$

35. Edge length =  $2r^+ + 2r^-$

$$\frac{508}{2} = r^+ + r^-; 254 = 110 + r^-$$

$$\therefore r^- = 254 - 110 = 144 \text{ pm.}$$

36. In fcc,  $4r = \sqrt{2} a$ ,

Where r = radius of the sphere

a = edge length of the unit cell = 620 pm

$$r = \frac{\sqrt{2} a}{4} = \frac{\sqrt{2} \times 620}{4} = 219.20 \text{ pm}$$

37. Volume occupied by one atom of radius 'r' =  $\frac{4}{3}\pi r^3$ .

In fcc unit cell, there are 4 atoms present.

$\therefore$  Total volume occupied by the atoms

$$\text{present in fcc unit cell} = 4 \times \frac{4}{3}\pi r^3 = \frac{16}{3}\pi r^3$$

38. Simple unit cell,  $r = a/2$

$$\text{Body-centered unit cell, } r = \frac{a\sqrt{3}}{4}$$

$$\text{Face-centered unit cell, } r = \frac{a}{2\sqrt{2}}$$



39. Radius of Na (in bcc lattice)  

$$= \frac{\sqrt{3}a}{4} = \frac{\sqrt{3} \times 4.29}{4} = 1.857 \text{ \AA} \approx 1.86 \text{ \AA}$$
40. 
$$N_0 = \frac{z \times M}{d \times a^3} = \frac{4 \times 100}{10 \times (10^{-8})^3} = 4 \times 10^{25}$$
41. 
$$d = \frac{z \times M}{a^3 \times N_0 \times 10^{-30}}$$

$$= \frac{2 \times 100}{(400)^3 \times (6.02 \times 10^{23}) \times 10^{-30}}$$

$$= 5.188 \text{ g/cm}^3$$
42. Since, there are four metal atoms in one unit cell, the given metal crystallizes in fcc lattice. For fcc lattice;  

$$r = \frac{\sqrt{2}a}{4} = \frac{\sqrt{2} \times 361}{4} = \frac{1.414 \times 361}{4}$$

$$= 127.6 \text{ pm} \approx 127 \text{ pm}$$
43. 
$$z = \frac{V \times N_0 \times d}{M}$$

$$= \frac{4.2 \times 8.6 \times 8.3 \times 10^{-24} \times 6.023 \times 10^{23} \times 3.3}{155}$$

$$= 3.84 \approx 4$$
44. For bcc structure,  $z = 2$   
Density of unit cell,  $d = \frac{z \times M}{a^3 \times N_0 \times 10^{-30}}$   
(when  $a$  is in pm)  

$$\therefore a = \left( \frac{z \times M}{d \times N_0 \times 10^{-30}} \right)^{\frac{1}{3}}$$

$$\therefore a = \left( \frac{2 \times 6.94 \text{ g mol}^{-1}}{0.530 \text{ g cm}^{-3} \times 6.02 \times 10^{23} \text{ mol}^{-1} \times 10^{-30}} \right)^{\frac{1}{3}}$$

$$= 351.7 \text{ pm} \approx 352 \text{ pm}$$
45. Mass of one unit cell = density  $\times$  volume  

$$= d \times a^3$$

$$= \frac{M \times z}{N_0 \times a^3} \times a^3$$

$$= \frac{58.5 \times 4}{6.023 \times 10^{23}}$$

$$\therefore \text{Number of unit cells in 1 g NaCl}$$

$$\frac{1}{\text{Mass of one unit cell}} = \frac{6.023 \times 10^{23}}{58.5 \times 4}$$

$$= 2.57 \times 10^{21} \text{ unit cells}$$
46. Metal has fcc lattice,  
 $\therefore z = 4$   

$$d = \frac{z \times M}{a^3 \times N_0}$$

$$2.72 = \frac{4 \times M}{(4.04 \times 10^{-8})^3 \times 6.02 \times 10^{23}}$$

$$M = \frac{2.72 \times (4.04)^3 \times 6.02 \times 10^{-1}}{4} = 27 \text{ g mol}^{-1}$$
47. A metal that crystallizes in bcc structure has a coordination number of 8.
49. Atoms of X per unit cell =  $8 \times \frac{1}{8} = 1$   
Atoms of Y per unit cell = 1  
Atoms of Z per unit cell =  $6 \times \frac{1}{2} = 3$   
Hence, the formula is  $XYZ_3$
50. A as corners of cube;  $\frac{1}{8} \times 8 = 1$ .  
B as faces of cube;  $\frac{1}{2} \times 6 = 3$   
A : B = 1 : 3  
 $\therefore$  The empirical formula for this compound would be  $AB_3$
51. W at corner;  $\frac{1}{8} \times 8 = 1$   
O at centres of edges;  $\frac{1}{2} \times 6 = 3$   
Na at centre of cube = 1  
Na : W : O  
1 : 1 : 3
52. Atoms A at the corners of cube;  $\frac{1}{8} \times 8 = 1$   
Atom B at the centre of cube = 1  
A : B at the centre of cube = 1  
A : B = 1 : 1
54. Let the number of atoms of element Y in hcp unit cell be  $n$ .  
 $\therefore$  Number of tetrahedral voids =  $2n$   
As  $\frac{2}{3}$ <sup>rd</sup> of the tetrahedral voids are occupied by atoms of element X,  
Number of atoms of element X =  $2n \times \frac{2}{3} = \frac{4n}{3}$   
 $\therefore$  Ratio of atoms of element X : atoms of element Y =  $\frac{4n}{3} : n = 4 : 3$   
The formula of the compound is  $X_4Y_3$ .



55. The number of ions of 'Y' in ccp unit cell = 4.  
 Number of octahedral voids in ccp unit cell = Number of ions of 'Y' in ccp unit cell = 4  
 Since, ions of 'X' occupy all the octahedral voids, the number of ions of 'X' in ccp unit cell = 4  
 $\therefore$  The ratio of number of ions of 'X' to the number of ions of 'Y' = 4 : 4 i.e., 1 : 1.  
 Hence, the molecular formula of the given compound is XY.

56. 'A' atoms are present at 8 corners and 6 face centres. Two face centre atoms are removed along one axis. Thus, total 4 face centred atoms are left out.

$$\text{Total number of 'A' atoms in one unit cell} = 8 \times \frac{1}{8} + 4 \times \frac{1}{2} = 3$$

'B' atoms occupy octahedral holes. There are 4 octahedral holes in fcc unit cell.

$\therefore$  Number of 'B' atoms in fcc unit cell = 4

$\therefore$  Stoichiometry =  $A_3B_4$

59. For ionic solids, radius ratio =  $\frac{r^+}{r^-} = \frac{A^+}{B^-}$

$$= \frac{0.98 \times 10^{-10} \text{ m}}{1.81 \times 10^{-10} \text{ m}} = 0.541$$

$\Rightarrow$  Coordination number = 6

$\therefore$  For the given ionic solid,  $A^+B^-$ , having equal number of cations and anions, the coordination number of each ion is 6.

64. For n-type, impurity added to silicon should have more than 4 valence electrons.

67.

	Substance	Magnetic property
(A)	Dioxygen	Paramagnetic
(B)	Chromium (IV) oxide	Ferromagnetic
(C)	Benzene	Diamagnetic
(D)	Dihydrogen monoxide	Diamagnetic

69. Mass of a single Ag atom = m

$\therefore$  Mass of fcc unit cell of silver = 4m

( $\because$  fcc type unit cell contains total 4 atoms)

Edge length of fcc unit cell = a

Volume of fcc unit cell =  $a^3$

$$\text{Density of silver (Ag)} = \frac{\text{Mass of fcc unit cell}}{\text{Volume of fcc unit cell}}$$

$$\therefore \text{Density of silver (Ag)} = \frac{4m}{a^3}$$

70. According to the given condition,

$$\begin{aligned} \text{Edge length (a)} &= \sqrt[3]{\text{Volume of one CsCl ion pair}} \\ &= \sqrt[3]{7.014 \times 10^{-23} \text{ cm}^3} \\ &= 4.12 \times 10^{-8} \text{ cm} \\ &= 4.12 \times 10^{-10} \text{ m} \\ &= 4.12 \text{ \AA} \approx 4 \text{ \AA} \end{aligned}$$

So, the smallest Cs to Cs internuclear distance is nearly 4 Å.

71. The number of particles of Y in ccp unit cell = 4. The formula of the solid is  $XY_3$ . Therefore, the ratio of number of X particles to the number of Y particles is 1 : 3. So, for the unit cell, the number of X particles =  $\frac{4 \times 1}{3} = 1.33$

Number of octahedral voids in ccp unit cell = Number of Y particles in ccp unit cell = 4

$\therefore$  Percentage of octahedral voids occupied by X particles =  $\frac{1.33}{4} \times 100 = 33\%$

72.

Type of unit cell	Packing efficiency	Examples
Simple cubic lattice	52.4%	Polonium
Body centred cubic lattice	68%	Iron, Tungsten
Face centred cubic lattice	74%	Aluminium

Hence, among the given metals, aluminium has the highest packing efficiency.

73. 58.5 g of NaCl = 1 mole =  $6.023 \times 10^{23}$  NaCl units. One unit cell of NaCl (fcc) contains 4 NaCl units.

Hence, the number of unit cells present

$$= \frac{6.023 \times 10^{23}}{4} = 1.5 \times 10^{23}$$



### Evaluation Test

2. The triclinic system has all the three sides different ( $a \neq b \neq c$ ) and all the three angles different ( $\alpha \neq \beta \neq \gamma \neq 90^\circ$ ). Hence, it is the most unsymmetrical crystal system.

3. Volume of unit cell =  $a^3 = (4.08 \times 10^{-8} \text{ cm})^3 = 6.79 \times 10^{-23}$



4. For fcc unit cell,  $z = 4$   
Weight of  $18 \times 10^{23}$  atoms = 150 g  
Atomic weight,  $M = 150 \times \frac{6.023 \times 10^{23}}{18 \times 10^{23}} = 50.19$   
Edge length =  $a = 100$  pm  
Density,  $d = \frac{z \times M}{a^3 \times 10^{-30} \times N_0} \text{ g cm}^{-3}$   
$$= \frac{4 \times 50.19}{(100)^3 \times 10^{-30} \times 6.023 \times 10^{23}} = 333.3 \text{ g cm}^{-3}$$
5. Density =  $\frac{z \times M}{a^3 \times N_0} \text{ g cm}^{-3}$   
$$2.7 \text{ g cm}^{-3} = \frac{z \times 26.98}{(4.05 \times 10^{-8})^3 \times 6.023 \times 10^{23}}$$
  
$$z = \frac{2.7 \times (4.05 \times 10^{-8})^3 \times 6.023 \times 10^{23}}{26.98} = 4$$
  
 $\therefore$  The cell is fcc unit cell.  
For fcc unit cell,  $4r = \sqrt{2} a$   
 $\therefore$  Radius of Al atom,  $r = \frac{\sqrt{2} a}{4} = \frac{1.414 \times 4.05 \text{ \AA}}{4}$   
$$= 1.432 \text{ \AA}$$
6. Density  $d = \frac{z \times M}{a^3 \times N_0} \text{ g cm}^{-3}$   
$$= \frac{4 \times 108}{(409 \times 10^{-10})^3 \times 6.022 \times 10^{23} \text{ mol}^{-1}} = 10.5 \text{ g cm}^{-3}$$
7. Density  $d = \frac{z \times M}{a^3 \times 10^{-30} \times N_0} \text{ g cm}^{-3}$   
$$5.56 \text{ g cm}^{-3} = \frac{z \times 143.32}{(555.2)^3 \times 10^{-30} \times 6.023 \times 10^{23}}$$
  
$$z = \frac{5.56 \times (555.2)^3 \times 10^{-30} \times 6.023 \times 10^{23}}{143.32} = 3.99 \approx 4$$
  
 $\therefore$  solid has face centred cubic system with  $z = 4$ .
8. Four P atoms from ccp arrangement contribute to one unit cell.  
Four Q atoms from all the octahedral voids and four Q atoms from half of the tetrahedral voids contribute to one unit cell.  
So formula of solid is  $P_4Q_8$ , so the simplest formula of the solid is  $PQ_2$ .
10. For fcc structure,  $4r = \sqrt{2} a$   
$$a = 2\sqrt{2} r = 2\sqrt{2} \times 130 \text{ pm} = 367.64 \text{ pm}$$
  
Density  $d = \frac{z \times M}{a^3 \times N_0} = \frac{4 \times 63.54}{(3.67 \times 10^{-8})^3 \times 6.023 \times 10^{23}} = 8.54 \text{ g cm}^{-3}$





11. From eight corner atoms, one atom (X) contributes to one unit cell.  
From six face centres, three atoms (Y) contributes to one unit cell.  
∴ The formula of the compound is  $XY_3$ .  
Molar mass (M) of  $XY_3 = 60 + 3 \times 90 = 330 \text{ g mol}^{-1}$   
Density of  $XY_3$  (d) =  $\frac{z \times M}{a^3 \times N_0} = \frac{1 \times 330}{(5 \times 10^{-8})^3 \times 6.023 \times 10^{23}} = 4.38 \text{ g/cm}^3$
12. Density  $d = \frac{z \times M}{a^3 \times N_0}$   
 $2 = \frac{4 \times M}{(7 \times 10^{-8})^3 \times 6.023 \times 10^{23}}$   
 $M = \frac{2 \times (7 \times 10^{-8})^3 \times 6.023 \times 10^{23}}{4} = 103.3 \text{ g/mol}$
13. As LiI has fcc arrangement,  $I^-$  ions will occupy the corners and face centres. These ions will touch each other along the face diagonal.  
∴ Face diagonal =  $4r = \sqrt{2} a$   
∴  $r = \frac{\sqrt{2}}{4} a = \frac{1.414}{4} \times 550 = 194.4 \text{ pm}$
14.  $\frac{d_{\text{bcc}}}{d_{\text{ccp}}} = \frac{\text{packing efficiency of bcc}}{\text{packing efficiency of ccp}} = \frac{67.92}{74.02} = 0.918$
16. Isomorphous substances have same crystal structure.
18. Radius ratio =  $\frac{r^+}{r^-} = \frac{95}{181} = 0.52$   
Since the radius ratio is in between 0.414 to 0.732, the coordination number of cation is 6.
20.  $Cl^-$  in CsCl adopt bcc type of packing hence the coordination of  $Cs^+$  is equal to that of  $Cl^-$ , that is 8.



## Hints



### Classical Thinking

5. A solution of “two or more metals” or “of a metal or metals with one or more non-metals” is called an alloy or solid solution.
7. Concentration of a solution is defined as the amount of solute dissolved in a specific amount of solvent.
9. Unsaturated solution contains less amount of solute than required for forming a saturated solution. Therefore, unsaturated solution can accommodate additional amount of solute added to it for dissolution, till the formation of a saturated solution.
11. Percentage by mass of solute  

$$= \frac{\text{mass of solute}}{\text{mass of solution}} \times 100$$
12. mass of solute = 50 g  
 mass of solvent = 950 g  
 mass of solution = (50 + 950) g  

$$= 1000 \text{ g}$$

$$\therefore 1000 \text{ g contains } 50 \text{ g solute}$$

$$\therefore 100 \text{ g contains } = \frac{50 \times 100}{1000}$$

$$= 5 \text{ g of solute}$$
14. Moles of  $\text{N}_2 = \frac{7}{28} = 0.25$   
 Moles of  $\text{O}_2 = \frac{16}{32} = 0.50$   

$$\therefore \text{Mole fraction of } \text{N}_2 = \frac{0.25}{0.25 + 0.50} = 0.33$$
16. Mole fractions of various components of a solution add up to 1.  

$$\therefore \text{In this case } x_{\text{solute}} + x_{\text{solvent}} = 1.$$

$$\therefore x_{\text{solute}} = 1 - 0.8 = 0.2$$
18.  $M_1 V_1 = M_2 V_2$   
 Initial      final  

$$\therefore 0.25 \times 250 = M_2 \times 500$$

$$\therefore M_2 = \frac{0.25 \times 250}{500} = 0.125 \text{ M}$$

19.  $M_1 V_1 = M_2 V_2, M_2 = \frac{0.4 \times 25}{600} = 0.0167 \text{ M}$
20.  $M_1 V_1 = M_2 V_2$   
 $20 \times M_{\text{HCl}} = 19.85 \times 0.01$   
 $M_{\text{HCl}} = \frac{19.85 \times 0.01}{20} = 0.0099 \text{ M}$
23. The solubility of  $\text{Na}_2\text{SO}_4$  decreases with increase of temperature.
27. According to Charles's law, volume of a given mass of a gas increases with increase in temperature. Hence, solubility of a gas decreases with increase in temperature and vice-versa.
35. According to Raoult's law, the relative lowering in vapour pressure of a dilute solution is equal to mole fraction of the solute present in the solution.
38.  $p_{\text{solution}} = p_{\text{solvent}}^\circ x_{\text{solvent}} \Rightarrow \therefore p_{\text{solution}} \propto x_{\text{solvent}}$
41. The expression for relative lowering of vapour pressure by Raoult's law is  $\frac{p_1^\circ - p}{p_1^\circ} = \frac{n}{n + N}$ ,  
 Where,  $p_1^\circ$  = vapour pressure of pure solvent  
 $p$  = vapour pressure of solution of non-volatile solute  
 $n$  = number of moles of solute  
 $N$  = number of moles of solvent
42.  $x_2 = \frac{p_1^\circ - p}{p_1^\circ} = \frac{50 - 45}{50} = \frac{5}{50} = 0.1$
46. For ideal solution,  
 $\Delta T_b = K_b \times \text{molality of solute in solution}$   

$$\therefore K_b = \frac{\Delta T_b}{\text{molality}}$$
49.  $K_b = \frac{\Delta T_b}{m} = \frac{373.23 - 373.15}{0.15} = \frac{0.08}{0.15}$   

$$= 0.53 \text{ K kg mol}^{-1}$$
54.  $\Delta T_f = K_f \times m$   

$$\therefore 0.184 = m \times 18.4$$

$$m = \frac{0.184}{18.4} = 0.01$$



56. Addition of solute to a solvent lowers the freezing point of solvent.
66. Beet cell solution will be less concentrated than concentrated NaCl solution. So, solvent molecules (water) will move from dilute solution of beet cells to concentrated NaCl solution, due to osmosis. Cell membrane will act as semipermeable membrane.
67. Osmotic pressure is a colligative property i.e., depends only on the number of particles in the solution. When mole fraction of the solvent decreases, mole fraction of solute increases, which in turn results in increase in osmotic pressure.
68. If  $\pi$  is the osmotic pressure of a dilute solution then,  $\pi V = nRT$  where  $n$  = moles of solute  
 $\therefore \pi = \frac{nRT}{V}$   
 $\therefore$  at constant  $T$  :  $\pi \propto \frac{1}{V}$   
 at constant  $V$  and  $n$  :  $\pi \propto T$  and  
 $\pi V = \text{constant}$  if  $T$  and  $n$  are constant  
 $\therefore$  The incorrect statement is  $\pi \propto V$  when  $T$  is constant.
72. Molecular mass of  $\text{CH}_3\text{COOH} = 60 \text{ g mol}^{-1}$   
 Hence, the molecular mass of acetic acid in benzene =  $2 \times 60 = 120 \text{ g mol}^{-1}$ .
73. Due to association, the number of particles decreases. Hence, van't Hoff factor also decreases.
74.  $\text{Na}_3\text{PO}_4$  gives a maximum of four ions, thus it will show highest van't Hoff factor.
81. Salt water contains relatively less number of water molecules per unit volume, as compared to the number of water molecules per unit volume in our body. Salts in sea water are in larger proportion than salts in our body. Solvent water flows out from the cells of our body into sea water. The cells of our body shrink in size making the skin appear wrinkled. This is due to osmosis.
84. Vapour pressure  $\propto \frac{1}{\text{Boiling point}}$   
 When vapour pressure decreases then boiling point increases and vice-versa.
87. The egg will shrink in the saturated NaCl solution due to osmosis.



### Critical Thinking

4. All the three states of matter i.e., solid, liquid and gas may play role of either solvent or solute.
6. 10% means 10 g glucose in 100 mL  
 Amount of glucose dissolved in 100 mL of solution = 10 g  
 Amount of glucose dissolved in 1 litre (1000 mL) of solution =  $\frac{1000 \times 10}{100} = 100 \text{ g}$
7. 10 % (W/V) solution means  
 10 g glucose is present in 100 mL solution.  
 $\therefore$  180 g glucose is present in  $x$  mL (1 mole)  
 Then  $\frac{10}{180} = \frac{100}{x}$   
 $\therefore x = 1800 \text{ mL} = 1.8 \text{ L}$   
 $\therefore$  Volume of glucose solution that contains 1 g mole glucose is 1.8 L.
8. Mole fraction of  $\text{H}_2\text{O} = \frac{\frac{80}{18}}{\frac{80}{18} + \frac{20}{34}} = \frac{68}{77}$
9. Molecular mass of  $\text{C}_2\text{H}_5\text{OH} = 24 + 5 + 16 + 1 = 46$   
 Molecular mass of  $\text{H}_2\text{O} = 18$   
 414 g of  $\text{C}_2\text{H}_5\text{OH}$  has  $\frac{414}{46} = 9$  mole  
 18 g of  $\text{H}_2\text{O}$  has =  $\frac{18}{18} = 1$  mole  
 Mole fraction of water =  $\frac{n_1}{n_1 + n_2} = \frac{1}{1+9} = \frac{1}{10} = 0.1$
10. Molarity =  $\frac{n_{\text{NaCl}}}{V_{\text{Litres}}} = \frac{0.01}{0.50} = \frac{1}{50} = 0.02 \text{ M}$
11.  $\text{NaCl} = 23 + 35.5 = 58.5$   
 Number of moles of  $\text{NaCl} = \frac{5.85}{58.5} = 0.1$   
 0.1 moles present in 200 mL.  
 Hence, 0.5 moles will be present in 1000 mL  
 $\therefore$  Concentration of the solution is 0.5 molar.



12.  $\text{H}_2\text{SO}_4$  in solution is 15 %  
If mass of  $\text{H}_2\text{SO}_4 = 15 \text{ g}$ ,  
Mass of water =  $(100 - 15) \text{ g}$   
 $= 85 \text{ g} = 85 \times 10^{-3} \text{ kg}$
- $$\therefore \text{Volume of solution} = \frac{\text{Mass of solution}}{\text{Density of solution}}$$
- $$= \frac{100 \text{ g}}{1.1 \text{ g/cm}^3} = 90.9 \text{ cm}^3$$
- $$= 90.9 \times 10^{-3} \text{ dm}^3$$
- Molarity of solution
- $$= \frac{\text{Mass of solute}}{\text{Molar mass of solute} \times \text{Volume of solution in dm}^3}$$
- $$= \frac{15 \times 10^{-3} \text{ kg}}{98 \times 10^{-3} \text{ kg/mol} \times 90.9 \times 10^{-3} \text{ dm}^3}$$
- $$= 1.68 \text{ mol/dm}^3 \text{ or } 1.68 \text{ M}$$
13.  $\text{Molarity} = \frac{\text{Mass}}{\text{Molar mass} \times \text{Volume in mL}} \times 1000$
- $$= \frac{5.56 \times 1000}{278 \times 250}$$
- $$= 0.08 \text{ M.}$$
14. Number of moles of  $\text{H}_2\text{O}_2 = \frac{5.0}{34}$
- $$= 0.147 \approx 0.15$$
- $$\therefore \text{Molarity} = \frac{\text{Number of moles of solute}}{\text{Volume of solution in L}} = \frac{0.15}{0.1}$$
- $$= 1.5 \text{ M}$$
15. Number of moles of  $\text{H}_2\text{O}$  in 1 g
- $$= \frac{1}{18} = 0.0555 \text{ mol/mL}$$
- $$\therefore \text{moles/L} = 0.0555 \times 1000 = 55.5$$
16.  $\text{CaCl}_2 \rightleftharpoons \text{Ca}^{++} + 2\text{Cl}^-$   
(1 mole) (2 moles)
- $$\therefore \text{In } 500 \text{ mL, number of moles of } \text{CaCl}_2 = 0.25$$
- $$\therefore \text{Number of } \text{Cl}^- \text{ ions is double, it will be}$$
- $$0.25 \times 2 = 0.50 \text{ moles}$$
17. 0.8 moles of solute are present in 1000 mL
- $$\therefore 0.1 \text{ moles of solute are present in } x \text{ mL}$$
- $$\therefore \frac{0.8}{0.1} = \frac{1000}{x}$$
- $$\therefore x = \frac{1000}{8} = 125 \text{ mL}$$
18.  $\text{Molarity} = \frac{\text{Number of moles of solute}}{\text{Volume of solution in L}} = \frac{n}{V_{\text{Litres}}}$
- $$\therefore n = \text{molarity} \times V_{\text{Litres}} = 3 \times 1 = 3 \text{ moles}$$

19. Molar solution has 1 mole or molar mass of solute in 1000 mL of its solution  
OR
- $$\text{Molarity} = \frac{n_{\text{solute}}}{\text{Volume in L}}$$
- and this value should be 1 for molar solution. Also,
- $$n_{\text{solute}} = \frac{\text{Mass of solute}}{\text{Molar mass}}$$
- (A) Molar mass of  $\text{C}_2\text{H}_5\text{OH}$
- $$= (2 \times 12) + (5 \times 1) + (1 \times 16) + 1 = 46 \text{ g}$$
- $$\therefore n_{\text{C}_2\text{H}_5\text{OH}} = \frac{0.46}{46} = 0.01 \text{ moles}$$
- $$\therefore \text{Molarity of } \text{C}_2\text{H}_5\text{OH} \text{ solution}$$
- $$= \frac{n_{\text{C}_2\text{H}_5\text{OH}}}{\text{Volume in L}} = \frac{0.01}{0.1} = 0.1 \text{ M}$$
- Thus, solution of ethyl alcohol is 0.1 M and not 1 M.
- (B) Molar mass of  $\text{CaCl}_2$  is
- $$= 39.98 + (2 \times 35.5) = 110.98 \text{ g}$$
- Now,  $n_{\text{CaCl}_2} = \frac{\text{Mass of } \text{CaCl}_2}{\text{Molar Mass}}$
- $$= \frac{110.98}{110.98} = 1 \text{ mole}$$
- Molarity of  $\text{CaCl}_2$  solution
- $$= \frac{n_{\text{CaCl}_2}}{\text{Volume in L}} = \frac{1 \text{ mole}}{1 \text{ L}} = 1 \text{ M}$$
- $$\therefore 1 \text{ mole } \text{CaCl}_2 \text{ solute is present in } 1 \text{ L solution.}$$
- $$\therefore \text{It is a molar solution.}$$
- (C) Molar mass of  $\text{CH}_3\text{OH}$
- $$= (1 \times 12) + (3 \times 1) + (1 \times 16) + (1 \times 1) = 32 \text{ g}$$
- $$\therefore n_{\text{CH}_3\text{OH}} = \frac{0.23}{32} = 0.0072 \text{ moles}$$
- Molarity of  $\text{CH}_3\text{OH}$  solution
- $$= \frac{n_{\text{CH}_3\text{OH}}}{\text{Volume in L}} = \frac{0.0072}{0.1} = 0.072 \text{ M}$$
- The solution of  $\text{CH}_3\text{OH}$  is 0.072 M and not 1 M.
- (D) Molar mass of  $\text{NaCl} = 23 + 35.5 = 58.5 \text{ g}$
- $$n_{\text{NaCl}} = \frac{5.85}{58.5} = 0.1 \text{ mole}$$
- Molarity of  $\text{NaCl}$  solution
- $$= \frac{n_{\text{NaCl}}}{\text{Volume in L}} = \frac{0.1}{1} = 0.1 \text{ M}$$
- Thus, the solution of  $\text{NaCl}$  is 0.1 M and not 1 M.



20.  $M_1 = 0.1 \text{ M}$ ,  $M_2 = 0.2 \text{ M}$   
 $V_1 = 100 \text{ mL}$ ,  $V_2 = 25 \text{ mL}$   
 Resulting Molarity =  $\frac{M_1 V_1 + M_2 V_2}{V_1 + V_2}$   
 $= \frac{(0.1 \times 100) + (0.2 \times 25)}{100 + 25}$   
 $= 0.12 \text{ M}$
21.  $n_{\text{glucose}} = \frac{18}{180} = 0.1$   
 1 L of  $\text{H}_2\text{O} \equiv 1000 \text{ mL} \equiv 1000 \text{ g} \equiv 1 \text{ kg}$   
 $(\because d = 1 \text{ g mL}^{-1})$   
 Molality =  $\frac{n_{\text{glucose}}}{W_{\text{solvent (kg)}}} = \frac{0.1}{1} = 0.1$
22. Molar mass of sugar =  $342 \times 10^{-3} \text{ kg/mol}$   
 $\therefore$  Mass of water in syrup =  $214.2 - 34.2 \text{ g}$   
 $= 180 \text{ g} = 180 \times 10^{-3} \text{ kg}$   
 $\therefore$  Number of moles of sugar  
 $= \frac{\text{Mass of sugar}}{\text{Molar mass of sugar}}$   
 $= \frac{34.2 \times 10^{-3} \text{ kg}}{342 \times 10^{-3} \text{ kg/mol}} = 0.1 \text{ mol}$   
 $\therefore$  Molality =  $\frac{\text{Moles of sugar}}{\text{Mass of solvent in kg}}$   
 $= \frac{0.1 \text{ mol}}{180 \times 10^{-3} \text{ kg}} = 0.55 \text{ mol/kg}$
23. ppm means parts per million.  
 To find parts by mass of fluoride ion in 1 million parts by mass of the toothpaste:  
 500 g toothpaste contains 0.2 g fluoride,  
 1000000 g toothpaste contains  $x$  g fluoride,  
 then  $\frac{500}{1000000} = \frac{0.2}{x}$   
 $\therefore x = \frac{0.2 \times 10^6}{500} = \frac{20 \times 10^4}{5 \times 10^2} = 4 \times 10^2 = 400 \text{ ppm}$
25. Henry's law states that "the mass of a gas dissolved per unit volume of the solvent at a constant temperature is directly proportional to the pressure of the gas in equilibrium with the solution".
26.  $\text{CO}_2$  reacts with water to form carbonic acid and  $\text{NH}_3$  reacts with water to form ammonium hydroxide.
29. According to Henry's law,  $S = KP$   
 Given  $S = 3.12 \times 10^{-4} \text{ mol dm}^{-3}$ ,  $P = 0.24 \text{ atm}$   
 $K = \frac{S}{P} = \frac{3.12 \times 10^{-4} \text{ mol dm}^{-3}}{0.24 \text{ atm}}$   
 $= 13 \times 10^{-4} \text{ mol dm}^{-3} \text{ atm}^{-1}$   
 $= 1.3 \times 10^{-3} \text{ mol dm}^{-3} \text{ atm}^{-1}$
30. According to Henry's law,  $S = KP$   
 $\therefore K = \frac{S}{P} = \frac{13.6 \times 10^{-4} \text{ mol dm}^{-3}}{2 \text{ atm}}$   
 $= 6.8 \times 10^{-4} \text{ mol dm}^{-3} \text{ atm}^{-1}$   
 Solubility of  $\text{N}_2$  if partial pressure of  $\text{N}_2$  is 1.56 atm,  
 $S = KP$   
 $S = 6.8 \times 10^{-4} \text{ mol dm}^{-3} \text{ atm}^{-1} \times 1.56 \text{ atm}$   
 $= 1.0608 \times 10^{-3} \text{ mol dm}^{-3}$
31. According to Henry's law,  $S = KP$   
 $\therefore P = \frac{S}{K} = \frac{1.43 \times 10^{-4} \text{ mol dm}^{-3}}{0.65 \times 10^{-3} \text{ mol dm}^{-3} \text{ atm}^{-1}} = 0.22 \text{ atm}$
32. Alloy of mercury with other metal in general is known as amalgam, as mercury is in liquid state.
38. Refractive index is an intensive property, which does not depend on the number of particles in solution.
40. Vapour pressure is independent of volume of the container. Since, all other factors remain same, vapour pressure of water remains unchanged.
41. The relative lowering of vapour pressure of a solution is equal to mole fraction of the solute.  
 $\frac{p_1^\circ - p}{p_1^\circ} = \frac{\Delta p}{p_1^\circ} = x$   
 Where,  $\Delta p = p_1^\circ - p =$  lowering of vapour pressure and  $\frac{p_1^\circ - p}{p_1^\circ} =$  relative lowering of vapour pressure.
42.  $\frac{p^\circ - p}{p^\circ} = N_2$   
 But  $N_1 + N_2 = 1$   
 $(\because \text{sum of the mole fractions of the solute and solvent is equal to one})$   
 $\therefore N_1 = 1 - N_2$   
 $\therefore N_1 = 1 - \left( \frac{p^\circ - p}{p^\circ} \right)$   
 $N_1 = \frac{p^\circ - p^\circ + p}{p^\circ}$   
 $\therefore p = p^\circ N_1$



43.  $p = 750 \text{ mm Hg}$   
 $p_1^\circ = 760 \text{ mm Hg at } 373 \text{ K}$   

$$x = \frac{p_1^\circ - p}{p_1^\circ} = \frac{760 - 750}{760} = \frac{10}{760} = \frac{1}{76}$$

44.

Solution	Concentration	Particles	Total particles
0.1 M urea	$x$	1	$x$
0.1 M KCl	$x$	2	$2x$
0.1 M $\text{Na}_2\text{SO}_4$	$x$	3	$3x$
0.1 M $\text{Na}_3\text{PO}_4$	$x$	4	$4x$

As the number of particles increases, colligative properties increases,

$\therefore$  Vapour pressure decreases.

45. 
$$\frac{p_1^\circ - p}{p_1^\circ} = \frac{W_2 \times M_1}{W_1 \times M_2}$$

$$\therefore \frac{640 - 600}{640} = \frac{2.175 \times 78}{39.08 \times M_2}$$

$$\therefore M_2 = 69.5 \text{ g mol}^{-1}$$

46. There are two volatile liquids A and B. Using Dalton's law of partial pressure for the vapour phase assuming vapour to behave ideally,

$$\therefore p_{\text{solution}} = p_A + p_B$$

$$\therefore p_{\text{solution}} = x_A p_A^\circ + x_B p_B^\circ \text{ (given } x_B = 0.2)$$

$$\therefore x_A = 1 - x_B = 1 - 0.2$$

$$\therefore x_A = 0.8 \text{ and } p_A^\circ = 70 \text{ Torr}$$

$$p_{\text{solution}} = 84 \text{ Torr (1 Torr = 1 mm of Hg)}$$

Now, 
$$p_{\text{solution}} = 0.8 \times 70 + 0.2 \times p_B^\circ$$

$$\therefore 84 = 0.8 \times 70 + 0.2 \times p_B^\circ$$

$$84 - (0.8 \times 70) = 0.2 \times p_B^\circ$$

$$\therefore p_B^\circ = \frac{84 - (0.8 \times 70)}{0.2} = \frac{84 - 56}{0.2} = \frac{28}{0.2} = 140 \text{ Torr}$$

$$p_B^\circ = \text{vapour pressure of pure B} = 140 \text{ Torr.}$$

47. Mass of benzene = volume  $\times$  density  

$$= 56.8 \times 0.889 = 50.495 \text{ g}$$

Moles of benzene = 
$$\frac{50.495}{78} = 0.6474$$

$$\frac{p_1^\circ - p}{p_1^\circ} = \frac{n_2}{n_1}$$

$$\therefore \frac{100 - 98.88}{100} = \frac{n_2}{0.6474}$$

$$\therefore n_2 = 0.007251$$

$$\therefore \text{Molality} = \frac{\text{Number of moles of solute}}{\text{Mass of solvent in kg}}$$
  

$$= \frac{0.007251}{50.495 \times 10^{-3}}$$
  

$$= 0.144 \text{ m}$$

48.  $p = 2985 \text{ N/m}^2$ ,  $p_1^\circ = 3000 \text{ N/m}^2$   
 From Raoult's law (for dilute solution),

$$\frac{p_1^\circ - p}{p_1^\circ} = \frac{n_2}{n_1}$$

$$\therefore \frac{(3000 - 2985) \text{ N/m}^2}{3000 \text{ N/m}^2} = \frac{\left(\frac{5}{M}\right)}{\left(\frac{100}{18}\right)}$$

(Here,  $M$  = molar mass of solute and  $18$  = molar mass of water)

$$\therefore 0.005 = \frac{5}{M} \times \frac{18}{100}$$

$$\therefore M = \frac{5 \times 18}{100 \times 0.005} = 180 \text{ g mol}^{-1}$$

49. 
$$\frac{p_1^\circ - p}{p_1^\circ} = \frac{W_2 \times M_1}{W_1 \times M_2}$$

$$\frac{10}{750} = \frac{2 \times 78}{78 \times M_2}$$

$$\therefore M_2 = \frac{2 \times 78 \times 750}{10 \times 78} = 150 \text{ g mol}^{-1}$$

50. 
$$\frac{p_1^\circ - p}{p_1^\circ} = \frac{W_2 \times M_1}{W_1 \times M_2}$$

$$\frac{0.3}{17.54} = \frac{20 \times 18}{100 \times M_2}$$

$$M_2 = \frac{20 \times 18 \times 17.54}{100 \times 0.3} = 210.48 \approx 210.5 \text{ g mol}^{-1}$$

51. In the first solution, number of the moles of

urea = 
$$\frac{\text{Mass of urea}}{\text{Molecular weight of urea}} \times \frac{1}{V}$$

$$= \frac{12}{60} \times \frac{1}{1} = 0.2 \text{ and}$$

In the second solution, number of moles of

cane sugar = 
$$\frac{\text{Mass of cane sugar}}{\text{Molecular weight of cane sugar}}$$

$$= \frac{68.4}{342} \times \frac{1}{1} = 0.2$$



52. Boiling point elevation is a colligative property.  $\text{BaCl}_2$  produces 3 moles of particles, which is highest compared to the rest and hence will have the highest boiling point among the given options.

$$53. \Delta T_b = K_b \times m = 0.513 \left( \frac{0.1}{200} \times 1000 \right) \\ = 0.2565 \text{ }^\circ\text{C}$$

$$\therefore T_b = (100 + 0.256) \text{ }^\circ\text{C} = 100.256 \text{ }^\circ\text{C}$$

$$54. \Delta T_b = K_b \times m = X \times 0.2 = \left( \frac{X}{5} \right) \text{ }^\circ\text{C}$$

$\therefore$  Boiling point of the solution = Boiling point of pure solvent +  $\Delta T_b = \left( A + \frac{X}{5} \right) \text{ }^\circ\text{C}$

55. Solvent is same in both solutions, hence,  $K_b$  is constant.

$$\therefore \Delta T_b = K_b \times m [\because \Delta T_b \propto m]$$

$$\therefore \text{for 0.1 molal solution : } \Delta T_b = (100.16 - 100) \text{ }^\circ\text{C} \\ = 0.16 \text{ }^\circ\text{C}$$

$$\therefore \text{for 0.5 molal solution : } \Delta T_b = (5 \times 0.16) \text{ }^\circ\text{C} \\ = 0.8 \text{ }^\circ\text{C}$$

Hence, boiling point of glucose solution =  $(100 + 0.8) \text{ }^\circ\text{C}$   
=  $100.8 \text{ }^\circ\text{C}$ .

$$56. M_B = \frac{K_b \times 1000 \times W_B}{W_A (\Delta T_b)} \\ = \frac{2.53 \times 1000 \times 10}{100 \times 1} \\ = 253 \text{ g mol}^{-1}$$

57. Molality (m)

$$= \frac{\text{Number of moles of solute (anthracene)}}{\text{Mass of solvent (chloroform) in kg}} \\ = \frac{\text{Mass of anthracene} \times 1000}{\text{Molar mass of anthracene} \times \text{Mass of chloroform in g}}$$

$$\therefore m = \frac{0.5143 \times 1000}{M \times 35}$$

$$\Delta T_b = K_b \times m$$

$$0.323 = 3.9 \times \frac{0.5143 \times 1000}{M \times 35}$$

$$M = \frac{3.9 \times 0.5143 \times 1000}{0.323 \times 35} = 177.42 \text{ g/mol}$$

$$58. m(\text{molality}) = \frac{\text{Number of moles of solute 'X'}}{\text{Mass of solvent in kg}} \\ = \frac{\text{Mass of solute 'X'} \times 1000}{\text{Molar mass of solute 'X'} \times \text{Mass of solvent in g}}$$

$$\therefore m = \frac{6 \times 1000}{M \times 100}$$

$$\Delta T_b = K_b \times m$$

$$0.52 = 0.52 \times \frac{6 \times 1000}{M \times 100}$$

$$M = \frac{0.52 \times 6 \times 1000}{0.52 \times 100} = 60 \text{ g mol}^{-1}$$

59. Lesser the number of particles in solution, lesser the depression in freezing point, i.e., freezing point is higher. As the colligative particles obtained in case of dissolving of sugar to form a solution is least compared to the others, 0.1 M sugar solution will have a higher freezing point.

60.  $\text{CaCl}_2$  gives maximum ions in solution hence, it has minimum freezing point.

62.  $\text{NaCl} \longrightarrow \text{Na}^+ + \text{Cl}^- = 2 \text{ ions}$

$\text{K}_2\text{SO}_4 \longrightarrow 2\text{K}^+ + \text{SO}_4^{2-} = 3 \text{ ions}$

$\text{K}_2\text{SO}_4$  gives maximum ions in solution, so it shows maximum depression in freezing point.

$$63. \Delta T_f = K_f m = 1.86 \times 0.05 = 0.093 \text{ K}$$

$$\therefore \text{Freezing point} = (273 - 0.093) \text{ K} = 272.907 \text{ K}$$

$$64. \Delta T_f = K_f \times m$$

$$\therefore 273 - (272.07) = \frac{1.86 \times 6.8}{0.1 \times \text{Molar mass}}$$

$$\therefore \text{Molar mass} = \frac{1.86 \times 6.8}{0.1 \times 0.93} = \frac{186 \times 68}{93} \\ = 2 \times 68 = 136 \text{ g mol}^{-1}$$

$$65. \Delta T_f = 0.93 \text{ K}$$

$$M_2 = \frac{K_f \times W_2 \times 1000}{\Delta T_f \times W_1}$$

$$= \frac{1.86 \times 6 \times 1000}{0.93 \times 100} = 120 \text{ g mol}^{-1}$$

$$\therefore \text{Molar mass of } x = 120 \text{ g mol}^{-1}$$

$$66. M_2 = \frac{1000 \times K_f \times W_2}{\Delta T_f \times W_1}$$

$$W_2 = \frac{M_2 \times \Delta T_f \times W_1}{1000 \times K_f}$$

$$W_2 = \frac{60 \times 0.186 \times 500}{1.86 \times 1000} = \frac{6 \times 5}{10} = \frac{30}{10} = 3 \text{ g}$$

$$67. W_2 = \frac{\Delta T_f \times W_1 \times M_2}{1000 \times K_f} \\ = \frac{1.05 \times 100 \times 9000}{1000 \times 4.9} \\ = 192.85 \text{ g} \approx 193 \text{ g}$$



68.  $\Delta T_f =$  Freezing point of solvent  
– Freezing point of solution

$$\Delta T_f = K_f \times m = 1.86 \times \frac{342}{342} = 1.86 \text{ }^\circ\text{C}$$

$\therefore$  Freezing point of solution  
= Freezing point of solvent –  $\Delta T_f$   
=  $(0 - 1.86)^\circ\text{C} = -1.86 \text{ }^\circ\text{C}$

69. 
$$M_2 = \frac{K_f \times 1000 \times W_2}{\Delta T_f \times W_1}$$

$$= \frac{5.12 \times 1000 \times 1}{0.40 \times 50} = 256 \text{ g mol}^{-1}$$

70. 
$$M_2 = \frac{K_f \times W_2}{\Delta T_f \times W_1}$$

$$= \frac{5.12 \times 0.440 \times 1000}{0.567 \times 22.2} = 178.9 \text{ g mol}^{-1}$$

71.  $\Delta T_f = 0.186 \text{ K}$

$$\Delta T_f = K_f \times m$$

$$\therefore m = \frac{\Delta T_f}{K_f} = \frac{0.186 \text{ K}}{1.86 \text{ K kg mol}^{-1}} = 0.1 \text{ mol kg}^{-1}$$

$$\Delta T_b = K_b \times m$$

$$\therefore \Delta T_b = 0.512 \text{ K kg mol}^{-1} \times 0.1 \text{ mol kg}^{-1}$$

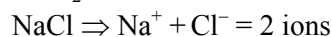
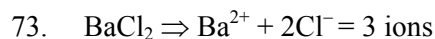
$$= 0.0512 \text{ K}$$

Boiling point of solution

$$= \text{Boiling point of water} + \Delta T_b$$

$$= (373 + 0.0512) \text{ K} = 373.0512 \text{ K}$$

72. NaCl gives maximum ions hence it will show highest osmotic pressure.



$\therefore$  Order of osmotic pressure:  $\text{BaCl}_2 > \text{NaCl} > \text{Glucose}$

75. 0.5 M ( $3.0 \text{ g L}^{-1}$ ) urea solution and 0.5 M ( $17.10 \text{ g L}^{-1}$ ) sucrose or sugar solution exhibit same osmotic pressure, hence, termed as isotonic solution.

76. 
$$\pi = CRT = \frac{n}{V} RT$$

$$= \frac{1.75}{\frac{342}{150}} \times 0.0821 \times 290$$

$$= \frac{1.75 \times 150}{342} \times 0.0821 \times 290$$

$$= 0.81 \text{ atm.}$$

77. Isotonic solution means molar concentrations are same.

$$C_{\text{boric acid}} = C_{\text{sucrose}}$$

$$\frac{1.63}{450} = \frac{20}{1000}$$

$$\therefore \frac{m}{450} = \frac{342}{1000}$$

$$\therefore m = \frac{1.63 \times 342 \times 1000}{20 \times 450}$$

78.  $\pi = C \times R \times T$

$$\therefore C = \frac{\pi}{RT} = \frac{2.5}{0.0821 \times 297} = 0.1025 \text{ M}$$

79. 
$$\pi = \frac{W}{M} \times \frac{1}{V} RT$$

$$\therefore 1.23 \text{ atm} = \frac{0.6 \text{ g}}{M} \times \frac{1}{0.1 \text{ L}}$$

$$\times 0.0821 \text{ L atm K}^{-1} \text{ mole}^{-1} \times 300 \text{ K}$$

$$\therefore M = \frac{0.6}{0.1} \times \frac{1}{1.23} \times 0.0821 \times 300 \text{ g/mole}$$

$$\therefore M = \frac{6}{12.3} \times 0.821 \times 300 = \frac{1 \times 82.1 \times 3}{2.05} = 40.05 \times 3$$

$$\therefore M = 120.15 \text{ g/mole}$$

80. 
$$C = \frac{\text{Mass in g}}{\text{Molar mass} \times \text{Volume in L}}$$

$$= \frac{3}{180 \times 0.06}$$

$$= 0.278$$

$$T = 273 + 15 = 288 \text{ K}$$

$$\pi = CRT = 0.278 \times 0.0821 \times 288 = 6.57 \text{ atm}$$

81. When two solutions are isotonic, their osmotic pressures are equal.

$$\pi_1 = \pi_x \text{ (assuming T constant and solution is dilute)}$$

$\therefore$  100 g solution has volume 100 mL

$\therefore$  density of water = 1g/cc

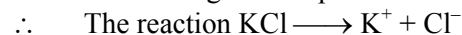
$$\frac{n_1 RT}{V} = \frac{n \times RT}{V}$$

$$\therefore \frac{5}{342} \times \frac{1}{0.100} = \frac{1}{M} \times \frac{1}{0.100}$$

$$\therefore M = \frac{342}{5} = 68.4 \text{ g/mole}$$

83.  $\text{AlCl}_3$  furnishes more ions than  $\text{CaCl}_2$  and thus shows higher boiling point i.e.,  $t_1 > t_2$ .

84. KCl undergoes complete dissociation in water.



1 mole of KCl, dissociates to form 2 mole particles.





- $\therefore i = 2$   
 $\Delta T = i \times K_f \times m$   
 (Given:  $K_f = 1.86 \text{ }^\circ\text{C kg mol}^{-1}$  ;  
 $\Delta T = 0 - (-10) = 10 \text{ }^\circ\text{C}$ ;  $i = 2$ )
- $\therefore 10 = 2 \times 1.86 \times m$   
 $m = \frac{10}{2 \times 1.86} = 2.68 \text{ mol/kg}$
- $\therefore$  Grams of KCl =  $2.68 \times 74.5 = 199.66 \text{ g per kg}$   
 $\therefore 199.66 \text{ g should be added to one kg of water.}$
85.  $\text{Na}_2\text{SO}_4 \longrightarrow 2\text{Na}^+ + \text{SO}_4^{2-}$
- |              |           |          |
|--------------|-----------|----------|
| 1            | 0         | 0        |
| $(1-\alpha)$ | $2\alpha$ | $\alpha$ |
- $\therefore i = (1 - \alpha) + \alpha + 2\alpha = 1 + 2\alpha$
86. (A)  $\text{K}_2\text{SO}_4 \longrightarrow 2\text{K}^+ + \text{SO}_4^{2-}$
- |         |        |       |
|---------|--------|-------|
| $(1-x)$ | $(2x)$ | $(x)$ |
|---------|--------|-------|
- $\therefore i = \frac{1-x+2x+x}{1} = 1+2x = 3 (\because x = 1)$
- (B)  $\text{NaHSO}_4 \longrightarrow \text{Na}^+ + \text{HSO}_4^-$   
 (weak electrolyte)  $x \neq 0$
- |         |       |       |
|---------|-------|-------|
| $(1-x)$ | $(x)$ | $(x)$ |
|---------|-------|-------|
- (C) Sugar  $\longrightarrow$  No ionization
- (D)  $\text{MgSO}_4 \longrightarrow \text{Mg}^{++} + \text{SO}_4^{--}$
- |         |       |       |
|---------|-------|-------|
| $(1-x)$ | $(x)$ | $(x)$ |
|---------|-------|-------|
- $\therefore i = \frac{1-x+x+x}{1} = 1+x = 2 (\because x = 1)$
87. The boiling occurs at lower temperature if atmospheric pressure is lower than 76 cm Hg.
88. As  $\Delta T_f$  in case of B is half that of A, the number of moles of particles in B must be less than that of A. This condition is possible only when B will be in associated state.
89. As solids are incompressible, change of pressure has no effect on solubility of solids in liquids.
90. van't Hoff factor (i)  
 $= \frac{\text{Experimental C.P.}}{\text{Calculated C.P.}}$   
 [C.P. = Colligative property]  
 $= 1 - \alpha + x\alpha + y\alpha$ ,  
 for KCl it is = 2 and for sugar it is equal to 1.
91. **Step I:**  
 Calculation of molar mass of sulphur:  
 $\Delta T_b = \text{elevation of boiling point} = 0.81 \text{ K}$

$$K_b = \text{molal elevation of boiling point constant} = 2.53 \text{ K kg mol}^{-1}$$

$$W_B = \text{mass of sulphur} = 3.24 \text{ g} = 3.24 \times 10^{-3} \text{ kg}$$

$$W_A = \text{mass of benzene} = 40 \text{ g} = 40 \times 10^{-3} \text{ kg}$$

$$M_B = \text{molar mass of sulphur}$$

$$\Delta T_b = K_b \frac{W_B}{M_B W_A};$$

$$0.81 = 2.53 \frac{3.24 \times 10^{-3}}{M_B \times 40 \times 10^{-3}};$$

$$M_B = 0.253 \text{ kg/mol} = 253 \text{ g/mol}$$

### Step II:

Calculation of the number of atoms present in sulphur molecule:

$$\begin{aligned} \text{Number of atoms} &= \frac{\text{Molar mass of sulphur } M_B}{\text{Atomic mass of sulphur}} \\ &= \frac{253}{32} \cong 8 \end{aligned}$$

$\therefore$  The molecular formula of sulphur is  $\text{S}_8$ .



### Competitive Thinking

- Amount of  $\text{AgNO}_3$  added in 60 mL of solution =  $60 \times 0.03 = 1.8 \text{ g}$
  - $5.8 \text{ g NaCl} = \frac{5.8}{58.5} \text{ mol} = 0.099 \text{ mol}$   
 $90 \text{ g H}_2\text{O} = \frac{90}{18} \text{ mol} = 5 \text{ mol}$   
 $\text{Mole fraction of NaCl} = \frac{0.099}{5 + 0.099} = 0.02.$
  - 20 % W/W aqueous sucrose solution means 100 g of solution contains 20 g of sucrose.  
 Let mass of solution = 100 g  
 $\therefore$  Mass of sucrose = 20 g  
 $\therefore$  Mass of solvent (water) =  $100 - 20 = 80 \text{ g}$   
 Number of moles of water ( $n_1$ )  
 $= \frac{\text{Mass of water}}{\text{Molar mass of water}} = \frac{80 \text{ g}}{18 \text{ g/mol}} = 4.4444 \text{ mol}$   
 Number of moles of sucrose ( $n_2$ )  
 $= \frac{20 \text{ g}}{342 \text{ g/mol}} = 0.0585 \text{ mol}$
- $\therefore$  Mole fraction of water =  $\frac{n_1}{n_1 + n_2}$   
 $= \frac{4.4444}{4.4444 + 0.0585} = \frac{4.4444}{4.5029} = 0.987$



4. Rectified spirit contains 95 % of ethanol by weight. Hence, if mass of ethanol is 95 g, mass of water is  $100 - 95 = 5$  g

$$\begin{aligned} \text{Number of moles of ethanol } (n_2) &= \frac{95}{46} \\ &= 2.065 \text{ mol} \end{aligned}$$

$$\begin{aligned} \text{Number of moles of water } (n_1) &= \frac{5}{18} \\ &= 0.278 \text{ mol} \end{aligned}$$

$$\begin{aligned} \text{Mole fraction of ethanol} &= \frac{n_2}{n_1 + n_2} \\ &= \frac{2.065}{2.343} = 0.88 \end{aligned}$$

$$\text{Mole fraction of water} = 1 - 0.88 = 0.12$$

5. 
$$\text{Molarity} = \frac{\text{Number of moles of solute}}{\text{Volume of solution in dm}^3}$$

6. 
$$\begin{aligned} \text{Molarity} &= \frac{\text{Mass}}{\text{Molar mass} \times \text{Volume in mL}} \times 1000 \\ &= \frac{5.0 \times 1000}{40 \times 100} \\ &= 1.25 \text{ mol dm}^{-3} \end{aligned}$$

7. 
$$\begin{aligned} \text{Molarity (M)} \\ &= \frac{\text{Mass of solute}}{\text{Molar mass of solute} \times \text{Volume of solution (L)}} \end{aligned}$$

$$\begin{aligned} \text{Mass of solute (in kg)} &= 15 \times 10^{-3} \text{ kg} \\ \text{Molar mass of solute (in kg mol}^{-1}\text{)} \\ &= 60 \times 10^{-3} \text{ kg mol}^{-1} \\ \text{Volume of solution } 500 \text{ cm}^3 &= 0.5 \text{ dm}^3 = 0.5 \text{ L} \\ \text{(Assuming that the volume of solution is same} \\ &\text{that of water)} \end{aligned}$$

$$\begin{aligned} \text{Molarity} &= \frac{15 \times 10^{-3}}{60 \times 10^{-3} \times 0.5} \\ &= 0.5 \text{ mol dm}^{-3} \end{aligned}$$

8. 
$$\begin{aligned} \text{Molarity} \\ &= \frac{\text{Mass of solute}}{\text{Molar mass of solute} \times \text{Volume of solution (L)}} \\ &= \frac{5}{40 \times 0.450} = 0.278 \text{ M} \end{aligned}$$

9. 
$$\begin{aligned} \text{Molarity} &= \frac{\text{Mass of solute (kg)}}{\text{Molar mass of solute (kg mol}^{-1}\text{)} \times \text{volume of solution (L)}} \end{aligned}$$

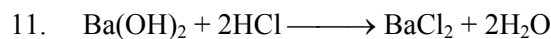
$$\therefore 0.2 = \frac{\text{Mass of solute}}{106 \times 10^{-3} \times 0.250}$$

$$\begin{aligned} \therefore \text{Mass of solute} &= 0.2 \times 106 \times 10^{-3} \times 0.250 \\ &= 0.0053 \text{ kg} = 5.3 \text{ g} \end{aligned}$$

10. 
$$\begin{aligned} \text{Number of moles of solute} \\ &= \frac{\text{Number of molecules}}{\text{Avogadro's number}} = \frac{6.02 \times 10^{20}}{6.02 \times 10^{23}} \end{aligned}$$

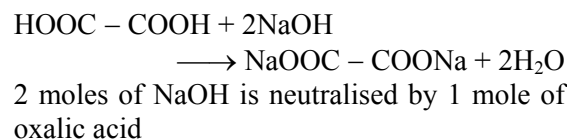
$$\text{Volume of solution} = 100 \text{ mL} = \frac{100}{1000} \text{ dm}^3$$

$$\begin{aligned} \text{Molarity} &= \frac{\text{Number of moles of solute}}{\text{Volume of solution in dm}^3} \\ &= \frac{6.02 \times 10^{20}}{\frac{100}{1000}} = 0.01 \text{ M} \end{aligned}$$



$$\begin{aligned} \text{Applying molarity equation, } \frac{M_1 V_1}{1} &= \frac{M_2 V_2}{2} \\ &\quad (\text{Ba(OH)}_2) \quad (\text{HCl}) \\ \therefore 25 \times M_1 &= \frac{0.1 \times 35}{2} \\ M_1 &= \frac{0.1 \times 35}{2 \times 25} \\ &= 0.07 \end{aligned}$$

12. 
$$\begin{aligned} \text{Number of moles of NaOH:} \\ 0.064 \text{ g NaOH} &= \frac{0.064}{40} \text{ moles of NaOH} \end{aligned}$$



$$\begin{aligned} \therefore \frac{0.064}{40} \text{ moles of NaOH will require} \\ \left( \frac{0.064}{40} \times \frac{1}{2} \right) &= 8.0 \times 10^{-4} \text{ moles of oxalic acid.} \end{aligned}$$

$$\therefore 25 \text{ cm}^3 \text{ of oxalic acid solution contains } 8.0 \times 10^{-4} \text{ moles of oxalic acid.}$$

$$\begin{aligned} \therefore \text{Molarity of oxalic acid solution} \\ &= \frac{\text{Moles of oxalic acid}}{\text{Volume of solution in L}} \\ &= \frac{8.0 \times 10^{-4}}{25 \times 10^{-3}} = 0.032 \text{ M} \end{aligned}$$

13. 
$$\begin{aligned} M_1 V_1 &= M_2 V_2 \\ \text{Initial} \quad \text{Final} \end{aligned}$$

$$\therefore 0.5 \times V_1 = 0.2 \times 1$$

$$\therefore V_1 = \frac{0.2 \times 1}{0.5} = 0.4 \text{ L} = 400 \text{ mL}$$

14. 
$$\begin{aligned} M_1 V_1 + M_2 V_2 &= M_3 V_3; \\ 1.5 \times 480 + 1.2 \times 520 &= M \times 1000 \\ M &= \frac{720 + 624}{1000} = 1.344 \text{ M.} \end{aligned}$$



15. Molar mass of  $\text{H}_2\text{SO}_4 = 98 \text{ g}$   
 $\therefore$  Number of moles of  $\text{H}_2\text{SO}_4$  in solution  
 $= \frac{\text{Mass of } \text{H}_2\text{SO}_4}{\text{Molar mass of } \text{H}_2\text{SO}_4} = \frac{98}{98} = 1$   
 Density =  $\frac{\text{Mass (M)}}{\text{Volume (V)}}$   
 $V = \frac{100}{1.84} = 54.34 \text{ mL} = 54.34 \times 10^{-3} \text{ L}$   
 Molarity =  $\frac{\text{Number of moles of } \text{H}_2\text{SO}_4}{\text{Volume of solution in litre}}$   
 $\therefore$  Molarity =  $\frac{1}{54.34} \times 10^3 = 18.4 \text{ M}$
16. Given Molarity = 3.60 M  
 $\text{H}_2\text{SO}_4$  solution is 29 % by mass.  
 Hence, if mass of  $\text{H}_2\text{SO}_4$  is 29 g  
 Mass of  $\text{H}_2\text{O}$  is  $(100 - 29) = 71 \text{ g}$   
 Now, Molarity  
 $= \frac{\text{Mass of solute}}{\text{Molar mass of solute} \times \text{Volume of solute in dm}^3}$   
 $\therefore$  Volume of solution in  $\text{dm}^3$   
 $= \frac{\text{Mass of solute}}{\text{Molarity} \times \text{Molar mass of solute}}$   
 $= \frac{29 \text{ g}}{3.60 \times 98 \text{ g/mol}} = 0.082 \text{ dm}^3 = 82 \text{ cm}^3$   
 Now; Density of solution  
 $= \frac{\text{mass of solution}}{\text{Volume of solution}}$   
 $= \frac{100}{82} \text{ [As mass was taken as 100 g]}$   
 $= 1.219 \approx 1.22 \text{ g/mL}$
17. Number of moles of  $\text{HNO}_3$   
 $= M \times V = \frac{2 \times 250}{1000} = 0.5$   
 Number of moles of  $\text{HNO}_3$   
 $= \frac{\text{Mass of } \text{HNO}_3}{\text{Molar mass of } \text{HNO}_3}$   
 $\therefore 0.5 = \frac{\text{Mass of } \text{HNO}_3}{63}$   
 $\therefore$  Mass of  $\text{HNO}_3 = 0.5 \times 63 = 31.5 \text{ g}$   
 Percentage by mass of  $\text{HNO}_3$   
 $= \frac{\text{Mass of } \text{HNO}_3}{\text{Mass of solution}} \times 100$   
 $\therefore 70 = \frac{31.5}{\text{Mass of solution}} \times 100$   
 Mass of solution =  $\frac{31.5 \times 100}{70} = 45 \text{ g}$

18. Molar mass of ethyl alcohol ( $\text{C}_2\text{H}_5\text{OH}$ )  
 $= 46 \text{ g mol}^{-1}$   
 Molarity of ethyl alcohol solution  
 $= \frac{\text{Number of moles of ethyl alcohol}}{\text{Volume of solution in dm}^3}$   
 $= \frac{\text{Mass of ethyl alcohol}}{\text{Molar mass of ethyl alcohol} \times \text{Volume of solution in dm}^3}$   
 $\therefore 0.5 \text{ M} = \frac{\text{Mass of ethyl alcohol}}{100 \times 10^{-3} \text{ dm}^3}$   
 $\left( \because \text{Number of moles of ethyl alcohol} = \frac{\text{Mass of ethyl alcohol}}{\text{Molar mass of ethyl alcohol}} \right)$   
 $\therefore 0.5 = \frac{\text{Mass of ethyl alcohol}}{46} \times 10$   
 $\therefore$  Mass of ethyl alcohol =  $\frac{0.5 \times 46}{10} = 2.3 \text{ grams}$   
 Density =  $\frac{\text{Mass}}{\text{Volume}}$   
 $\therefore$  Density of given ethyl alcohol = 1.15 g/cc  
 $\therefore 1.15 \text{ g/cc} = \frac{2.3 \text{ grams}}{\text{Volume in cc}}$   
 $\therefore$  Volume in cc =  $\frac{2.3 \text{ grams}}{1.15 \text{ g/cc}}$   
 $\therefore$  Volume in cc = 2  
 $\therefore$  2 cc of given ethyl alcohol needs to be added to water in order to prepare 100 cc of 0.5 M ethyl alcohol solution.
19. Mass of the solute urea =  $200 \times 10^{-3} \text{ g}$   
 Molar mass of the solute urea =  $60 \text{ g mol}^{-1}$   
 Number of moles of the solute  
 $= \frac{\text{Mass of solute}}{\text{Molar mass of solute}} = \frac{200 \times 10^{-3}}{60} = 3.33 \times 10^{-3}$   
 40 g of water contains  $3.33 \times 10^{-3}$  moles of urea  
 $\therefore$  Number of moles of urea present in 1000 g of water  
 $= \frac{3.33 \times 10^{-3} \times 1000}{40} = 0.08325$
20. Molality =  $\frac{\text{Number of moles of solute}}{\text{Mass of solvent in g}} \times 1000$   
 $= \frac{\text{Mass of solute}}{\text{Molar mass of solute}} \times \frac{1000}{\text{Mass of solvent in g}}$   
 $= \frac{18 \times 1000}{180 \times 500} = 0.2 \text{ mol kg}^{-1}$



$$\begin{aligned}
 21. \text{ Molality} &= \frac{\text{Number of moles of solute}}{\text{Mass of solvent in g}} \times 1000 \\
 &= \frac{\text{Mass of solute}}{\text{Molar mass of solute}} \\
 &\quad \times \frac{1000}{\text{Mass of solvent in g}} \\
 &= \frac{15.20 \times 1000}{60 \times 150} \\
 &= 1.689 \text{ mol kg}^{-1}
 \end{aligned}$$

22. 10 % W/W of NaOH solution means 100 g of solution contains 10 g of NaOH.

Let mass of solution = 100 g

∴ Mass of NaOH = 10 g

∴ Mass of solvent (H<sub>2</sub>O) = 100 - 10 = 90 g  
 $= 90 \times 10^{-3} \text{ kg}$

Molar mass of NaOH = 23 + 16 + 1  
 $= 40 \text{ g mol}^{-1}$

$$\begin{aligned}
 \text{Molality} &= \frac{\text{Number of moles of NaOH}}{\text{Mass of solvent in kg}} \\
 &= \frac{10}{40} = \frac{0.25}{90 \times 10^{-3}} = 2.778 \text{ m}
 \end{aligned}$$

23. Molality refers to the number of moles of solute present in 1 kg of the solvent.

∴ Number of moles of NaOH present in 1.25 molal solution = 1.25

But Number of moles of NaOH

$$= \frac{\text{Mass of NaOH}}{\text{Molar mass of NaOH}}$$

∴ Mass of NaOH = Number of moles  
 $\times$  Molar mass of NaOH  
 $= 1.25 \times 40 \times 10^{-3} \text{ kg}$   
 $= 0.05 \text{ kg}$

Percentage by weight of NaOH

$$\begin{aligned}
 &= \frac{\text{Mass of the solute}}{(\text{Mass of solute} + \text{Mass of solvent})} \times 100 \\
 &= \frac{0.05}{(0.05 + 1)} \times 100 = 4.76
 \end{aligned}$$

24. 2 % (W/W) aqueous KI solution means 100 g of solution contains 2 g of KI.

Let mass of solution = 100 g

∴ Mass of KI = 2 g

∴ Mass of solvent (H<sub>2</sub>O) = 100 - 2 = 98 g  
 $= 0.098 \text{ kg}$

$$\begin{aligned}
 \text{Molality} &= \frac{\text{Number of moles of KI}}{\text{Mass of solvent in g}} \\
 &= \frac{2}{0.098} \\
 &= 0.1229 \text{ m (i.e., approximately equal to 0.15 m).}
 \end{aligned}$$

25. Mass of water (W) = 1000 g; Number of moles of solute (n) = 1 mole

$$\begin{aligned}
 \text{Number of moles of water (N)} &= \frac{W}{M} \\
 &= \frac{1000}{18} = 55.55
 \end{aligned}$$

$$\begin{aligned}
 \text{Mole fraction of solute, } x_{\text{solute}} &= \frac{n}{n + N} \\
 &= \frac{1}{1 + 55.55} \\
 &= 0.0177
 \end{aligned}$$

26. Number of moles of NaOH (n<sub>1</sub>) = 0.2

Mass of solvent (water) = 1 kg

Number of moles of water (n<sub>2</sub>)

$$\begin{aligned}
 &= \frac{\text{Mass of water}}{\text{Molar mass of water}} \\
 &= \frac{1}{18 \times 10^{-3}} = 55.55
 \end{aligned}$$

$$\begin{aligned}
 \text{Mole fraction of NaOH} &= \frac{n_1}{n_1 + n_2} \\
 &= \frac{0.2}{0.2 + 55.55} \\
 &= 3.58 \times 10^{-3} \approx 3.6 \times 10^{-3}
 \end{aligned}$$

27. Molarity is volume dependent and volume varies with change in temperature.

28. The solubility of KNO<sub>3</sub>, NaNO<sub>3</sub> and KBr increases significantly with increase in temperature. The solubility of NaBr increases very slowly with increase in temperature.

$$32. \quad \frac{p_1^\circ - p}{p_1^\circ} = x_2 \quad \therefore \quad \frac{0.2}{0.8} = 0.25 = x_2$$

33. Relative lowering of vapour pressure,

$$\begin{aligned}
 \frac{\Delta p}{p_1^\circ} = x_2 &= \frac{\frac{W_2}{M_2}}{\frac{W_1}{M_1} + \frac{W_2}{M_2}} = \frac{\frac{9}{180}}{\frac{90}{18} + \frac{9}{180}} \\
 &= \frac{0.05}{5 + 0.05} = 0.0099
 \end{aligned}$$



34. Mass of  $\text{CCl}_4 = \text{Density of } \text{CCl}_4$

$\times \text{Volume of } \text{CCl}_4$

$$\therefore W_1 = 1.58 \text{ g/cm}^3 \times 100 \text{ cm}^3 = 158 \text{ g}$$

$$\frac{p_1^\circ - p}{p_1^\circ} = \frac{W_2 \times M_1}{M_2 \times W_1}$$

$$\frac{143 - p}{143} = \frac{0.5 \times 153.82}{65 \times 158}$$

$$143 - p = \frac{0.5 \times 153.82}{65 \times 158} \times 143$$

$$\therefore p = 141.93 \text{ mm}$$

35.  $p_B = p_B^\circ x_B$  ;

$$\frac{78}{78 + 92}$$

$$\therefore p_B = 75 \times \frac{78}{78 + 92}$$

$$\therefore p_B = 50 \text{ torr}$$

36. Vapour pressure of pure solvent i.e., water ( $p_1^\circ$ )

$$= 17.53 \text{ mm}$$

Vapour pressure of solution ( $p$ ) = 17.22 mm

Mass of solvent ( $W_1$ ) = 100 g =  $100 \times 10^{-3}$  kg

Molar mass of solvent ( $M_1$ )

$$= 18 \text{ g mol}^{-1} = 18 \times 10^{-3} \text{ kg mol}^{-1}$$

Mass of solute ( $W_2$ ) = 18 g =  $18 \times 10^{-3}$  kg

$$\frac{p_1^\circ - p}{p_1^\circ} = \frac{W_2 M_1}{W_1 M_2}$$

$$\therefore \frac{17.53 - 17.22}{17.53} = \frac{18 \times 10^{-3} \times 18 \times 10^{-3}}{100 \times 10^{-3} \times M_2}$$

$$\therefore \text{Molar mass of solute } (M_2) = \frac{18 \times 10^{-3} \times 18 \times 10^{-3}}{100 \times 10^{-3} \times 0.0177}$$

$$= 0.183 \text{ kg mol}^{-1}$$

$$= 183 \text{ g mol}^{-1}$$

37. Vapour pressure of pure acetone  $p_1^\circ = 185$  torr

Vapour pressure of solution,  $p = 183$  torr

Molar mass of solvent i.e., acetone ( $\text{CH}_3\text{COCH}_3$ ),  $M_1 = 58 \text{ g mol}^{-1}$

$$\frac{p_1^\circ - p}{p_1^\circ} = \frac{W_2 \times M_1}{W_1 \times M_2}$$

$$\therefore \frac{185 - 183}{185} = \frac{1.2 \times 58}{100 \times M_2}$$

$$\therefore M_2 = \frac{1.2}{2} \times \frac{58}{100} \times 185$$

$$= 63.38 \text{ g mol}^{-1} \approx 64 \text{ g mol}^{-1}$$

$$38. \frac{p_1^\circ - p}{p_1^\circ} = \frac{W_2 \times M_1}{W_1 \times M_2}$$

$$\frac{195 - 192.5}{195} = \frac{1 \times 58}{100 \times M_2}$$

$$M_2 = \frac{58 \times 195 \times 1}{2.5 \times 100} = 45.24 \text{ g mol}^{-1}$$

$$39. \frac{p_1^\circ - p}{p_1^\circ} = \frac{W_2 \times M_1}{W_1 \times M_2}$$

$$\frac{660 - 600}{660} = \frac{3.6 \times 10^{-3} \times 78}{40 \times 10^{-3} \times M_2}$$

$$M_2 = \frac{3.6 \times 10^{-3} \times 78}{40 \times 10^{-3} \times 0.09} = 78.0 \text{ g mol}^{-1}$$

40. Molecular weight of glucose ( $\text{C}_6\text{H}_{12}\text{O}_6$ ) = 180

$$\therefore \text{Number of moles of glucose } (n_B) = \frac{18}{180} = 0.1$$

$\therefore$  Molecular weight of water ( $\text{H}_2\text{O}$ ) = 18

$$\therefore \text{Number of moles of water } (n_A) = \frac{178.2}{18} = 9.9$$

$$\therefore \text{Mole fraction of water } (x_{\text{H}_2\text{O}}) = \frac{n_A}{n_A + n_B}$$

$$= \frac{9.9}{9.9 + 0.1} = \frac{9.9}{10}$$

$$\therefore p_{\text{H}_2\text{O}} = x_{\text{H}_2\text{O}} p_{\text{H}_2\text{O}}^\circ$$

$$\therefore p_{\text{H}_2\text{O}} = \frac{9.9}{10} \times 760 \text{ mm (considering at boiling point of water)}$$

$$\therefore p_{\text{H}_2\text{O}} = 752.4 \text{ mm} = 752.4 \text{ torr}$$

( $\therefore 1 \text{ torr} = 1 \text{ mm of Hg}$ )

41.  $\Delta T_b = K_b \cdot m$  (where,  $m = \text{molarity}$ )

$$= K_b \cdot \left( \frac{W_2}{M_2} \times \frac{1}{W_1} \right)$$

Rearranging,

$$M_2 = \frac{K_b \times W_2}{\Delta T_b \times W_1}$$

where,

$K_b = \text{Ebullioscopic constant}$

$\Delta T_b = \text{Elevation of boiling point}$

$M_2 = \text{Molar mass of solute}$

$W_2 = \text{Mass of solute}$

$W_1 = \text{Mass of solvent}$

43. Due to higher pressure inside the pressure cooker, the boiling point is elevated.



44.  $\Delta T_b = \text{Boiling point of solution}$   
 – Boiling point of pure solvent (water)  
 $= 100.052^\circ\text{C} - 100^\circ\text{C}$   
 $= 0.052^\circ\text{C}$  or  $0.052\text{ K}$   
 $\Delta T_b = K_b \times m$   
 $\therefore m = \frac{\Delta T_b}{K_b} = \frac{0.052\text{K}}{0.52\text{ kg mol}^{-1}\text{K}} = 0.1\text{ m}$
45.  $\Delta T_b = i \cdot K_b \cdot m$   
 $m = \frac{13.44}{134.4 \times 1} = 0.1$   
 $\text{CuCl}_2 \longrightarrow \text{Cu}^{+2} + 2\text{Cl}^-$   

1	0	0
$(1-\alpha)$	$\alpha$	$2\alpha$

 $\therefore i = 1 + 2\alpha$   
 $\therefore i = 3$  (taking 100 % ionisation)  
 $\therefore \Delta T_b = 3 \times 0.52 \times 0.1 = 0.156 \approx 0.16$
46.  $M_2 = \frac{K_b W_2}{\Delta T_b W_1} = \frac{0.6 \times 3}{0.52 \times 0.2} = 17.3\text{ g/mol}$
47.  $\Delta T_b = \text{elevation of boiling point} = 0.1^\circ\text{C} = 0.1\text{ K}$   
 $K_b = \text{molal elevation of boiling point constant}$   
 $= 2.16\text{ K kg mol}^{-1}$   
 $W_2 = \text{mass of solute} = 0.11\text{ g}$   
 $W_1 = \text{mass of solvent} = 15\text{ g} = 15 \times 10^{-3}\text{ kg}$   
 $M_2 = \text{molar mass of solute} = ?$   
 $\Delta T_b = K_b \frac{W_2}{M_2 W_1}; 0.1 = 2.16 \frac{0.11}{M_2 \times 15 \times 10^{-3}}$   
 $M_2 = \frac{2.16 \times 0.11}{0.1 \times 15 \times 10^{-3}}$   
 $= 158.40\text{ g mol}^{-1} \approx 158\text{ g mol}^{-1}$
49.  $K_f$  is independent of solution concentration.  $K_f$  depends only on the nature of the solvent.
50.  $\text{La}(\text{NO}_3)_3$  will furnish four ions and thus, will undergo more lowering in freezing point, whereas glucose gives only one particle and thus minimum lowering in freezing point.
51. On dissolution in water, one molecule of  $\text{KCl}$ ,  $\text{C}_6\text{H}_{12}\text{O}_6$ ,  $\text{Al}_2(\text{SO}_4)_3$  and  $\text{K}_2\text{SO}_4$  gives two, one, five and three particles respectively. Depression in freezing point is a colligative property and depends on the number of particles. Among the given options, all the aqueous solutions are of the same concentrations i.e.,  $0.10\text{ m}$  but  $\text{Al}_2(\text{SO}_4)_3$  gives the highest number of particles and hence, shows the largest freezing point depression.
52.  $\text{Na}_2(\text{SO}_4)$  gives three ions in solution which is highest compared to the equimolar solutions of the other salts. Since, the colligative properties are directly proportional to the number of particles in solution, sodium sulphate solution exhibits the maximum depression in freezing point.
53.  $K_f = \frac{\Delta T_f M_2 W_1}{W_2} = \frac{0.15 \times 60 \times 0.1}{6} = 0.15$
54.  $\Delta T_f = \text{molality} \times K_f \times (1+\alpha)$   
 $\alpha = 0.2$ , Molality =  $0.2$ ,  $K_f = 1.86$   
 $\Delta T_f = 0.2 \times 1.2 \times 1.86 = 0.4464^\circ\text{C} \approx 0.45^\circ\text{C}$   
 Freezing point =  $-0.45^\circ\text{C}$ .
55.  $\Delta T_f = \frac{K_f W_2}{M_2 W_1} = \frac{1.86 \times 0.08}{62 \times 10^{-3} \times 400 \times 10^{-3}} = 6\text{ K}$   
 Freezing point of mixture  
 $= \text{Freezing point of water} - \Delta T_f$   
 $= 273.15 - 6 = 267.15\text{ K}$
56.  $\Delta T_f = T^\circ - T$   
 $\Delta T_f = 0^\circ\text{C} - (-0.186^\circ\text{C})$   
 $\Delta T_f = +0.186^\circ\text{C}$  or  $0.186\text{ K}$   
 $\Delta T_f = K_f \times m$   
 $0.186 = 1.86 \times m$   
 $\therefore m = 0.1$   
 Substituting the value of  $m$  in,  
 $\Delta T_b = K_b \times m$   
 $\Delta T_b = 0.521 \times (0.1) = 0.0521\text{ K}$
57.  $M_2 = \frac{K_f \times W_2}{\Delta T_f \times W_1} = \frac{5.1 \times 4.8}{(5.5 - 4.48) \times 60 \times 10^{-3}}$   
 $= \frac{5.1 \times 4.8}{1.02 \times 60 \times 10^{-3}}$   
 $= 400\text{ g mol}^{-1}$
58.  $M_2 = \frac{K_f W_2}{\Delta T_f W_1} = \frac{1.86 \times 0.1}{(273.15 - 272.813) \times 21.7 \times 10^{-3}}$   
 $= \frac{1.86 \times 0.1}{0.337 \times 21.7 \times 10^{-3}}$   
 $= 25.4\text{ g/mol}$
59.  $\text{Na}_2\text{SO}_4$  solution has more osmotic pressure than  $\text{NaCl}$  solution because  $\text{Na}_2\text{SO}_4$  gives 3 ions whereas  $\text{NaCl}$  gives 2 ions.
63.  $\pi = CRT$   
 $\pi = \frac{nRT}{V}$   
 $= \frac{\frac{34.2}{342} \times 0.082 \times 293}{1}$   
 $= 2.40\text{ atm}$



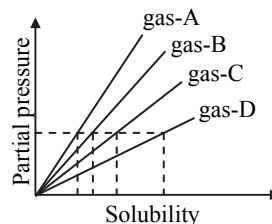
64. For isotonic solution,  $C_1 = C_2$
- $$\frac{W_{\text{urea}}}{M_{\text{urea}} \times V_{\text{urea solution}}} = \frac{W_{\text{cane sugar}}}{M_{\text{cane sugar}} \times V_{\text{cane sugar solution}}}$$
- $$\frac{30 \times 10^{-4}}{60 \times 0.5} = \frac{W_{\text{cane sugar}}}{342 \times 1}$$
- $$W_{\text{cane sugar}} = \frac{30 \times 10^{-4} \times 342 \times 1}{60 \times 0.5}$$
- $$= 0.0342 \text{ kg} = 34.2 \text{ g}$$
65. On complete dissociation, barium hydroxide  $\text{Ba}(\text{OH})_2$  gives three ions. Hence, van't Hoff factor (i) is 3.
66. Aluminium chloride ( $\text{AlCl}_3$ );  $i = 4$   
Potassium sulphate ( $\text{K}_2\text{SO}_4$ );  $i = 3$   
Ammonium chloride ( $\text{NH}_4\text{Cl}$ );  $i = 2$   
Urea ( $\text{NH}_2\text{CONH}_2$ );  $i = 1$   
Since urea is a non-electrolyte, it has the lowest value of van't Hoff factor.
67. Considering 100% ionisation of given species,  $\text{Al}_2(\text{SO}_4)_3$  dissociates as  $2\text{Al}^{3+} + 3\text{SO}_4^{2-}$  thus 1 molecule dissociates into five particles. In the similar way  $\text{K}_4[\text{Fe}(\text{CN})_6]$  also gives five particles per molecule by dissociating as  $4\text{K}^+ + [\text{Fe}(\text{CN})_6]^{4-}$ .
- 68.
- |                      |                           |                   |                            |     |              |
|----------------------|---------------------------|-------------------|----------------------------|-----|--------------|
|                      | $\text{CH}_2\text{FCOOH}$ | $\longrightarrow$ | $\text{CH}_2\text{FCOO}^-$ | $+$ | $\text{H}^+$ |
| Initial moles        | 1                         |                   | 0                          |     | 0            |
| Moles at equilibrium | $1 - \alpha$              |                   | $\alpha$                   |     | $\alpha$     |
- $\therefore i = 1 - \alpha + \alpha + \alpha = 1 + \alpha$
69. For  $\text{Ba}(\text{NO}_3)_2$ ,  $i = 2.74$  ....(given)  
 $n' = 3$   
Degree of dissociation ( $\alpha$ )  
 $= \frac{i-1}{n'-1} = \frac{2.74-1}{3-1} = 0.87$   
 $\therefore$  Degree of dissociation = 87 %
71. The extent of depression in freezing point varies with the number of solute particles for a fixed solvent only, and it is a characteristic feature of the nature of solvent also. So for two different solvents the extent of depression may vary even if number of solute particles dissolved be same.

72. According to Henry's law, 'the solubility of a gas in a liquid at constant temperature is proportional to the pressure of the gas above the solution.'

$$S \propto P$$

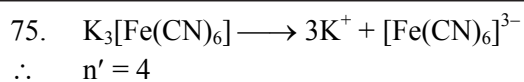
Where  $S$  is the solubility of the gas in  $\text{mol dm}^{-3}$  and  $P$  is the pressure of the gas in atmosphere.

If several gases are present, then the solubility of any gas may be evaluated by using  $P$  as partial pressure of that gas in the mixture.



From given graph it is observed that at any given partial pressure, gas-A has the least solubility.

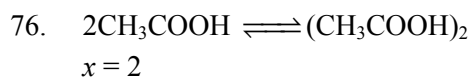
73. When 10 mL of 0.1 M aqueous solution of  $\text{NaCl}$  is divided into 1000 drops of equal volume, the concentration of the solution will not change. So, the concentration of one drop of solution will be 0.1 M. Hence, option (B) is the correct answer.
74.  $\Delta T_b = K_b \cdot m$   
Substituting the given values in above equation,  
 $0.05 = 0.5 \times m$   
 $\therefore m = \frac{0.05}{0.5}$   
 $\therefore m = 0.1$   
But molality =  $\frac{\text{number of moles of the solute}}{\text{mass of solvent in kg}}$   
Also, number of moles of solute  
 $= \frac{\text{Amount of solute in grams}}{\text{Molecular weight of solute}}$   
Let 'x' be the amount of solute dissolved.  
 $\therefore \text{molality (m)} = \frac{\frac{x}{100}}{100 \times 10^{-3}}$   
( $\because$  100 g of water is taken as solvent and molecular weight of solute is 100).  
 $\therefore 0.1 = \frac{x}{100} \times 10 \quad \therefore x = 1 \text{ g}$   
 $\therefore$  To observe an elevation of boiling point of  $0.05^\circ\text{C}$ , the amount of solute (Mol. Wt. = 100) to be added to 100 g of water ( $K_b = 0.5$ ) is 1 g.



$$\text{Degree of dissociation } (\alpha) = \frac{i-1}{n'-1}$$

$$= \frac{3.333-1}{4-1} = 0.78$$

$\therefore$  Percent dissociation =  $0.78 \times 100 = 78\%$



$$i = 1 + \left(\frac{1}{x} - 1\right)\alpha \quad i = 1 + \left(\frac{1}{2} - 1\right)\alpha$$

$$i = 1 - \frac{\alpha}{2}$$

Now,  $\Delta T_f = i.m.K_f$

$\Delta T_f = 0.45^\circ\text{C}$  or  $0.45\text{ K}$

$\text{mass}_{(\text{solute})} = 0.2\text{ g}$

$\text{mass}_{(\text{solvent})} = 20\text{ g} = 0.02\text{ kg}$

$$0.45 = i \left(\frac{0.2}{0.02}\right) 5.12 \quad \therefore i = 0.527$$

i.e.,  $0.527 = 1 - \frac{\alpha}{2} \quad \therefore \alpha = 0.946$

$\therefore$  Degree of association =  $94.6\%$

77. For isotonic solutions, the number of moles of solutes are equal (i.e., molar concentrations are same).

$0.06\%$  (W/V) aqueous solution of urea means 100 mL of solution contains 0.06 g of urea.

Let volume of solution = 100 mL

$\therefore$  Mass of urea = 0.06 g

Number of moles of urea =  $\frac{0.06}{60} = 0.001\text{ mol}$

$\therefore$  Molarity =  $\frac{\text{Number of moles of solute}}{\text{Volume of solution in L}}$

$$= \frac{0.001}{0.1} = 0.01\text{ M}$$

$\therefore$  Among the given options, 0.01 M glucose solution is isotonic with the given solution of urea.

78. van't Hoff factor (i)

$$= \frac{\text{Theoretical molecular mass}}{\text{Observed molecular mass}}$$

$\therefore 0.5 = \frac{\text{Theoretical molecular mass}}{\text{Observed molecular mass}}$

Observed molecular mass

$$= \frac{\text{Theoretical molecular mass}}{0.5}$$

=  $2 \times$  (Theoretical molecular mass)

The observed molecular mass is twice the theoretical molecular mass. This indicates that in the given solution, two molecules of benzoic acid associate to form a dimer.

80.  $16.9\%$  (W/V)  $AgNO_3$  solution means 100 mL of solution contains 16.9 g of  $AgNO_3$ .

Molar mass of  $AgNO_3 = 169.3\text{ g mol}^{-1}$

$\therefore$  Number of moles of  $AgNO_3 = \frac{16.9\text{ g}}{169.3\text{ g mol}^{-1}}$

$$= 0.0998\text{ mol}$$

Molarity =  $\frac{\text{Number of moles of } AgNO_3}{\text{Volume of solution in L}}$

$$= \frac{0.0998\text{ mol}}{0.1\text{ L}} = 0.998\text{ M}$$

Now, 50 mL of  $AgNO_3$  solution is used.

$\therefore$  Number of moles of  $AgNO_3$

$$= \text{Molarity} \times \text{Vol. of solution in L}$$

$$= 0.998 \times 0.05 = 0.0499\text{ mol} \approx 0.05\text{ mol}$$

$5.8\%$  (W/V)  $NaCl$  solution means 100 mL of solution contains 5.8 g of  $NaCl$ .

Molar mass of  $NaCl = 58.5\text{ g mol}^{-1}$

$\therefore$  Number of moles of  $NaCl = \frac{5.8\text{ g}}{58.5\text{ g mol}^{-1}}$

$$= 0.0991\text{ mol}$$

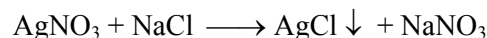
Molarity =  $\frac{0.0991\text{ mol}}{0.1\text{ L}} = 0.991\text{ M}$

Now, 50 ml of  $NaCl$  solution is used.

$\therefore$  Number of moles of  $NaCl = 0.991 \times 0.05$

$$= 0.04955\text{ mol}$$

$$\approx 0.05\text{ mol}$$



According to the balanced chemical equation, 1 mol of  $AgNO_3$  reacts with 1 mol of  $NaCl$  to form 1 mol of  $AgCl$  (as precipitate).

$\therefore$  When 0.05 mol of  $AgNO_3$  reacts with 0.05 mol of  $NaCl$ , 0.05 mol of  $AgCl$  is formed.

$\therefore$  The mass of the precipitate formed

$$= 0.05\text{ mol} \times 142.8\text{ g mol}^{-1}$$

$$= 7.14\text{ g} \approx 7\text{ g}$$





81.  $p_A^\circ = 760 \text{ mm Hg}$   
 $p_T = 732 \text{ mm Hg}$   
 $\therefore$  relative lowering of vapour pressure will be,

$$\frac{p_A^\circ - p_T}{p_A^\circ} = \frac{W_B M_A}{M_B W_A}$$

$$\therefore M_B = \frac{W_B M_A p_A^\circ}{W_A (p_A^\circ - p_T)}$$

$$= \frac{6.5 \times 18 \times 760}{100(760 - 732)} = 31.757$$

$$\text{Now, } \Delta T_b = K_b \frac{W_B 1000}{M_B W_A}$$

$$= 0.52 \times \frac{6.5 \times 1000}{31.757 \times 100} = 1.06$$

$$\therefore \text{Boiling point of solution} = 100 + 1.06$$

$$= 101.06 \text{ }^\circ\text{C} \approx 101 \text{ }^\circ\text{C}$$



### Evaluation Test

1. Number of moles of  $\text{O}_2$  ( $n_A$ ) =  $\frac{W_A}{M_A} = \frac{8}{32} = 0.25$

Number of moles of  $\text{H}_2$  ( $n_B$ ) =  $\frac{W_B}{M_B} = \frac{2}{2} = 1.0$

Mole fraction of  $\text{H}_2$  ( $x_{\text{H}_2}$ ) =  $\frac{n_B}{n_A + n_B} = \frac{1.0}{0.25 + 1.0} = \frac{1}{1.25} = 0.8$

2. Number of moles of acetic acid ( $n_A$ ) =  $\frac{W_A}{M_A} = \frac{25}{60} = 0.416 \approx 0.42$

Number of moles of ethanol ( $n_B$ ) =  $\frac{W_B}{M_B} = \frac{57}{46} = 1.239 \approx 1.24$

Percentage of water in the solution =  $100 - (25 + 57) = 18$

Number of moles of water ( $n_C$ ) =  $\frac{W_C}{M_C} = \frac{18}{18} = 1$

Mole fraction of acetic acid =  $\frac{n_A}{n_A + n_B + n_C} = \frac{0.42}{0.42 + 1.24 + 1} = \frac{0.42}{2.66} = 0.157 \approx 0.16$

Mole fraction of ethanol =  $\frac{n_B}{n_A + n_B + n_C} = \frac{1.24}{2.66} = 0.466 \approx 0.47$

Mole fraction of water =  $\frac{n_C}{n_A + n_B + n_C} = \frac{1}{2.66} = 0.375 \approx 0.38$

3. Molarity =  $\frac{\text{Number of moles of solute}}{\text{Volume of solution in litre}}$

$\therefore$  Volume of solution in litre =  $\frac{\text{Number of moles of solute}}{\text{Molarity}} = \frac{1.0}{4.0} = 0.25 \text{ litre} = 250 \text{ mL}$

4.  $M_1 = 0.2 \text{ M}$ ,  $M_2 = 0.3 \text{ M}$

$V_1 = 45 \text{ mL}$ ,  $V_2 = 60 \text{ mL}$

Resulting molarity =  $\frac{M_1 V_1 + M_2 V_2}{V_1 + V_2}$

$$= \frac{(0.2 \times 45) + (0.3 \times 60)}{45 + 60} = 0.26 \text{ M}$$



$$\begin{aligned} 5. \quad \text{ppm of Na}_2\text{CO}_3 &= \frac{\text{Mass of Na}_2\text{CO}_3}{\text{Total mass of Na}_2\text{CO}_3 \text{ solution}} \times 10^6 \\ &= \frac{10}{1000} \times 10^6 = 10,000 \text{ ppm.} \end{aligned}$$

$$\begin{aligned} 6. \quad \frac{p_1^\circ - p}{p_1^\circ} &= \frac{W_2 M_1}{W_1 M_2} \\ \frac{p_1^\circ - p}{180} &= \frac{25 \times 78}{250 \times 342} \end{aligned}$$

$$\text{The vapour pressure lowering} = p_1^\circ - p = \frac{25 \times 78 \times 180}{250 \times 342} = 4.1 \text{ mm Hg}$$

$$7. \quad \text{Mass of acetone} = \text{Volume} \times \text{Density} = 64.5 \text{ cm}^3 \times 0.791 \text{ g/cm}^3 = 51 \text{ g}$$

$$\text{Moles of acetone} = \frac{\text{Mass of acetone}}{\text{Molar mass of acetone}} = \frac{51}{58} = 0.8793$$

$$\begin{aligned} \frac{p_1^\circ - p}{p_1^\circ} &= \frac{n_2}{n_1} \\ \frac{285 - 260}{285} &= \frac{n_2}{0.8793} \end{aligned}$$

$$\frac{25}{285} = \frac{n_2}{0.8793}$$

$$n_2 = \frac{25 \times 0.8793}{285} = 0.0771$$

$$\text{Molality} = \frac{\text{Number of moles of solute}}{\text{Mass of solvent in kg}} = \frac{0.0771}{51 \times 10^{-3}} = 1.51 \text{ M}$$

$$8. \quad p_A = p_A^\circ x_A \quad \dots\text{(i)}$$

$$p_B = p_B^\circ x_B \quad \dots\text{(ii)}$$

Equal moles of A and B in the vapour means  $p_A = p_B$

$$\therefore p_A^\circ x_A = p_B^\circ x_B \quad \dots\text{(iii)}$$

Substituting  $x_A = x$  and  $x_B = 1 - x$  in (iii),

$$0.95 \times x = 0.15 (1 - x)$$

$$0.95x = 0.15 - 0.15x$$

$$0.95x + 0.15x = 0.15$$

$$1.1x = 0.15$$

$$x = \frac{0.15}{1.1} = 0.1363 \approx 0.14$$

9. Total pressure above the solution is,

$$p_{\text{total}} = p_{\text{cp}}^\circ x_{\text{cp}} + p_{\text{ch}}^\circ x_{\text{ch}}$$

$$= 331 \times \left(\frac{1}{4}\right) + 113 \times \left(\frac{3}{4}\right) = 82.75 + 84.75 = 167.5 \text{ mm Hg}$$

$$\text{Mole fraction of cyclopentane in the vapour} = \frac{82.75 \text{ mm Hg}}{167.5 \text{ mm Hg}} = 0.49$$



$$10. \quad K_b = \frac{\Delta T_b}{m} = \frac{(100.51 - 100)}{0.3} = \frac{0.51}{0.3} = 1.7 \text{ K kg mol}^{-1}$$

$$\Delta T_b \text{ for } 0.7 \text{ m aqueous solution of sucrose} = K_b \times m = 1.7 \times 0.7 = 1.19$$

$$\therefore \text{The boiling point of } 0.7 \text{ m aqueous solution of sucrose} = (100 + 1.19)^\circ\text{C} = 101.19^\circ\text{C}$$

$$11. \quad \Delta T_b = \frac{K_b W_2}{M_2 W_1} = \frac{\left(\frac{19.4}{10} \text{ K kg mol}^{-1} \times 0.524 \text{ g}\right)}{152 \text{ g mol}^{-1} \times (36.8 \times 10^{-3}) \text{ kg}} = 0.18 \text{ K}$$

$$\text{Boiling point of ether} = (34.6 + 273) \text{ K} = 307.6 \text{ K}$$

$$\begin{aligned} \text{The boiling point of solution} &= \text{boiling point of ether} + \Delta T_b \\ &= 307.6 \text{ K} + 0.18 \text{ K} = 307.78 \text{ K} \end{aligned}$$

12. The number of moles of ions obtained from dissociation of 1 mole of the given solute:  
glucose ( $\text{C}_6\text{H}_{12}\text{O}_6$ ) = 1, sodium chloride ( $\text{NaCl}$ ) = 2, sodium sulphate ( $\text{Na}_2\text{SO}_4$ ) = 3,  
sodium phosphate ( $\text{Na}_3\text{PO}_4$ ) = 4.

$$\therefore \text{The ratio} = 1 : 2 : 3 : 4$$

13. 5% Aqueous solution refers to 5 g of solute 'A' in 100 g of solution.

$$W_1 = 100 - 5 = 95 \text{ g} = 95 \times 10^{-3} \text{ kg}$$

$$\Delta T_f \text{ (for A)} = \frac{K_f W_2}{M_A W_1} = \frac{K_f \times 5}{M_A \times 95 \times 10^{-3}} \quad \dots\text{(i)}$$

- 3% Aqueous solution refers to 3 g of solute 'B' in 100 g of solution.

$$W_1 = 100 - 3 = 97 \text{ g} = 97 \times 10^{-3} \text{ kg}$$

$$\Delta T_f \text{ (for B)} = \frac{K_f W_2}{M_B W_1} = \frac{K_f \times 3}{72 \times 97 \times 10^{-3}} \quad \dots\text{(ii)}$$

Since  $\Delta T_f$  is equal for two solutions, (i) = (ii)

$$\frac{5K_f}{M_A \times 95 \times 10^{-3}} = \frac{3K_f}{72 \times 97 \times 10^{-3}}$$

$$M_A = \frac{5 \times 72 \times 97}{3 \times 95} = 122.52 \text{ g/mol}$$

14.  $\Delta T_f = K_f \times m$   
 $0.153 \text{ K} = 1.68 \text{ K kg mol}^{-1} \times m$

$$m = \frac{0.153 \text{ K}}{1.68 \text{ K m}^{-1}} = 0.09 \text{ m}$$

$$\begin{aligned} \Delta T_b &= \text{Boiling point of solution} - \text{Boiling point of solvent} \\ &= (304.52 - 303) \text{ K} = 1.52 \text{ K} \end{aligned}$$

$$\Delta T_b = K_b m$$

$$\therefore K_b = \frac{\Delta T_b}{m} = \frac{1.52}{0.09} = 16.8 \text{ K m}^{-1}$$

$$15. \quad M_{XY_2} = \frac{K_f W_2}{\Delta T_f W_1} = \frac{5.1 \times 1}{2.3 \times 20 \times 10^{-3}} = 110.87 \text{ g mol}^{-1}$$

$$M_{XY_4} = \frac{K_f W_2}{\Delta T_f W_1} = \frac{5.1 \times 1}{1.3 \times 20 \times 10^{-3}} = 196.15 \text{ g mol}^{-1}$$

Let x and y be the atomic masses of 'X' and 'Y' respectively.

$$M_{XY_2} = x + 2y = 110.87 \quad \dots\text{(i)}$$

$$M_{XY_4} = x + 4y = 196.15 \quad \dots\text{(ii)}$$



Subtracting (i) from (ii),

$$M_{XY_4} - M_{XY_2} = (x + 4y) - (x + 2y) = 196.15 - 110.87$$

$$\therefore 2y = 85.28$$

$$y = 42.64 \text{ g mol}^{-1}$$

substituting  $y = 42.64$  in (i)

$$x + (2 \times 42.64) = 110.87$$

$$x + 85.28 = 110.87$$

$$x = 110.87 - 85.28 = 25.59 \text{ g mol}^{-1}$$

$$16. \quad \pi V = \frac{W}{M} RT$$

$$5.2 \times 10^{-4} \times 1 = \frac{3.56}{M} \times 0.082 \times 300$$

$$M = \frac{3.56 \times 0.082 \times 300}{5.2 \times 10^{-4}} = 1.68 \times 10^5 \text{ g mol}^{-1}$$

17. For two isotonic, non-electrolytic solution,  $C_1 = C_2$

$$\therefore \frac{W_{\text{glucose}}}{M_{\text{glucose}} \times V_{\text{glucose solution}}} = \frac{W_{\text{solute}}}{M_{\text{solute}} \times V_{\text{solution of solute}}}$$

$$\frac{9.2}{180 \times 1} = \frac{3 \times 1000}{M_{\text{solute}} \times 100}$$

$$M_{\text{solute}} = \frac{3 \times 1000 \times 180 \times 1}{9.2 \times 100} = 587 \text{ g mol}^{-1}$$

$$18. \quad \pi = \frac{W}{M} \times \frac{RT}{V}$$

$$\frac{600}{760} = \frac{10}{M} \times \frac{R \times 300}{250 \times 10^{-3}}$$

$$M = \frac{10 \times 300 \times 760 \times R}{250 \times 10^{-3} \times 600} = \frac{22800 \times R}{1.5}$$

19.  $m \times d = M$  if  $d > 1 \text{ kg dm}^{-3}$ , then  $M > m$

20. Vapour pressure of a solvent is lowered by the presence of solute in it. Lowering in vapour pressure is a colligative property i.e., it depends on the number of particles present in the solution.  $\text{Cu}(\text{NO}_3)_2$  gives the maximum number of ions. (i.e., 3) so it causes the greatest lowering in vapour pressure of water.

21.  $\Delta T_b = K_b \times m$  [given  $K_b$  for water =  $0.513 \text{ }^\circ\text{C kg mol}^{-1}$  and molality ( $m$ ) =  $0.69 \text{ m}$ ]

$$\therefore \Delta T_b = 0.513 \times 0.69 = 0.354 \text{ }^\circ\text{C}$$

$\therefore$  The elevated boiling point

$$= 99.725 \text{ }^\circ\text{C} + 0.354 \text{ }^\circ\text{C}$$

$$= 100.079 \text{ }^\circ\text{C}.$$

22. For isotonic solution  $C_1 = C_2$  thus, number of moles in both the solutions are equal.

$$\frac{3.42}{342} = \frac{500}{M_2}$$

$$\therefore M_2 = \frac{500 \times 342}{3.42} = 50000 \text{ g mol}^{-1}$$

$$23. \quad \frac{\pi_2}{\pi_1} = \frac{T_2}{T_1}$$

$$\pi_2 = \frac{546 \times 2.5}{276} = 4.94 \approx 5.0 \text{ atm}$$

Chemical Thermodynamics and  
Energetics

## Hints



## Classical Thinking

6. Internal energy is an extensive property (whose magnitude depends on the amount of matter present in the system) while refractive index, viscosity and temperature are examples of intensive property (whose magnitude is independent of the amount of matter present in the system).
7. The intensive property is mass/volume i.e., density.
9. For isothermal process,  $\Delta T = 0$   
 $\therefore \Delta U = 0$
10. In an isobaric process, pressure of the system remains constant.
13. In cyclic process, a system in a given state goes through a series of different processes, but in the end returns to its initial state.
16. This is an irreversible process.  
 $\therefore W = -p_{\text{ex}}(V_2 - V_1) = -p_{\text{ex}}(x - y) \text{ L-atm.}$
17. At 10 °C melting of ice is irreversible process. Diffusion is a spontaneous process, hence it is very difficult to make this process reversible. A solid NaCl spontaneously dissolves in water. At 373 K and 1 atm pressure, condensation and evaporation both take place simultaneously, hence it is a reversible process.  
 $\text{H}_2\text{O}_{(l)} \rightleftharpoons \text{H}_2\text{O}_{(g)}$  at 373 K and 1 atm  
Rate of forward = Rate of backward
20.  $q = 920 \text{ J}$ ,  $\Delta U = 460 \text{ J}$ ,  
According to first law of thermodynamics for compression;  
 $\Delta U = q + W$   
 $\therefore W = \Delta U - q = 460 - 920 = -460 \text{ J.}$
21.  $\Delta U = q + W$   
 $q = 54 \text{ J}$  and  $W = -238 \text{ J}$  (work done by a system or work done on the surroundings)  
 $\therefore \Delta U = 54 - 238 = -184 \text{ J}$   
Thus, the system loses its internal energy.
22.  $\Delta U = q + W = 200 + (-1000) = -800 \text{ cal}$

26. Enthalpy is defined by the equation,  
 $H = U + PV$
27.  $\Delta H = \Delta U + \Delta nRT$ ; For liquids  $\Delta n = 0$   
 $\therefore \Delta H = \Delta U$
28.  $\Delta H = \Delta U + P\Delta V$  OR  $\Delta H = \Delta U + \Delta nRT$   
Conditions for  $\Delta H = \Delta U$  are:  
i.  $P = 0$  ii.  $\Delta V = 0$  iii.  $\Delta n = 0$   
In case of,  
(A)  $\Delta n = 0$  (Since all the reactants and products are in solution)  
 $\therefore \Delta H = \Delta U$   
(B)  $\Delta V = 0$  (Since the reaction is carried out in a closed vessel)  
 $\therefore \Delta H = \Delta U$   
(C)  $\Delta n = 0$  (Since the number of moles of gaseous reactants and products are equal)  
 $\therefore \Delta H = \Delta U$   
(D)  $\Delta P = 0$  (Since the reaction is carried out at constant pressure)  
 $\therefore \Delta H = \Delta U + P\Delta V \quad \therefore \Delta H \neq \Delta U$
29.  $\text{C}_6\text{H}_{6(g)} + \frac{15}{2}\text{O}_{2(g)} \longrightarrow 6\text{CO}_{2(g)} + 3\text{H}_2\text{O}_{(g)}$   
 $\Delta n = 6 + 3 - 1 - \frac{15}{2} = +\frac{1}{2}$ .
30.  $\Delta n = \text{number of moles of product} - \text{number of moles of reactant} = 2 - 3 = -1$   
By the definition of enthalpy:  
 $\Delta H = \Delta U + \Delta nRT$  i.e.,  $\Delta H = \Delta U + (-1)RT$   
 $\Delta H = \Delta U - RT$
31. Enthalpy of fusion is the enthalpy change in converting 1 mole of the substance from solid state to liquid state at its freezing point.
36. A negative  $\Delta H$  indicates that reaction is exothermic. Thus, in reaction (i) heat is evolved while in reaction (ii) heat is absorbed.
37. Change of liquid to vapour takes energy in the form of heat, so it is endothermic reaction.
38. For exothermic reactions,  $H_P < H_R$ .  
For endothermic reactions,  $H_P > H_R$ .



39. For endothermic reaction,  $\Delta H = +ve$
42.  $n = \frac{3600}{18} = 200$   
 $\therefore \Delta H$  for 200 moles  $= -284.5 \times 200 = -56900$  kJ
44. The enthalpies of all elements in their standard state at  $25^\circ\text{C}$  or  $298$  K are zero.  
 Enthalpies of elements i.e., enthalpies of formation of elements is zero at standard state i.e.,  $298$  K and external atmospheric pressure of  $1$  bar i.e.,  $10^5$   $\text{Nm}^{-2}$ .
47. i. It cannot be called as heat of combustion, since,  $2$  moles of reactants are present.  
 ii. It cannot be heat of formation, since,  $2$  moles of products are formed.  
 Thus, the given  $\Delta H$  represents heat of reaction.
48.  $\Delta H/\text{mole of FeS} = \frac{3.77 \times 56}{2.1} = 100.5 = -100.5$  kJ
52.  $\Delta S = +ve$  then the system is more disordered.
54. In case of gas, randomness is maximum, therefore entropy is maximum in case of steam (water vapours).
59. Spontaneous change shows  $\Delta G = -ve$ .
60. When  $\Delta G = -ve$ , then the reaction is spontaneous in nature.
61. For equilibrium,  $\Delta G = 0$ .
64.  $\text{H}_2\text{O}_{(s)} \longrightarrow \text{H}_2\text{O}_{(l)}$ ,  $\Delta H = +ve$   
 i.  $\Delta H = +ve$  (i.e., enthalpy increases)  
 ii.  $\Delta G = -ve$  (i.e., free energy decreases)  
 iii.  $\Delta U = +ve$  (internal energy increases)
65.  $\Delta G = \Delta H - T\Delta S$   
 $\Delta G = -382.64 - (-145.6) \times 10^{-3} \times 298$   
 $= -339.3$  kJ  $\text{mol}^{-1}$
66.  $K_p = e^{-\frac{\Delta G^\circ}{RT}}$



### Critical Thinking

2. Closed system is the type of system, which can exchange energy but not matter with the surroundings. The boundary between the system and surrounding is sealed but not insulated.

9. The process in which pressure remains constant is known as isobaric process. Reversible process is one in which change is carried out so slowly that the system and surrounding are always in equilibrium with each other.
11. In adiabatic process, there is no heat exchange therefore energy required for expansion is supplied by lowering temperature. As volume increases, pressure decreases.
13. When a real gas is forced through a porous plug into a region of low pressure, it is found that due to expansion, the gas on the side of low pressure gets cooled.  
 The phenomenon of producing lowering of temperature when a gas is made to expand adiabatically from a region of high pressure into a region of low pressure is known as Joule-Thomson effect.
14.  $W = -p_{\text{ex}} \cdot \Delta V$   
 $= -1(101 - 1)\text{L} = -100$  L  
 $= -100 \times 24.2$  cal  $= -2420$  cal  $= -2.42$  kcal
15.  $W = -p_{\text{ex}} \Delta V = -5 \times 10^5 (8 - 2.5) \times 10^{-3}$   
 $= -5 \times 5.5 \times 10^2 = -2.750$  kJ.
16.  $V_2 = 100$   $\text{cm}^3 = 0.1$   $\text{dm}^3 = 0.1 \times 10^{-3}$   $\text{m}^3$   
 $V_1 = 1$   $\text{dm}^3 = 1 \times 10^{-3}$   $\text{m}^3$   
 $W = -p_{\text{ex}} \Delta V = -3.2 \times 10^5 (0.1 - 1) \times 10^{-3}$   
 $= +2.88 \times 10^2$  J
17.  $W = -p_{\text{ex}} \Delta V$   
 $\therefore -\frac{9.09 \times 10^3}{(8 - 23) \times 10^{-3}} = p_{\text{ex}}$   
 $\therefore p_{\text{ex}} = 6.06 \times 10^5$   $\text{N/m}^2$ .
18. Since, work is done against constant pressure, the process is irreversible. Work done for a irreversible process is given by,  
 $W_{\text{irr}} = -p_{\text{ex}} (V_2 - V_1) = -5 \times (15 - 3)$   
 $= -60$  L - atm  $= -60 \times 101.3$  J  
 $= -6.078 \times 10^3$  J
19.  $W = p \cdot \Delta V$  (as work is done on the system)  
 $= (3.039 \times 10^5 \text{Nm}^{-2}) (30 - 20) \text{dm}^3$   
 $= 3.039 \times 10^5 \text{Nm}^{-2} \times 10 \times 10^{-3} \text{m}^3$   
 $= 3039$  Nm  $= 3039$  J  
 $= (3039 \times 0.239)$  cal  
 $= 726.3$  cal



20. The work done in reversible isothermal expansion process =  $-2.303nRT \log_{10} \frac{P_1}{P_2}$
- $$= -2.303 \times 2 \times 8.314 \times 330 \times \log \frac{5}{1}$$
- $$= -2.303 \times 8.314 \times 660 \times \log 5 \text{ J}$$
21. An ideal gas undergoing expansion in vacuum shows,  $\Delta U = 0$ ,  $W = 0$  and  $q = 0$ .
22. Expression for work, when an ideal gas expands isothermally and reversibly is given by
- $$W_{\max} = -2.303nRT \log_{10} \frac{V_2}{V_1}$$
- For same mass, temperature,  $V_1$  and  $V_2$
- $$W_{\max} \propto n$$
- where,  $n = \text{number of moles} = \frac{\text{Mass}}{\text{Molar mass}}$
- $$n \propto \frac{1}{\text{Molar mass}}$$
- $\therefore$  Lower the molar mass, higher is the magnitude of work.
23.  $P_1 = 10 \text{ atm}$ ,  $P_2 = 1 \text{ atm}$ ,  $T = 300 \text{ K}$ ,  $n = 1$ ,  
 $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$   
 By using the formula,
- $$W = -2.303 nRT \log_{10} \frac{P_1}{P_2}$$
- $$= -2.303 \times 1 \times 8.314 \times 300 \log_{10} 10$$
- $$W = -5744.1 \text{ Joule}$$
24.  $W_{\max} = -2.303 nRT \log_{10} \frac{V_2}{V_1}$
- $$-831.4 = -2.303 \times 1 \times 8.314 \times T \times \log \left( \frac{20}{2} \right)$$
- $$T = \frac{831.4}{2.303 \times 8.314} = 43.42 \text{ K}$$
- $\therefore T = 43.42 \text{ K}$
25.  $W_{\text{rev}} = -2.303nRT \log_{10} \frac{V_2}{V_1}$
- $$= -2.303 \times n \times 8.314 \times 298$$
- $$\times \log_{10} \frac{40}{20} \text{ J/mole}$$
- $$= -2.303 \times 8.314 \times 10^7 \times 298 \times \log_{10} 2$$
- $$\times n \text{ ergs/mole. } (\because 1 \text{ Joule} = 10^7 \text{ ergs})$$
26. Mass = 16 g  
 $\therefore n = 0.5$
- $$W = -2.303nRT \log_{10} \frac{V_2}{V_1}$$
- $\therefore W = -2.303nRT \log_{10} 3 \quad (V_2 = 3V_1)$
- $$= -2.303 \times 0.5 \times 8.314 \times 300 \times 0.4771$$
- $$= -1370.26 \text{ J} = -1.370 \text{ kJ.}$$
27.  $\Delta U = U_{\text{products}} - U_{\text{reactants}}$   
 When  $\Delta U$  is negative then,  $U_{\text{reactants}} > U_{\text{products}}$   
 i.e., heat is evolved in the reaction.
28.  $W = +600 \text{ J}$   
 $\Delta U = U_2 - U_1 = q + W$
- $\therefore U_2 = U_1 + (-450) + 600$
- $\therefore U_2 = U_1 + 150 \text{ J}$
29. Since work is done by the system,  $W$  is taken as negative.  
 $\Delta U = q + W = 2500 - 3500 = -1000 \text{ cal}$
30. Internal energy change,  $\Delta U = q + W$  is a state function.
31.  $\Delta U = q_p + W$   
 $\Delta U = q_p - p_{\text{ex}} \cdot \Delta V \quad (\because W = -p_{\text{ex}} \cdot \Delta V)$
- $\therefore q_p = \Delta U + p_{\text{ex}} \cdot \Delta V$
32. For isochoric process,  $\Delta V = 0$  so  $q_v = \Delta U$  i.e., heat given to a system under constant volume is used up in increasing its internal energy.
33. In adiabatic expansion, no heat is allowed to enter or leave the system, hence  $q = 0$ .  
 According to first law of thermodynamics;  
 $\Delta U = q + W$
- $\therefore \Delta U = W$   
 Work is done at the expense of internal energy. Hence, the system gets cooled.
35. Enthalpy is an extensive property.
36. In the reaction,  $\text{H}_{2(\text{g})} + \frac{1}{2} \text{O}_{2(\text{g})} \longrightarrow \text{H}_2\text{O}_{(l)}$ ;
- $$\Delta n = 0 - \left( 1 + \frac{1}{2} \right) = -1.5$$
- $\therefore \Delta H = \Delta U - 1.5 RT$
- $\therefore \Delta H < \Delta U$
37. In the reaction,  $\text{PCl}_{5(\text{g})} \longrightarrow \text{PCl}_{3(\text{g})} + \text{Cl}_{2(\text{g})}$ ;
- $$\Delta n = 2 - 1 = +1$$
- $$\Delta H = \Delta U + \Delta n RT \quad \therefore \Delta H > \Delta U$$
38.  $\text{C}_4\text{H}_{10(\text{g})} + \frac{13}{2} \text{O}_{2(\text{g})} \longrightarrow 4\text{CO}_{2(\text{g})} + 5\text{H}_2\text{O}_{(l)}$
- $$\Delta n = 4 - \left( 1 + \frac{13}{2} \right) = -3.5$$
- $\therefore \Delta U > \Delta H \quad (\because \Delta n = -ve)$



39. For the reaction,  $2\text{CO}_{(g)} + \text{O}_{2(g)} \longrightarrow 2\text{CO}_{2(g)}$ ;  
 $\Delta n = 2 - 3 = -1$   
 $\therefore \Delta H = \Delta U - RT$   
 $\therefore \Delta H < \Delta U$
40.  $\Delta n = 0$  so,  $\Delta U = \Delta H$ .
41.  $\Delta n = 1 - 0 = 1$   
 $\Delta U = \Delta H - \Delta nRT$   
 $\Delta U = +176 - 1 \times \frac{8.314}{1000} \times 1250 = 165.6 \text{ kJ}$ .
42.  $\Delta H = \Delta U + \Delta nRT$   
 $\Delta n = 6 - 9 = -3$   
 $R = 0.002 \text{ kcal} = 2 \times 10^{-3} \text{ kcal}$ ,  $T = 298 \text{ K}$   
 Substituting the values:  
 $-936.9 = \Delta U - (2 \times 10^{-3} \times 298 \times 3) \text{ kcal}$
43. 7.8 g  $\text{C}_6\text{H}_6$  gives 40 kJ heat  
 78 g  $\text{C}_6\text{H}_6$  (1 mole) gives  $\frac{40 \times 78}{7.8} = 400 \text{ kJ heat}$   
 Thus,  $\Delta U = -400 \text{ kJ mol}^{-1}$  at 300 K for  
 $\text{C}_6\text{H}_{6(l)} + \frac{15}{2} \text{O}_{2(g)} \longrightarrow 6\text{CO}_{2(g)} + 3\text{H}_2\text{O}_{(l)}$   
 Now,  $\Delta n = 6 - \frac{15}{2} = -\frac{3}{2}$   
 $\therefore \Delta H = \Delta U + \Delta nRT$   
 $= -400 - \left[ \frac{3}{2} \times \frac{8.314 \times 300}{10^3} \right] \text{ kJ mol}^{-1}$   
 $\Delta H = -403.74 \text{ kJ mol}^{-1}$ .
44. The reaction for the combustion can be given as  
 $\text{C}_6\text{H}_5\text{COOH}_{(s)} + \frac{15}{2} \text{O}_{2(g)} \longrightarrow 7\text{CO}_{2(g)} + 3\text{H}_2\text{O}_{(l)}$   
 $\Delta n_g = 7 - \frac{15}{2} = -\frac{1}{2}$   
 Here,  $T = 27 + 273 = 300 \text{ K}$   
 $q_p = q_v + \Delta n_g RT$   
 $\therefore q_p = -321.30 + \left( -\frac{1}{2} \right) \times 300 \times R$   
 $= (-321.30 - 150) \text{ kJ}$
47. As formation of graphite is an exothermic reaction, there is lowering of energy. So it is more stable than diamond.
48.  $\Delta_{\text{fus}}H = 1.435 \text{ kcal mol}^{-1}$   
 i.e., 1 mole of  $\text{H}_2\text{O}$  fusion  $\equiv 1.435 \text{ kcal}$   
 18 g of  $\text{H}_2\text{O} \equiv 1435 \text{ cal required}$   
 $\therefore 1 \text{ g of H}_2\text{O} \equiv 80 \text{ cal required}$   
 $\Delta_{\text{freez}}H = -\Delta_{\text{fus}}H$
49. In Born-Haber cycle, Hess's law is applied to a series of reactions, beginning with the elements in their standard states and ending with the ionic compound in its standard state, to determine the crystal lattice enthalpy.
50.  $2\text{C}_2\text{H}_{6(g)} + 7\text{O}_{2(g)} \longrightarrow 4\text{CO}_{2(g)} + 6\text{H}_2\text{O}_{(l)}$ ;  
 $\Delta H = -3129 \text{ kJ}$   
 $\Delta H = \sum H_{f(\text{Products})} - \sum H_{f(\text{Reactants})}$   
 $-3129 = [4(-395) + 6(-286)] - [2\Delta_f H(\text{C}_2\text{H}_6) + 0]$   
 $[\because H_f(\text{O}_2) = 0]$   
 $= -1580 - 1716 - 2x$   
 $2x = -1580 - 1716 + 3129 = -167$   
 $x = -83.5 \text{ kJ}$
51.  $\Delta_f H$  refers to the formation of one mole of  $\text{NH}_3$ .  
 $\therefore \Delta_f H$  for 4 moles  $= 4 \times -46 = -184 \text{ kJ}$ .
52.  $\Delta H_{\text{reaction}} = \sum \Delta_f H^\circ_{(\text{products})} - \sum \Delta_f H^\circ_{(\text{reactants})}$   
 $\Delta_f H^\circ_{(\text{Si})} = 0$ ,  $\Delta_f H^\circ_{(\text{Mg})} = 0$  because they are in their standard states.  
 $\Delta H_{\text{reaction}} = \Delta_f H^\circ_{(\text{MgO})} - \Delta_f H^\circ_{(\text{SiO}_2)}$   
 $= 2(-34.7) - (-48.4) = -21 \text{ kJ}$
53. The molar mass of  $\text{CO}_2$  is 44 g. If 11 g yield 100 kJ of heat, 44 g will yield 400 kJ heat. Since the reaction is exothermic, it is  $-400 \text{ kJ}$ .
54.  $\text{CO} + \frac{1}{2} \text{O}_2 \longrightarrow \text{CO}_2$   
 $\Delta H = \Delta_f H^\circ(\text{CO}_2) - \left[ \Delta_f H^\circ(\text{CO}) + \frac{1}{2} \Delta_f H^\circ(\text{O}_2) \right]$   
 $= -94.0 - (-26.4) = -67.6 \text{ kcal}$ .
55.  $\text{CH}_4 + 2\text{O}_2 \longrightarrow \text{CO}_2 + 2\text{H}_2\text{O}$   
 Molecular mass of  $\text{CH}_4 = 12 + 4 = 16 \text{ g}$   
 $\therefore$  Heat liberated on the combustion of 2.0 g of methane  $= 25.0 \text{ kcal}$   
 $\therefore$  Heat liberated on the combustion of 16.0 g  
 $= \frac{25 \times 16}{2} = 200 \text{ kcal}$ .
56. 78 g of benzene on combustion produces heat  $= 3264.6 \text{ kJ}$   
 $\therefore 39 \text{ g of benzene will produce} = \frac{3264.6}{2}$   
 $= 1632.3 \text{ kJ}$ .



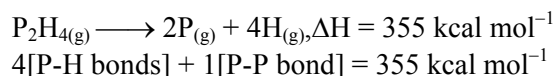


57. Exothermic products  $\equiv$  more stable  
Endothermic products  $\equiv$  less stable  
More magnitude of  $\Delta H \equiv$  more is stability in exothermic reaction  
More magnitude of  $\Delta H \equiv$  less is stability in endothermic reaction

$\therefore$  Order of stability :  $O_3 < HI < NH_3 < CO_2$ .

58.  $PH_3(g) \longrightarrow P(g) + 3H(g)$ ,  $\Delta H = 228 \text{ kcal mol}^{-1}$   
For breaking three P-H bonds  $\equiv 228 \text{ kcal mol}^{-1}$

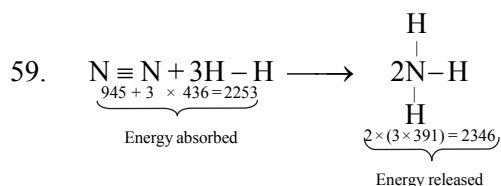
$\therefore$  One P-H bond  $\equiv \frac{228}{3} \equiv 76 \text{ kcal mol}^{-1}$



$$4[\text{P-H bonds}] + 1[\text{P-P bond}] = 355 \text{ kcal mol}^{-1}$$

$\therefore 4(76) + \text{P-P bond} = 355 \text{ kcal mol}^{-1}$

$\therefore \text{P-P bond} = 355 - 4(76) = 51 \text{ kcal mol}^{-1}$



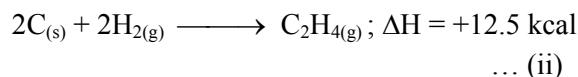
Net energy released =  $2346 - 2253 = 93 \text{ kJ}$   
i.e.,  $\Delta H = -93 \text{ kJ}$ .

60. Required equation:

$H_2(g) + S(s) + 2O_2(g) \longrightarrow H_2SO_4(l)$ ; is obtained by adding all the equations (i), (ii), (iii) and (iv),

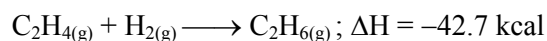
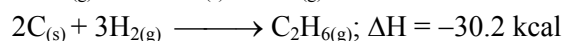
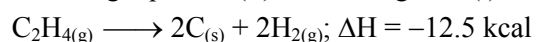
$\therefore \Delta_f H (H_2SO_4) = (-298.2 - 98.7 - 130.2 - 287.3) \text{ kJ}$   
 $= -814.4 \text{ kJ}$

61.  $2C(s) + 3H_2(g) \longrightarrow C_2H_6(g)$ ;  $\Delta H = -30.2 \text{ kcal}$  ... (i)

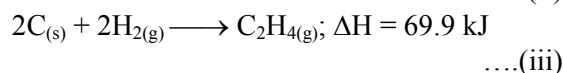
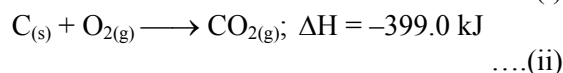


Required equation:

$C_2H_4(g) + H_2(g) \longrightarrow C_2H_6(g)$ ; is obtained by reversing equation (ii) and adding it to (i),



62.  $H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l)$ ;  $\Delta H = -285.0 \text{ kJ}$  ... (i)



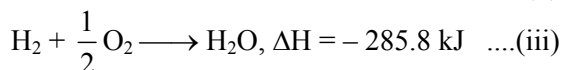
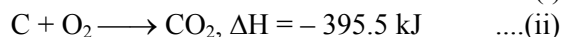
Required equation:

$C_2H_4(g) + 3O_2(g) \longrightarrow 2CO_2(g) + 2H_2O(l)$ ; is obtained by reversing equation (iii), multiplying equation (i) and (ii) by 2 and adding all the equations.

$$\Delta_c H (C_2H_4) = [-69.9 + (2 \times -285) + (2 \times -399.0)] \text{ kJ}$$

$$= -1437.9 \text{ kJ}$$

63.  $CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O$ ,  $\Delta H = -890.4 \text{ kJ}$  ... (i)



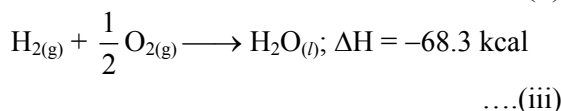
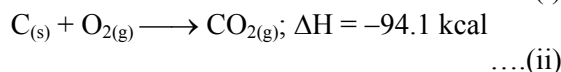
from (i), (ii), (iii).

$$\Delta_c H (CH_4) = \Delta_f H (CO_2) + 2\Delta_f H (H_2O) - \Delta_f H (CH_4) - 2\Delta_f H (O_2)$$

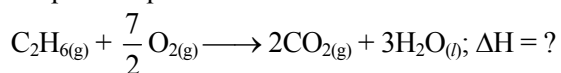
$$-890.4 = -395.5 + 2(-285.5) - \Delta_f H (CH_4) - 2 \times 0$$

$$\Delta_f H (CH_4) = -76.1 \text{ kJ mol}^{-1}$$

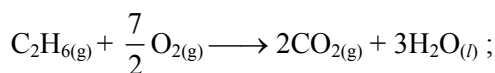
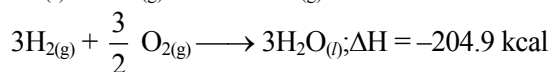
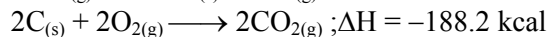
64.  $2C(s) + 3H_2(g) \longrightarrow C_2H_6(g)$ ;  $\Delta H = -21.1 \text{ kcal}$  ... (i)



Required equation:



Required equation is obtained by reversing equation (i), multiplying equation (ii) by 2 and equation (iii) by 3 and adding all the equations.



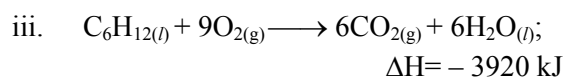
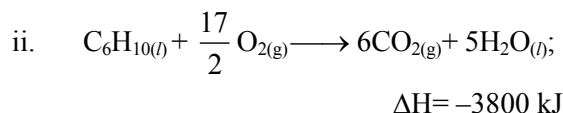
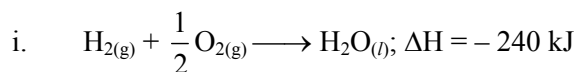
$$\Delta H = -372 \text{ kcal}$$

65. equation (i) + equation (ii) and dividing by 2;  
 $\frac{490 + 424}{2} = \frac{914}{2}$

66. The required reaction is  $2C(s) + H_2(g) \longrightarrow C_2H_2(g)$ , Applying the operation (i) + (ii) + (-iii), by Hess's law of heat summation; we get,  
 $\Delta H = \Delta H_1 + \Delta H_2 + \Delta H_3$   
 $= (-767) + (-266) + (1290) = 257 \text{ kJ}$ .



67. Given:



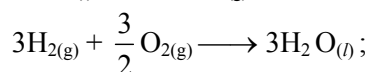
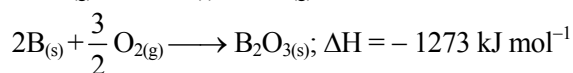
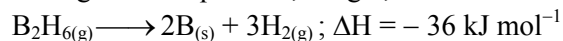
Required equation is  $\text{C}_6\text{H}_{10(\text{l})} + \text{H}_{2(\text{g})} \longrightarrow \text{C}_6\text{H}_{12(\text{l})};$   
 $\Delta H = ?$

It may be achieved by the operation (i) + (ii) - (iii).

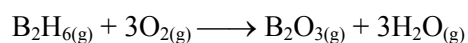
$$\Delta H = (-240) + (-3800) - (-3920)$$

$$= -4040 + 3920 = -120 \text{ kJ}$$

68. Reverse equation (iv), rewrite equation (i), multiply equation (iii) and (ii) by 3, and adding all the equations, we get,

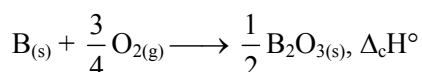
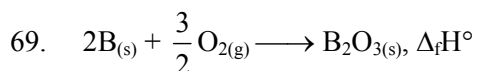


$$\Delta H = -286 \times 3 = -858 \text{ kJ mol}^{-1}$$



$$\Delta H = -36 - 1273 + 132 - 858$$

$$= -2167 + 132 = -2035 \text{ kJ mol}^{-1}$$



$$\Delta_c H^\circ = \frac{1}{2} \Delta_f H^\circ$$

70. When  $\Delta S = +ve$ , the change is spontaneous.

72. Randomness decreases in the case of crystallization of sucrose from solution.

73.  $\Delta_{\text{vap}} S = \frac{\Delta_{\text{vap}} H}{T} = \frac{37.3 \text{ kJ mol}^{-1}}{373 \text{ K}}$   
 $= 0.1 \text{ kJ mol}^{-1} \text{ K}^{-1} = 100 \text{ J mol}^{-1} \text{ K}^{-1}$

74.  $\Delta_{\text{vap}} S = \frac{\Delta_{\text{vap}} H}{T} = \frac{840 \text{ J mol}^{-1}}{100 \text{ K}} = 8.4 \text{ J mol}^{-1} \text{ K}^{-1}$

75.  $\Delta_{\text{vap}} S = \frac{(900 \times 18)}{373} = 43.4 \text{ JK}^{-1} \text{ mol}^{-1}$

76.

$\therefore$  Latent heat of vaporization of 1 g of water =  $x$  J

$\therefore$  Latent heat of vaporization of 9 g of water =  $9x$  J

$$\Delta S = \frac{q_{\text{rev}}}{T}$$

$$\Delta S = \frac{9x}{(100 + 273)} = \frac{9x}{373} = \frac{1}{2} \times \frac{18x}{373}$$

77. Because solid  $\longrightarrow$  solid,  $\Delta S$  is -ve and  $\Delta H$  is also -ve.

78. For reverse reaction, sign will change.

79.  $\Delta G = 0$ , for equilibrium process.

82.  $\Delta G = \Delta H - T\Delta S = 145600 - 300 \times 116$   
 $= 145600 - 34800$   
 $= 110.8 \text{ kJ / mol}$

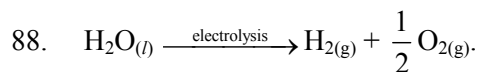
83.  $\Delta G = \Delta H - T\Delta S = 9.08 - (298 \times 0.0357)$   
 $= -1.56 \text{ kJ mol}^{-1}$

Since, the value of  $\Delta G$  is negative, the reaction is spontaneous at 298 K.

Also,  $\Delta H = +ve$ , therefore, the reaction is endothermic.

84. If  $\Delta G = -ve$ , reaction is spontaneous.

87. The compressor has to run for longer time releasing more heat to the surroundings.



89.  $\text{CaO}_{(\text{s})} + \text{H}_2\text{O}_{(\text{l})} \longrightarrow \text{Ca(OH)}_2$  is exothermic.

92.  $W = -p_{\text{ex}} \Delta V$   
 $= -1 \text{ atm}(6\text{L} - 2\text{L})$   
 $= -1 \text{ atm}(4\text{L})$   
 $= -4 \text{ L.atm} = -4 \times 101.3 \text{ J} = -405.2 \text{ J}$

$$\Delta U = q + W = 800 \text{ J} + (-405.2) \text{ J} = 394.8 \text{ J}$$

93. Since one mole of an ideal gas is compressed isothermally,  $\Delta U = 0$  for reversible process.

$\therefore \Delta U = q + W = 0$

$\therefore q = -W$

$$W = -2.303 nRT \log \left( \frac{P_1}{P_2} \right)$$

$$= -2.303 \times 1 \times 8.314 \times 302 \times \log \left( \frac{2}{10} \right)$$

$$= -2.303 \times 1 \times 8.314 \times 302 \times (-0.6989)$$

$$= 4041.74 \text{ J}$$

$$= (4041.74 \times 0.239) \text{ cal} = 966 \text{ cal}$$

$\therefore q = -966 \text{ cal}$



94. 50% of 880 kJ = 440 kJ  
 Since  $\Delta_{\text{evp}}H = 44 \text{ kJ mol}^{-1}$ , 440 kJ will require  $\frac{440}{44} = 10$  moles of water.  
 One mole of water = 18 g  
 $\therefore 10 \text{ moles} = 10 \times 18 = 180 \text{ g}$
95. Energy = Power  $\times$  time  
 $= 400 \text{ W} \times (5 \times 60 \text{ sec})$   
 $= 400 \times 5 \times 60 \text{ J}$   
 $(400 \times 5 \times 60) \text{ J} \equiv 50 \text{ g of H}_2\text{O} (50 \text{ mL H}_2\text{O})$   
 $x \text{ J} \equiv 18 \text{ g of H}_2\text{O} (1 \text{ mole})$   
 $\therefore x = \Delta_{\text{vap}} H(\text{H}_2\text{O}) = \frac{400 \times 5 \times 60 \times 18}{50}$   
 $= 43200 \text{ J} = 43.2 \text{ kJ mol}^{-1}$



### Competitive Thinking

4. Thermodynamics is a reversible process in which surroundings are always in equilibrium with system.
6. 1 L atm = 101.3 J  
 1 cal = 4.18 J  
 $\therefore 1 \text{ J} = \frac{1}{4.18} = 0.239 \text{ cal}$   
 1 L atm =  $0.239 \times 101.3 = 24.2 \text{ cal}$
7.  $p_{\text{ex}} = 101.325 \text{ kPa} = 101.325 \times 10^3 \text{ Pa}$   
 $V_1 = 10 \text{ dm}^3 = 10 \times 10^{-3} \text{ m}^3 = 0.01 \text{ m}^3$   
 $V_2 = 2 \text{ m}^3$   
 $w = -p_{\text{ex}} \cdot \Delta V$   
 $= -101.325 \times 10^3 \times (2 - 0.01)$   
 $= -201.6 \times 10^3 \text{ J}$   
 $= -201.6 \text{ kJ}$
8.  $V_1 = 5 \text{ m}^3, V_2 = 1 \text{ dm}^3 = 10^{-3} \text{ m}^3 = 0.001 \text{ m}^3$   
 $W = -p\Delta V = -100 \times 10^3 (0.001 - 5)$   
 $= 499.9 \times 10^3 \text{ J} = 499.9 \text{ kJ}$
9.  $\text{CH}_{4(g)} + 2\text{O}_{2(g)} \longrightarrow \text{CO}_{2(g)} + 2\text{H}_2\text{O}_{(l)}$   
 Methane    Oxygen    Carbon dioxide  
 $\Delta n = 1 - (1 + 2) = -2$   
 $W = -P\Delta V = -\Delta nRT = -[-2 \times 8.314 \times 300]$   
 $= +4988.4 \text{ J}$   
 This is the work done for combustion of 1 mole of methane.  
 $\therefore$  Work done for combustion of 0.5 mole of methane will be  $= +4988.4 \times 0.5$   
 $= +2494.2 \text{ J}$
10. The work done in chemical reaction is given as,  
 $W = -\Delta n_g RT$   
 For a combustion of ethane, the reaction is,  
 $2\text{C}_2\text{H}_6(g) + 7\text{O}_2(g) \longrightarrow 4\text{CO}_2(g) + 6\text{H}_2\text{O}(l)$   
 $\Delta n_g = 4 - (2+7)$   
 $= -5$   
 $W = -\Delta n_g RT = -(-5) \times 8.314 \times 300$   
 $= 12471 \text{ J}$   
 $= 12.471 \text{ kJ}$   
 $\therefore$  The work done during combustion of 2 mole (i.e.  $2 \times 30 \text{ g}$ ) of  $\text{C}_2\text{H}_6 = 12.471 \text{ kJ}$   
 $\therefore$  The work done during combustion of 90 g of  $\text{C}_2\text{H}_6 = \frac{90 \times 12.471}{2 \times 30}$   
 $= 18.706 \text{ kJ} \approx 18.71 \text{ kJ}$
11. 1 dm = 0.1 m  
 $\therefore 10 \text{ dm}^3 = 0.01 \text{ m}^3$   
 $W = -p_{\text{ex}} \Delta V$   
 $= -100 (0.01 - 1)$   
 $= 99 \text{ kJ}$
12. At 300 K, the reaction is  
 $\text{C}_2\text{H}_5\text{OH}_{(l)} + 3\text{O}_{2(g)} \rightarrow 2\text{CO}_{2(g)} + 3\text{H}_2\text{O}_{(l)}$   
 Therefore,  
 $\Delta n = 2 - 3 = -1$   
 $W = -p_{\text{ex}} \cdot \Delta V$   
 $= -\Delta nRT$   
 $= -(-1) \times 8.314 \times 300$   
 $= 2494 \text{ J}$   
 This work is done during the combustion of 1 mole of ethanol.  
 Now, 0.138 kg of ethanol = 138 g of ethanol  
 $= \frac{138}{46} \text{ mol of ethanol}$   
 $= 3 \text{ mol of ethanol}$   
 Work done for combustion of 3 moles of ethanol is  
 $W = 2494 \times 3 = 7482 \text{ J}$
13.  $n = \frac{\text{Mass of O}_2}{\text{Molar mass of O}_2} = \frac{1.6 \times 10^{-2} \text{ kg}}{3.2 \times 10^{-2} \text{ kg}} = 0.5$   
 $W = -2.303 nRT \log_{10} \left( \frac{V_2}{V_1} \right)$   
 $= -2.303 \times 0.5 \times 8.314 \times 300 \times \log \left( \frac{100}{10} \right)$   
 $= -2,872 \text{ J}$
14.  $U = U_{\text{electrical}} + U_{\text{nuclear}} + U_{\text{chemical}} + U_{\text{potential}} + U_{\text{kinetic}} (U_t + U_v + U_r)$ .



15.  $A \xrightarrow{-40} B$                        $A \xleftarrow{-40} B$   
 $\Delta H = 40 - 40 = 0$ .
17.  $\Delta U = q + W$   
 $\therefore$  On removal of heat ( $q$ ) and work ( $W$ ) from the system, the internal energy change ( $\Delta U$ ) will become negative, i.e., the internal energy of the system will decrease.
19.  $\Delta U = q + W$   
 $\Delta U = q - p_{\text{ex}} \cdot \Delta V$                       ( $\because W = -p_{\text{ex}} \cdot \Delta V$ )  
 For an isochoric process,  $\Delta V = 0$ ,  
 $\therefore \Delta U = q_v$
20.  $\Delta U = q + w$   
 $0 = q + w$  ( $\because \Delta U = 0$ , for isothermal process)  
 $\therefore q = -w$
21. In an adiabatic process, no heat is allowed to enter or leave the system. Hence,  $q = 0$ .  
 According to first law of thermodynamics,  
 $\Delta U = q + w$   
 $\therefore \Delta U = w$
22. In an adiabatic process, there is no exchange of heat between the system and its surroundings.  
 So,  $q = 0$ .  
 According to first law of thermodynamics,  
 $\Delta U = q + W$   
 $\therefore \Delta U = W$  or  $-\Delta U = -W$  (For adiabatic process)  
 Since, the given process is adiabatic expansion, the work is done by the system on the surroundings at the expense of system's internal energy. Hence, the internal energy of the system decreases in this process.  
 $\therefore$  For adiabatic expansion,  $-\Delta U = -W$ .  
 i.e.,  $\Delta U < 0$
23.  $\Delta U = q + W$   
 For isobaric condition,  
 $\Delta U = q_p + W$   
 $\Delta U = q_p - p_{\text{ex}} \cdot \Delta V$                       ( $\because W = -p_{\text{ex}} \cdot \Delta V$ )
24. As the system is closed and insulated, no heat enters or leaves the system, i.e.,  $q = 0$ ;  
 $\therefore \Delta U = q + W = W$ .
25. Enthalpy ( $H$ ) is defined as the sum of internal energy and energy due to pressure and volume,  $U + PV$
26.  $\Delta H = \Delta U + \Delta nRT$   
 $H_2 - H_1 = U_2 - U_1 + n_2 - n_1(RT)$   
 $\therefore H_2 - H_1 + U_1 - U_2 = n_2RT - n_1RT$
27. If  $\Delta n = -ve$ , then  $\Delta H < \Delta U$ .
28.  $\Delta n_g = 1 - \frac{3}{2} = \frac{-1}{2}$ , As  $\Delta n_g$  is negative,  
 $\Delta H < \Delta U$ .
29. In the given reaction,  $\Delta n = 0$   
 $\therefore \Delta H = \Delta U = 2.8 \text{ kJ}$
30. For this reaction,  $\Delta n = 0$                        $\therefore \Delta U = \Delta H$ .
31.  $\Delta H = \Delta U + \Delta nRT$   
 Since  $\Delta n = -2$   
 Then  $\Delta H = \Delta U - 2RT$ .
32. In the given reaction,  $\Delta n = 3 - (5 + 1) = -3$   
 $\therefore \Delta H = \Delta U - 3RT$                        $\therefore \Delta H - \Delta U = -3RT$
33. In the given reaction,  $\Delta n = \left(1 - \frac{1}{2}\right) = +0.5$   
 $\Delta H = \Delta U + \Delta nRT$   
 $\Delta H - \Delta U = \Delta nRT$   
 $= 0.5 \times 0.002 \text{ kcal} \times T$   
 $= 1 \times 10^{-3} \text{ kcal} \times T = T \text{ cal}$
34. For the formation of HCl,  
 $H_{2(g)} + Cl_{2(g)} \longrightarrow 2HCl_{(g)}$ ;  
 $\Delta n = 2 - 2 = 0$   
 $\therefore \Delta H = \Delta U$
35. In the formation of acetaldehyde from its constituent elements,  
 $2C_{(s)} + 2H_{2(g)} + \frac{1}{2} O_{2(g)} \longrightarrow CH_3CHO_{(l)}$ ;  
 $\Delta n = 0 - \left(2 + \frac{1}{2}\right) = -2.5$
36.  $CO_{(g)} + \frac{1}{2} O_{2(g)} \longrightarrow CO_{2(g)}$ ,  $\Delta n = 1 - \left(1 + \frac{1}{2}\right)$   
 $= -\frac{1}{2}$   
 $\Delta H = \Delta U + \Delta nRT$   
 $\Delta H = -283.3 - \frac{1}{2} \times \frac{8.314}{1000} \times 290 = -284.5 \text{ kJ}$ .
37.  $C_6H_{6(l)} + \frac{15}{2} O_{2(g)} \longrightarrow 6CO_{2(g)} + 3H_2O_{(l)}$ ;  
 $\Delta H = -781.1 \text{ kcal}$   
 $\Delta H = \Delta U + \Delta nRT$   
 $\Delta U = \Delta H - \Delta nRT$  (Here  $\Delta n = 6 - \frac{15}{2} = -1.5$ ,  
 $R = 1.98 \times 10^{-3} \text{ kcal K}^{-1} \text{ mol}^{-1}$ )  
 $\Delta U = -781.1 - (-1.5 \times 1.98 \times 10^{-3} \times 298)$   
 $= -780.1 \text{ kcal/mol}$



42. Greater the magnitude of the heat of formation, more stable is the compound formed.
43. Amount of water decomposed by 272 kJ = 18g = 1 mole  
Amount of water decomposed by 750 kJ  

$$= \frac{18 \times 750}{272} = \frac{49.6}{18} = 2.75 \text{ mole}$$
44. From the given reaction,  $\Delta H$  for the formation of 2 mole HCl = -184 kJ  
 $\therefore \Delta H$  for the formation of 1 mole HCl (i.e.,  
 $36.54 \times 10^{-3} \text{ kg}) = -\frac{184}{2} = -92 \text{ kJ}$   
 $\therefore \Delta H$  for the formation of 0.365 kg  

$$= \frac{0.365 \times (-92)}{36.54 \times 10^{-3}} = -920 \text{ kJ}$$
45.  $\text{S} + \text{O}_2 \longrightarrow \text{SO}_2$ ;  $\Delta H = -298 \text{ kJ}$   
Heat of formation for 1 mole (i.e., 64 g) of  $\text{SO}_2 = -298 \text{ kJ}$   
 $\therefore$  Heat of formation for 4 g of  $\text{SO}_2 = \frac{4 \times (-298)}{64}$   

$$= -18.6 \text{ kJ}$$
46.  $\Delta_r H^\circ = \sum \Delta_f H^\circ_{(\text{products})} - \sum \Delta_f H^\circ_{(\text{reactants})}$   

$$= [\Delta_f H^\circ(\text{CaO}) + \Delta_f H^\circ(\text{CO}_2)] - \Delta_f H^\circ(\text{CaCO}_3)$$
  

$$= [-635 + (-393)] - (-1207)$$
  

$$= -1028 + 1207$$
  

$$= +179 \text{ kJ mol}^{-1}$$
47.  $2\text{PCl}_5 \longrightarrow 2\text{P} + 5\text{Cl}_2$ ;  $\Delta H = -340 \text{ kJ}$  .....(i)  
Required equation is:  
 $\text{P} + \frac{5}{2}\text{Cl}_2 \longrightarrow \text{PCl}_5$ ;  $\Delta H = ?$   
The required equation is obtained by reversing equation (i) and dividing it by 2.  
 $\therefore \Delta H = \frac{340}{2} = 170 \text{ kJ}$ .
48. Heat of combustion of 1 mole (i.e., 16 g) of  $\text{CH}_4 = -800 \text{ kJ}$   
 $\therefore$  Heat of combustion of  $4 \times 10^{-4} \text{ kg}$  of  $\text{CH}_4 = \frac{4 \times 10^{-4} \times (-800)}{16 \times 10^{-3}} = -20 \text{ kJ}$
49. Given: Weight of iron burnt = 4g;  
Heat liberated = 29.28 kJ and atomic weight of iron (Fe) = 56.  
In ferric oxide ( $\text{Fe}_2\text{O}_3$ ), 2 moles of iron or  $2 \times 56 = 112 \text{ g}$  of iron are burnt.

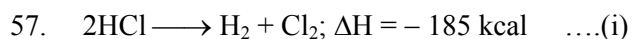
Thus, when 4 grams of iron are burnt, then heat liberated = 29.28 kJ, therefore when 112 grams of the iron are burnt, then heat liberated

$$= \frac{29.28 \times 112}{4} = -819.8 \text{ kJ (Minus sign due to liberation of heat)}$$

50. For 1 mole of  $\text{CS}_2$ ,  $\Delta H = 22.0 \text{ kcal}$ .  
But heat evolved for 24 g C and 128 g S is 2 mole of  $\text{CS}_2$ ;  $\Delta H = 22.0 \times 2 = 44 \text{ kcal}$ .
51.  $\text{C} + \text{O}_2 \longrightarrow \text{CO}_2$ ;  $\Delta H = -393.5 \text{ kJ}$   
Heat released in the formation of 1 mole (i.e., 44 g) of  $\text{CO}_2$  is -393.5 kJ  
 $\therefore$  Heat released in the formation of 35.2 g of  $\text{CO}_2 = \frac{-393.5 \times 35.2}{44}$   

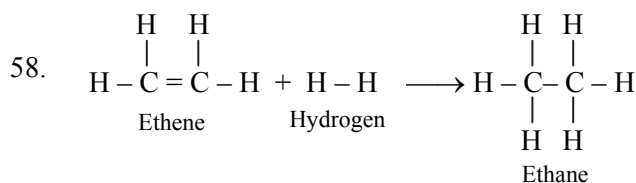
$$= -314.8 \text{ kJ}$$
  

$$\approx -315 \text{ kJ}$$
52. Amount of heat liberated when 1 mole i.e., 18 g of water is decomposed = +68 kcal ( $\because$  given reaction is formation of 1 mole of water)  
Amount of heat liberated when 7.2 g of water is decomposed is  $\frac{7.2 \times (+68)}{18} = +27.2 \text{ kcal}$
53. Both Xe and  $\text{F}_2$  are gaseous elements at 25 °C and in their standard states and form  $\text{XeF}_{4(\text{g})}$  hence,  
 $\Delta_f H^\circ = \Delta H^\circ$ .
54. 4g  $\text{H}_2 = 2$  moles.  
Bond energy for 1 mole of  $\text{H}_2 = \frac{208}{2} = 104 \text{ kcal}$ .
55. Enthalpy change of a reaction is given as  
 $\Delta H^\circ_{(\text{reaction})} = \text{Energy required to break reactant bonds} - \text{energy required to break product bonds}$   
 $\therefore \Delta H^\circ_{(\text{reaction})} = \sum H^\circ_{(\text{reactant bonds})} - \sum H^\circ_{(\text{product bonds})}$
56.  $\frac{1}{2}\text{H}_2 + \frac{1}{2}\text{Cl}_2 \longrightarrow \text{HCl}$ ,  $\Delta H = -90 \text{ kJ}$   
 $\therefore \Delta H = \frac{1}{2}E_{\text{H-H}} + \frac{1}{2}E_{\text{Cl-Cl}} - E_{\text{HCl}}$   
 or  $-90 = \frac{1}{2} \times 430 + \frac{1}{2} \times 240 - E_{\text{HCl}}$   
 $\therefore E_{\text{H-Cl}} = 425 \text{ kJ mol}^{-1}$ .

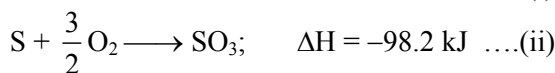


Required equation;  $\frac{1}{2}\text{H}_2 + \frac{1}{2}\text{Cl}_2 \longrightarrow \text{HCl}$  is obtained by reversing equation (i) and dividing it by 2.

$\therefore \Delta_f H$  of HCl =  $\frac{185}{2} = 92.5 \text{ kcal}$ .



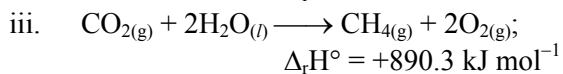
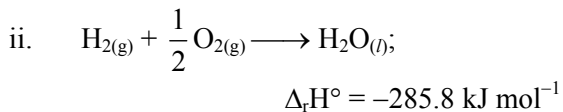
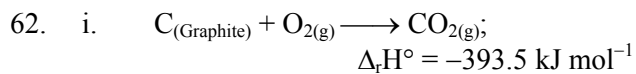
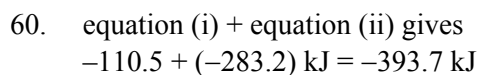
$$\begin{aligned} \Delta H &= \Sigma \Delta H_{(\text{reactant bonds})} - \Sigma \Delta H_{(\text{product bonds})} \\ &= [\Delta H(\text{C}=\text{C}) + 4 \Delta H(\text{C}-\text{H}) + \Delta H(\text{H}-\text{H})] \\ &\quad - [6 \Delta H(\text{C}-\text{H}) + \Delta H(\text{C}-\text{C})] \\ &= [1 \text{ mol} \times 600 \text{ kJ mol}^{-1} + 4 \text{ mol} \times 410 \text{ kJ mol}^{-1} \\ &\quad + 1 \text{ mol} \times 400 \text{ kJ mol}^{-1}] - [6 \text{ mol} \times 410 \text{ kJ mol}^{-1} \\ &\quad + 1 \text{ mol} \times 350 \text{ kJ mol}^{-1}] \\ &= [600 + 1640 + 400] - [2460 + 350] \\ &= 2640 - 2810 \\ &= -170 \text{ kJ} \end{aligned}$$



Required equation  $\text{SO}_2 + \frac{1}{2}\text{O}_2 \longrightarrow \text{SO}_3$  is

obtained by reversing (i) and adding (ii),

$\therefore \Delta H = 298.2 + (-98.2) \text{ kJ} = +200 \text{ kJ}$



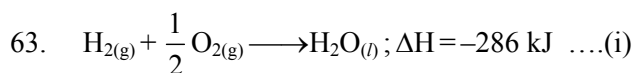
Required equation is



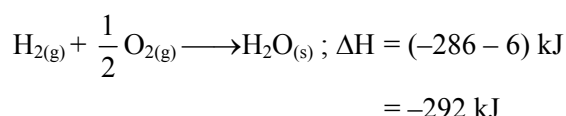
This can be obtained by applying the operation:

(i) + 2(ii) + (iii)

$\therefore \Delta_r H^\circ = -393.5 + 2(-285.8) + 890.3 = -74.8 \text{ kJ mol}^{-1}$



Equation (i) + Reverse of Equation (ii) gives,

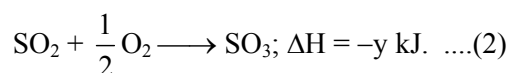
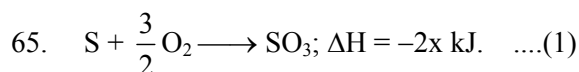


$\therefore \Delta H$  for formation of 1 mol of ice is  $-292 \text{ kJ}$ .

i.e,  $\Delta H$  for formation of 18 g of ice is  $-292 \text{ kJ}$ .

$\therefore \Delta H$  for formation of 100 g of ice

$= -292 \times \frac{100}{18} = -1622 \text{ kJ}$ .



For reaction (2),

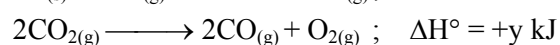
$\Delta H = \Delta_f H_{(\text{SO}_3)} - \Delta_f H_{(\text{SO}_2)}$

$\therefore \Delta_f H_{(\text{SO}_2)} = \Delta_f H_{(\text{SO}_3)} - \Delta H = -2x + y$  or  $y - 2x$

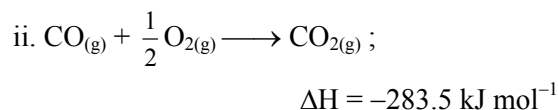
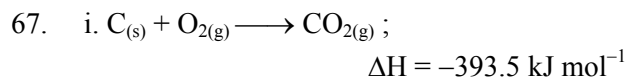
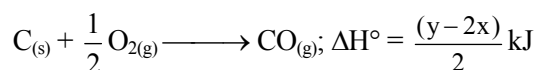


Required equation:  $\text{C}_{(\text{s})} + \frac{1}{2}\text{O}_{2(\text{g})} \longrightarrow \text{CO}_{(\text{g})};$

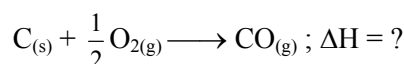
is obtained by multiplying equation (i) by 2 and subtracting reverse of equation (ii) from it and dividing the equation so formed by 2.



Required equation:



Required equation is



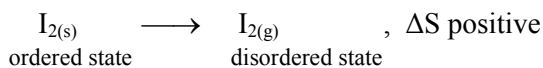
It may be achieved by applying the operation:

(i) + (-ii).

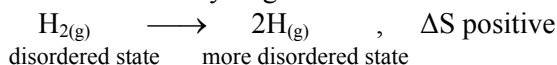
$\therefore \Delta H = -393.5 + (+283.5) = -110.0 \text{ kJ mol}^{-1}$



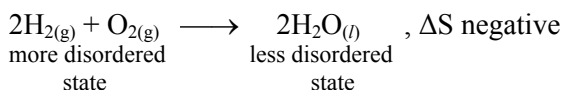
68. Sublimation of iodine:



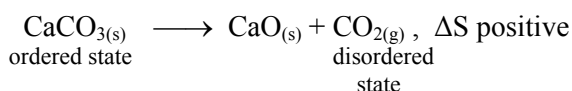
Dissociation of hydrogen:



Formation of water:

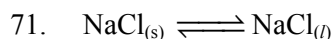


Thermal decomposition of calcium carbonate:



69.  $\Delta S = \frac{q_{\text{rev}}}{T} \quad \therefore \text{unit of } S \text{ is } \text{J K}^{-1} \text{ mol}^{-1}.$

70.  $\Delta S = \frac{q_{\text{rev}}}{T} = \frac{6000}{273} = 21.98 \text{ J K}^{-1} \text{ mol}^{-1}$



Given :  $\Delta H = 30.5 \text{ kJ mol}^{-1}$

$\Delta S = 28.8 \text{ J K}^{-1} = 28.8 \times 10^{-3} \text{ kJ K}^{-1}$

By using  $\Delta S = \frac{\Delta H}{T}$ ;

$T = \frac{\Delta H}{\Delta S} = \frac{30.5}{28.8 \times 10^{-3}} = 1059 \text{ K}$

72. The entropy change =  $\frac{\text{heat of vaporisation}}{\text{temperature}}$

$\therefore \text{heat of vaporization} = 540 \text{ cal/g}$   
 $= 540 \times 18 \text{ cal mol}^{-1}$

Temperature of water =  $100 + 273 = 373 \text{ K}$

$\therefore \text{Entropy change} = \frac{540 \times 18}{373} = 26.06 \text{ cal mol}^{-1} \text{ K}^{-1}$

73.  $\Delta_{\text{vap}}S = \frac{186.5}{373} = 0.5 \text{ kJ K}^{-1} \text{ mol}^{-1}.$

74. The entropy change of a system in a process is equal to the amount of heat transferred to it in a reversible manner divided by the temperature at which the process occurs.

$\therefore \Delta S = \frac{q_{\text{rev}}}{T}$

Now,  $q_{\text{rev}}$  for an isothermal change is given as:

$$q_{\text{rev}} = -w = nRT \ln \left( \frac{P_i}{P_f} \right)$$

$$\therefore \Delta S = \frac{nRT \ln \left( \frac{P_i}{P_f} \right)}{T}$$

$$= nR \ln \left( \frac{P_i}{P_f} \right)$$

75. Standard entropy of formation of  $\text{CO}_{2(g)}$   
 $= \text{standard entropy of } \text{CO}_{2(g)} - [\text{standard entropy of } (\text{C})_{(s)} + \text{standard entropy of } \text{O}_{2(g)}]$   
 $= 213.5 - [5.740 + 205] = 2.76 \text{ J/K}.$

78. As the randomness of particles reduces, entropy decreases.

80. During the adsorption of gas, degree of randomness decreases as the gas molecules adhere together. Thus,  $\Delta S$  is negative which implies that  $\Delta H$  is also highly negative ( $\because \Delta G = \Delta H - T\Delta S$  and for spontaneous process,  $\Delta G < 0$ )

83.  $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = 58040 - (298 \times 176.7)$   
 $= 58040 - 52656$   
 $= 5384 \text{ J} = 5.38 \text{ kJ}$

84.  $\Delta G = \Delta H - T\Delta S$

$\Delta G = 0$  at equilibrium

$\therefore \Delta H = T\Delta S$  or  $30.56 = T \times 0.066$

$T = 463 \text{ K}.$

85.  $\Delta G = \Delta H - T\Delta S$

$\Delta H = 30.58 \text{ kJ}, \Delta S = 66.1 \text{ J K}^{-1} = 0.0661 \text{ kJ K}^{-1}$

At equilibrium,  $\Delta G = 0$

$\therefore 0 = \Delta H - T\Delta S$

$T = \frac{\Delta H}{\Delta S} = \frac{30.58}{0.0661} = 462.6 \text{ K}$

86.  $\Delta H = -400 \text{ kJ mol}^{-1}$   
 $\Delta S = -20 \text{ kJ mol}^{-1} \text{ K}^{-1}$

Since, both  $\Delta H$  and  $\Delta S$  are negative, the reaction will be spontaneous at lower temperatures.

The temperature at which change over between spontaneous and non-spontaneous

behaviour occurs is calculated as :  $T = \frac{\Delta H}{\Delta S}$

$\therefore T = \frac{-400 \text{ kJ mol}^{-1}}{-20 \text{ kJ mol}^{-1} \text{ K}^{-1}}$

$\therefore T = 20 \text{ K}$

Thus, the given reaction is spontaneous below 20 K.



87.  $\Delta G = \Delta G^\circ + RT \ln Q$  ....(i)

At equilibrium  $\Delta G = 0$  and  $Q = K$ ,  
thus equation (i) becomes,

$$0 = \Delta G^\circ + RT \ln K$$

$$\therefore \Delta G^\circ = -RT \ln K = -2.303 RT \log_{10} K$$

88.  $K < 1.0$  indicates that the concentration of reactants is greater than that of the products, i.e., the reaction does not proceed in the forward direction. Hence, the reaction is non-spontaneous and  $\Delta G^\circ$  is positive.

89.  $\Delta G^\circ = -2.303 RT \log_{10} K_{sp}$

$$63.3 = -2.303 \times 8.314 \times 10^{-3} \times 298 \times \log_{10} K_{sp}$$

$$\log_{10} K_{sp} = \frac{63.3}{2.303 \times 8.314 \times 10^{-3} \times 298}$$

$$\log_{10} K_{sp} = -11.09$$

$$K_{sp} = \text{Antilog}(-11.09) = 8.0 \times 10^{-12}$$

90.  $\Delta H = \Delta U + \Delta nRT$

$$\Delta H = 2.1 + (2 \times 1.98 \times 10^{-3} \times 300)$$

$$\therefore \Delta H = 3.28 \text{ kcal}$$

$$\Delta G = \Delta H - T\Delta S$$

$$= 3.28 - (300 \times 20 \times 10^{-3})$$

$$= -2.72 \text{ kcal}$$

$$\approx -2.7 \text{ kcal}$$

91. According to III law of thermodynamics.

92. Third law of thermodynamics helps in calculating entropy of different temperatures.

93. It does not violate the first law of thermodynamics but violates the second law of thermodynamics.

94.  $\Delta_{\text{soln}}H = \Delta_L H + \Delta_{\text{hydra}}H$

$$= 777.8 - 774$$

$$= 3.8 \text{ kJ mol}^{-1}$$

The free energy change ( $\Delta G$ ) in dissolving one mole of NaCl is calculated as follows:

$$\Delta G = \Delta H - T\Delta S$$

$$\Delta H = 3.8 \text{ kJ mol}^{-1}; \Delta S = 0.043 \text{ kJ K}^{-1} \text{ mol}^{-1}$$

$$\therefore \Delta G = 3.8 - (298 \times 0.043)$$

$$= -9.014 \text{ kJ mol}^{-1}$$

$$\approx -9.1 \text{ kJ mol}^{-1}$$

95. For the given reaction,  $X_2Y_{4(l)} \longrightarrow 2XY_{2(g)}$

$$\Delta n = 2 - 0 = 2$$

For the given reaction,

$$\Delta H = \Delta U + \Delta nRT \quad \dots(i)$$

Substituting the values in equation (i),

$$\Delta H = 2 + [2 \times (2 \times 10^{-3}) \times 300]$$

$$(\because R = 1.987 \text{ cal K}^{-1} \text{ mol}^{-1} \approx 2 \text{ cal K}^{-1} \text{ mol}^{-1})$$

$$\approx 2 \times 10^{-3} \text{ kcal K}^{-1} \text{ mol}^{-1})$$

$$\Delta H = 2 + [1.2] = 3.2 \text{ kcal} = 3.2 \times 10^3 \text{ cal}$$

$$\Delta G = \Delta H - T\Delta S \quad \dots(ii)$$

Substituting the values in equation (ii),

$$\Delta G = 3.2 \times 10^3 - (300 \times 20) = 3200 - 6000$$

$$\Delta G = -2800 \text{ cal}$$

96. In liquid state, the constituent particles are held together by intermolecular forces of attraction. Energy is required to overcome these attractive forces between the particles in liquid state and to convert it to gaseous state. The value of heat of vaporization gives the quantity of heat absorbed when one mole of a substance in liquid state is converted to its gaseous state. Larger the value of heat of vaporization, stronger is the intermolecular forces between the particles. Hence, the order of intermolecular forces in the given liquids is  $H_2O > C_2H_5OH > CS_2$ .

97.  $q_{\text{rev}} = -W_{\text{max}} = 2.303 \times nRT \log_{10} \frac{V_2}{V_1}$

$$n=2, R=8.314 \text{ J K}^{-1} \text{ mol}^{-1}, T=27+273=300 \text{ K}$$

$$V_1 = 10 \text{ L}, V_2 = 100 \text{ L}$$

$$\therefore q_{\text{rev}} = 2.303 \times 2 \times 8.314 \times 300 \times \log_{10} \left( \frac{100}{10} \right)$$

$$= 2.303 \times 2 \times 8.314 \times 300 \times \log_{10} (10)$$

$$= 2.303 \times 2 \times 8.314 \times 300$$

$$\Delta S = \frac{q_{\text{rev}}}{T}$$

$$\therefore \Delta S = \frac{2.303 \times 2 \times 8.314 \times 300}{300}$$

$$= 38.3 \text{ J K}^{-1}$$

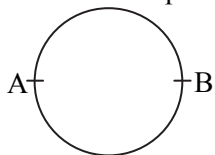




## Evaluation Test

1. The enthalpy change for a reaction does not depend upon the nature of intermediate reaction steps. This is in accordance with Hess's law.

2. Reversible path



Irreversible path

For cyclic process, the net change in internal energy is equal to zero. The change in internal energy does not depend upon the path.

3. For same mass, temperature, pressure and volume,

$$W_{\max} \propto \frac{1}{\text{Molecular mass}}$$

Lower the molecular mass, higher is the magnitude of work. Among the options given, hydrogen has the least molecular mass and thus the maximum work is done in the case of hydrogen.

5.  $C_{(s)} + \frac{1}{2} O_{2(g)} \longrightarrow CO_{(g)} \quad \Delta n = 1 - \frac{1}{2} = \frac{1}{2}$

$$\Delta H = \Delta U + \Delta nRT \quad \therefore \Delta H - \Delta U = \frac{1}{2} \times 8.314 \times 298 = 1238.78 \text{ J/mol.}$$

6. To decide the spontaneity of a process, both  $\Delta H$  and  $\Delta S$  must be considered. An endothermic process can become spontaneous at high temperatures (when  $T \cdot \Delta S > \Delta H$ ). Similarly, an exothermic process can be non-spontaneous at high temperatures.

7.  $\frac{1}{2} X_2 + \frac{3}{2} Y_2 \longrightarrow XY_3$

$$\begin{aligned} \Delta S_{\text{reaction}}^{\circ} &= \Sigma \Delta S_{\text{products}}^{\circ} - \Sigma \Delta S_{\text{reactants}}^{\circ} \\ &= 50 - \left( \frac{1}{2} \times 60 + \frac{3}{2} \times 40 \right) \\ &= 50 - \frac{1}{2} \times 60 - \frac{3}{2} \times 40 \text{ J K}^{-1} \text{ mol}^{-1} \end{aligned}$$

Using equation,  $\Delta G = \Delta H - T\Delta S$

$\Delta H = -30 \text{ kJ}$ ,  $\Delta S = -40 \text{ J K}^{-1} \text{ mol}^{-1}$  and at equilibrium,  $\Delta G = 0$

$$\therefore T = \frac{\Delta H}{\Delta S} = \frac{-30 \times 1000}{-40} = 750 \text{ K}$$

8. Stronger the acid, more will be heat of neutralisation. Negative sign indicates evolution of heat.

9. Formation of HCl  $\equiv \frac{1}{2} H_2 + \frac{1}{2} Cl_2 \longrightarrow HCl$

$$\text{B.E. (kcal)} \equiv \frac{1}{2} \times 104 + \frac{1}{2} \times 58 \longrightarrow 103$$

$$\begin{aligned} \Delta H_{(HCl)} &= \Sigma \text{B.E.}_{\text{Reactants}} - \Sigma \text{B.E.}_{\text{Products}} \\ &= 52 + 29 - 103 = -22 \text{ kcal/mole.} \end{aligned}$$



10.  $\Delta H = \Delta U + \Delta nRT$   
 $\therefore \Delta H - \Delta U = \Delta nRT$   
 $= (12 - 15) \times 8.315 \times 298 = -7.432 \text{ kJ}$
11.  $\text{C}_{(s)} + \text{O}_{2(g)} \longrightarrow \text{CO}_{2(g)}$   $\Delta H = -394 \text{ kJ/mol}$  = heat of formation of  $\text{CO}_2$ . (in the form of graphite)
12. Vapourisation of  $\text{H}_2\text{O}$ :  $\text{H}_2\text{O}_{(l)} \longrightarrow \text{H}_2\text{O}_{(g)}$ ;  $\Delta H = 10.52 \text{ kcal}$   
 $\Delta H = \Delta_f H_{(\text{H}_2\text{O}_{(g)})} - \Delta_f H_{(\text{H}_2\text{O}_{(l)})}$   
 $\Delta_f H_{(\text{H}_2\text{O}_{(g)})} = \Delta H + \Delta_f H_{(\text{H}_2\text{O}_{(l)})} = 10.52 + (-68.32) = -57.80 \text{ kcal/mol}$
13.  $\text{Ag}_2\text{O} \longrightarrow 2\text{Ag} + \frac{1}{2} \text{O}_{2(g)}$ ;  $q_v = \Delta U = 30.66 \text{ kJ}$   
 $q_p = q_v + \Delta nRT$   
 $\Delta n_g RT > 0$   
 $\therefore q_p > q_v$  i.e.,  $q_p > 30.66 \text{ kJ}$ .
14. More positive the heat of formation, less will be the stability associated with the product.
15. There are 4 N – H bonds present in  $\text{N}_2\text{H}_4$ .  
 $\therefore$  Bond energy =  $391 \times 4 = 1564 \text{ kJ mol}^{-1}$   
 $\therefore$  Bond energy of N – N in  $\text{N}_2\text{H}_4 = (1724 - 1564) \text{ kJ mol}^{-1} = 160 \text{ kJ mol}^{-1}$
16. (i)  $\text{H}_{2(g)} + \frac{1}{2} \text{O}_{2(g)} \longrightarrow \text{H}_2\text{O}_{(l)}$ ,  $\Delta H_1 = -a_1 \text{ kJ}$   
(ii)  $\text{H}_{2(g)} + \frac{1}{2} \text{O}_{2(g)} \longrightarrow \text{H}_2\text{O}_{(g)}$ ;  $\Delta H_2 = -a_2 \text{ kJ}$   
In case of reaction (i),  
 $\Delta n_1 = n_{\text{products}(g)} - n_{\text{reactants}(g)}$   
 $= 0 - \left(1 + \frac{1}{2}\right) = -1.5$   
 $\Delta H_1 = \Delta U + \Delta n_1 RT$   
 $-a_1 = \Delta U - 1.5 RT \quad \dots(1)$   
In case of reaction (ii),  
 $\Delta n_2 = n_{\text{products}(g)} - n_{\text{reactants}(g)}$   
 $= 1 - \left(1 + \frac{1}{2}\right) = -0.5$   
 $\Delta H_2 = \Delta U + \Delta n_2 RT$   
 $-a_2 = \Delta U - 0.5 RT \quad \dots(2)$   
Comparing equations (1) and (2),  $a_2 < a_1$
17. For an endothermic reaction, a minimum amount of energy equal to  $\Delta H$  must be supplied.
18. Since the reaction is non-spontaneous ( $\Delta G$  is +ve)  
As  $\Delta S$  is positive (given),  $\Delta H$  must be +ve. It means reaction is endothermic.
19.  $\Delta H$  has minimum value at equilibrium i.e., at  $\Delta G = 0$   
Since,  $\Delta G = \Delta H - T\Delta S$   
 $\therefore \Delta H = T\Delta S$   
 $\therefore \Delta H = 298 \times 150 = 44700 \text{ J} = 44.7 \text{ kJ}$



20.  $\Delta G = \Delta H - T\Delta S$   
 $= -270.6 - [300 \times (-139 \times 10^{-3})] = -270.6 + 41.7 = -228.9 \text{ kJ/mol}$
21. Crystallisation involves arrangement of molecules in a perfectly ordered manner i.e., minimum randomness.
22. At 298 K,  $\Delta H$  is  $\Delta H^\circ$  i.e., standard heat of formation,  
 For,  $\text{CCl}_4(\text{g}) + 2\text{H}_2\text{O}(\text{g}) \longrightarrow \text{CO}_2(\text{g}) + 4\text{HCl}(\text{g}); \Delta H^\circ = ?$   
 $\Delta H^\circ_{\text{reaction}} = \Delta H^\circ_{\text{Products}} - \Delta H^\circ_{\text{Reactants}}$   
 $= \Delta_f H^\circ_{(\text{CO}_2)} + 4 \times \Delta_f H^\circ_{(\text{HCl})} - \Delta_f H^\circ_{(\text{CCl}_4)} - 2 \times \Delta_f H^\circ_{(\text{H}_2\text{O})}$   
 $= -94.1 + 4 \times (-22.1) - (-25.5) - 2 \times (-57.8)$   
 $= -41.4 \text{ kcal}$
23. For a reversible, isothermal expansion, temperature of system and surroundings are same. Heat absorbed by the system is equal to heat lost by surroundings so that total entropy change is zero.  
 $\Delta S_{\text{sys}} + \Delta S_{\text{surr}} = 0$   
 $\therefore \Delta S_{\text{sys}} = -\Delta S_{\text{surr}}$
24. For reversible process, under isothermal conditions,  
 $W = -2.303 nRT \log_{10} \frac{P_1}{P_2}$   
 $= -2.303 \times 3 \times 8.314 \times 300 \log_{10} \frac{1.01 \times 10^5}{5.05 \times 10^6}$   
 $= +2.9277 \times 10^4 \text{ J}$
25.  $W_{\text{max}} = -2.303 nRT \log \frac{V_2}{V_1}$   
 $-831.4 = -2.303 \times 1 \times 8.314 \times T \times \log \left( \frac{20}{2} \right)$   
 $T = \frac{-831.4}{-2.303 \times 8.314} = 43.42 \text{ K}$

# 04 Electrochemistry



## Hints



## Classical Thinking

2. Oxidation is a process in which a species loses electron(s). In 'A', 'B' and 'D' the species accepts electron(s). Therefore, these are reduction reactions while the reaction in option 'C' is oxidation reaction.
3. A reducing agent itself undergoes oxidation. In the given reaction, nickel undergoes oxidation.  

$$\text{Ni} \longrightarrow \text{Ni}^{2+} + 2\text{e}^-$$
 Hence, Ni serves as a reducing agent.
5. Electrolyte is a substance which in aqueous or fused state conducts electricity.
8. Sulphuric acid being strong electrolyte undergoes complete ionization and hence produces more ions.  
 Therefore it will be the best conductor of electricity.
11. Conductance is reciprocal of resistance.  

$$R = \frac{1}{C}$$
 $\therefore$  for highest resistance, lowest conductance is required.  
 $\therefore$  electrolyte with lowest conductance of  $9.2 \times 10^{-9} \text{ ohm}^{-1} \text{ cm}^{-1}$  will offer higher resistance.
12. Molar conductivity =  $\frac{1000X}{M}$ .
16. cell constant,  $b = \frac{l}{a} = \frac{3}{4}$
17. Cell constant,  $b = \kappa \times R$   
 $\therefore b = 0.002765 \times 400 = 1.106 \text{ m}^{-1}$
18. Molar conductance,  $\wedge = \frac{1000\kappa}{C}$   

$$= \frac{1000 \times 6.3 \times 10^{-2}}{0.1}$$

$$= 630 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$$
19.  $\wedge_{\text{m}}^{\circ}(\text{CH}_3\text{COOH}) = \wedge_{\text{m}}^{\circ}(\text{CH}_3\text{COONa}) + \wedge_{\text{m}}^{\circ}(\text{HCl}) - \wedge_{\text{m}}^{\circ}(\text{NaCl})$   

$$= 91 + 426.16 - 126.45$$

$$= 390.71 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$$

$$20. \alpha = \frac{\wedge}{\wedge_{\circ}} = \frac{50}{250} = 0.2$$

$$\alpha = 0.2 \times 100 = 20 \%$$

$$21. \wedge_{\text{m}}^{\circ}(\text{C}_6\text{H}_5\text{COOH}) = \wedge_{\text{m}}^{\circ}(\text{C}_6\text{H}_5\text{COO}^-) + \wedge_{\text{m}}^{\circ}(\text{H}^+)$$

$$= 42 + 288.42$$

$$= 330.42$$

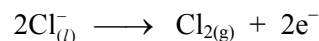
$$\% \alpha = \frac{\wedge}{\wedge_{\circ}} = \frac{128}{330.42} \times 100$$

$$\therefore \alpha \approx 39 \%$$

22. Depending upon the type of electrochemical cell, anode and the cathode may be positive or negative.

23. Cell used for metal plating is a type of electrolytic cell whereas lead storage cell, fuel cells and nickel – cadmium cell (NICAD) are a type of voltaic (galvanic) cells.

27. In the electrolysis of aqueous NaCl solution,  
 At anode:



This is true for electrolysis of both aqueous NaCl and molten NaCl.

33.  $W = z \cdot I \cdot t = z \cdot Q$   
 When  $Q = 1$  coulomb i.e.,  $I = 1$  ampere and  $t = 1$  second,

$$W = z$$

i.e., amount of substance liberated is equal to electrochemical equivalent.

34.  $W = zIt$  ;

$$z = \frac{W}{It} = \frac{W}{Q} = \frac{\text{gram}}{\text{Coulomb}} \quad [\because Q = It]$$

Where,

$W$  = amount of substance liberated in gram.

$Q$  = quantity of electricity passed in Coulomb.

$z$  = electrochemical equivalent.

$I$  = current in amperes.

$t$  = time in seconds.

35. One faraday is the charge on one mole of electrons.  
 $\therefore$  1 mole of electrons i.e.  $6.023 \times 10^{23}$  electrons are involved when a faraday of electricity is passed.



36.  $z = \frac{E}{96500}$   
 $\therefore E = z \times 96,500$   
 But,  $z = \frac{W}{I \times t}$   
 $\therefore E = \frac{W \times 96,500}{I \times t}$
37. Equivalent mass =  $\frac{\text{Atomic mass}}{\text{Valency}} = \frac{65}{2} = 32.5$
38.  $Q = 36,000 \text{ C}$ ,  $I = 10 \text{ A}$   
 $Q = I \times t$   
 $t = \frac{Q}{I} = \frac{36,000}{10} = 3600 \text{ s} = 1 \text{ hour.}$
39. Electricity required  
 = number of gm equivalent  $\times$  96500 Coulombs  
 =  $0.5 \times 96500$   
 = 48250 C
40. 108 g of Ag  $\equiv$  1 mole of Ag  
 $\text{Ag}_{(\text{aq})}^+ + e^- \longrightarrow \text{Ag}_{(\text{s})}$   
 $\therefore$  Charge on 1 mole of electrons i.e., 1 F of electricity is required to liberate 1 mole of Ag from  $\text{AgNO}_3$  solution.
41. 1 Faraday of electricity liberates 1g equivalent of hydrogen.  
 $\therefore$  2 g hydrogen  $\equiv$  2 g equivalent of hydrogen.  
 $\therefore$  2 Faradays of electricity are required to liberate 2 g of hydrogen.
42.  $\text{Cu}^{2+} + 2e^- \longrightarrow \text{Cu}$   
 $\therefore$  Charge of 2 moles of  $e^-$  is required to reduce 1 mole of  $\text{Cu}^{+2}$  to Cu.  
 $\therefore$  Charge on 2 mole of  $e^- = 2 \times 96500 \text{ C}$   
 $= 193000 \text{ C}$   
 $= 1.93 \times 10^5 \text{ C}$
43.  $E = z \times 96500$   
 $= 3.4 \times 10^{-7} \times 96500$   
 $= 3.281 \times 10^{-2} \text{ kg}$
44.  $W = \frac{E \times I \times t}{96500}$   
 $\therefore 1.8 = \frac{E \times 3 \times 50 \times 60}{96500}$   
 $\therefore E = \frac{1.8 \times 96500}{3 \times 50 \times 60}$   
 $\therefore E = 19.3$

45.  $\text{Al}^{3+} + 3e^- \longrightarrow \text{Al}$   
 Therefore, one Al atom absorbs 3 electrons.  
 So, one mole  $\text{Al}^{3+}$  will absorb charge of 3 moles of electrons i.e., 3 F.  
 $3F \equiv 1 \text{ mol of Al} \equiv 6.023 \times 10^{23} \text{ atoms of Al}$   
 $\therefore 1F \equiv \frac{1}{3} \text{ mole of Al}$   
 $\equiv \frac{1}{3} (6.023 \times 10^{23} \text{ atoms}) \text{ of Al}$   
 $\equiv 2.008 \times 10^{23} \text{ atoms of Al}$
46.  $\text{Al}_{(\text{aq})}^{3+} + 3e^- \longrightarrow \text{Al}_{(\text{s})}$   
 For aluminium,  
 1 gm atom  $\equiv$  1 mole.  
 $\therefore$  1 mole i.e., 27 g of Al is deposited by charge of 3 moles of electrons.  
 $\therefore$  3 N electrons are required to deposit 1 g atom of Al.
47.  $\text{Fe}_{(\text{aq})}^{3+} + 3e^- \longrightarrow \text{Fe}_{(\text{s})}$   
 $\therefore$  56 g of Fe is deposited by 3 Faraday of electricity.  
 So, 0.6 Faraday will deposit =  $\frac{56 \times 0.6}{3} = 11.2 \text{ g}$
48. Equivalent mass of Al =  $\frac{\text{Atomic mass}}{\text{Valency}}$   
 $= \frac{27}{3} = 9$   
 $W = \frac{ItE}{96500}$   
 $100 = \frac{125 \times t \times 9}{96500}$   
 $\therefore t = \frac{100 \times 96500}{125 \times 9}$   
 $= 8577.77 \text{ s} = 143 \text{ min}$
49.  $W = zIt$   
 $z = \frac{E}{96500}$   
 $E = \frac{\text{atomic mass}}{\text{valency}} = \frac{58.7}{2}$   
 $\therefore I = \frac{W \times 96500}{E \times t}$   
 $= \frac{11.74 \times 96500 \times 2}{58.7 \times 1000}$   
 $= 38.6 \text{ A.}$



$$50. \quad W = zQ; \quad z = \frac{E}{96500}$$

$$z = \frac{63.5}{2 \times 96500}$$

(1 atom of Cu gives 2 electrons as it is divalent, so  $E = \frac{63.5}{2}$ )

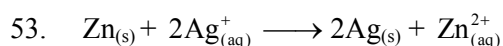
$$W = 0.1 \text{ g atom;}$$

For copper,

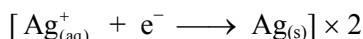
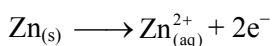
$$1 \text{ g atom} = 63.5 \text{ g}$$

$$\therefore 0.1 \text{ g atom} = 6.35 \text{ g}$$

$$\therefore Q = \frac{W}{z} = \frac{6.35 \times 2 \times 96500}{63.5} = 19300 \text{ coulombs}$$

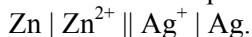


The two half cell reactions are –



Therefore, Zn is oxidised and acts as negative electrode (anode) whereas,  $\text{Ag}^+$  ions are reduced and acts as positive electrode (cathode).

Hence the cell representation is



$$58. \quad E_{\text{cell}}^{\circ} = E_{\text{red(cathode)}}^{\circ} - E_{\text{red(anode)}}^{\circ}$$

$$= 0.337 - (-0.44)$$

$$= 0.337 + 0.44$$

$$= 0.777 \text{ V}$$

59. Electrical potential is an intensive property. Thus, whenever the half reaction is multiplied by a numerical factor to balance the number of electrons, the corresponding  $E^{\circ}$  value is not to be multiplied by that factor (i.e.,  $E_{\text{el}}^{\circ}$  is always fixed or constant).

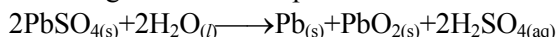
62. Electric work = amount of charge  $\times$  cell potential  
 $W_{\text{max}} = nF \times E_{\text{cell}} = nFE_{\text{cell}}$

64. Pt,  $\text{H}_{2(g)}$  | HCl is a standard hydrogen electrode (SHE). By definition, SHE is reversible with respect to  $\text{H}^+$  ions. The reaction is

$$\frac{1}{2} \text{H}_{2(g)} \rightleftharpoons \text{H}_{(aq)}^+ + e^-$$

70.  $\text{H}_2\text{SO}_4$  is used in lead storage battery as an electrolyte.

71. During the recharging of lead storage cell following reaction takes place.



Lead sulphate concentration decreases while the concentration of  $\text{H}_2\text{SO}_4$ ,  $\text{PbO}_2$  and Pb increases.

78. Smaller (more negative) the reduction potential, more will be the tendency to get oxidised. Conversion of metal to electropositive ion is oxidation. Since, D has lowest reduction potential among the given options, it will be strongly electropositive.



### Critical Thinking

1. When a species acts as an oxidising agent, the oxidation number of at least one of the atoms in it decreases.
2. In electrochemical cell, reduction is always a cathodic reaction.
3. In solid state, NaCl do not have free ions to conduct electricity.
4. Acetic acid is a weak electrolyte. Glucose, Sucrose and urea are non-electrolytes.

$$8. \quad 1\text{S} = 1 \Omega^{-1} = 1 \text{AV}^{-1} = 1 \text{CV}^{-1}\text{s}^{-1}$$

$$9. \quad \kappa = \frac{1}{R} \times b$$

where,  $\kappa$  = conductivity

$R$  = resistance

$b$  = cell constant

$$\kappa = \frac{8.76}{1000}$$

$$\kappa = 8.76 \times 10^{-3} \text{ ohm}^{-1} \text{ cm}^{-1}$$

$$10. \quad \kappa = \frac{1}{R} \times b$$

where,  $\kappa$  = conductance

$R$  = resistance

$b$  = cell constant

$$\therefore \kappa = \frac{1.15}{250} = 0.0046 \text{ ohm}^{-1} \text{ cm}^{-1}$$

The molar conductance of the solution is given by,

$$\wedge = \frac{1000\kappa}{C}$$

Where  $C = 0.1 \text{ mol L}^{-1}$

Hence,

$$\wedge = \frac{1000(\text{cm}^3 \text{L}^{-1}) \times 0.0046(\text{ohm}^{-1} \text{cm}^{-1})}{0.1(\text{mol L}^{-1})}$$

$$= 46 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$$

11. Kohlraush's law of independent migration of ions is applicable for electrolytes at infinite dilution i.e., at zero concentration.



13.  $\Lambda_{\infty}(\text{HCl}) = 426.15$   
According to Kohlrausch's law,  
 $\Lambda_{\infty}(\text{H}^+) + \Lambda_{\infty}(\text{Cl}^-) = 426.15 \dots(\text{i})$   
 $\Lambda_{\infty}(\text{NaCl}) = 126.15$   
 $\Lambda_{\infty}(\text{Na}^+) + \Lambda_{\infty}(\text{Cl}^-) = 126.15 \dots(\text{ii})$   
Subtract eqn (i) from eqn (ii)  
 $\Lambda_{\infty}(\text{H}^+) - \Lambda_{\infty}(\text{Na}^+) = 300$   
 $\Lambda_{\infty}(\text{H}^+) = 300 + \Lambda_{\infty}(\text{Na}^+)$   
 $\therefore \Lambda_{\infty}(\text{H}^+) > \Lambda_{\infty}(\text{Na}^+)$
15.  $\lambda_{\text{ClCH}_2\text{COOH}} = \lambda_{\text{ClCH}_2\text{COONa}} + \lambda_{\text{HCl}} - \lambda_{\text{NaCl}}$   
 $= 224 + 203 - 38.2$   
 $= 388.8 \text{ ohm}^{-1} \text{ cm}^2 \text{ gm eq}^{-1}$
16. Electrode at which oxidation takes place is anode and electrode at which reduction takes place is cathode. In electrochemical cell electrons flow from anode to cathode.
17. For setting up an electrochemical cell, redox reaction is required.  
 $\text{AgNO}_3 + \text{NaCl} \longrightarrow \text{AgCl} + \text{NaNO}_3$   
It is not a redox reaction and hence, cannot be used to set up the electrochemical cell.
19. A salt bridge contains a saturated solution of KCl or  $\text{NH}_4\text{NO}_3$  and 5% agar solution.
20. At anode, oxidation of anions takes place.
21. During electrolysis, inert electrodes like Pt, Hg and graphite are used.
22. Faraday's first law of electrolysis gives the relation between amount of a substance deposited or dissolved and the quantity of electricity. Mathematically Faraday's first law of electrolysis can be expressed as  $W \propto Q$  where,  $W$  = amount of substance deposited or dissolved in grams,  
 $Q$  = Quantity of electricity passed in Coulombs.
25. The charge on  $\text{N}_3^-$  is  $-1$ . The charge on this anion is due to one excess electron. Charge on 1 electron =  $1.6 \times 10^{-19} \text{ C}$
26. Charge on 1 electron =  $1.6022 \times 10^{-19} \text{ C}$   
 $1 \text{ C} = \frac{1}{1.6022 \times 10^{-19}} \text{ electrons}$   
 $= 0.6241 \times 10^{19}$   
 $= 6.241 \times 10^{18} \text{ electrons}$   
One coulomb is equal to charge on  $6.241 \times 10^{18} \text{ electrons}$
27. Electrochemical equivalent  
 $= \frac{\text{Equivalent weight}}{96500}$   
Equivalent weight of O =  $\frac{\text{Atomic weight}}{\text{Valency}}$   
 $= \frac{16}{2}$   
 $= 8 \text{ g}$   
 $= 8 \times 10^{-3} \text{ kg}$   
 $\therefore \text{Electrochemical equivalent} = \frac{8 \times 10^{-3}}{96500} \text{ kg/C}$
28.  $22.4 \text{ dm}^3$  of  $\text{Cl}_2$  at STP  $\equiv 1$  mole of  $\text{Cl}_2$   
 $\therefore 0.224 \text{ dm}^3$  of  $\text{Cl}_2$  at STP  $\equiv 0.01$  mole of  $\text{Cl}_2$   
In order to deposit one mole of chlorine (i.e., 71 grams), two faraday of electricity is required.  
 $\therefore 96500 \text{ C} \equiv 35.5 \text{ g} \equiv 0.5$  moles of  $\text{Cl}_2$   
i.e.,  $\frac{1}{2}$  moles of  $\text{Cl}_2 \equiv 96500 \text{ C}$   
 $\therefore 0.01$  moles of  $\text{Cl}_2 \equiv 96500 \times 0.01 \times 2$   
 $= 965 \times 2 \text{ C}$
29. Electrolysis of water :  
 $2\text{H}_2\text{O} \longrightarrow 4\text{H}^+ + 4\text{e}^- + \text{O}_2$   
4 F charge will produce = 1 mole  $\text{O}_2$   
 $= 32 \text{ g } \text{O}_2$   
1 F charge will produce =  $\frac{32}{4} = 8 \text{ g } \text{O}_2$ .
30. 1 Faraday will liberate half gram atom of the metal.  
 $\therefore$  Charge on 2 mole of electrons i.e., 2 Faradays is required to liberate 1 mole of metal. This indicates that metal needs to be dipositive. Among the given option, Ba in  $\text{BaCl}_2$  is dipositive.
31. Valency of M in  $\text{M}_2(\text{SO}_4)_3$  is +3  
Equivalent mass of M =  $\frac{x}{3}$   
 $\therefore \text{electrochemical equivalent} = \frac{\text{equivalent mass}}{96500 \text{ C}}$   
 $= \frac{x}{3F}$   
( $\because 1\text{F} = 96500 \text{ C}$ )
32.  $\text{Ni}_{(\text{aq})}^{2+} + 2\text{e}^- \longrightarrow \text{Ni}_{(\text{s})}$   
 $\therefore 2$  Faraday ( $2 \times 96500 \text{ C}$ ) of charge is required to deposit 1 mole i.e., 58.8 g of Ni.  
 $\therefore 48250 \text{ C}$  of electricity will deposit  
 $= \frac{48250 \times 58.8}{2 \times 96500} = 14.7 \text{ g of Ni.}$



33.  $I = 2 \text{ A}$ ,  $t = 965 \text{ s}$   
 $W = z \times I \times t \quad \dots(i)$   
 But  $z = \frac{E}{96500}$  [E = Equivalent mass of Cu]  
 $E = \frac{63.5}{2}$  [ $\because$  In  $\text{CuSO}_4$ , Cu is in +2 state]  
 Substituting in (i),  
 $W = \frac{63.5}{2} \times \frac{2 \times 965}{96500} = 0.635 \text{ g}$
34. Chemical equivalent of a substance is equivalent weight of the substance in grams.  
 For oxygen, equivalent weight  
 $= \frac{\text{Atomic weight}}{\text{Valency}} = \frac{16}{2} = 8$   
 $96,500 \text{ C or } 1 \text{ F}$  will liberate 1 equivalent of  $\text{O}_2$ .  
 1 equivalent of  $\text{O}_2 = 8 \text{ g}$ .  
 $32 \text{ g} = 22.4 \text{ L}$ ;  $8 \text{ g} = \frac{22.4 \times 8}{32} = 5.6 \text{ L}$
35.  $I = 3 \text{ A}$ ,  $t = 60 \text{ min} = 60 \times 60 \text{ s}$ ,  $W = 2.98 \text{ g}$ ,  
 Atomic mass = 106.4  
 $W = \frac{I \times t \times E}{96500}$   
 $\therefore E = \frac{W \times 96500}{I \times t}$   
 $= \frac{2.98 \times 96500}{3 \times 3600} = 26.63$   
 $\text{Valency } (n) = \frac{\text{Atomic mass}}{E}$   
 $= \frac{106.4}{26.63}$   
 $\therefore n \approx 4$
36. Mass of chlorine deposited can be calculated according to Faraday's first law of electrolysis  
 $W = \frac{ItE}{96500}$  ( $I = 300 \text{ mA} = 300 \times 10^{-3} \text{ A}$ )  
 $= \frac{300 \times 10^{-3} \times 60 \times 35.5}{96500}$  ( $t = 1 \text{ min} = 60 \text{ s}$ )  
 $= 6.621 \times 10^{-3} \text{ g}$   
 Number of chlorine molecules  
 $= \text{number of moles} \times \text{Avogadro number}$   
 $= \frac{6.621 \times 10^{-3} \times 6.023 \times 10^{23}}{71}$   
 $= 5.6 \times 10^{19} \text{ molecules}$   
 $\left( \begin{array}{l} \therefore \text{Number of moles of chlorine} \\ = \frac{\text{Weight in grams}}{\text{Molecular weight}} \end{array} \right)$

37.  $I = 10 \text{ A}$ ,  $t = 330 \text{ s}$ ,  $W = 1.950 \text{ g}$   
 $\therefore W = \frac{ItE}{96500}$   
 $\therefore E = \frac{W \times 96500}{It} = \frac{1.950 \times 96500}{10 \times 330} = 57.02$   
 Molten salt is  $\text{MF}_2$   
 Valency of fluorine =  $(-1) \times 2 = -2$   
 $\therefore$  Valency of M = +2  
 $E = \frac{\text{Atomic mass}}{\text{Valency}}$   
 $\therefore \text{Atomic mass} = E \times \text{Valency}$   
 $= 57.02 \times 2 \approx 114.0$
38.  $W = 39.4 \text{ g}$ ,  $t = 3600 \text{ s}$   
 $E \text{ for } \text{Au}^{3+} = \frac{197}{3} = 65.66$   
 $W = \frac{E}{96,500} \times I \times t$   
 $I = \frac{W \times 96,500}{E \times t} = \frac{39.4 \times 96,500}{65.66 \times 3,600} \approx 16 \text{ A}$
39.  $\text{H}_2\text{O} \rightleftharpoons \text{H}_2 + \frac{1}{2} \text{O}_2$   
 $\therefore 18 \text{ g (1 mole)}$  liberates 1 mole of  $\text{H}_2$  (i.e., 2 g)  
 $E = \frac{\text{At.mass}}{\text{Valency}} = \frac{1}{1} = 1$   
 $\therefore z = \frac{1}{96500}$   
 $I = 3 \text{ A}$ ,  $W = 2 \text{ g}$   
 $\therefore W = zIt$   
 $\therefore t = \frac{W}{zI} = \frac{2}{\frac{1}{96500} \times 3} = \frac{2 \times 96500}{3}$   
 $= 64333 \text{ s} = \frac{64332}{3600} \text{ hrs} = 17.9 \text{ hrs} \approx 18 \text{ hrs}$
40. Cell I:  
 Mercuric perchlorate  $\text{Hg}(\text{ClO}_4)_2 \rightarrow \text{Hg}^{2+}$   
 Cell II:  
 Mercuric nitrate  $\text{Hg}(\text{NO}_3)_2 \rightarrow \text{Hg}^{2+}$   
 Cell III:  
 Mercurous perchlorate  $\text{Hg}_2(\text{ClO}_4)_2 \rightarrow \text{Hg}^+$   
 $\text{Hg}^{2+} + 2\text{e}^- \rightarrow \text{Hg}$   
 $\text{Hg}^+ + \text{e}^- \rightarrow \text{Hg}$   
 $W_{\text{Hg}^{2+}} : W_{\text{Hg}^{2+}} : W_{\text{Hg}^+} =$   
 $(\text{mole ratio})_{\text{Hg}^{2+}} : (\text{mole ratio})_{\text{Hg}^{2+}} : (\text{mole ratio})_{\text{Hg}^+}$   
 $= \frac{1}{2} : \frac{1}{2} : 1$   
 $\therefore$  The amount of mercury deposited, will be same in cell I and II but more in cell III.





41.  $2\text{H}^+ + 2\text{e}^- \longrightarrow \text{H}_2$   
 mole ratio =  $\frac{\text{moles of product}}{\text{moles of e}^-} = \frac{1}{2}$   
 $\text{Ca}^{2+} + 2\text{e}^- \longrightarrow \text{Ca}$   
 mole ratio =  $\frac{\text{moles of product}}{\text{moles of e}^-} = \frac{1}{2}$   
 $\frac{\text{moles of H}_2 \text{ produced}}{\text{moles of Ca produced}} = \frac{\text{mole ratio of H}_2}{\text{mole ratio of Ca}}$   

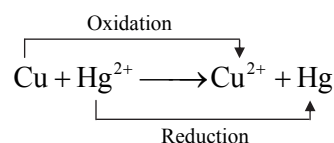
$$= \frac{\frac{1}{2}}{\frac{1}{2}} = \frac{1}{1}$$
  
 $\therefore \frac{\text{Mass of hydrogen liberated}}{\text{Mass of Ca liberated}}$   

$$= \frac{\text{moles of H}_2 \text{ produced} \times \text{its molar mass}}{\text{moles of Ca produced} \times \text{its molar mass}}$$
  

$$\therefore = \frac{1}{1} \times \frac{2}{40}$$
  
 $\therefore \text{H} : \text{Ca} = 1:20$
42. Valency of Fe in ferric salt = 3  
 Valency of Fe in ferrous salt = 2  
 According to faraday's second law,  
 $\frac{W_1}{W_2} = \frac{\text{Equivalent weight of ferrous ions}}{\text{Equivalent weight of ferric ions}}$   
 Let 'x' be the atomic mass of Fe  
 $\therefore \frac{W_1}{W_2} = \frac{x/2}{x/3}, \quad \frac{W_1}{W_2} = \frac{x}{2} \times \frac{3}{x}$   

$$\left( \because \text{Equivalent weight} = \frac{\text{Atomic mass}}{\text{Valency}} \right)$$
  
 The ratio of iron deposited at respective cathodes is 3 : 2
43. Reaction at cathode,  
 $\text{Ca}^{2+} + 2\text{e}^- \longrightarrow \text{Ca}$   
 Equivalent mass of Ca =  $\frac{40}{2} = 20$   
 $\text{Al}^{3+} + 3\text{e}^- \longrightarrow \text{Al}$   
 Equivalent mass of Al =  $\frac{27}{3} = 9$   
 According to Faraday's second law of electrolysis  
 $\frac{W_{\text{Al}}}{W_{\text{Ca}}} = \frac{E_{\text{Al}}}{E_{\text{Ca}}}$   
 $\therefore W_{\text{Al}} = \frac{40 \times 9}{20} = 18 \text{ kg}$

45.  $\text{Cu}_{(s)} | \text{Cu}^{2+}_{(aq)} || \text{Hg}^{2+}_{(aq)} | \text{Hg}_{(l)}$   
 Oxidation always occurs at anode while reduction occurs at cathode.



46. Anode: {Ag, AgCl(s), Cl<sup>-</sup> = reacting species}  
 metal with sparingly soluble salt  
 Cathode: {Ag, Ag<sup>+</sup> = reacting species}  
 metal in metal ion.  
 Anode:  $\text{Ag}_{(s)} + \text{Cl}^-_{(aq)} \longrightarrow \text{AgCl}_{(s)} + \cancel{\text{e}^-}$   
 Cathode:  $\text{Ag}^+_{(aq)} + \cancel{\text{e}^-} \longrightarrow \text{Ag}_{(s)}$   
 Cell reaction  $\text{Ag}^+_{(aq)} + \text{Cl}^-_{(aq)} \longrightarrow \text{AgCl}_{(s)}$
47. H<sub>2</sub> undergoes oxidation and AgCl(Ag<sup>+</sup>) undergoes reduction.
48. In Daniel cell, electrons flow from Zn to Cu, through an external circuit hence, the current (reverse direction of electrons) passes from Cu to Zn through an external circuit. Passage of current is reverse to that of flow of electrons.
50. In galvanic cell, the two solutions are connected by a salt bridge which is represented by a double vertical line.
51. Since the reduction potential of Ag is more than Zn, Ag will get reduced and Zn will oxidise. Hence the reaction is,  
 $\text{Zn}_{(s)} + 2\text{Ag}^+_{(aq)} \longrightarrow \text{Zn}^{2+}_{(aq)} + 2\text{Ag}_{(s)}$
52.  $\text{Mg}_{(s)} | \text{Mg}^{2+}_{(aq)} || \text{Cl}^-_{(aq)} | \text{Cl}_{2(g)} (1\text{atm}) | \text{Pt}$   
 Oxidation :  $\text{Mg} \longrightarrow \text{Mg}^{2+} + 2\text{e}^-$   
 Reduction :  $\text{Cl}_2 + 2\text{e}^- \longrightarrow 2\text{Cl}^-$   
 Cell reaction:  $\text{Mg}_{(s)} + \text{Cl}_{2(g)} \longrightarrow \text{Mg}^{2+}_{(aq)} + 2\text{Cl}^-_{(aq)}$   
 Nernst equation:  

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.0592}{2} \log \frac{[\text{Cl}^-]^2 [\text{Mg}^{2+}]}{P_{\text{Cl}_2}}$$

$$= E^\circ_{\text{cell}} - \frac{0.0592}{2} \log \frac{[\text{Cl}^-]^2 [\text{Mg}^{2+}]}{1}$$

$$= E^\circ_{\text{cell}} - \frac{0.0592}{2} \log [\text{Cl}^-]^2 [\text{Mg}^{2+}]$$



54.  $\text{pH} = 3$   
 $\therefore [\text{H}^+] = 10^{-3}$   
 The reaction is,  $\text{H}_{(\text{aq})}^+ + \text{e}^- \rightarrow \frac{1}{2} \text{H}_{2(\text{g})}$   
 At 25 °C,  

$$E_{\text{cell}} = E^\circ - \frac{0.0592}{1} \log \frac{[\text{H}_2]^{\frac{1}{2}}}{[\text{H}^+]}$$

$$= 0 - 0.0592 \times (3) = -0.177 \text{ V}$$
55. 
$$E_{\text{el}} = E_{\text{el}}^\circ - \frac{0.0592}{n} \log \frac{[\text{Zn}]}{[\text{Zn}^{2+}]}$$

$$= -0.76 - \frac{0.0592}{2} \log \frac{1}{0.1}$$

$$= -0.76 - 0.0296$$

$$= -0.789 \text{ V}$$
56. The cell may be represented as,  
 $\text{Zn}_{(\text{s})} | \text{Zn}^{2+} (0.1 \text{ M}) || \text{Cu}^{2+} (10^{-9} \text{ M}) | \text{Cu}_{(\text{s})}$   
 $E^\circ$  of the cell =  $E_{\text{Zn/Zn}^{2+}}^\circ - E_{\text{Cu/Cu}^{2+}}^\circ = +1.10 \text{ V}$   
 $\text{Zn} + \text{Cu}^{2+} \longrightarrow \text{Zn}^{2+} + \text{Cu}$   
 On applying Nernst Equation  

$$E_{\text{cell}} = E_{\text{cell}}^\circ - \frac{0.0592}{n} \log \frac{C_{\text{Zn}^{2+}}}{C_{\text{Cu}^{2+}}}$$

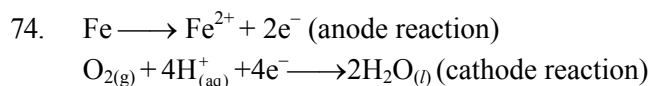
$$= 1.10 - \frac{0.0592}{2} \log \frac{0.1}{10^{-9}}$$

$$= 1.10 - 0.236 = 0.864 \text{ V}$$
57. Overall cell reaction for a Daniel cell can be given as,  
 $\text{Zn}_{(\text{s})} + \text{Cu}_{(\text{aq})}^{2+} \longrightarrow \text{Zn}_{(\text{aq})}^{2+} + \text{Cu}_{(\text{s})}$   
 At 298 K,  

$$\therefore E_{\text{cell}} = E_{\text{cell}}^\circ - \frac{0.0592}{2} \log \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]}$$
  
 $\therefore$  When the concentrations of both  $\text{Zn}^{2+}$  and  $\text{Cu}^{2+}$  are doubled, the ratio  $\frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]}$  remains unaltered.  
 $\therefore$  e.m.f of the cell remains constant.
58.  $\text{M} \longrightarrow \text{M}^{2+} + 2\text{e}^-$  (oxidation)  
 $2\text{H}^+ + 2\text{e}^- \longrightarrow \text{H}_2$  (reduction)  
 $n = 2$   

$$E_{\text{cell}} = E_{\text{cell}}^\circ - \frac{0.0592}{2} \log \frac{[\text{M}^{2+}]}{[\text{H}^+]^2}$$

$$= E_{\text{cell}}^\circ - \frac{0.0592}{2} \log \frac{0.1}{1}$$
- 1.5 =  $E_{\text{cell}}^\circ + \frac{0.0592}{2}$   
 $E_{\text{cell}}^\circ = 1.5 - \frac{0.0592}{2}$   
 $E_{\text{cell}}^\circ = 1.47 \text{ V}$   
 $E_{\text{cell}}^\circ = E_{\text{Cathode}}^\circ - E_{\text{Anode}}^\circ$   
 $= E_{\text{SHE}}^\circ - E_{\text{M}^{2+}/\text{M}}^\circ$   
 $\therefore 1.47 = 0 - E_{\text{M}^{2+}/\text{M}}^\circ$   
 $\therefore E_{\text{M}^{2+}/\text{M}}^\circ = -1.47 \text{ V}$
59. The maximum work will be done by the given cell using free energy.  
 $-\Delta G = nFE_{\text{cell}}$   
 $= 2 \times 96500 \times 1.1$   
 $= 212300 \text{ J}$   
 $= 212.30 \text{ kJ}$
63. During the use of lead storage battery (i.e., discharging of the cell)  $\text{SO}_4^{2-}$  ions (from  $\text{H}_2\text{SO}_4$ ) are consumed by  $\text{Pb}^{2+}$  ions to form  $\text{PbSO}_4$ .
65. During recharging of a lead storage cell, electrical energy is supplied to it from external source i.e., the cell functions as electrolytic cell and the external emf is greater than the emf of the cell.
67. Fuel cells can work continuously as long as the reacting substances are continuously supplied to the electrodes.
68. Since,  $E_{\text{A/A}^-}^\circ$  has large negative value, the tendency of A to be reduced to  $\text{A}^-$  is very small. In other words tendency of  $\text{A}^-$  to be oxidized to A is very large.
71. The standard electrode potentials of Ag and Cu are greater than the standard electrode potential of hydrogen. Therefore, the aqueous solutions of  $\text{Ag}^+$  and  $\text{Cu}^{2+}$  can oxidize hydrogen ( $\text{H}_2$ ) to  $\text{H}^+$ .
72. For the reaction,  $\text{A}^+ + \text{B} \rightarrow \text{A} + \text{B}^+$ ,  
 $E_{\text{cell}}^\circ = E_{\text{cathode}}^\circ - E_{\text{anode}}^\circ = +3.03 - (-0.70)$   
 $= 3.73 \text{ V}$   
 Since the standard cell potential is positive, the reaction is spontaneous. For other given reactions, the standard cell potentials are negative.
73. Rusting of iron occurs in acidic medium. The  $\text{H}^+$  ions are supplied by the reaction of atmospheric  $\text{CO}_2$  with water to form  $\text{H}_2\text{CO}_3$ .  
 $\therefore \text{H}^+$  ions catalyze rusting of iron.



76. For 1g Mg, it costs ₹ 3.00  
 One equivalent of Mg =  $\frac{24}{2} = 12$  g,

[∵ One atom of Mg can give two electrons as it is divalent]

∴ Cost to deposit one equivalent of Mg =  $12 \times 3 = ₹ 36.00$

The same amount of electricity and hence the same cost will deposit an equivalent of Al,

i.e.,  $\frac{27}{3} = 9$  g.

[According to Faraday's second law]

∴ For 8 g of Al, it costs  $\frac{8}{9} \times 36 = ₹ 32.00$



### Competitive Thinking

2. As temperature increases, the resistance of metallic or electronic conductors increases and hence, electrical conductivity decreases.

3. Hydrochloric acid is a strong electrolyte which is almost completely ionized in its aqueous solution. Hence, among the given options, aqueous solution of HCl is the best conductor of electric current.

4. The SI unit of conductivity is  $\text{S m}^{-1}$ .

5.  $G \propto \frac{a}{l}$

$$G = \kappa \frac{a}{l}$$

∴  $G = \kappa \cdot a \cdot l^{-1}$

6. Since molar conductance  $\propto \frac{1}{\text{Molarity}}$ ,

lower the concentration, higher will be molar conductance. So molar conductance will be maximum for 0.001 M solution.

7. Halogen substituted acetic acid is more acidic than acetic acid. More the number of electronegative halogen atoms, more is the acidic strength and hence more will be the ionisation. So difluoroacetic acid which has comparatively more number of halogen atoms (two fluorine atoms) will show highest electrical conductivity among the given options.

8. Since the conductivity given is not molar conductance, the conductivity decreases on dilution.

9. The cell constant is determined by using 1 M, 0.1 M (i.e.,  $10^{-1}$  M) or 0.01 M (i.e.,  $10^{-2}$  M) KCl solution.

$$\begin{aligned} \Lambda_m^\circ(\text{NaBr}) &= \Lambda^\circ(\text{NaCl}) + \Lambda^\circ(\text{KBr}) - \Lambda^\circ(\text{KCl}) \\ &= 126 + 152 - 150 \\ &= 128 \text{ S cm}^2 \text{ mol}^{-1} \end{aligned}$$

$$\begin{aligned} \text{11. Molar conductivity } (\Lambda) &= \frac{1000\kappa}{C} \\ &= \frac{1000 \text{ cm}^3 \text{ L}^{-1} \times 1.41 \times 10^{-3} \text{ S cm}^{-1}}{0.1 \text{ mol L}^{-1}} \\ &= 14.1 \text{ S cm}^2 \text{ mol}^{-1} \end{aligned}$$

$$\begin{aligned} \text{12. Conductivity (electrolytic)} &= \kappa \\ &= 5.76 \times 10^{-3} \text{ S cm}^{-1} \end{aligned}$$

$$\begin{aligned} \Lambda_m &= \frac{\kappa \times 1000}{C} = \frac{5.76 \times 10^{-3} \times 1000}{0.5} \\ &= 11.52 \text{ S cm}^2 \text{ mol}^{-1} \end{aligned}$$

13. i. For given 0.2 M solution,  
 Resistance (R) = 50 Ω,  
 Specific conductance ( $\kappa$ ) =  $1.4 \text{ S m}^{-1}$   
 The cell constant (b) =  $\kappa \times R$   
 $= 1.4 \text{ S m}^{-1} \times 50 \Omega$   
 $= 70 \text{ m}^{-1}$

ii. For given 0.5 M solution,  
 resistance (R) = 280 Ω  
 Specific conductance ( $\kappa$ ) =  $\frac{b}{R} = \frac{70 \text{ m}^{-1}}{280 \Omega}$   
 $= 0.25 \text{ S m}^{-1}$

$$\begin{aligned} \text{Concentration (C)} &= 0.5 \frac{\text{mol}}{\text{dm}^3} \\ &= 0.5 \times 10^3 \frac{\text{mol}}{\text{m}^3} \\ &= 500 \text{ mol m}^{-3} \end{aligned}$$

Molar conductivity ( $\Lambda_m$ )

$$\begin{aligned} &= \frac{\kappa}{C} \text{ S m}^2 \text{ mol}^{-1} \\ &= \frac{0.25 \text{ S m}^{-1}}{500 \text{ mol m}^{-3}} \\ &= 5 \times 10^{-4} \text{ S m}^2 \text{ mol}^{-1} \end{aligned}$$



$$14. \text{ Degree of dissociation } (\alpha) = \frac{\wedge}{\wedge_0}$$

$$= \frac{150}{500}$$

$$= 0.3$$

$$\text{Dissociation constant of HF } (K_a) = \frac{\alpha^2 C}{1 - \alpha}$$

$$= \frac{(0.3)^2 \times 0.007}{1 - 0.3}$$

$$= 9 \times 10^{-4}$$

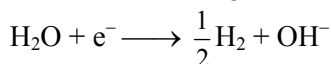
15. Here, since the cell is galvanic cell, the +ve electrode is the cathode, where the reduction reaction occurs.

∴ The reaction that occurs at +ve electrode is  $\text{Fe}^{+3} + \text{e}^- \longrightarrow \text{Fe}^{2+}$   
Since, the electrode is  $\text{Fe}^{3+}, \text{Fe}^{2+} | \text{Pt}$

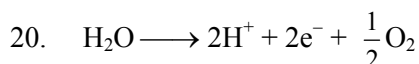
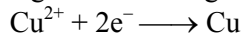
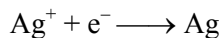
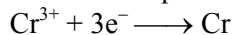
16. During electrolysis of fused sodium chloride (NaCl), oxidation reaction occurs at anode wherein two electrons are given up to the anode by chloride ( $\text{Cl}^-$ ) ions to form chlorine ( $\text{Cl}_2$ ) molecule.

17. In the electrolysis of concentrated aqueous solution of NaCl,  $\text{Na}^+$  ions combine with  $\text{OH}^-$  ions to form NaOH solution. Thus, the resulting solution is basic and it turns red litmus into blue.

18.  $\text{Ca}^{2+}$  ( $E^\circ = -2.87 \text{ V}$ ) has lower reduction potential than water ( $E^\circ = -0.83 \text{ V}$ ). Hence it cannot be reduced in aqueous solution. Instead water will get reduced to liberate  $\text{H}_2$ .



$\text{Ag}^+$  ( $E^\circ = 0.80 \text{ V}$ ),  $\text{Cu}^{2+}$  ( $E^\circ = 0.34 \text{ V}$ ) and  $\text{Cr}^{3+}$  ( $E^\circ = -0.74 \text{ V}$ ) have higher reduction potential than water. Hence they can be reduced in aqueous solution to obtain metals.



For the oxidation of one mole of water to dioxygen, 2 mole electrons are required.

Electricity required (Q)

$$= \text{Moles of electrons actually passed} \times 96500 \text{ C/mol e}^-$$

$$\therefore Q = 2 \text{ mol e}^- \times 96500 \text{ C/mol e}^-$$

$$= 1.93 \times 10^5 \text{ C}$$

21.  $\text{Ca}^{2+} + 2\text{e}^- \longrightarrow \text{Ca}$   
2 F will deposit 1 mole Ca (i.e., 40 g of Ca)  
Hence, 0.5F of electricity will be required to deposit 10 g of Ca from molten  $\text{CaCl}_2$  when inert electrodes are used.

22.  $2\text{H}^+ + 2\text{e}^- \longrightarrow \text{H}_2$   
2 F will deposit 2 g of hydrogen  
∴ 4 F will deposit 4 g of hydrogen

23. Number of moles of electrons passed

$$= \frac{I \times t}{96500}$$

$$= \frac{2 \times 20 \times 60}{96500}$$

$$= 2.487 \times 10^{-2} \text{ mol e}^-$$

24.  $\text{Al}^{3+} + 3\text{e}^- \longrightarrow \text{Al}^0$   
∴ To deposit 1 mole of Al i.e., 27 g of Al, 3 Faraday of charge is required.

∴ for  $5.12 \times 10^3 \text{ g}$  of Al,  
charge required =  $\frac{5.12 \times 10^3 \times 3}{27}$   
= 568.9 Faraday of charge  
=  $568.9 \times 96500$   
=  $5.49 \times 10^7 \text{ C}$

25.  $\text{Ag}_{(\text{aq})}^+ + \text{e}^- \longrightarrow \text{Ag}_{(\text{s})}$   
1 Faraday i.e., 96500 C will deposit 108 g of Ag.  
∴ 9650 C will deposit 10.8 g of Ag

26.  $\text{Zn}^{2+} + 2\text{e}^- \longrightarrow \text{Zn}$   
 $\text{Al}^{3+} + 3\text{e}^- \longrightarrow \text{Al}$   
 $\text{Ag}^+ + \text{e}^- \longrightarrow \text{Ag}$   
∴ The quantity of electricity needed to separately electrolyze 1 M solution of  $\text{ZnSO}_4$ ,  $\text{AlCl}_3$  and  $\text{AgNO}_3$  completely is in the ratio of 2 : 3 : 1.

27.  $\text{Ag}^+ + \text{e}^- \longrightarrow \text{Ag}$   
∴ Equivalent weight of Ag =  $\frac{\text{Atomic weight}}{\text{Valency}}$   
$$= \frac{108}{1} = 108.$$

∴ 96500 C i.e., 1F of charge deposits 108 g of Ag.

∴ 1C of charge will deposit =  $\frac{108}{96500}$  of Ag  
= 1 electrochemical equivalent of silver



28. In  $\text{CuSO}_4$  solution, the reduction reaction of Cu can be given as,  
 $\text{Cu}^{2+} + 2e^- \longrightarrow \text{Cu}$   
 $\therefore$  To deposit 1 mole of Cu, 2 F i.e.,  $2 \times 96500$  coulombs of electricity is required.  
 $\therefore$  Moles of copper deposited on passing of 9650 coulombs  

$$= \frac{9650}{2 \times 96500} = 0.05 \text{ moles}$$
29. At anode:  $2\text{Cl}^- \longrightarrow \text{Cl}_2 + 2e^-$   
 $\therefore$  2F (i.e.,  $2 \times 96500$  C) of electricity is required to produce 1 mol of  $\text{Cl}_2$  gas.  
 $\therefore$  0.2 F (i.e.,  $0.2 \times 96500$  C) of electricity will be required to produce 0.1 mol of  $\text{Cl}_2$  gas.  
 Now,  $Q = I \times t$   
 $\therefore 0.2 \times 96500 = 3 \times t$   
 $\therefore t = 6433.3 \text{ seconds} = 107.2 \text{ minutes}$   
 $\approx 110 \text{ minutes}$
30. Reaction for electrolysis of water is  
 $2\text{H}_2\text{O} \rightleftharpoons 4\text{H}^+ + 2\text{O}^{2-}$   
 $2\text{O}^{2-} \longrightarrow \text{O}_2 + 4e^-$   
 $4\text{H}^+ + 4e^- \longrightarrow 2\text{H}_2$   
 $n = 4$ , so 4 Faraday of charge will liberate 1 mole i.e.,  $22.4 \text{ dm}^3$  of oxygen  
 $\therefore$  1 Faraday charge will liberate  $\frac{22.4}{4} = 5.6 \text{ dm}^3 \text{ O}_2$
31. Charge  $Q = I \times t$   
 $= 10 \times 80 \times 60$   
 $= 48000 \text{ C}$   
 $1 \text{ F} = 96500 \text{ C}$   
 $\therefore x\text{F} = 48000 \text{ C}$   
 $x = \frac{48000}{96500}$   
 $x = 0.5 \text{ Faraday.}$   
 $2\text{H}^+ + 2e^- \longrightarrow \text{H}_2$   
 $\therefore$  Charge of 2 Faraday will release one mole of  $\text{H}_2$  i.e.,  $22.4 \text{ L}$  of  $\text{H}_2$  at STP.  
 $\therefore$  Charge of 0.5 Faraday will release  
 $= \frac{0.5 \times 22.4}{2} = 5.6 \text{ L of H}_2$
32. Given, Current = 241.25 coulomb  
 $96500 \text{ C}$  current will deposit 108g of Ag  
 $\therefore$  1 coulomb current will deposit =  $\frac{108}{96500}$   
 $= 1.118 \times 10^{-3} \text{ g Ag.}$   
 $\therefore$  241.25 current will deposit  
 $= 1.118 \times 10^{-3} \times 241.25 = 0.27 \text{ g silver.}$
33.  $\text{Fe}^{3+} + 3e^- \longrightarrow \text{Fe}^{2+}$   
 $\therefore$  3 F will deposit 56 g of Fe  
 So, 0.6 F will deposit =  $\frac{0.6 \times 56}{3} = 11.2 \text{ g}$
34. Weight deposited =  $\frac{E \times I \times t}{F}$   
 $= \frac{108 \times 0.5 \times 10 \times 60}{96500} = 0.336 \text{ g}$
35. At cathode  $\text{Ca}^{+2}$  ions from  $\text{CaCl}_2$  get reduced as follows:  
 $\text{Ca}^{+2} + 2e^- \rightarrow \text{Ca}$   
 Equivalent weight (E) =  $\frac{\text{Atomic mass}}{\text{Valency}}$   
 $= \frac{40}{2} = 20$   
 $\text{weight} = \frac{E \times I \times t}{F}$   
 $= \frac{20 \times 0.005 \times 200}{96500}$   
 $= 0.0002073 \text{ g of Ca}$
36. Weight of 1 mol of  $\text{H}_2$  gas = 2 g.  
 $\therefore$  0.01 mol of  $\text{H}_2$  will weigh 0.02 g.  
 Weight deposited =  $\frac{E \times I \times t}{F}$   
 $0.02 = \frac{10 \times 10^{-3} \times t}{96500}$   
 $t = \frac{0.02 \times 96500}{10^{-2}} = 19.3 \times 10^4 \text{ s}$
37.  $\text{Cu}^{2+} + 2e^- \longrightarrow \text{Cu}$   
 So, 2 F charge deposits 1 mol of Cu.  
 $\therefore$  Mass deposited = 63.5 g.
38.  $\text{Al}^{3+} + 3e^- \longrightarrow \text{Al}$   
 $\therefore$  3 Faraday charge is required to deposit 27 g of Al.  
 $\therefore$  x Faraday of charge is required to deposit  $4.5 \times 10^{-5} \text{ g of Al.}$   
 $\therefore x = \frac{3 \times 4.5 \times 10^{-5}}{27} \text{ Faraday}$   
 $1 \text{ Faraday} = \text{charge on } 6.022 \times 10^{23} \text{ electrons}$   
 $\therefore$  number of electrons required  
 $= \frac{3 \times 4.5 \times 10^{-5}}{27} \times 6.022 \times 10^{23}$   
 $= 3.0 \times 10^{18} \text{ electrons.}$



39. 0.1 M  $\text{FeSO}_4$  is given i.e., 1000 mL of solution contains 0.1 mole of  $\text{FeSO}_4$   
 $\therefore$  20 mL of solution will contain =  $2 \times 10^{-3}$  moles of  $\text{FeSO}_4$   
 $2 \times 10^{-3}$  moles of  $\text{FeSO}_4$  contains  $2 \times 10^{-3}$  moles of  $\text{Fe}^{2+}$ .  
 The oxidation reaction of  $\text{Fe}^{2+}$  can be given as,  
 $\text{Fe}^{2+} \longrightarrow \text{Fe}^{3+} + \text{e}^-$   
 $\therefore$  1 mole of  $\text{Fe}^{2+}$  gives 1 mole of  $\text{e}^-$  on oxidation.  
 $\therefore$  moles of electrons required to oxidise  $2 \times 10^{-3}$  moles of  $\text{Fe}^{2+} = 1 \times 2 \times 10^{-3}$   
 $= 2 \times 10^{-3}$  moles of electrons  
 $\therefore$  number of electrons  
 $= 2 \times 10^{-3} \times 6.022 \times 10^{23}$   
 $= 12.04 \times 10^{20}$   
 $= 1.204 \times 10^{21}$  electrons.
40. The magnitude of charge on an electron  
 $= 1.6 \times 10^{-19} \text{ C}$   
 $\therefore$  One coulomb equals the charge of  
 $\frac{1}{1.6 \times 10^{-19}} = 6.25 \times 10^{18}$  electrons  
 $1 \text{ C} = 1 \text{ Ampere} \times 1 \text{ second}$   
 $\therefore 6.25 \times 10^{18}$  electrons  $\equiv 1 \text{ Ampere} \times 1 \text{ second}$   
 $\therefore$  Current of 1 ampere in 60 seconds  
 $\equiv 6.25 \times 10^{18} \times 60 = 3.75 \times 10^{20}$  electrons
41. weight =  $z I t$   
 $z = \frac{\text{weight}}{I t}$   
 $= \frac{0.34}{0.5 \times 200} = 0.0034 \text{ gm C}^{-1}$
42. Electrochemical equivalent ( $z$ )  
 $= \frac{\text{Equivalent weight}}{96500}$   
 $z = \frac{\text{Atomic weight}}{\text{valency} \times 96500}$   
 $\therefore$  Atomic weight =  $z \times \text{valency} \times 96500$   
 In  $\text{CuSO}_4$ , Cu is in +2 oxidation state  
 $\therefore$  valency = +2.  
 $\therefore$  Atomic weight =  $3.29 \times 10^{-4} \times 2 \times 96500$   
 $= 63.49 = 63.5$
43. At STP,  
 22,400 mL of  $\text{O}_2 \equiv 32 \text{ g}$  of  $\text{O}_2$  (1 mol of  $\text{O}_2$ ).  
 $\therefore$  5600 mL of  $\text{O}_2 \equiv 8 \text{ g}$  of  $\text{O}_2$  at STP.  
 $\therefore$  Weight of  $\text{O}_2$  displaced ( $W_{\text{O}_2}$ ) in grams  
 $= 8 \text{ grams}$   
 Equivalent weight of silver ( $E_{\text{Ag}} = \frac{108}{1} = 108$ )

$$\text{Equivalent weight of } \text{O}_2 (E_{\text{O}_2}) = \frac{\frac{1}{2} \times 32}{2} = 8$$

$$\therefore \frac{W_{\text{Ag}}}{W_{\text{O}_2}} = \frac{E_{\text{Ag}}}{E_{\text{O}_2}}$$

...(Faraday's second law of electrolysis)

$$\therefore W_{\text{Ag}} = \frac{108}{8} \times 8 = 108 \text{ g}$$

44. Ferrous chloride :  $\text{FeCl}_2$   
 $\therefore$  equivalent weight of Fe in  $\text{FeCl}_2$   
 $= \frac{\text{Atomic weight of Fe}}{\text{Valency}}$   
 $= \frac{\text{Atomic weight of Fe}}{2}$   
 Ferric chloride :  $\text{FeCl}_3$   
 $\therefore$  equivalent weight of Fe in  $\text{FeCl}_3$   
 $= \frac{\text{Atomic weight of Fe}}{\text{Valency}}$   
 $= \frac{\text{Atomic weight of Fe}}{3}$   
 $\frac{\text{weight of } \text{Fe}^{2+} \text{ deposited}}{\text{weight of } \text{Fe}^{3+} \text{ deposited}}$   
 $= \frac{\text{equivalent weight of Fe in } \text{FeCl}_2}{\text{equivalent weight of Fe in } \text{FeCl}_3}$   
 $= \frac{\text{Atomic weight of Fe}}{2} \times \frac{3}{\text{Atomic weight of Fe}} = \frac{3}{2}$

45.  $\frac{\text{Weight of Cu}}{\text{Weight of Cr}} = \frac{\text{Equivalent weight of Cu}}{\text{Equivalent weight of Cr}}$   
 $= \frac{\text{electrochemical equivalent of Cu} \times \cancel{96500}}{\text{electrochemical equivalent of Cr} \times \cancel{96500}}$   
 $\frac{z_1}{z_2} = \frac{0.375}{0.30} = 1.25$

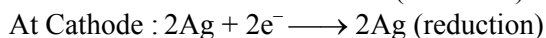
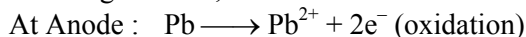
46. Nickel chloride:  $\text{NiCl}_2$   
 Equivalent weight of Ni =  $\frac{\text{Atomic weight of Ni}}{\text{Valency}}$   
 $= \frac{58.5}{2} = 29.25$   
 Aluminium chloride :  $\text{AlCl}_3$   
 Equivalent weight of Al =  $\frac{\text{Atomic weight of Al}}{\text{Valency}}$   
 $= \frac{27}{3} = 9$



$$\frac{\text{Weight of Ni deposited}}{\text{Weight of Al deposited}} = \frac{\text{Equivalent weight of Ni}}{\text{Equivalent weight of Al}}$$

$$\therefore \text{Weight of Ni deposited} = \frac{29.25}{9} \times 18 = 58.5 \text{ g}$$

47. For the given cell,



$\therefore$  Pb is undergoing oxidation and hence, acting as a reducing agent.

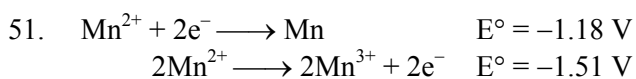
50. The electrode with higher reduction potential forms cathode.

So  $\text{Sn}^{4+} | \text{Sn}^{2+}$  is cathode and  $\text{Cr}^{3+} | \text{Cr}$  is anode.

$$E_{\text{cell}}^{\circ} = E_{\text{cathode}}^{\circ} - E_{\text{anode}}^{\circ}$$

$$= +0.15 - (-0.74)$$

$$= +0.15 + 0.74 = +0.89 \text{ V}$$



As  $E^{\circ}$  value is negative the reaction will not occur.

52. Since,  $\text{Cu}^{2+}$  undergoes reduction it is cathodic reaction while Mg undergoes oxidation and hence it is anodic reaction.

$$E_{\text{cell}} = E_{\text{Cu}^{2+}|\text{Cu}}^{\circ} - E_{\text{Mg}^{2+}|\text{Mg}}^{\circ}$$

$$= 0.337 - (-2.37)$$

$$= 0.337 + 2.37$$

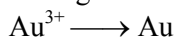
$$= 2.707 \text{ V} \approx 2.7 \text{ V}$$

53.  $E_{\text{Au}^{3+}|\text{Au}}^{\circ} = 1.5 \text{ V}$

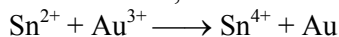
$$E_{\text{Sn}^{4+}|\text{Sn}^{2+}}^{\circ} = 0.15 \text{ V}$$

Since  $E_{\text{Au}^{3+}|\text{Au}}^{\circ}$  is greater than  $E_{\text{Sn}^{4+}|\text{Sn}^{2+}}^{\circ}$ ,

$\text{Au}^{3+}$  will undergo reduction while  $\text{Sn}^{2+}$  will undergo oxidation.



$\therefore$  net reaction is,



54. The reduction potential of an electrode is always equal to its oxidation potential with the sign reversed.

Therefore, reduction potentials of  $\text{Zn} = -0.76 \text{ V}$  and that of  $\text{Cu} = +0.34 \text{ V}$

The electrode with higher reduction potential forms cathode. So, Cu is cathode and Zn is anode.

$$E_{\text{cell}}^{\circ} = E_{\text{cathode}}^{\circ} - E_{\text{anode}}^{\circ}$$

$$= +0.34 - (-0.76) = +1.10 \text{ V}$$

55.  $E_{\text{Ag}|\text{Ag}^{+}}^{\circ} = -0.799 \text{ V}$

$\therefore E_{\text{Ag}^{+}|\text{Ag}}^{\circ} = 0.799 \text{ V}$

$$E_{\text{cell}}^{\circ} = E_{\text{(cathode)}}^{\circ} - E_{\text{(anode)}}^{\circ}$$

$$= 0.799 - 0$$

$$E_{\text{cell}}^{\circ} = 0.799 \text{ V}$$

56. Copper is placed above hydrogen in electrochemical series and has reduction potential of  $+0.153 \text{ V}$  while zinc is placed below hydrogen and has potential of  $-0.763 \text{ V}$ .

$\therefore$  The cell potential with Zn as electrode will be  $0.763 \text{ V}$  while the cell potential with copper as electrode will be  $0.153 \text{ V}$ . Hence the cell potential will decrease.

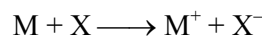
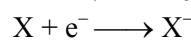
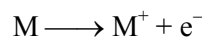
57.  $E_{\text{cell}}^{\circ} = E_{\text{(cathode)}}^{\circ} - E_{\text{(anode)}}^{\circ}$

$$0.769 = 0 - E_{\text{(anode)}}^{\circ}$$

$$E_{\text{anode}}^{\circ} = -0.769 \text{ V}$$



The two half-cell reactions can be given as –



$$E_{\text{M}^{+}|\text{M}}^{\circ} = 0.44 \text{ V}$$

$$E_{\text{X}|\text{X}^{-}}^{\circ} = 0.33 \text{ V}$$

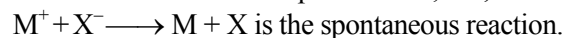
$$E_{\text{cell}} = E_{\text{X}|\text{X}^{-}}^{\circ} - E_{\text{M}^{+}|\text{M}}^{\circ}$$

$$= 0.33 - 0.44$$

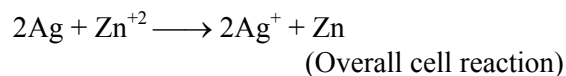
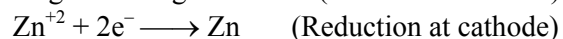
$$E_{\text{cell}} = -0.11 \text{ V}$$

Since  $E_{\text{cell}}$  is negative, the reaction is non-spontaneous.

$\therefore$  The reverse reaction is spontaneous; i.e.,



59. For the given electrochemical cell, the oxidation reaction at anode, reduction reaction at cathode and overall cell reaction are as follows:



$\therefore$  The emf of the cell is given by

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.0592}{n} \log_{10} \frac{[\text{Ag}^{+}]^2}{[\text{Zn}^{+2}]}$$

Substituting the values in above equation,



$$E_{\text{cell}} = -1.562 - \frac{0.0592}{2} \log_{10} \frac{(0.1)^2}{(0.1)}$$

$$= -1.562 - \frac{0.0592}{2} \log_{10} 10^{-1}$$

$$= -1.562 - (-1) \frac{0.0592}{2}$$

$$= -1.562 + 0.0296 = -1.5324 \text{ V}$$

60. The cell reaction is  $\text{Zn} + \text{Cu}^{2+} \longrightarrow \text{Zn}^{2+} + \text{Cu}$

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.059}{2} \log \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]}$$

When  $[\text{Zn}^{2+}]$  is increased and  $[\text{Cu}^{2+}]$  is decreased, the term  $\log \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]}$  increases.

Thus,  $E_1 > E_2$ .

61.  $\text{Fe}^{2+} | \text{Fe}$ ,  $E^{\circ} = -0.44 \text{ V}$  and

$\text{Fe}^{3+} | \text{Fe}^{2+}$ ,  $E^{\circ} = 0.77 \text{ V}$ .

Since,  $\text{Fe}^{3+} | \text{Fe}^{2+}$  electrode has higher potential than  $\text{Fe}^{2+} | \text{Fe}$ ,  $\text{Fe}^{3+} | \text{Fe}^{2+}$  acts as cathode and  $\text{Fe}^{2+} | \text{Fe}$  acts as anode.

Oxidation at anode:  $\text{Fe} \rightarrow \text{Fe}^{2+} + 2e^{-}$ ,  $E^{\circ} = 0.44 \text{ V}$

Reduction at cathode:  $2\text{Fe}^{3+} + 2e^{-} \rightarrow 2\text{Fe}^{2+}$ ,  $E^{\circ} = 0.77 \text{ V}$

Overall reaction:  $\text{Fe} + 2\text{Fe}^{3+} \rightarrow 3\text{Fe}^{2+}$ ,  $E^{\circ} = 1.21 \text{ V}$

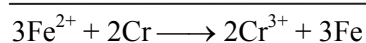
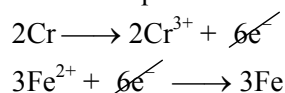
$E^{\circ}$  for overall reaction is positive, hence the overall reaction is spontaneous. Therefore, if  $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$  and Fe blocks are kept together, it will lead to decrease in  $\text{Fe}^{3+}$ .

63. The half-cell reactions can be given as

At anode:  $\text{Cr} \longrightarrow \text{Cr}^{3+} + 3e^{-}$  .... (i)

At cathode:  $\text{Fe}^{2+} + 2e^{-} \longrightarrow \text{Fe}$  .... (ii)

Multiply (i) by 2 and (ii) by 3 and adding the resultant equations



$$E_{\text{cell}}^{\circ} = E_{\text{Fe}^{2+}|\text{Fe}}^{\circ} - E_{\text{Cr}^{3+}|\text{Cr}}^{\circ}$$

$$= -0.42 - (-0.72) = 0.3 \text{ V}$$

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.0592}{n} \log \frac{[\text{Cr}^{3+}]^2}{[\text{Fe}^{2+}]^3}$$

$$= 0.3 - \frac{0.0592}{6} \log \frac{(0.1)^2}{(0.01)^3}$$

$$= 0.3 - \frac{0.0592}{6} \log 10^4$$

$$= 0.3 - 0.0394$$

$$E_{\text{cell}} = 0.26 \text{ V}$$

64. When the cell is fully discharged,

$$E_{\text{cell}} = 0$$

$$\therefore E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.0592}{2} \log \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]}$$

$$\frac{1.10 \times 2}{0.0592} = \log \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]}$$

$$37.2 = \log \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]}$$

$$\frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]} = 10^{37.2}$$

65.  $\text{Pt} | \text{H}_2(\text{P}_1) | \text{H}^+(\text{aq}) | \text{H}_2(\text{P}_2) | \text{Pt}$

At anode:  $\text{H}_2 \longrightarrow 2\text{H}^+ + 2e^{-}$

At cathode:  $2\text{H}^+ + 2e^{-} \longrightarrow \text{H}_2$

$$\text{emf} = \frac{RT}{nF} \ln \frac{[\text{H}^+]_{\text{P}_1}}{[\text{H}^+]_{\text{P}_2}}$$

$$\text{emf} = \frac{RT}{nF} \ln \frac{P_1}{P_2}$$

$$\therefore n = 2$$

$$\text{emf} = \frac{RT}{2F} \ln \frac{P_1}{P_2}$$

66.  $2\text{H}^+(\text{aq}) + 2e^{-} \longrightarrow \text{H}_2(\text{g})$

$$E = E^{\circ} - \frac{0.0592}{n} \log \frac{P_{(\text{H}_2)}}{[\text{H}^+]^2}$$

$$= 0 - \frac{0.0592}{2} \log \frac{2}{(1)^2}$$

$$E = \frac{-0.0592}{2} \log(2)$$

67. For  $\text{H}_2$  electrode,  $2\text{H}^+ + 2e^{-} \rightarrow \text{H}_2(\text{g})$

$$\therefore E_{\text{H}^+/\text{H}_2} = E^{\circ} - \frac{0.0591}{2} \times \log \frac{P_{\text{H}_2}}{[\text{H}^+]^2}$$

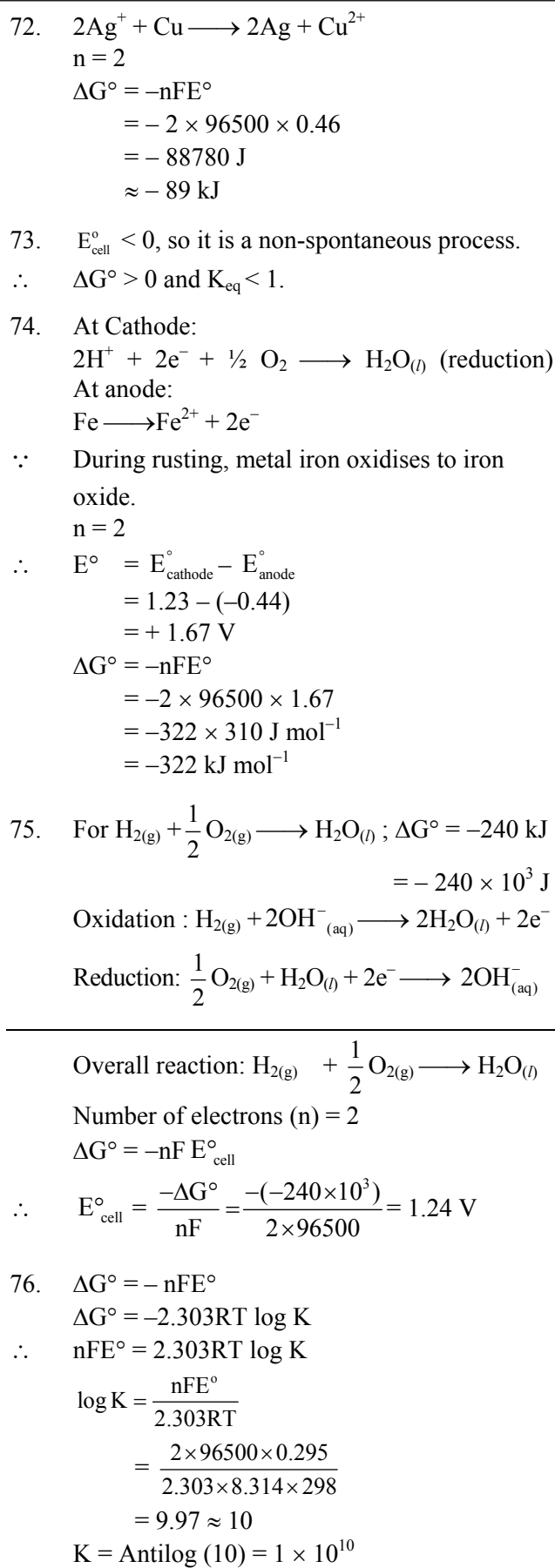
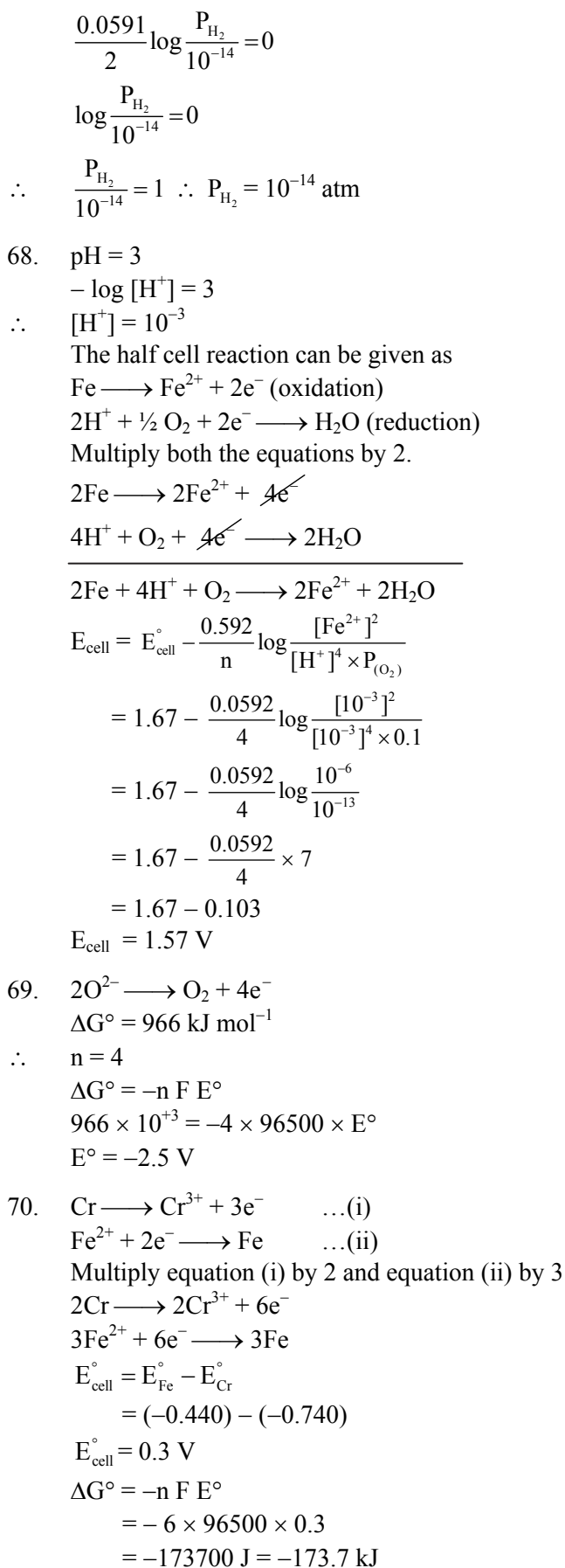
Now,  $E^{\circ} = 0$  for  $\text{H}_2$  electrode.

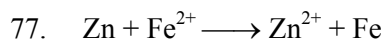
To make the potential of  $\text{H}_2$ -electrode,

$$E_{\text{H}^+/\text{H}_2} = 0,$$

$$0 = 0 - \frac{0.0591}{2} \times \log \frac{P_{\text{H}_2}}{(10^{-7})^2}$$







$$E = E^\circ - \frac{0.0592}{2} \log \frac{[\text{Zn}^{2+}]}{[\text{Fe}^{2+}]}$$

$$\begin{aligned} E^\circ &= E + \frac{0.0592}{2} \log \frac{[\text{Zn}^{2+}]}{[\text{Fe}^{2+}]} \\ &= 0.2905 + \frac{0.0592}{2} \log \frac{10^{-2}}{10^{-3}} \\ &= 0.32 \text{ V} \end{aligned}$$

At equilibrium,

$$\therefore E^\circ = \frac{0.0592}{2} \log K = 0.0296 \log K$$

$$\therefore \log K = \frac{0.32}{0.0296}$$

$$\therefore K = 10^{\frac{0.32}{0.0296}}$$

78.  $E^\circ = \frac{0.0592}{2} \log K$

$$0.295 = \frac{0.0592}{2} \log K$$

$$\begin{aligned} \log K &= \frac{0.295 \times 2}{0.0592} \\ &= 9.96 \end{aligned}$$

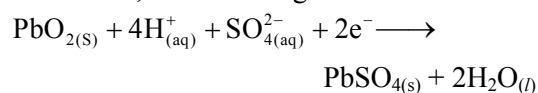
$$\log K \approx 10$$

$$\begin{aligned} K &= \text{Antilog} [10] \\ &= 1 \times 10^{10} \end{aligned}$$

79. To prepare  $\text{H}_2$  electrode, hydrogen is adsorbed on platinised plate. Hence, platinised plate act as adsorbent.

84. During the construction of lead accumulator, the electrodes are dipped in an aqueous solution of  $\text{H}_2\text{SO}_4$  (38% mass) having density approx 1.2 g/mL.

85. At cathode, the following reaction occurs:



Therefore,  $\text{Pb}^{4+}$  is reduced to  $\text{Pb}^{2+}$ .

92. From the values of standard reduction potentials, Li is the strongest reducing agent. Therefore  $\text{Li}^+$  is the weakest oxidizing agent.

93. The element with lowest reduction potential will displace the elements of higher reduction potential. Among A, B, C and D, D has the least reduction potential and hence it will displace all the other three elements.

94. The element with lowest reducing power will displace the elements of higher reducing power. Among A, B, C and D, A has the least reducing power and hence it will displace all the other three elements.

95. The ability of metals to act as reducing agent decreases as the standard reduction potential ( $E^\circ_{\text{red}}$ ) values become more positive.

$\therefore$  The correct order is  $\text{B} > \text{C} > \text{A}$ .

$$-0.80 \text{ V} \quad -0.46 \text{ V} \quad 0.34 \text{ V}$$

96.  $E^\circ_{\text{Zn}^{2+}|\text{Zn}} = -0.76 \text{ V}$

$$E^\circ_{\text{Ni}^{2+}|\text{Ni}} = -0.23 \text{ V}$$

$$E^\circ_{\text{Fe}^{2+}|\text{Fe}} = -0.44 \text{ V}$$

Since, the reduction potential of  $\text{Ni}^{2+}/\text{Ni}$  is highest it will undergo reduction.

Similarly among the given three, Zn has the least reduction potential. So Zn will undergo oxidation.

So for the reaction  $\text{X} + \text{Y}^{2+} \longrightarrow \text{X}^{2+} + \text{Y}$  to be spontaneous,

$\text{X} = \text{Zn}$  and  $\text{Y} = \text{Ni}$

97. Change in oxidation state from +2 to +3 happens in the process of oxidation.

Lower the reduction potential higher is its reducing power.

The increasing  $E^\circ_{\text{M}^{3+}|\text{M}^{2+}}$  values is

$$-0.41 < +0.77 < +1.57 < +1.97$$

$\therefore$  Cr with lowest reduction potential will easily change its oxidation state from +2 to +3.

98. Since,  $\text{Ag}^+$  ions are reduced to Ag and  $E^\circ_{\text{Ag}^+|\text{Ag}} > E^\circ_{\text{Cu}^{2+}|\text{Cu}}$ ; Cu is oxidized to  $\text{Cu}^{2+}$ , which imparts blue colour to the solution.

99. The standard oxidation potentials of A, B, C and D are given.

$\therefore$  Their corresponding standard reduction potential will be 0.03 V, -0.108 V, 0.07 V and -0.1 V respectively. B has the lowest reduction potential while C has the highest reduction potential. Hence, the spontaneous cell reaction takes place between B and C.



## Evaluation Test

$$2. \quad b = \frac{l}{a} = \frac{1.5 \text{ cm}}{0.75 \text{ cm}^2} = 2.0 \text{ cm}^{-1}$$

$$3. \quad \wedge = \frac{1000 \kappa}{C}$$

$$\therefore \kappa = \frac{l}{a} \frac{1}{R} = \frac{0.5}{50} = 1 \times 10^{-2}$$

$$\therefore \wedge = \frac{1000 \times 1 \times 10^{-2}}{1} \\ = 10 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$$

$$4. \quad n = 3$$

$$I = 5 \text{ A}$$

$$t = 10 \times 60 \text{ sec}$$

$$W = 1.18 \text{ g}$$

$$\therefore \text{Equivalent wt. (E)} = \frac{\text{Atomic mass (M)}}{\text{Valency}(n)}$$

$$\therefore E = \frac{M}{3}$$

$$\therefore W = \frac{E \times I \times t}{96500}$$

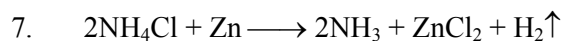
$$1.18 = \frac{M \times 10 \times 60 \times 5}{3 \times 96500}$$

$$\therefore M = \frac{1.18 \times 3 \times 96500}{10 \times 60 \times 5}$$

$$\therefore M = 113.87 \approx 114$$

$\therefore$  The identity of the metal is indium.

6. More negative the reduction potential, higher will be the reducing property. Since Zn has more negative reduction potential than the other given options, Zn will be the strongest reducing agent.



10. Oxidation state of X and Y are  $\text{X}^{3+}$  and  $\text{Y}^{+2}$  respectively.

Ratio of atomic mass of X to Y = 1 : 2

$\therefore$  Valency of X = +3

Valency of Y = +2

$$\therefore \text{Equivalent ratio of X : Y} = \frac{1}{3} : \frac{2}{2} = \frac{1}{3} : 1$$

$\therefore$  ratio of liberated mass of X to Y = Equivalent ratio of X to Y

$$\frac{W_X}{W_Y} = \frac{\frac{1}{3}}{1} = \frac{1}{3} = 1 : 3$$



11.  $W = 90\text{g}$ ,  $I = 965\text{ A}$ ,

$$W = zIt; t = \frac{W}{zI}; z = \frac{\text{Equivalent mass}}{96500}$$

$$\text{For Al, Equivalent mass} = \frac{27}{3}$$

[ $\because$  In  $\text{Al}_2\text{O}_3$ , Al is in +3 state]

$$\therefore z = \frac{27}{3 \times 96500}$$

$$t = \frac{90 \times 3 \times 96500}{27 \times 965}$$

$$= 1000\text{ s}$$

$$= 16\text{ min. } 40\text{ s}$$

12.  $E_{\text{Zn}^{2+}/\text{Zn}}^\circ = -0.76\text{ V}$

$$E_{\text{Mg}^{2+}/\text{Mg}}^\circ = -2.37\text{ V}$$

$$E_{\text{Fe}^{2+}/\text{Fe}}^\circ = -0.44\text{ V}$$

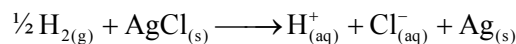
$$E_{\text{Mg}^{2+}/\text{Mg}}^\circ < E_{\text{Zn}^{2+}/\text{Zn}}^\circ < E_{\text{Fe}^{2+}/\text{Fe}}^\circ$$

$\therefore$  Zn will reduce  $\text{Fe}^{2+}$

$$\therefore E_{\text{Zn}^{2+}/\text{Zn}}^\circ > E_{\text{Mg}^{2+}/\text{Mg}}^\circ$$

Zn cannot reduce  $\text{Mg}^{2+}$ . Mg and Zn will reduce Fe but not oxidise Fe since their  $E^\circ$  values are lesser than Fe.

13. In the reaction,



the  $\text{H}_2$  undergoes oxidation while Ag undergoes reduction.

$\therefore$  The galvanic cell can be represented as:  $\text{Pt} | \text{H}_{2(\text{g})} | \text{HCl}_{(\text{soln})} || \text{AgCl}_{(\text{s})} | \text{Ag}$

14.  $\Delta_{\text{HOAc}}^\infty = \Delta_{\text{NaOAc}}^\infty + \Delta_{\text{HCl}}^\infty - \Delta_{\text{NaCl}}^\infty$

$$= 91.0 + 426.2 - 126 = 390.7\text{ S cm}^2\text{ mol}^{-1}$$

15.  $E_{\text{ele}} = E^\circ - \frac{0.0592}{n} \log \frac{1}{[\text{H}^+]}$

$$= 0 - \frac{0.0592}{1} \log \frac{1}{10^{-1}} [\because \text{pH} = 1, [\text{H}^+] = 10^{-1}]$$

$$= -0.0592\text{ V}$$

$$E_{\text{ele}} = -59.25\text{ mV}$$

16. Equivalent weight of A =  $\frac{\text{Atomic mass}}{\text{Valency}} = \frac{112}{x}$

$$\text{Equivalent weight of B} = \frac{\text{Atomic mass}}{\text{Valency}} = \frac{27}{3} = 9$$

$$\frac{\text{mass of A}}{\text{mass of B}} = \frac{\text{Equivalent wt. of A}}{\text{Equivalent wt. of B}} = \frac{5.6}{0.9}$$

$$= \frac{112/x}{9} = \frac{112}{9x}$$

$$\therefore x = \frac{112 \times 0.9}{9 \times 5.6} = 2$$

Valency of A = 2



17. The electrolysis of  $\text{Ni}(\text{NO}_3)_2$  in the presence of Ni electrode will bring in following changes.  
At anode :  $\text{Ni} \longrightarrow \text{Ni}^{2+} + 2\text{e}^-$   
At cathode :  $\text{Ni}^{2+} + 2\text{e}^- \longrightarrow \text{Ni}$   
 $\therefore$  Equivalent of  $\text{Ni}^{2+}$  formed = Equivalent of  $\text{Ni}^{2+}$  lost  
Thus, there will be no change in concentration of  $\text{Ni}(\text{NO}_3)_2$  solution during electrolysis i.e.,  
It will remain 2 M solution.
18. 
$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.0592}{2} \log \frac{[\text{Sn}^{2+}]}{[\text{Ag}^+]^2}$$
  
So to increase  $E_{\text{cell}}$ ,  $\log \frac{[\text{Sn}^{2+}]}{[\text{Ag}^+]^2}$  should decrease.  
i.e.,  $\text{Ag}^+$  ion concentration should increase.  
 $\therefore$  Increase in the concentration of  $\text{Ag}^+$  ions will increase the voltage of the cell.
19. Metal with lower oxidation potential (or higher standard reduction potential) gets deposited (reduced) first.  
Hence the sequence of deposition of metals will be  
 $\text{Ag} > \text{Hg} > \text{Cu} > \text{Mg}$ .
20. After removing cathode, no electricity flows, hence ions will behave in normal manner i.e., move randomly.

# 05 Chemical Kinetics



## Hints



### Classical Thinking

2. As the reaction progresses, the concentration of the reactants decreases and the concentration of the product increases.
3. Negative sign indicates the decrease in concentration of the reactant with time.
6. Rate of reaction  $= -\frac{\Delta x}{\Delta t} = -\left[\frac{0.1-0.2}{10}\right] = \frac{0.1}{10}$   
 $= 0.01 \text{ mol dm}^{-3}\text{min}^{-1}$
7. Rate of reaction  $= \frac{1}{2} \frac{d[C]}{dt}$   
 $= \left(\frac{1}{2} \times 1.0\right) \text{ mol L}^{-1} \text{ s}^{-1}$   
 $= 0.5 \text{ mol L}^{-1} \text{ s}^{-1}$ .
8.  $-\frac{d[\text{N}_2\text{O}_5]}{dt} = 0.03 \text{ M/s}$   
 rate  $= -\frac{1}{2} \frac{d[\text{N}_2\text{O}_5]}{dt} = \frac{1}{4} \frac{d[\text{NO}_2]}{dt}$   
 $\therefore$  rate of formation of  $\text{NO}_2 = \frac{d[\text{NO}_2]}{dt}$   
 $= 2 \left[ \frac{-d[\text{N}_2\text{O}_5]}{dt} \right]$   
 $= 2 \times (0.03 \text{ M/s})$   
 $= 0.06 \text{ M/s}$
10. Rate constant is independent of concentration of reactants. It is the rate of reaction at unit concentration of reactants, therefore remains constant.
11. rate  $= k[A][B]^2$   
 Rate  $= 0.125 \text{ M/s}$ ;  $[A] = 2.0 \text{ M}$ ,  $[B] = 0.4 \text{ M}$   
 Substituting the values in the equation:  
 rate  $= k[A][B]^2$   
 $0.125 \text{ Ms}^{-1} = k \times 2.0 \text{ M} \times (0.4 \text{ M})^2$   
 $\therefore k = \frac{0.125 \text{ M/s}}{2 \text{ M} \times 0.16 \text{ M}^2} = 0.39 \text{ M}^{-2}\text{s}^{-1}$
12. Rate  $= 9 \times 10^{-5} \text{ A}$  (given)  
 $\therefore$  Rate  $= 9 \times 10^{-5} (0.25)^2$   
 $= 5.6 \times 10^{-6} \text{ mol/L s}$
13. Estimation of amount of heat evolved is a thermodynamic aspect. Hence rate law cannot be used to estimate the amount of heat evolved.  
 Rate law can predict the rate of reaction for any composition of reaction. The overall order of the reaction is the sum of the exponents of the concentration terms of reactants in the rate law.



16. If the surface area of reactant increases, the reaction proceeds at faster rate, but does not affect the order of the reaction.

17. Order of a reaction = sum of the exponents of the concentration terms

$$\therefore \text{Order of reaction} = \frac{3}{2} + (-1) = \frac{3}{2} - 1 = \frac{1}{2}$$

18. Order of a reaction = sum of the exponents of the concentration terms

$$\begin{aligned} \therefore \text{Order of reaction} &= \frac{1}{2} + \frac{1}{3} + 1 \\ &= \frac{3+2+6}{6} = \frac{11}{6} \end{aligned}$$

19. Order of a reaction = sum of the exponents of the concentration terms

$$\therefore \text{Order of the reaction} = \frac{3}{2} + \left(-\frac{1}{2}\right) = \frac{2}{2} = 1.$$

$$\begin{aligned} 20. \quad k &= \frac{\text{Rate}}{[\text{Concentration}]} \\ &= \frac{7.5 \times 10^{-4}}{0.5} = 1.5 \times 10^{-3} \text{ min}^{-1} \end{aligned}$$

$$\begin{aligned} 21. \quad \text{Rate}_1 &= k[A]^x \\ \text{Rate}_2 &= k[8A]^x \\ \text{Rate}_2 &= 2 \text{ Rate}_1 \\ k[8A]^x &= 2k[A]^x \\ k8^x [A]^x &= 2k[A]^x \\ 2^{3x} &= 2 \end{aligned}$$

$$\therefore x = \frac{1}{3}$$

23. Integrated rate law for the first order reaction is given by the equation,

$$k = \frac{2.303}{t} \log_{10} \frac{[A]_0}{[A]_t}$$

The unit of k will be given by reciprocal of time as  $\log_{10} \frac{[A]_0}{[A]_t}$  is a unitless quantity.

$$\therefore k = \text{time}^{-1}$$

25. For 1<sup>st</sup> order reaction,  $t_{1/2}$  is independent of initial concentration.

26. Given,

$$a = 100, x = 80, \text{ when } t = 10 \text{ min.}$$

Substituting these values in the first order rate equation

$$\begin{aligned} k &= \frac{2.303}{t} \log \frac{a}{a-x}, \text{ we get} \\ k &= \frac{2.303}{10 \times 60} \log \frac{100}{100-80} = \frac{2.303}{10 \times 60} \log 5 \\ &= \frac{2.303}{600} \times 0.6989 \\ k &= 0.00268 \text{ s}^{-1} \approx 0.0027 \text{ s}^{-1} \end{aligned}$$



27. Given reaction is first order.

Let the reaction be  $A \longrightarrow \text{Products}$ .

$\therefore$  In flask I,

$$[A]_0 = 1 \text{ M}; [A]_t = 0.25 \text{ M}$$

$$\begin{aligned}\therefore k_1 &= \frac{2.303}{t} \log \frac{[A]_0}{[A]_t} \\ &= \frac{2.303}{8} \log \frac{1}{0.25} \\ &= \frac{2.303}{8} \log 4 = \frac{2.303}{8} \times 2 \log 2 \\ &= \frac{2.303}{4} \log 2\end{aligned}$$

Similarly in flask II,

$$[A]_0 = 0.6 \text{ M}; [A]_t = 0.3 \text{ M}$$

$$\begin{aligned}\therefore k_2 &= \frac{2.303}{t} \log \frac{0.6}{0.3} \\ &= \frac{2.303}{t} \log 2\end{aligned}$$

Since, the rate of the reaction is constant (i.e.,  $k_1 = k_2$ )

$$\therefore \frac{2.303}{4} \log 2 = \frac{2.303}{t} \log 2$$

$$\therefore t = 4 \text{ hours.}$$

**Alternate method:**

Flask 1:  $[A]_0 = 1 \text{ M}$

$$[A]_t = 0.25 \text{ M} \left( \frac{1}{4^{\text{th}}} \text{ of original concentration} \right)$$

$$\therefore 2 t_{\frac{1}{2}} = 8 \text{ hrs}$$

$$t_{\frac{1}{2}} = 4 \text{ hrs}$$

Flask 2:  $[A]_0 = 0.6 \text{ M}$

$$[A]_t = 0.3 \text{ M}$$

$$\text{Time} = t_{\frac{1}{2}} = 4 \text{ hrs}$$

$$28. t_{1/2} = \frac{0.693}{k} = \frac{0.693}{2} = 0.347 \text{ min}$$

$$\begin{aligned}29. \text{ For a first order reaction, } t_{1/2} &= \frac{0.693}{k} \\ &= \frac{0.693}{0.693 \text{ hr}^{-1}} \\ &= 1 \text{ hour}\end{aligned}$$

30. Half life of a first order reaction is constant and is independent of the reactant concentration. So, the time taken by 10 g of reactant to reduce its half is 10 years.





33. For a zero order reaction,  
 $A \longrightarrow \text{Products}$   
 Let  $[A]_0 =$  concentration at  $t = 0$   
 and  $[A]_t =$  concentration at  $t = t$   
 From the rate law of zero order reaction,  

$$k = \frac{[A]_0 - [A]_t}{t}$$

$$[A]_0 - [A]_t = kt$$

$$[A]_t = -kt + [A]_0$$
35. Reaction:  $A \longrightarrow \text{Products}$   
 Rate law for a zero order reaction, is given by  

$$\text{Rate} = -\frac{d[A]}{dt} = k[A]^0 = k$$
  
 $\therefore$  Rate constant and rate of the reaction will have the same unit, which is  $\text{mol L}^{-1} \text{t}^{-1}$ .
37. Hydrolysis of methyl acetate can be represented as,  
 $\text{CH}_3\text{COOCH}_3(\text{aq}) + \text{H}_2\text{O}(\text{l}) \longrightarrow \text{CH}_3\text{COOH}(\text{aq}) + \text{CH}_3\text{OH}(\text{aq})$   
 The solvent ( $\text{H}_2\text{O}$ ) participates in the reaction, and it is expected to have second order kinetics. But it follows first order kinetics, as the presence of huge amount of water, keeps its concentration unchanged.  
 $\therefore [\text{H}_2\text{O}] = \text{constant} = k_1$   
 $\therefore \text{rate} = k [\text{CH}_3\text{COOCH}_3] k_1$
38. Molecularity of an elementary reaction is defined as the number of reactant molecules taking part in the reaction, hence it can only have integral values.
39. Molecularity =  $2 + 1 = 3$ .
41. The rate law for the given elementary reaction can be given by;  $\text{rate} = k[A][B]^2$ , i.e., the powers that are raised are those which are given as coefficient of reactant.
42. For elementary reaction,  
 $2A + B \rightarrow C + D$   
 $\text{rate} = k [A]^2[B]$   
 $\therefore$  When concentration of A is tripled by keeping B constant,  
 $\text{rate}_1 = k [3A]^2[B] = k 9 [A]^2[B] = 9 k [A]^2[B]$   
 $\text{rate}_1 = 9 \text{ rate}$   
 $\therefore$  rate of reaction increases by 9 times.
43. The slowest intermediate step is also known as the rate determining step (RDS) and it governs the overall rate of reaction.
44. The rate determining step is the slowest one in a reaction mechanism. This step determines the rate of the overall reaction and the order as well.  
 $\therefore \text{rate} = k[A_2]$   
 $\therefore \text{order} = 1$
49. In Arrhenius equation,  $k = Ae^{-E_a/RT}$ , the pre-exponential factor i.e., A has the unit of  $\text{s}^{-1}$ .
50. The given reaction is exothermic reaction.  
 $\therefore E_{a(\text{reverse})} = E_{a(\text{forward})} + \Delta H$   
 $\therefore$  Activation energy for the reverse reaction  
 $= 38 \text{ kcal} + 20 \text{ kcal} = 58 \text{ kcal}$ .



53.  $\frac{k_{35^\circ}}{k_{34^\circ}} > 1$   
 $\therefore k_{35^\circ} > k_{34^\circ}$   
 $\therefore$  Rate of reaction at  $35^\circ$  is greater than the rate at  $34^\circ$ . i.e., rate increases with the rise in temperature.
54. Rate constant at 280 K =  $k_2$   
 Rate constant at 300 K =  $k_1$   
 The difference in temperature is 20 K.  
 For every 10 K rise in temperature, the rate constant doubles so for 20 K it will be 4 times.  
 $\therefore k_1 = 4k_2$   
 $\therefore k_2 = \frac{k_1}{4} \quad \therefore k_2 = 0.25 k_1$
57. The catalyst does react with the reactants to form intermediate of low activation energy. The intermediate then decomposes to form the product along with the regeneration of catalyst. Thus it reduces energy of activation and provides alternate path for the reaction.

**Critical Thinking**

- Feasibility of a reaction is dealt by thermodynamics.
- $2A + B \longrightarrow C + D$   

$$\text{Rate} = -\frac{1}{2} \frac{d[A]}{dt} = -\frac{d[B]}{dt} = \frac{d[C]}{dt} = \frac{d[D]}{dt}$$

Thus  $\frac{1}{2}$  rate of disappearance of A = rate of disappearance of B.
- $2A + B \longrightarrow 3C + D$   

$$\therefore \text{Rate} = -\frac{1}{2} \frac{d[A]}{dt} = -\frac{d[B]}{dt} = \frac{1}{3} \frac{d[C]}{dt} = \frac{d[D]}{dt}$$

$\frac{d[C]}{dt}$  is change in concentration of C per unit time. Since C is product, its concentration increases and hence  $\frac{d[C]}{dt}$  term is positive.
- $2\text{SO}_{2(g)} + \text{O}_{2(g)} \longrightarrow 2\text{SO}_{3(g)}$   
 Rate of the reaction is represented as:  

$$-\frac{d[\text{O}_2]}{dt} = -\frac{1}{2} \frac{d[\text{SO}_2]}{dt} = \frac{1}{2} \frac{d[\text{SO}_3]}{dt}$$

$$\therefore 2.5 \times 10^{-4} = -\frac{1}{2} \frac{d[\text{SO}_2]}{dt}$$

$$\therefore \text{rate of disappearance of SO}_2 \text{ i.e., } -\frac{d[\text{SO}_2]}{dt}$$

$$= 5.0 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$$
- $\text{N}_2 + 3\text{H}_2 \longrightarrow 2\text{NH}_3$   

$$\text{rate} = \frac{-\Delta[\text{N}_2]}{\Delta t} = -\frac{1}{3} \frac{\Delta[\text{H}_2]}{\Delta t} = \frac{1}{2} \frac{\Delta[\text{NH}_3]}{\Delta t}$$

$$\therefore \text{rate of reaction in terms of change in concentration of N}_2$$

$$= \frac{-\Delta[\text{N}_2]}{\Delta t} = \frac{1}{2} \times \frac{\Delta[\text{NH}_3]}{\Delta t}$$

$$= \frac{1}{2} \times 4.0 \times 10^{-4} = 2 \times 10^{-4} \text{ mole L}^{-1} \text{ s}^{-1}$$



rate of reaction in terms of change in concentration of  $H_2$

$$\begin{aligned} &= \frac{-\Delta[H_2]}{\Delta t} = \frac{3}{2} \times \frac{\Delta[NH_3]}{\Delta t} \\ &= \frac{3}{2} \times 4 \times 10^{-4} = 6 \times 10^{-4} \text{ mole L}^{-1} \text{ s}^{-1} \end{aligned}$$

7. For the reaction  $aA + bB \longrightarrow cC + dD$ ; rate of reaction =  $k[A]^x [B]^y$   
where 'k' is rate constant and sum of  $x$  and  $y$  are order of reaction with respect to 'A' and 'B' respectively.  
Hence, rate of reaction and rate constant are related through definite expression depending upon order of the reaction.

$$9. \text{ rate} = -\frac{d}{dt}[C_6H_5N_2^+Cl^-] = \frac{d}{dt}[C_6H_5Cl] = \frac{d[N_2]}{dt}$$

rate of evolution of  $N_2$  becomes two times faster than the initial i.e.,  $(\text{rate})_2 = 2(\text{rate})_1$ ; when concentration of salt is doubled i.e.,  $[C_6H_5N_2^+Cl^-]_2 = 2[C_6H_5N_2^+Cl^-]_1$

Let the order of reaction be  $x$ .

$$\therefore \text{rate} = k[C_6H_5N_2^+Cl^-]^x$$

$$(\text{rate})_1 = k[C_6H_5N_2^+Cl^-]_1^x$$

$$(\text{rate})_2 = k[C_6H_5N_2^+Cl^-]_2^x = k2^x [C_6H_5N_2^+Cl^-]_1^x$$

$$\therefore \frac{(\text{rate})_1}{(\text{rate})_2} = \frac{k[C_6H_5N_2^+Cl^-]_1^x}{k \cdot 2^x [C_6H_5N_2^+Cl^-]_1^x}$$

$$\frac{1}{2} = \frac{1}{2^x} \quad \therefore x = 1$$

- $\therefore$  The reaction is first order reaction.

10. Let the rate of reaction depends on  $x^{\text{th}}$  power of  $[A]$ . Then

$$r_1 = k[A]^x \text{ and } r_2 = k[2A]^x$$

$$\therefore \frac{r_1}{r_2} = \frac{[A]^x}{[2A]^x}$$

$$\frac{r_1}{r_2} = \frac{1}{2^x}$$

$$\therefore \frac{1}{4} = \frac{1}{2^x} \quad (\because r_2 = 4 r_1)$$

$$\therefore x = 2$$

Rate of reaction remains unaffected if concentration of 'B' is doubled. So the reaction rate does not depend upon the concentration of B. Hence, the correct rate law will be:  $\text{rate} = k[A]^2[B]^0 = k[A]^2$

11. Rate =  $k[A]^2$ , According to the problem,

$$(\text{Rate})_2 = k[2A]^2 = 4k[A]^2 = 4k[A]^2$$

$$\therefore (\text{Rate})_2 = 4 \times \text{Rate}$$

i.e., the rate of formation of B will increase by a factor of 4.

12. Let the initial concentration be C and rate be R.

According to the given condition,

$$\text{When } C_1 = 2C, R_1 = 4R$$

$$\text{When } C_2 = 3C, R_2 = 9R$$



Let the order be  $x$ .

$$\therefore \text{Rate} \propto [\text{Reactant}]^x$$

$$R_1 = k (C_1)^x$$

$$4R = k (2C)^x \quad \dots\text{(i)}$$

$$R_2 = k (C_2)^x$$

$$9R = k (3C)^x \quad \dots\text{(ii)}$$

Dividing (i) by (ii), we get

$$\frac{4R}{9R} = \frac{(2C)^x}{(3C)^x}$$

$$\frac{4}{9} = \left(\frac{2}{3}\right)^x$$

$$\therefore x = 2 \quad \therefore \text{order} = 2$$

13. Let the rate of the given reaction be

$$\text{rate, } r = k[G]^x[H]^y \quad \dots\text{(i)}$$

According to 1<sup>st</sup> condition,

$$8r = k[2G]^x[2H]^y \quad \dots\text{(ii)}$$

According to 2<sup>nd</sup> condition

$$2r = k[2G]^x[H]^y \quad \dots\text{(iii)}$$

Dividing equation (ii) by (iii), we get

$$\frac{8r}{2r} = \frac{k[2G]^x[2H]^y}{k[2G]^x[H]^y}$$

$$4 = 2^y$$

$$\therefore y = 2$$

Substituting the value of  $y$  in equation (i), we get

$$8r = k[2G]^x(2)^2[H]^2$$

$$\frac{8r}{4} = k[2G]^x[H]^2$$

$$2r = k[2G]^x[H]^2 \quad \dots\text{(iv)}$$

Dividing equation (iv) by substituted equation (i)

$$\frac{2r}{r} = \frac{k[2G]^x[H]^2}{k[G]^x[H]^2}$$

$$2 = 2^x \quad \therefore x = 1$$

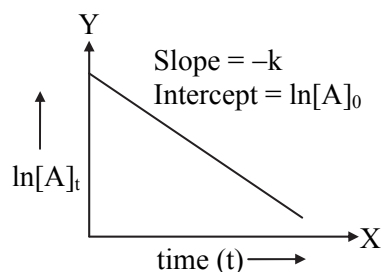
$$\therefore \text{overall order} = x + y = 1 + 2 = 3$$

14. For integrated rate equation,

$$kt = \ln[A]_0 - \ln[A]_t$$

$$\ln[A]_t = -kt + \ln[A]_0$$

On comparing the above equation with  $y = mx + c$





$$15. \quad k = \frac{2.303}{t} \times \log_{10} \frac{a}{a-x}$$

$$\frac{kt}{2.303} = \log_{10} a - \log_{10} (a-x)$$

$$\therefore \log_{10} (a-x) = -\frac{kt}{2.303} + \log_{10} a \quad [\text{comparing with } y = mx + c \text{ where } m = \text{slope.}]$$

$$\therefore \text{Slope} = -\frac{k}{2.303}$$

$$\therefore \text{Negative slope} = \frac{k}{2.303}$$

$$16. \quad t = \frac{2.303}{k} \log \frac{[A]_0}{[A]_t}$$

$$= \frac{2.303}{6} \log \frac{0.5}{0.05} = \frac{2.303}{6} \times \log 10$$

$$= \frac{2.303}{6} = 0.3838 \text{ s} \cong 0.384 \text{ s}$$

17. For the reaction,  $A \longrightarrow \text{products}$

When the volume of vessel changes into  $\frac{1}{3}$  of its initial value then concentration of reactant increases three times its initial concentration.

The rate of reaction for first order reaction is proportional to concentration. So, rate of reaction will increase three times.

$$18. \quad k = \frac{0.693}{30} = 0.0231$$

$$t = \frac{2.303}{k} \log \left( \frac{100}{100-75} \right)$$

$$t = \frac{2.303}{0.0231} \log 4 = 60 \text{ minutes}$$

$$19. \quad t_{1/2} = \frac{0.693}{k}$$

t (for completion of 99.9 %)

99.9% complete means 0.1% remaining

$$t = \frac{2.303}{k} \log_{10} \frac{100}{0.1}$$

$$\therefore \frac{t}{t_{1/2}} = \frac{k}{0.693} \times \frac{2.303}{k} \log_{10} [10^3]$$

$$\therefore \frac{t}{t_{1/2}} = \frac{2.303 \times 3}{0.693} = \frac{6.909}{0.693} = 9.969 \approx 10.$$

20.  $t_{1/2} = 120$  minutes

$$\therefore k = \frac{0.693}{120} \quad \dots (i)$$

Now for 90% completion

$$k = \frac{2.303}{t} \log \frac{a}{0.1a} = \frac{2.303}{t} \quad \dots (ii)$$



$$\therefore \frac{0.693}{120} = \frac{2.303}{t} \quad [\text{From (i) and (ii)}]$$

$$t = \left[ \frac{2.303 \times 120}{0.693} \right] \text{ minutes} \\ = 398.78 \text{ min} \approx 400 \text{ minutes}$$

$$21. [A]_0 = 100, [A]_t = 100 - 75 = 25$$

$$\therefore k = \frac{2.303}{t} \times \log \frac{100}{25} = \frac{2.303}{30} \times \log 4$$

$$\therefore k = \frac{2.303 \times 2 \log 2}{30} \quad \dots \text{(i)}$$

$$[A]_{t_1} = 100 - 93.75 = 6.25$$

$$k = \frac{2.303}{t_1} \log \frac{100}{6.25}$$

$$k = \frac{2.303}{t_1} \log 16 = \frac{2.303}{t_1} 4 \log 2 \quad \dots \text{(ii)}$$

Equating (i) and (ii)

$$\frac{2.303 \times 2 \log 2}{30} = \frac{2.303}{t_1} \times 4 \log 2 \quad (\because k = \text{constant})$$

$$t_1 = 60 \text{ mins.}$$

$$22. t_{1/2} = \frac{0.693}{k} = \frac{0.693}{1.155 \times 10^{-3}} = 600 \text{ s}$$

$$23. \text{At } \frac{3}{4} \text{ life,}$$

$$a - x = \frac{1}{4}$$

$$k = \frac{2.303}{t_{\frac{3}{4}}} \log_{10} \left[ \frac{1}{\frac{1}{4}} \right]$$

$$t_{\frac{3}{4}} = \frac{2.303}{k} \log_{10} 4$$

$$24. t_{1/2} = \frac{0.693}{k} = \frac{0.693}{1.7 \times 10^{-5}} \text{ s} = 40764.7 \text{ s} \\ = \frac{40764.7}{3600} \text{ hr} = 11.32 \text{ hr} \approx 11.3 \text{ hr.}$$

$$25. \text{Rate} = k[\text{Concentration}]$$

$$\text{Rate} = \frac{0.693}{t_{1/2}} [\text{Concentration}].$$

$$\therefore t_{1/2} = \frac{0.693[\text{Concentration}]}{\text{Rate}}$$

$$t_{1/2} = \frac{0.693 \times 0.2}{0.69 \times 10^{-2}} = 20 \text{ min} = 1200 \text{ s.}$$



26.  $t_{1/2} = 10 \text{ min}$

$$\therefore k = \frac{0.693}{t_{1/2}} = \frac{0.693}{10} = 0.0693$$

$$\begin{aligned} \text{Again, } t &= \frac{2.303}{k} \log \frac{[A]_0}{[A]_t} \\ &= \frac{2.303}{0.0693} \times \log \frac{0.08}{0.01} = 30 \text{ min.} \end{aligned}$$

27.  $k = \frac{2.303}{t} \log_{10} \left( \frac{a}{a-x} \right)$

$$\therefore \frac{0.693}{\frac{t_1}{2}} = \frac{2.303}{11} \log_{10} \left( \frac{a}{a-x} \right)$$

[ $\because$  Hydrolysis of cane sugar is a pseudo first order reaction]

$$\therefore \frac{0.693}{4} = \frac{2.303}{11} \log_{10} \left( \frac{a}{a-x} \right)$$

$$\therefore \log_{10} \left( \frac{a}{a-x} \right) = \frac{0.693 \times 11}{2.303 \times 4} = 0.827$$

$$\therefore \frac{a}{a-x} = \text{Antilog}(0.827) = 6.714$$

$$\therefore \frac{a-x}{a} = \frac{1}{6.714} = 0.1489$$

$$\therefore \text{Fraction of sucrose that undergoes hydrolysis} = 1 - 0.1489 = 0.8511$$

**Note:**

$$\frac{a-x}{a} = \text{fraction remaining unhydrolysed}$$

$$\therefore 1 - \left( \frac{a-x}{a} \right) = \text{fraction hydrolysed.}$$

29. For zero order reaction,

$$k = \frac{[A]_0 - [A]}{t}$$

where  $[A]_0$  = Initial concentration of reactant

$[A]_t$  = Concentration of reactant at time 't'

After completion,  $[A]_t = 0$

$$\therefore t = \frac{[A]_0 - 0}{k}$$

$$t = \frac{a}{k} \quad \dots [\because \text{initial concentration is } a]$$

30. Half life of a reaction is defined as the time needed for the reactant concentration to degenerate to one half of its initial value.

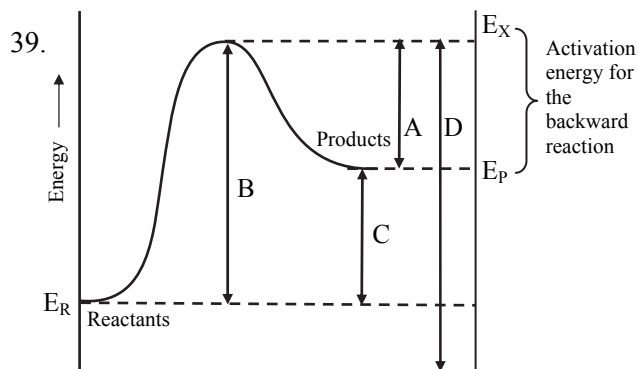
31. Roughly calculated 75% completion of a reaction takes approximately double the half life period of first order.



32. Molecularity of a reaction is the number of reactant molecules taking part in the reaction, and hence cannot be a fraction.
34. Molecularity = 2 + 1 = 3
37. Energy of activation is always positive.
38. Enthalpy change,  $\Delta H = E_f - E_b$

$$= 150 - 260$$

$$= -110 \text{ kJ mol}^{-1}$$



41. Larger the value of  $E_a$  smaller is the rate constant.

$$k' = 2 k'' \quad (\text{given})$$

$$\therefore k' > k''$$

$$\therefore E'_a < E''_a$$

43.  $k = A e^{\frac{-E_a}{RT}}$

For  $E_a = \text{Zero}$

$$k = A e^0 = A$$

44. For the reaction to proceed more rapidly,  $k$  should increase which can be brought about by decrease in  $E_a$ .

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

$$\log \left( \frac{6.90 \times 10^{-3}}{3.45 \times 10^{-5}} \right) = \frac{E_a}{2.303 \times 8.314} \times \frac{40}{300 \times 340}$$

$$\therefore E_a = \frac{2.303 \times 8.314 \times 300 \times 340 \times \log 200}{40}$$

$$= 112.34 \text{ kJ}$$

46. Effect of Catalyst

i. Increases rate of reaction:

[In case of reversible reaction increases rate of forward as well as backward reaction to same extent]

ii. Decreases the time of completion [In case of reversible reaction, decreases the time to achieve equilibrium]

iii. Catalyst does not alter the Gibbs energy change of the reaction.

iv. Decreases energy of activation by forming new transition state

v. Increases rate constant

vi. Decrease half-life period

47. Catalyst affect only activation energy. It decreases the activation energy of the reaction. A catalyst does not affect equilibrium constant, Gibbs energy change ( $\Delta G$ ) and enthalpy change ( $\Delta H$ ) of the reaction.





48.  $\text{Rate} \propto \frac{1}{t}$   
 As temperature increases, rate increases  
 $\therefore$  As rate increases,  $t$  (or even  $t_{1/2}$ ) decreases  
 $\therefore$  As temperature increases,  $t_{1/2}$  decreases.
49. i. Threshold energy of a reaction  
 = Activation energy of forward reaction + potential energy of reactants  
 = 15 kJ + 10kJ = 25 kJ
- ii. Potential energy of Y = Threshold energy of reaction – Activation energy of backward reaction  
 Potential energy of Y = 25 – 9  
 $\therefore$  P.E of Y = 16 kJ.  
 Heat of reaction = Activation energy of forward reaction – Activation energy of backward reaction  
 = 15 – 9 = 6 kJ.
50. Enzyme being a biological catalyst, it always decreases the activation energy.



### Competitive Thinking

2.  $\text{N}_{2(\text{g})} + 3\text{H}_{2(\text{g})} \rightarrow 2\text{NH}_{3(\text{g})}$   
 $\text{rate} = -\frac{d[\text{N}_2]}{dt} = -\frac{1}{3} \frac{d[\text{H}_2]}{dt} = \frac{1}{2} \frac{d[\text{NH}_3]}{dt}$   
 $\therefore -\frac{1}{3} \frac{d[\text{H}_2]}{dt} = \frac{1}{2} \frac{d[\text{NH}_3]}{dt}$   
 $\frac{d[\text{NH}_3]}{dt} = -\frac{2}{3} \frac{d[\text{H}_2]}{dt}$
3. For the given reaction,  
 $3\text{A} \longrightarrow 2\text{B}$   
 $\text{Rate} = -\frac{1}{3} \frac{d[\text{A}]}{dt} = \frac{1}{2} \frac{d[\text{B}]}{dt}$   
 $\therefore \frac{d[\text{B}]}{dt} = -\frac{2}{3} \frac{d[\text{A}]}{dt}$
4.  $2\text{N}_2\text{O}_5 \longrightarrow 4\text{NO}_2 + \text{O}_2$   
 $\text{Rate} = \frac{-1}{2} \frac{d[\text{N}_2\text{O}_5]}{dt} = \frac{1}{4} \frac{d[\text{NO}_2]}{dt} = \frac{d[\text{O}_2]}{dt}$   
 $\therefore \text{Rate} = +\frac{1}{2} k[\text{N}_2\text{O}_5] = \frac{1}{4} k'[\text{N}_2\text{O}_5] = k''[\text{N}_2\text{O}_5] \quad \dots(i)$   
 $\therefore +\frac{1}{2} k[\text{N}_2\text{O}_5] = \frac{1}{4} k'[\text{N}_2\text{O}_5] \quad [\text{from i}]$   
 $\therefore \frac{1}{2} k = \frac{1}{4} k'$   
 $\therefore k' = 2k$   
 $\frac{1}{2} k[\text{N}_2\text{O}_5] = k''[\text{N}_2\text{O}_5] \quad [\text{from i}]$   
 $\therefore \frac{1}{2} k = k''$



5. Increase in concentration of B =  $5 \times 10^{-3} \text{ mol L}^{-1}$ ; Time = 10 s

$$\begin{aligned}\text{Rate of appearance of B} &= \frac{\text{Increase of [B]}}{\text{Time taken}} \\ &= \frac{5 \times 10^{-3} \text{ mol L}^{-1}}{10 \text{ s}} \\ &= 5 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}\end{aligned}$$

6.  $2\text{N}_2\text{O}_5(\text{g}) \longrightarrow 4\text{NO}_2(\text{g}) + \text{O}_2(\text{g})$

$$\text{Rate} = -\frac{1}{2} \frac{d[\text{N}_2\text{O}_5]}{dt} = \frac{1}{4} \frac{d[\text{NO}_2]}{dt} = \frac{d[\text{O}_2]}{dt}$$

$$\therefore \frac{d[\text{NO}_2]}{dt} = \frac{4}{2} \left( -\frac{d[\text{N}_2\text{O}_5]}{dt} \right) = \frac{4}{2} \times 0.02 = 0.04 \text{ M/s}$$

7.  $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \longrightarrow 2\text{NH}_3(\text{g})$

$$\begin{aligned}\text{Rate of disappearance of hydrogen} &= -\frac{\Delta[\text{H}_2]}{\Delta t} \\ &= \frac{6 \times 10^{-2}}{10}\end{aligned}$$

$$\text{Rate} = -\frac{\Delta[\text{N}_2]}{\Delta t} = -\frac{1}{3} \frac{\Delta[\text{H}_2]}{\Delta t} = \frac{1}{2} \frac{\Delta[\text{NH}_3]}{\Delta t}$$

$$\therefore \frac{\Delta[\text{NH}_3]}{\Delta t} = -\frac{2}{3} \frac{\Delta[\text{H}_2]}{\Delta t} = \frac{2}{3} \times \frac{6 \times 10^{-2}}{10}$$

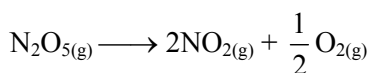
$$\frac{\Delta[\text{NH}_3]}{\Delta t} = 0.4 \times 10^{-2} \text{ mole}$$

$$\Delta[\text{NH}_3] = 0.4 \times 10^{-2} \times 10 = 4 \times 10^{-2} \quad [\because \Delta t = 10]$$

In 10 minutes, number of moles formed  
 $= 4 \times 10^{-2}$

$$\therefore \text{In 0.3 minutes, number of moles of NH}_3 \text{ formed} = \frac{4 \times 10^{-2}}{10} \times 0.3 = 1.2 \times 10^{-3}$$

8.  $\frac{-d[\text{N}_2\text{O}_5]}{dt} = 6.25 \times 10^{-3}$



$$\therefore \text{Rate} = -\frac{d[\text{N}_2\text{O}_5]}{dt} = \frac{1}{2} \frac{d[\text{NO}_2]}{dt} = 2 \frac{d[\text{O}_2]}{dt} \quad \dots(i)$$

$$\begin{aligned}\therefore \frac{d[\text{NO}_2]}{dt} &= 2 \times -\frac{d[\text{N}_2\text{O}_5]}{dt} \\ &= 2 \times 6.25 \times 10^{-3} \\ &= 1.25 \times 10^{-2} \text{ mol L}^{-1} \text{ s}^{-1}\end{aligned}$$

$$\frac{d[\text{O}_2]}{dt} = \frac{1}{2} \times -\frac{d[\text{N}_2\text{O}_5]}{dt} \quad [\text{from i}]$$

$$\begin{aligned}&= \frac{1}{2} \times 6.25 \times 10^{-3} \\ &= 3.125 \times 10^{-3} \text{ mol L}^{-1} \text{ s}^{-1}\end{aligned}$$



$$9. \quad -\frac{\Delta[\text{Br}^-]}{\Delta t} = 0.05 \text{ mol L}^{-1} \text{ min}^{-1}$$

For the given reaction,

$$\text{Average rate of reaction} = -\frac{1}{5} \frac{\Delta[\text{Br}^-]}{\Delta t} = -\frac{\Delta[\text{BrO}_3^-]}{\Delta t}$$

$$\begin{aligned} \therefore -\frac{\Delta[\text{BrO}_3^-]}{\Delta t} &= \frac{1}{5} \times 0.05 \\ &= 0.01 \text{ mol L}^{-1} \text{ min}^{-1} \end{aligned}$$

11. Order can be fractional, zero, negative and positive.

12. There are few reactions of third order and reactions of higher order are unknown. The reason is that the collisions in which three or more molecules all come together at the same time are very unlikely.

13. The overall order of the given reaction is 3 and the order of the reaction with respect to X is 2.

$$\begin{aligned} \therefore \text{Order of the reaction with respect to Y} &= 3 - 2 \\ &= 1 \end{aligned}$$

\(\therefore\) The differential rate equation is

$$-\frac{d[\text{X}]}{dt} = k[\text{X}]^2[\text{Y}]$$

$$\begin{aligned} 14. \quad \text{Rate} &= k[\text{A}]^2[\text{B}] \\ 0.22 &= k(1)^2(0.25) \\ 0.22 &= k \times \frac{1}{4} \\ k &= 0.88 \text{ M}^{-2}\text{s}^{-1} \end{aligned}$$

15. If the reaction is taken as  $\text{A} \longrightarrow \text{Products}$ .

$$\begin{aligned} \text{Rate} &= k[\text{A}] \\ &= 3 \times 10^{-6} \text{ s}^{-1} \times 0.10 \text{ M} = 3 \times 10^{-7} \text{ Ms}^{-1} \end{aligned}$$

$$\begin{aligned} 16. \quad k &= 6.2 \times 10^{-1} \text{ s}^{-1} \\ \text{Rate} &= k[\text{N}_2\text{O}_5] = 6.2 \times 10^{-1} \times 1.25 = 0.775 \\ &= 7.75 \times 10^{-1} \text{ mole L}^{-1}\text{s}^{-1} \end{aligned}$$

17.  $2\text{A} + \text{B} \longrightarrow \text{C} + \text{D}$

$$\text{Rate} = \frac{-1}{2} \frac{d[\text{A}]}{dt} = -\frac{d[\text{B}]}{dt} = \frac{d[\text{C}]}{dt} = \frac{d[\text{D}]}{dt}$$

$$\text{Let rate of reaction} = k[\text{A}]^x[\text{B}]^y$$

$$\text{Or, } \frac{d[\text{C}]}{dt} = k[\text{A}]^x[\text{B}]^y$$

Now from table,

$$1.2 \times 10^{-3} = k[0.1]^x[0.1]^y \quad \dots\text{(i)}$$

$$1.2 \times 10^{-3} = k[0.1]^x[0.2]^y \quad \dots\text{(ii)}$$

$$2.4 \times 10^{-3} = k[0.2]^x[0.1]^y \quad \dots\text{(iii)}$$

Dividing equation (i) by (ii)

$$\therefore \frac{1.2 \times 10^{-3}}{1.2 \times 10^{-3}} = \frac{k[0.1]^x[0.1]^y}{k[0.1]^x[0.2]^y}$$

$$\therefore 1 = \left[\frac{1}{2}\right]^y \quad \therefore y = 0$$



Now Dividing equation (i) by (iii)

$$\therefore \frac{1.2 \times 10^{-3}}{2.4 \times 10^{-3}} = \frac{k[0.1]^x [0.1]^y}{k[0.2]^x [0.1]^y}$$

$$\therefore \left[\frac{1}{2}\right]^1 = \left[\frac{1}{2}\right]^x \quad \therefore x = 1$$

$$\text{Hence, } \frac{d[C]}{dt} = k[A]^1[B]^0$$

$$\therefore \frac{d[C]}{dt} = k[A]$$

18. Let the rate of given reaction be:

$$(\text{rate})_1 = k[A]^x[B]^y$$

Doubling the concentration of A increases the rate by 4.

$$\therefore (\text{rate})_2 = k[2A]^x[B]^y = 2^x k[A]^x[B]^y$$

$$(\text{rate})_2 = 2^x \times (\text{rate})_1$$

$$\frac{(\text{rate})_2}{(\text{rate})_1} = 2^x$$

$$4 = 2^x$$

$$\therefore x = 2$$

Doubling the concentration of B doubles the reaction rate.

$$(\text{rate})_3 = k[A]^x[2B]^y$$

$$(\text{rate})_3 = 2^y k[A]^x[B]^y$$

$$(\text{rate})_3 = 2^y (\text{rate})_1$$

$$\frac{(\text{rate})_3}{(\text{rate})_1} = 2^y$$

$$2 = 2^y$$

$$\therefore y = 1$$

$$\therefore \text{Overall order} = x + y = 2 + 1 = 3$$

$$19. \quad 9r = k(3.24 \times 10^{-2})^n \quad \dots(i)$$

$$r = k(1.2 \times 10^{-3})^n \quad \dots(ii)$$

Dividing (i) by (ii),

$$9 = \left(\frac{3.24 \times 10^{-2}}{1.2 \times 10^{-3}}\right)^n \quad \text{or } 9 = (27)^n$$

$$\text{or } (3)^2 = (3^3)^n = (3)^{3n}$$

$$\text{Hence, } 3n = 2 \text{ or } n = 2/3.$$

20. Rate of the given reaction is doubled when concentration of 'A' is doubled and it is quadrupled when concentration of 'A' and 'B' is raised four times.

$$\text{Let the rate } (R) = k[A]^x[B]^y \quad \dots(i)$$

$\therefore$  When concentration of A is doubled, the new rate<sub>1</sub> (R<sub>1</sub>) will be

$$\text{Rate}_1 (R_1) = k[2A]^x[B]^y \quad \dots(ii)$$

$$\text{But rate}_1(R_1) = 2 \text{ rate}(R)$$

$$\therefore k[2A]^x[B]^y = 2k[A]^x[B]^y \quad \dots[\text{From (i) and (ii)}]$$

$$\therefore k 2^x[A]^x[B]^y = 2k[A]^x[B]^y$$

$$\therefore 2^x = 2 \text{ and thus } x = 1$$



Similarly when concentration of both A and B is quadrupled, the new rate<sub>2</sub> (R<sub>2</sub>) will be

$$\text{Rate}_2 (R_2) = k[4A]^x [4B]^y \quad \dots(\text{iii})$$

$$\text{But rate}_2 (R_2) = 4 \text{ Rate}(r)$$

$$\therefore k[4A]^x [4B]^y = 4k[A]^x [B]^y \quad \dots[\text{From (i) and (iii)}]$$

$$\cancel{k} 4^x [\cancel{A}]^x 4^y [\cancel{B}]^y = 4 \cancel{k} [\cancel{A}]^x [\cancel{B}]^y$$

$$\therefore 4^x \cdot 4^y = 4$$

$$\therefore 4 \cdot 4^y = 4 \quad (\because x = 1)$$

$$\therefore 4^y = 1 \text{ and thus } y = 0$$

Substituting the values of x and y in (i), the rate expression for the given reaction is rate (R) = k[A]<sup>1</sup> [B]<sup>0</sup>

$$\therefore \text{rate}(R) = k[A]$$

Thus, the order of the given reaction with respect to:

i. 'A' is 1 and ii. 'B' is 0.

The overall order of the given reaction is 1.

$$21. k = [\text{NO}]^2 [\text{O}_2]$$

As volume is halved concentration gets doubled

$$\therefore k_1 = [2\text{NO}]^2 [2\text{O}_2] = 4[\text{NO}]^2 2[\text{O}_2] \\ = 8 [\text{NO}]^2 [\text{O}_2] = 8k$$

$$22. t = 40 \text{ min}, [X]_0 = 0.1 \text{ M}, [X] = 0.025 \text{ M}$$

$$\therefore k = \frac{2.303}{t} \log \frac{0.1}{0.025} \\ = \frac{2.303}{40} \times \log 4 = \frac{2.303}{40} \times 2 \log 2 \\ = \frac{2.303 \times 2 \times 0.3010}{40} = 0.03467 \text{ min}^{-1}$$

$$\therefore \text{Rate} = k [x] = (0.03467 \times 0.01) \text{ M min}^{-1} \\ = 3.467 \times 10^{-4} \text{ M min}^{-1} \\ \approx 3.47 \times 10^{-4} \text{ M min}^{-1}$$

$$23. [A]_0 = 100, [A]_t = 100 \times \frac{1}{10} = 10$$

$$\text{For first order reaction, } k = \frac{2.303}{t} \log \frac{[A]_0}{[A]_t}$$

$$\therefore t = \frac{2.303}{k} \log \frac{[A]_0}{[A]_t} = \frac{2.303}{2.303 \times 10^{-2}} \log \left( \frac{100}{10} \right) \\ = \frac{1}{10^{-2}} \times \log(10) = 10^2 = 100 \text{ seconds}$$

$$24. k_1 = \frac{2.303}{15} \log \frac{0.8}{0.4} = \frac{2.303}{15} \log 2$$

$$\text{Similarly } k_2 = \frac{2.303}{t} \times \log \frac{0.1}{0.025} = \frac{2.303}{t} \log 4$$

Now,  $k_1 = k_2$

$$\therefore \frac{2.303}{15} \log 2 = \frac{2.303}{t} \times 2 \log 2$$

or,  $t = 30 \text{ mins}$



25.  $k = 10^{-2} \text{ s}^{-1}$

$$t = \frac{2.303}{k} \log_{10} \frac{[A]_0}{[A]_t}$$

$$t = \frac{2.303}{10^{-2}} \log_{10} \left( \frac{20}{5} \right)$$

$$= 138.65 \text{ s} \approx 138.6 \text{ s}$$

26. The unit of rate constant for 1<sup>st</sup> order reaction is  $\text{time}^{-1}$ .

27.  $2A + B \longrightarrow \text{Products}$

When concentration of B was doubled, there is no change in the half-life i.e., half life is independent of concentration of B.

$\therefore$  With respect to B, the reaction follows first order.

When the concentration of A is doubled, the rate increases two times.

So, the reaction follows first order with respect to A.

$\therefore$  Overall order is  $1 + 1 = 2$

$\therefore$  Rate =  $k[A][B]$

$$k = \frac{\text{Rate}}{[A][B]}$$

$\therefore$  Unit of  $k = \frac{(\text{mol/L})(\text{s}^{-1})}{(\text{mol/L})(\text{mol/L})}$

$$\text{Unit of } k = \text{L mol}^{-1} \text{ s}^{-1}$$

30. The half life of first order reaction is given by equation  $t_{1/2} = \frac{0.693}{k}$

The equation implies that the half life of a first order reaction is constant and is independent of the reactant concentration. Since, in given reaction, change in concentration does not affect its half life; it must be a first order reaction.

31. Half life period of first order reaction is given as;

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

$$\therefore k = \frac{0.693}{t_{\frac{1}{2}}} = \frac{0.693}{6.93 \text{ hr}}$$

$$k = 0.1 \text{ hr}^{-1}$$

Thus, the value of rate constant for the given reaction is  $0.1 \text{ hr}^{-1}$ .

32.  $t_{1/2} = 1386 \text{ sec}$

$$k = \frac{0.693}{1386} = 5 \times 10^{-4} \text{ s}^{-1} = 0.5 \times 10^{-3} \text{ s}^{-1}$$

33. The rate constant for a first order reaction is independent of concentration.

$$\begin{aligned} \text{It is given as } k &= \frac{0.693}{t_{1/2}} \\ &= \frac{0.693}{7.0 \times 10^{-4}} \\ &= 990 \text{ s} \end{aligned}$$



34. 60% of a first order reaction was completed

∴ If  $a = 100$  then

$$a - x = 40$$

and time,  $t = 60$  min

$$\therefore k = \frac{2.303}{60} \log \frac{100}{40}$$

$$= \frac{2.303}{60} \log 2.5 = 0.0153$$

$$k = \frac{0.693}{t_{1/2}} \quad \dots (\because 50\% \text{ is completed})$$

$$t_{1/2} = \frac{0.693}{0.0153} = 45.29 \approx 45 \text{ min}$$

35.  $t_{1/2} = 6.93$  min

If  $a = 100$

$$a - x = 1$$

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{6.93} = 0.1$$

$$k = \frac{2.303}{t} \log \frac{a}{a-x}$$

$$t = \frac{2.303}{k} \log \frac{a}{a-x} = \frac{2.303}{0.1} \log \frac{100}{1}$$

$$= \frac{2.303}{0.1} \times 2 = 46.06 \text{ min}$$

$$36. k = \frac{0.693}{t_{1/2}} = \frac{0.693}{138}$$

$$k = \frac{2.303}{t} \log \left( \frac{1.28}{0.04} \right)$$

$$t = \frac{138 \times 2.303}{0.693} \log 32 = \frac{138 \times 2.303}{0.693} \log 2^5$$

$$= \frac{138 \times 2.303 \times 5 \times 0.3010}{0.693}$$

$$t = 690 \text{ s}$$

37. For the given first order reaction, the concentration of the reactant is reduced to 12.5% in 1 h.

∴ If  $[A]_0 = 100$ , then  $[A]_t = 12.5$  and

$$t = 1 \text{ h} = 60 \text{ min}$$

$$k = \frac{2.303}{t} \log_{10} \frac{[A]_0}{[A]_t}$$

$$= \frac{2.303}{60} \log_{10} \frac{100}{12.5} = 0.03466 \text{ min}^{-1}$$

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

$$\therefore t_{1/2} = \frac{0.693}{0.03466} = 19.99 \approx 20 \text{ min}$$

∴ The reaction was half completed in 20 min.



38. For a first order reaction, Rate =  $k[A]$

$$\therefore [A] = \frac{\text{Rate}}{k}$$

$$\therefore \text{At } t = 10 \text{ s, } [A]_0 = \frac{0.04 \text{ mol L}^{-1} \text{ s}^{-1}}{k \text{ s}^{-1}}$$

At  $t = 20 \text{ s}$ , i.e., after 10 s,

$$[A]_t = \frac{0.03 \text{ mol L}^{-1} \text{ s}^{-1}}{k \text{ s}^{-1}}$$

$$\therefore k = \frac{2.303}{t} \log \left( \frac{[A]_0}{[A]_t} \right)$$

$$\therefore k = \frac{2.303}{10} \log \frac{\frac{0.04}{k}}{\frac{0.03}{k}}$$

$$\therefore k = \frac{2.303}{10} \log \frac{0.04}{0.03} = \frac{2.303}{10} \times 0.1249$$

$$\therefore t_{1/2} = \frac{0.693}{k} = \frac{0.693 \times 10}{2.303 \times 0.1249}$$
$$= 24.09 \text{ s} \approx 24.1 \text{ s}$$

39.  $k = \frac{2.303}{t_{1/4}} \log \left( \frac{1}{3/4} \right)$

$$t_{1/4} = \frac{2.303}{k} \log \left( \frac{4}{3} \right)$$

$$t_{1/4} = \frac{0.29}{k}$$

40.  $\frac{1}{4}$  of initial concentration is obtained after two half-life.

i.e.,  $2 \times t_{1/2} = 20 \text{ min}$

$$t_{1/2} = 10 \text{ min}$$

$\frac{1}{16}$  of initial concentration is obtained after 4 half life. i.e.,  $\frac{1}{16} = \frac{1}{2} \times \frac{1}{2} \times \frac{1}{2} \times \frac{1}{2}$

$$\therefore \text{time required} = 4 \times t_{1/2} = 4 \times 10 = 40 \text{ min}$$

41.  $t_{1/2} = 10 \text{ min}$

$$\therefore 20 \text{ min} = 2 \text{ half lives}$$

After two half lives, concentration of reactant reduces to  $\frac{1}{4}$  th of initial concentration.

$$\therefore \text{Concentration after } 20 \text{ min} = \frac{1}{4} \times 12 = 3 \text{ M}$$

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{10}$$

$$k = 0.0693 \text{ min}^{-1}$$

For a first order reaction,

$$\text{rate} = k[\text{concentration of reactant}]$$

$$= 0.0693 \times 3 \text{ M min}^{-1}$$





$$42. \quad 0.5 \text{ M} \Rightarrow 0.125 \text{ M} \quad \dots \frac{1}{4} \text{ concentration}$$

$$\Rightarrow 2t_{1/2} = 50 \text{ min}$$

$$\therefore t_{1/2} = 25 \text{ min}$$

$$\therefore \text{Rate constant (k)} = \frac{0.693}{t_{1/2}}$$

$$k = \frac{0.693}{25} \text{ min}^{-1}$$

$$\text{Rate of H}_2\text{O}_2 \text{ decomposition} = k[\text{H}_2\text{O}_2]$$

$$\therefore -\frac{d[\text{H}_2\text{O}_2]}{dt} = \frac{0.693}{25} (0.05)$$



$$\begin{aligned} \therefore \frac{d[\text{O}_2]}{dt} &= -\frac{1}{2} \frac{d[\text{H}_2\text{O}_2]}{dt} \\ &= +\frac{1}{2} \frac{(0.693)}{25} (0.05) \\ &= 6.93 \times 10^{-4} \text{ M min}^{-1} \end{aligned}$$

43. The decomposition of  $\text{PH}_3$  on tungsten at low pressure is a first order reaction. So, rate is directly proportional to the concentration of  $\text{PH}_3$ .

$$\text{Rate} = k[\text{PH}_3]$$

At low pressure, surface area covered is proportional to partial pressure of  $\text{PH}_3$  and hence, rate is directly proportional to the surface coverage.

46. For a zero order reaction,

$$t_{1/2} = \frac{[\text{A}]_0}{2k}$$

$$\therefore k = \frac{2}{2 \times 1} = 1 \text{ h}^{-1}$$

$$k = \frac{[\text{A}]_0 - [\text{A}]_t}{t}$$

$$t = \frac{[\text{A}]_0 - [\text{A}]_t}{k} = \frac{0.50 - 0.25}{1}$$

$$t = 0.25 \text{ h}$$

47. For 1<sup>st</sup> order reaction

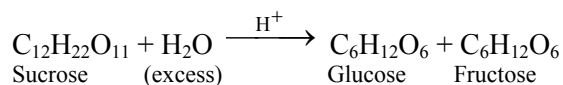
$$k_1 = \frac{0.693}{t_{1/2}} = \frac{0.693}{40} = 0.01732 \text{ s}^{-1}$$

For zero order reaction

$$k_0 = \frac{[\text{a}]}{2t_{1/2}} = \frac{1.386}{2 \times 20} = 0.03465 \text{ mol dm}^{-3} \text{ s}^{-1}$$

$$\frac{k_1}{k_0} = \frac{0.01732}{0.03465} = 0.5 \text{ mol}^{-1} \text{ dm}^3$$

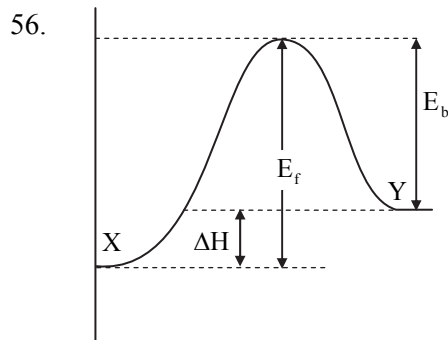
50. Inversion of cane sugar is the reaction in which sucrose (cane sugar) is hydrolysed to a mixture of glucose and fructose.



This is pseudo first order reaction as water is in excess.



53. Since NO is formed during reaction and again consumed, it is intermediate.
55. The rate law expression is written for the slowest step in the reaction mechanism. So, the rate of the given reaction is  
rate =  $k_1 [\text{ClO}^-]^2$ .



For an endothermic reaction

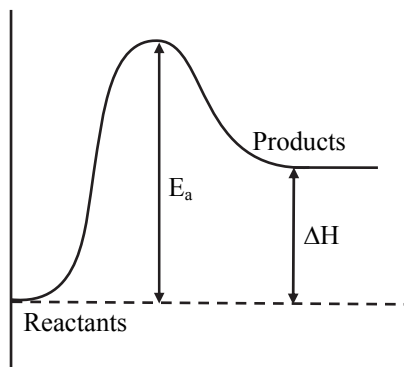
$$E_b = E_f - \Delta H$$

$$\therefore E_b < E_f$$

57.  $\Delta H = E_{a(\text{forward})} - E_{a(\text{reverse})}$

$$\therefore \Delta H = 0 \quad \left[ \because E_{a(\text{forward})} = E_{a(\text{reverse})} \right]$$

58. For an endothermic reaction, the energy of products will be more than that of reactants.



$$\therefore E_a > \Delta H$$

59. (A)  $k$  is rate constant.  
(B)  $A$  is Arrhenius parameter.  
(C)  $R$  is universal gas constant

60. Arrhenius equation is given as,

$$k = A \cdot e^{-E_a/RT}$$
$$= \frac{A}{e^{E_a/RT}}$$

62. By Arrhenius equation

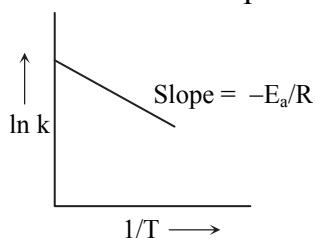
$$k = A e^{-E_a/RT}$$

By taking logarithms on both sides,

$$\ln k = \ln A - \frac{E_a}{RT}$$



On plotting  $\ln k$  vs  $\frac{1}{T}$

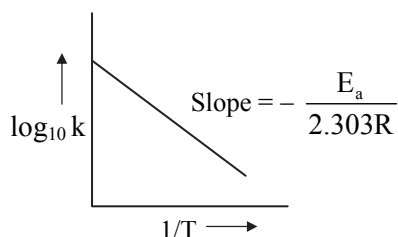


$\therefore$  By knowing slope, activation energy can be determined.

$$63. \log_{10} k = \log_{10} A - \frac{E_a}{2.303RT}$$

$$\log_{10} k = \frac{-E_a}{2.303R} \times \frac{1}{T} + \log_{10} A$$

A plot of  $\log_{10} k$  against  $\frac{1}{T}$  is a straight line with a slope equal to  $\frac{-E_a}{2.303R}$  and intercept equal to  $\log_{10} A$ .



65. Rate doubles for every  $10^\circ\text{C}$  rise.

$\therefore$  When temperature is raised by  $50^\circ\text{C}$ , the rate will increase by  $= 2^5 = 32$  times.

66. The relationship can be written as

$$k = Ae^{\frac{-E_a}{RT}}$$

$$\text{as } T \rightarrow \infty; \frac{1}{T} \rightarrow 0; \quad \therefore k \rightarrow A$$

$\therefore$  At  $T = \infty$ ,  $k = A = 6.0 \times 10^{14} \text{ s}^{-1}$

$$67. k = Ae^{-E_a/RT}$$

$$\therefore k_1 = Ae^{-E_{a1}/RT} \text{ and } k_2 = Ae^{-E_{a2}/RT}$$

$$\therefore \frac{k_2}{k_1} = e^{\left(\frac{E_{a1} - E_{a2}}{RT}\right)}$$

$$\ln \frac{k_2}{k_1} = \frac{E_{a1} - E_{a2}}{RT} = \frac{10,000}{8.314 \times 300} = 4$$

68.  $k_1 = k_2$

$$10^{16} \cdot e^{-2000/T} = 10^{15} \cdot e^{-1000/T}$$

$$10 = \frac{e^{-1000/T}}{e^{-2000/T}} = e^{\frac{2000}{T} - \frac{1000}{T}}$$

$$10 = e^{1000/T}$$

$$\ln 10 = \frac{1000}{T}$$

$$2.303 \log 10 = \frac{1000}{T}$$

$$2.303 = \frac{1000}{T} \quad \therefore T = \frac{1000}{2.303} \text{ K}$$



69. Activation energy ( $E_a$ ) = 600 R;

$$T_1 = 27^\circ\text{C} = 300\text{ K}$$

$$T_2 = 327^\circ\text{C} = 600\text{ K}$$

$$\begin{aligned}\ln \frac{k_2}{k_1} &= \frac{E_a}{R} \left[ \frac{T_2 - T_1}{T_1 \times T_2} \right] \\ &= \frac{600 R}{R} \left[ \frac{600 - 300}{300 \times 600} \right] \\ &= 600 \left[ \frac{300}{300 \times 600} \right] = 1\end{aligned}$$

$$\therefore \frac{k_2}{k_1} = e^1 = e$$

$$70. \log \frac{k_2}{k_1} = \frac{E_a}{2.303R} \left[ \frac{T_2 - T_1}{T_1 \times T_2} \right]$$

$$\log 2 = \frac{E_a}{2.303 \times 8.314} \left[ \frac{310 - 300}{300 \times 310} \right]$$

$$\begin{aligned}\therefore E_a &= \frac{\log 2 \times 2.303 \times 8.314 \times 300 \times 310}{10} \\ &= \frac{0.3010 \times 2.303 \times 8.314 \times 300 \times 310}{10} \\ &= 53,598\text{ J} = 53.59\text{ kJ} \approx 54\text{ kJ}\end{aligned}$$

71. Temperature dependence of rate is given by Arrhenius equation

$$k = Ae^{-E_a/RT}$$

$$\log k = \log A - \frac{E_a}{RT \times 2.303}$$

$$\therefore \log k = -\left( \frac{E_a}{2.303R} \right) \frac{1}{T} + \log A \dots (i)$$

$$\log k = -(2000) \frac{1}{T} + 6.0 \dots (ii) \text{ [Given]}$$

Comparing equation (i) and (ii),

$$\frac{E_a}{2.303R} = 2000$$

$$\begin{aligned}\therefore E_a &= 2000 \times 8.314 \times 2.303 \\ &= 38294\text{ J mol}^{-1} = 38.29\text{ kJ mol}^{-1} \\ &= 38.3\text{ kJ mol}^{-1}\end{aligned}$$

$$\log A = 6.0$$

$$A = \text{Antilog}(6.0)$$

$$A = 10^6 = 1.0 \times 10^6\text{ s}^{-1}$$

72. Rate of reaction =  $k$ [concentration of reactants]

When a catalyst increases the rate of a chemical reaction, there is no change in initial concentration of reactants.

So, when rate of reaction increases, the rate constant also increases.



73. Rate  $r = k[\text{H}^+]^n$   
 New rate,  $r' = 100 r$
- $$\therefore \frac{r'}{r} = 100$$
- $\text{pH} = -\log_{10}[\text{H}^+] \quad \dots(i)$
- $\therefore$  When  $\text{pH} = 3$ , equation (i) becomes  
 $3 = -\log_{10}[\text{H}^+]$
- $\therefore \log_{10}[\text{H}^+] = -3$   
 Taking antilog on both sides  
 $[\text{H}^+] = \text{Antilog } \bar{3} = 10^{-3} \text{ M}$   
 Similarly when  $\text{pH} = 1$ ,  $[\text{H}^+] = 10^{-1} \text{ M}$   
 $\text{pH}$  changes from 3 to 1  
 i.e.,  $[\text{H}^+] = 10^{-3} \text{ M}$  changes to  $[\text{H}^+]' = 10^{-1} \text{ M}$   
 i.e., concentration increases 100 times.
- $$\frac{[\text{H}^+]'}{[\text{H}^+]} = \frac{10^{-1}}{10^{-3}} = 100$$
- $\therefore \frac{r'}{r} = \frac{k[\text{H}^+]'^n}{k[\text{H}^+]^n}$
- $\therefore \frac{r'}{r} = \left(\frac{[\text{H}^+]'}{[\text{H}^+]}\right)^n$  or  $100 = (100)^n$  or  $n = 1$



### Evaluation Test

- For a first order reaction  

$$k = \frac{2.303}{t} \log \frac{a}{(a-x)} \quad \left[ \because t_{1/2} = \frac{0.693}{k} \Rightarrow k = \frac{0.693}{t_{1/2}} \right]$$

$$t = \frac{2.303}{k} \log \frac{100}{(100-90)}$$

$$= \frac{2.303 \times t_{1/2}}{0.693} \times \log \frac{100}{10}$$

$$= 3.3 \times t_{1/2} \times \log 10 = 3.32 t_{1/2} \approx 3.3 t_{1/2}$$
- $$k = \frac{2.303}{t} \times \log \frac{[\text{A}]_0}{[\text{A}]_t}$$

$$= \frac{2.303}{500} \log \frac{\text{M}/10}{\text{M}/100}$$

$$= \frac{2.303}{500} \times \log 10 = \frac{2.303}{500} = 0.004606$$

$$= 4.606 \times 10^{-3} \text{ s}^{-1}$$
- The rate of reaction depends upon concentration of reactant, surface area of reactant, temperature, presence of light and catalyst. Gases being compressible, their concentration vary with pressure. A concentration of solids and liquids are not affected by change in pressure. So, the rate of reaction which do not contain any gases is not dependent on pressure.



5. From 1<sup>st</sup> and 2<sup>nd</sup> set of data it is found that change in concentration of C does not affect the rate. So, the order with respect to C is zero.

$$\text{Let, Rate} \propto [\text{B}]^x \quad \therefore \text{Rate} = k_1[\text{B}]^x$$

In 1<sup>st</sup> and 3<sup>rd</sup> set of data

$$5.0 \times 10^{-3} = k_1 (0.005)^x \quad \dots(\text{i})$$

$$1.0 \times 10^{-2} = k_1 [0.01]^x \quad \dots(\text{ii})$$

Dividing equation (ii) by (i),

$$\left( \frac{1.0 \times 10^{-2}}{5.0 \times 10^{-3}} \right) = \left( \frac{0.01}{0.005} \right)^x$$

$$\left( \frac{10}{5} \right) = \left( \frac{10}{5} \right)^x$$

$$\therefore x = 1$$

$$\text{Let, Rate} \propto [\text{A}]^y$$

$$\therefore \text{Rate} = k_2[\text{A}]^y$$

From 1<sup>st</sup> and 4<sup>th</sup> set of data

$$(5.0 \times 10^{-3}) = k_2 [0.010]^y \quad \dots(\text{iii})$$

$$(1.25 \times 10^{-3}) = k_2 [0.005]^y \quad \dots(\text{iv})$$

Dividing equation (iv) by (iii),

$$\frac{1.25 \times 10^{-3}}{5.0 \times 10^{-3}} = \left( \frac{0.005}{0.010} \right)^y$$

$$\left( \frac{1.25}{5} \right) = \left( \frac{0.5}{1} \right)^y$$

$$\left( \frac{0.25}{1} \right) = \left( \frac{0.5}{1} \right)^y$$

$$y = 2$$

$$\therefore \text{Rate} = k [\text{A}]^2 [\text{B}]^1 [\text{C}]^0$$

7. Given rate of the reaction ( $\sim 7.3 \times 10^{-2}$ ) is constant i.e., the concentration of reactant does not change with time. So, the reaction follows zero order.

8. At half life,  $a = 0.5$ ,  $a - x = \frac{0.5}{2}$

$$k = \frac{2.303}{t_{1/2}} \log \left[ \frac{0.5}{0.5/2} \right]$$

$$t_{1/2} = \frac{2.303}{k} \log 2 \quad t_{1/2} = \frac{\ln 2}{k}$$

9. The unit of rate constant for zero order reaction is  $\text{mol dm}^{-3} \text{sec}^{-1}$ .

10.  $\text{rate} = k[\text{A}]^n [\text{B}]^m$

New rate,  $r'$

$$r' = k[2\text{A}]^n [\text{B}/2]^m = k[2]^n [\text{A}]^n \frac{[\text{B}]^m}{[2]^m}$$

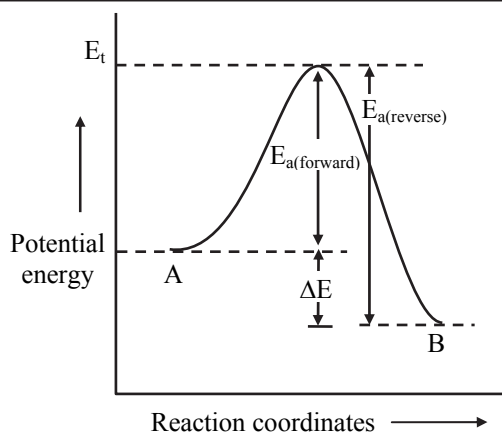
$$= k \frac{[2]^n}{[2]^m} [\text{A}]^n [\text{B}]^m = 2^{(n-m)} k[\text{A}]^n [\text{B}]^m$$

$$= 2^{(n-m)} \text{rate}$$

- $\therefore$  The ratio of new rate ( $r'$ ) to earlier rate of reaction i.e.,  $\frac{r'}{\text{rate}} = 2^{(n-m)}$



$$\begin{aligned}
 11. \quad E_{a(\text{forward})} + \Delta E &= E_{a(\text{reverse})} \\
 17 + 40 &= E_{a(\text{reverse})} \\
 E_{a(\text{reverse})} &= 57 \text{ kJ}
 \end{aligned}$$



12. Molecularity of a reaction is the number of molecules of the reactants taking part in a single step chemical reaction. It will have integral values and can be determined theoretically by stoichiometric equation of the elementary reaction.

The sum of exponents of the molar concentrations of the reactants in the rate equation is called order of that reaction.

13.  $A_0$  = Amount of element initially present.  
 $A_t$  = Amount of element present at time 't'.

$$\begin{aligned}
 n = \text{number of half lives} &= \frac{\text{time period}}{\text{one half life}} \\
 &= \frac{560}{140} = 4
 \end{aligned}$$

$$\therefore \frac{[A]_t}{[A]_0} = \frac{1}{2^4} = \frac{1}{16} \text{ g}$$

14. Average rate and instantaneous rate can be equal for zero order reactions.

$$15. \quad \frac{-d[N_2]}{dt} = \frac{-1}{3} \frac{d[H_2]}{dt} = \frac{1}{2} \frac{d[NH_3]}{dt}$$

Rate of conversion of  $H_2$

$$= \frac{-d[H_2]}{dt} = \frac{3}{2} \frac{d[NH_3]}{dt}$$

$$= \frac{3}{2} \times 0.001 = 0.0015 \text{ kg/hr}$$



## Hints



## Classical Thinking

- Noble metals like gold, platinum, etc., being unreactive, are found in free state.
- When oil, water and air are mixed up, they produce froth. Hence, pine oil is used as foaming agent.
- In order to separate two sulphide ores by froth floatation process, proportion of oil to water is adjusted or certain depressant like NaCN is added.
- Silica is an acidic flux used to remove basic impurities.
- For the formation of metal oxide,  $\Delta G^\circ$  increases with the increase in temperature.  

$$2M_{(s)} + O_{2(g)} \longrightarrow 2MO_{(s)}$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$
 Here,  $\Delta H^\circ = -ve$  (since all combustion reactions are exothermic).  
 $\Delta S^\circ = -ve$  (gaseous reactant converted into solid product i.e.,  $O_{2(g)}$  converted to  $MO_{(s)}$ ).  
 At low temperature  $\Delta G^\circ$  may be negative but it becomes positive (i.e., increases) with increase in temperature.
- The relative tendency of the metals to undergo oxidation is in the following order,  
 $Mg > Al > Cr > Fe > Ag$   
 Therefore, the decreasing order of the stabilities of the metal oxides is  
 $MgO > Al_2O_3 > Cr_2O_3 > FeO > Ag_2O$ .
- Metals like bismuth (m.p. of Bi: 544.3K), lead (m.p. of Pb: 600.4 K), mercury (m.p. of Hg: 234.6 K), etc. are separated from their crude form by liquation.
- Tin (melting point: 504.8 K) and lead (melting point: 600.4 K) have lower melting point as compared to the melting point of impurities present in their respective ores. Hence, liquation process is used.
- Liquation process is the refining method used to obtain pure tin metal. The pure tin metal obtained by this method is called pig tin.
- In electrolytic refining, anode is made up of impure metal and cathode is made up of strip of the same metal in the pure form. Anode and cathode are suspended in a suitable electrolytic bath containing soluble salt of the same metal.
- $$Ni + 4CO \xrightarrow{330-350K} Ni(CO)_4$$

volatile

 Nickel when heated with carbon monoxide forms nickel tetra carbonyl complex which is highly volatile.
- In van Arkel method, the impure metal is heated in a vessel with little iodine to form iodide of metal which is covalent and volatile.
- In column chromatography, the mixture whose different components are to be separated is dissolved in suitable liquid or gaseous solvent (called moving/mobile phase) and then it is moved through the stationary phase [alumina ( $Al_2O_3$ ) or silica ( $SiO_2$ )] and eluted out using eluents.
- The concentrated ore containing trace elements can be best purified by chromatography technique like gas chromatography, thin layer chromatography, paper chromatography, etc.
- Wrought iron contains least percentage of carbon  $<0.2\%$  and is the purest form of iron.
- Impurities of  $SiO_2$  (acidic) is present in the iron ore, so basic flux limestone ( $CaCO_3$ ) is added during the extraction of iron.





44. The various changes taking place in the blast furnace at different temperature are given below:

Temperature (K)	Changes taking place	Reactions
500 K	Ore loses moisture	
900 K	Reduction of ore by CO	$\text{Fe}_2\text{O}_3 + 3\text{CO} \rightarrow 2\text{Fe} + 3\text{CO}_2$
1200 K	Limestone decomposes	$\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2$
1500 K	Reduction of ore by C	$\text{Fe}_2\text{O}_3 + 3\text{C} \rightarrow 2\text{Fe} + 3\text{CO}$
1500 K	Fusion of iron and slag formation.	$\text{CaO} + \text{SiO}_2 \rightarrow \text{CaSiO}_3$
2000 K	Combustion of coke	$2\text{C} + \text{O}_2 \rightarrow 2\text{CO}$

48. Sapphire (blue colour) contains  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$  and  $\text{TiO}_2$ .
49. Corundum ( $\text{Al}_2\text{O}_3$ ) is a mineral of aluminium whereas malachite ( $\text{Cu}(\text{OH})_2 \cdot \text{CuCO}_3$ ), cuprite ( $\text{Cu}_2\text{O}$ ) and azurite ( $\text{Cu}(\text{OH})_2 \cdot 2\text{CuCO}_3$ ) are minerals of copper.
50. During smelting of copper pyrites, the roasted ore is mixed with powdered coke and sand (charge) and it is then heated strongly in the blast furnace.
51. After bessemerization, as the molten copper solidifies,  $\text{SO}_2$  (sulphur dioxide) escapes and leaves blisters on the surface. The solid metal thus obtained is called as blister copper.

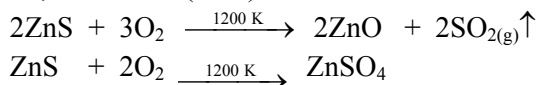


### Critical Thinking

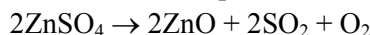
2. The various steps involved in the extraction of pure metals from their ores are as follows:
- Concentration of an ore/ore benefaction/ore dressing.
  - Extraction of crude metal from concentrated ore (either by conversion of ores into oxides or other desired compounds or by reduction of ores).
  - Purification or refining of the metal.
4. Cassiterite contains wolframite ( $\text{FeWO}_4$ ) which is a magnetic component and stannic oxide ( $\text{SnO}_2$ ) which is a non-magnetic component. Hence, it is concentrated by magnetic separation process.
10. Calcination process involves decomposition of carbonate ores to their respective metal oxides and carbon dioxide.
14.  $\text{SiO}_2$  is an acidic flux.
15. Slag is a light material and forms separate layer above molten metal.
16.  $\text{C}_{(s)} + \text{O}_{2(g)} \longrightarrow \text{CO}_{2(g)}$   
 Here,  $\Delta G^\circ = \Delta H^\circ - T\Delta S \quad \dots(i)$   
 For this reaction,  $\Delta H^\circ$  is -ve and  $\Delta S^\circ \approx 0$   
 $\therefore T\Delta S^\circ$  in equation (i) becomes zero, thus  $\Delta G^\circ$  does not vary much with the temperature.
17. From Ellingham diagram, it can be deduced that any metal can reduce the oxide of other metal which appears above it in the diagram.
18. From Ellingham diagram, it can be deduced that any metal can reduce the oxide of other metal which appears above it in the diagram. Also the graph of formation of silver oxide is at the upper part of diagram indicating positive  $\Delta G^\circ$  value and possible decomposition at moderate temperature. Thus, if the newly discovered metal 'M' is found to have its graph of formation of oxide above the graph line of silver, then it can be reduced by silver and also it can be easily decomposed at moderate temperature.
20. Liquation process for refining of crude metal is used when the metal has lower melting point and impurity has higher melting point.



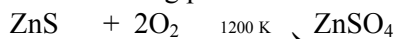
22. The fact that impurities are more soluble in the molten state than in the solid state of the metal is used in zone refining. Zone refining is also called fractional crystallization.
24. Zone refining is employed for preparing extremely pure metals especially metalloids for the preparation of semiconductors. Gallium arsenide is a semiconductor and hence zone refining is used for its purification.
27. During roasting of concentrated zinc sulphide (ZnS) ore at about 1200 K and in the presence of excess of air, zinc oxide (ZnO) and some amount of zinc sulphate (ZnSO<sub>4</sub>) may also get formed.



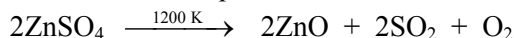
In order to decompose ZnSO<sub>4</sub> formed, care is taken to complete the roasting at 1200 K.



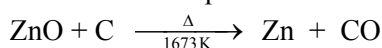
28. In the roasting process of zinc ore, zinc sulphate may get formed as follows:



In order to decompose this ZnSO<sub>4</sub>, care is taken to complete the roasting at 1200 K.

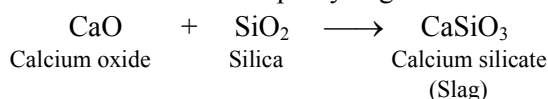


29. Modern vertical process is used to carry out smelting (i.e., it involves reduction of metal oxide).



Zinc oxide                      Zinc (Spelter)

31. In metallurgy of iron, charge consisting of roasted ore, coke and calcium carbonate (limestone) in the approximate ratio of 12:5:3 is introduced in the blast furnace.
32. In the blast furnace, cone enables the uniform distribution of charge and cup prevents the loss of gases. Introduction of pre-heated air into the furnace is done through tuyers.
33. In the extraction of iron, limestone is used as a flux. Calcium oxide obtained by the decomposition of limestone combines with silica impurity to give calcium silicate which is a slag.

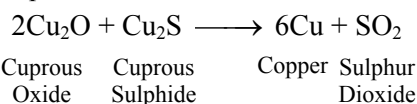


34. During the smelting of iron in blast furnace all the processes viz., oxidation (coke burns to give carbon monoxide), reduction (oxide ore is reduced to metal) and decomposition (limestone which acts as a flux, first gets decomposed to CaO and CO<sub>2</sub>). However, it does not involve process of sublimation.
35. Conversion of ferrous oxide (FeO) to ferric oxide (Fe<sub>2</sub>O<sub>3</sub>) occurs during roasting and not during extraction of iron in blast furnace.

44. Oxides of some metals are difficult to reduce by carbon. In such cases, aluminothermite process is used. Aluminothermite process involves reduction of oxides such as Fe<sub>2</sub>O<sub>3</sub>, Mn<sub>3</sub>O<sub>4</sub>, Cr<sub>2</sub>O<sub>3</sub>, etc., to metals with aluminum.



47. In the extraction of copper, copper matte is transferred to a Bessemer converter where autoreduction reaction takes place as follows.



48. Blister copper is 99% pure copper and mainly contains impurities of Ag and Au. It is further refined to 99.99% purity by carrying out electrolysis.





24. The van Arkel method is used for metals like Zr and Ti.

Combustion zone	2000 K
Fusion zone	1500 K
Slag zone	1500 K
Reduction zone	900 K

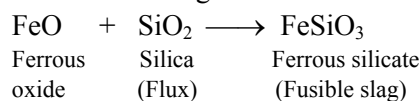
33. Corundum ( $\text{Al}_2\text{O}_3$ ) is an ore of Al.

37. Hoopé's process is used to refine aluminium.

39. Among cuprite [ $\text{Cu}_2\text{O}$ ], copper glance [ $\text{Cu}_2\text{S}$ ], chalcopyrite [ $\text{CuFeS}_2$ ] and malachite [ $\text{Cu}(\text{OH})_2 \cdot \text{CuCO}_3$ ], only chalcopyrite is an ore which contains both Fe and Cu.

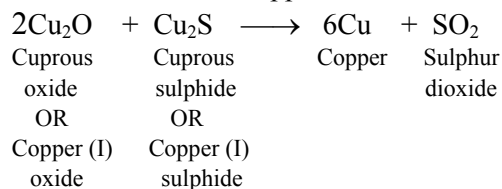
40. Copper pyrite  $\text{CuFeS}_2$  (Chalcopyrite)

41. During smelting of roasted copper pyrites, ferrous oxide is produced which combines with silica (flux) to form fusible slag.

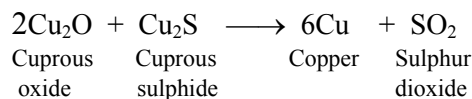


The molten material obtained after roasting and smelting of copper ore from the blast furnace consists of sulphides of  $\text{Cu}^+$ ,  $\text{Fe}^{+2}$ , coke and sand which is called matte.

42. In the extraction of copper, auto reduction reaction takes place as follows:



43. Auto reduction: Reduction of an oxide ore of a metal by its own sulphide.



45. Pyrolusite –  $\text{MnO}_2$

Malachite –  $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$

Diaspore –  $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$

Cassiterite –  $\text{SnO}_2$

Hence, malachite is the only carbonate ore in the given options.

47. In metallurgy of iron, the flux used is  $\text{CaCO}_3$ .



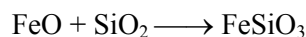
### Evaluation Test

1. Cryolite ( $\text{Na}_3\text{AlF}_6$ )  $\longrightarrow$  Halide ore

Galena ( $\text{PbS}$ )  
Copper glance ( $\text{Cu}_2\text{S}$ ) } Sulphide ores

Bauxite  $\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$   $\longrightarrow$  Oxide ore

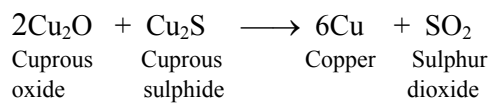
3. Haematite contains  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$  and phosphates as gangue (impurity). Ferrous oxide ( $\text{FeO}$ ) can combine with  $\text{SiO}_2$  to form  $\text{FeSiO}_3$  (slag) during smelting.



To prevent this, the ferrous oxide is converted to ferric oxide during roasting.



5. Cryolite ( $\text{Na}_3\text{AlF}_6$ ) is also called sodium hexafluoro aluminate (III) or sodium aluminium fluoride.
8. In Hall and Heroult's process, aluminium is liberated at cathode whereas the oxygen evolved at anode combines with the carbon of the anode to produce carbon monoxide which either burns to carbon dioxide or escapes out.
14. Magnesite is  $\text{MgCO}_3$ .
15. Auto reduction: Reduction of an oxide ore of a metal by its own sulphide.



# 07 p-Block Elements



## Hints

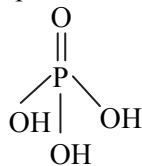


### Classical Thinking

5. The hydrides of the elements of group 15 are covalent in nature.
7. 
$$\text{NH}_4\text{Cl}_{(\text{aq})} + \text{NaNO}_2_{(\text{aq})} \xrightarrow{\Delta} \text{N}_{2(\text{g})}\uparrow + \text{NaCl}_{(\text{aq})} + 2\text{H}_2\text{O}_{(\text{l})}$$
 Ammonium chloride      Sodium nitrite      Nitrogen
8. Higher the bond dissociation energy, lower the reactivity and vice-versa.
9. 
$$\text{CaCN}_2 + 3\text{H}_2\text{O} \xrightarrow{\Delta} \text{CaCO}_3 + 2\text{NH}_3$$
 Calcium cyanamide      Calcium carbonate      Ammonia
11. 
$$4\text{NH}_3 + 5\text{O}_2 \xrightarrow[1100\text{K}]{\text{Pt}} 4\text{NO} + 6\text{H}_2\text{O}$$
 Ammonia      Nitrogen Monoxide
13. With Nessler's reagent (an alkaline solution of  $\text{K}_2\text{HgI}_4$ ) ammonia and ammonium salts give brown precipitate due to the formation of Millon's base.
- $$2\text{K}_2\text{HgI}_4 + \text{NH}_3 + 3\text{KOH} \longrightarrow \text{H}_2\text{N} - \text{Hg} - \text{O} - \text{Hg} - \text{I} + 7\text{KI} + 2\text{H}_2\text{O}$$
 Nessler's Reagent      (Iodide of Millon's base)
15. 
$$\text{Fe}^{2+} + \text{NO} + 5\text{H}_2\text{O} \longrightarrow [\text{Fe}(\text{H}_2\text{O})_5\text{NO}]^{2+}$$
 Ferrous ion      Nitric oxide      Pentaaquanitrosyl iron (II) ion (Brown complex)
16.  $\text{N}_2\text{O}$  is a linear molecule.
- 18.

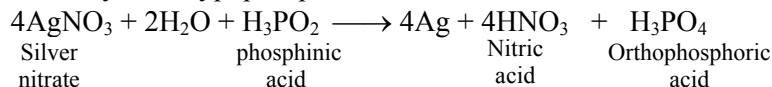
Formula	Oxidation State of N
$\text{N}_2\text{O}$	+1
$\text{N}_2\text{O}_3$	+3
$\text{NO}_2$	+4
$\text{N}_2\text{O}_5$	+5

22. White phosphorus is soluble in  $\text{CS}_2$  while red phosphorus is insoluble.
27. 
$$\text{PCl}_5 + \text{H}_2\text{O} \longrightarrow \text{POCl}_3 + 2\text{HCl} \quad ; \quad \text{POCl}_3 + 3\text{H}_2\text{O} \longrightarrow \text{H}_3\text{PO}_4 + 3\text{HCl}$$
 Phosphorus pentachloride      Phosphorus oxychloride      Phosphorus oxychloride      Orthophosphoric acid
28. Oxidation state of phosphorus in orthophosphorus acid = +3; hypophosphorus acid = +1; orthophosphoric acid = +5; poly metaphosphoric acid = +5
29. Orthophosphoric acid is





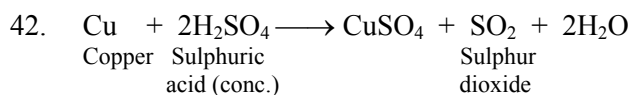
31. Hypophosphorus acid acts as a reducing agent. The acids which contain P–H bonds have strong reducing tendency. The hypophosphorus acid which contains two P–H bonds reduces  $\text{AgNO}_3$  to metallic silver.



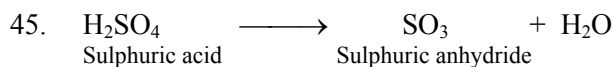
35. On going down the group – 16, the size of the central atom increases and therefore, its tendency to form stable covalent bond with hydrogen decreases as a result thermal stability decreases.
36. Oxygen can be absorbed to a considerable extent in alkaline solution of pyrogallol.
39. Ozone is bluish black liquid, has pungent odour, bleaching and sterilizing agent and powerful oxidizing agent (next to  $\text{F}_2$ ).

40.  $\text{O}_2$  is paramagnetic whereas  $\text{O}_3$  is diamagnetic.

41. The S – S – S bond angle in  $\text{S}_8$  molecule is  $107^\circ$ .

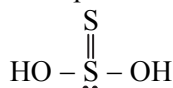


43.  $2\text{ZnS} + 3\text{O}_2 \longrightarrow 2\text{ZnO} + 2\text{SO}_2$   
 $\text{SO}_2$  gas is produced as a byproduct of the roasting of pyrites and blends.

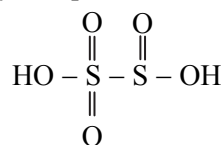


50. Sulphuric acid is a strong oxidising agent.

52. (A) Thiosulphurous acid ( $\text{H}_2\text{S}_2\text{O}_2$ )



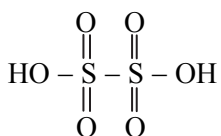
(B) Pyrosulphurous acid ( $\text{H}_2\text{S}_2\text{O}_5$ )



(C) Dithionous acid ( $\text{H}_2\text{S}_2\text{O}_4$ )



(D) Dithionic acid ( $\text{H}_2\text{S}_2\text{O}_6$ )



Only thiosulphurous acid contains S = S bond.

54. Most electronegative fluorine shows only –1 oxidation state. Chlorine, bromine and iodine show –1, +1, +3, +5 and +7 oxidation states.

Chlorine and bromine also exhibit +4 and +6 oxidation states. Halogens possess low melting and boiling points.

55. Electron gain enthalpies of halogens are negative. Hence halogens liberate maximum heat by gain of electrons as compared to the elements in the corresponding periods.

57. Chlorine is slightly soluble in water. The reactivity of halogens is of the order  $\text{F}_2 > \text{Cl}_2 > \text{Br}_2 > \text{I}_2$ .

59. Fluorine is the strongest oxidizing agent.

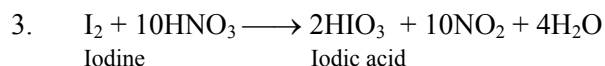


65.  $\text{Ca(OH)}_2 + \text{Cl}_2 \longrightarrow \text{CaOCl}_2 + \text{H}_2\text{O}$   
Slaked lime                                      Bleaching powder
67. Interhalogen compounds behave as strong oxidizing agent.
68. Interhalogens of type  $\text{XX}'_3$  have  $\text{sp}^3\text{d}$  hybridization. They have two lone pairs of electrons on central atom X.
69. Chlorine does not exist in +2 oxidation state.
72. The oxidizing power of oxyacids of Cl decreases as  $\text{HOCl} > \text{HClO}_2 > \text{HClO}_3 > \text{HClO}_4$   
So, HOCl is the strongest oxidising agent.
75. Inert elements have large positive values of electron gain enthalpy because they have no tendency to accept electrons (as they have stable electronic configuration).
76. Noble gases have completely filled valence shell. Large amount of energy is required to remove an electron from completely filled valence shell. Hence they have very high values of ionization enthalpies. On moving down the group, the ionization enthalpy decreases from He to Rn due to increase in atomic size. Hence, He has the highest ionization energy.
77. With increasing atomic size, the polarizability of atom increases. Hence, xenon is most polarised.
78. With increase in the atomic number, the liquefaction tendency increases from He to Rn due to increase in the strength of van der Waal's forces. Thus, the ease of liquefaction of noble gases decreases in the order  $\text{Xe} > \text{Kr} > \text{Ar} > \text{Ne} > \text{He}$ .
79. With increase in the atomic number, heat of vaporization increases from He to Rn due to increase in the strength of van der Waal's forces. Hence, radon is the inert gas with highest heat of vaporization.
84. Phosphorus forms  $\text{P}_4$  molecule.
85. Due to smaller size of fluorine it forms stable compound which does not undergo hydrolysis easily.

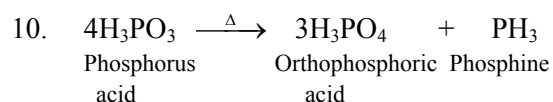
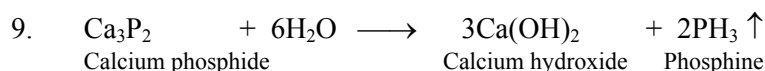
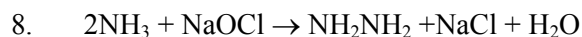
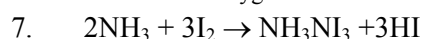
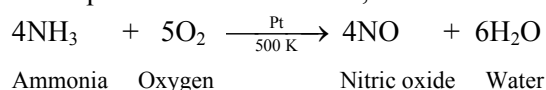


### Critical Thinking

2. In the large scale preparation of nitric acid by Ostwald's process, NO is formed as a byproduct.

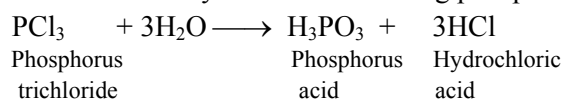


6. In the presence of Pt at 500 K, ammonia is oxidized to nitric oxide.

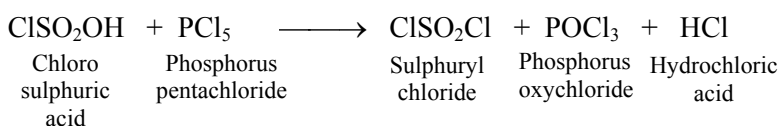
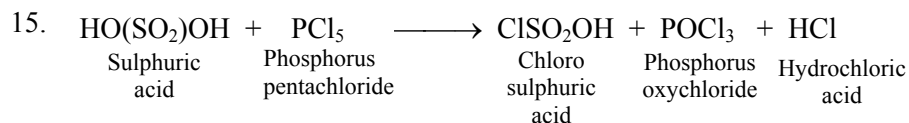


12.  $\text{PH}_3$  is stronger reducing agent than  $\text{NH}_3$ .

14. It reacts violently with water forming phosphorus acid.

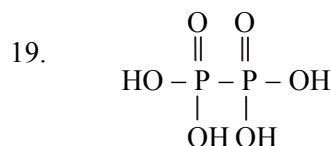
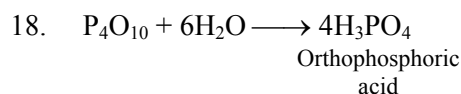






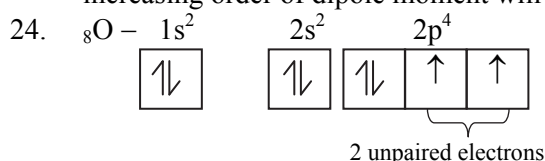
Hence, the reaction shows that  $\text{H}_2\text{SO}_4$  contains two hydroxyl groups in its molecule.

17. Three equatorial P–Cl bonds are equivalent with bond length of 202 pm.

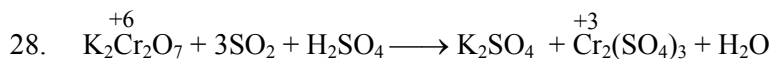


Hypophosphoric acid ( $\text{H}_4\text{P}_2\text{O}_6$ )

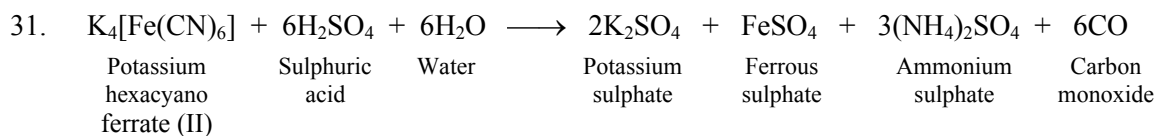
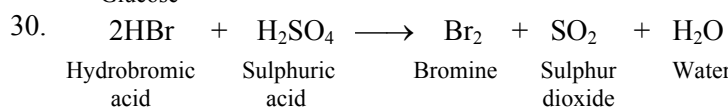
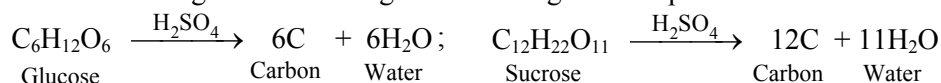
23. Dipole moment depends upon the electronegativity of the atoms in the molecule. Oxygen is the second most electronegative element and the electronegativity decreases on moving down the group. So, the increasing order of dipole moment will be  $\text{H}_2\text{Te} < \text{H}_2\text{Se} < \text{H}_2\text{S} < \text{H}_2\text{O}$



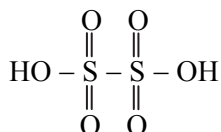
26. NO,  $\text{N}_2\text{O}$  and CO are examples of neutral oxides.



29. Concentrated sulphuric acid is a powerful dehydrating agent due to its strong affinity for water. It removes water from a large number of organic and inorganic compounds.



32. Dithionic acid



Oxidation state of S: +5

34.  $\text{OF}_2$  molecule can be shown as F – O – F. Oxygen has 2 lone pairs while each fluorine atom has 3 lone pairs each. Hence, there are 2 bond pairs and 8 lone pairs of electrons.

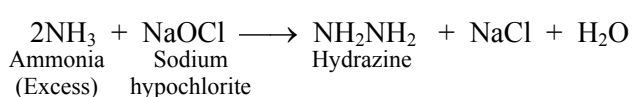
35. Cryolite is  $\text{Na}_3\text{AlF}_6$ .



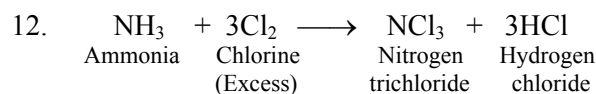
39.  $\text{IF}_5$  can further form  $\text{IF}_7$
42. Fluorine forms only one oxyacid i.e., HOF (hypofluorous acid)
43. Oxidising power of halogens follow the order  $\text{Cl}_2 > \text{Br}_2 > \text{I}_2$ .
46. As the number of shells increases, size increases and the effective nuclear charge on the outermost electron decreases. Thus, I.E. decreases.
48. Zero group elements show less chemical activity because elements of this group have stable electronic configuration.
53. Very few compounds of krypton are known.  $\text{KrF}_2$  is studied in detail. True compounds of Ar, Ne and He are not known till date.

**Competitive Thinking**

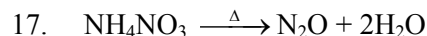
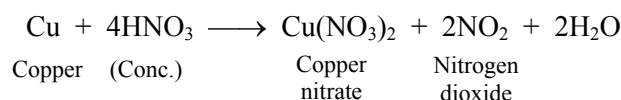
4. For group 15 elements, the decrease in the stability and solubility of hydrides is from  $\text{NH}_3$  to  $\text{BiH}_3$ .
5. Nitrogen forms  $p\pi - p\pi$  multiple bonds as d-orbitals are absent. Other elements form  $d\pi - p\pi$  multiple bonds.
8. By the thermal decomposition of barium azide, dinitrogen obtained is in the pure form.
9. Nitrogen does not have empty d-orbitals like other elements of group 15. Hence, it does not exist as tetra atomic molecule.
10. Excess of ammonia with sodium hypochlorite solution in the presence of glue or gelatine gives hydrazine ( $\text{NH}_2\text{NH}_2$ ).



11.  $\underset{\substack{\text{Calcium} \\ \text{carbide}}}{\text{CaC}_2} + \underset{\substack{\text{Dinitrogen}}}{\text{N}_2} \xrightarrow[1000\text{K}/1\text{atm}]{500-600\text{K}/6-8\text{atm}} \underset{\substack{\text{Calcium} \\ \text{cyanamide}}}{\text{CaCN}_2} + \underset{\substack{\text{Carbon}}}{\text{C}}$



15. Copper reacts with conc.  $\text{HNO}_3$  to form nitrogen dioxide as the gaseous byproduct along with copper nitrate.



20.

Substance	Oxidation state of nitrogen
Nitrogen gas ( $\text{N}_2$ )	0
Ammonia ( $\text{NH}_3$ )	-3
Nitrous oxide ( $\text{N}_2\text{O}$ )	+1
Nitric oxide (NO)	+2

21. (A) Nitric oxide       $\text{NO} + 2$                       (B) Nitrous oxide       $\text{N}_2\text{O} + 1$   
 (C) Nitrogen dioxide  $\text{NO}_2 + 4$                       (D) Nitrogen trioxide  $\text{N}_2\text{O}_3 + 3$



22. Let the oxidation state of nitrogen be  $x$ .

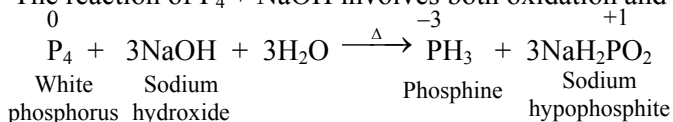
$$\therefore 2(x) + 4(-2) = 0 \text{ i.e., } 2x - 8 = 0$$

$$x = \frac{8}{2} = 4$$

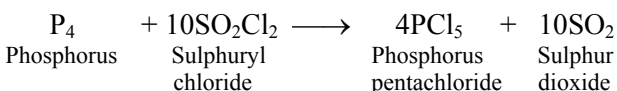
$\therefore$  Oxidation state of nitrogen in  $N_2O_4$  is +4.

25. For group 15 elements, the decrease in the stability and solubility of hydrides is from  $NH_3$  to  $BiH_3$ .

27. The reaction of  $P_4 + NaOH$  involves both oxidation and reduction of P-atoms.



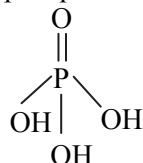
28. Sulphuryl chloride ( $SO_2Cl_2$ ) reacts with white phosphorus ( $P_4$ ) to give  $PCl_5$  and  $SO_2$  as products.



30.  $PH_3$  reacts with  $Cl_2$  to form spontaneously  $PCl_3$  and  $PCl_5$  and the mixture warms up.

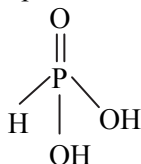
33.  $PH_3$  is stable molecule, it is basic towards litmus and has odour of rotten fish. It is sparingly soluble in water.

36. In orthophosphoric acid ( $H_3PO_4$ ), three  $-OH$  groups are present.



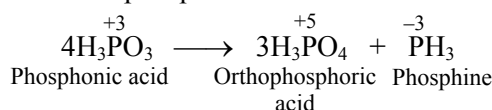
Orthophosphoric acid ( $H_3PO_4$ )

37. Orthophosphorus acid ( $H_3PO_3$ ) contains two  $O-H$  bonds. Hence, its basicity is two.

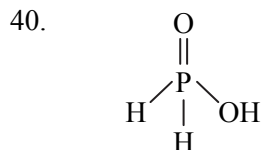


Orthophosphorus acid ( $H_3PO_3$ )

38. Oxoacid of phosphorous in +3 oxidation state shows a tendency to disproportionate.

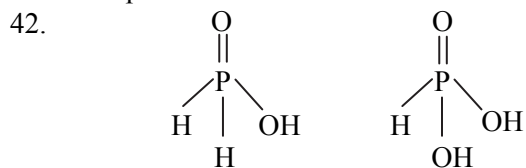


39. The oxidation state of phosphorus in phosphinic acid is +1.



Hypophosphorus acid ( $H_3PO_2$ )

$H_3PO_2$  is a monobasic acid since it contains one  $P-OH$  bond. It shows strong reducing behaviour due to the presence of two  $P-H$  bonds.



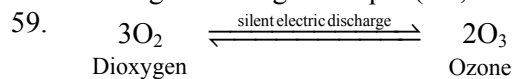
Phosphinic acid has one  $P-OH$  bond, and it can provide one proton, hence it is monoprotic acid. Whereas phosphonic acid has two  $P-OH$  bonds and it is diprotic acid.



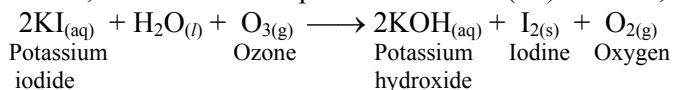
46. Selenium exists in many allotropic modifications like in crystalline form red monoclinic and grey metallic, in amorphous form dark brown, vitreous and red amorphous selenium, etc.
49.  $\text{H}_2\text{O}$  is very stable molecule,  
 $\Delta H_{\text{diss}}(\text{O} - \text{H}) = 463 \text{ kJ mol}^{-1}$ . Therefore, it does not act as a reducing agent.
50. Generally, acidic oxides are the binary compounds of oxygen with non-metals whereas basic oxides are the binary compounds of oxygen with highly electropositive metals.
51.  $\text{ZnO}$  and  $\text{Al}_2\text{O}_3$  are amphoteric oxides.  
 $\text{N}_2\text{O}_5$  is an acidic oxide.  
 $\text{MgO}$  is a basic oxide.
52.  $\text{SnO}$ ,  $\text{ZnO}$  and  $\text{PbO}$  are amphoteric oxides while  $\text{MgO}$  is a basic oxide.
53.  $\text{SO}_2 \rightarrow$  Acidic oxide  
 $\text{BaO} \rightarrow$  Basic oxide  
 $\text{N}_2\text{O} \rightarrow$  Neutral oxide  
 $\text{CO}_2 \rightarrow$  Acidic oxide

54.

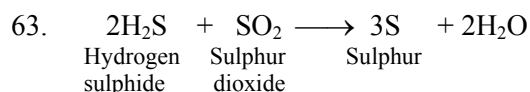
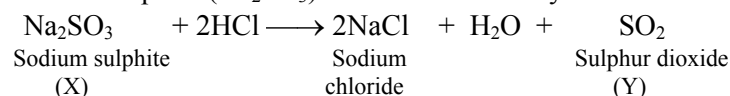
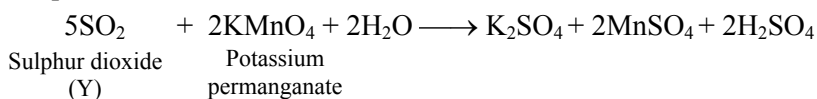
Element	Nature of oxide
Calcium	Basic
Zinc	Amphoteric
Carbon	Acidic
Sulphur	Acidic

55. In presence of acid ( $\text{CO}_2$ ),  $\text{ZnO}$  acts as a base and in presence of base ( $\text{Na}_2\text{O}$ ), it acts as an acid.57. Ozone molecule is angular with  $\text{O} - \text{O} - \text{O}$  bond angle as  $116.8^\circ$  ( $\approx 117^\circ$ ). Both  $\text{O} - \text{O}$  bonds are identical having bond length 128 pm (i.e.,  $1.28 \text{ \AA}$ ) [Since,  $1 \text{ \AA} = 10^{-10} \text{ m}$  and  $1 \text{ pm} = 10^{-12} \text{ m}$ ].

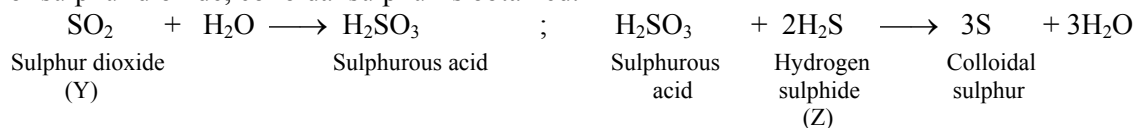
Thus, 3 volumes of oxygen give two volumes of ozone. Hence, 6 volumes of oxygen will give 4 volumes of ozone.

60. Ozone, on reaction with potassium iodide (KI) solution, oxidises iodide ions to iodine ( $\text{I}_2$ ).

62. Sulphur dioxide is not a dehydrating agent.

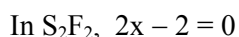
64. Sodium sulphite ( $\text{Na}_2\text{SO}_3$ ) reacts with dilute hydrochloric acid to liberate sulphur dioxide ( $\text{SO}_2$ ) gas.Sulphur dioxide decolourises acidified  $\text{KMnO}_4$ .

Sulphur dioxide is highly soluble in water. When hydrogen sulphide gas is passed into an aqueous solution of sulphur dioxide, colloidal sulphur is obtained.



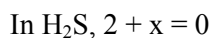


65. Let 'x' be the oxidation number of sulphur.  $S_8$  is the elemental form of sulphur. Hence, oxidation state is zero.

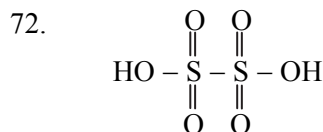
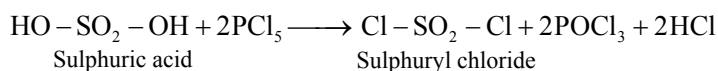
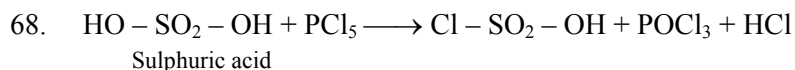


$$\therefore 2x = 2$$

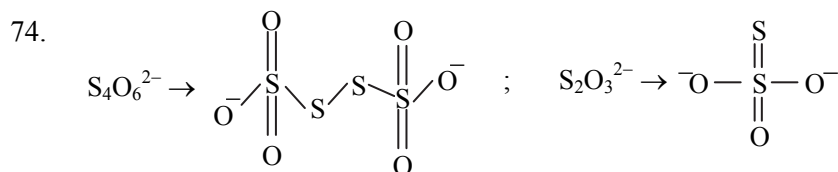
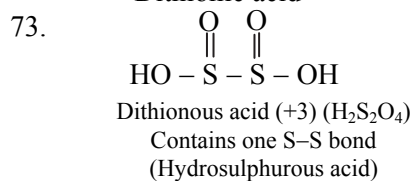
$$x = 1$$



$$x = -2$$



Dithionic acid



75. Most electronegative fluorine shows only  $-1$  oxidation state. Chlorine, bromine and iodine show  $-1$ ,  $+1$ ,  $+3$ ,  $+5$  and  $+7$  oxidation states.

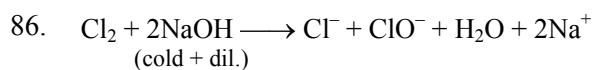
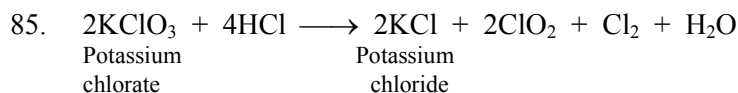
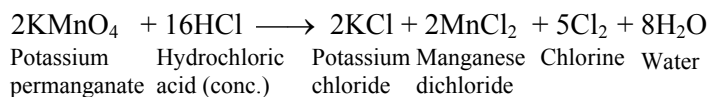
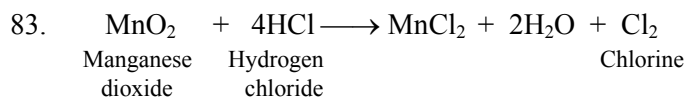
Chlorine and bromine also exhibit  $+4$  and  $+6$  oxidation states.

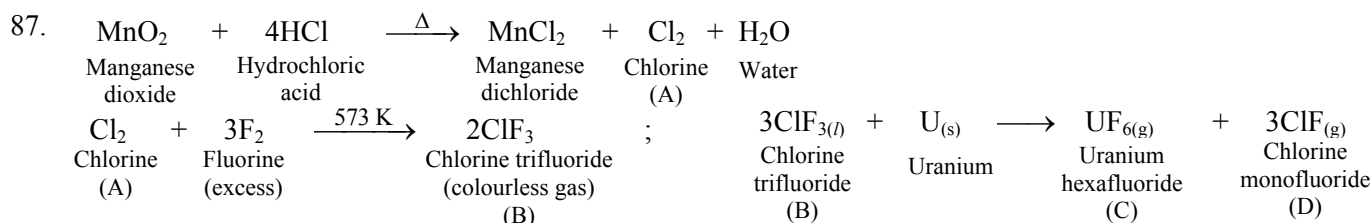
77. Due to smaller size of fluorine, it shows inter electronic repulsion among its electrons. Hence, electron gain enthalpy of F is less negative than Cl. The value of electron gain enthalpy becomes less negative going down the group from Cl. Thus, chlorine has the highest value of negative electron gain enthalpy.

78. The acid strength increases in the order  $HF < HCl < HBr < HI$ . Hence, HF is the weakest acid.

81. The decreasing order of the ionic character of the M-X bond in metal halides is:  $MF_n > MCl_n > MBr_n > MI_n$  (Where M is metal and n is its valency).

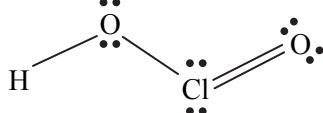
82. Bond dissociation energy:  $F_2 < Cl_2 > Br_2 > I_2$   
Bond dissociation energy    159   243   192   151  
values (kJ/mole):





In the given series of reactions, the gases A, B, C and D are  $\text{Cl}_2$ ,  $\text{ClF}_3$ ,  $\text{UF}_6$  and  $\text{ClF}$  respectively.

89. Interhalogen compounds are more reactive than halogens. This is because X–X' bonds present in them are weaker than X–X or X'–X' bonds.
92. Among halogens, only chlorine forms the halous acid like chlorous acid wherein the chlorine atom is in tripositive oxidation state.



Chlorous acid  
(Oxidation state of Cl: +3)

93.  $2\text{HClO}_4 \longrightarrow \text{H}_2\text{O} + \text{Cl}_2\text{O}_7$
94. The increasing order of charge delocalization in the anions of oxoacids of chlorine is,  
 $\text{ClO}^- < \text{ClO}_2^- < \text{ClO}_3^- < \text{ClO}_4^-$ .

With increase in charge delocalisation, the stability of the ion increases and the basicity of the anion decreases. Thus,  $\text{ClO}^-$  is the strongest base and  $\text{ClO}_4^-$  is the weakest base. A weak base has strong conjugate acid and vice versa. Hence,  $\text{HClO}$  (conjugate acid of  $\text{ClO}^-$ ) is the weakest acid and  $\text{HClO}_4$  (conjugate acid of  $\text{ClO}_4^-$ ) is the strongest acid. Hence, the correct increasing order of acid strength is  $\text{HClO} < \text{HClO}_2 < \text{HClO}_3 < \text{HClO}_4$ .

95. Argon is a monoatomic gas.

96.

Gas	Abundance in air by volume (ppm)
Helium	5.2
Neon	18.2
Argon	93.4
Krypton	1.1
Xenon	0.09

97. The valence shell electronic configuration of p-block elements is  $ns^2np^{1-6}$ , except helium, which has  $1s^2$  configuration. Helium contains completed duplet and hence, one molecule of He consists of only one atom (i.e., it is a monoatomic element).
98. Boiling point (in K) of inert gases:

He	Ne	Ar	Kr	Xe	Rn
4.0	27.0	87.0	121	165.0	211

100. The noble gas which forms maximum number of compounds is Xe.  
eg.  $\text{XeF}_2, \text{XeOF}_2, \text{XeF}_4, \text{XeOF}_4, \text{XeF}_6, \text{XeO}_3$ .
102. Helium is non-inflammable but it is heavier than hydrogen.
103. Argon is used to provide inert atmosphere for welding and several metallurgical processes.
104. On moving down the group, the atomic size increases. Due to this, the electron density, the electron donor capacity and the basic strength decreases.  $\text{NH}_3$  is distinctly basic.  $\text{PH}_3$  is a very weak base.  $\text{AsH}_3, \text{SbH}_3$  and  $\text{BiH}_3$  do not show any basic property.
105. Sulphur exists in many allotropic forms such as rhombic sulphur, monoclinic sulphur, plastic sulphur, milk of sulphur and colloidal sulphur.





## Hints



### Classical Thinking

7.  $\text{Cr}_2\text{O}_3$  – Chrome ore  
 $\text{FeCr}_2\text{O}_4$  – Chromite  
 $\text{PbCrO}_4$  – Crocoisite  
 $\text{MnO}_2$  – Pyrolusite
8. Transition metals have high density.
10. Cr, Mo and W have maximum number of unpaired d-electrons. Therefore, these metals are very hard. However, Cd is not very hard as it does not contain unpaired d-electrons.
14. Mn exhibits oxidation state of + 7.
15. Fe, Cu and Mn show variable oxidation states whereas Zn shows only + 2 as stable oxidation state.
18.  $x + 4(-2) = 0$   
 $x - 8 = 0$   
 $x = +8$
20. For the same oxidation state, the ionic radii generally decreases with increase in nuclear charge. Therefore, the decreasing order of ionic radii of given options will be:  
 $\text{Sc}^{3+} > \text{Ti}^{3+} > \text{Mn}^{3+} > \text{Co}^{3+}$   
 73 pm   67 pm   65 pm   61 pm  
 So,  $\text{Sc}^{3+}$  has highest ionic radii.
22. Sc :  $[\text{Ar}] 3d^1 4s^2$   
 $\text{Sc}^{3+}$  :  $[\text{Ar}] 3d^0 4s^0 \Rightarrow 0$  unpaired electron hence, colourless  
 Ti :  $[\text{Ar}] 3d^2 4s^2$   
 $\text{Ti}^{3+}$  :  $[\text{Ar}] 3d^1 4s^0 \Rightarrow 1$  unpaired electron hence, coloured  
 Ni :  $[\text{Ar}] 3d^8 4s^2$   
 $\text{Ni}^{2+}$  :  $[\text{Ar}] 3d^8 4s^0 \Rightarrow 2$  unpaired electrons hence, coloured  
 Cu :  $[\text{Ar}] 3d^{10} 4s^1$   
 $\text{Cu}^+$  :  $[\text{Ar}] 3d^{10} 4s^0 \Rightarrow 0$  unpaired electron hence, colourless  
 Co :  $[\text{Ar}] 3d^7 4s^2$   
 $\text{Co}^{2+}$  :  $[\text{Ar}] 3d^7 4s^0 \Rightarrow 3$  unpaired electrons hence, coloured
23.  $\text{Ni}^{2+}$  and  $\text{Cr}^{3+}$  are coloured due to the presence of 2 and 3 unpaired electrons respectively. But  $\text{Zn}^{2+}$  is colourless because of absence of unpaired electrons.
26.  $\text{Fe}^{3+}$  ion is  $[\text{Ar}] 3d^5 4s^0$ . It has 5 unpaired electrons.  
 $\therefore$  Magnetic moment,  $\mu = \sqrt{n(n+2)} = \sqrt{5(5+2)} = 5.9$  B.M. (where B.M. – Bohr magneton)
28. Defects in the crystal lattice of transition metals result in presence of vacant spaces which are also known as interstitial spaces. Small atoms are trapped inside these vacant spaces resulting in formation of interstitial compounds.
29. The small H atoms occupy the vacant spaces in the lattice of Ti metal to form interstitial compound  $\text{TiH}_{1.73}$
32. Stainless steel is an alloy of iron with chromium, vanadium, molybdenum, tungsten and manganese.





33. The conversion of dichromate to chromate.  

$$\text{K}_2\text{Cr}_2\text{O}_7 + 2\text{KOH} \longrightarrow \underbrace{2\text{K}_2\text{CrO}_4}_{\text{Yellow}} + \text{H}_2\text{O}$$
35.  $\text{K}_2\text{Cr}_2\text{O}_7$  is a good oxidising agent. It is used in estimation of ferrous ions ( $\text{Fe}^{2+}$ ) and chloride ion ( $\text{Cl}^-$ ) as these ions can be oxidised to  $\text{Fe}^{3+}$  and  $\text{Cl}_2$  respectively whereas  $\text{Fe}^{3+}$  cannot be oxidised further.
36. Pyrolusite ore ( $\text{MnO}_2$ ) when fused with  $\text{KOH}$  a green coloured  $\text{K}_2\text{MnO}_4$  is obtained.  

$$\begin{array}{ccccccc} 2\text{MnO}_2 & + & 4\text{KOH} & + & \text{O}_2 & \longrightarrow & 2\text{K}_2\text{MnO}_4 & + & 2\text{H}_2\text{O} \\ \text{Manganese} & & \text{Potassium} & & \text{Oxygen} & & \text{Potassium} & & \text{Water} \\ \text{dioxide} & & \text{hydroxide} & & & & \text{manganate} & & \\ (\text{pyrolusite ore}) & & & & & & & & \end{array}$$
46. Tb ( $Z = 65$ ):  $[\text{Xe}] 4f^9 5d^0 6s^2$   
 Tb shows +3 oxidation state by losing electrons from its 6s and 4f orbitals.
48. When lanthanoids (Ln) are heated with sulphur, they form corresponding sulphides.  

$$2\text{Ln} + 3\text{S} \longrightarrow \text{Ln}_2\text{S}_3$$
50.  $\text{Yb}^{3+}$  ( $Z = 70$ ) <  $\text{Pm}^{3+}$  ( $Z = 61$ ) <  $\text{Ce}^{3+}$  ( $Z = 58$ ) <  $\text{La}^{3+}$  ( $Z = 57$ ). Atomic number decreases from Yb to La. Hence, ionic radii increases from  $\text{Yb}^{3+}$  to  $\text{La}^{3+}$ .
56. The elements having atomic number higher than uranium ( $Z = 92$ ) are collectively called transuranic elements.
61. Among lanthanoids, only promethium is radioactive. In actinoid series, all elements are radioactive.
62. Pr is f-block element, As is p-Block element (representative element), Rb is an alkali metal and Mo is a transition element.
64. Colour absorption is based on d-d transition.
65.  $\text{Zr}^{4+}$  and  $\text{Hf}^{4+}$  possess almost the same ionic radii due to lanthanide contraction.  $\text{La}(\text{OH})_3$  is the most basic among lanthanide hydroxides. The oxide  $\text{Ln}_2\text{O}_3$  reacts with water to form insoluble hydroxides. Except promethium, rest of the lanthanoids occur in nature.



### Critical Thinking

1. Since Zn, Cd and Hg have completely filled ( $n - 1$ ) d orbitals in their elementary states as well as in the form of ions, they are excluded from transition series.
3.  $[\text{Ne}] 3s^2 3p^5$  is a p-block element as last electron enters the p-orbital.
4. Cr : 24  $\longrightarrow$   $[\text{Ar}] 3d^5 4s^1$   
 Cu : 29  $\longrightarrow$   $[\text{Ar}] 3d^{10} 4s^1$
5. Cr :  $[\text{Ar}] 3d^5 4s^1$   

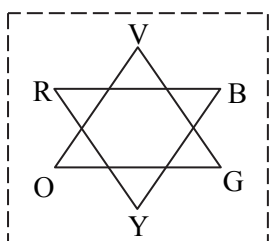
$$\begin{array}{|c|c|c|c|c|} \hline \uparrow & \uparrow & \uparrow & \uparrow & \uparrow \\ \hline \end{array} \quad \begin{array}{|c|} \hline \uparrow \\ \hline \end{array}$$
8. In a transition series, the first ionization enthalpy remains almost unchanged or slightly increases from left to right, due to decrease in size of the atom from left to right. However, the ionization enthalpy of the last element (i.e., Zn) is high in spite of its large atomic size. This is due to extra stability gained because of completely filled d-orbitals.
11.  $\text{Cr}^{2+}$  :  $[\text{Ar}] 3d^4 4s^0$   
 $\text{Co}^{3+}$  :  $[\text{Ar}] 3d^6 4s^0$   
 $\text{Mn}^{3+}$  :  $[\text{Ar}] 3d^4 4s^0$   
 $\text{Fe}^{3+}$  :  $[\text{Ar}] 3d^5 4s^0$
12. Manganese (Mn) : 25  $\longrightarrow$   $[\text{Ar}] 3d^5 4s^2$



13.  $\text{TiCl}_3 \longrightarrow \text{Ti}^{3+} : [\text{Ar}] 3d^1 4s^0 \longrightarrow 1 \text{ unpaired } e^-$   
 $\text{MnCl}_2 \longrightarrow \text{Mn}^{2+} : [\text{Ar}] 3d^5 4s^0 \longrightarrow 5 \text{ unpaired } e^-$   
 $\text{FeSO}_4 \longrightarrow \text{Fe}^{2+} : [\text{Ar}] 3d^6 4s^0 \longrightarrow 4 \text{ unpaired } e^-$   
 $\text{CuSO}_4 \longrightarrow \text{Cu}^{2+} : [\text{Ar}] 3d^9 4s^0 \longrightarrow 1 \text{ unpaired } e^-$
14.  $\overset{x}{\text{V}} \overset{-2}{\text{O}} \overset{-1}{\text{Cl}}_3$   
 Oxidation state of V:  
 $x + (-2) + (-1) \times 3 = 0$   
 $x - 2 - 3 = 0$   
 $x = +5$   
 In  $\text{VCl}_4$ ,  $\text{VCl}_3$  and  $\text{VCl}_2$ , vanadium exhibits oxidation state of +4, +3 and +2 respectively.
15. Mn shows the highest oxidation state of +7. The outermost electronic configuration of Mn is  $3d^5 4s^2$ .
16. In potassium ferrate ( $\text{K}_2\text{FeO}_4$ ), chromyl chloride ( $\text{CrO}_2\text{Cl}_2$ ) and sodium chromate ( $\text{NaCrO}_4$ ), the oxidation state of transition metal is +6.
18. The oxidation number of Cr in the following compounds can be given as:  
 $+1 \quad x \quad -2$   
 $\text{K}_2\text{CrO}_4 : 2(+1) + x + 4(-2) = 0 \Rightarrow x = +6$   
 $x \quad -2$   
 $\text{CrO}_2 : x + 2(-2) = 0 \Rightarrow x = +4$   
 $x \quad -1$   
 $\text{CrF}_3 : x + 3(-1) = 0 \Rightarrow x = 3$   
 $x \quad -1$   
 $\text{CrCl}_3 : x + 3(-1) = 0 \Rightarrow x = 3$

For same element, as the charge on the cations increases, the size of the cation decreases. Hence, ionic radius of Cr with +6 charge is smallest.

20. Colour absorbed orange ( $6000 \text{ \AA}$ ), emits out blue colour as complementary colour.

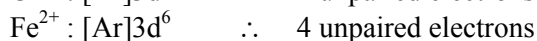
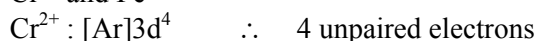
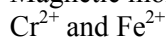


V = Violet  
 B = Blue  
 G = Green  
 Y = Yellow  
 O = Orange  
 R = Red

21. Cuprous ( $\text{Cu}^+$ ) has  $3d^{10} 4s^0$  configuration (colourless) whereas cupric ( $\text{Cu}^{2+}$ ) has  $3d^9 4s^0$  configuration, hence coloured.
23.  $\text{Cu}^{2+} : [\text{Ar}] 3d^9 4s^0 \longrightarrow 1 \text{ unpaired } e^-$  ;  $\text{Ni}^{2+} : [\text{Ar}] 3d^8 4s^0 \longrightarrow 2 \text{ unpaired } e^-$   
 $\text{Ti}^{4+} : [\text{Ar}] 3d^0 4s^0 \longrightarrow 0 \text{ unpaired } e^-$  ;  $\text{Mn}^{2+} : [\text{Ar}] 3d^5 4s^0 \longrightarrow 5 \text{ unpaired } e^-$   
 Hence,  $\text{Ti}^{4+}$  is diamagnetic as it does not have unpaired electrons.
24.  $\text{Mn}^{2+} : 3d^5 \longrightarrow 5$  unpaired element in d-subshell so it has highest paramagnetic character.
25.  $\text{Cu} : [\text{Ar}] 3d^{10} 4s^1$   
 $\text{Cu}^{2+} : [\text{Ar}] 3d^9 4s^0 \quad \therefore 1 \text{ unpaired electron}$   
 $\text{V} : [\text{Ar}] 3d^3 4s^2$   
 $\text{V}^{2+} : [\text{Ar}] 3d^3 4s^0 \quad \therefore 3 \text{ unpaired electrons}$   
 $\text{Cr} : [\text{Ar}] 3d^5 4s^1$   
 $\text{Cr}^{2+} : [\text{Ar}] 3d^4 \quad \therefore 4 \text{ unpaired electrons}$   
 $\text{Mn} : [\text{Ar}] 3d^5 4s^2$   
 $\text{Mn}^{2+} : [\text{Ar}] 3d^5 \quad \therefore 5 \text{ unpaired electrons}$   
 Greater the number of unpaired electrons, greater will be its paramagnetic property. Hence the order of increase in the paramagnetic property is  $\text{Cu}^{2+} < \text{V}^{2+} < \text{Cr}^{2+} < \text{Mn}^{2+}$ .



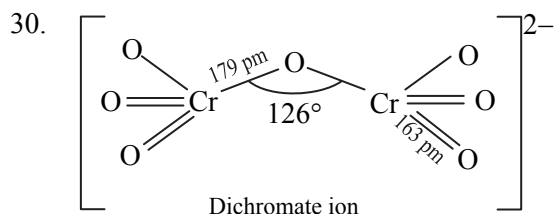
26. Magnetic moment will be equal if the ions have same number of unpaired electrons.



27. If d-orbital contains 7-electrons, it has 3 unpaired electrons.

$$\therefore \text{Magnetic moment } (\mu) = \sqrt{n(n+2)} = \sqrt{3(3+2)} = \sqrt{3 \times 5} = \sqrt{15} = 3.87 \text{ B.M.}$$

29. Acidified potassium dichromate is treated with hydrogen sulphide. In the reaction, the oxidation number of chromium decreases from +6 to +3.



There are six equivalent Cr – O bonds and one Cr – O – Cr bond.

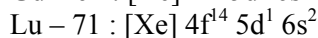
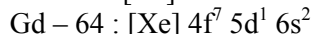
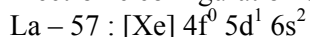
31. Number of electrons lost or gained = 5

$$\text{Equivalent mass} = \frac{\text{molecular mass}}{\text{electrons lost or gained}} = \frac{M}{5}$$

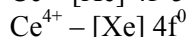
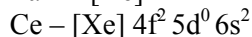
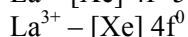
32. In acidic medium, the reaction is  $\text{MnO}_4^- + 8\text{H}^+ \longrightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O}$

Oxidation state of Mn changes from +7 to +2 in acidic medium i.e., one mole of it accepts 5 mole of electrons.

34. Electronic configuration of



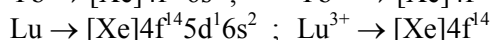
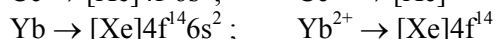
35. La –  $[\text{Xe}] 4f^0 5d^1 6s^2$



- 36.

Symbol	Atomic Number	Expected electronic configuration	Observed electronic configuration
Ce	58	$[\text{Xe}] 4f^1 5d^1 6s^2$	$[\text{Xe}] 4f^2 5d^0 6s^2$
Pr	59	$[\text{Xe}] 4f^2 5d^1 6s^2$	$[\text{Xe}] 4f^3 5d^0 6s^2$
Ho	67	$[\text{Xe}] 4f^{10} 5d^1 6s^2$	$[\text{Xe}] 4f^{11} 5d^0 6s^2$
Gd	64	$[\text{Xe}] 4f^7 5d^1 6s^2$	$[\text{Xe}] 4f^7 5d^1 6s^2$

38. Ce  $\rightarrow$   $[\text{Xe}]4f^2 6s^2$ ; Ce<sup>4+</sup>  $\rightarrow$   $[\text{Xe}]$



Eu<sup>2+</sup> has 7 unpaired electrons. Hence, it is paramagnetic.

39. Lanthanide contraction = Radius of La<sup>3+</sup> – Radius of Lu<sup>3+</sup> = x – y

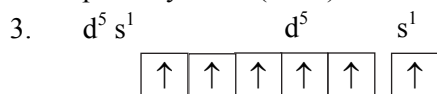
43. The electronic configuration of thorium (Z = 90) is  $[\text{Rn}] 5f^0 6d^2 7s^2$ . It does not contain any 5f-electron.



45. Nobelium (No) is very stable in +2 oxidation state due to  $f^{14}$  configuration.  
 $\text{No} \Rightarrow [\text{Rn}] 5f^{14} 6d^0 7s^2$   
 $\text{No}^{2+} \Rightarrow [\text{Rn}] 5f^{14}$
46. The atomic number of Kr = 36  
 Hence, atomic number of the given element =  $36 + 7 + 2 = 45$  and its tripositive ion will contain,  
 $45 - 3 = 42$  electrons.
47. The colour of Ni-DMG complex is due to charge transfer transition.
48. For lanthanoids, basicity decreases in the order of  $\text{La}(\text{OH})_3 > \text{Ce}(\text{OH})_3 > \dots > \text{Lu}(\text{OH})_3$

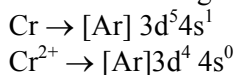
**Competitive Thinking**

2. Transition elements are those elements which have partially filled  $(n - 1)$  d-subshell in their elementary form. Hence, among the given options, only the  $1s^2, 2s^2 2p^6, 3s^2, 3p^6 3d^2, 4s^2$  electronic configuration has partially filled  $(n - 1)$  d-subshell i.e.,  $3d^2$ .



This configuration is more stable because of symmetrical distribution of  $e^-$  and exchange energy.

4. Electronic configuration of chromium



5. The expected electronic configuration of Cu (29) is  $[\text{Ar}] 3d^9 4s^2$  but actually it is found to be  $[\text{Ar}] 3d^{10} 4s^1$ . This is because fully filled d-orbitals are more stable than incompletely filled d-orbitals. So, there is a migration of one  $e^-$ , from 4s orbital to 3d orbital to give a more stable configuration.

7.  $\text{Ti} : [\text{Ar}] 3d^2 4s^2 \Rightarrow \text{Ti}^{1+} : [\text{Ar}] 3d^2 4s^1$   
 $\text{V} : [\text{Ar}] 3d^3 4s^2 \Rightarrow \text{V}^{1+} : [\text{Ar}] 3d^3 4s^1$   
 $\text{Cr} : [\text{Ar}] 3d^5 4s^1 \Rightarrow \text{Cr}^{1+} : [\text{Ar}] 3d^5 4s^0$   
 $\text{Mn} : [\text{Ar}] 3d^5 4s^2 \Rightarrow \text{Mn}^{1+} : [\text{Ar}] 3d^5 4s^1$

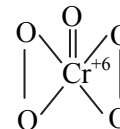
In Cr, for second ionisation, the electron needs to be removed from stable half-filled orbital and hence requires more energy. As the atomic number increases the size of cations of same charge decreases and hence, the ionisation energy will increase.

Hence, the order of decreasing second ionisation enthalpy is  $\text{Cr} > \text{Mn} > \text{V} > \text{Ti}$ .

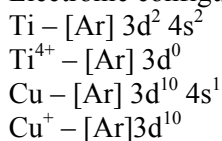
8.  ${}_{25}\text{Mn} = [\text{Ar}] 3d^5 4s^2$

After losing two electrons, electronic configuration will be  $[\text{Ar}] 3d^5$  and this is most stable configuration due to half filled orbitals hence, third ionization enthalpy will be highest.

10.  $\text{CrO}_5$  has two  $(-\text{O}-\text{O}-)$  bonds. Thus,  $[\text{O}-\text{O}]^{-2}$  and oxidation state of Cr in  $\text{CrO}_5$  is +6.



11. Electronic configurations:



Since, there are no unpaired electrons in  $\text{Ti}^{4+}$  and  $\text{Cu}^+$ , their compounds are colourless.

12.  $\text{Sc}^{3+} \rightarrow [\text{Ar}] 3d^0$   
 $\text{Fe}^{2+} \rightarrow [\text{Ar}] 3d^6$   
 $\text{Ti}^{3+} \rightarrow [\text{Ar}] 3d^1$   
 $\text{Mn}^{2+} \rightarrow [\text{Ar}] 3d^5$

Due to absence of unpaired electrons,  $\text{Sc}^{3+}$  ion will be colourless.

13.  $\text{CuSO}_4$  will be absorbing orange-red colour and emits out blue colour.



14.  $\text{Sc} \longrightarrow [\text{Ar}] 3d^1 4s^2$   
 $\text{Sc}^{3+} \longrightarrow [\text{Ar}] 3d^0$   
 Due to absence of unpaired electrons, compounds of  $\text{Sc}^{3+}$  are colourless.
15.  $\text{CrCl}_3 : x + 3(-1) = 0 \Rightarrow x = 3$   
 $\text{Cr} : [\text{Ar}] 3d^5 4s^1$   
 $\text{Cr}^{3+} : [\text{Ar}] 3d^3 4s^0$   
 $\text{Cr}^{3+}$  contains three unpaired electrons. Hence,  $\text{CrCl}_3$  will be coloured.
16. In Fischer-Tropsch process (for the synthesis of gasoline), Co-Th alloy is used as a catalyst.
17.  $\text{Sc}^{3+} \longrightarrow [\text{Ar}] 3d^0$   
 Due to absence of unpaired electrons, it is diamagnetic.

18.

Ion	Outer electronic configuration	Number of unpaired electrons
$\text{Ni}^{2+}$	$3d^8$	2
$\text{Ti}^{3+}$	$3d^1$	1
$\text{Cr}^{2+}$	$3d^4$	4
$\text{Co}^{2+}$	$3d^7$	3

The magnetic moment  $\mu = \sqrt{n(n+2)}$  B.M., Where  $n$  = number of unpaired electrons.

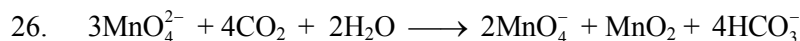
When  $n = 2$ ;  $\mu = \sqrt{2(2+2)} = \sqrt{8} = 2.84$  B.M.

$\therefore$  Magnetic moment 2.84 B.M. is given by  $\text{Ni}^{2+}$ .

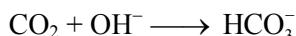
19. Magnetic moment =  $\sqrt{n(n+2)}$  (where  $n$  = number of unpaired electrons)

Ion	Outer electronic configuration	Number of unpaired electrons	Calculated value of magnetic moment (in B.M.)
$\text{Fe}^{3+}$	$3d^5$	5	5.92
$\text{Cr}^{3+}$	$3d^3$	3	3.87
$\text{Ti}^{3+}$	$3d^1$	1	1.73
$\text{Co}^{3+}$	$3d^6$	4	4.90

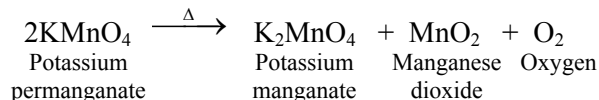
20. Transition metallic carbides are chemically inert.
21. Chromite ore is  $\text{FeCr}_2\text{O}_4$  (or  $\text{FeO} \cdot \text{Cr}_2\text{O}_3$ ).
22. Sodium chromate is converted to sodium dichromate by treatment with concentrated sulphuric acid.  
 $2\text{Na}_2\text{CrO}_4 + \text{H}_2\text{SO}_4 \longrightarrow \text{Na}_2\text{Cr}_2\text{O}_7 + \text{Na}_2\text{SO}_4 + \text{H}_2\text{O}$
23. In acidic medium, Cr(VI) of potassium dichromate gains 3 electrons and is reduced to Cr(III) of chromium sulphate. Thus, potassium dichromate is a good oxidizing agent.  
 $\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6\text{e}^- \longrightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O}$   
 Thus, oxidation state of chromium changes by  $(+6) - (+3) = 3$
24. When  $\text{SO}_2$  gas is passed through acidified  $\text{K}_2\text{Cr}_2\text{O}_7$  solution, it is oxidized to sulphuric acid. Colour of the solution changes to green due to formation of  $\text{Cr}_2(\text{SO}_4)_3$ .  
 $\text{K}_2\text{Cr}_2\text{O}_7 + 3\text{SO}_2 + \text{H}_2\text{SO}_4 \longrightarrow \text{K}_2\text{SO}_4 + \text{Cr}_2(\text{SO}_4)_3 + \text{H}_2\text{O}$
25.  $\text{K}_2\text{Cr}_2\text{O}_7 + 6\text{H}_2\text{SO}_4 + 4\text{NaCl} \longrightarrow 2\text{KHSO}_4 + 4\text{NaHSO}_4 + 2\text{CrO}_2\text{Cl}_2 + 3\text{H}_2\text{O}$   
 Potassium      Sulphuric      Sodium      Potassium      Sodium      Chromyl      Water  
 dichromate      acid      chloride      hydrogen      hydrogen      chloride  
    sulphate      sulphate



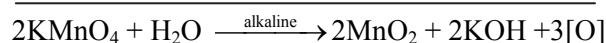
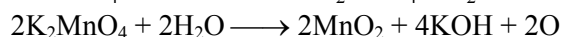
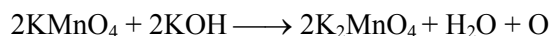
The  $\text{OH}^-$  ions formed, react with  $\text{CO}_2$  to form  $\text{HCO}_3^-$  ions.



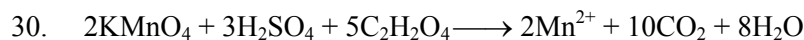
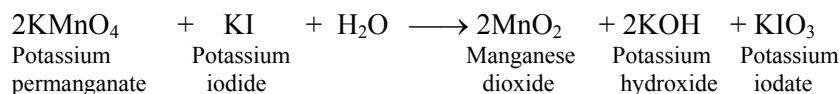
27. When heated to 473 K, potassium permanganate decomposes to give  $\text{K}_2\text{MnO}_4$ ,  $\text{MnO}_2$  and  $\text{O}_2$ .



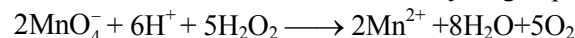
28.  $\text{KMnO}_4$  is first reduced to manganate and then to insoluble manganese dioxide. Colour changes first from purple to green and finally becomes colourless.



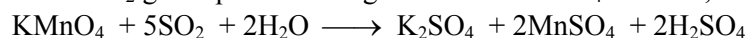
29. In alkaline medium



31. In acidic medium,  $\text{KMnO}_4$  oxidizes hydrogen peroxide. Thus, this reaction gives  $\text{Mn}^{2+}$  and  $\text{O}_2$  as products.



32. When  $\text{SO}_2$  gas is passed through acidified  $\text{KMnO}_4$  solution, the solution turns colourless.

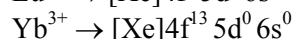
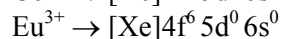
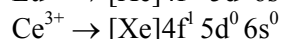
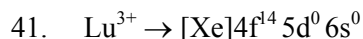


33. Manganate ion ( $\text{MnO}_4^{2-}$ ) is green in colour and is paramagnetic as it contains one unpaired electron.

36. Alkaline  $\text{KMnO}_4$  is also known as Baeyer's reagent, which is used for testing unsaturation in organic compounds.

37. As sixth period can accommodate only 18 elements in the table, 14 members of 4f series (atomic number 58 to 71) are separately accommodated in a horizontal row below the periodic table. These are called as lanthanoids.

38. The observed electronic configuration of Ce is  $[\text{Xe}] 4f^2 5d^0 6s^2$ . Therefore, the electronic configuration of  $\text{Ce}^{3+}$  ion is  $[\text{Xe}] 4f^1$ .

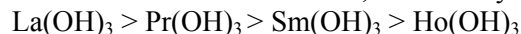


$\text{Lu}^{3+}$  does not have any unpaired electrons and hence, it is not paramagnetic.

42.  $\text{Yb}^{2+}$  has an electronic configuration of  $4f^{14}$ . Since there is absence of unpaired electron, it is diamagnetic in nature.

44. Due to poor shielding of 4-f electrons, increased nuclear charge is experienced and the valence shell is pulled slightly towards nucleus thereby resulting in the lanthanoid contraction.

46. Due to lanthanoid contraction, the basicity of hydroxides decreases in the following order:

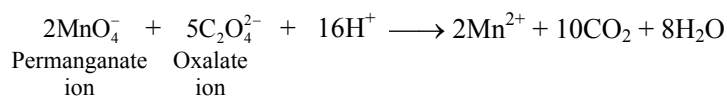
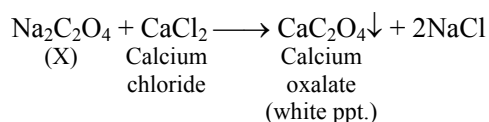
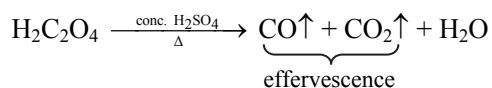
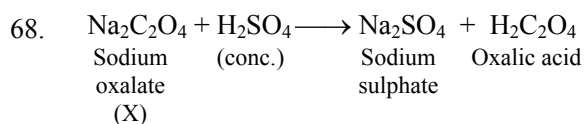


47. Due to lanthanoid contraction, Zr and Hf possess similar properties. This is due to similar number of valence electrons, atomic radii and almost same size of these elements. Thus, they are also called 'chemical twins'.

48.  $\text{Zr}^{4+}$  (4d) and  $\text{Hf}^{4+}$  (5d) series-size almost same due to lanthanoid contraction.

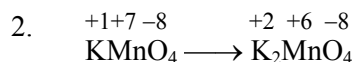


50. Zr is present in period 5 while Hf is present in period 7.
51. Terbium ( $Z = 65$ ) is lanthanide as it belongs to 4f-series having configuration  $[\text{Xe}] 4s^9 6s^2$ . The other elements belong to 5f-series (actinides).
55. 4f and 5f belongs to different energy levels, hence the shielding effect on them is not the same. Shielding of 4f is more than 5f.
56. Elements having unpaired electrons in their outermost orbit are termed as paramagnetic. In 3d series elements, number of unpaired electrons increases from Sc to Mn and then decreases from Fe to Zn. Therefore, paramagnetic character increases from Sc to Mn and then decreases from Fe to Zn.
57. The element in +3 oxidation state has the electronic configuration  $[\text{Ar}] 3d^3$ . So the electronic configuration in elemental form is  $[\text{Ar}] 3d^6$ . So, the atomic number is sum of atomic number of Ar and 6 electrons in 3d subshell i.e.,  $18 + 6 = 24$ .
58. The basic character of any element changes with the oxidation state, low oxidation states are more basic and high oxidation state are more acidic. For example,  $\text{MnO}$  and  $\text{Mn}_2\text{O}_3$  are basic while  $\text{Mn}_2\text{O}_7$  is acidic in nature.
59.  $\text{Fe}^{3+}$  is easily hydrolysed than  $\text{Fe}^{2+}$  due to more positive charge.
60. Basic character of oxide decreases from left to right in a period of periodic table.
62. In acidic medium,  $\text{KMnO}_4$  gives 5 oxygen while acidic  $\text{K}_2\text{Cr}_2\text{O}_7$  gives 3 oxygen.
63. Most of the trivalent lanthanoid compounds except that of  $\text{La}^{3+}$  and  $\text{Lu}^{3+}$  are coloured both in the solid state and in the aqueous solution. The colour of these ions can be attributed due to the presence of f-electrons.
64. (B) The extent of actinoid contraction is greater than lanthanoid contraction. This is due to lesser shielding of 5f-electrons in actinoids as compared to the shielding of 4f-electrons in lanthanoids.  
(C) In general, both lanthanoids and actinoids show variable oxidation states.  
(D) Ce exhibits +4 oxidation state.  $\text{Ce}^{4+}$  is a good oxidising agent.
65. Since Zn, Cd and Hg have completely filled  $(n - 1)$  d orbitals in their ground states as well as in the form of ions, they are excluded from transition series. Hence, among the given options, only Au is a transition element.
66. The oxides of lanthanoids ( $\text{Ln}_2\text{O}_3$ ) react with water to form corresponding hydroxides  $[\text{Ln}(\text{OH})_3]$ , which are basic in nature. The basicity of these hydroxides decreases from  $\text{La}(\text{OH})_3$  to  $\text{Lu}(\text{OH})_3$ . Therefore, among the given options,  $\text{La}_2\text{O}_3$  has the maximum basicity.
67. In general, the earlier members of lanthanoids have reactivity similar to calcium but, with increasing atomic number, their reactivity is similar to aluminium.

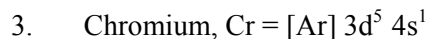




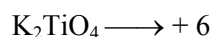
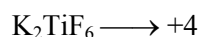
## Evaluation Test



$$\text{Equivalent weight} = \frac{\text{molecular mass}}{\text{total of } e^- \text{ gained or lost}} = \frac{M}{1} = M$$

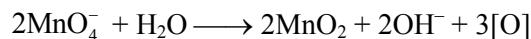


4. Oxidation state of Ti in the given compounds is as follows:

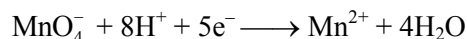


The oxidation states exhibited by Ti is +2, +3, +4. So K<sub>2</sub>TiO<sub>4</sub> does not exist.

5. In alkaline medium, KMnO<sub>4</sub> is first reduced to manganate and then to insoluble manganese dioxide.



In acidic medium, manganous sulphate is formed.



No unpaired electron hence will show diamagnetic character and will be repelled, resulting into less weight.

7. In this reaction



5 time quantity of Fe<sup>2+</sup> is consumed.

So, 5 time of FeSO<sub>4</sub> will be equivalent to 50 mL

9. KMnO<sub>4</sub> will not be oxidized further by ozone as manganese is already present in its highest possible oxidation state i.e., +7.

10.

Sr.No.	Ion	Outer electronic configuration	Number of unpaired electrons
i.	Cu <sup>+2</sup>	3d <sup>9</sup>	1
ii.	Ni <sup>+2</sup>	3d <sup>8</sup>	2
iii.	Co <sup>+2</sup>	3d <sup>7</sup>	3
iv.	Fe <sup>+2</sup>	3d <sup>6</sup>	4

$$\mu = \sqrt{n(n+2)} \text{ (magnetic moment)}$$

$$\mu \propto \sqrt{n}$$

Cu<sup>+2</sup> there is only 1 unpaired electron so its magnetic moment is least. 12. [Xe] 4f<sup>0</sup> 5d<sup>1</sup> 6s<sup>2</sup> is an electronic configuration of Lanthanum (La) – 57 which is not an inner transition element.





13. (B) Hydroxides of actinoids are more basic than hydroxides of lanthanoids.  
(C) The extent of actinoid contraction is relatively more as compared to lanthanoid contraction.  
(D) Actinoids show greater tendency to form complexes as compared to lanthanoids.
14. Compounds containing Ni(II) are thermodynamically more stable than compounds containing Pt(II). Less amount of energy is required for the ionization of Ni to  $\text{Ni}^{2+}$ , than the energy required for the ionization of Pt to  $\text{Pt}^{2+}$ .  
Compounds containing Pt(IV) are thermodynamically more stable than compounds containing Ni(IV). Less amount of energy is required for the ionization of Pt to  $\text{Pt}^{4+}$  than the energy required for the ionization of Ni to  $\text{Ni}^{4+}$ .



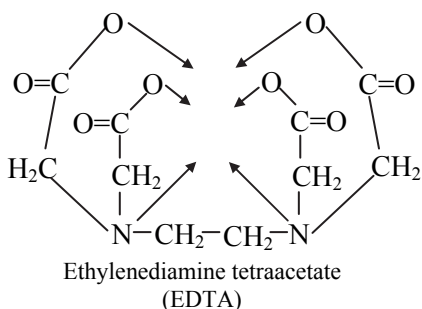
## Hints



### Classical Thinking

3. According to Werner's theory, most metals exhibit two types of valences:
  - i. primary valence
  - ii. secondary valence
4. Primary valence is also known as ionizable valence.
5. Secondary valence has directional properties and is designated by dotted lines. It corresponds to the coordination number of the central metal.
6. Inner sphere is known as the first sphere or coordination sphere and the outer sphere is known as the second sphere or the ionization sphere.
8.  $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3 \rightleftharpoons \underbrace{[\text{Co}(\text{NH}_3)_6]^{3+} + 3\text{Cl}^-}_{(4 \text{ ions})}$
9. Ammonia and methylamine are neutral ligands. Hydrazinium is a positive ligand.

12.

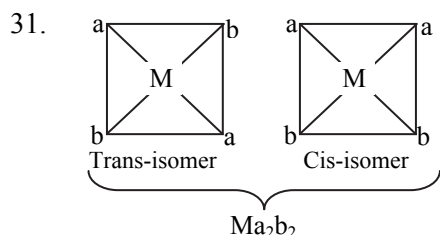


14. en is a bidentate ligand. Hence, the coordination number =  $2 \times$  number of bidentate ligands  
 $= 2 \times 3 = 6$
16. Coordination number acts as deciding factor to govern the geometry or shape of the complex compounds.
19. Complex ions carrying a net positive charge are known as cationic complexes.
20. Let the oxidation number of Ni be 'x'. As CO is a neutral ligand, charge on it is zero. Thus, the oxidation number can be calculated as:  
 $x + 4 \times 0 = 0$   
 $\therefore x = 0$
23.  $\text{K}_4[\text{Fe}(\text{CN})_6] + 2\text{CuSO}_4 \longrightarrow \text{Cu}_2[\text{Fe}(\text{CN})_6] + 2\text{K}_2\text{SO}_4$   
 Copper ferrocyanide
26. EAN = atomic number – oxidation number of metal ion + number of electrons donated by ligands.  
 $86 = x - (4) + (2 \times 6)$   
 $86 = x - 4 + 12$   
 $x = 78$



27. The complex ion is the anion and bears four negative charges. Thus, iron atom must have an oxidation number of +2. Hence, the compound is potassium hexacyanoferrate (II) and is commonly called as potassium ferrocyanide.

30.  $\text{NH}_3$  (Ammonia) is a neutral ligand with zero charge and named “ammine”.



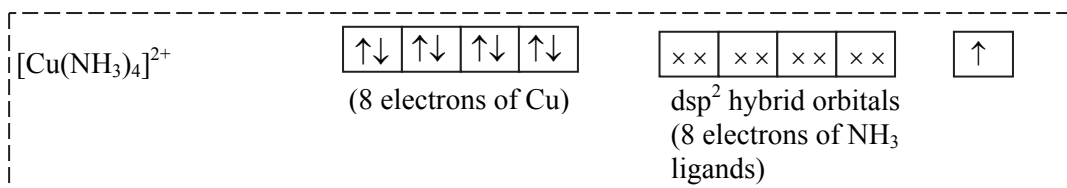
32. Tetrahedral complexes do not exhibit geometrical isomerism.

34. In ionization isomerism, there is exchange of ions inside and outside the coordination sphere. They have the same formula but produce different ions in solution.

35. In linkage isomerism, the same ligand is bonded to the central metal atom/ion, through different atoms. They have same molecular formula but differ in the linkage of the ligand to central metal atom.

36. Coordination isomerism is observed in the coordination compounds having both cationic and anionic complex ions. The ligands are interchanged in both the cationic and anionic ions to form isomers.

40. The central atom is surrounded by four ammonia molecules (ligands) exhibiting square planar configuration with  $\text{Cu}^{2+}$  oxidation state as paramagnetic (one unpaired electron).

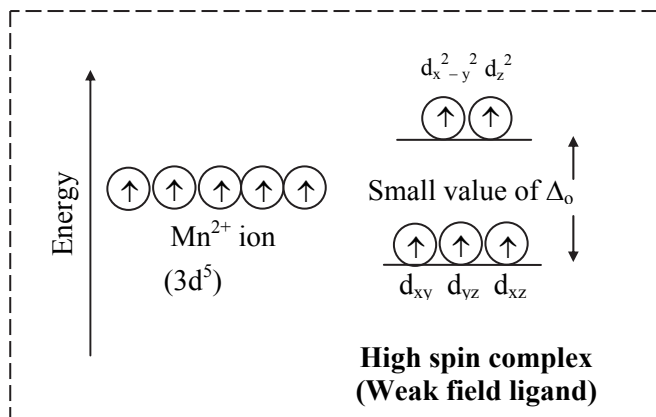


42. Valence bond theory cannot distinguish between weak field and strong field ligands.

46.  $\text{Mn} (Z = 25) \longrightarrow [\text{Ar}] 3d^5 4s^2$

$\text{Mn}^{2+} \longrightarrow [\text{Ar}] 3d^5$

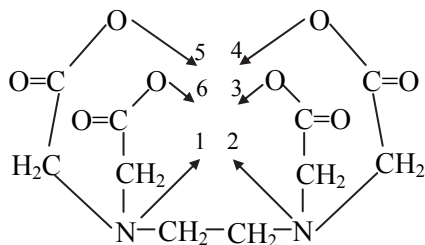
In presence of weak ligand field, there will be no pairing of electrons. So, it will form a high spin complex. i.e., the number of unpaired electrons will be 5.







8.

Ethylenediamine tetraacetate  
(EDTA)

1, 2 are donor N atoms and 3, 4, 5, 6 are donor O atoms.

9. While forming a complex, either N or O of  $\text{NO}_2^-$  can get linked with a metal. Hence,  $\text{M-ONO}$  or  $\text{M-NO}_2$  are the possible linkages.11. Let the oxidation state of Fe in  $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$  be  $x$ .  
The charge on  $\text{C}_2\text{O}_4$  ligands is  $-2$ . Thus, the oxidation number can be calculated as:

$$x + 3(-2) = -3$$

$$x - 6 = -3$$

$$x = 3$$

Thus, iron in  $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$  has +3 oxidation state while in  $\text{K}_2[\text{Ni}(\text{CN})_4]$ ,  $\text{K}_4[\text{Fe}(\text{CN})_6]$  and  $[\text{Cu}(\text{NH}_3)_4]^{2+}$ ; the central metal atom exhibits an oxidation state of +2.

12. Six monodentate ligands are attached to the central metal atom. Hence, the coordination number is 6.

Let the oxidation number of metal be  $x$ . $\text{NH}_3$  is neutral molecule,  $\text{SO}_4$  has charge of  $-2$  and  $\text{Cl}$  has charge of  $-1$ .

$$\therefore x + 5(0) + (-2) + (-1) = 0$$

$$x = +3$$

 $\therefore$  Coordination number is 6 and oxidation number is +3.14. Mohr's salt ( $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ ) is a double salt.

15. Atomic number of Pd = 46

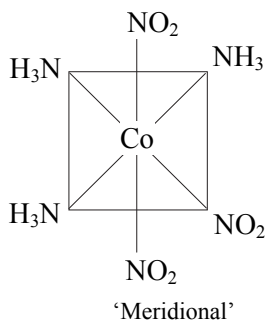
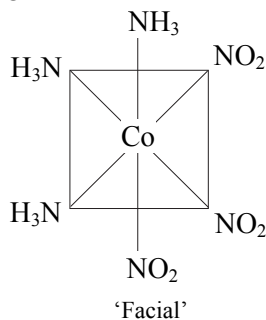
$$\therefore \text{Pd}^{4+} = 46 - 4 = 42$$

Each  $\text{NH}_3$  ligand donates 2 electrons.

$$\therefore \text{Electrons from } 6\text{NH}_3 = 2 \times 6 = 12$$

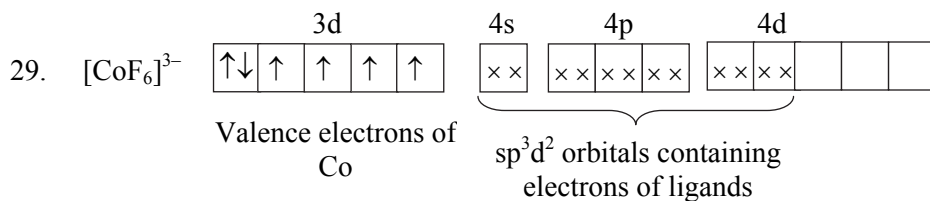
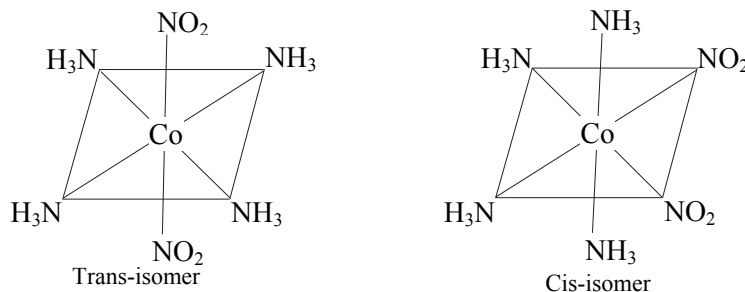
$$\therefore \text{EAN} = 42 + 12 = 54$$

54 is the atomic number of Xenon.

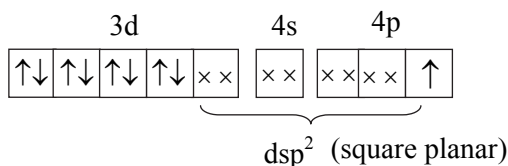
22. In complexes with coordination number 4, geometrical isomerism is shown by complex with formula  $\text{Ma}_2\text{b}_2$ . Hence,  $[\text{Pt}(\text{NH}_3)_2(\text{H}_2\text{O})_2]^{2+}$  and  $[\text{Co}(\text{en})_2\text{Cl}_2]$  will show geometrical isomerism.In octahedral complex with coordination number 6, complexes of the type  $\text{Ma}_6$  and  $\text{Ma}_5\text{b}$  do not show geometrical isomerism while the other types show such isomerism. So  $[\text{Cr}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$  being of type  $\text{Ma}_5\text{b}$  will not show geometrical isomerism.23. Complexes of type  $[\text{Ma}_3\text{b}_3]^{n\pm}$  exhibit two geometrical isomers (i) facial and (ii) meridional. In facial isomer, three identical ligands are on one triangular face and the other three identical ligands are placed on the opposite triangular face. In meridional isomer, each set of three identical ligands occupies a plane passing through the metal atom.



27. The complex is an octahedral complex of the type  $[M(AA)_2ab]^{n+}$  and hence can exhibit cis-trans isomerism. SCN and  $\text{NO}_2$  being ambidentate ligands, enable the complex to show linkage isomerism. The complex can show ionization isomerism with  $[\text{Co}(\text{en})_2(\text{SCN})\text{Br}]\text{NO}_2$
28. i.  $\text{NO}_2$  is an ambidentate ligand. It can show linkage isomerism.  
 ii. The complex can show ionization isomerism with the complex  $[\text{Co}(\text{NH}_3)_4\text{NO}_2\text{Cl}]\text{NO}_2$   
 iii. The complex shows geometrical isomerism.



30.  $[\text{Cu}(\text{NH}_3)_4]^{2+}$  complex is formed by  $\text{dsp}^2$  hybridization and one electron is shifted to 4p-orbital.



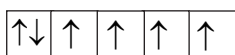
32.  $[\text{CoF}_6]^{3-}$  : Fluoride has uninegative charge, hence

$$x + 6(-1) = -3$$

$$x - 6 = -3$$

$$x = +3$$

Co is present in +3 state, resulting into 4 unpaired  $e^-$



34. In octahedral complex, the ligands approach along the axes and hence, the  $d_z^2$  and  $d_{x^2-y^2}$  orbitals experience maximum electrostatic repulsion due to ligands. Hence, the energy of these orbitals increases.
35. According to spectrochemical series, the strength of the ligands can be given as  $\text{CN}^- > \text{OH}^- > \text{F}^- > \text{Br}^-$
36.  $\text{Fe}(\text{CO})_5$  has  $\text{dsp}^3$ -hybridisation; so it shows trigonal bipyramidal geometry.
39. In a complex, metal ion is Lewis acid and ligand is Lewis base.
41. Higher the magnitude of charge and smaller the size of the ion, more is the charge density on the metal ion and greater is the stability of the complex. The magnitude of positive charge on  $\text{Cu}^{2+}$  and  $\text{Cd}^{2+}$  is same; however, the ionic radius of  $\text{Cu}^{2+}$  ion is less than that of  $\text{Cd}^{2+}$  ion. Hence, the charge density on  $\text{Cu}^{2+}$  ion is greater than that of  $\text{Cd}^{2+}$  ion. Thus, the complexes formed by  $\text{Cu}^{2+}$  ion are more stable than those formed by  $\text{Cd}^{2+}$  ion.
43. Detection and estimation of  $\text{Ni}^{2+}$  ions is done by complexing with dimethylglyoxime to obtain red precipitate.
47. Since the isomer gives one mole of  $\text{AgCl}$ , the isomer will contain one ionisable chlorine atom. So, among the given options, (C) is the answer.



48. Since no precipitate of AgCl with AgNO<sub>3</sub> is obtained, all the chloride ions are inside the coordination sphere. PtCl<sub>4</sub>.2NH<sub>3</sub> gives zero ions in the solution. Hence, all the ligands are present inside the coordination sphere. Thus, the structure is [Pt(NH<sub>3</sub>)<sub>2</sub>Cl<sub>4</sub>]. PtCl<sub>4</sub>.2KCl gives 3 moles of ions in solution.

$K_2[PtCl_6] \rightleftharpoons 2K^+ + [PtCl_6]^{2-}$ . Hence, the structure is K<sub>2</sub>[PtCl<sub>6</sub>].

49. [Fe(H<sub>2</sub>O)<sub>6</sub>]<sup>2+</sup> is paramagnetic while [Fe(CN)<sub>6</sub>]<sup>4-</sup> is diamagnetic. [Fe(H<sub>2</sub>O)<sub>6</sub>]<sup>2+</sup> has pale green colour while [Fe(CN)<sub>6</sub>]<sup>4-</sup> has yellow colour.

50. Magnetic moment =  $\sqrt{n(n+2)}$  (n = unpaired electrons)

Cr<sup>3+</sup> – [Ar]3d<sup>3</sup> : 3 unpaired electrons ; Fe<sup>2+</sup> – [Ar]3d<sup>6</sup> : 4 unpaired electrons

∴ Magnetic moment =  $\sqrt{3 \times 5} = \sqrt{15}$  ∴ Magnetic moment =  $\sqrt{4 \times 6} = \sqrt{24}$

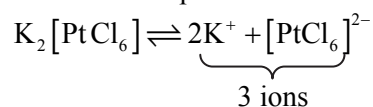
Ni<sup>2+</sup> – [Ar]3d<sup>8</sup> : 2 unpaired electrons ;

∴ Magnetic moment =  $\sqrt{2 \times 4} = \sqrt{8}$  ; Mn<sup>2+</sup> – [Ar]3d<sup>5</sup> : 5 unpaired electrons

∴ Magnetic moment =  $\sqrt{5 \times 7} = \sqrt{35}$

51. The complex is K<sub>2</sub>[PtCl<sub>6</sub>].

When the complex is dissolved in water, it ionises as:



Hence, each molecule will give 3 ions.

As Cl<sup>-</sup> ions are not present in the ionisation sphere, Cl<sup>-</sup> ions will not be formed and hence, AgCl will not be precipitated.



### Competitive Thinking

1.

Composition	Formula of the complex	No. of Cl <sup>-</sup> ions precipitated by AgNO <sub>3</sub>
CoCl <sub>3</sub> .3NH <sub>3</sub>	[CoCl <sub>3</sub> (NH <sub>3</sub> ) <sub>3</sub> ]	0
CoCl <sub>3</sub> .4NH <sub>3</sub>	[CoCl <sub>2</sub> (NH <sub>3</sub> ) <sub>4</sub> ]Cl	1
CoCl <sub>3</sub> .5NH <sub>3</sub>	[CoCl(NH <sub>3</sub> ) <sub>5</sub> ]Cl <sub>2</sub>	2
CoCl <sub>3</sub> .6NH <sub>3</sub>	[Co(NH <sub>3</sub> ) <sub>6</sub> ]Cl <sub>3</sub>	3

Therefore, CoCl<sub>3</sub>.3NH<sub>3</sub> will not give test for chloride ions with silver nitrate.

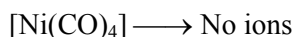
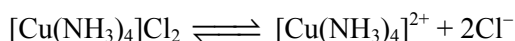
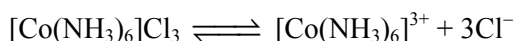
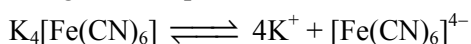
2. CoCl<sub>3</sub>.6NH<sub>3</sub> contains 3 Cl<sup>-</sup> ions in ionization sphere.

CoCl<sub>3</sub>.5NH<sub>3</sub> contains 2 Cl<sup>-</sup> ions in ionization sphere.

CoCl<sub>3</sub>.4NH<sub>3</sub> contains 1 Cl<sup>-</sup> ion in ionization sphere.

3. On dissolution of one mole of complex, three moles of ions are formed. Hence, there will be two groups in the ionization zone. Since two moles of AgCl get precipitated, the complex has two ionizable chlorine atoms. So the complex is [Co(NH<sub>3</sub>)<sub>5</sub>Cl]Cl<sub>2</sub>.

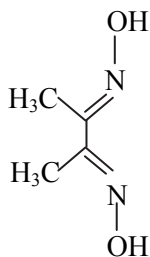
4. The given compounds will ionize as follows:



Since, K<sub>4</sub>[Fe(CN)<sub>6</sub>] gives maximum number of ions (i.e., 5 ions) in the solution, it will show maximum ionic conductivity among the given compounds.

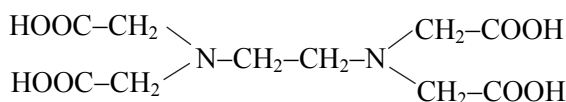


5. DMG is a bidentate ligand, which binds the central atom and forms 5 membered ring. Hence, it is a chelating ligand while  $\text{H}_2\text{O}$ ,  $\text{OH}^-$  and  $\text{Cl}^-$  are monodentate ligands.
6. The structure of dimethylglyoximato is

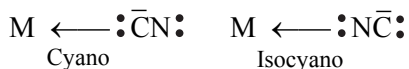


Dimethylglyoximato is a bidentate ligand because it has two donor N atoms.

7. Structure of EDTA is



8. Ambidentate ligands have two or more donor atoms but in forming complexes only one donor atom is attached to metal ion.



10.  $\left[ \text{AuCl}_4 \right]^{-}$

$$x + 4(-1) = -1$$

$$\therefore x = +3$$

11. Charge on the ligand  $\text{C}_2\text{O}_4^{2-}$  is  $-2$  and charge on the complex ion is  $-4$ .

Let the oxidation number of Ni be  $x$ .

$$\therefore x + 3 \times (-2) = -4$$

$$x = +2$$

Oxidation number of Ni in  $[\text{Ni}(\text{C}_2\text{O}_4)_3]^{4-} = +2$

12. The complex is  $[\text{Fe}(\text{CN})_6]^{3-}$

$$x + 6(-1) = -3$$

$$\therefore x = +3$$

Since there are 6  $\text{CN}^-$  ligands attached to Fe, the coordination number of Fe is 6.

13.  $[\text{E}(\text{en})_2(\text{C}_2\text{O}_4)]\text{NO}_2$

The complex has two molecules of en and one  $\text{C}_2\text{O}_4^{2-}$  ion. Thus, the complex has three bidentate ligands in all.

$$\therefore \text{Coordination number} = 2 \times \text{number of bidentate ligands.}$$

$$= 2 \times 3 = 6$$

Let the oxidation number of metal 'E' in the complex be 'x'.

The charges on complex ion, en and  $\text{C}_2\text{O}_4^{2-}$  are +1, 0 and  $-2$  respectively.

$$\text{Hence, } x + 0 - 2 = +1$$

$$x = 3$$

14.  $[\text{M}(\text{en})_2(\text{C}_2\text{O}_4)]\text{Cl}$

The complex has two molecules of en and one  $\text{C}_2\text{O}_4^{2-}$  ion. Thus, the complex has three bidentate ligands in all.

$$\therefore \text{Coordination number} = 2 \times \text{number of bidentate ligands.} = 2 \times 3 = 6$$

Let the oxidation number of metal 'M' in the complex be 'x'.

The charge on complex ion, en and  $\text{C}_2\text{O}_4^{2-}$  are +1, 0 and  $-2$  respectively.

$$\text{Hence, } x + 0 - 2 = +1$$

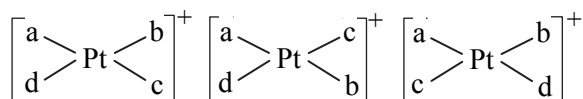
$$x = 3$$

$$\therefore \text{The sum of coordination number and oxidation number of the metal M} = 6 + 3 = 9.$$



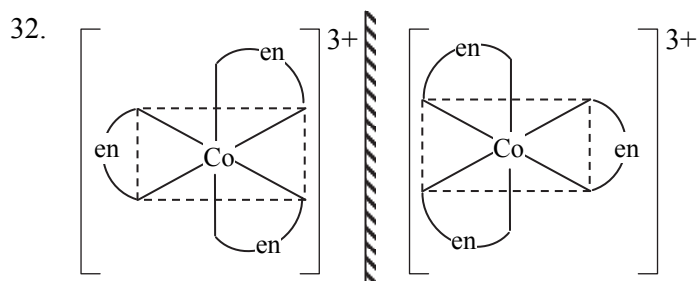


16. In  $K_4[Fe(CN)_6]$ , the species retains its identity in solid as well as in solution state. Hence, it is a complex salt.
17. Mohr's salt is  $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$ .  
When it is dissolved in excess of water, one molecule forms one  $Fe^{2+}$  ion, two  $NH_4^+$  ions and two  $SO_4^{2-}$  ions (i.e., total five ions per molecule).
18. EAN = Atomic number – oxidation state +  $2 \times$  coordination number  
Hence, EAN of Ni in  $Ni(CO)_4$  is equal to  $28 - 0 + 2 \times 4 = 36$
19.  $Z - 3 + 12 = 33$   
 $Z = 24$
20. EAN of  $[Pt(NH_3)_6]^{4+} = 78 - 4 + 12 = 86$   
EAN of  $[Fe(CN)_6]^{4-} = 26 - 2 + 12 = 36$   
EAN of  $[Zn(NH_3)_4]^{2+} = 30 - 2 + 8 = 36$   
EAN of  $[Cu(NH_3)_4]^{2+} = 29 - 2 + 8 = 35$   
Hence,  $[Cu(NH_3)_4]^{2+}$  is an exception to EAN rule.
26.  $[Co(H_2O)_4(NH_3)_2]Cl_3$  : Diamminetetraaquacobalt (III) chloride.
27.  $[Cr(en)_2Br_2]Br$  : Dibromidobis(ethylenediamine)chromium (III) bromide.
28. For square planar complexes of the type  $[Mabcd]^{n\pm}$  where all the four ligands are different, three geometrical isomers are possible. So, for the given square planar complex  $[Pt(Cl)(py)(NH_3)(NH_2OH)]^+$ , following three geometrical isomers are possible:

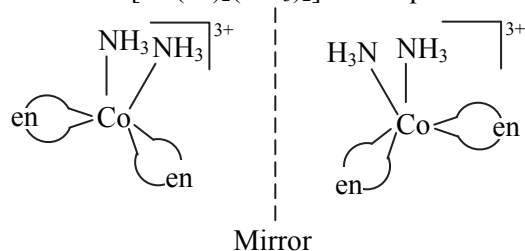


where  $a = Cl$ ,  $b = py$ ,  $c = NH_3$  and  $d = NH_2OH$ .

29. For square planar complexes of the type  $MABCD$  where all the four ligands are different, three geometrical isomers are possible.
30. Octahedral complexes of the type  $[MA_4B_2]$ ,  $[MA_2B_4]$ ,  $[MA_3B_3]$  exhibit geometrical isomerism.
31. Two geometrical isomers are found in  $MA_4B_2$  complexes.

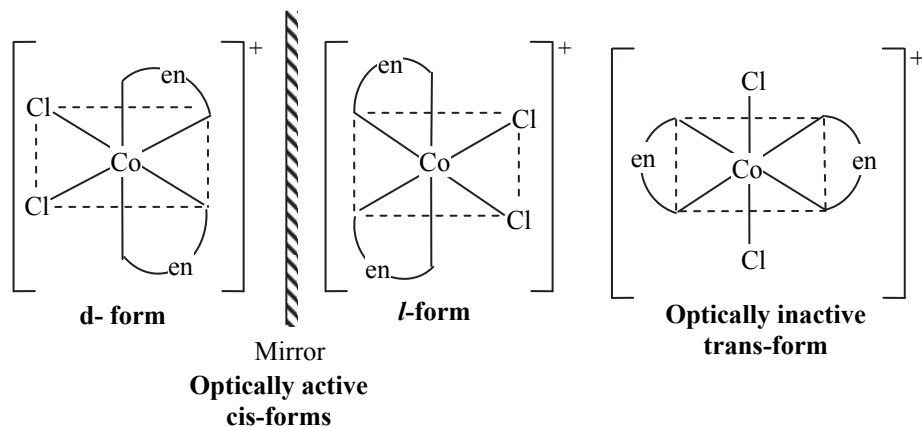


33. cis-form  $[Co(en)_2(NH_3)_2]^{3+}$  has optical isomers.



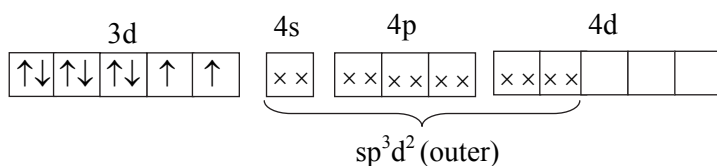


34. Cis isomer of  $[\text{Co}(\text{en})_2\text{Cl}_2]^+$  is optically active whereas trans isomer contains a plane of symmetry and is optically inactive.
35.  $[\text{Co}(\text{en})_2\text{Cl}_2]^+$  is optically active in cis isomer. Trans isomer contains a plane of symmetry and is therefore optically inactive. The resolution of cis isomer in *d* and *l*-form is possible.

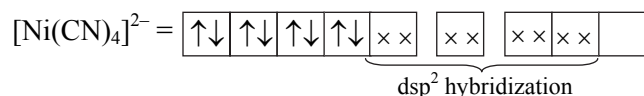


36. The ionisation isomer for the given compound will be obtained by exchanging ligand with counter ion as:  $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2](\text{NO}_2)$ .
37.  $\text{SCN}^-$  ion can coordinate through the sulphur or nitrogen atom. Such possibilities give rise to linkage isomerism in coordination compounds.  
 $\text{M} \leftarrow \text{SCN}$  Thiocyanato or thiocyanato-S ;  $\text{M} \leftarrow \text{NCS}$  Isothiocyanato or thiocyanato-N

40. oxidation state of metal = +2  
 $[\text{Ni}(\text{NH}_3)_6]^{2+}$

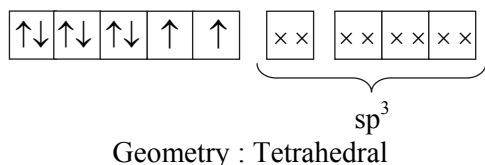


41. In  $[\text{Ni}(\text{CN})_4]^{2-}$ , Ni has +2 oxidation state.  
 $\text{Ni}^{2+} \Rightarrow [\text{Ar}] 3d^8 4s^0$



42. In  $[\text{MnO}_4]^-$ , Mn is in +7 oxidation state.  
 $\text{Mn} = [\text{Ar}] 3d^5 4s^2$   
 $\therefore \text{Mn}^{7+} = [\text{Ar}] 3d^0 4s^0$   
 Thus,  $[\text{MnO}_4]^-$  has no 'd' electrons.

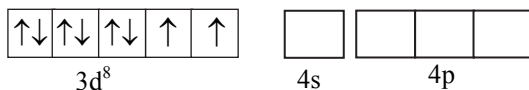
43. oxidation state of metal : + 2  
 $[\text{NiX}_4]^{2-}$



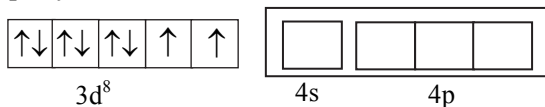


44. In the paramagnetic and tetrahedral complex  $[\text{NiCl}_4]^{2-}$ , the nickel is in +2 oxidation state and the ion has the electronic configuration  $3d^8$ . The hybridisation scheme is as shown below:

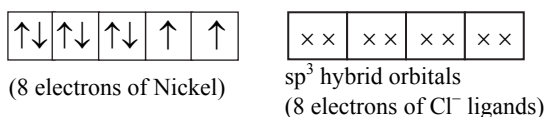
$\text{Ni}^{+2}$



$sp^3$  hybridisation



$[\text{NiCl}_4]^{2-}$  high spin complex

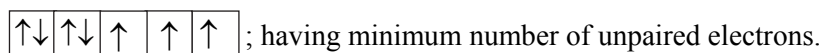


$$\text{Magnetic moment } (\mu) = \sqrt{n(n+2)},$$

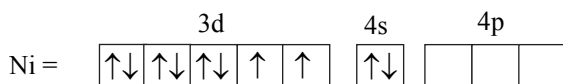
(n = number of unpaired electrons)

$$\mu = \sqrt{n(n+2)} = \sqrt{2(2+2)} = 2.82 \text{ B.M.}$$

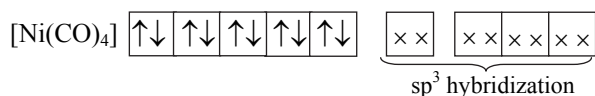
45.  $\text{Co}^{2+} \rightarrow 3d^7 4s^0$



- 46.

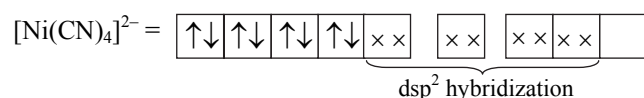


In  $[\text{Ni}(\text{CO})_4]$ , Ni has 0 oxidation state

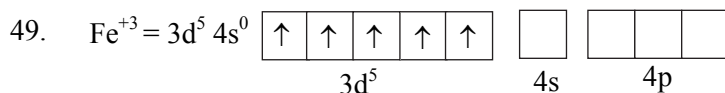


In  $[\text{Ni}(\text{CN})_4]^{2-}$ , Ni has +2 oxidation state

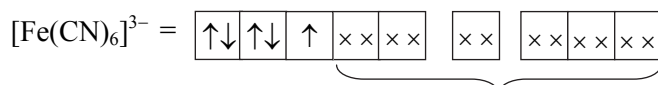
$$\therefore \text{Ni}^{2+} - 1s^2 2s^2 2p^6 3s^2 3p^6 3d^8 4s^0$$



48. The magnitude of  $\Delta_o$  (CFSE in octahedral field) will be maximum for  $[\text{Co}(\text{CN})_6]^{3-}$  as  $\text{CN}^-$  is a strong field ligand.



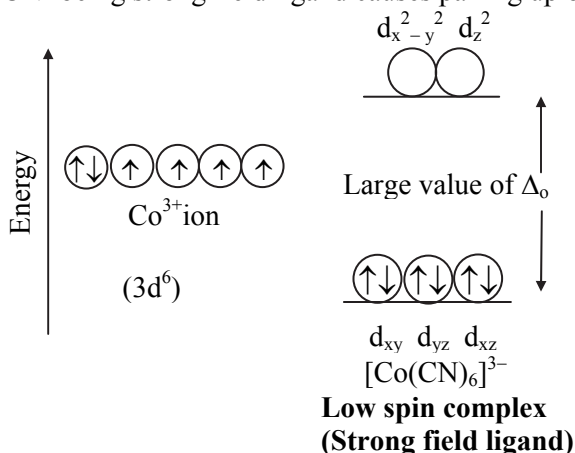
$\text{CN}^-$  being strong field ligand causes pairing up of electrons.



Electrons of ligands in  $d^2sp^3$  hybridized orbitals

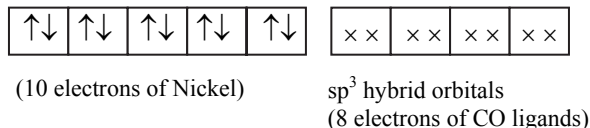


50. In  $[\text{Co}(\text{CN})_6]^{3-}$ , Co has +3 oxidation state.  
 $\text{Co}^{3+} \longrightarrow [\text{Ar}] 3d^6$   
 $\text{CN}^-$  being strong field ligand causes pairing up of d-electrons.

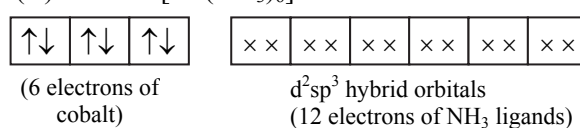


Thus,  $[\text{Co}(\text{CN})_6]^{3-}$  has no unpaired electrons and will be in a low-spin configuration (i.e., it forms low spin complex).

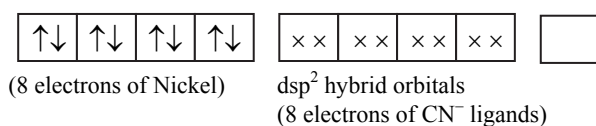
51. (A) Ni in  $[\text{Ni}(\text{CO})_4]$



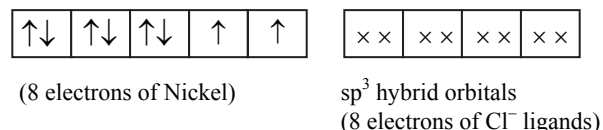
- (B)  $\text{Co}^{3+}$  in  $[\text{Co}(\text{NH}_3)_6]^{3+}$



- (C)  $\text{Ni}^{2+}$  in  $[\text{Ni}(\text{CN})_4]^{2-}$



- (D)  $\text{Ni}^{2+}$  in  $[\text{NiCl}_4]^{2-}$



$\text{CO}$ ,  $\text{NH}_3$  and  $\text{CN}^-$  are strong ligands, thus they induce pairing of electrons and their complexes are diamagnetic.  $\text{Cl}^-$  is a weak ligand, thus it does not induce the pairing of electrons and its complex is paramagnetic.

52. The magnetic moment of a substance increases with increase in the number of unpaired electrons. For the complexes  $[\text{Fe}(\text{CN})_6]^{3-}$  and  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ , the central metal ion is  $\text{Fe}^{3+}$  with outer electronic configuration  $3d^5$ .  $\text{CN}^-$  is a strong field ligand while  $\text{H}_2\text{O}$  is a weak field ligand. Therefore,  $[\text{Fe}(\text{CN})_6]^{3-}$  has magnetic moment of a single unpaired electron while  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$  has magnetic moment of five unpaired electrons.
- For the complexes  $[\text{Co}(\text{CN})_6]^{3-}$  and  $[\text{CoF}_6]^{3-}$ , the central metal ion is  $\text{Co}^{3+}$  with outer electronic configuration  $3d^6$ .  $\text{CN}^-$  is a strong field ligand while  $\text{F}^-$  is a weak field ligand. Therefore,  $[\text{Co}(\text{CN})_6]^{3-}$  is diamagnetic (no unpaired electrons) while  $[\text{CoF}_6]^{3-}$  has magnetic moment of four unpaired electrons. Thus, among the given complexes,  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$  has the highest magnetic moment value.

53. Magnetic moment ( $\mu$ ) =  $\sqrt{n(n+2)}$ ,

(n = number of unpaired electrons)

Therefore, complexes having same number of unpaired electrons will have same magnetic moment. By considering  $\text{H}_2\text{O}$  and  $\text{Cl}^-$  to be weak field ligands:

Complex	Central metal ion	No. of unpaired electrons
$[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$	$\text{Cr}^{2+}$ ( $3d^4$ )	4
$[\text{CoCl}_4]^{2-}$	$\text{Co}^{2+}$ ( $3d^7$ )	3
$[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$	$\text{Fe}^{2+}$ ( $3d^6$ )	4
$[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$	$\text{Mn}^{2+}$ ( $3d^5$ )	5

$[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$  and  $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$  have the same magnetic moment.

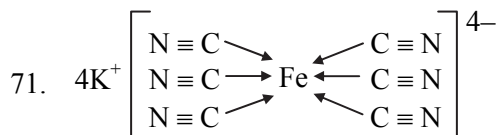


54. Only  $\text{Cr}^{3+}$  in the complex has unpaired electrons in the d orbital, while  $\text{Sc}^{3+}$ ,  $\text{Ti}^{4+}$  and  $\text{Zn}^{2+}$  do not have d electrons.
55.  $[\text{Ni}(\text{CN})_4]^{2-}$  is not expected to absorb visible light as unpaired electron in  $\text{Ni}^{+2}$  is zero.
56. In  $[\text{TiF}_6]^{2-}$ ,  $\text{Ti}^{4+}$ :  $3d^0$ , colourless; as there is no unpaired electron  
 In  $[\text{CoF}_6]^{3-}$ ,  $\text{Co}^{3+}$ :  $3d^6$ , coloured; as there are 4 unpaired electrons  
 In  $\text{Cu}_2\text{Cl}_2$ ,  $\text{Cu}^+$ :  $3d^{10}$ , colourless; as there is no unpaired electron  
 In  $[\text{NiCl}_4]^{2-}$ ,  $\text{Ni}^{2+}$ :  $3d^8$ , coloured; as there are 2 unpaired electrons  
 Thus, among the given options, two species ( $[\text{TiF}_6]^{2-}$  and  $\text{Cu}_2\text{Cl}_2$ ) are colourless.
57. The strength of ligands is in order  $\text{en} > \text{NH}_3 > \text{H}_2\text{O}$ .  
 Therefore, the wavelength of absorption will be  
 $[\text{Co}(\text{en})_3]^{3+} < [\text{Co}(\text{NH}_3)_6]^{3+} < [\text{Co}(\text{H}_2\text{O})_6]^{3+}$
59. The cyano and ammine complexes are far more stable than those formed by halide ions. This is due to the fact that  $\text{NH}_3$  and  $\text{CN}^-$  are strong Lewis bases.
60.  $\text{CuSO}_4$  solution contains  $\text{Cu}^{2+}$  ions. When this solution is treated with excess of KCN, cyano complex having formula  $\text{K}_2[\text{Cu}(\text{CN})_4]$  is formed.
61. The compound  $\text{cis}[\text{PtCl}_2(\text{NH}_3)_2]$  is also known as cisplatin.
64. The formula of the complex is  $[\text{M}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl}$ .  
 $0.1 \times V = 0.01 \times 200$   
 $\therefore V = 20 \text{ mL}$
65. Number of moles of complex =  $\frac{\text{Weight of complex}}{\text{molar mass of complex}} = \frac{2.675}{267.5} = 0.01$   
 Molar mass of  $\text{AgCl} = 108 + 35.5 = 143.5 \text{ g}$ .  
 Number of moles of  $\text{AgCl} = \frac{\text{Weight of AgCl}}{\text{molar mass of AgCl}} = \frac{4.78}{143.5} = 0.03$   
 This shows that three  $\text{Cl}^-$  ions are ionizable in the complex.
66. Mol of  $\text{Cl}^-$  ions =  $\frac{1.2 \times 10^{22}}{6.022 \times 10^{23}} = 0.02 \text{ mol}$   
 Mol of  $\text{COCl}_3 \cdot 6\text{H}_2\text{O} = \frac{100 \times 0.1}{1000} = 0.01 \text{ mol}$   
 1 mole complex produces =  $\frac{0.02}{0.01}$   
 $= 2 \text{ mol Cl}^-$  ions  
 There are two  $\text{Cl}^-$  ions as primary valence in the given complex. Hence, the formula of the given complex will be  $[\text{Co}(\text{H}_2\text{O})_5\text{Cl}]\text{Cl}_2 \cdot \text{H}_2\text{O}$ .
67. Chelated complex is more stable than unchelated complex. More the chelation, more is the stability.
68. In metal carbonyls, the donation of a pair of electrons from the filled d-orbital of metal to vacant antibonding  $\pi^*$  orbital of CO ligand (back bonding) reduces the bond order of C–O bond from the triple bond to double bond. This results in increase in C–O bond length from  $1.128 \text{ \AA}$  to  $1.15 \text{ \AA}$ . Among these four options, the central metal ion  $\text{Fe}^{2+}$  in  $[\text{Fe}(\text{CO})_4]^{2-}$  has maximum electron density and back bonding will be more pronounced in this complex. Thus, C–O bond length in  $[\text{Fe}(\text{CO})_4]^{2-}$  is the longest.
69.  $\text{Ca}^{2+}$  forms an octahedral complex with just one molecule of EDTA as it has four donor oxygen atoms and two donor nitrogen atoms in each molecule.



70. In the complex ion  $[\text{Co}^{(\text{III})}(\text{NH}_3)_5\text{Cl}]^x$ , charge on the complex ion is  
 $x = 3 + (0 \times 5) + (-1)$   
 $x = 3 - 1 = 2$

Hence, it will combine with that species which has  $-2$  charge to produce a neutral complex salt. So, it will combine with  $2\text{Cl}^-$  to produce  $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$  complex.

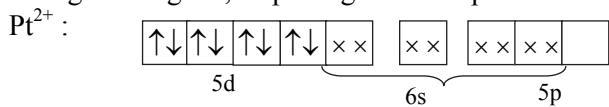


Bond between  $\text{K}^+$  and  $[\text{Fe}(\text{CN})_6]^{4-}$  is ionic.

Bond between C and N in  $\text{CN}^-$  ions is covalent.

Bond between  $\text{CN}^-$  ions and Fe is coordinate covalent.

72. Outer electronic configuration of Pt is  $5d^9 6s^1$ . Outer electronic configuration of  $\text{Pt}^{2+}$  is  $5d^8$ . As  $\text{CN}^-$  is strong field ligand, so pairing will take place.



$dsp^2$  hybridised orbitals containing  
electrons of  $\text{CN}^-$  ligands

73. Crystal field stabilization energy (CFSE)

$$= 4 Dq \times (\text{number of electrons in } t_{2g} \text{ orbital}) - 6 Dq \times (\text{number of electrons in } e_g \text{ orbital})$$

Complex	Outer electronic configuration	CFSE
$[\text{Mn}(\text{H}_2\text{O})_6]^{3+}$	$3d^4 (t_{2g}^3 e_g^1)$	$4Dq(3) - 6Dq(1) = 6 Dq$
$[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$	$3d^5 (t_{2g}^3 e_g^2)$	$4Dq(3) - 6Dq(2) = 0 Dq$
$[\text{Co}(\text{H}_2\text{O})_6]^{2+}$	$3d^7 (t_{2g}^5 e_g^2)$	$4Dq(5) - 6Dq(2) = 8 Dq$
$[\text{Co}(\text{H}_2\text{O})_6]^{3+}$	$3d^6 (t_{2g}^4 e_g^2)$	$4Dq(4) - 6Dq(2) = 4 Dq$

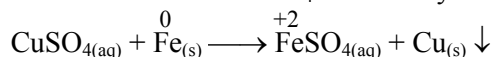
74. The increasing order of energies of light is  
red < yellow < green < blue.

Higher the energy of light absorbed, higher is the ligand strength.

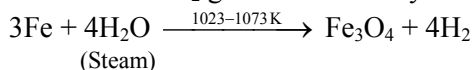
Hence, the increasing order of ligand strength is  $L_1 < L_3 < L_2 < L_4$

75. Rusting (corrosion) of iron involves redox reaction where iron (Fe) forms rust ( $\text{Fe}_2\text{O}_3 \cdot x \text{H}_2\text{O}$ ), i.e., Fe is oxidised to  $\text{Fe}^{3+}$ .

Decolourization of  $\text{CuSO}_4$  solution by iron involves oxidation of Fe.



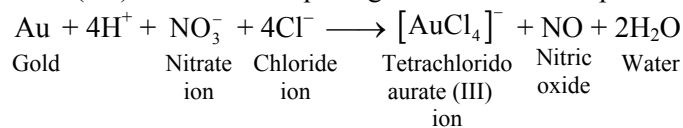
Liberation of  $\text{H}_2$  gas from steam by iron at high temperature involves oxidation of Fe. (Lane's process)



In  $\text{Fe}(\text{CO})_5$ , oxidation number of Fe is zero (0). Therefore, formation of  $\text{Fe}(\text{CO})_5$  from Fe involves no change in the oxidation state of Fe.

76. A mixture of three parts of concentrated hydrochloric acid and one part of concentrated  $\text{HNO}_3$  is known as aqua regia.

Gold (Au) dissolves in aqua regia to form the complex ion,  $[\text{AuCl}_4]^-$ .



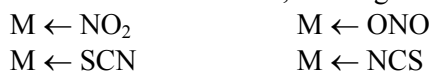


## Evaluation Test

1. Primary valencies are also known as oxidation state. Thus the oxidation state of metal ion in  $\text{Na}_2[\text{Co}(\text{CN})_4]$ , can be given as

$$2 + x - 4 = 0 \\ \Rightarrow x = +2$$

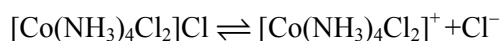
2. There are certain ligands which have two or more donor atoms but in forming complexes only donor atoms is attached to metal ion, such ligands are called ambidentate ligands.



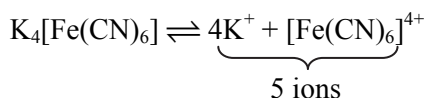
3. As the number of ions, formed from complex compounds when dissolved in water, increases, molar conductivity also increases.

i. 1 mole of  $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$  gives zero moles of ions (because it is a neutral molecule)

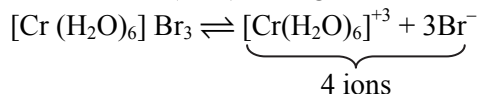
ii. 1 mole of  $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$  gives two mole of ions



iii. 1 mole of  $\text{K}_4[\text{Fe}(\text{CN})_6]$  gives five moles of ions

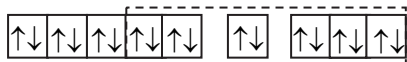
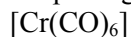


iv. 1 mole of  $[\text{Cr}(\text{H}_2\text{O})_6] \text{Br}_3$  gives 4 moles of ions



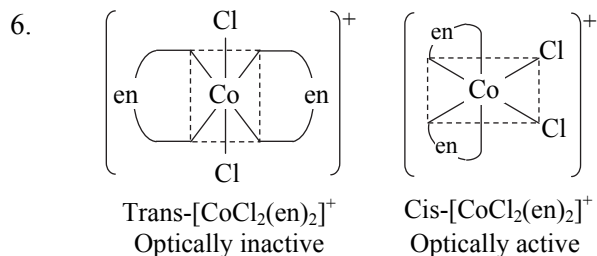
More the number of ions, more is the molar conductivity. Hence,  $\text{K}_4[\text{Fe}(\text{CN})_6]$  has the highest molar conductivity.

5. The chromium is in zero oxidation state having configuration  $[\text{Ar}] 3d^5 4s^1$ . The CO is a strong field ligand so the pairing of electrons occur. Thus, the complex has  $d^2sp^3$  hybridisation and is diamagnetic.



Rearrangement  $d^2sp^3$  hybridization

$$\mu_{B.M} = \sqrt{n(n+2)} = 0 \text{ as there is no unpaired electrons.}$$



7. One 'en' molecule provides 2 pairs of electrons for bonding. Hence three 'en' molecule will provide 6 pairs of electrons for bonding.

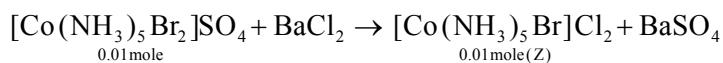
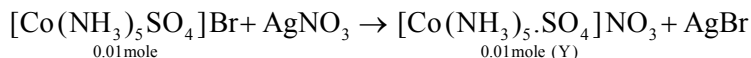
Hence the coordination number is 6.

Oxidation number of Cr in  $\text{K}_3[\text{Cr}(\text{C}_2\text{O}_4)_3]$  is

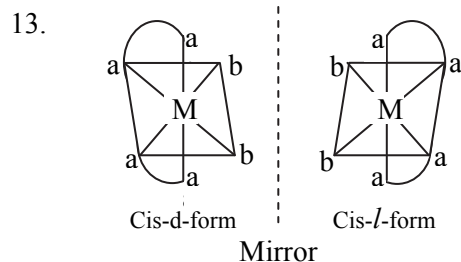
$$x + 3(-2) + 3(+1) = 0 \Rightarrow x = +3$$



8. 2 litre of solution contains 0.02 mol of  $[\text{Co}(\text{NH}_3)_5\text{SO}_4]\text{Br}$  and  $[\text{Co}(\text{NH}_3)_5\text{Br}]\text{SO}_4$  each.  
 $\therefore$  1 litre of solution will contain 0.01 mol of  $[\text{Co}(\text{NH}_3)_5\text{SO}_4]\text{Br}$  and  $[\text{Co}(\text{NH}_3)_5\text{Br}]\text{SO}_4$  each.



- $\therefore$  On using one litre solution, we will get 0.01 mole Y and 0.01 mole Z.
10. Nitrite ( $\text{NO}_2^-$ ) is a negative ligand, while hydroxylamine ( $\text{NH}_2\text{OH}$ ) and methylamine ( $\text{CH}_3\text{NH}_2$ ) are neutral molecule. Nitrosylium ( $\text{NO}^+$ ) is the positive ion.
11. The complex  $[\text{Co}(\text{en})_3]\text{Cl}_3$  will dissociate as,  $[\text{Co}(\text{en})_3]\text{Cl}_3 \rightleftharpoons [\text{Co}(\text{en})_3]^{3+} + 3 \text{Cl}^-$   
 The net charge carried by the complex ion is its charge number. Hence the charge number is  $-3$ .  
 Let  $x$  be the oxidation number of Co. 'en' is a neutral ligand with charge 0. So for  $[\text{Co}(\text{en})_3]\text{Cl}_3$ ,  
 $x + 3(0) + 3(-1) = 0$   
 $x = 3$   
 $\therefore$  oxidation number is 3.  
 One 'en' molecule provides 2 pairs of electrons for bonding. Hence three 'en' molecule will provide 6 pairs of electrons for bonding.  
 Hence the coordination number is 6.
12.  $\Delta T_f = i \times K_f \times m = i \times 1.86 \times 0.1$   
 $\therefore 0.372 = 0.186 \times i$   
 $\therefore i = 2$   
 This shows that the complex gives two ions in solution.  
 Thus the formula of the complex is  $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$   
 $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl} \rightleftharpoons [\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+ + \text{Cl}^-$



Trans form of  $\text{M}(\text{aa})_2\text{b}_2$  does not show optical isomerism.

14. The complex  $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$  contains in all three chlorine atoms.  
 Dissociation of  $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$  gives two chloride ions in the solution.  
 $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2 \longrightarrow [\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+} + 2\text{Cl}^-$   
 $\therefore$  fraction of  $\text{Cl}^-$  ion precipitated by  $\text{AgNO}_3$  solution =  $\frac{2}{3}$
15. CO has strong  $\text{M} \longrightarrow \text{L} \pi$  - bonding ability so it can accept electron pairs (thus acting as Lewis acid) from metal ion So, it is a  $\pi$  - acid ligand.
16. The EAN of  $[\text{Co}(\text{NH}_3)_6]^{3+}$ ,  $[\text{Zn}(\text{NH}_3)_4]^{2+}$  and  $[\text{Ni}(\text{CO})_4]$  are 36 each, which is equal to the atomic number of krypton. The EAN of  $[\text{Fe}(\text{CN})_6]^{3-}$  is 35.
17. In linkage isomerism, the ambidentate ligands have two donor atoms, but at a time, only one atom is directly linked to central metal atom of the complex.
20. The magnitude of  $\Delta_o$  (CFSE in octahedral field) will be minimum for  $[\text{CoF}_6]^{3-}$  as  $\text{F}^-$  is the weakest ligand among the other given ligands.



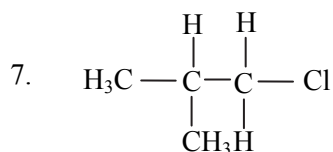
Halogen Derivatives of Alkanes  
and Arenes

## Hints

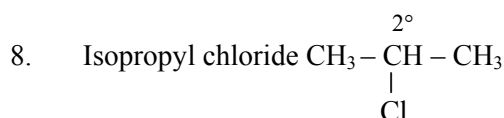


## Classical Thinking

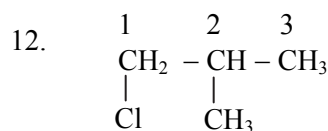
4. Haloforms are trihalogen derivatives of methane. **eg.**  $\text{CHI}_3$ ,  $\text{CHCl}_3$ , etc.
6. Monohalogenes are also called alkyl halides. They can be primary, secondary and tertiary according to the nature of the 'C' atom to which the halogen atom is attached.



In this structure, the chlorine atom is attached to a primary carbon atom (a carbon atom which is further attached to only one carbon atom). Hence, among the given options  $(\text{CH}_3)_2\text{CHCH}_2\text{Cl}$  is the primary alkyl halide.



Chlorine atom is attached to  $2^\circ$  carbon atom as it is attached to two carbon atoms.



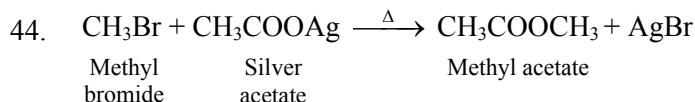
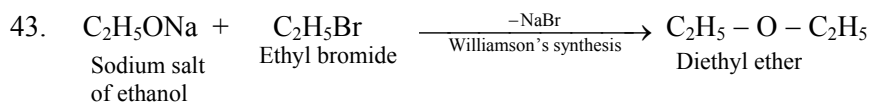
(1-Chloro-2-methylpropane)

13. C-X bonds are being formed by overlap of  $\text{sp}^3$  orbital of carbon atom, with half filled p-orbital of the halogen atom ( $4p_z$  in case of Br)
14. Chlorination of an alkane in direct sunlight can be explosive, it is done only in the presence of diffused sunlight or UV-light or at high temperature.
16. Iodination is a reversible reaction and hydroiodic acid formed during iodination is a strong reducing agent, which reduces alkyl iodide back to alkane. Presence of strong oxidising agent (**eg.**  $\text{HgO}$ ,  $\text{HIO}_3$ ) decomposes hydroiodic acid and prevents the backward reaction.
18. 
$$\text{H}_3\text{C} - \text{CH} = \text{CH} - \text{CH}_3 + \text{HBr} \longrightarrow \text{CH}_3 - \text{CH}_2 - \underset{\text{(A)}}{\text{CHBr}} - \text{CH}_3 \text{ or } \text{CH}_3 - \underset{\text{(B)}}{\text{CHBr}} - \text{CH}_2 - \text{CH}_3$$

Since the alkene is symmetrical, only one product is possible. (A) and (B) both are same products.

19. Reaction being addition reaction by nature, 'A' should possess unsaturation. Since only one molecule of HBr is added, 'A' contains one double bond.  
 $\therefore$  It is an alkene.
21. The bromide atom does not get attached to the carbon atom, with lesser number of H-atoms, in the presence of peroxide as predicted by Markownikoff's rule. This phenomenon is also known as peroxide effect or anti-Markownikoff's rule or Kharasch effect.
22. In presence of peroxide the addition of HBr to an asymmetrical alkene follows the anti-Markownikoff's rule. HCl and HI always add according to Markownikoff's rule.

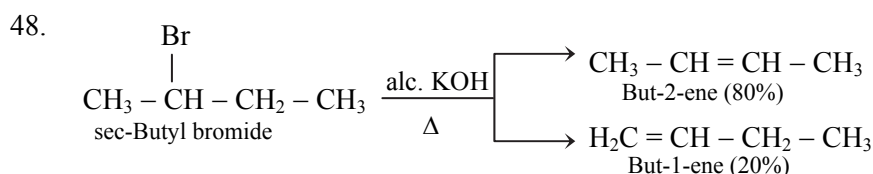
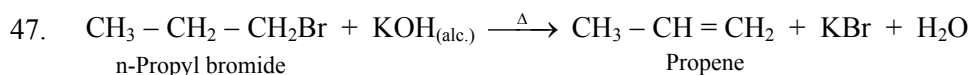




45. Since the reaction involves the removal of one hydrogen and one halide atom, it is an elimination reaction.



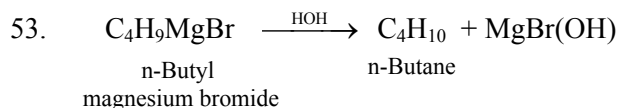
Dehydrohalogenation is a process in which both hydrogen and halogen are removed from a molecule of alkyl halide. ['De' means removal; 'hydro' is for hydrogen and 'halogen' is for halogen groups]



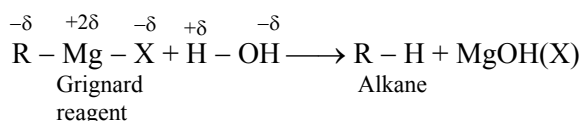
Since two different types of hydrogen atoms are present to the adjacent C atoms of secondary carbon containing Br group, two products are possible.

49. Alkyl iodides have the weakest C – X bond, hence can be broken easily.

51. In an organometallic compound, the metal is directly bonded to any one of the carbon atoms of the chain.



Grignard reagent is very sensitive to moisture. When it comes into contact with water, it is converted to the corresponding alkane.

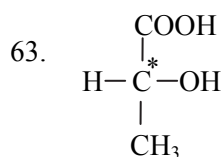


54. From alkyl halides, alkanes can be prepared by Wurtz synthesis, alkenes are prepared by dehydrohalogenation and alcohols are formed by using aqueous alkali.

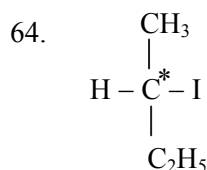
55. A single wavelength means a light of single colour, which is also known as a monochromatic light (Mono = one, chrome = colour).

58. d- and l -forms of an optically active compound differ in their specific rotation. d-form rotates the plane of polarised light to the right and l -form to the left. Both have similar specific gravity, boiling and melting points.

61. Object - Mirror image  
 P                      Q

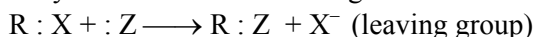


Presence of an asymmetric carbon atom (marked \*) in lactic acid results in optical isomerism.



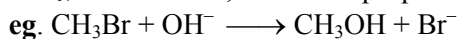
Secondary butyl iodide has one asymmetric carbon atom (marked \*) and is therefore capable of exhibiting enantiomerism.

66. Alkyl halides react with a large number of nucleophilic reagents, both organic and inorganic.



Depending on the nature of alkyl halide, the nucleophilic substitution is either  $\text{S}_{\text{N}}1$  or  $\text{S}_{\text{N}}2$ .

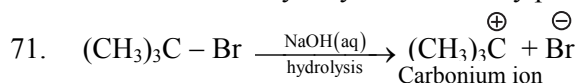
67. In  $\text{S}_{\text{N}}2$  mechanism, the rate is proportional to concentration of the reactants; substrate and reagent.



$$\text{Rate} = k[\text{CH}_3\text{Br}]^1 [\text{OH}]^1 \text{ (order} = 1 + 1 = 2\text{)}$$

The reaction is said to follow second order kinetics, since rate is dependent on the concentration of two substances and sum of powers to which concentration terms are raised is 2.

70. Primary alkyl halides readily undergo  $\text{S}_{\text{N}}2$  reaction. Of the other three, one is tertiary alkyl halide form and two are secondary alkyl halides. They preferably undergo  $\text{S}_{\text{N}}1$  reaction by forming carbocation.

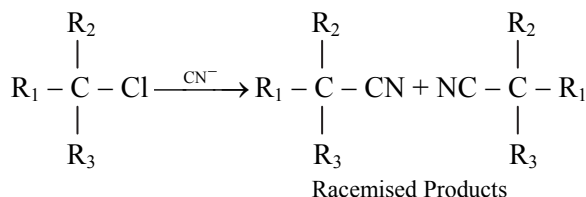


72. In  $\text{S}_{\text{N}}1$  reaction, the incoming nucleophile can attack from the back and front sides because it is a 2 step process; in 1<sup>st</sup> step carbocation is formed and in 2<sup>nd</sup> step nucleophile attacks, for which both sides are available for attack. Hence, there is inversion as well as retention of configuration.

73. Reactivity is directly related to the rates of formation of carbocations. Rate of formation of carbocation is  $3^\circ > 2^\circ > 1^\circ > \text{CH}_3$ . Greater the number of alkyl groups, the more stable the carbocation. This is due to the (+ I) inductive effect of the alkyl group.

74. As alkyl groups show + I effect, the formation of carbonium ion is easier.  $\text{S}_{\text{N}}1$  reaction proceeds via carbonium ion intermediate. Hence, it is favoured by polar solvents and bulky groups on the reaction centre.

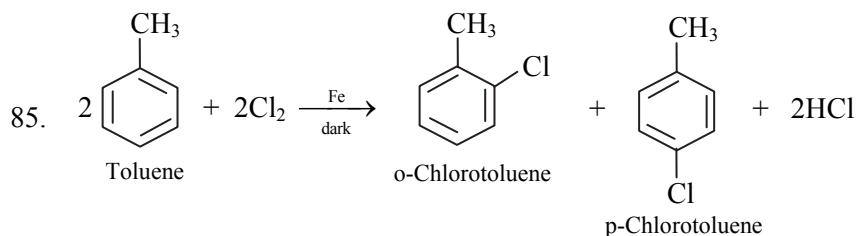
75. When an optically active halide follows  $\text{S}_{\text{N}}1$  mechanism, partially racemised products are formed.

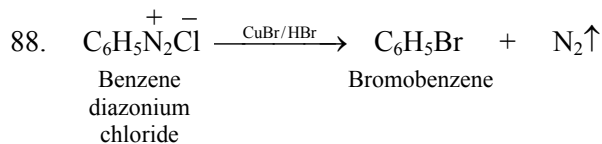
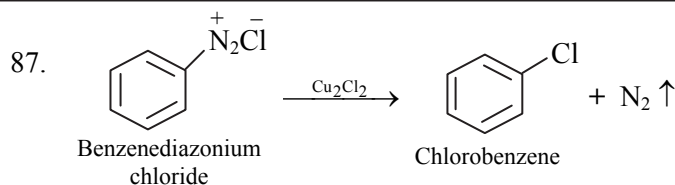


$3^\circ$  halides are more susceptible to  $\text{S}_{\text{N}}1$  mechanism.

82. In Chlorobenzene, C – Cl bond acquires a partial double bond character because of resonance, hence becomes slightly shorter as well as stronger than C – Cl bond in methyl chloride.

83. Due to double bond character of C – X bond in aryl halide, the C – X bond is shorter and stronger. But in structure (D) the Cl is attached to benzyl group, hence weaker.



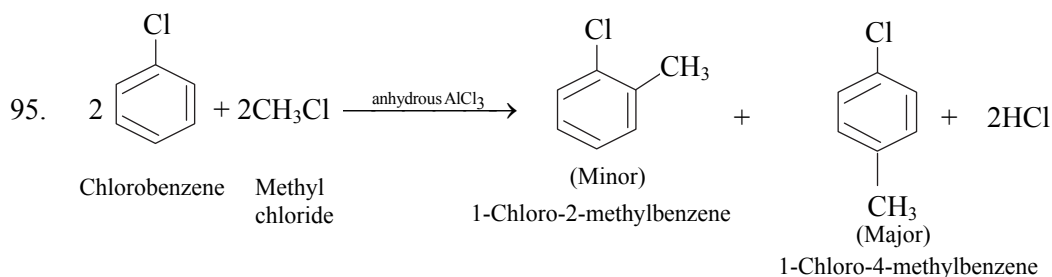
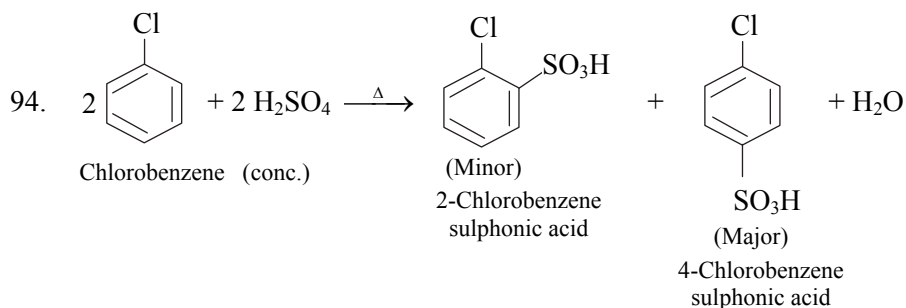


89. The shorter bond length and its strength due to sp<sup>2</sup>-hybridization, needs more energy to be broken, Hence, lower is the reactivity of aryl halides towards nucleophilic substitution compared to alkyl halides.

91. Inductive effect depends upon the tendency of a substituent to release or withdraw electrons from the shared pair. The effect in which atoms or groups have electron donating tendency is called positive inductive effect or + I effect (eg. Alkyl groups.)

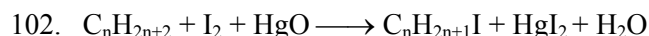
92. Bonding in which a bonding pair of electron is spread over a number of atoms, rather than localised over a definite bond is known as delocalized bonding. Hence, resonance is a situation where more than one structure is written for a species and true structure cannot be written at all.

93. Chlorobenzene when heated with nitrating mixture (conc. H<sub>2</sub>SO<sub>4</sub> + conc. HNO<sub>3</sub>) yields both ortho and para chloronitrobenzene, with para derivative as the major product.

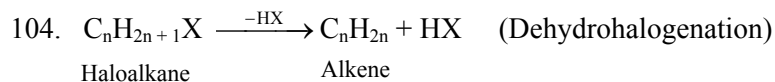
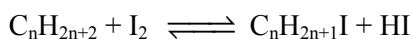


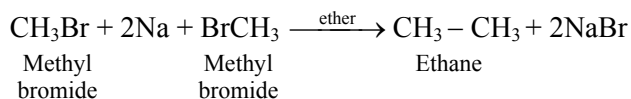
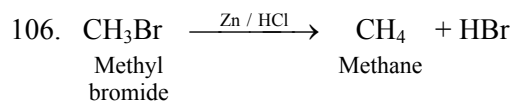
96. The above reaction is known as Wurtz-Fittig reaction.

97. The product is diphenyl, formed by Wurtz-Fittig reaction.

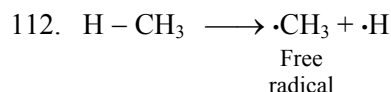


The presence of HgO takes the reaction in forward direction. Otherwise the reaction becomes reversible due to formation of HI which is a good reducing agent.





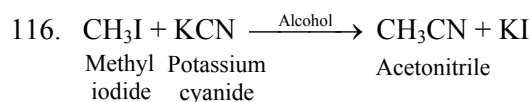
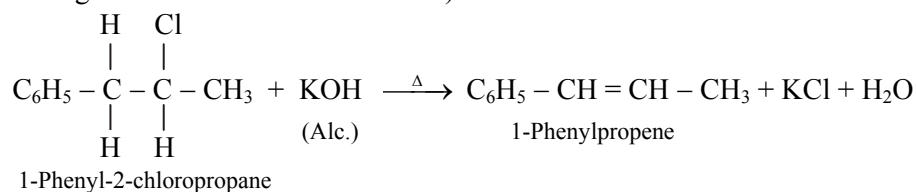
108. They are position isomers as both have the same molecular formula and only differ by the position of the halide group, which act as a functional group here.



113. Nucleophiles are electron rich groups capable of donating electrons to electron deficient centres. All the mentioned groups are capable of donating electrons.

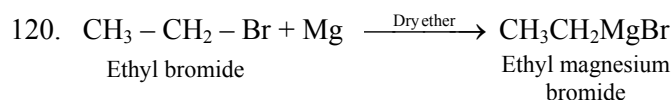
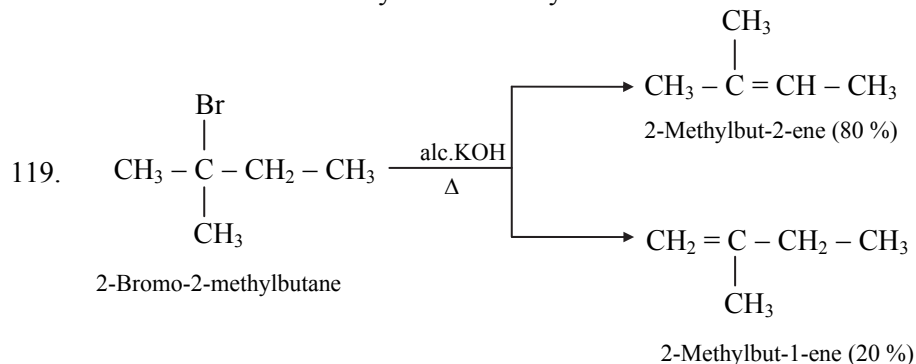
114. For inductive effect to be operational, there should be a difference in electronegativity between the participating atoms and  $\text{F}_2$  is a molecule made of atoms of same electronegativity.

115. 1-Phenyl-2-chloropropane, on heating with alcoholic KOH, gives mainly 1-phenylpropene (i.e., the product having more substituted double bond).



117. In Hoffmann's ammonolysis reaction, When excess of ammonia is used, primary amine is obtained as a major product whereas when an alkyl halide is in excess, quaternary ammonium salt is obtained as the major product.

118. Dehydrohalogenation is the removal of hydrogen and halogen altogether from an alkyl halide, and the reaction can be effectively carried out by alcoholic KOH.



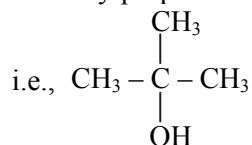
This is the method for preparation of Grignard reagent.





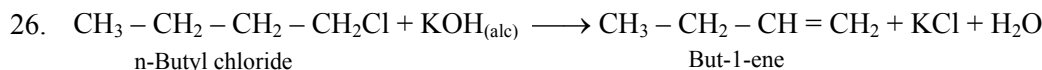
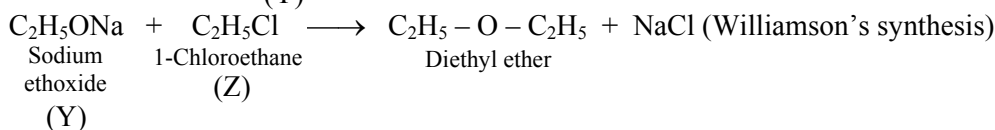
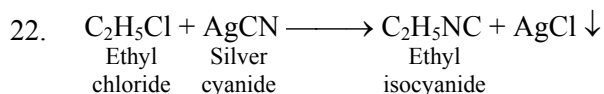
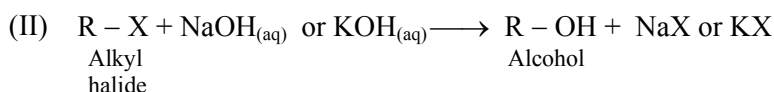
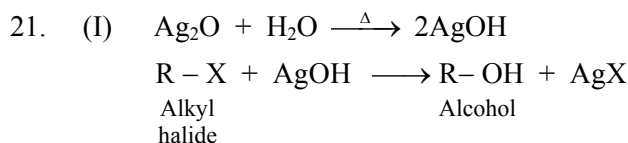
15. The reactivity of alcohols with HBr is in the order  $3^\circ > 2^\circ > 1^\circ$ .

2-Methylpropan-2-ol is a tertiary alcohol.

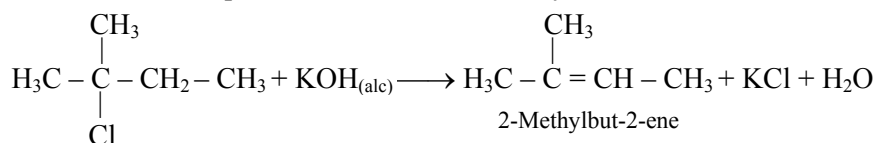


Hence, it reacts fastest with HBr. Propan-1-ol and 2-Methylpropan-1-ol are primary alcohols. Propan-2-ol is a secondary alcohol.

18. With increased branching, surface area decreases, hence, van der Waal's forces of attraction also decreases. As a result boiling point among the isomeric alkyl halides follows the order :-  $1^\circ > 2^\circ > 3^\circ$ .
19. Physical properties depend upon the nature of alkyl chain if the halogen atom is same. For the same halogen, boiling point increases as the molecular weight increases. Hence,  $\text{CH}_3\text{Br}$  has the lowest boiling point.
20. For halogen derivatives of alkanes, as molecular weight increases, the melting point increases.

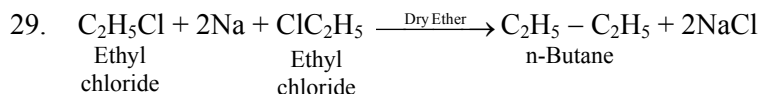
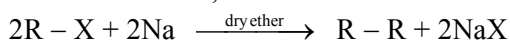


27. Elimination takes place in accordance with Saytzeff's rule.



2-Chloro-2-methylbutane

28. Wurtz reaction is,

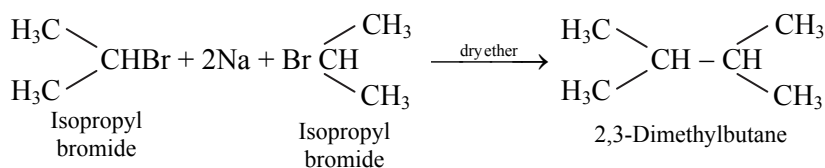
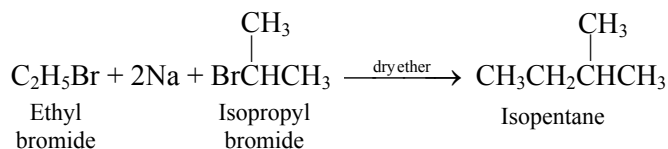
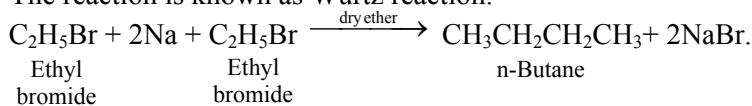






30. The probable reactions are,  
 $\text{CH}_3\text{I} + \text{Na} + \text{CH}_3\text{I} \longrightarrow \text{C}_2\text{H}_6 + \text{NaI}$   
 $\text{CH}_3\text{I} + \text{Na} + \text{C}_2\text{H}_5\text{I} \longrightarrow \text{C}_3\text{H}_8 + \text{NaI}$   
 $\text{C}_2\text{H}_5\text{I} + \text{Na} + \text{C}_2\text{H}_5\text{I} \longrightarrow \text{C}_4\text{H}_{10} + \text{NaI}$

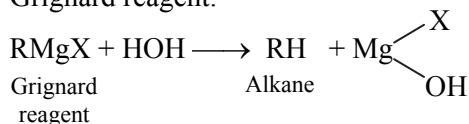
31. The reaction is known as Wurtz reaction.



But n-Hexane cannot be formed.

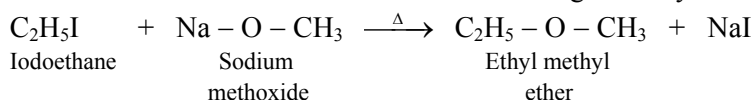
32.  $\text{C}_2\text{H}_5\text{Cl} + \text{LiAlH}_4 \longrightarrow \text{C}_2\text{H}_6$   
Ethane

33. A Grignard reagent is very sensitive to moisture (water vapour) and forms alkane corresponding to R of Grignard reagent.



35. 1.4 L = 1 g  
 22.4 L = 16 g. Hence, gas is methane and  $\text{RMgX}$  is  $\text{CH}_3\text{MgBr}$ , as the gas formed will be  $\text{CH}_4$ .

36. Iodoethane on reaction with sodium methoxide gives ethyl methyl ether.



37. Amount of rotation is directly proportional to the concentration.
38. Racemic mixture is optically inactive due to external compensation.  
 When the enantiomers are mixed together, the rotation caused by one enantiomer is nullified by equal and opposite rotation caused by the other enantiomer. This is known as external compensation.
39. The *d* and *l* forms of a compound are non-superimposable mirror image of each other. Such pairs are known as enantiomers or enantiomorphs or optical anti-podes. They have the same chemical properties though they have different rates of reaction. They differ only in the direction of optical rotation.
40. Compound containing asymmetric carbon atom i.e., carbon atom attached to 4 different groups, shows optical isomerism.

41.  $\begin{array}{c} \text{CH}_3 \\ | \\ \text{C}_2\text{H}_5 - \overset{*}{\text{C}} - \text{H} \\ | \\ \text{COOH} \end{array}$                    $\begin{array}{c} \text{CH}_3 \\ | \\ \text{H} - \overset{*}{\text{C}} - \text{C}_2\text{H}_5 \\ | \\ \text{COOH} \end{array}$

All the four groups attached to the carbon atom are different. Hence, it is asymmetric and it can exist in two enantiomeric forms.



42. (A)  $\begin{array}{c} \text{Cl} \\ | \\ \text{H}_3\text{C} - \text{C}^* - \text{CH}_2\text{Cl} \\ | \\ \text{H} \end{array}$  (\* Asymmetric carbon, optically active)
- (B)  $\begin{array}{c} \text{Cl} \\ | \\ \text{H}_3\text{C} - \text{CH}_2 - \text{C} - \text{Cl} \\ | \\ \text{H} \end{array}$  (No asymmetric carbon, optically inactive)
- (C)  $\begin{array}{c} \text{Cl} \\ | \\ \text{H}_3\text{C} - \text{C} - \text{CH}_3 \\ | \\ \text{Cl} \end{array}$  (No asymmetric carbon, optically inactive)
- (D)  $\begin{array}{c} \text{Cl} \qquad \text{Cl} \\ | \qquad \quad | \\ \text{H}_2\text{C} - \text{CH}_2 - \text{CH}_2 \end{array}$  (No asymmetric carbon, optically inactive)

46. A nucleophile is rich in electrons and hence can also be termed as a Lewis base. A Lewis acid is a species, which is deficient in electrons and is an electron acceptor. A Lewis base is an electron rich species and is an electron donor.

47. Nucleophilic reagents are nucleus loving and electron rich species. As they donate lone pair of electrons they act as Lewis bases.

49. Alkaline hydrolysis of 1-Bromopropane takes place according to  $S_N2$  mechanism. Rate is given by,

$$\text{Rate} \left( \frac{-dc}{dt} \right) = k[\text{C}_3\text{H}_7\text{Br}]^1 [\text{OH}^-]^1$$

From the above rate expression, if we double the concentration of any one of the reactant (i.e. either alkyl halide or alkali), the rate will be doubled.

50. The given product is laevo rotatory due to 100% inversion.

51. Alkaline hydrolysis of tertiary alkyl halide follows  $S_N1$  mechanism. It involves two steps (i) formation of carbonium ion and (ii) attack of nucleophile resulting in the formation of the product.

52. Alkaline hydrolysis of tert-butyl bromide follows  $S_N1$  mechanism.

$$\text{Rate} = k [(\text{CH}_3)_3\text{C} - \text{Br}]$$

The presence of methyl groups restricts the entry of the nucleophile from the rear side. Hence, the alkyl halide first undergoes heterolysis, which is a slow process. The heterolysis produces a carbocation, which is immediately attacked by the new nucleophile. Hence, in the slowest step of the reaction only one molecule is involved and therefore rate is dependent only on its concentration.

53. In  $S_N1$  reaction,  $\Delta H$  is negative, order of reactivity of alkyl halide is  $3^\circ > 2^\circ > 1^\circ$  and polar solvents are favoured.

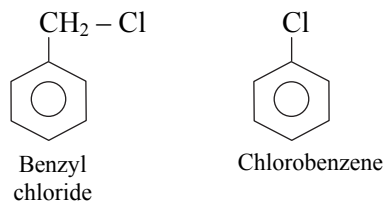
54. In  $S_N1$  mechanism, formation of carbonium ion is rate determining step. So, increase in concentration of nucleophilic reagent will not affect the rate of reaction. Thus, rate depends only on the substrate.

55. Hydrolysis of tertiary halide will take place by  $S_N1$  mechanism where formation of carbonium ion is the rate determining step of the reaction. Carbonium ion is  $sp^2$ - hybridized. It is unimolecular as the rate of reaction depends upon the concentration of substrate and not the attacking nucleophile.

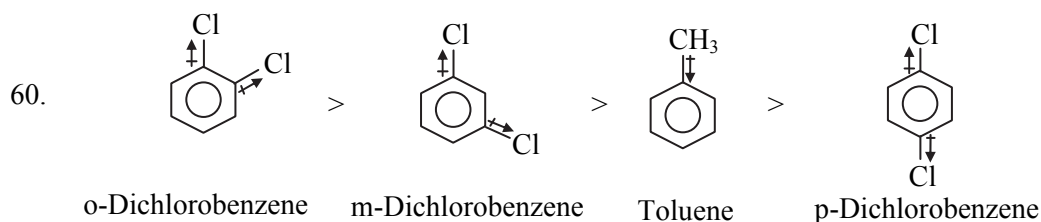
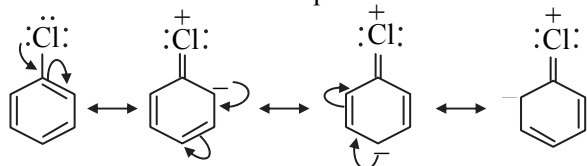
56. After  $S_N1$  reaction, 50% retention, 50% inversion, results in a racemic mixture.



59. Chlorobenzene is less reactive than benzyl chloride.

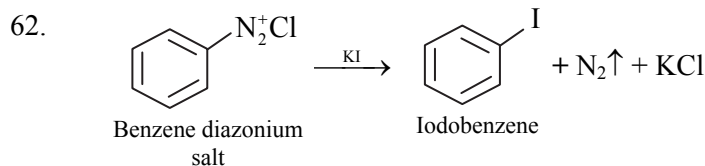


In Chlorobenzene, the lone pairs present on Cl-atom get involved in resonance with  $\pi$  electrons of benzene due to which C – Cl bond acquires double bond character. Hence, reactivity decreases.



Dipole moments are vector quantities which add up to give net dipole moment.

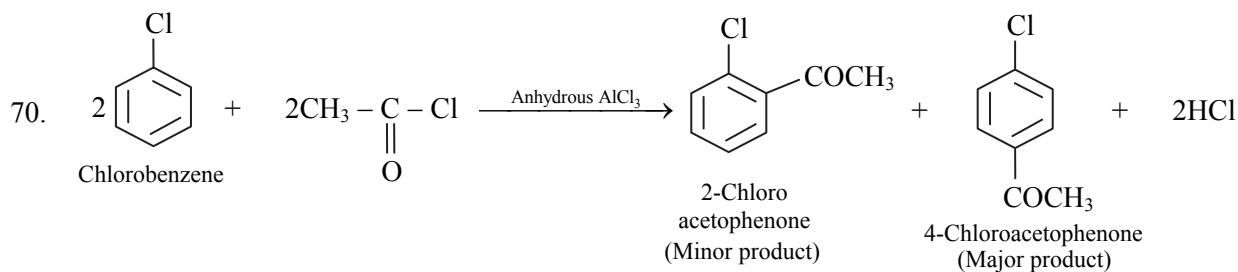
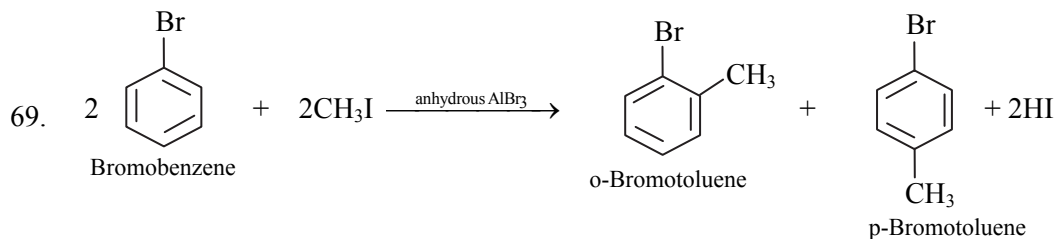
61. Fluoro compounds cannot be prepared by direct halogenation of benzene as fluorine is highly reactive.



63. Any atom or a group if attracts electrons more strongly than hydrogen, it is said to have – I effect.  
(eg. : –  $\text{NO}_2$ , –  $\text{Cl}_2$ , – Br, – I)

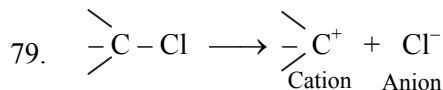
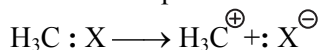
64. – I effect is due to affinity for electrons. This is shown by electronegative atoms or groups having electronegative atoms.

66. It has been found that presence of electron withdrawing groups like –  $\text{NO}_2$ , –  $\text{COOH}$ , –  $\text{CN}$  at o – and/or p – position with respect to halogen atom greatly activates haloarenes to undergo nucleophilic displacement reactions.





72. DDT is not readily metabolized.
76. Nucleophiles are electron rich reagents which attack positively charged carbocations (electrophiles), whereas electrophiles are electron loving species and attack negatively charged species.
77. The hydrogen atom replacing  $\text{Br}^-$  is not a nucleophile.
78. In heterolytic fission, the bonding pair of electrons goes to a single atom or group and thus electrically charged ions are formed. Charged species which accept electrons are electrophiles and which donate electrons are nucleophiles.

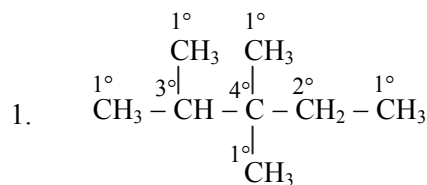


During heterolytic fission, asymmetrical breaking of covalent bond takes place where formation of positive and negative ions occurs.

80. Alkaline hydrolysis of tert-Butyl bromide follows  $\text{S}_{\text{N}}1$  mechanism.
- $\therefore$  Rate of reaction  $\propto [(\text{CH}_3)_3\text{C} - \text{Br}]$
- $\therefore$  Rate is doubled if the concentration of alkyl halide is doubled.



### Competitive Thinking



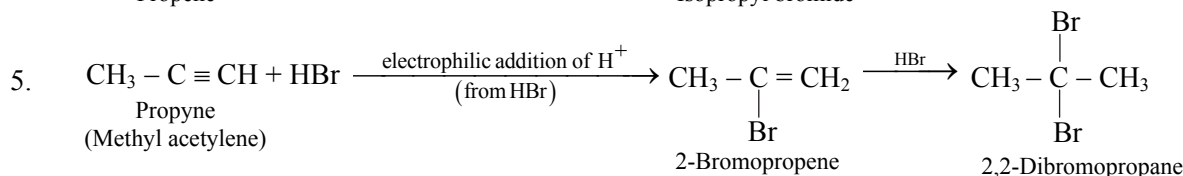
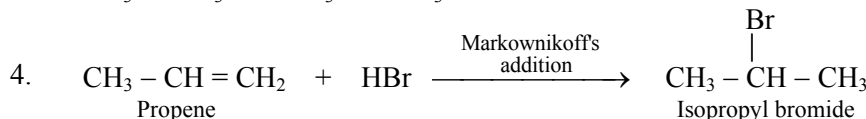
2,3,3-Trimethylpentane

2.  $\text{CH}_3\text{F} > \text{CH}_3\text{Cl} > \text{CH}_3\text{Br} > \text{CH}_3\text{I}$   
The  $\text{sp}^3$  orbital of carbon cannot penetrate into larger p-orbitals ( $3^{\text{rd}}$ ,  $4^{\text{th}}$ ,  $5^{\text{th}}$  orbitals) sufficiently to form strong bonds. Hence, C-F bond will be the strongest and C-I the weakest.

3.

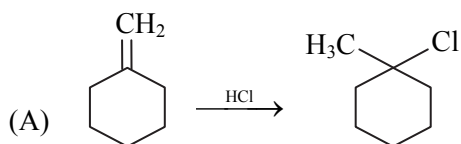
Halomethane	C-X Bond Enthalpy (kJ/mol)
$\text{CH}_3 - \text{F}$	452
$\text{CH}_3 - \text{Cl}$	351
$\text{CH}_3 - \text{Br}$	293
$\text{CH}_3 - \text{I}$	234

Thus, the C-X bond energy (bond enthalpy) increases in the order:  
 $\text{CH}_3\text{I} < \text{CH}_3\text{Br} < \text{CH}_3\text{Cl} < \text{CH}_3\text{F}$

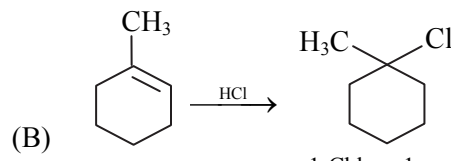




7. According to Markownikoff's rule, when an unsymmetrical reagent (like HCl) adds to an unsymmetrical alkene, the negative part of the reagent gets attached to that unsaturated carbon atom which carries lesser number of hydrogen atoms.

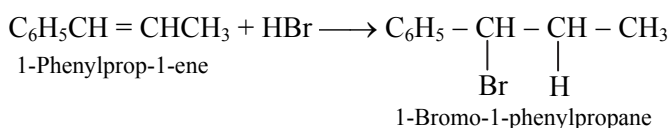


1-Chloro-1-methylcyclohexane



1-Chloro-1-methylcyclohexane

8. Both of the doubly bonded carbon atoms carry equal number of hydrogen atoms. However, benzyl carbocation is more stable than 2° alkyl carbocation, hence option (A) is the correct answer.

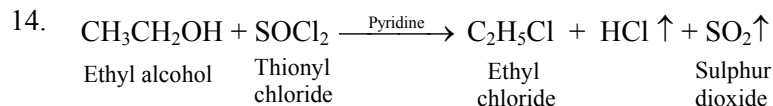
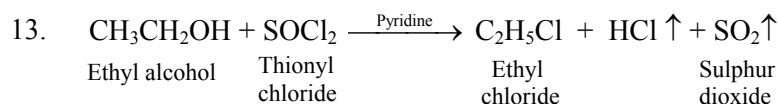


10. Peroxide effect is shown by unsymmetrical alkenes like  $\text{CH}_2=\text{CH}-\text{CH}_3$ .

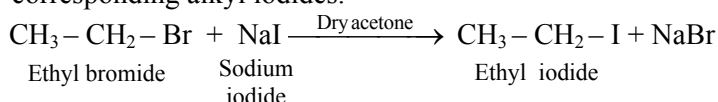


Reactivity order of alcohols for a particular halogen acid is  $3^\circ > 2^\circ > 1^\circ$

12. Reactivity order of halogen acids with a particular alcohol is  $\text{H}-\text{I} > \text{H}-\text{Br} > \text{H}-\text{Cl} > \text{H}-\text{F}$



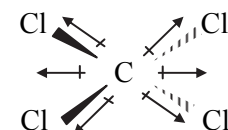
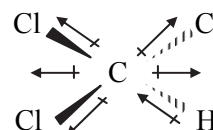
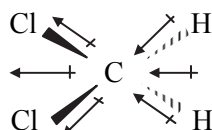
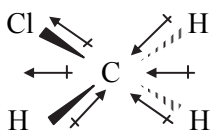
15. In Finkelstein reaction, alkyl chlorides or bromides are treated with sodium iodide in dry acetone to give corresponding alkyl iodides.



17. Preparation of alkyl fluorides by heating alkyl bromides or chlorides in the presence of metallic fluorides is known as Swarts reaction. Hence, among the given options, (C) is Swarts reaction.

18. Higher members of alkyl halides are liquids or solids.  $\text{CH}_3\text{F}$ ,  $\text{CH}_3\text{Cl}$ ,  $\text{CH}_3\text{Br}$  and  $\text{C}_2\text{H}_5\text{Cl}$  are gases at room temperature.  $\text{CH}_3\text{I}$  is a liquid at room temperature and solidifies at  $-66.5^\circ\text{C}$ .

19. The three dimensional structure of the given compounds along with the direction of dipole moment in each of their bonds is given below:



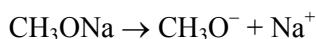
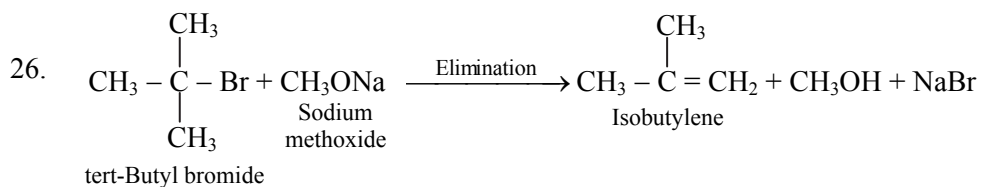
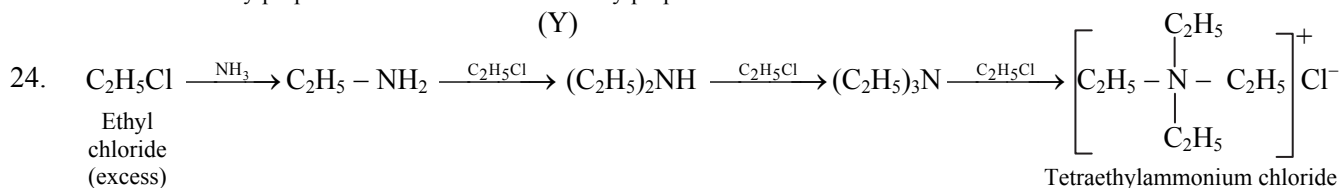
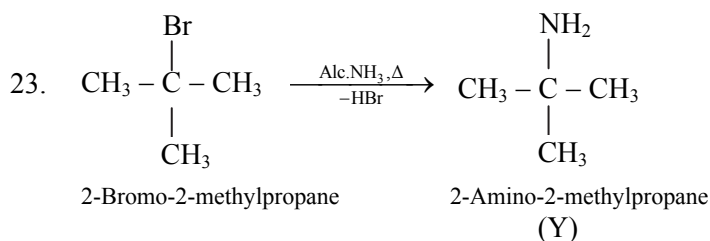
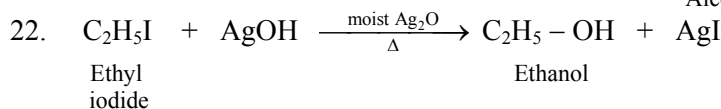
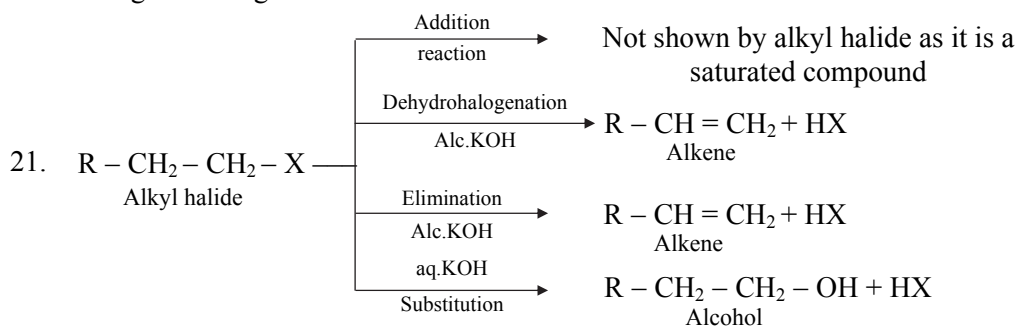
In  $\text{CH}_2\text{Cl}_2$ , the resultant of two C-Cl dipole moments is reinforced by resultant of two C-H dipoles. Therefore,  $\text{CH}_2\text{Cl}_2$  has a dipole moment higher than that in the other given options.



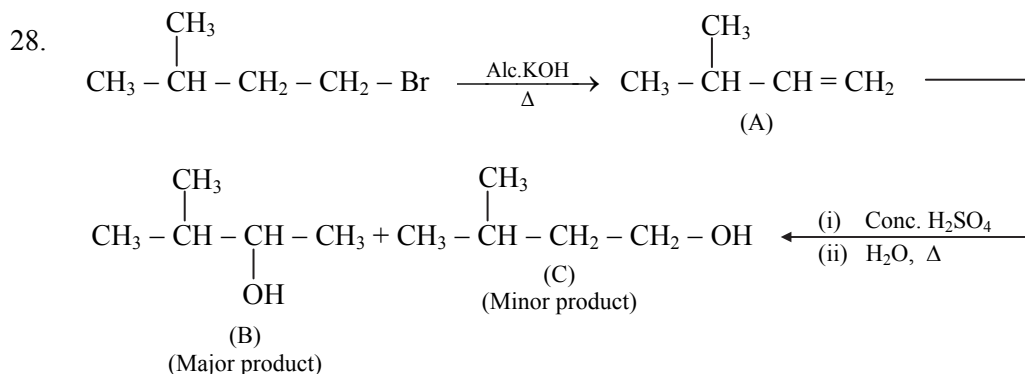
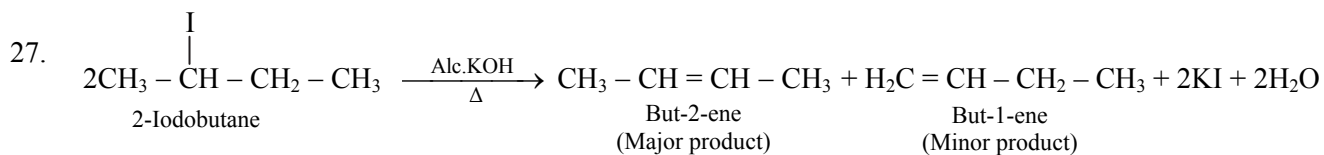
20. Order of reactivity:

For given alkyl group:  $R - I > R - Br > R - Cl$

For given halogen atom:  $3^\circ > 2^\circ > 1^\circ$



Methoxide ion ( $CH_3O^{-}$ ) is a strong base, therefore it abstracts proton from  $3^\circ$  alkyl halide and favours elimination reaction.



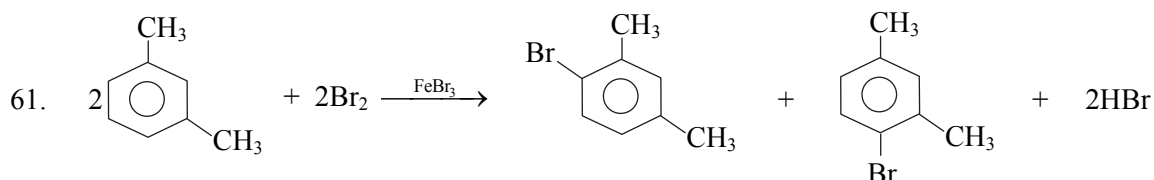
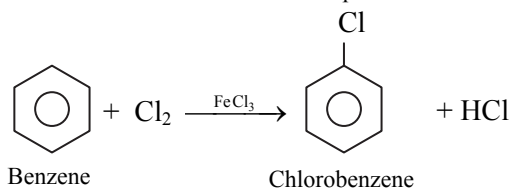
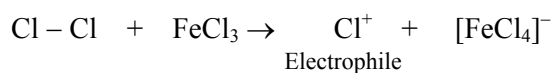




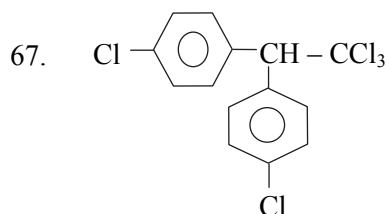




60. Arenes undergo electrophilic substitution reaction.



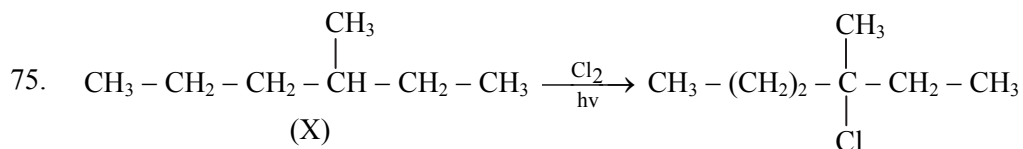
64. Vapours of carbon tetrachloride ( $\text{CCl}_4$ ) are non-inflammable (i.e., do not catch fire). Hence, it is used as fire extinguishers under the name pyrene.



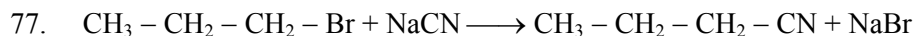
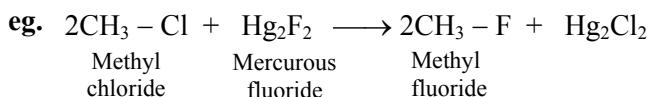
DDT (Dichlorodiphenyltrichloroethane)

68. Chlorofluorocarbon is used in air-conditioning and in domestic refrigerators for cooling purposes. The main drawback of CFC is ozone depletion.

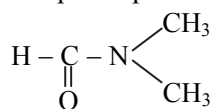
74. The compounds in which the metal atom is directly bonded to the carbon atom are known as organometallic compounds. In  $\text{CH}_3\text{ONa}$  and  $\text{C}_2\text{H}_5\text{SNa}$ , the sodium atom is not directly bonded to the carbon atom. However, in  $\text{CH}_3\text{MgI}$ , the magnesium atom is directly bonded to the carbon atom. Hence,  $\text{CH}_3\text{MgI}$  is an organometallic compound.



76. Alkyl fluorides can be prepared by the action of mercurous fluoride ( $\text{Hg}_2\text{F}_2$ ), silver fluoride ( $\text{AgF}$ ), cobalt fluoride ( $\text{CoF}_3$ ) or antimony trifluoride  $\text{SbF}_3$  on alkyl chloride or bromide. This reaction is known as "Swarts Reaction".



This is  $\text{S}_{\text{N}}2$  reaction for which polar aprotic solvent is suitable for faster rate of reaction. Among the given options, DMF is a polar aprotic solvent, which is polar enough to dissolve the substrate and nucleophile but do not participate in hydrogen bonding with the nucleophile.

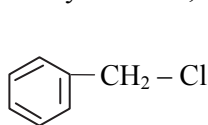


N,N-Dimethylformamide

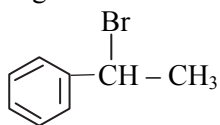
78. Chlorination of ethane is carried out in the presence of ultraviolet light or diffused sunlight or at high temperature.



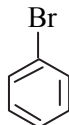
79. In allylic halide, the halogen atom is attached to  $sp^3$  carbon atom next to a carbon-carbon double bond.



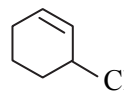
Benzyl chloride



(1-Bromoethyl)benzene



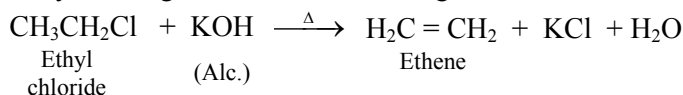
1-Bromobenzene



3-Chlorocyclohex-1-ene

Among the given options, 3-chlorocyclohex-1-ene is an allylic halide.

81. Dehydrohalogenation of  $\text{CH}_3\text{CH}_2\text{Cl}$  gives ethene as the main product.



Molar mass of  $\text{CH}_3\text{CH}_2\text{Cl}$  = 64.5 g/mol and Molar mass of ethene ( $\text{C}_2\text{H}_4$ ) = 28 g/mol

$$\therefore \text{Number of moles of } \text{CH}_3\text{CH}_2\text{Cl} = \frac{6.45 \text{ g}}{64.5 \text{ g/mol}} = 0.1 \text{ mol}$$

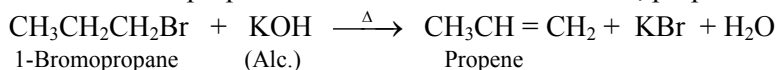
0.1 mol of  $\text{CH}_3\text{CH}_2\text{Cl}$  will give 0.1 mol of ethene.

However, only 50% of the reagent is used. So, only 50% of product will be formed, i.e., 0.05 mol of ethene.

$$\therefore \text{Weight of main product (ethene) obtained} = 0.05 \text{ mol} \times 28 \text{ g/mol} = 1.4 \text{ g}$$

82. The reaction of but-1-ene with HBr gives 2-bromobutane as the major product as the reaction proceeds according to Markownikoff's rule.

83. When 1-bromopropane is heated with alcoholic KOH, propene is obtained.



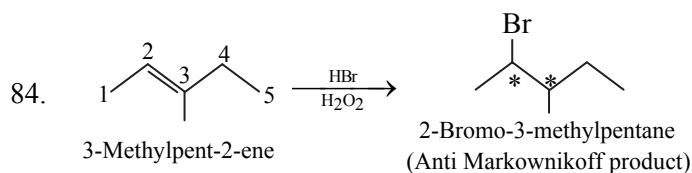
Molar mass of  $\text{CH}_3\text{CH}_2\text{CH}_2\text{Br}$  = 123 g/mol and Molar mass of propene ( $\text{CH}_3\text{CH}=\text{CH}_2$ ) = 42 g/mol

$$\therefore \text{Number of moles of } \text{CH}_3\text{CH}_2\text{CH}_2\text{Br} = \frac{12.3 \text{ g}}{123 \text{ g/mol}} = 0.1 \text{ mol}$$

0.1 mol of  $\text{CH}_3\text{CH}_2\text{CH}_2\text{Br}$  will give 0.1 mol of propene.

$$\therefore \text{Mass of propene obtained will be } 0.1 \times 42 = 4.2 \text{ g} \quad \text{However, yield obtained is 50\%}$$

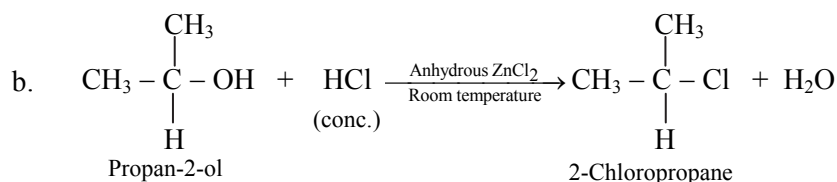
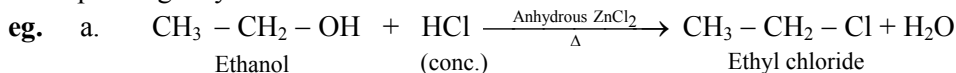
$$\therefore \text{Mass of propene obtained} = 4.2 \times \frac{50}{100} = 2.1 \text{ g}$$



Four stereoisomers are possible due to the presence of 2 chiral centres in the addition product.

85. Grignard's reagent is an example for organometallic compound having sigma bond while ferrocene, cobaltocene and ruthenocene are organometallic  $\pi$  complexes.

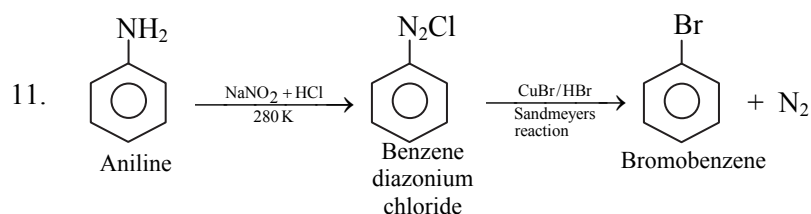
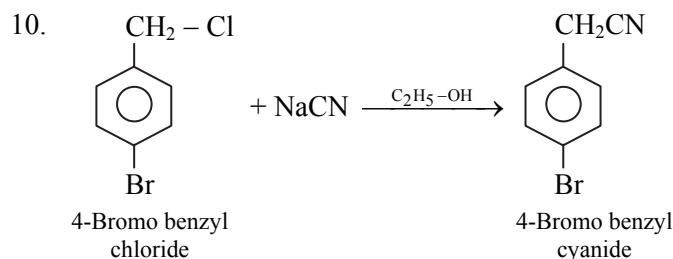
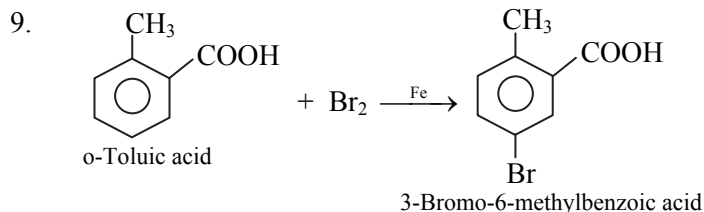
86. i. Primary and secondary alcohols react with concentrated HCl and anhydrous  $\text{ZnCl}_2$  to give the corresponding alkyl chlorides.



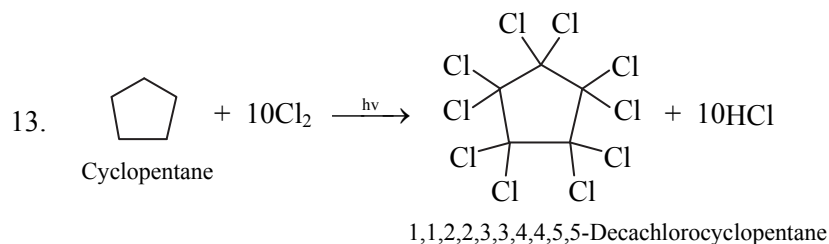




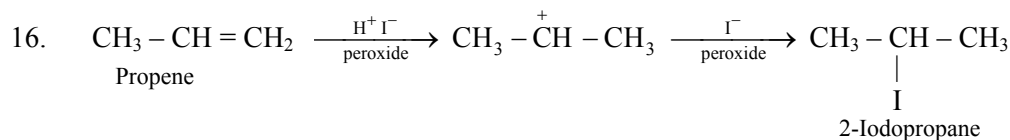
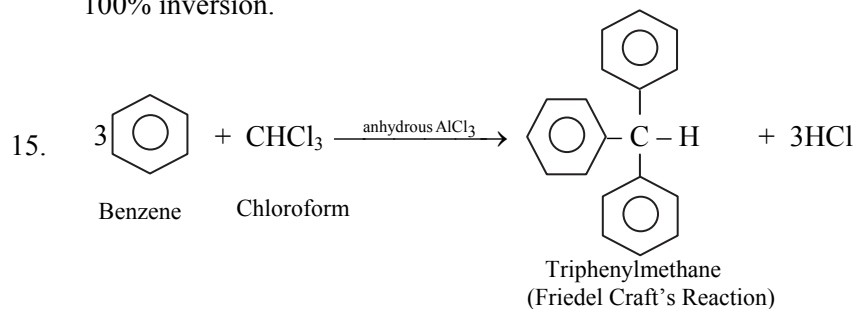
8. Presence of electron withdrawing group ( $\text{NO}_2$ ) facilitates the benzene ring towards nucleophilic substitution reaction.



12. Due to o- and p-directing - Cl group, all the products given in the option (A), (B) and (C) will be formed.



14.  $\text{CH}_3 - \underset{\text{Cl}}{\text{CH}} - \text{CH}_2 - \text{CH}_3$  (2-Chlorobutane) optically active compound undergoes  $\text{SN}^2$  mechanism with 100% inversion.



17. Primary alkyl halides undergo  $\text{SN}^2$  reaction which involves the complete stereochemical inversion.



18. 
$$\text{CH}_3 - \text{CH}_2 - \underset{\text{CH}_3}{\text{CH}} - \text{CH}_2\text{Cl} \xrightarrow[\text{peroxide}]{\text{C}_2\text{H}_5\text{ONa}/\text{C}_2\text{H}_5\text{OH}} \text{CH}_3 - \text{CH}_2 - \underset{\text{CH}_3}{\text{C}} = \text{CH}_2 \xrightarrow{\text{H}_2/\text{Catalyst}} \text{CH}_3 - \text{CH}_2 - \underset{\text{CH}_3}{\text{CH}} - \text{CH}_3$$
  
 1-Chloro-2-methylbutane 2-Methylbutane
19. 
$$\text{C}_6\text{H}_5\text{CH}_2\text{Br} \xrightarrow{\text{Mg, ether}} \text{C}_6\text{H}_5\text{CH}_2\text{MgBr} \xrightarrow{\text{H}_3\text{O}^+} \text{C}_6\text{H}_5\text{CH}_3 + \text{Mg} \begin{matrix} \text{Br} \\ \text{OH} \end{matrix}$$
  
 Benzyl bromide Benzyl magnesium bromide Toluene
20. 
$$2\text{CH}_3(\text{CH}_2)_2 - \underset{\text{I}}{\text{CH}} - \text{CH}_2\text{CH}_3 + 2\text{Na} \xrightarrow{\text{Wurtz reaction}} \text{CH}_3(\text{CH}_2)_2 - \underset{\text{C}_2\text{H}_5}{\text{CH}} - \underset{\text{C}_2\text{H}_5}{\text{CH}} - (\text{CH}_2)_2\text{CH}_3 + 2\text{NaI}$$
  
 3-Iodohexane 4,5-Diethyloctane
21. Freon ( $\text{CCl}_2\text{F}_2$ ), teflon [ $(\text{CF}_2 - \text{CF}_2)_n$ ] and iodoform ( $\text{CHI}_3$ ) are halogen derivatives of alkane. Vinyl chloride ( $\text{CH}_2 = \text{CH} - \text{Cl}$ ) is not a haloalkane.



## Hints



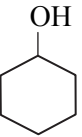
### Classical Thinking

- In alcohols (i.e., hydroxyl derivatives of hydrocarbons), one or more hydrogen atoms are replaced by – OH group.
- Glycols are dihydric alcohols (having two hydroxyl groups). Ethylene glycol is the first member of this series.  

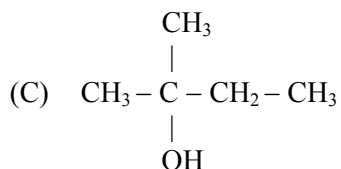
$$\begin{array}{c} \text{CH}_2\text{OH} \\ | \\ \text{CH}_2\text{OH} \end{array}$$
 Ethylene glycol
- $\text{CH}_2 - \underset{\text{OH}}{\text{CH}} - \underset{\text{OH}}{\text{CH}_2}$  Glycerol is trihydric alcohol as it contains three hydroxyl groups.  

$$\begin{array}{ccc} | & | & | \\ \text{OH} & \text{OH} & \text{OH} \end{array}$$
- $1^\circ \text{CH}_2 - \text{OH}$  (one secondary and two primary alcoholic groups.)  

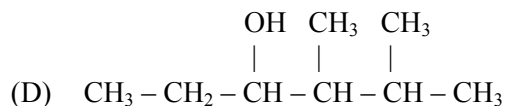
$$\begin{array}{c} | \\ 2^\circ \text{CH} - \text{OH} \\ | \\ 1^\circ \text{CH}_2 - \text{OH} \end{array}$$
- In a primary alcohol (–CH<sub>2</sub>OH), the alcoholic group is attached to the sp<sup>3</sup> hybridized primary carbon atom.
- |  |  |
|--|--|
| (A) $\begin{array}{c} \text{OH} \\   \\ \text{H}_3\text{C} - \text{CH} - \text{CH}_3 \\ \text{Propan-2-ol} \\ \text{(Secondary alcohol)} \end{array}$              | (B) $\begin{array}{c} \text{OH} \\   \\ \text{H}_2\text{C} - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{CH}_3 \\ \text{Pentan-1-ol} \\ \text{(Primary alcohol)} \end{array}$  |
| (C) $\begin{array}{c} \text{OH} \\   \\ \text{H}_3\text{C} - \text{CH} - \text{CH}_2 - \text{CH}_3 \\ \text{Butan-2-ol} \\ \text{(Secondary alcohol)} \end{array}$ | (D) $\begin{array}{c} \text{OH} \quad \text{CH}_3 \quad \text{CH}_3 \\   \quad   \quad   \\ \text{H}_3\text{C} - \text{CH}_2 - \text{CH} - \text{CH} - \text{CH} - \text{CH}_3 \\ \text{4,5-Dimethylhexan-3-ol} \\ \text{(Secondary alcohol)} \end{array}$ |
- Isopropyl alcohol has structural formula  

$$\begin{array}{c} \text{CH}_3 - \underset{\text{CH}_3}{\text{CH}} - \text{OH} \end{array}$$
 The C bearing – OH group is 2° because it is attached to two other carbon atoms.
- 
 Cyclohexanol is a secondary alcohol because (– OH) group is linked to 2° carbon.
- In case of tertiary alcohols, (–OH) group should be attached to tertiary carbon atom.
 

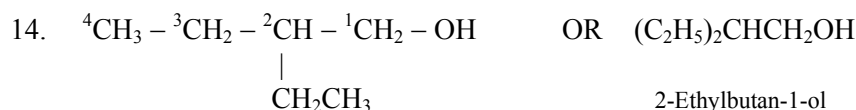
(A) $\begin{array}{c} \text{CH}_3 - \text{CH}_2 - \underset{\text{OH}}{\text{CH}} - \text{CH}_2 - \text{CH}_3 \\ \text{Pentan-3-ol (Secondary alcohol)} \end{array}$	(B) $\begin{array}{c} \text{CH}_2 - \underset{\text{OH}}{\text{CH}} - \underset{\text{OH}}{\text{CH}} - \underset{\text{OH}}{\text{CH}_2} \\ \text{Propane-1,2,3-triol (Trihydric alcohol)} \end{array}$
--	--



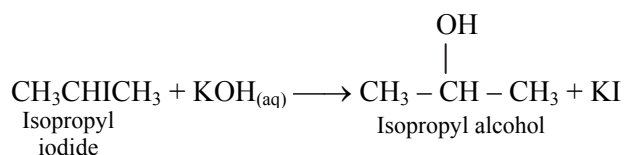
2-Methylbutan-2-ol (Tertiary alcohol)



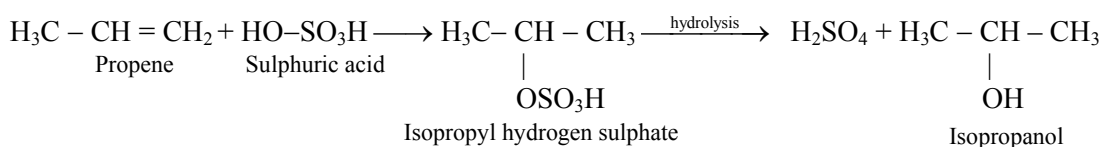
4,5-Dimethylhexan-3-ol (Secondary alcohol)



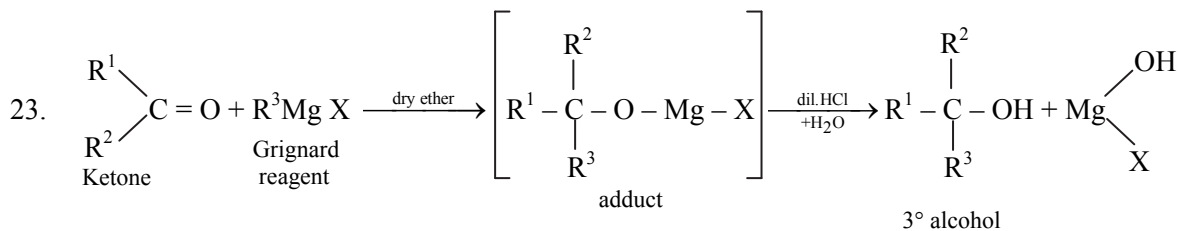
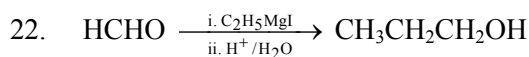
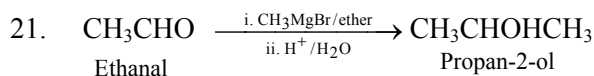
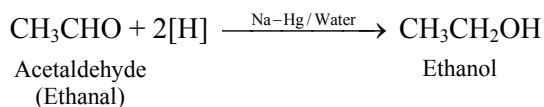
17. An alkyl halide on hydrolysis with aqueous KOH gives an alcohol. A primary alkyl halide is converted to a primary alcohol and a secondary alkyl halide is converted to a secondary alcohol.



18. This process effectively results in the addition of a molecule of water across a double bond. Hence it is a hydration reaction. Alkanes cannot undergo addition reactions.

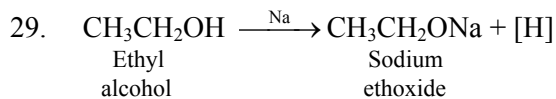
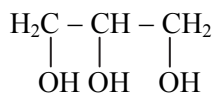


19. Sodium amalgam in water acts as a reducing agent. It reduces  $\text{>C} = \text{O}$  to  $\text{>CHOH}$  i.e., an aldehyde is reduced to a primary alcohol and a ketone is reduced to a secondary alcohol.



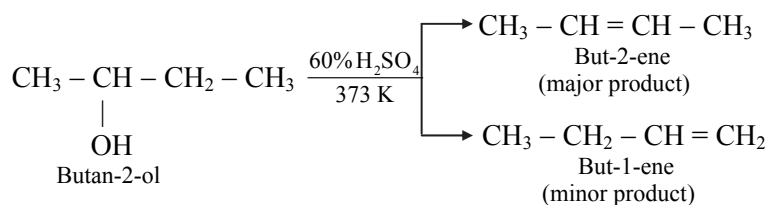
26. The higher member of alcohols are least soluble in water.

27. Glycerol shows greater hydrogen bonding.

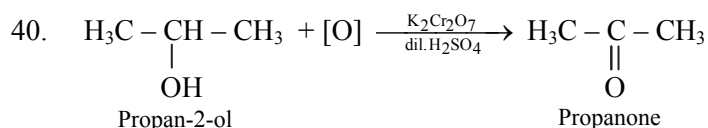
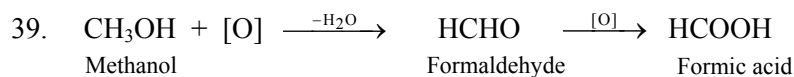
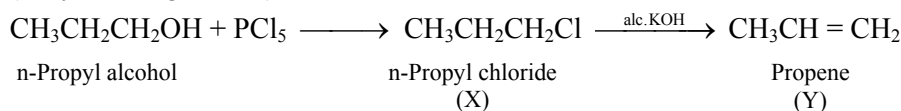




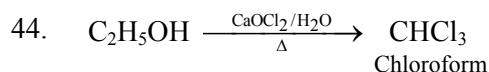
31.  $\text{CH}_3 - \text{OH} + \text{CH}_3 - \text{COCl} \xrightarrow{\text{conc. H}_2\text{SO}_4} \text{CH}_3 - \text{COO} - \text{CH}_3 + \text{HCl}$   
Methyl alcohol Methyl acetate
32. The reaction proceeds by the protonation of the hydroxyl group followed by loss of water to give a carbocation which then reacts with  $\text{X}^-$  to form the alkyl halide. More the acid strength of the halogen acid, greater is the protonating ability. Since the order of strength of halogen acids is  $\text{HI} > \text{HBr} > \text{HCl}$ , the order of reactivity is also the same.
33. Order of reactivity of alcohols towards a given hydrogen halide,  $\text{HX}$  is  $3^\circ > 2^\circ > 1^\circ$ .
34. According to Saytzeff rule, but-2-ene will be the major product.



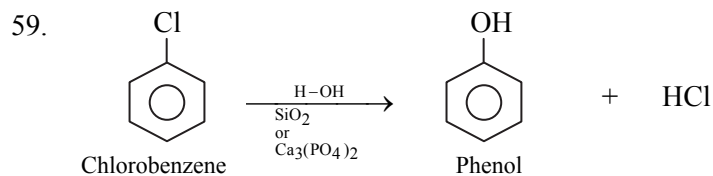
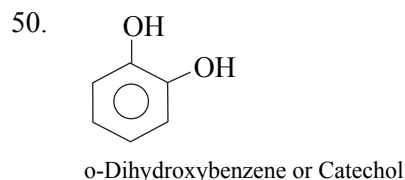
35. The order of ease of dehydration of alcohols is  $3^\circ > 2^\circ > 1^\circ$ .
36.  $\text{H}_3\text{C} - \text{CH}_2 - \text{OH} \xrightarrow{\text{Al}_2\text{O}_3, 623\text{K}} \text{H}_2\text{C} = \text{CH}_2 + \text{H}_2\text{O}$   
Ethanol Ethylene
37. Alcohols are converted to alkyl chlorides by  $\text{PCl}_5$ . Alcoholic  $\text{KOH}$  converts alkyl halides to alkenes (dehydrohalogenation).



41.  $3^\circ$  alcohols undergo oxidation under drastic conditions.
43. As the number of replaceable H atom increases, the ease of oxidation increases.



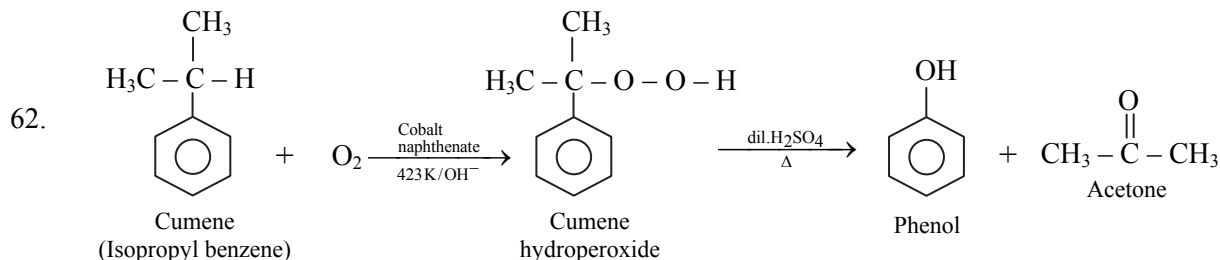
When ethyl alcohol is distilled with moist bleaching powder, chloroform is obtained. It is also used in the manufacture of alcoholic beverages and as a fuel in spirit lamps and stoves.



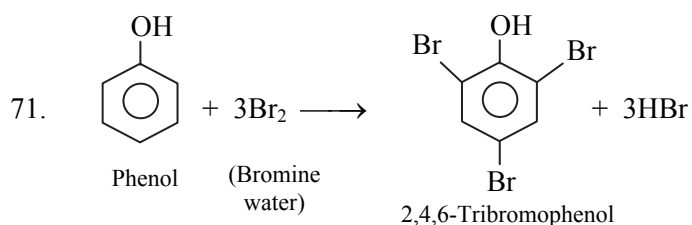
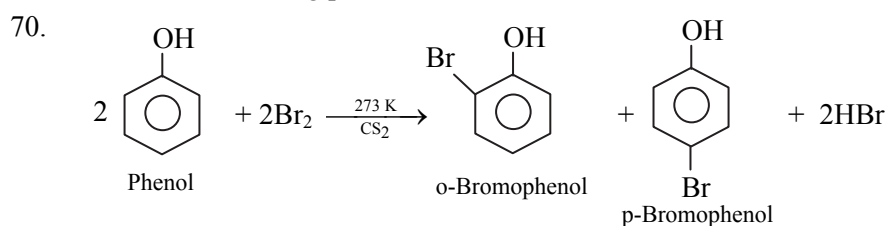




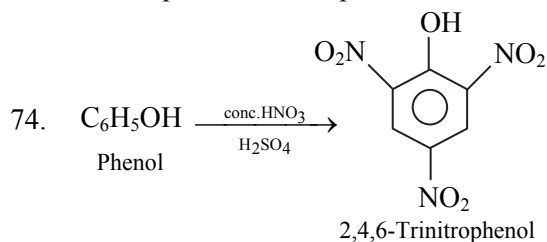
61. Phenol is obtained from cumene by atmospheric oxidation followed by hydrolysis. Cumene itself is prepared from benzene and propene. Both benzene and propene are cheaply available from petroleum sources. Air is abundantly available. Further decomposition is simple and involves converting the alkaline medium to an acidic one. Most importantly acetone is obtained as a valuable by-product which finds use as industrial solvent. All the remaining processes involve high temperature and high pressure making them highly expensive.



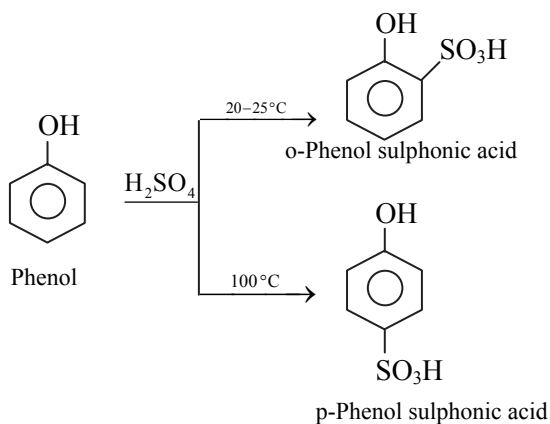
67. Phenol has a boiling point of 455 K.



73. Nitration reaction of phenol is aromatic electrophilic substitution reaction. It involves attack of  $\text{NO}_2^+$ , an electrophile.  $-\text{NO}_2$  replaces H – atoms of phenol ring. Hence it is an electrophilic substitution.

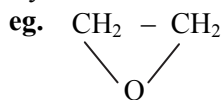


75. Phenol does not react with dilute  $\text{H}_2\text{SO}_4$ . It reacts only with conc.  $\text{H}_2\text{SO}_4$ . The products depend on the temperature at which the reaction is carried out. This reaction takes place at atmospheric pressure.



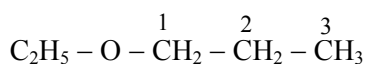


78. Phenol gives violet colour with neutral  $\text{FeCl}_3$  solution, while alcohols do not give violet colour.
82.  $\text{R}-\text{O}-\text{R}'$  Ethers      If  $\text{R} = \text{R}'$ , Simple ether      If  $\text{R} \neq \text{R}'$ , Mixed ether
83. Since  $\text{CH}_3-\text{O}-\text{C}_2\text{H}_5$  contains two alkyl i.e., methyl and ethyl in its chain, so it is Methoxyethane.
87. Cyclic ethers are called epoxides.



Epoxide (Also known as Oxirane, IUPAC name)

88. The general form of the IUPAC name of ether is alkoxyalkane where the alkyl with larger number of carbons is considered as parent.

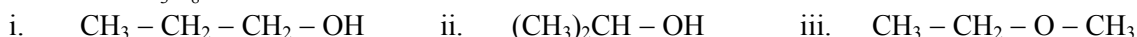


- $\therefore$  1-Ethoxypropane is the IUPAC name.

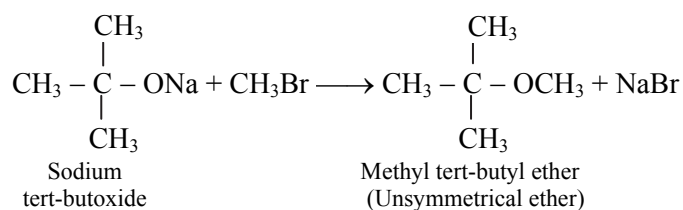


89.  $\begin{array}{c} \text{H}_3\text{C} - \text{O} - \overset{2}{\text{CH}} - \overset{3}{\text{CH}_3} \\ | \\ \text{CH}_3 \end{array}$   
2-Methoxypropane

91. Ethers can be considered as derivatives of water molecule replaced by alkyl groups. Alkyl groups being bulkier than hydrogen atom causes repulsion and slightly increases the bond angle, which becomes slightly greater than tetrahedral angle.
95. Diethyl ether ( $\text{C}_2\text{H}_5-\text{O}-\text{C}_2\text{H}_6$ ) is a metamer of 1-methoxypropane ( $\text{CH}_3-\text{O}-\text{CH}_2-\text{CH}_2-\text{CH}_3$ )
96. Propan-1-ol ( $\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{OH}$ ) and methoxyethane ( $\text{CH}_3-\text{O}-\text{CH}_2-\text{CH}_3$ ) are functional isomers of each other.
97. Isomers of  $\text{C}_3\text{H}_8\text{O}$ :



99.  $\text{CH}_3\text{ONa} + \text{Br}-\text{CH}_3 \longrightarrow \text{CH}_3-\text{O}-\text{CH}_3 + \text{NaBr}$   
Sodium methoxide                      Dimethyl ether (Symmetrical ether)



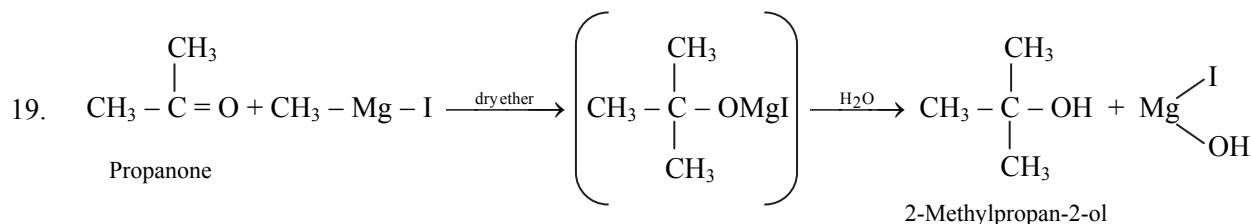
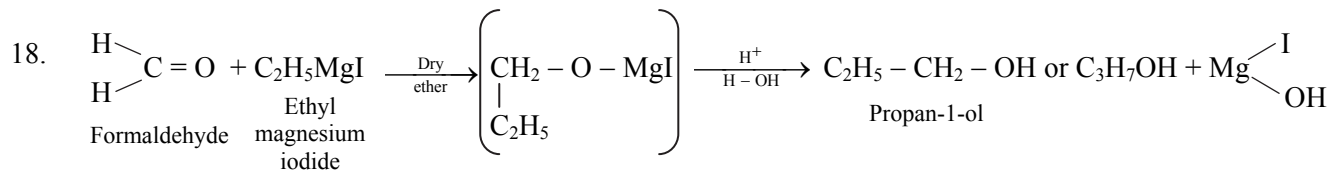
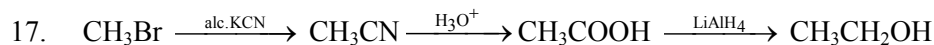
101.  $\begin{array}{c} \text{OH} \\ | \\ \text{C}_6\text{H}_5 \end{array} \xrightarrow{\text{NaOH}} \begin{array}{c} \text{ONa} \\ | \\ \text{C}_6\text{H}_5 \end{array} \xrightarrow{\text{CH}_3\text{I}} \begin{array}{c} \text{OCH}_3 \\ | \\ \text{C}_6\text{H}_5 \end{array} + \text{NaI}$   
Phenol                      Sodium phenoxide                      Anisole

103.  $\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{OH} + \text{CH}_2\text{N}_2 \xrightarrow[\Delta]{\text{HBF}_4} \text{CH}_3-\text{CH}_2-\text{CH}_2-\text{O}-\text{CH}_3 + \text{N}_2\uparrow$   
Propan-1-ol                      Diazomethane                      1-Methoxypropane

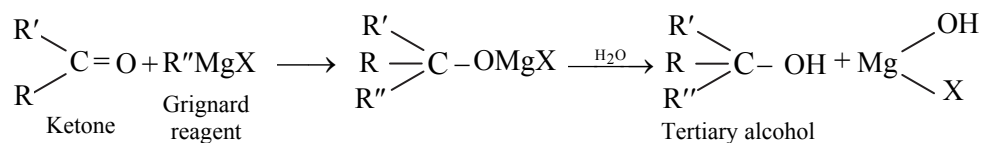
104. Only methyl ethers are obtained by diazomethane method.
105. The O - atom in ether contains two lone pairs of electrons. The diethyl ether is sparingly soluble in water due to H - bonding. Diethyl ether is very inert and a good solvent. Hence it is used as an inert medium to dissolve reactants and carry out reactions. Most of the organic compounds including ethers are inflammable.







20. Ketone gives tertiary alcohol on treatment with Grignard reagent.



21. The oxygen atom carries two lone pairs of electrons. Hence due to repulsion between these lone pairs, the bond angle is slightly less than tetrahedral.

22. As the size of the alkyl group increases, solubility decreases.

24. As compared to alkanes, alcohols have high boiling points. This is because in alcohols, there is inter-molecular H-bonding leading to association of a large number of molecules. Hence the boiling point of n-Pentane (B) is the least. Among isomeric alcohols, boiling point depends upon the molecular structure. Highly branched structures have less efficient packing of molecules which causes the boiling points to decrease. Hence the more branched an alcohol, the lower is its boiling point.

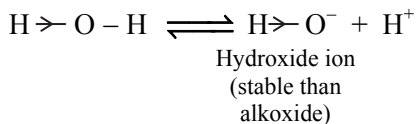
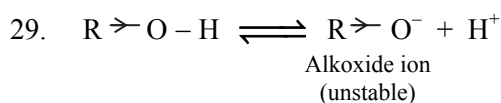
25. Hydrogen bonding is formed only by that hydrogen atom which is attached to electronegative element like F, O, N etc. More the electronegativity of the atom, stronger will be the H-bond. Electronegativity difference between S and H is not much i.e., S(2.5) and H(2.1). Hence hydrogen bond is not formed in between C<sub>2</sub>H<sub>5</sub>SH molecules.

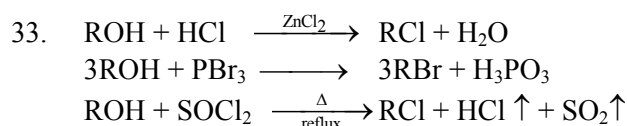
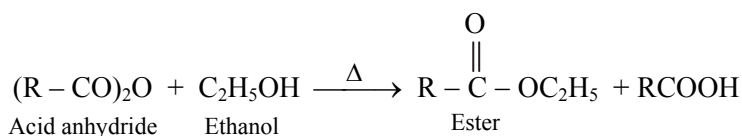
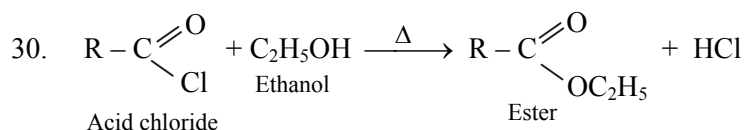
High polarity in -OH group arises due to the high electronegativity difference between oxygen (3.5) and hydrogen (2.1). By H-bonding, molecules of alcohol are associated with one another. To break this association, more energy is required and hence boiling point of ethyl alcohol is higher than that of C<sub>2</sub>H<sub>5</sub>SH.

26. In general, compounds which have stable conjugate base are acidic.

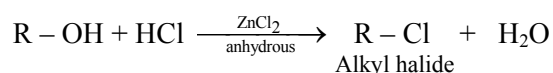
In carboxylic acids, the conjugate base is carboxylate ion, which is stabilized by resonance.

27. Cl ←← CH<sub>2</sub> ←← CH<sub>2</sub> ←← O<sup>-</sup> H<sup>+</sup>; Negative charge on oxygen is dispersed and thus ion is more stable.



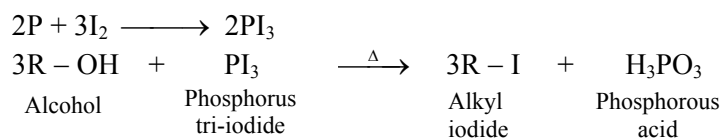


34. Alcohols react with concentrated HCl in presence of  $\text{ZnCl}_2$  (Lucas reagent) to form alkyl halides.

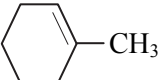


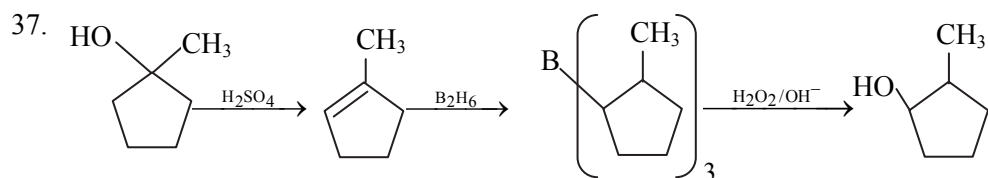
This reaction proceeds through the formation of carbocation. More stable the carbocation greater is the order of reactivity. Benzyl alcohol forms the benzyl cation which is stabilised by resonance. The presence of electronegative F in the chain destabilizes the carbocation. Closer the electronegative atom to the carbon with positive charge, more unstable the carbocation. Hence stability of cation formed is in the order, (iv) > (iii) > (ii) > (i).

35. Alcohols react with phosphorus tri-iodide ( $\text{PI}_3$ ) to yield alkyl iodide.



36. In the reaction carbocation formed is primary, which gets converted to tertiary which is more stable,

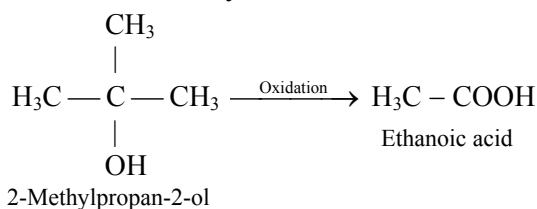
hence the product formed is 



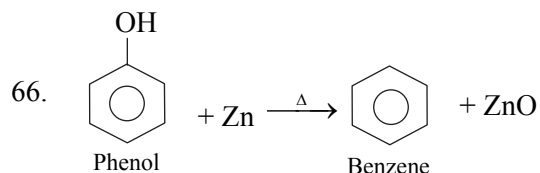
38. Secondary alcohols on oxidation gives ketones.

39. Tertiary alcohols are not easily oxidised.

40. 2-Methylpropan-2-ol is a tertiary alcohol. These are very difficult to oxidise and require very drastic conditions. They are first dehydrated then oxidised to a ketone and finally to the carboxylic acid. Both the ketone and carboxylic acid have lesser number of carbon atoms than the original alcohol.



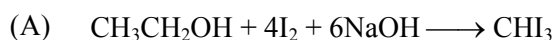




67. Phenol and ethyl alcohol are distinguished by

**Alcohol**

**Phenol**

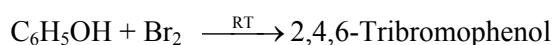
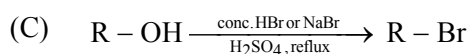


Phenols do not give iodoform test.

Iodoform is obtained



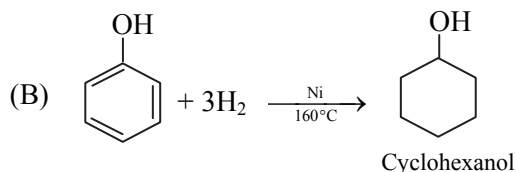
Deep violet colouration.



(White ppt)

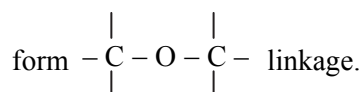
(D) Both phenol and ethyl alcohol will be soluble in NaOH. Hence, can't be distinguished.

68. (A) Phenol is used in the preparation of antiseptic like dettol, savlon, etc.

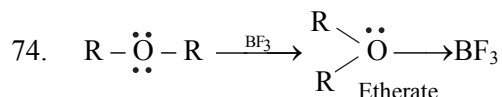


(C) Bakelite is a phenol-formaldehyde resin.

71. Ethers are organic derivatives of water, in which two hydrogen atoms are replaced by two alkyl group to

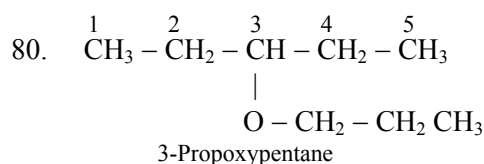


73.  $\text{C}_2\text{H}_5\text{OH}$  (Ethanol) and  $\text{CH}_3 - \text{O} - \text{CH}_3$  (Dimethyl ether) have the same molecular formula i.e.,  $\text{C}_2\text{H}_6\text{O}$ , but different functional groups. Hence, they are functional group isomers.



75. Anisole ( $\text{C}_6\text{H}_5 - \text{O} - \text{CH}_3$ ) is an aromatic ether as well as mixed ether.

76. The smaller alkyl group along with oxygen atom is named as alkoxy group and the position of the alkoxy group is indicated by the minimum number.

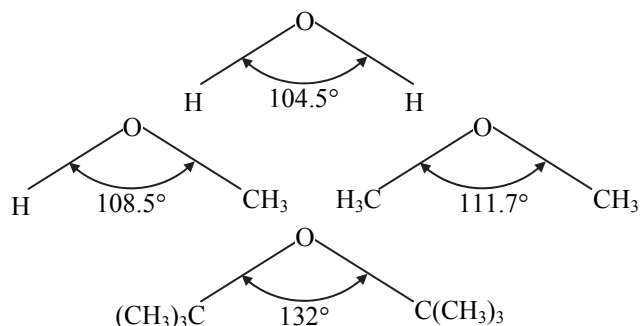


In ether, oxy-group is named as smaller alkyl group. Hence it is 3-Propoxy pentane.

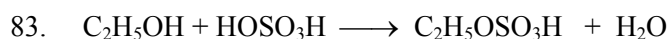




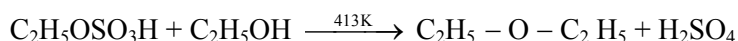
81.



In all these compounds oxygen is  $sp^3$ -hybridized. As the size of the alkyl group increases, the lone pair-lone pair repulsion is out weighted by steric hindrance and hence the angle increases in the following manner.  $H_2O < CH_3OH < CH_3OCH_3 < (CH_3)_3C - O - C(CH_3)_3$

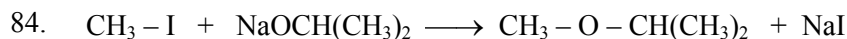
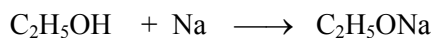
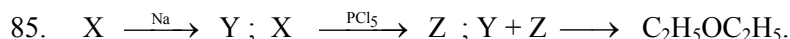


Ethanol

Ethyl hydrogen  
sulphateEthyl hydrogen  
sulphate

Diethyl ether

$H_2SO_4$  is regenerated. Hence the process becomes continuous. Since only a single alcohol is used, only simple ethers can be prepared.

Methyl  
iodideSodium  
isopropoxideIsopropyl methyl  
ether

Ethyl alcohol

Sodium ethoxide

(X)

(Y)

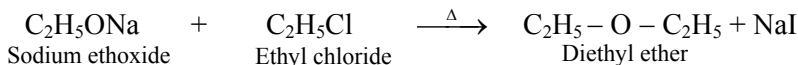


Ethyl alcohol

Ethyl chloride

(X)

(Z)



Sodium ethoxide

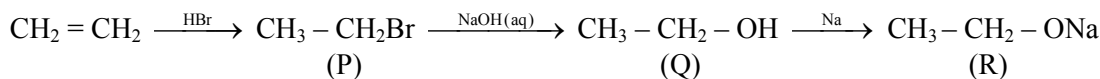
Ethyl chloride

Diethyl ether

(Y)

(Z)

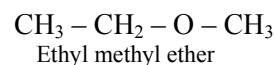
87. Since, the last step is the Williamson's ether synthesis, hence alkanes cannot be obtained.



(P)

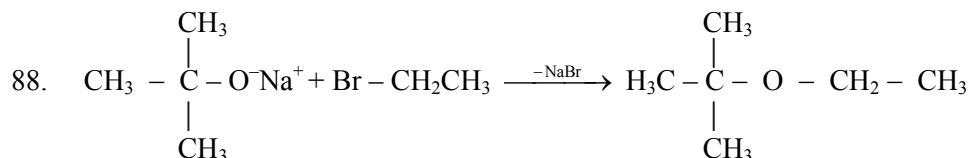
(Q)

(R)

$$\downarrow CH_3I$$


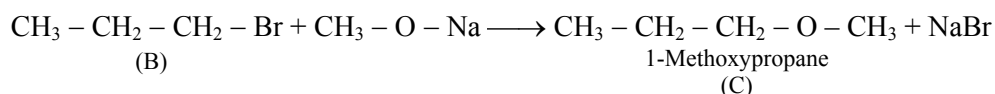
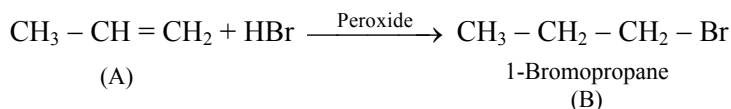
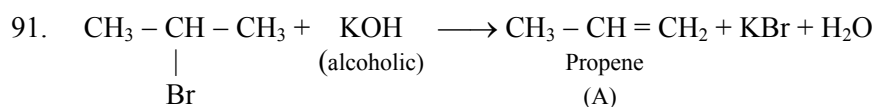
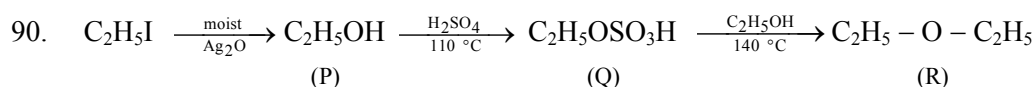
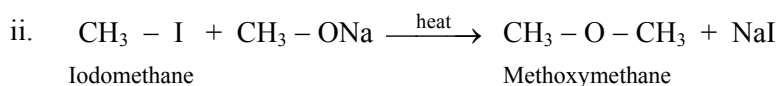
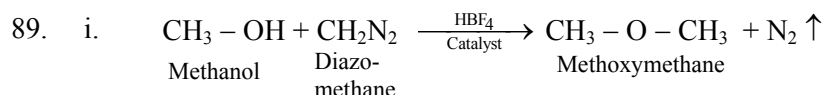
Ethyl methyl ether

(S)

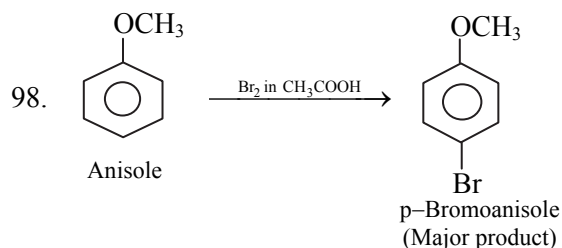
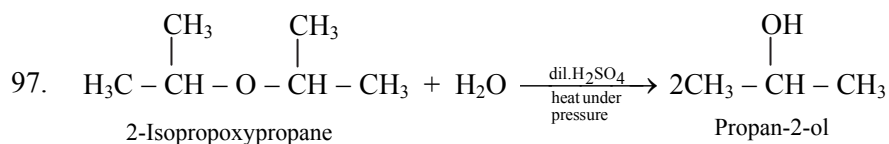
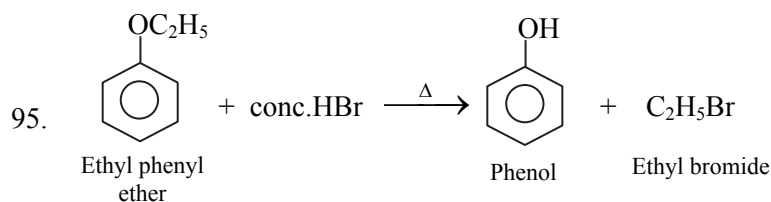


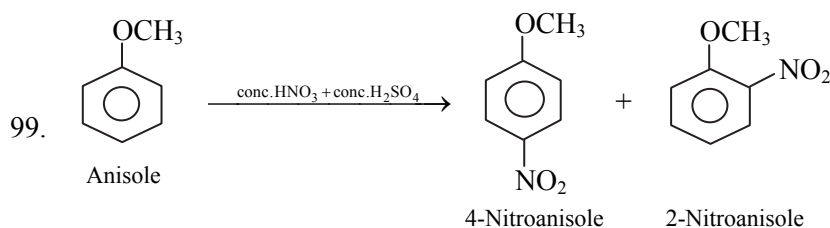
tert-Alkyl halides undergo elimination reaction with sodium alkoxides (strong bases) easily.

$(\text{CH}_3)_3\text{CBr} \xrightarrow{\text{RONa}} (\text{H}_3\text{C})_2\text{C} = \text{CH}_2 + \text{ROH} + \text{NaBr}$ . This will be the product in 'B'. 3° alcohols in presence of  $\text{H}_2\text{SO}_4$  can be easily dehydrated. Hence the alkene will result rather than the ether. An alkyl halide and an alcohol do not react to give ether.



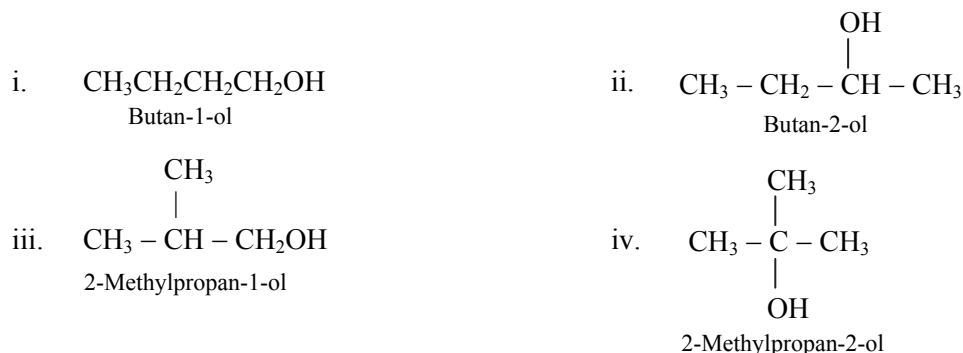
94. Ethers do not react with sodium. Ethers are inert and therefore used as solvents. They are highly inflammable and must be handled very carefully. They can be considered as dialkyl derivatives of water.



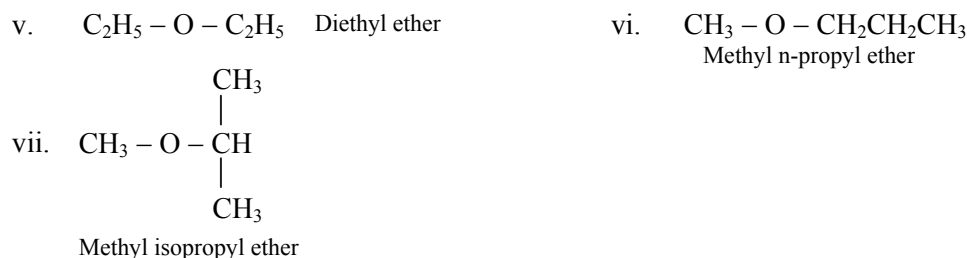


103. Methanol and ethanol is formed which are homologous to each other.

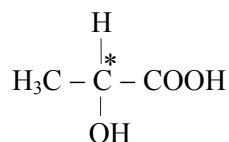
104. **Isomers of alcohol :**



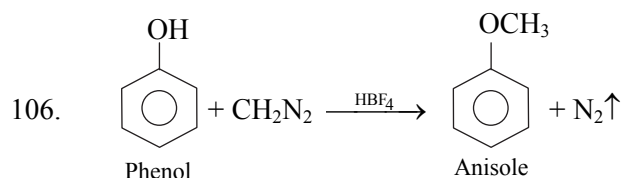
**Isomers of Ether :**



105.  $\text{CH}_3\text{CHOHCOOH}$  i.e., Lactic acid can be represented as

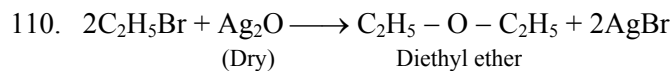
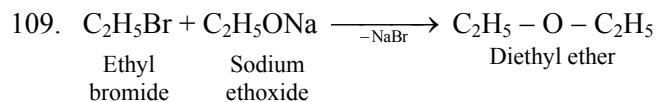


One carbon is attached to four different groups. The presence of this asymmetric carbon makes lactic acid optically active. Since none of the other molecules possesses an asymmetric carbon, they do not show optical activity.

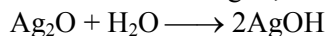


108. The CORRECT statements are:

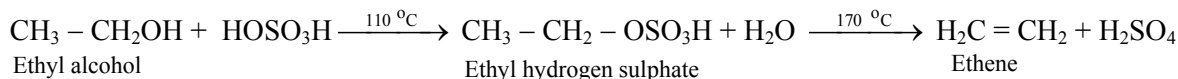
- (A) Phenol is carboic acid.
- (B) Monohydric alcohols are those, which contain one  $-\text{OH}$  group and which can be on primary, secondary or tertiary carbon atoms.
- (C) Boiling points of alcohols are higher than those of ethers because of hydrogen bonding between two alcohol molecules.
- (D) Ethers are prepared by Williamson's synthesis.



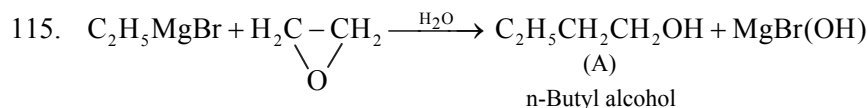
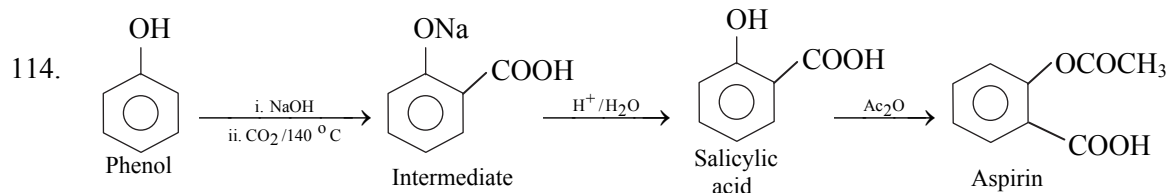
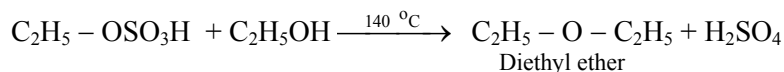
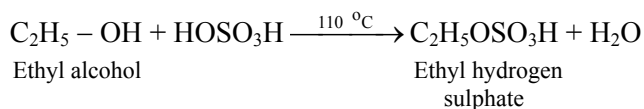
If we take moist  $\text{Ag}_2\text{O}$ , then alcohol is formed



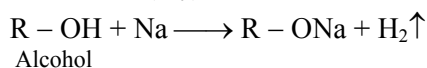
112. Ethyl alcohol is dehydrated to ethylene by conc.  $\text{H}_2\text{SO}_4$ .



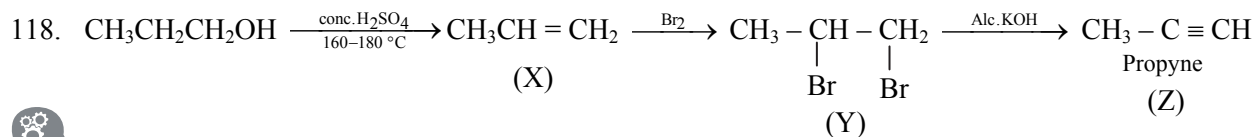
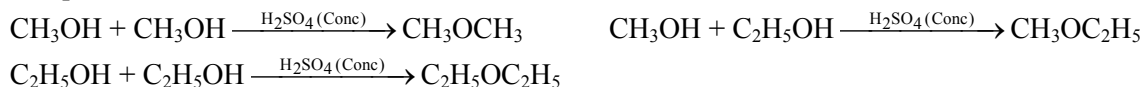
In excess of ethanol, continuous etherification takes place at  $140^\circ\text{C}$ .



116. Alcohol + Benzene  $\longrightarrow$  Soluble  
(Dry)

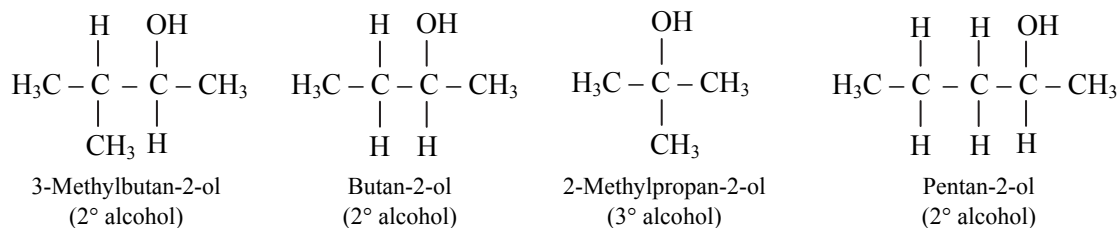


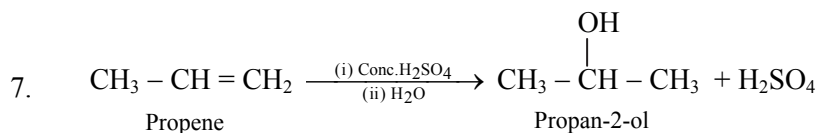
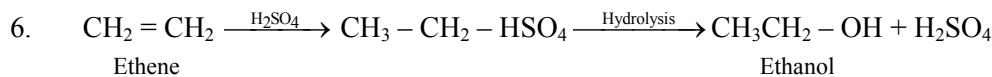
117. The product will contain a mixture of three ethers.



### Competitive Thinking

3.





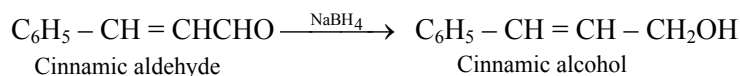
8. Except ethene, all alkenes on acid catalyzed hydration gives more stable alcohols i.e., secondary or tertiary alcohols. Ethene gives ethanol (primary alcohol).



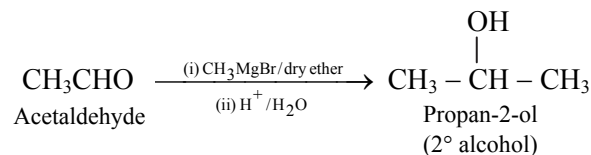
10. Hydroboration oxidation (Industrial preparation of alcohol)



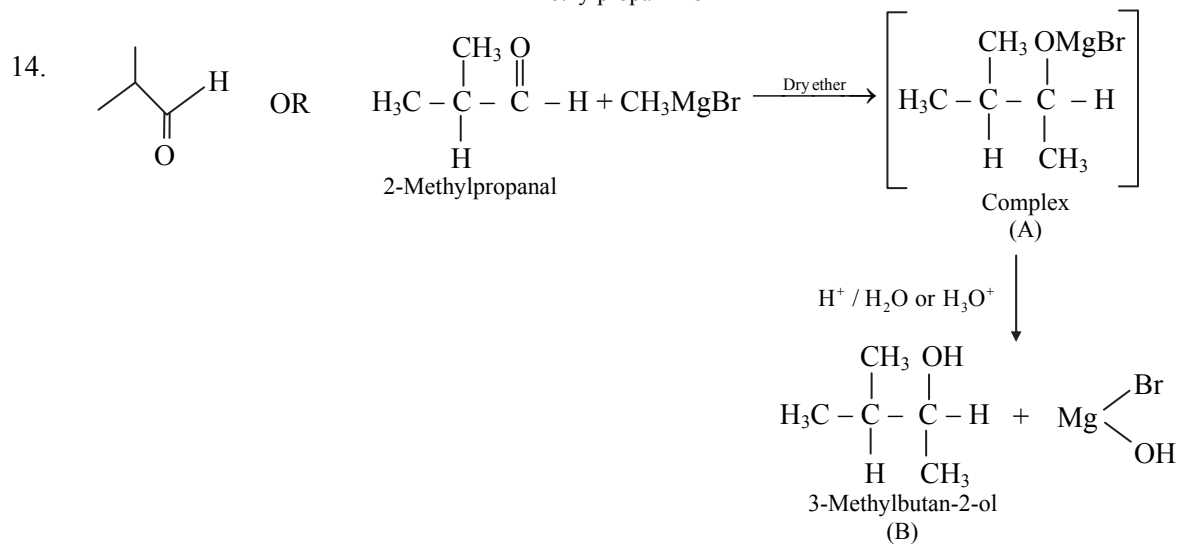
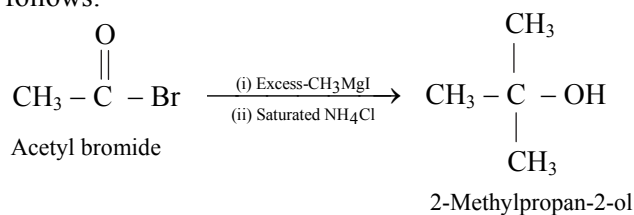
11.  $\text{NaBH}_4$  and  $\text{LiAlH}_4$  attacks only carbonyl group and reduces it into alcohol group. They do not attack on double bond.

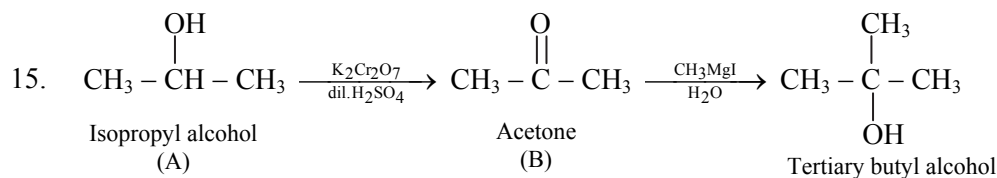


12. Aldehydes (other than formaldehyde) react with Grignard reagent, followed by acid hydrolysis, to form secondary alcohols. Therefore, among the given options, acetaldehyde will give a secondary alcohol upon treatment with methyl magnesium bromide followed by acid hydrolysis.



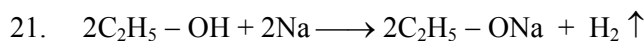
13. Considering that saturated solution of  $\text{NH}_4\text{Cl}$  behaves as acidic solution, the reaction will proceed as follows:



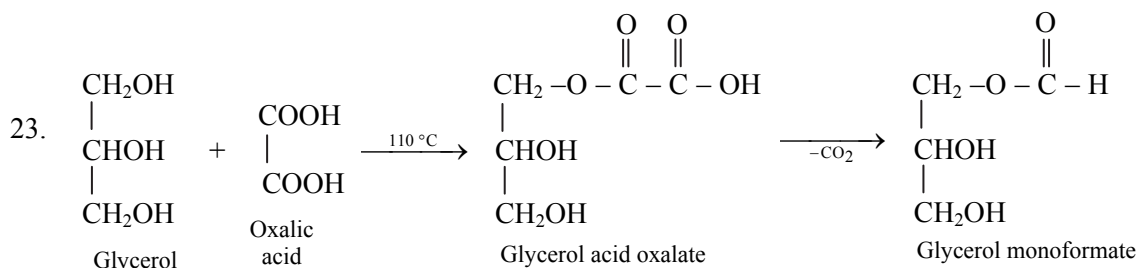
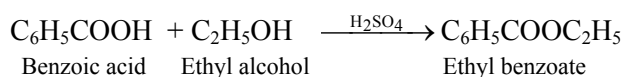


16. The correct order of boiling point for primary, secondary and tertiary alcohols is,  $1^\circ$  alcohol  $>$   $2^\circ$  alcohol  $>$   $3^\circ$  alcohol

17. Boiling point decreases with an increase in branching. Amongst all the isomers of butyl alcohol, tert-Butyl alcohol has the maximum branching and hence, it has the lowest boiling point.

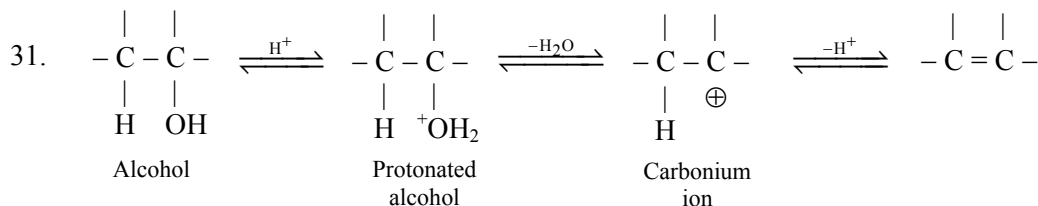
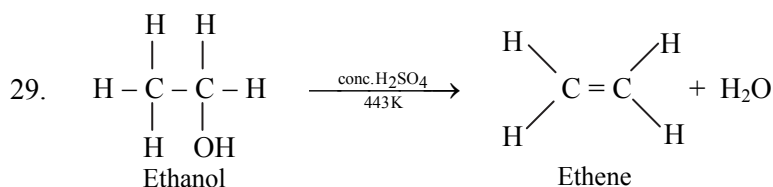


22. When benzoic acid reacts with ethyl alcohol in the presence of sulphuric acid, ethyl benzoate is formed. This is known as esterification.

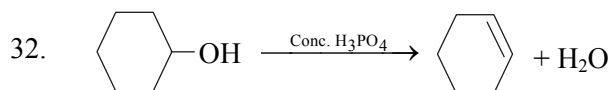


24. Tertiary alcohols react immediately with Lucas reagent and give turbidity.

25. Tertiary alcohols give immediate turbidity on shaking with HCl at room temperature.

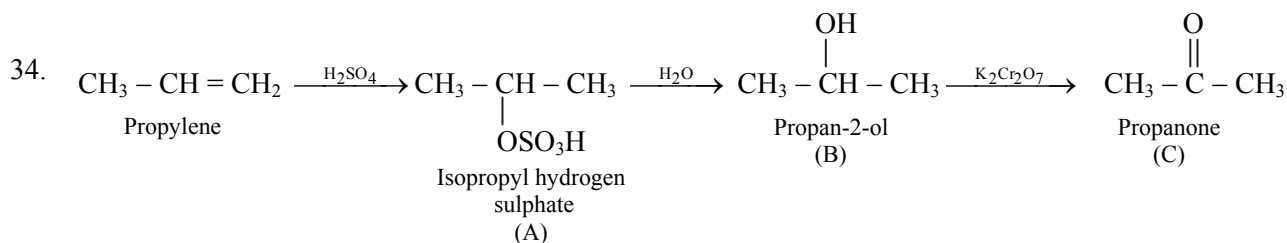


In all cases intermediate is carbonium ion, and there may be 1,2-Hydride or 1,2-Methyl shift to form more stable carbonium ion.



Because conc.  $\text{H}_3\text{PO}_4$  acts as a dehydrating agent.

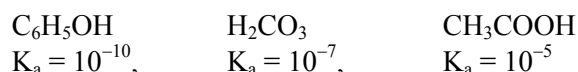
33. PCC being a mild oxidising agent, oxidises primary alcohols to corresponding aldehydes without further oxidation to carboxylic acids.



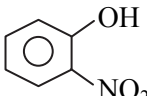
35. Glycol is used as an antifreeze for automobile radiators because it lowers down the melting point of water.

38. 5% aqueous solution of phenol at room temperature is called as carbolic acid.

45. Phenol is weaker acid than carbonic acid

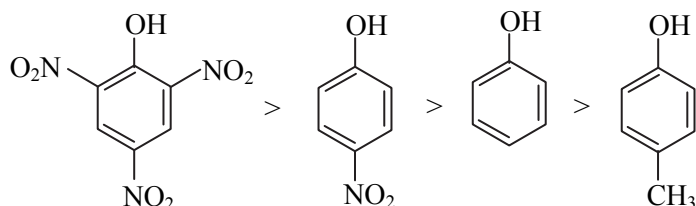


46. Phenols are more acidic than alcohols. Further, phenols with electron-withdrawing substituents (like  $-\text{NO}_2$  group) are more acidic than phenols with electron-donating substituents (like  $-\text{CH}_3$  group).

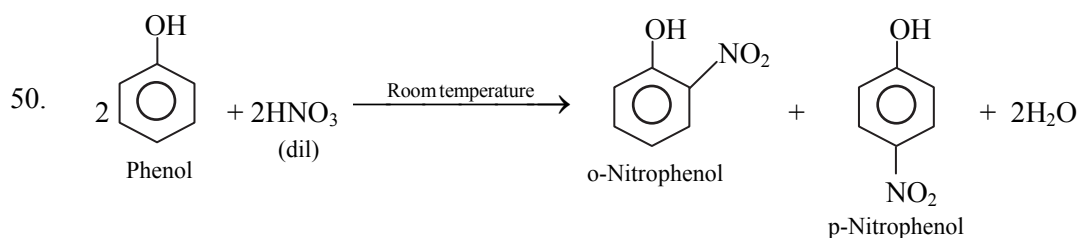
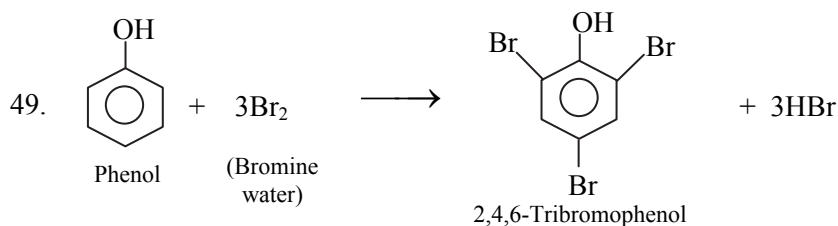
Hence, among the given options, the strongest acid is 

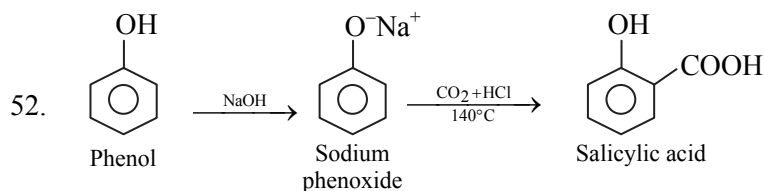
47. Presence of electron releasing group like  $-\text{NH}_2$  decreases the acidic strength of phenol. Therefore, phenol is more acidic than p-aminophenol. Presence of electron withdrawing group increases the acidic strength of the phenol. When electron withdrawing group like  $-\text{NO}_2$  is present at p-position, then it exerts both  $-I$  and  $-R$  effect whereas when it is present at m-position, it exerts only  $-I$  effect. Hence, p-nitrophenol is a stronger acid than m-nitrophenol. Therefore, the most acidic phenolic compound is p-nitrophenol.

48. The order of acidity for the given compounds follows the order,

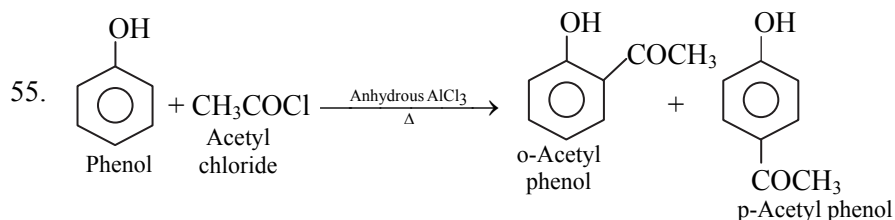
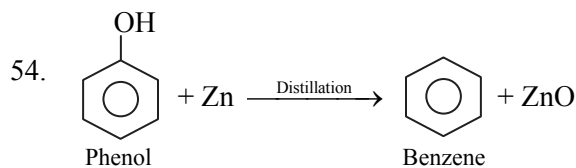
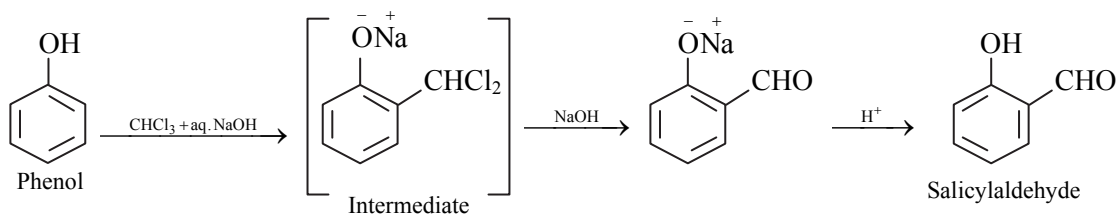


More  $-I$ ,  $-M$  effect, more acidic is the compound.



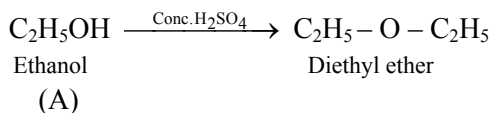
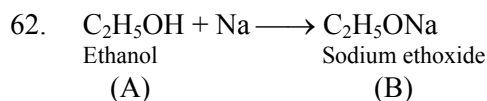
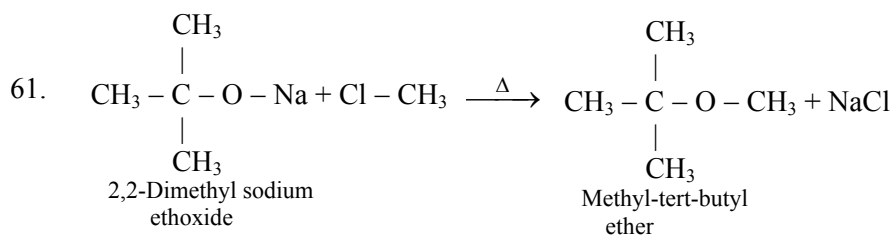
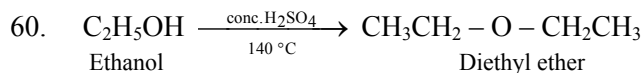


53. On treating phenol with chloroform in the presence of sodium hydroxide, a  $-\text{CHO}$  group is introduced at ortho position of benzene ring. This reaction is known as Reimer-Tiemann reaction.

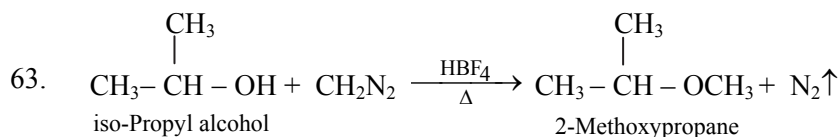


58. Ethers are isomeric with alcohols. Aldehydes and ketones are isomers of each other.

59. The molecular formula  $\text{C}_4\text{H}_{10}\text{O}$  can represent 4 alcohols and 3 ethers i.e., total 7 isomers. Since it is given that the compound  $\text{C}_4\text{H}_{10}\text{O}$  represents three isomers, these 3 isomers will be ethers showing metamerism.  
Ethers :  $\text{CH}_3\text{OC}_3\text{H}_7$  ;  $\text{C}_2\text{H}_5\text{OC}_2\text{H}_5$  ;  $\text{H}_3\text{COCH}(\text{CH}_3)_2$

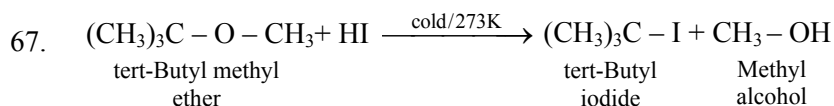
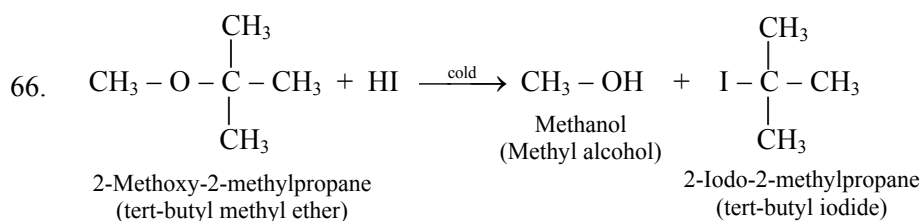
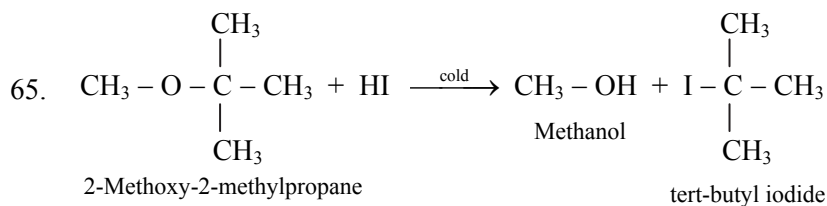




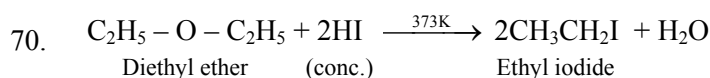
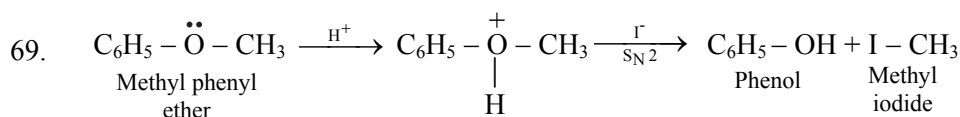
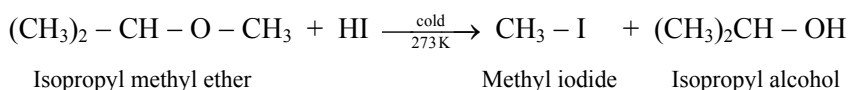


Only methyl ethers are prepared by this method.

64.  $\text{CH}_3\text{OCH}_3$  and  $\text{C}_2\text{H}_5\text{OCH}_3$  are gases while  $\text{C}_2\text{H}_5\text{OC}_2\text{H}_5$  (boiling point 308 K) is low boiling liquid.

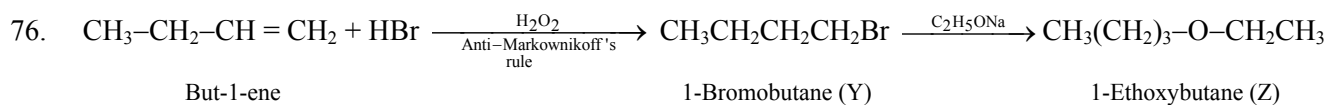
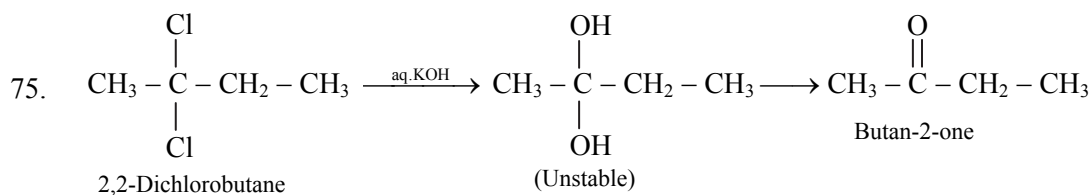


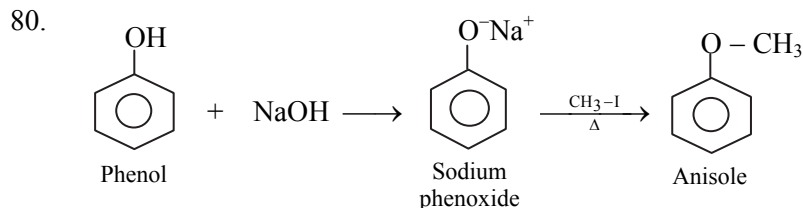
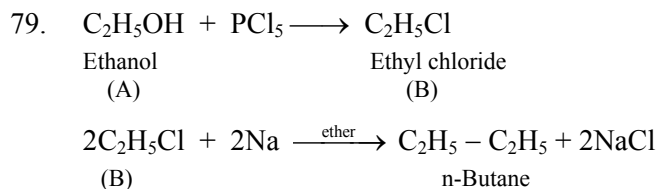
68. In this reaction, a mixture of an alkyl halide containing smaller alkyl group and an alcohol is obtained.



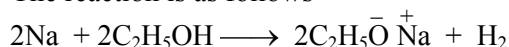
At high temperature, the ether is completely cleaved by concentrated HI to give the corresponding alkyl iodide.

73. Name of the compound is 18-crown-6.





81. The reaction is as follows



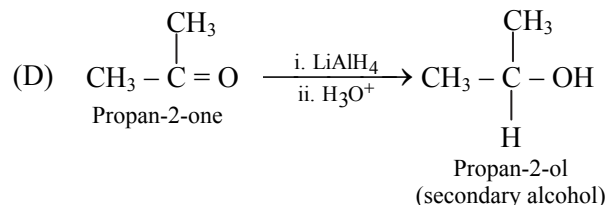
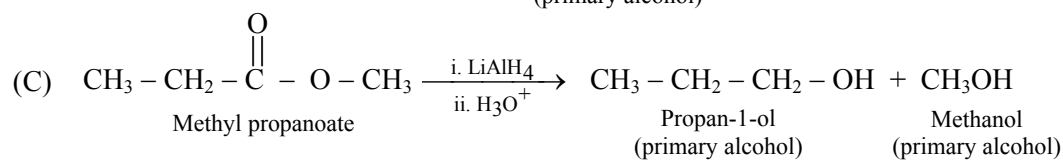
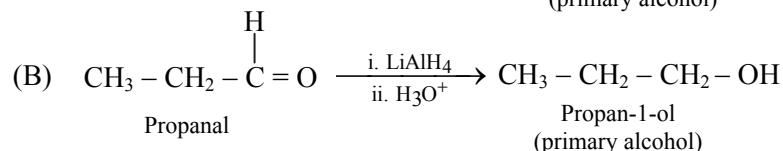
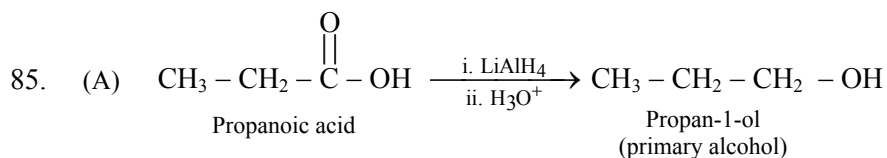
$$\therefore 2 \text{ mol Na} = 1 \text{ mol H}_2$$

$$46 \text{ g Na} \equiv 2 \text{ mol Na}$$

$$\therefore 46 \text{ g Na} = 2 \text{ g H}_2 = 2 \times 10^{-3} \text{ kg H}_2$$

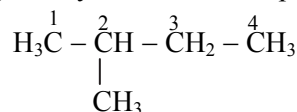
82. The ortho and para isomers of nitrophenols can be separated by steam distillation. o-Nitrophenol is steam volatile due to intramolecular hydrogen bonding while p-nitrophenol is less volatile due to intermolecular hydrogen bonding which causes association of molecule.

83.  $\text{C}_2\text{H}_5\text{OH}$  and  $\text{CH}_3 - \text{O} - \text{CH}_3$  are isomers.



86. Alcohols have higher boiling points than corresponding alkanes, alkyl halides, aldehydes, ketones and ethers of nearly same molecular mass. This is due to intermolecular hydrogen bonding in alcohols.

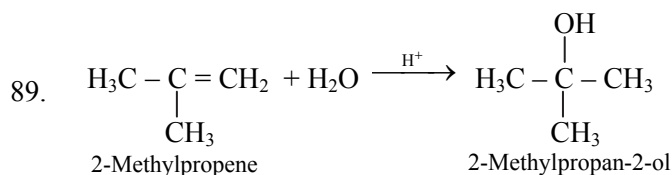
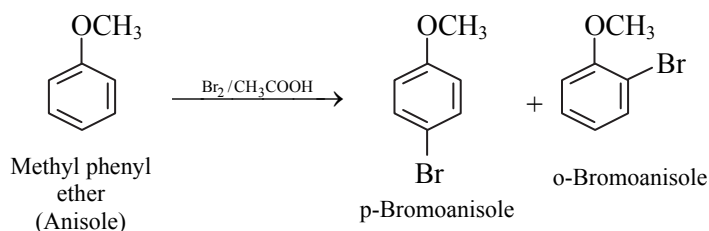
87. The given hydrocarbon is isopentane.



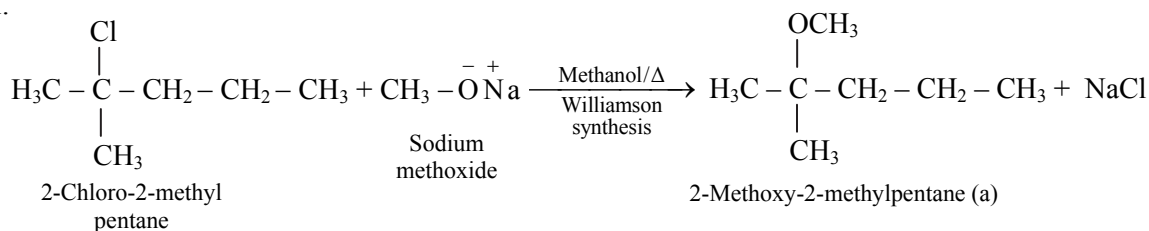
H-atom attached to C-1, C-2, C-3 or C-4 can get replaced by hydroxy group. Thus, there are 4 different monohydroxy derivatives possible for the given hydrocarbon.



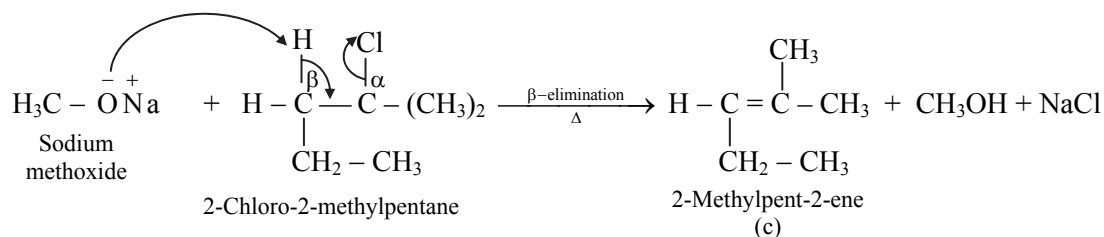
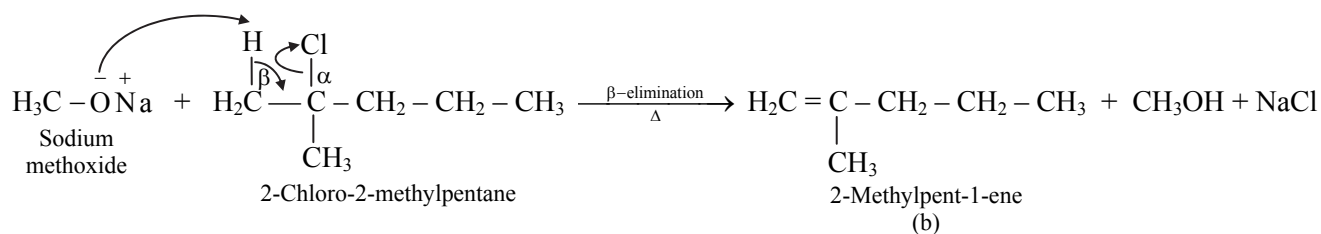
88. Methyl phenyl ether (anisole) undergoes bromination with bromine in acetic acid to form p-bromoanisole (major product) and o-bromoanisole (minor product).



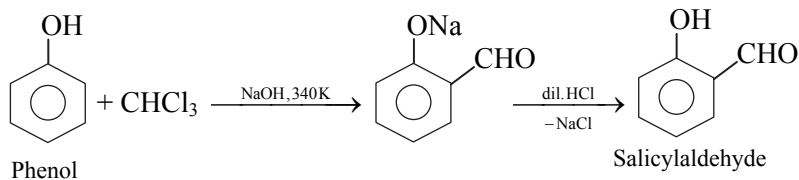
91. i.



- ii. In case of secondary or tertiary alkyl halides, Williamson synthesis is sterically difficult (crowding effect). Hence,  $\beta$ -elimination is predominant in the presence of stronger bases like alkoxides resulting in the formation of corresponding alkene. In 2-chloro-2-methylpentane, two different products are formed due to elimination of  $\beta$ -hydrogen from  $-\text{CH}_3$  and  $-\text{CH}_2-$  groups respectively as given below:



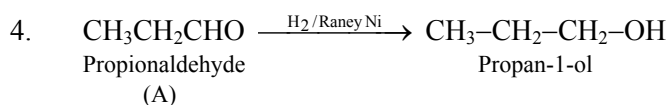
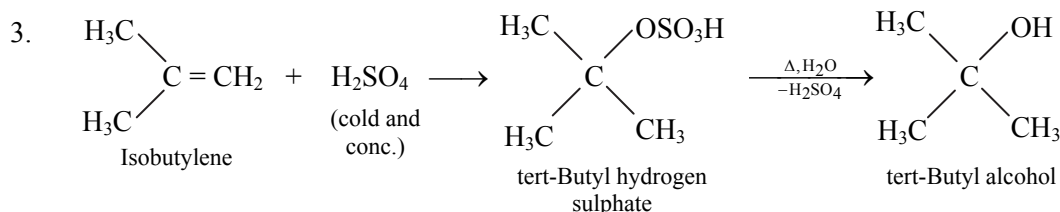
92. Reimer-Tiemann reaction involves the carbon carbon bond formation.



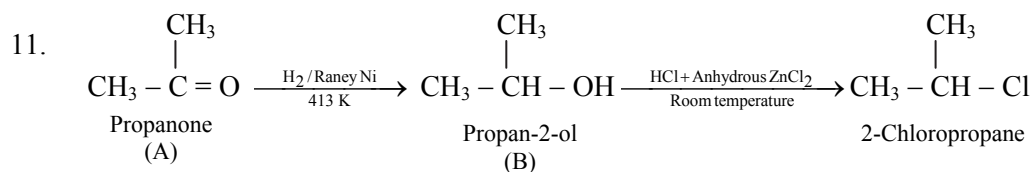


## Evaluation Test

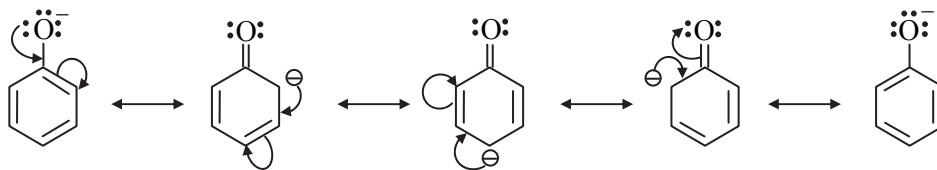
1. In the carbinol system, monohydric alcohols are named as derivatives of methyl alcohol,  $\text{CH}_3\text{OH}$  (which is known as carbinol).
2. Reactivity of alkyl halides having same halide group, but different alkyl group is tertiary > secondary > primary.



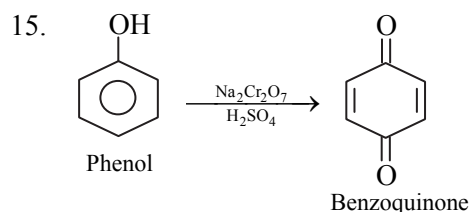
6. The solubility of isomeric alcohols increases with increase in branching.
7. At room temperature, tertiary alcohols react with Lucas reagent readily, secondary alcohols react slowly while primary alcohols do not react with Lucas reagent at room temperature.
8. Pyridine catalyses the reaction by neutralizing the hydrogen chloride produced.
9. Tertiary alcohols undergo oxidation under drastic conditions.
10. Alcohols which form the most stable carbocation undergo dehydration more readily. Tertiary-butyl alcohol forms the most stable tert-butyl carbocation among the given alcohols.



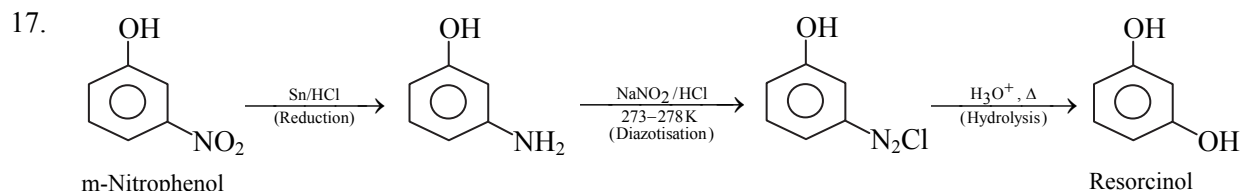
12. Primary alcohols give the best yield of dialkyl ether on treatment with sulphuric acid.
13. Due to delocalization of negative charge over the ortho and para position, phenoxide ion is more stable than phenol.



14.  $\text{Br}^+$  is the electrophile in the bromination of phenol.

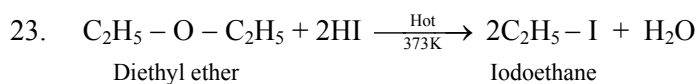
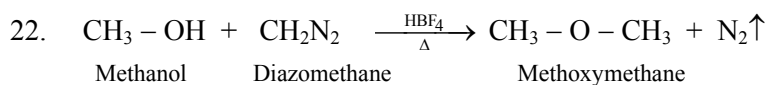
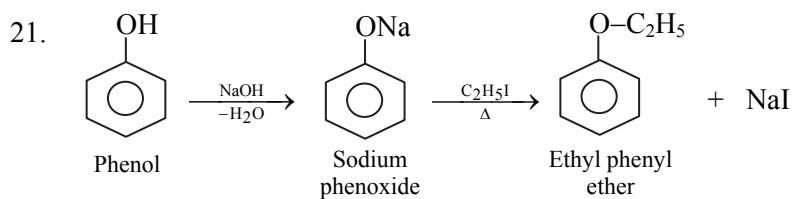
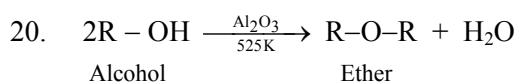


16. Phenols react with neutral  $\text{FeCl}_3$  to give purple colouration.



18. Due to almost identical sizes of 2p-orbitals of C and F, +R effect and -I effect of F almost balance each other, thus p-fluorophenol is almost as acidic as phenol. p-chlorophenol and p-nitrophenol are more acidic than phenol. p-nitrophenol is a much stronger acid than p-chlorophenol due to -R and -I effect of -NO<sub>2</sub> group.

19. Electron withdrawing groups like -NO<sub>2</sub>, -Cl increase the acidity of phenols while electron releasing groups like -CH<sub>3</sub>, -OCH<sub>3</sub> decrease the acidity of phenols.

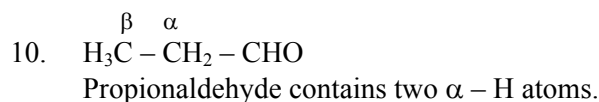
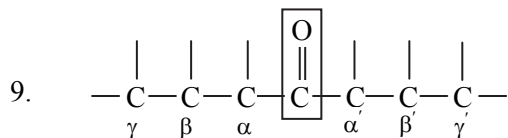
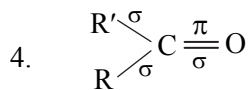




## Hints

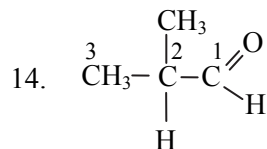


### Classical Thinking

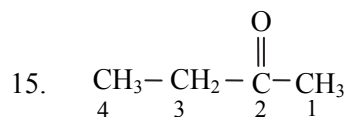


12. Aldehydes are named as alkanals and the name of an individual aldehyde is obtained by dropping the terminal 'e' from the name of the hydrocarbon and adding the suffix 'al'.

13. Ketones are named as alkanones and the name of an individual member is obtained by dropping 'e' of the parent hydrocarbon and adding the suffix 'one'.

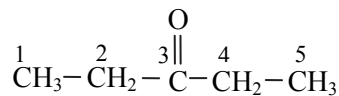


2-Methylpropanal



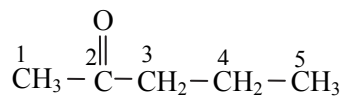
Butan-2-one

16. Diethyl ketone is  $CH_3CH_2COCH_2CH_3$  i.e.,

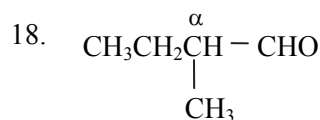


Pentan-3-one

17. Methyl n-propyl ketone is  $CH_3COCH_2CH_2CH_3$  i.e.,



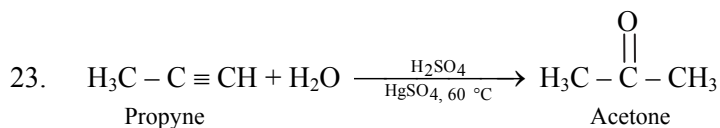
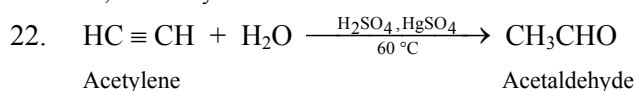
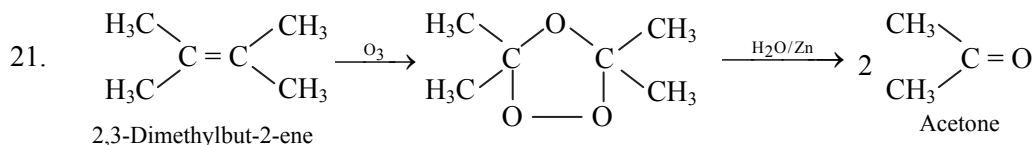
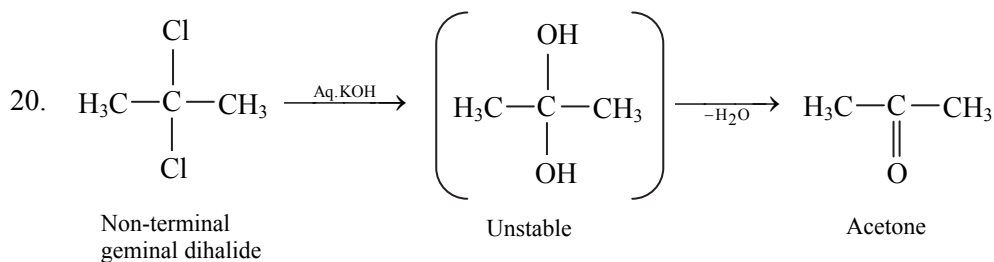
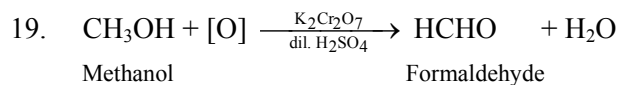
Pentan-2-one



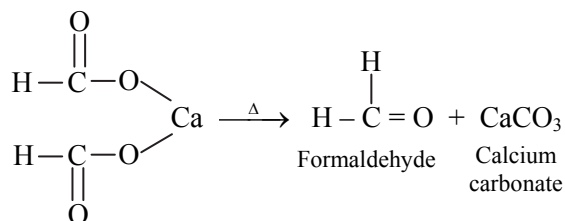
2-Methylbutanal

or

$\alpha$ -Methyl butyraldehyde

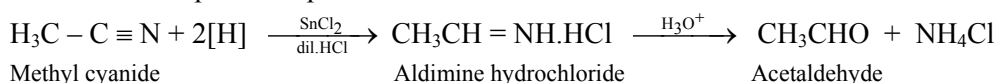


24. Dry distillation of calcium formate gives formaldehyde and calcium carbonate.



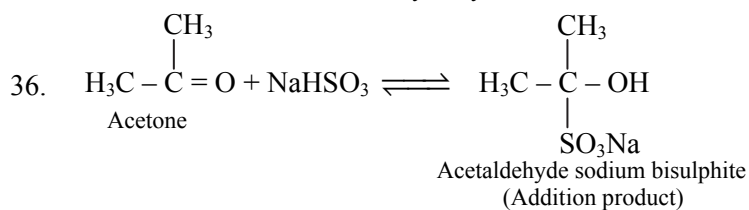
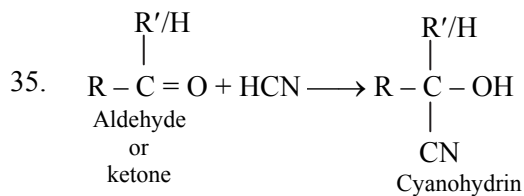
Calcium formate

25. This is an example of Stephen reaction.



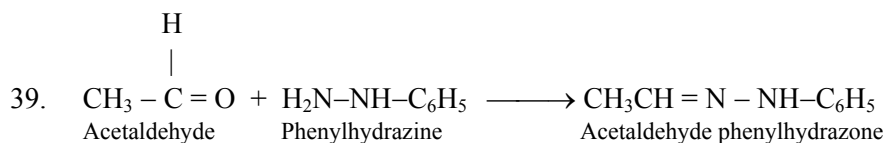
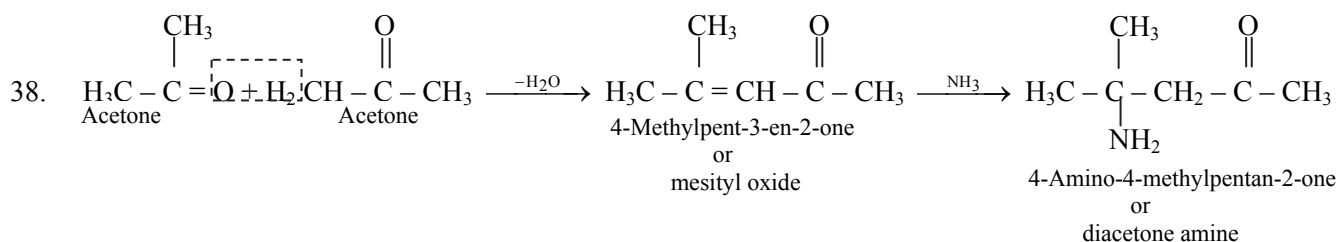
32. A 40% aqueous solution of formaldehyde is called formalin. It is used to preserve biological specimens.

33. Higher aldehydes are insoluble in water.

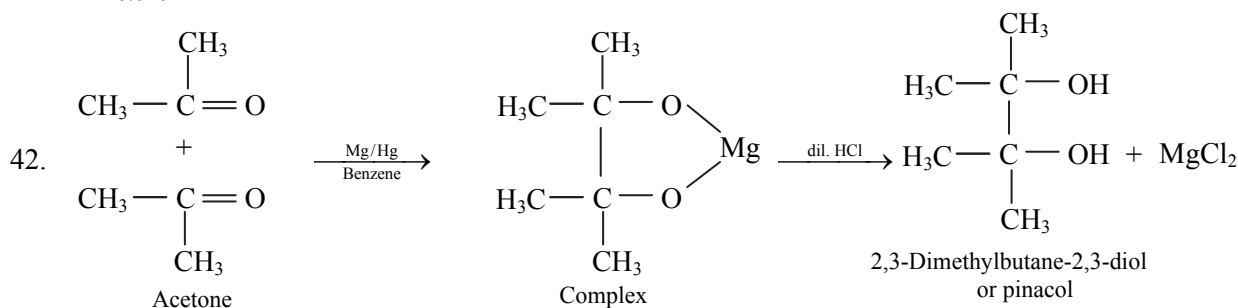
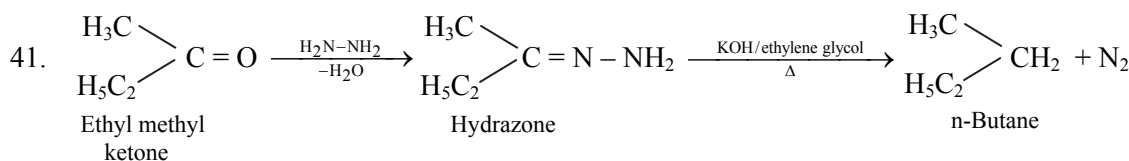
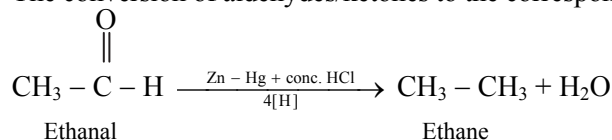




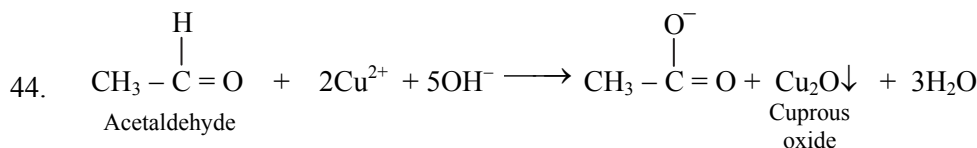
37. Ketals are the products of reaction between ketones with alcohols.



40. The conversion of aldehydes/ketones to the corresponding hydrocarbon is achieved by Clemmensen's reduction.

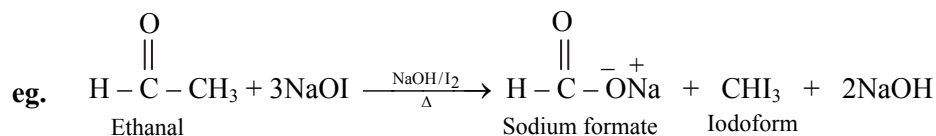


43. Only aldehydes get oxidized by Tollen's reagent while ketones, ethers or alcohols do not get oxidized by Tollen's reagent.



45. Ketones (i.e., acetone) do not get oxidized by mild oxidizing agents like Schiff reagent, as they have no hydrogen atom directly attached to the carbonyl carbon atom.

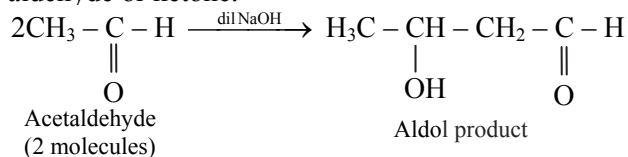
46. Among ethanal and propanal, only ethanal will react with  $\text{I}_2$  in presence of base, because haloform reactions give positive test to only methyl ketone containing compound i.e.,  $\text{H}_3\text{C}-\overset{\text{O}}{\parallel}{\text{C}}-\text{group}$



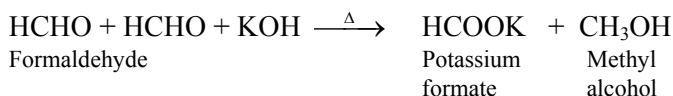




47. Aldol condensation is shown by aldehydes and ketones having  $\alpha$ -H atoms. The nucleophile formed by the removal of a proton from the  $\alpha$ -C attacks the carbonyl carbon of the second molecule, to form a  $\beta$ -hydroxy aldehyde or ketone.



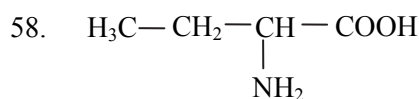
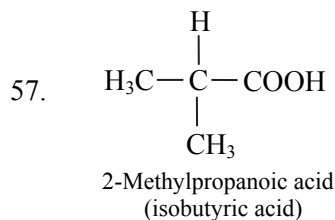
48. Formaldehyde does not contain  $\alpha$ -C and  $\alpha$ -H atoms. Hence, in presence of concentrated KOH, it undergoes self oxidation-reduction to form one molecule of potassium salt of carboxylic acid and one molecule of alcohol. This is an auto redox reaction called as Cannizzaro reaction.



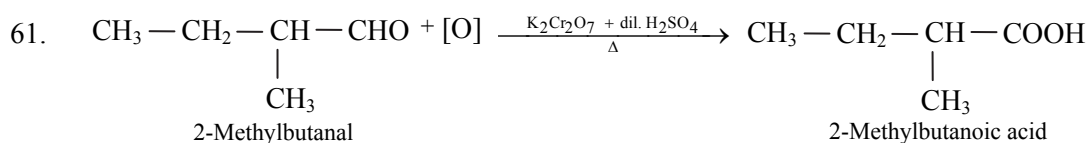
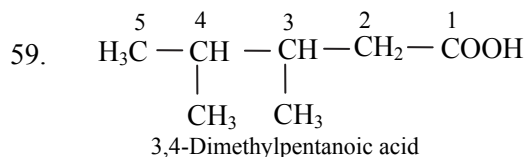
49. Cannizzaro reaction takes place for only those compounds which do not contain  $\alpha$ -hydrogen atoms.

53. Carboxyl ( $-\overset{\text{O}}{\parallel}{\text{C}}-\text{OH}$ ) group is a combination of carbonyl ( $-\overset{\text{O}}{\parallel}{\text{C}}-$ ) and hydroxyl ( $-\text{OH}$ ) group.

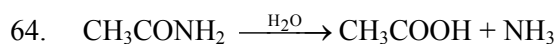
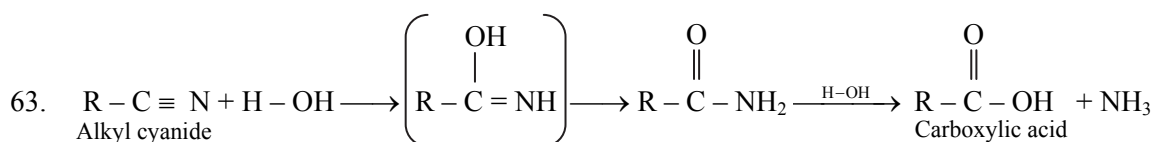
55. Valeric acid has five carbon atoms, i.e.,  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{COOH}$   
 $\therefore$  IUPAC name is n-pentanoic acid.

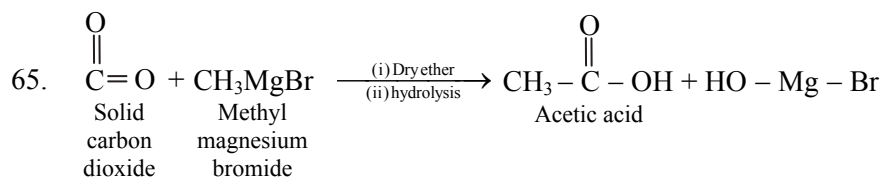


Preferred functional group is carboxyl ( $-\text{COOH}$ ). By IUPAC nomenclature, the name of the compound is 2-aminobutanoic acid.

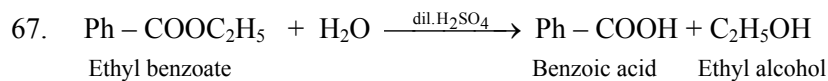


62. Anisole is an ether which cannot be oxidized by alkaline  $\text{KMnO}_4$  to give benzoic acid.



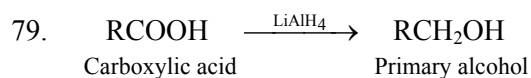
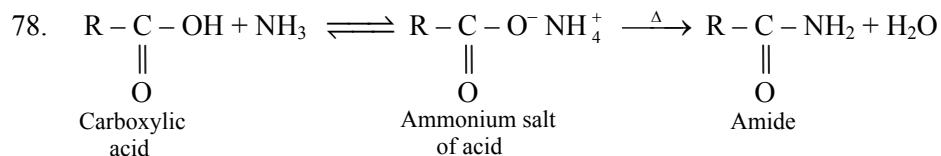
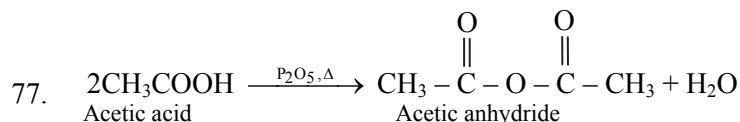
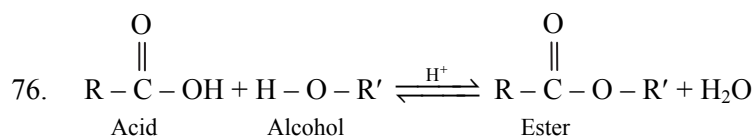
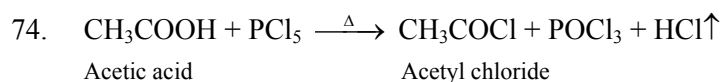
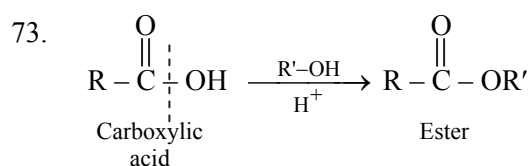


66. The given reaction is carried out in the presence of a base like pyridine or NaOH to remove the HCl generated.

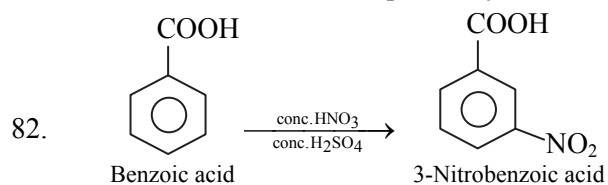


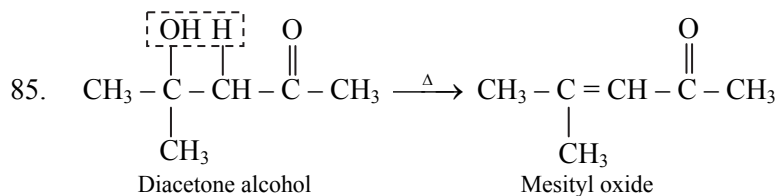
70. Carboxylic acids form H-bonding by means of two highly electronegative atoms present in it.

72. Presence of methyl group decreases the acidic character of acetic acid due to positive inductive effect (+I).



81. In this reaction,  $\alpha$ -H is replaced by chlorine.





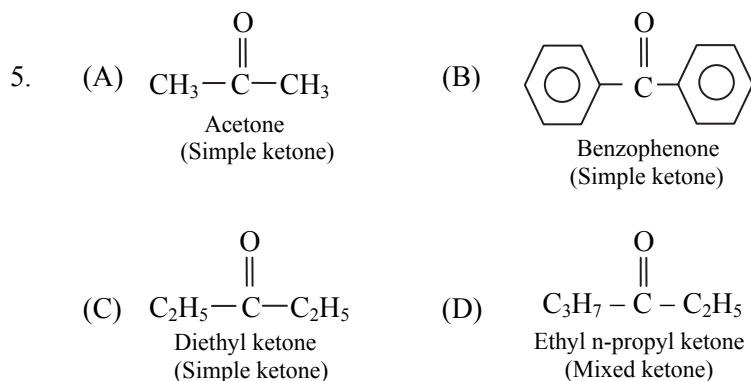
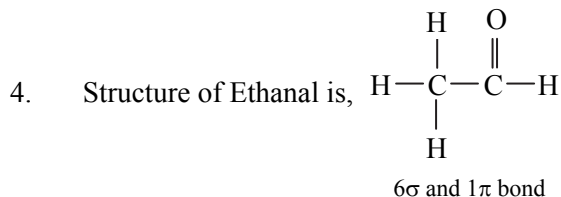
86. In the reaction of acetaldehyde with Benedict or Fehling solution, cupric ion is converted to cuprous oxide i.e.,  $\text{Cu}^{+2} \longrightarrow \text{Cu}^+$



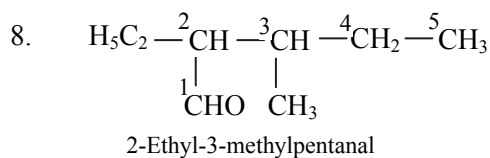
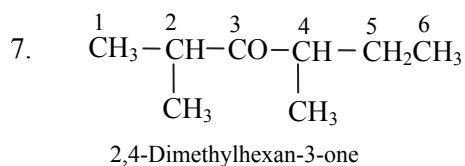
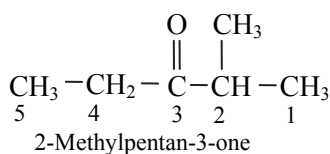
### Critical Thinking

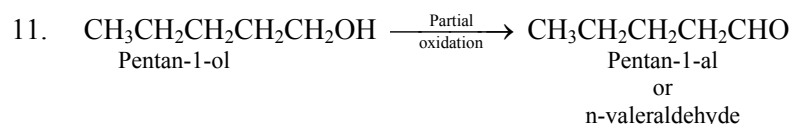
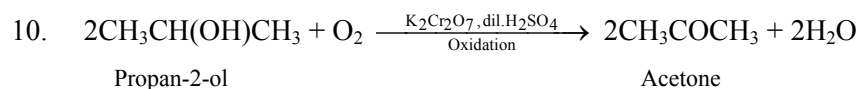
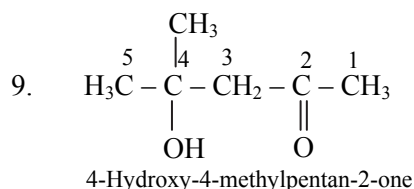
1. Saturated aliphatic aldehydes and ketones have general formula  $\text{C}_n\text{H}_{2n}\text{O}$ .

3. In the homologous series of ketones, acetone ( $\text{CH}_3 - \overset{\text{O}}{\parallel} \text{C} - \text{CH}_3$ ) is the first member, butanone ( $\text{CH}_3 - \text{CO} - \text{CH}_2 - \text{CH}_3$ ) is the second member, while pentan-2-one ( $\text{CH}_3 - \text{CO} - \text{CH}_2 - \text{CH}_2 - \text{CH}_3$ ) and pentan-3-one ( $\text{CH}_3 - \text{CH}_2 - \text{CO} - \text{CH}_2 - \text{CH}_3$ ) are the third members.

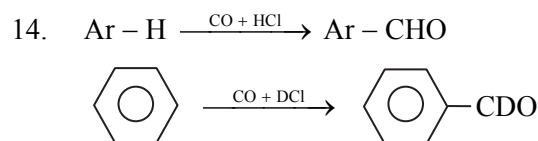
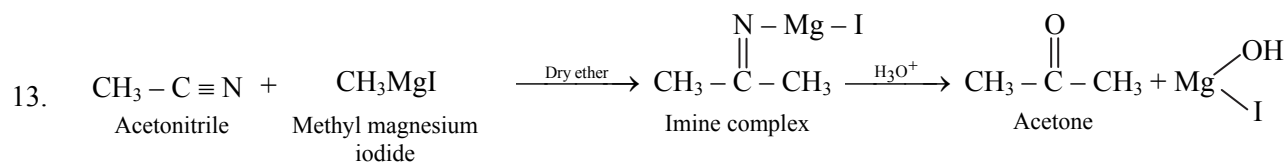
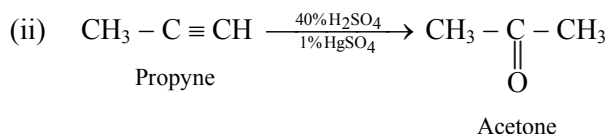
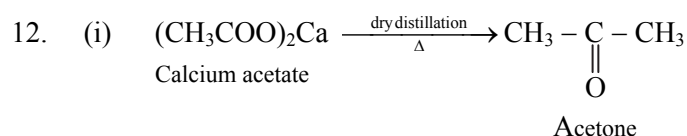


6. Ethyl isopropyl ketone is



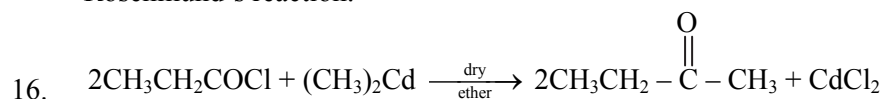


Partial oxidation of pentan-1-ol gives n-valeraldehyde whereas complete oxidation gives pentanoic acid.



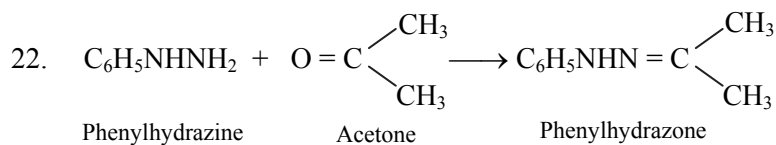
DCl = heavy hydrogen chloride (Deuterium chloride)

15. Only acyl chlorides are hydrogenated in the presence of  $\text{H}_2/\text{Pd}-\text{BaSO}_4$  to give the formation of aldehydes in Rosenmund's reaction.



19. Aldehydes and ketones being highly polar compounds have higher boiling points than non-polar hydrocarbons of comparable molecular masses. This is due to the weak molecular association in aldehydes and ketones arising because of dipole-dipole interactions.

20. Generally in nucleophilic addition reactions, aldehydes are more reactive than ketones due to both steric and electronic reasons.

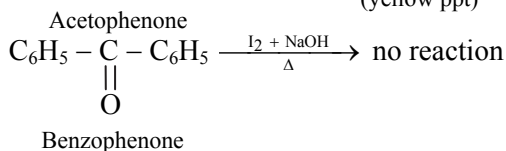
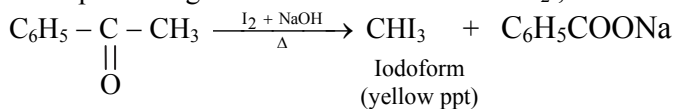




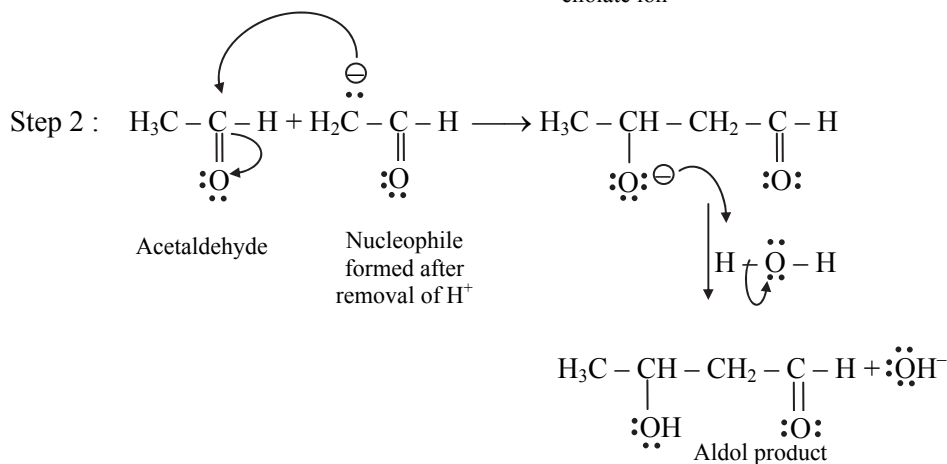
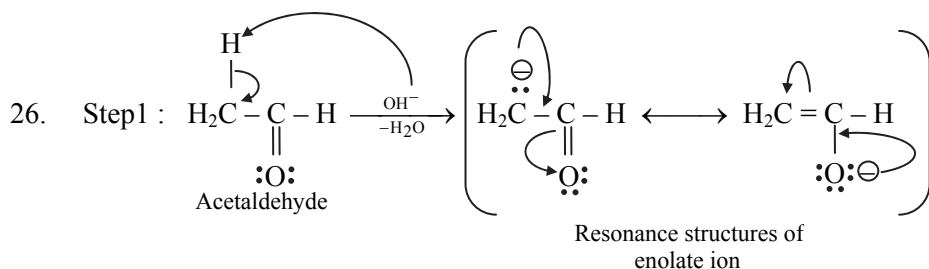
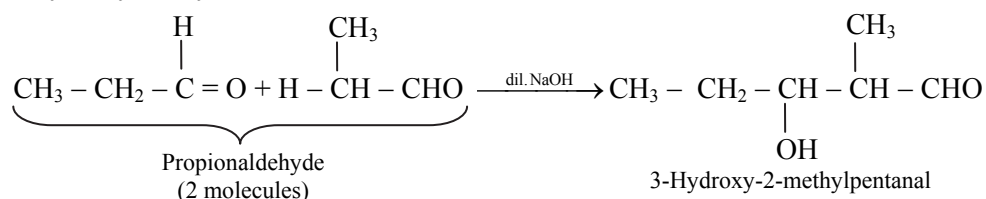
23. Pentan-2-one ( $\text{CH}_3 - \overset{\text{O}}{\parallel} \text{C} - \text{CH}_2 - \text{CH}_2 - \text{CH}_3$ ) is a methyl ketone, thus gives positive iodoform test.

Pentan-3-one ( $\text{CH}_3 - \text{CH}_2 - \overset{\text{O}}{\parallel} \text{C} - \text{CH}_2 - \text{CH}_3$ ) is not a methyl ketone, thus does not give positive iodoform test.

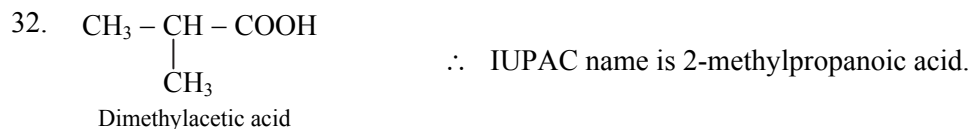
24. Acetophenone gives iodoform with alkaline  $\text{I}_2$ , whereas benzophenone does not give the reaction.



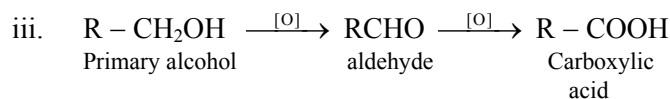
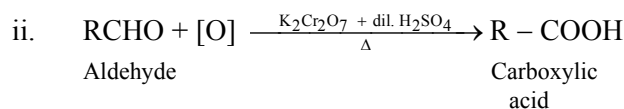
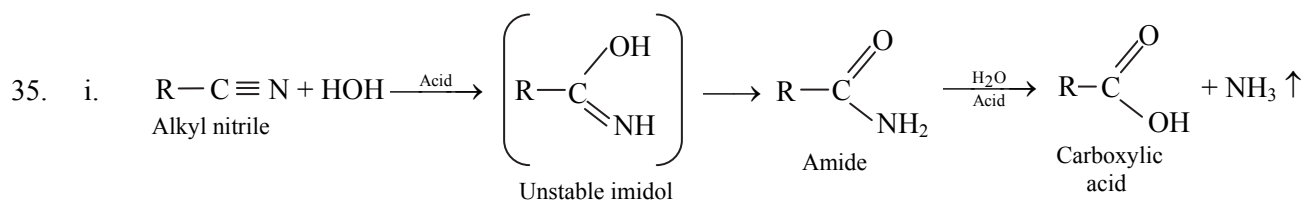
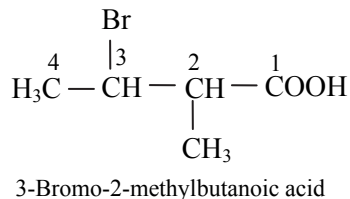
25. An aldehyde having  $\alpha$ -H atoms in presence of dilute alkali undergoes aldol condensation to give a  $\beta$ -hydroxyaldehyde.



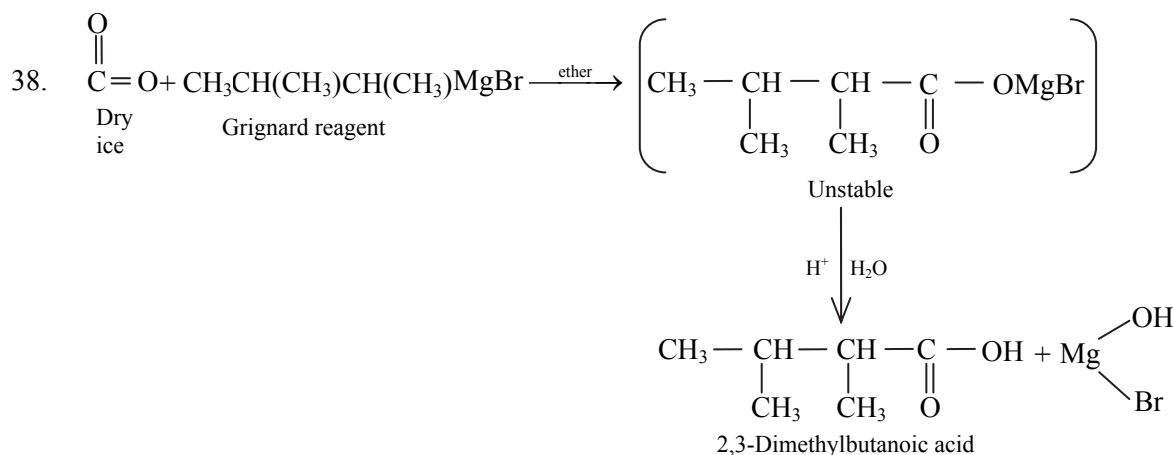
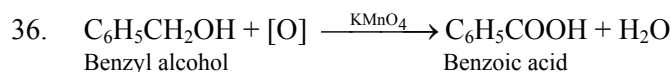
28. Acetone gives mesityl oxide on aldol condensation.
29. Aliphatic monocarboxylic acids are also called as fatty acids because many of them, particularly higher members (eg. palmitic and stearic acids) are obtained from fats.



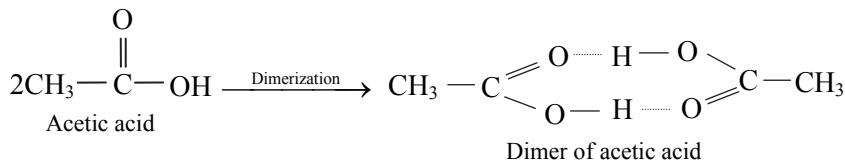
33. Always acid group is given first preference.



iv. A tertiary alcohol is resistant to oxidation in neutral or alkaline solution.



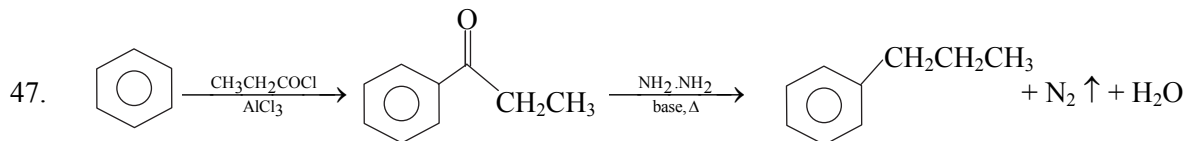
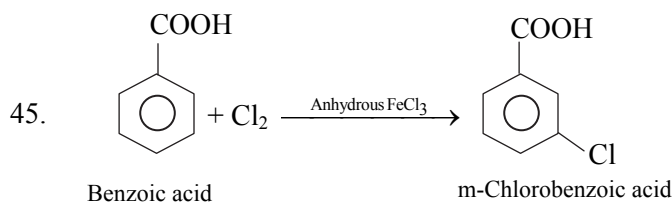
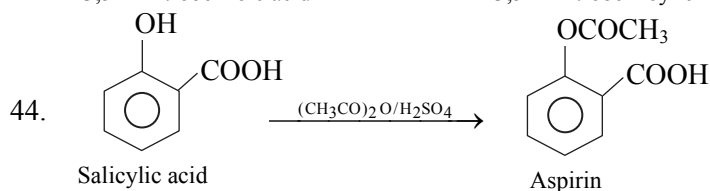
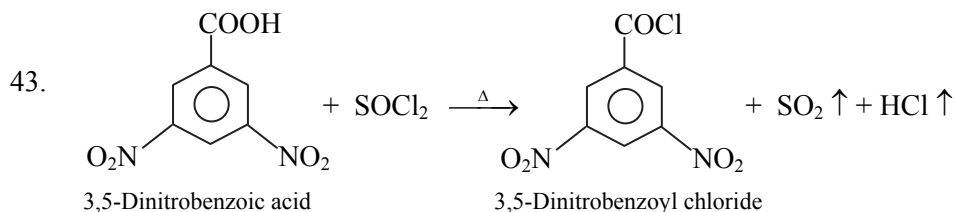
39. Molecular mass increases due to dimer formation.



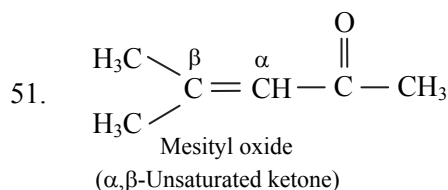
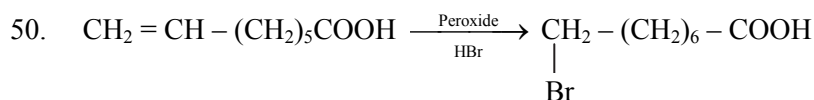
40. All the reactions are showing the acidic property of carboxylic acid. Carboxylic acid forms the sodium salts with all i.e., alkali metals, NaOH and  $\text{Na}_2\text{CO}_3$  etc. and removes the acidic proton from the carboxylic acid.



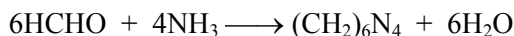
41. Among given options,  $\text{BrCH}_2\text{CH}_2\text{COOH}$  is least acidic or has less  $K_a$  i.e., dissociation constant because in aliphatic carboxylic acids the inductive effect decreases rapidly as the substituents move farther from the carboxyl group.



49. Acetic acid forms dimer in benzene due to which molecular mass becomes double.

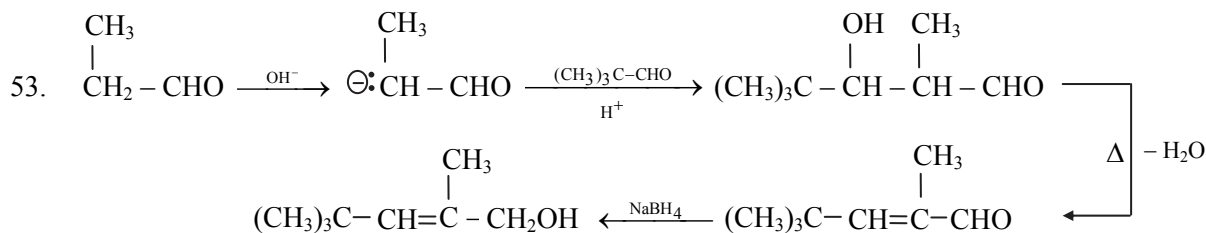


52. Product obtained by dry distillation of calcium formate is formaldehyde which on reacting with  $\text{NH}_3$  yields hexamethylene tetramine or urotropine.



Formaldehyde

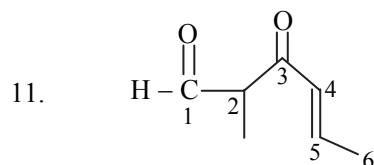
Hexamethylene  
tetramine  
(urotropine)



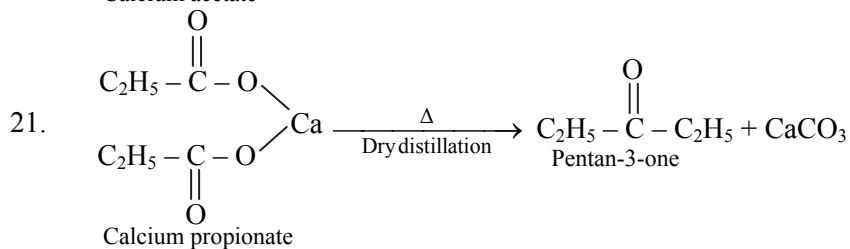
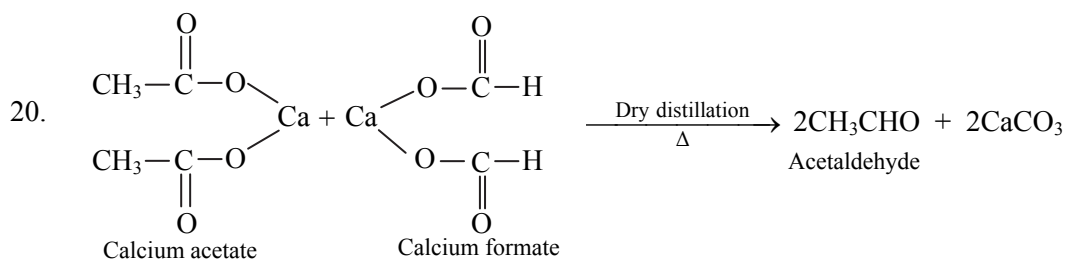
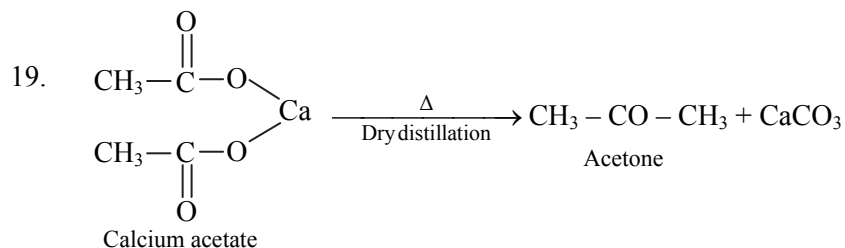
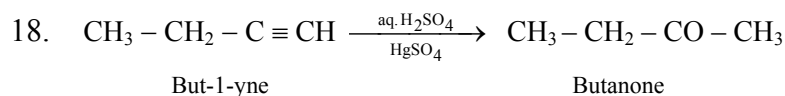
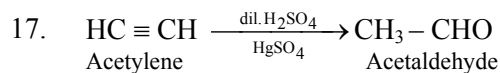
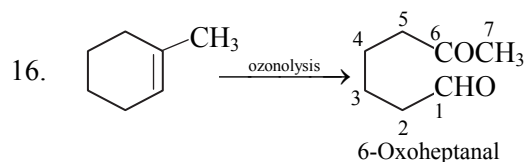
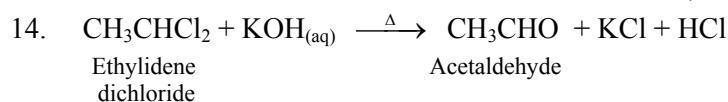
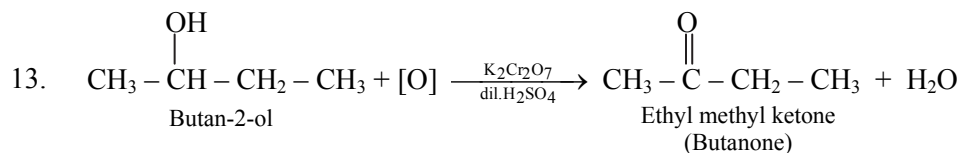
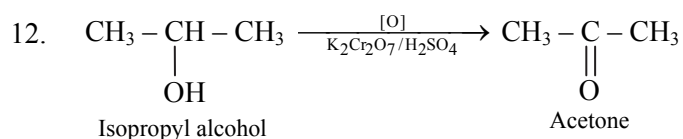
54. Tollen's reagent cannot be used to detect unsaturation. It is used to detect aldehydes like glucose, acetaldehyde etc. To detect unsaturation, bromine water or alkaline  $\text{KMnO}_4$  is used.

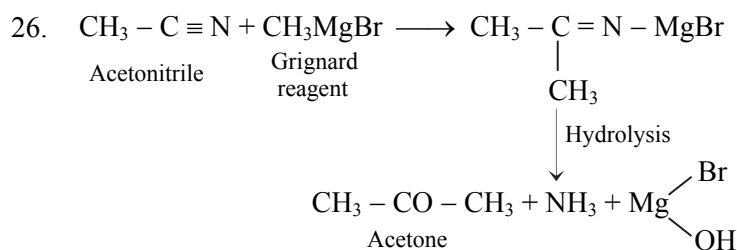
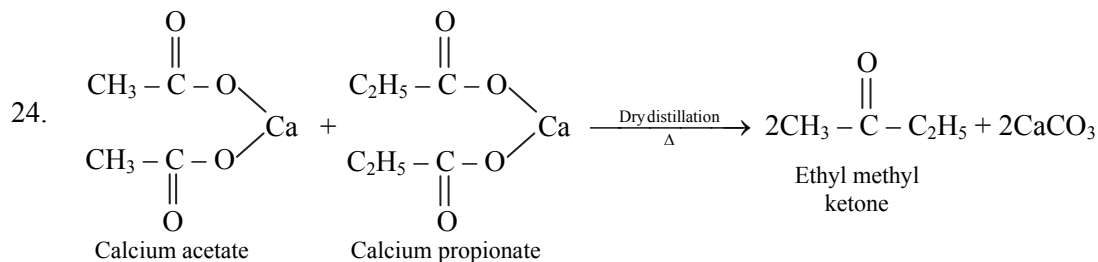
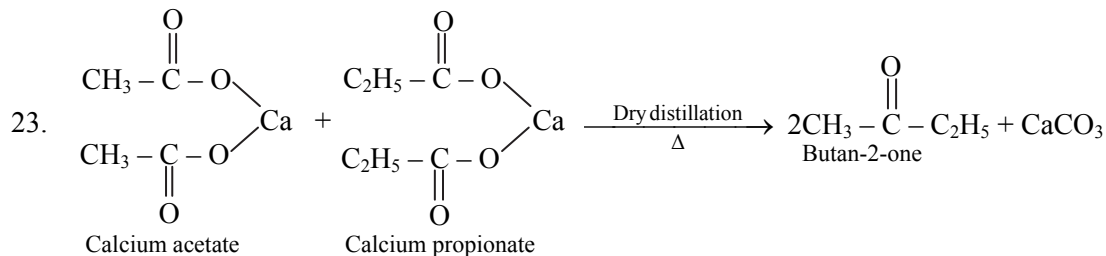
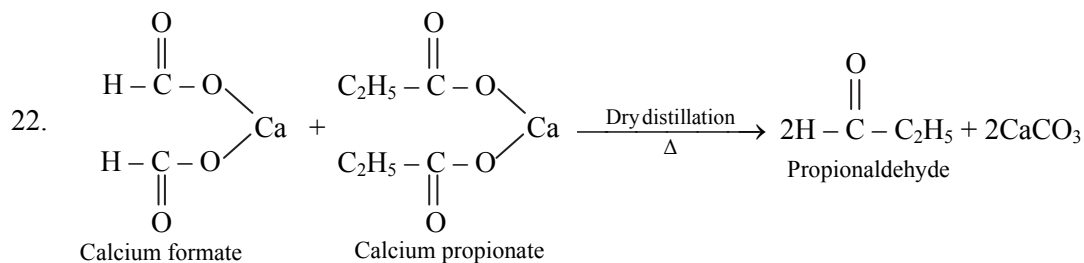






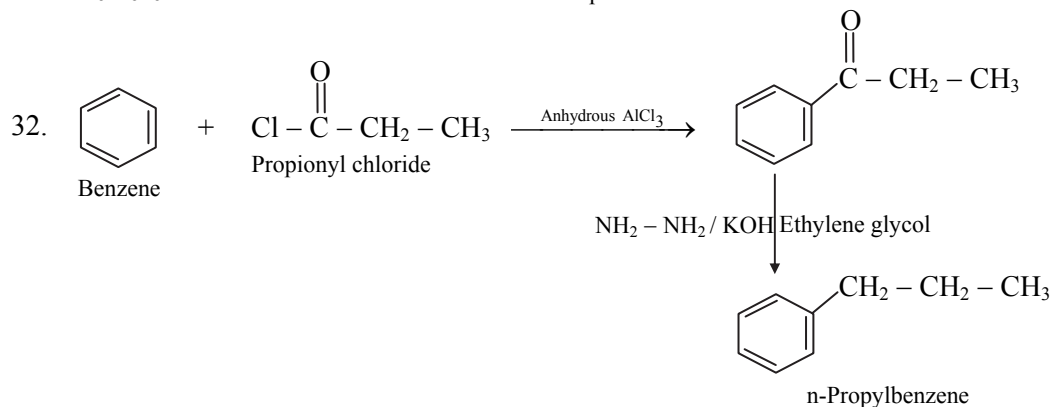
3-Keto-2-methylhex-4-en-1-al

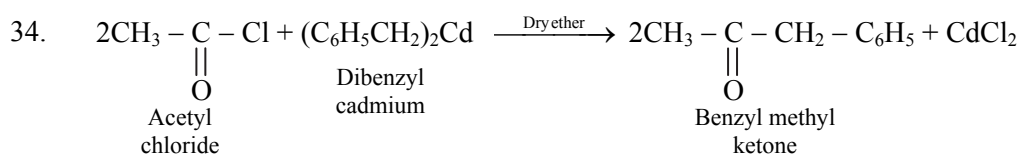
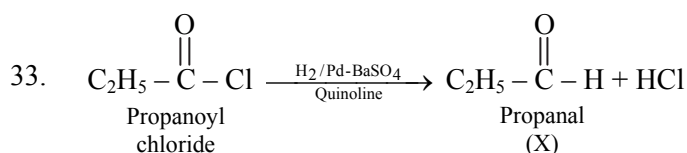




27. DIBAL - H is an electrophilic reducing agent which reduces cyanide, esters, lactone, amide, carboxylic acids, etc. into corresponding aldehyde (partial reduction).

28. In Etard reaction, toluene is oxidised to benzaldehyde by using chromyl chloride ( $\text{CrO}_2\text{Cl}_2$ ) in  $\text{CCl}_4$  or  $\text{CS}_2$ .



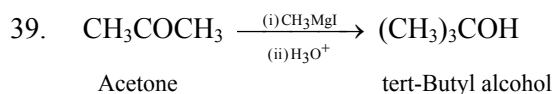


35. The lower members of aldehydes and ketones, i.e., formaldehyde, acetaldehyde and acetone are soluble in water in all proportions because they form hydrogen bonds with water.

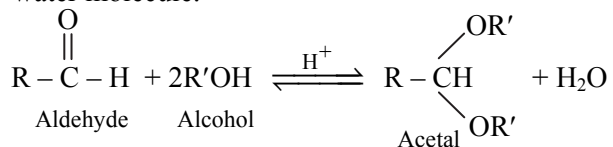
36. Benzaldehyde ( $\text{C}_6\text{H}_5\text{CHO}$ ) is more reactive towards nucleophilic addition than acetophenone ( $\text{C}_6\text{H}_5\text{COCH}_3$ ). Presence of electron withdrawing group like  $-\text{NO}_2$  favours nucleophilic attack.

37. Aldehydes are more reactive than ketones towards nucleophilic addition reaction. The order is  $\text{HCHO} > \text{CH}_3\text{CHO} > \text{CH}_3\text{CH}_2\text{CHO} > \text{CH}_3\text{CH}_2\text{COCH}_2\text{CH}_3$

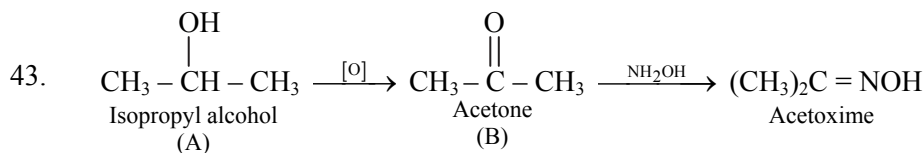
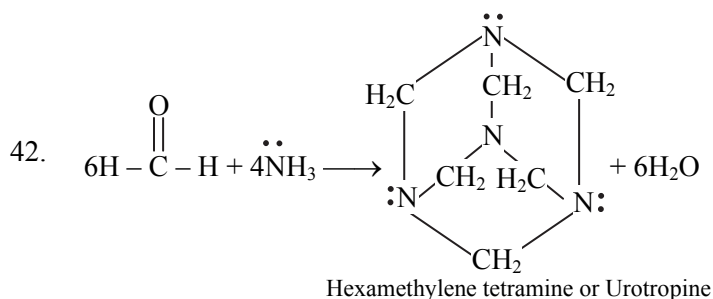
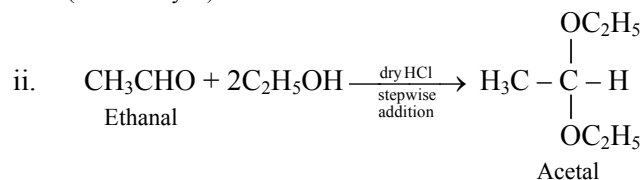
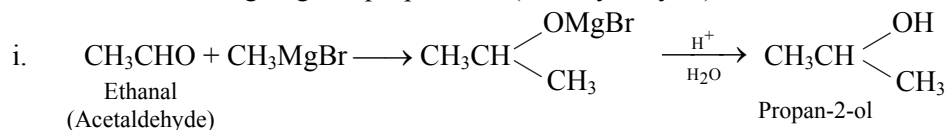
38. Generally in nucleophilic addition reactions, aldehydes are more reactive than ketones due to both steric and electronic reasons. Reaction of aldehydes and ketones with hydrogen cyanide forms corresponding cyanohydrins. It is a reversible reaction and the order of reactivity is formaldehyde  $>$  other aldehydes  $>$  ketones.



40. Two molecules of alcohol are added to carbonyl group of an aldehyde to form acetal by elimination of one water molecule.

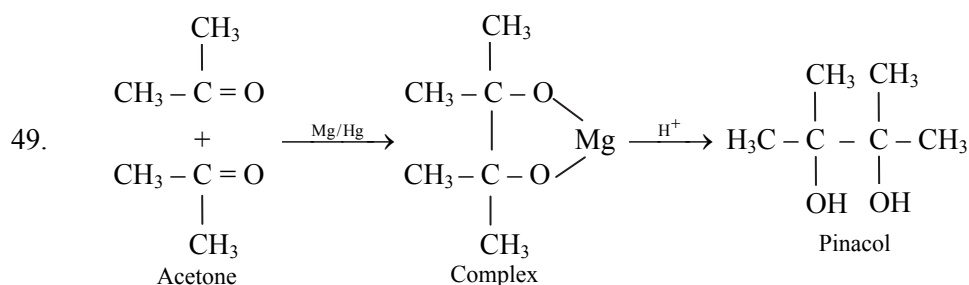
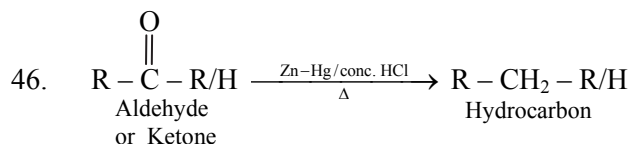
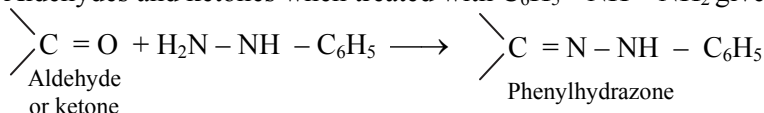


41. Ethanal with  $\text{CH}_3\text{MgBr}$  gives propan-2-ol (after hydrolysis) and with  $\text{C}_2\text{H}_5\text{OH}$ , it gives acetal.

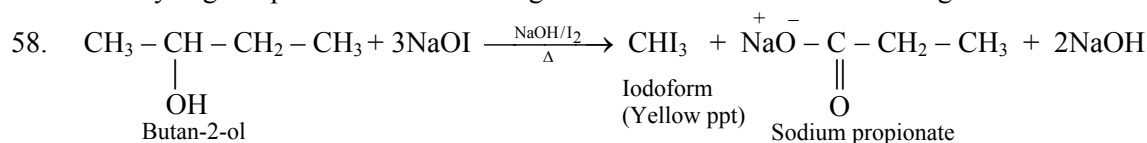




45. Aldehydes and ketones when treated with  $C_6H_5-NH-NH_2$  give phenylhydrazone as follows:



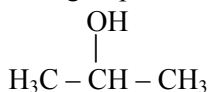
50. Aldehyde gives positive test for Fehling solution whereas ketone does not give the test with Fehling solution.



59. Ketones and secondary alcohols with free methyl group and acetaldehyde give iodoform reaction. Hence,  $C_2H_5 - CH - C_2H_5$  does not give iodoform test.

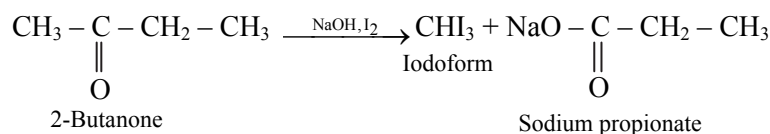


60. Alcohols with formula  $-CH(OH)CH_3$  give positive iodoform test. Acetaldehyde and ketones with at least one  $-CH_3$  group attached to carbonyl carbon will give positive iodoform test. The structure of isopropyl alcohol is,

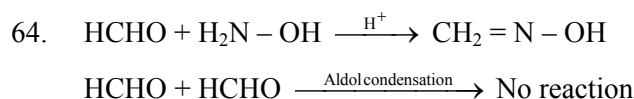
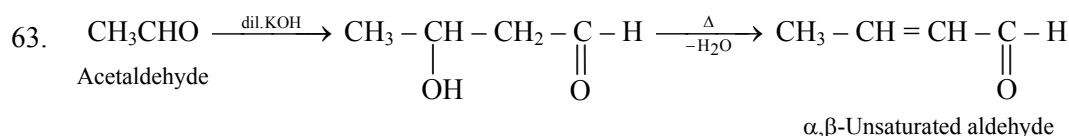
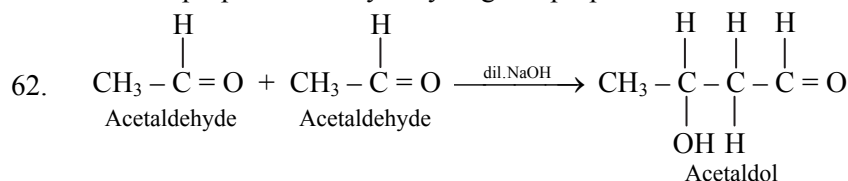


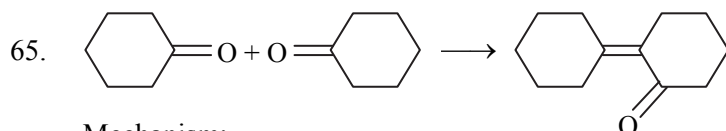
Hence, it gives positive iodoform test.

61. This is an example of haloform reaction.

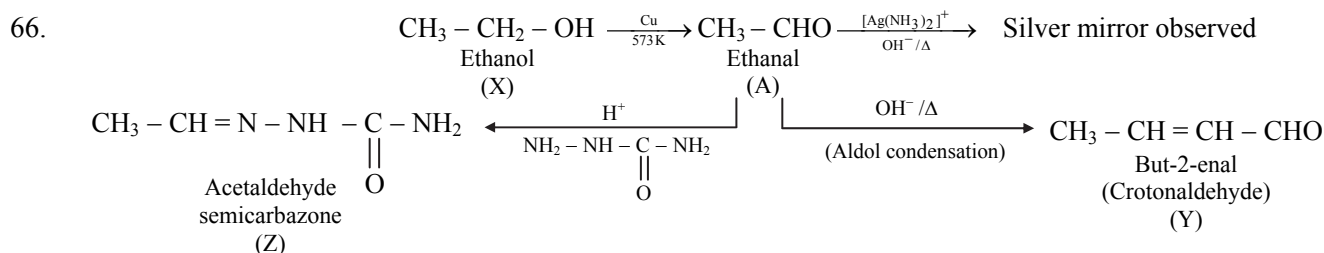
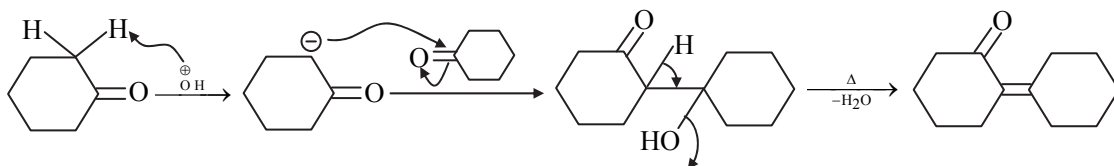


Sodium propionate on hydrolysis gives propanoic acid.

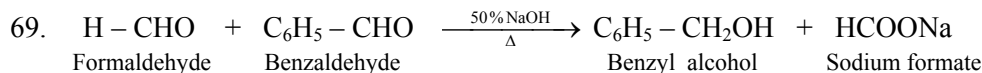




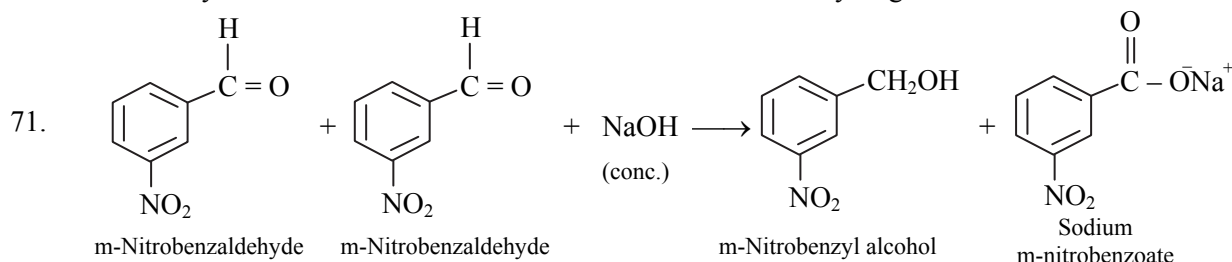
Mechanism:



67. Cannizzaro reaction is given by aldehydes which do not have  $\alpha$ -hydrogen atom.

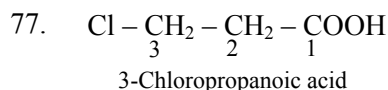
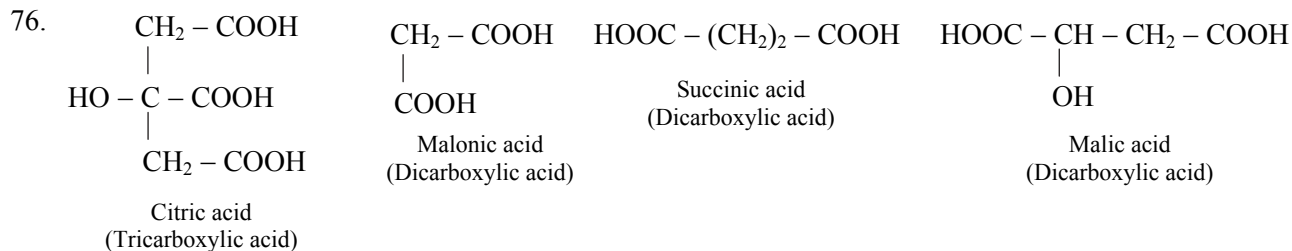
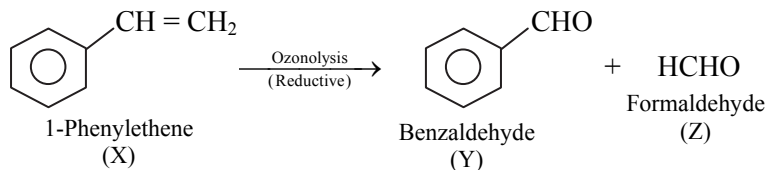


70. Acetaldehyde does not show Cannizzaro's reaction as it has  $\alpha$ -hydrogen atom.



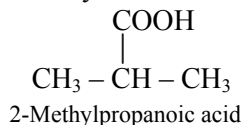
72. Carbonyl compounds containing  $\alpha$ -hydrogen atom undergo self aldol condensation. Hence, among the given options, HCHO does not undergo self aldol condensation.

73. Product of Etard reaction is benzaldehyde. Thus, in the given reaction Y is benzaldehyde. Z undergoes disproportionation reaction with concentrated alkali (i.e., Cannizzaro reaction). Thus, Z can be either benzaldehyde or formaldehyde. Among the given options, only option (B) yields formaldehyde and benzaldehyde as products of its ozonolysis and hence is a correct option.





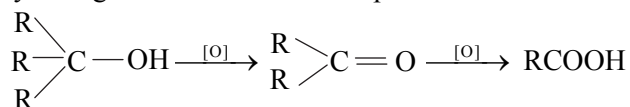
78. Isobutyric acid has structure as,



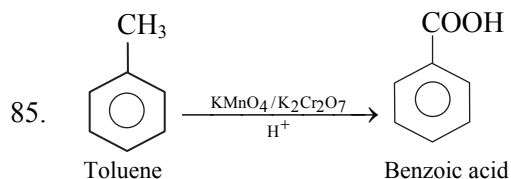
81.  $\text{CH}_3\text{CHO} \xrightarrow[\text{H}_2\text{SO}_4]{\text{K}_2\text{Cr}_2\text{O}_7} \text{CH}_3\text{COOH}$   
Acetaldehyde                      Acetic acid

82.  $\text{C}_2\text{H}_5\text{OH} \xrightarrow{[\text{O}]} \text{CH}_3\text{COOH}$   
Ethanol                      Acetic acid

83. Tertiary alcohols are not oxidised easily but on drastic conditions, these oxidise to give first ketone and then acid by losing one carbon at each step.



84. Aldehydes are easily oxidised to carboxylic acids on treatment with common oxidising agents like nitric acid, potassium permanganate and dichromate, etc.



86.  $\text{CH}_3 - \text{C} \equiv \text{N} + \text{H}_2\text{O} \xrightarrow{\text{Hydrolysis}} \text{CH}_3 - \overset{\text{O}}{\parallel} \text{C} - \text{NH}_2 \xrightarrow[\text{Hydrolysis}]{\text{H}_2\text{O}} \text{CH}_3 - \overset{\text{O}}{\parallel} \text{C} - \text{OH} + \text{NH}_3$   
Acetonitrile                      Acetamide                      Acetic acid

87.  $\text{R} - \text{Mg} - \text{X} \xrightarrow[\text{ether}]{\text{CO}_2} \left[ \text{R} - \overset{\text{O}}{\parallel} \text{C} - \text{OMgX} \right] \xrightarrow[\text{Dil. HCl}]{\text{H}_2\text{O}} \text{R} - \overset{\text{O}}{\parallel} \text{C} - \text{OH} + \begin{array}{c} \text{X} \\ \diagup \\ \text{Mg} \\ \diagdown \\ \text{OH} \end{array}$   
Grignard reagent                      Carboxylic acid

88.  $\text{C}_6\text{H}_5\text{MgBr} \xrightarrow[\text{(ii) H}_3\text{O}^+]{\text{(i) CO}_2} \text{C}_6\text{H}_5\text{COOH}$

89.  $\text{CO}_2 + \text{C}_3\text{H}_7\text{MgBr} \xrightarrow{\text{Hydrolysis}} \text{C}_3\text{H}_7\text{COOH} + \text{Mg} \begin{array}{c} \text{Br} \\ \diagup \\ \text{OH} \end{array}$

90. Addition of Grignard reagent increases the number of carbon atom by one. Methanoic acid (HCOOH) has only one carbon atom. Hence, it cannot be prepared using Grignard reagent and carbon dioxide.

92. Vinegar is 6 – 8% aqueous solution of acetic acid.

93. Acetic acid freezes at 16.6 °C while water freezes at 0 °C. So glacial acetic acid is obtained by crystallizing, separating and melting acetic acid.

94.  $\text{CH}_3\text{COOH} + \text{NaHCO}_3 \longrightarrow \text{CH}_3\text{COONa} + \text{H}_2\text{O} + \text{CO}_2 \uparrow$

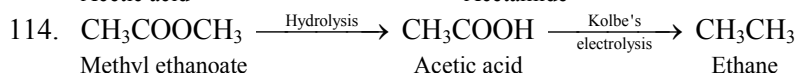
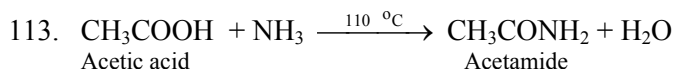
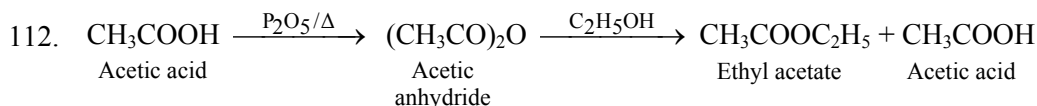
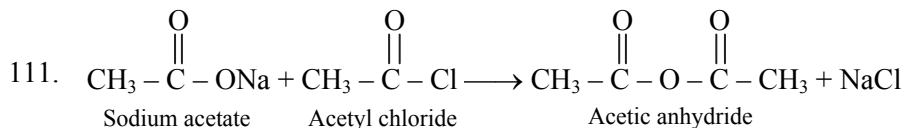
95.  $\text{CH}_3 - \text{CH}_2 - \overset{\text{O}}{\parallel} \text{C} - \text{OH} + \text{NaHCO}_3 \longrightarrow \text{CH}_3 - \text{CH}_2 - \overset{\text{O}}{\parallel} \text{C} - \text{O}^- \text{Na}^+ + \text{H}_2\text{O} + \text{CO}_2 \uparrow$   
Propionic acid                      Sodium bicarbonate                      Sodium propanoate

The C-atom of the evolved  $\text{CO}_2$  gas comes from sodium bicarbonate ( $\text{NaHCO}_3$ ).

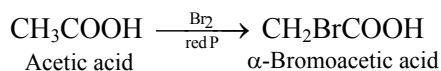




109. Correct order of reactivity is  
 $\text{CH}_3\text{CH}_2\text{COOH} > (\text{CH}_3)_2\text{CHCOOH} > (\text{C}_2\text{H}_5)_2\text{CHCOOH} > (\text{CH}_3)_3\text{CCOOH}$



115. When  $\text{Cl}_2$  or  $\text{Br}_2$  reacts with carboxylic acid in the presence of red phosphorus then  $\alpha$ -hydrogen of carboxylic acid is replaced by Cl or Br.



This reaction is known as Hell-Volhard-Zelinsky reaction.

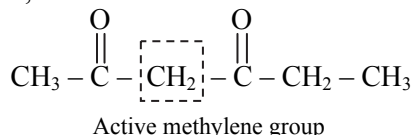
116. Acetic acid is a chief constituent of vinegar.

117. Formic acid,  $\text{HCOOH}$  shows reducing property.

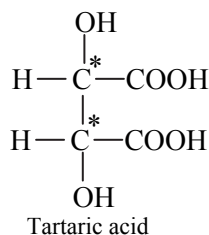
118. Acetylene first gives acetaldehyde which on aldol condensation gives product i.e., option (D).

120. Presence of electronegative  $-\text{Cl}$  group, increases the electrophilicity of carbonyl group.

121. 2,4-Hexanedione contains active methylene group, hence it contains most acidic hydrogen:



122. Tartaric acid has the chiral carbon (marked by asterisk) atom (\*). Hence it is optically active.

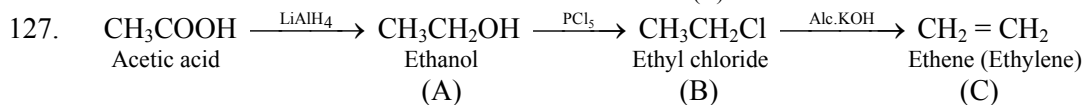
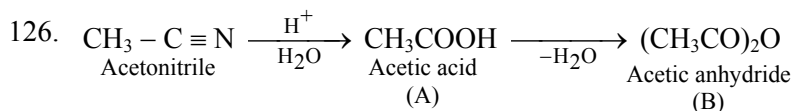


124. The order of reactivity of acid derivatives towards different reactions decreases in the order,  
 $\text{RCOCl} > (\text{RCO})_2\text{O} > \text{RCOOR}' > \text{RCONH}_2$

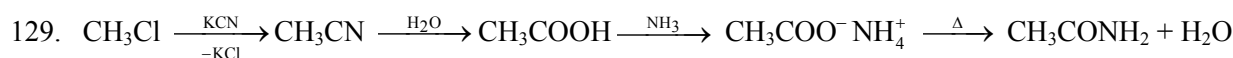
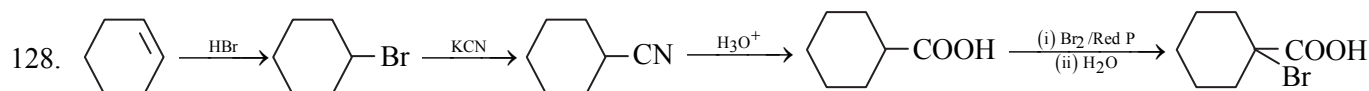
In other words, the reactivity decreases as the basicity of the leaving group increases i.e.,  
 $\text{Cl}^- < \text{RCOO}^- < \text{RO}^- < \text{NH}_2^-$

i.e.,  $\text{Cl}^-$  is good leaving group whereas  $\text{NH}_2^-$  is poor leaving group.

125. Esters have fruity odour.

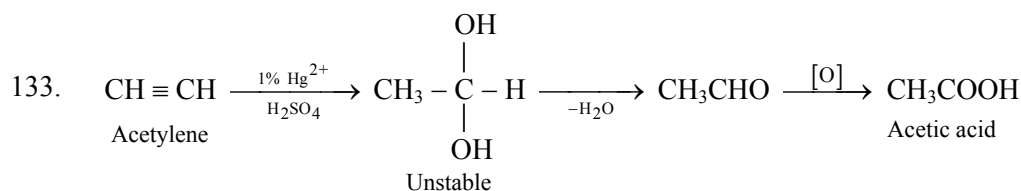
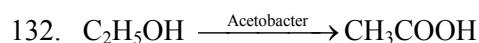
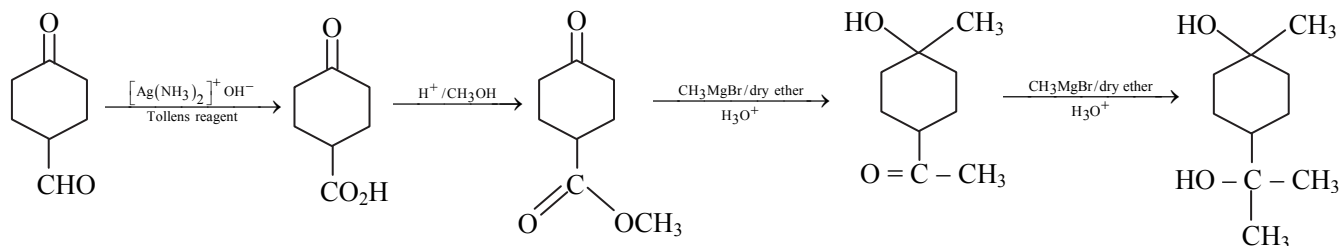




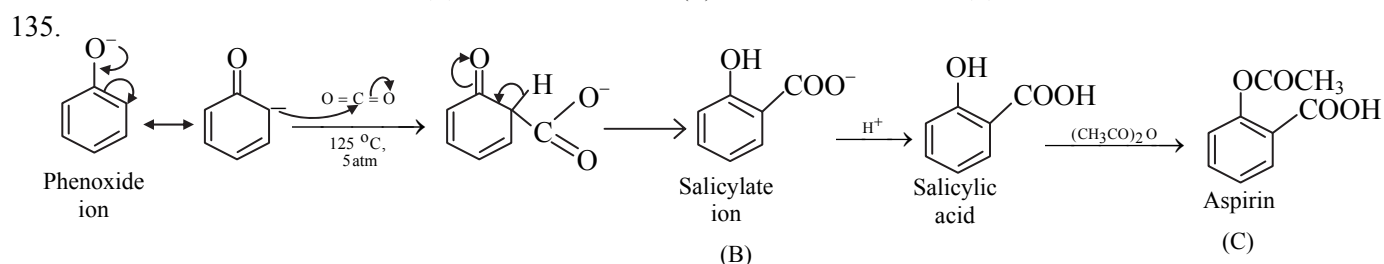
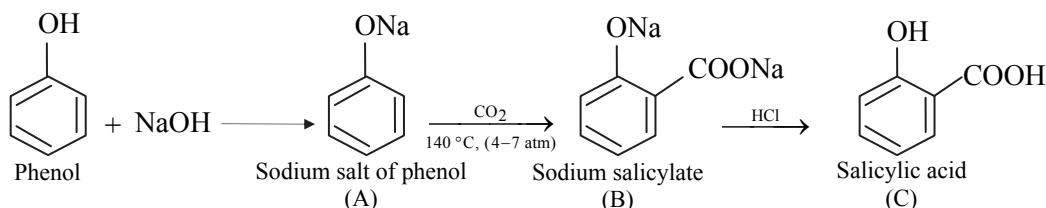


130. Amide, on treating with  $\text{HNO}_2$ , give acids.

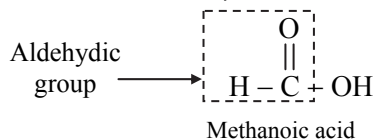
131.



134. Treatment of sodium salt of phenol with  $\text{CO}_2$  under pressure bring about substitution of the carbonyl group  $-\text{COOH}$ , for the hydrogen of the ring. This is called as Kolbe's reaction.

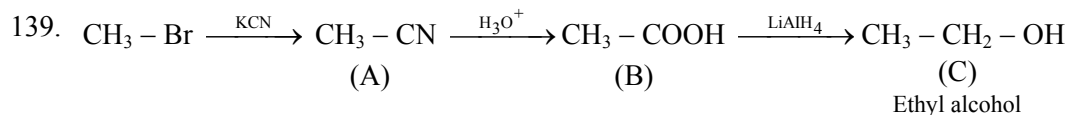


136. In methanoic acid, there is an aldehydic group present.

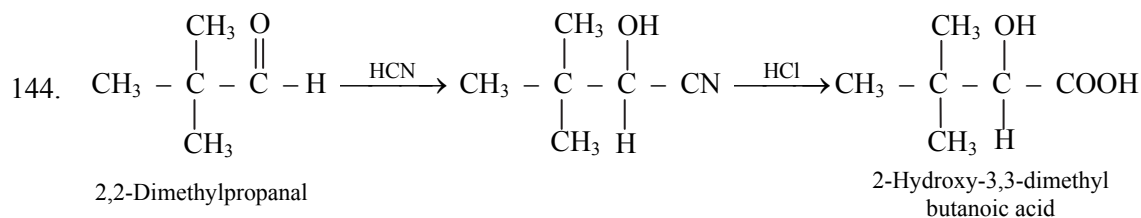
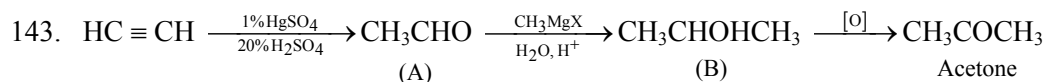
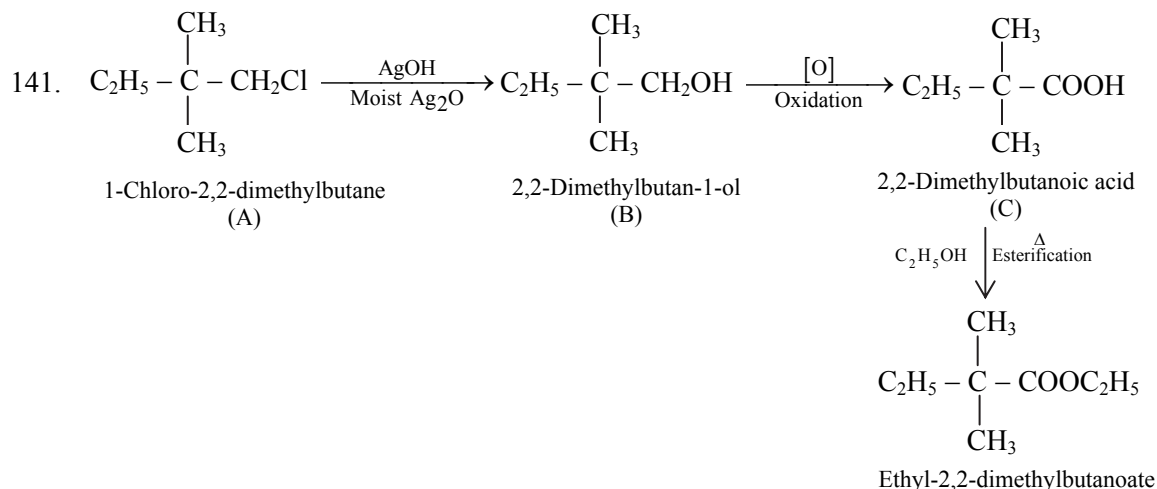
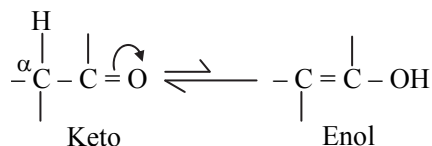


Hence, methanoic acid ( $\text{HCOOH}$ ) reduces ammoniacal silver nitrate solution, i.e., Tollen's reagent but ethanoic acid ( $\text{CH}_3\text{COOH}$ ) does not.

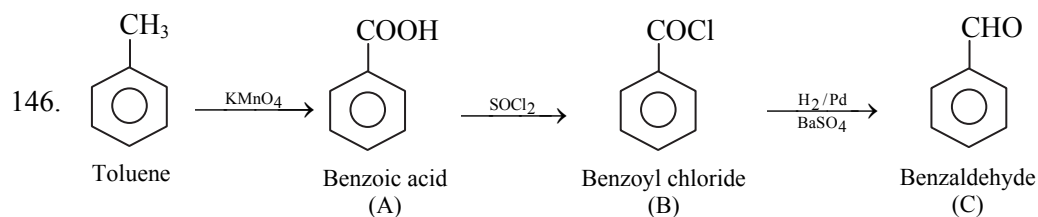
137. Acetic acid reacts with  $\text{FeCl}_3$  to form a red coloured complex along with  $\text{HCl}$  which interfere with each other. Higher acidity can interfere in the result and hence, it should be made neutral before performing the test with  $\text{FeCl}_3$  solution. Usually,  $\text{NaOH}$  is used to neutralize the acid yielding sodium acetate and water.



140. Keto-enol tautomerism is represented as:



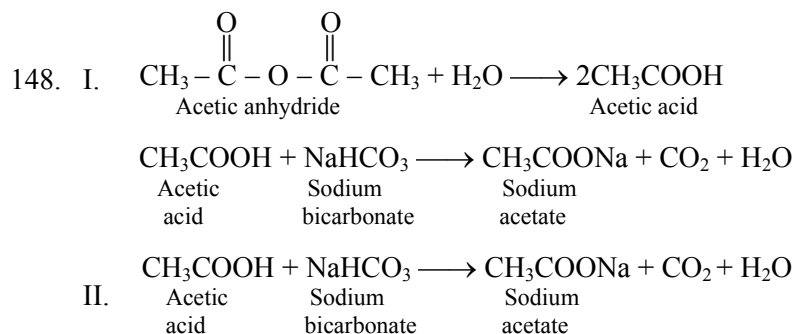
145. Methyl salicylate occurs in natural essential oils like winter green.



147.

	Option	Will not be compound 'X' because
(A)	Pentanal	it will give positive Tollen's test
(B)	Pentan-2-one	will give positive iodoform test as its a methyl ketone
(D)	n-Amyl alcohol	(i) will not yield phenyl hydrazone due to absence of carbonyl group (ii) will not yield n-pentane as a product on its reduction

Thus, only option (C) satisfies all the given conditions and hence is the correct answer.

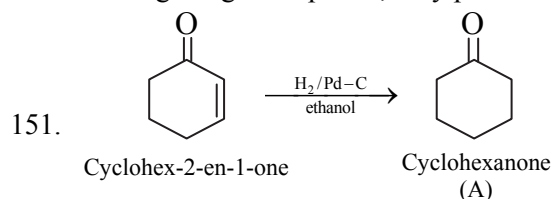


149.

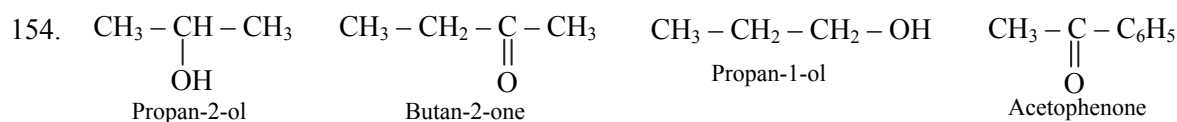
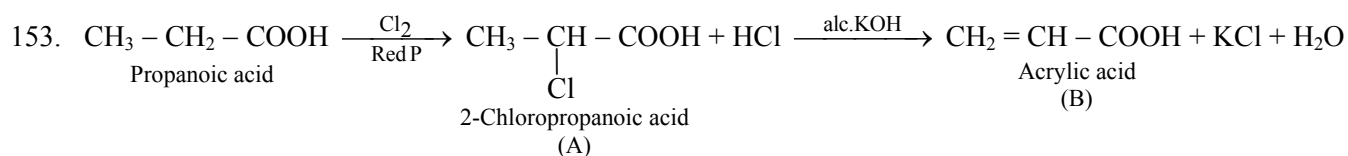
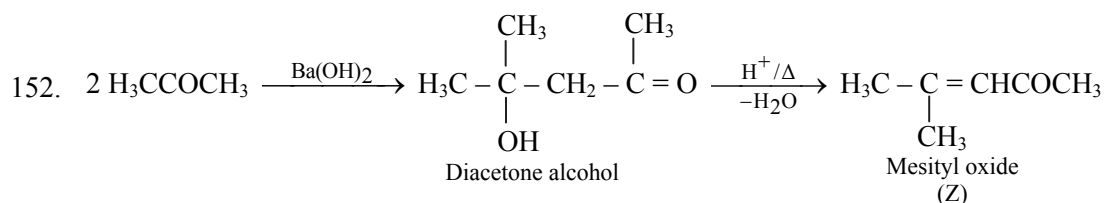
Compound	Structure
Ethanoic acid	$\text{CH}_3 - \text{COOH}$
Picric acid	

Compound	Structure
Benzoic acid	
Salicylic acid	

Among the given options, only picric acid does not have  $-\text{COOH}$  group.



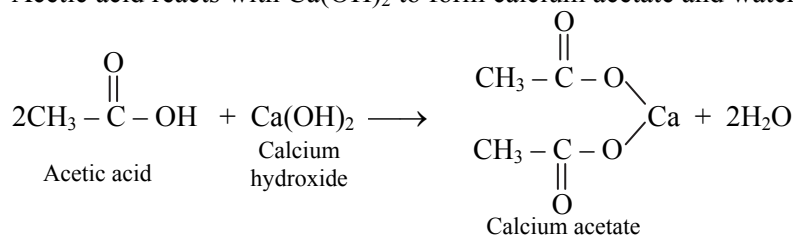
In this reaction, selective reduction of  $\text{C} = \text{C}$  double bond takes place.



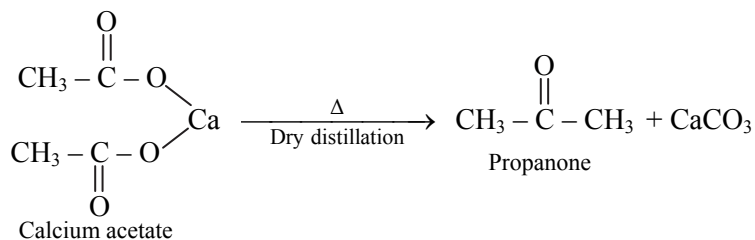
Methyl ketones and alcohols having structure  $\text{R}-\text{CH}(\text{OH})\text{CH}_3$  where R may be hydrogen, methyl group or aryl group forms iodoform. Thus, among the given options, propan-1-ol cannot be used to prepare iodoform.



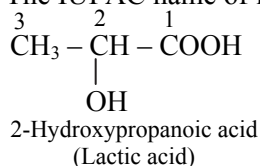
155. Acetic acid reacts with  $\text{Ca}(\text{OH})_2$  to form calcium acetate and water.



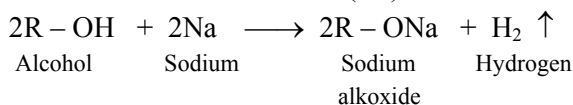
Calcium acetate on dry distillation gives propanone.



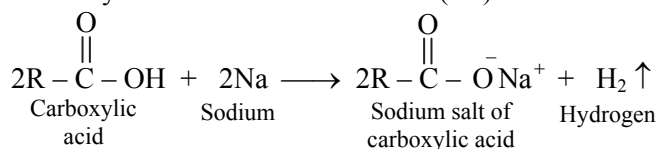
156. The IUPAC name of lactic acid is 2-hydroxypropanoic acid.



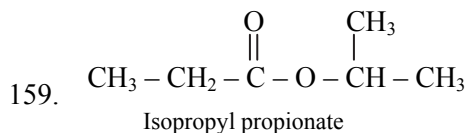
157. Alcohols react with sodium (Na) metal to form corresponding sodium alkoxides liberating hydrogen gas.



Carboxylic acids react with sodium (Na) metal to form corresponding sodium salts liberating hydrogen gas.



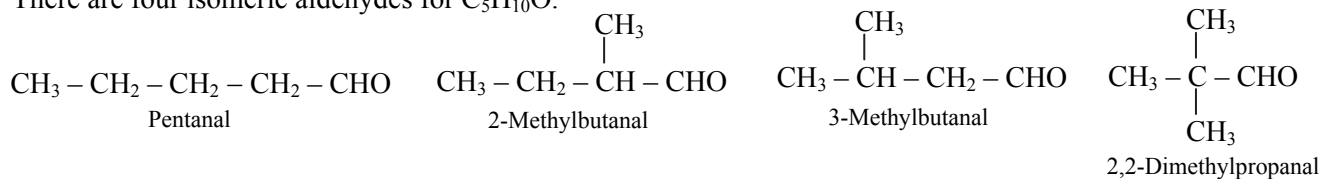
Thus, among the given options, only  $\text{CH}_3 - \text{O} - \text{CH}_3$  (an ether) does not react with sodium.

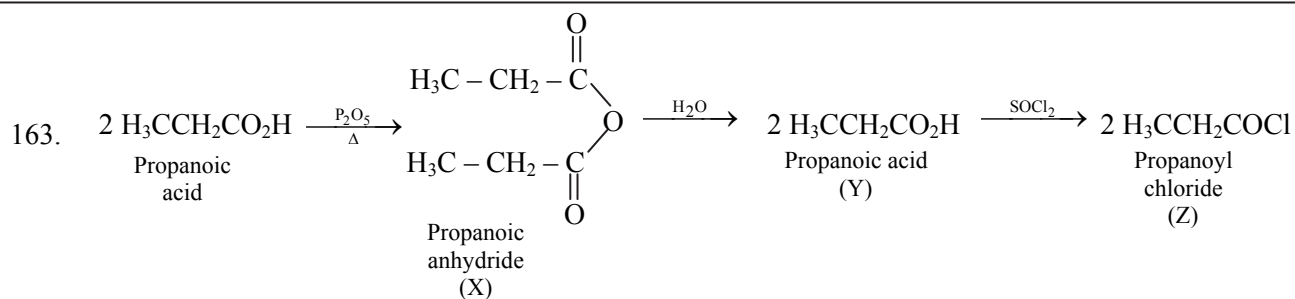


There are six C-atoms in isopropyl propionate.

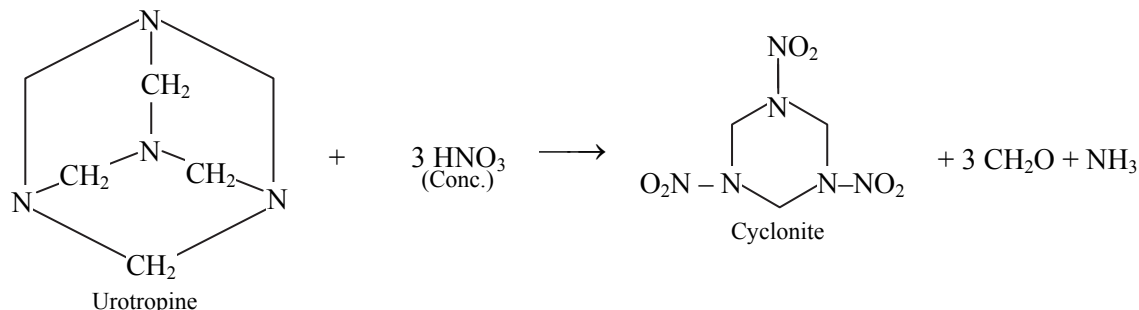
160.  $(\text{CH}_3)_2\text{CO}$  does not have hydrogen atom directly attached to carbonyl carbon atom. Hence, it does not react with Fehling's solution.

161. There are four isomeric aldehydes for  $\text{C}_5\text{H}_{10}\text{O}$ .





165. Urotropine reacts with conc.  $\text{HNO}_3$  to give explosive cyclonite (RDX).



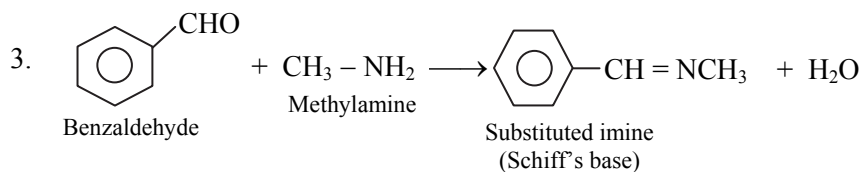
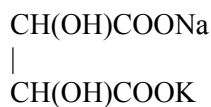
166. The given organic compound,  $\text{C}_3\text{H}_6\text{O}$  is neither a carbonyl compound (does not give test for hydrazine) nor an alcohol (does not react with sodium) and thus, it may be ether.



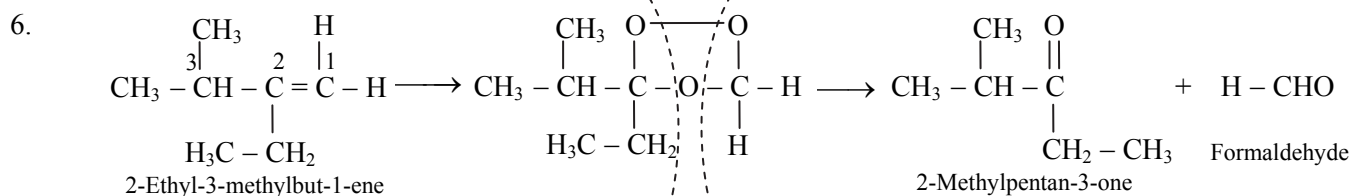
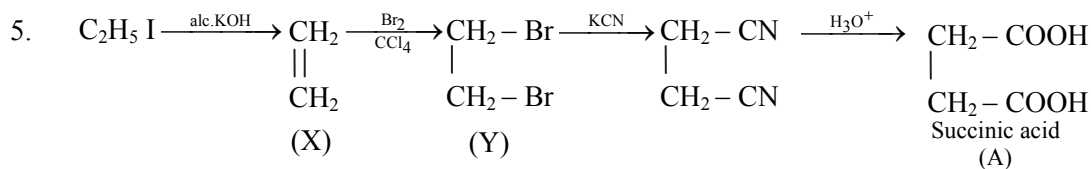
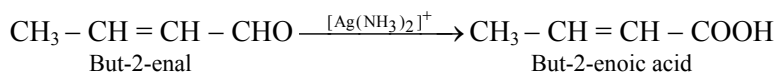
### Evaluation Test

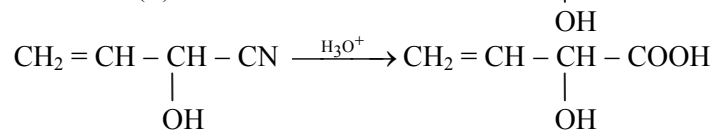
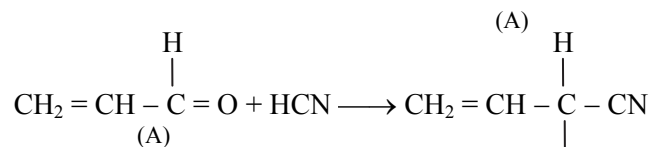
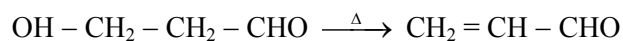
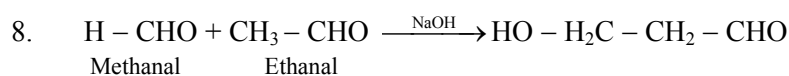
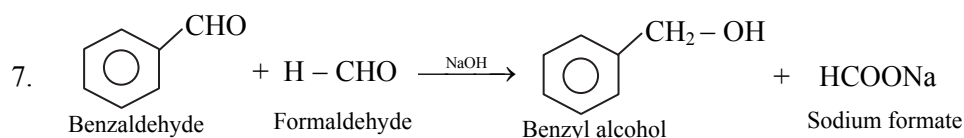
1. For keto-enol tautomerism the presence of  $\alpha$  hydrogen atom is required. In benzoquinone, hydrogen atom is bonded to  $\text{sp}^2$  hybridised C-atom, which is difficult to ionise.

2. Fehling's solution consists of  $\text{CuSO}_4$  mixed with Rochelle salt i.e., sodium potassium tartrate.



4. Tollen's Reagent oxidises only  $-\text{CHO}$  group to  $-\text{COOH}$  group.

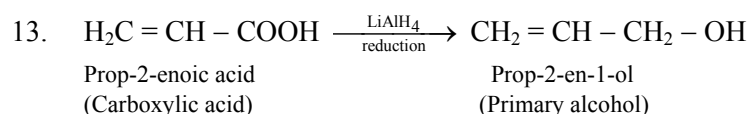
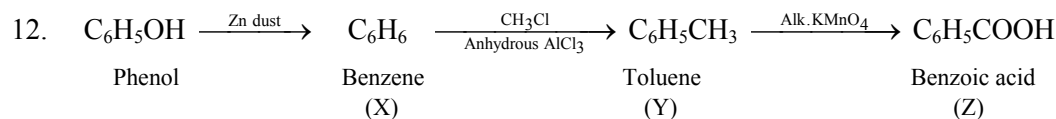
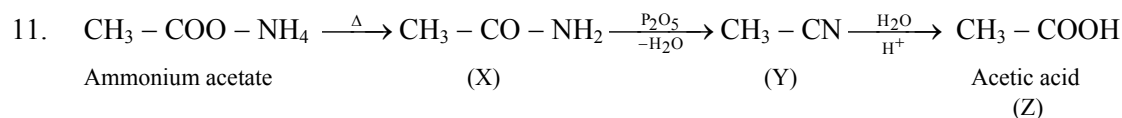




2-Hydroxybut-3-enoic acid  
(B)

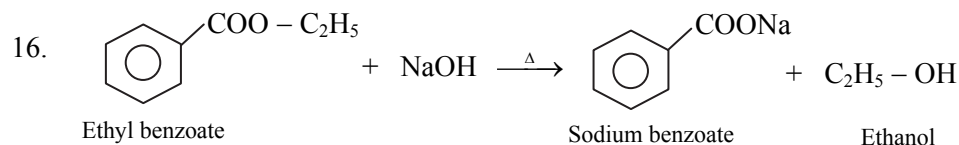
9. Addition of HCN to carbonyl compounds is a nucleophilic addition. The lower reactivity of ketones over aldehydes is due to +I effect of the alkyl group and steric hindrance. The aromatic aldehydes and ketones are less reactive than their aliphatic analogues.

10. -COOH is m-directing and electron withdrawing group.



14. H-COOH is the strongest acid among the given set of acids, hence it has lower pK<sub>a</sub> value.

15. Acid derivatives have electron deficient carboxylic carbon but there is no electron deficient site in ethers.

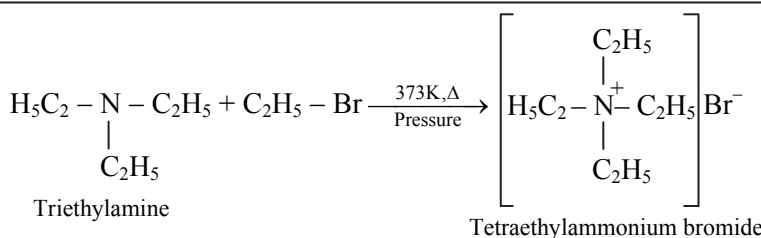


17. The smallest ketone is acetone which being a symmetrical ketone forms only one oxime. The next homologue of acetone, being butanone forms two oximes i.e., cis and trans butanone oxime, as it is an unsymmetrical ketone. Thus, in all there are three oximes formed.

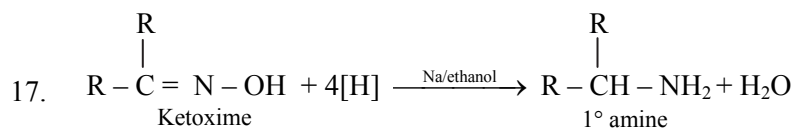
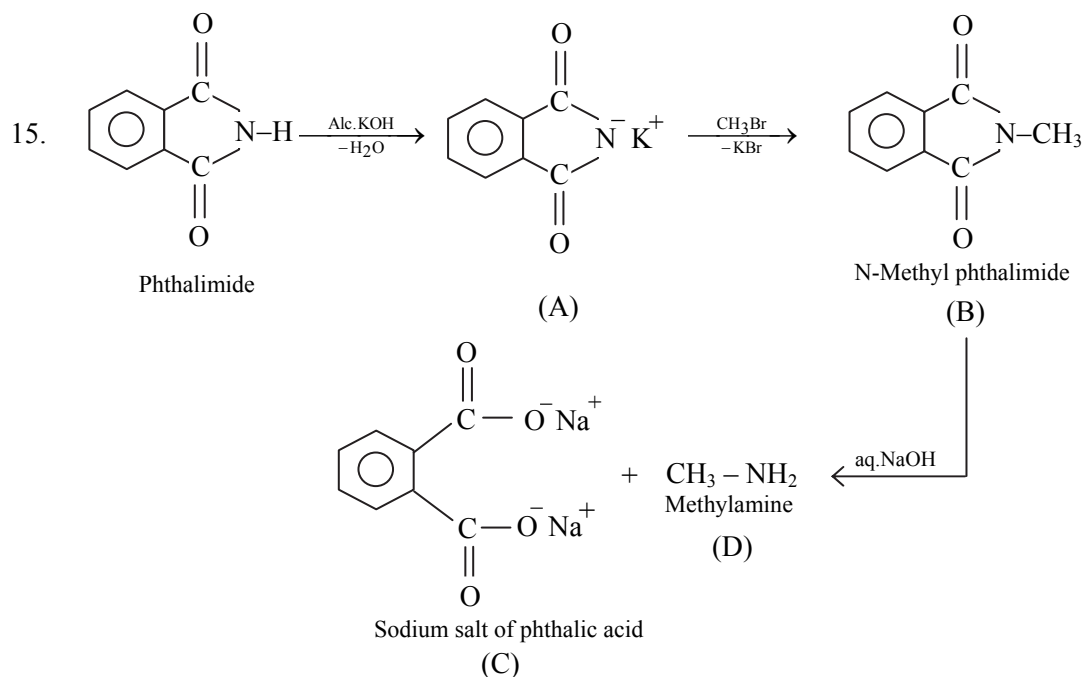
18. For cross Cannizzaro reaction, both the aldehydes must not have α-hydrogen. Hence, C<sub>6</sub>H<sub>5</sub>CHO and HCHO.

19. NH<sub>3</sub> gives urotropine on reacting with HCHO, CH<sub>3</sub>CH=NH with acetaldehyde and diacetone amine on reacting with acetone.

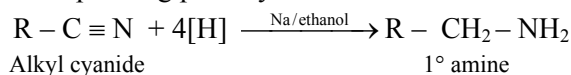




14. Three molecules of methyl bromide react with ethylamine to give quaternary ammonium salt.



19. Mendius reduction: Alkyl cyanides or cyanoalkanes on reduction by sodium and ethanol give corresponding primary amine.



21. Aliphatic amines having upto six C-atoms are soluble in water due to formation of H-bonds. However, solubility decreases with increase in molar mass.
23. Primary and secondary amines are associated by intermolecular hydrogen bonds. The association is more in primary amines than that in secondary amines as there are two hydrogen atoms on nitrogen. Tertiary amines cannot form intermolecular hydrogen bonds due to absence of hydrogen atoms on nitrogen. Hence, the order of boiling points is  $1^\circ > 2^\circ > 3^\circ$ .
24. The order of boiling point is  $1^\circ > 2^\circ > 3^\circ$  for isomeric amines. Ethylamine and propan-1-amine are primary amines, ethylmethylamine is a secondary amine while N,N-dimethylmethanamine is a tertiary amine. Hence N,N-dimethylmethanamine has the lowest boiling point.
26. Nitrogen atom of  $-\ddot{\text{N}}\text{H}_2$  group carries a lone pair of electrons in its hybrid orbital. They have a tendency to donate this lone pair of electrons to the electron deficient compounds and, therefore, behave as bases.
27. Aqueous solutions of amines are basic in nature and thus they turn red litmus paper into blue.

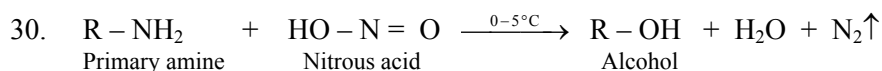




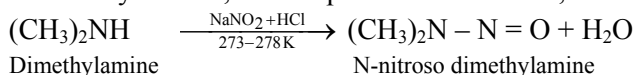
28. Since alkyl groups are electron releasing, electron density on the nitrogen atom is increased and alkylamines are more basic than ammonia. As a result, the basic character should decrease in the order,  $3^\circ$  amine  $>$   $2^\circ$  amine  $>$   $1^\circ$  amine. But due to the combined effect i.e., inductive effect (+I), steric hindrance and solvation of ions, the basicity decreases in the order,  $2^\circ$  amine  $>$   $1^\circ$  amine  $>$   $3^\circ$  amine  $>$   $\text{NH}_3$  for lower aliphatic amines.

29. Higher the value of  $K_b$ , stronger is the base and also due to the combined effect i.e., inductive effect (+I) and steric hindrance, the basicity decreases in the order,  $2^\circ$  amine  $>$   $1^\circ$  amine  $>$   $3^\circ$  amine  $>$   $\text{NH}_3$  for lower aliphatic amines.

$\therefore$  Among the given options, dimethylamine is the strongest base.

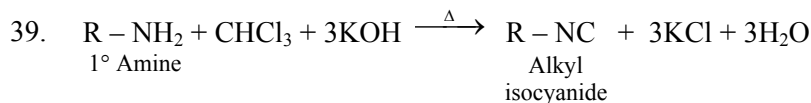
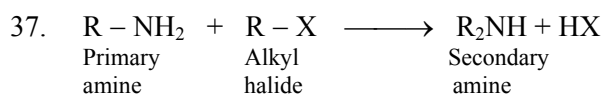
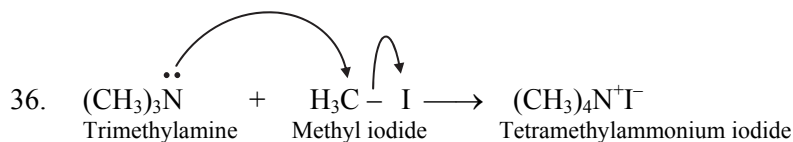


31. Secondary amines, both aliphatic and aromatic, react with nitrous acid to give yellow oily N-nitroso amines.

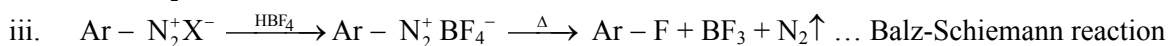
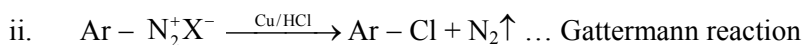
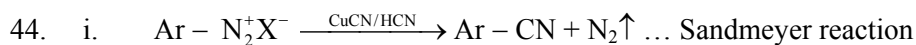


32. Acetylation of tertiary amines is not possible due to non-availability of replaceable hydrogen atom hence can be distinguished with primary as well as secondary amines.

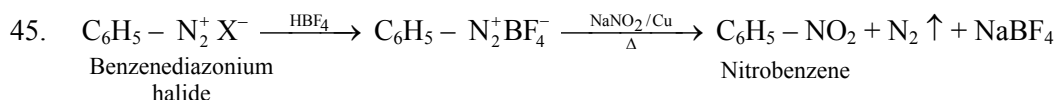
34. Due to availability of only one replaceable H-atom, secondary amines produce only monoacetyl derivatives on acetylation.



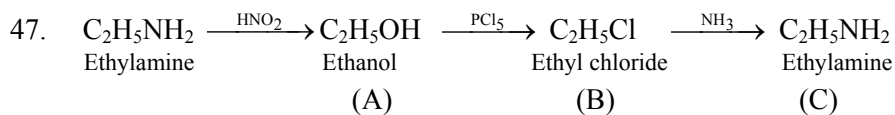
Secondary or tertiary amines do not give this test.



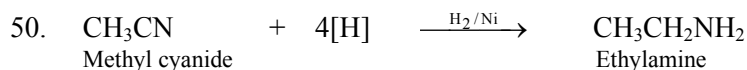
iv. Clemmensen's reduction does not involve diazonium salt.



46. Aromatic compounds do not undergo nucleophilic substitution reaction easily but nucleophile can easily be introduced by using diazonium salt.



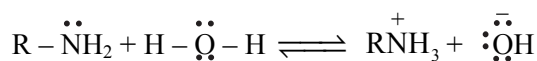
48. The basic strength of amines depend on the number of alkyl or aryl groups attached to the N-atom of the amine.



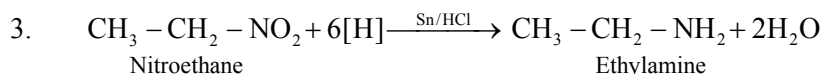
Cyanides on reduction give higher amines.



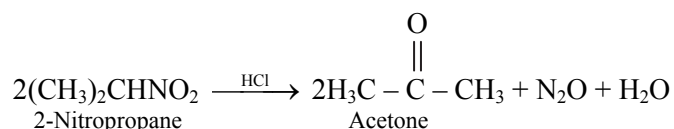
51. Nitroso compounds are water insoluble yellow oily liquids.
52. Tertiary amines do not undergo substitution reaction since there are no replaceable hydrogen atoms.
53. Amines react reversibly with water to form alkyl substituted ammonium ion and hydroxide ion.

**Critical Thinking**

1. Nitroalkanes are considered as the derivatives of alkanes in which one or more hydrogen atoms are replaced by nitro group (-NO<sub>2</sub>).



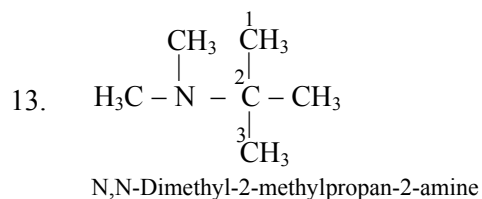
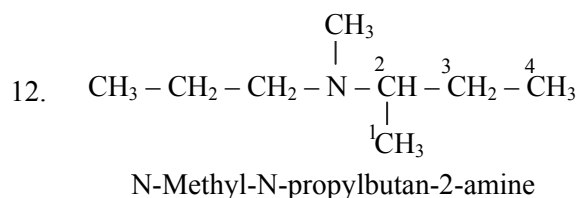
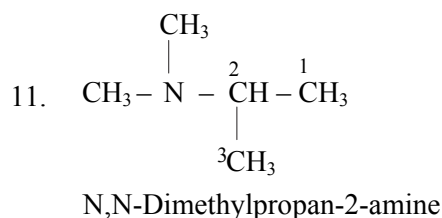
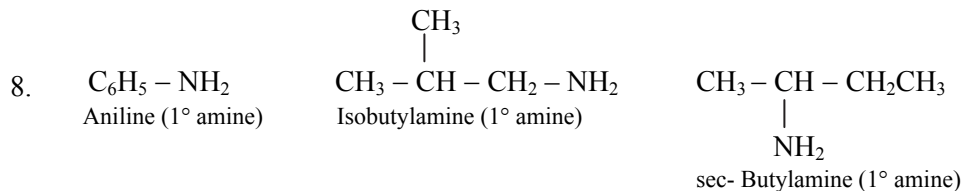
4. Secondary nitroalkanes on boiling with hydrochloric acid form corresponding ketones and nitrous acid.



5. Primary nitroalkanes react with nitrous acid to form blue coloured nitroso-nitroalkanes (aci form) which dissolves in sodium hydroxide to give red solution.

Secondary nitroalkanes react with nitrous acid to give blue coloured nitroso-nitroalkanes, which no more contain replaceable α-hydrogen atom, thereby are insoluble in water as well as in alkali.

Tertiary nitroalkanes do not react with nitrous acid because there is no replaceable α-hydrogen atom on the carbon atom carrying the -NO<sub>2</sub> group.



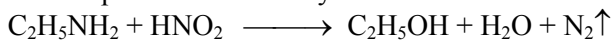


15.  $RX + alc. NH_3 \xrightarrow[sealed\ tube]{100\ ^\circ C} R - NH_2 + HX$   
 Alkyl (Excess) halide  $\quad\quad\quad$   $1^\circ$  amine (Y)
16.  $CH_3CH = NOH + 4[H] \xrightarrow{Na/alc.} CH_3CH_2NH_2 + H_2O$   
 Acetaldoxime  $\quad\quad\quad$  Ethylamine (primary amine)
17.  $Sn + 2HCl \longrightarrow SnCl_2 + 2[H]$   
 $C_6H_5NO_2 + 6[H] \xrightarrow[\Delta]{Sn+HCl} C_6H_5NH_2 + 2H_2O$   
 Nitrobenzene  $\quad\quad\quad$  Aniline
18. (A)  $R - C \equiv N + 4[H] \xrightarrow{Pt} R - CH_2 - NH_2$   
 Alkyl cyanide  $\quad\quad\quad$  Primary amine
- (B)  $\begin{array}{c} H \\ | \\ R - C = N - O - H \end{array} + 4[H] \xrightarrow{LiAlH_4} R - CH_2 - NH_2 + H_2O$   
 Aldoxime  $\quad\quad\quad$  Primary amine
- (C)  $\begin{array}{c} O \\ // \\ R - N \\ \searrow \\ O \end{array} + 6[H] \xrightarrow[\Delta]{Sn+conc.HCl} R - NH_2 + 2H_2O$   
 Nitroalkane  $\quad\quad\quad$  Primary amine
- (D)  $Alkene + H_2 \xrightarrow[\Delta]{Raney\ Ni} Alkane$
19.  $CH_3 - CO - NH_2 \xrightarrow[Hoffmann's\ bromamide\ degradation]{NaOH/Br_2} CH_3 - NH_2$   
 Acetamide (Amide)  $\quad\quad\quad$  Methylamine (Amine)
21. The order of boiling point is  $1^\circ > 2^\circ > 3^\circ$  for isomeric amines.  
 $\therefore$  The correct order for given amines is  
 n-Propylamine > ethylmethylamine > trimethylamine
22.  $R - NH_2 + HO - N = O \xrightarrow[273K-278K]{NaNO_2+HCl} R - OH + H_2O + N_2 \uparrow$  [Effervescence due to nitrogen gas]  
 $1^\circ$  amine  $\quad\quad\quad$  Alcohol
- $R_2 - NH + HO - N = O \xrightarrow[273K-278K]{NaNO_2+HCl} R_2N - N = O + H_2O$  [Yellow oil]  
 $2^\circ$  amine  $\quad\quad\quad$  Nitroso amine
- $R_3N + HNO_2 \xrightarrow[273K-278K]{NaNO_2+HCl} R_3N^+HNO_2^-$  [No visible reaction]  
 $3^\circ$  amine  $\quad\quad\quad$  Trialkylammonium nitrite
23.  $R_4N^+X^- + AgOH \xrightarrow{\Delta} R_4N^+OH^-$
24.  $R - NH_2 + CHCl_3 + 3KOH_{(alc.)} \xrightarrow{\Delta} RNC + 3KCl + 3H_2O$   
 Primary amine  $\quad\quad\quad$  Alkyl isocyanide
25. i. Offensive smell with  $CHCl_3$  and  $KOH$   
 $\therefore$  The compound must be an isocyanide. Only primary amine forms isocyanide.  
 $R - NH_2 + CHCl_3 + 3KOH \xrightarrow{\Delta} RNC + 3KCl + 3H_2O$   
 Primary amine  $\quad\quad\quad$  Alkyl isocyanide (offensive odour)

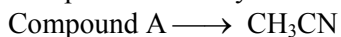


ii. Formation of ethyl alcohol with nitrous acid

∴ the compound must be ethylamine



∴ Compound B is ethylamine ( $\text{C}_2\text{H}_5\text{NH}_2$ ).

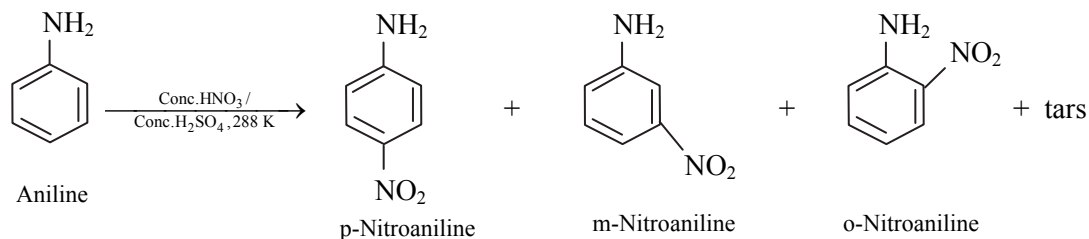


∴ Compound A is methyl cyanide.

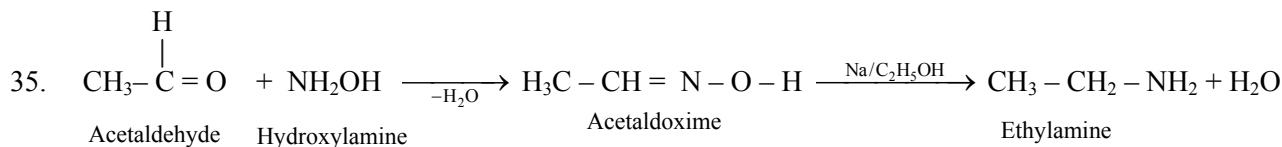
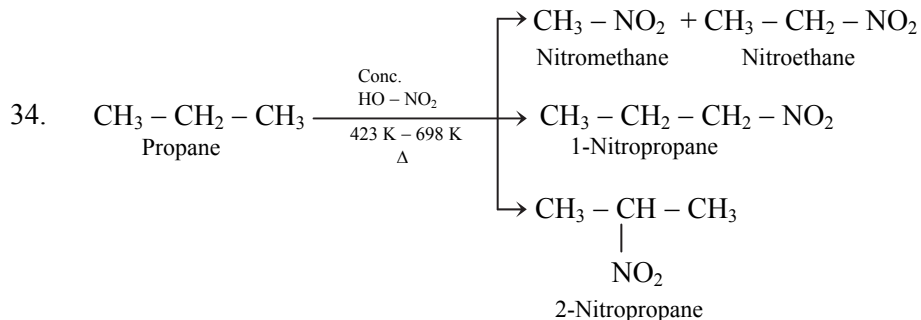
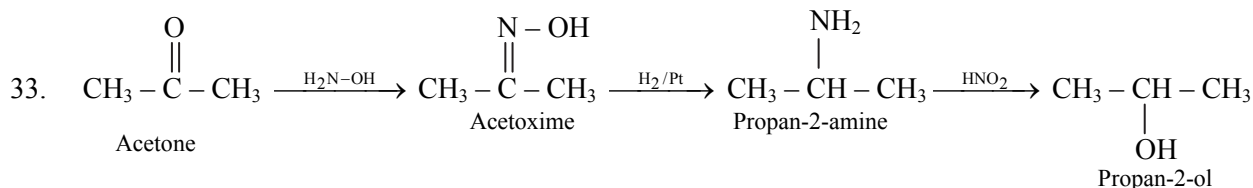
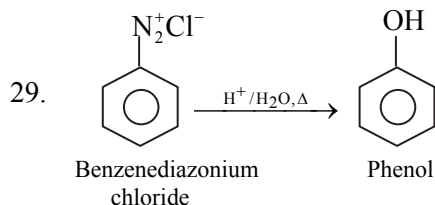
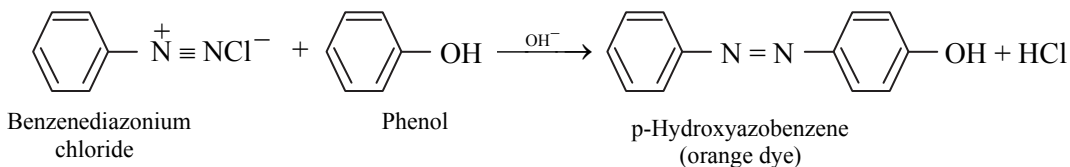
27. In direct nitration of aniline with concentrated nitric acid at 288 K in the presence of sulphuric acid, a mixture of ortho, meta and para isomers of nitroaniline is obtained as product.

Also, dark coloured tars are obtained due to oxidation.

m-Nitroaniline is obtained due to protonation of aniline in acidic medium (which gives anilinium ion containing meta directing  $-\text{NH}_3^+$  group).

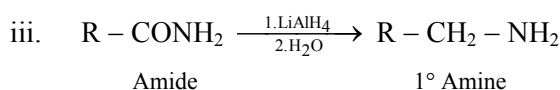
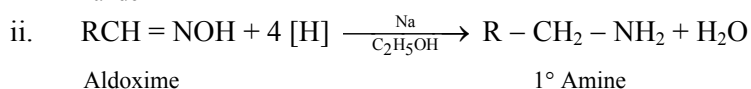
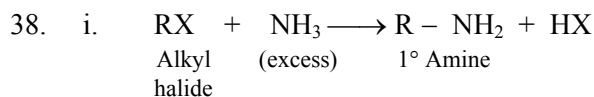
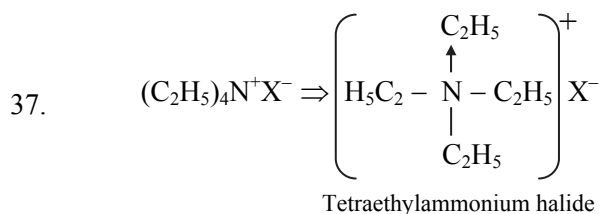


28. Benzenediazonium chloride reacts with phenol molecule and its para position gets coupled with the diazonium salt to form p-Hydroxyazobenzene. This type of reaction is known as coupling reaction.





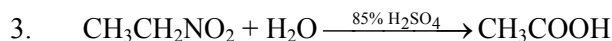
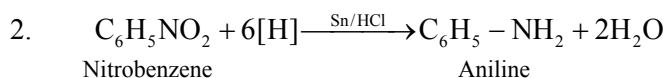
36. Schiff bases are the products of primary amines.



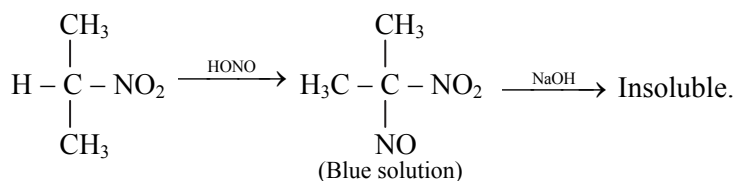
Alkyl cyanides on hydrolysis do not yield amine.



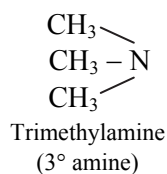
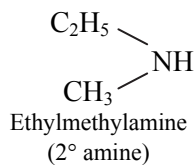
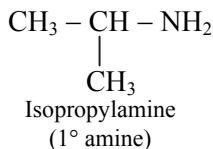
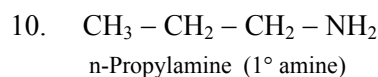
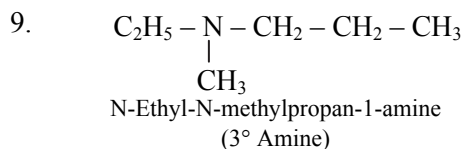
### Competitive Thinking



4. Secondary nitroalkanes react with nitrous acid to form blue coloured nitroso-nitroalkanes, which no more contain  $\alpha$ -hydrogen atom hence are insoluble in sodium hydroxide.

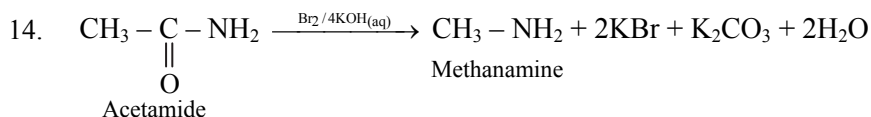


5. Primary and secondary nitroalkanes react with nitrous acid while tertiary nitroalkanes do not react with nitrous acid. The compound given in option (D) is a tertiary nitroalkane and hence, it does not react with nitrous acid.

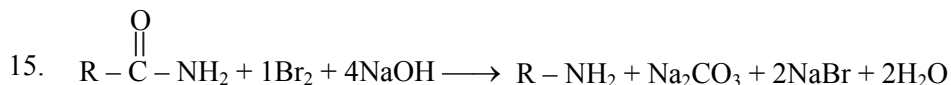




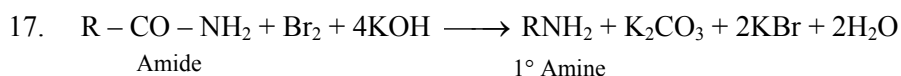
13.  $\text{LiAlH}_4$  is the strongest reducing agent and reduces amide to corresponding primary amine.



This reaction is known as Hoffmann's hypobromamide reaction.



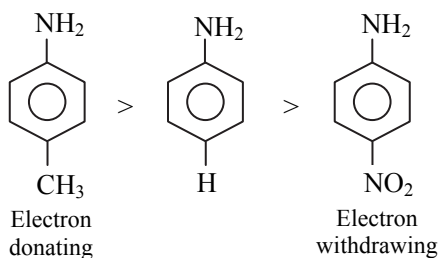
16. Hoffmann bromamide degradation is used only in the preparation of primary amines. It is useful for decreasing the length of carbon chain by one carbon atom. In this reaction, amides are treated with bromine and aqueous or alcoholic  $\text{KOH}$  /  $\text{NaOH}$  to obtain primary amine.



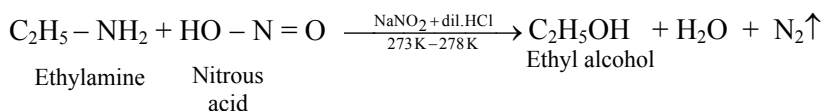
18. In amines nitrogen has a lone pair of  $e^-$ . It can donate an electron pair. So amines behave as a Lewis bases.

20. In case of substituted aniline, electron releasing groups like  $-\text{OCH}_3$ ,  $-\text{CH}_3$ ,  $-\text{NH}_2$  increase the basic strength while electron withdrawing groups like  $-\text{NO}_2$ ,  $-\text{C}_6\text{H}_5$ ,  $-\text{SO}_3$ ,  $-\text{COOH}$ ,  $-\text{CN}$ ,  $-\text{X}$  decrease the basicity of amines.

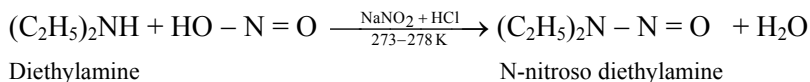
21. Order of basic strength for the mentioned compounds is,



22. Aliphatic primary amines react with nitrous acid ( $\text{HNO}_2$ ) to give brisk effervescence due to evolution of  $\text{N}_2$  gas.

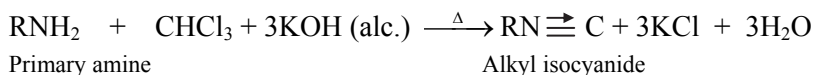


23. 2° amines form N-nitroso amines which are yellow oily liquids insoluble in water.

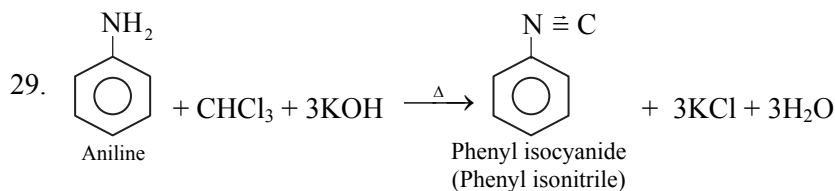


24. Secondary amines, both aliphatic and aromatic, react with nitrous acid at low temperature to give yellow oily N-nitroso amines.

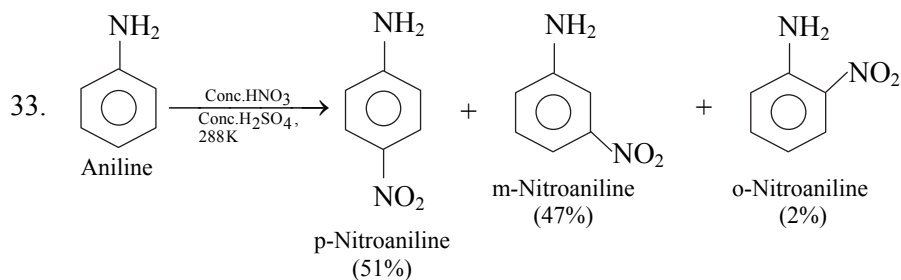
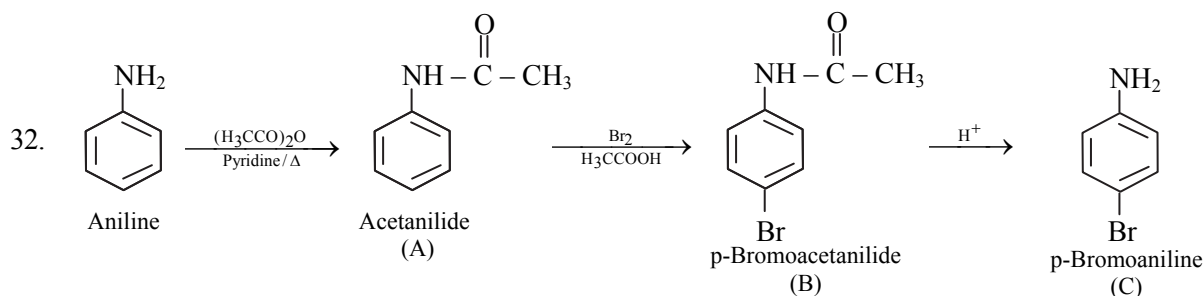
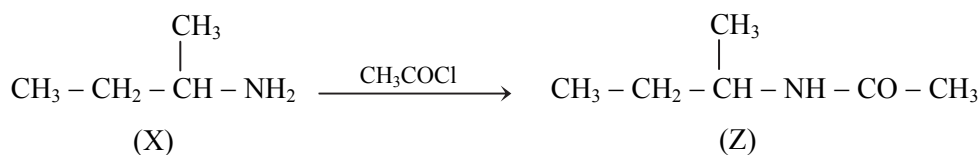
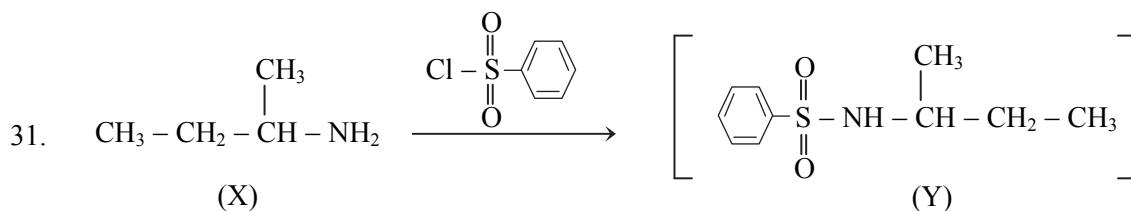
27.  $\text{CHCl}_3$  gives carbylamine test.



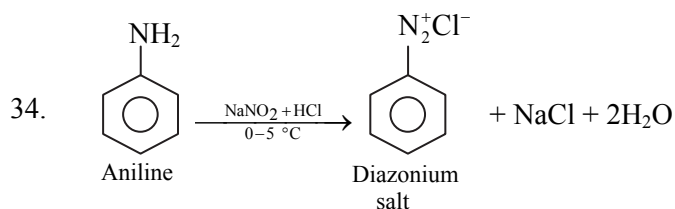
28. When aliphatic or aromatic primary amines are heated with chloroform and alcoholic potassium hydroxide, foul smelling alkyl isocyanides or carbylamines are formed. Secondary or tertiary amines do not undergo such reaction. This reaction is known as Hoffmann's carbylamine test or isocyanide test.



30. Tertiary amines do not react with benzenesulphonyl chloride due to absence of hydrogen atom directly attached to the nitrogen atom. The unreacted tertiary amine is insoluble in aqueous KOH but soluble in acid. Among the given options, tripropylamine is a tertiary amine and hence, option (A) is the correct answer.



This is because in acidic condition, protonation of  $-\text{NH}_2$  group gives anilinium ion ( $\text{Ar}-\text{NH}_3^+$ ), which is m-directing.

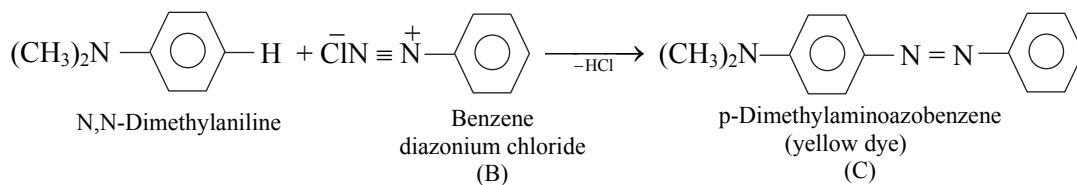
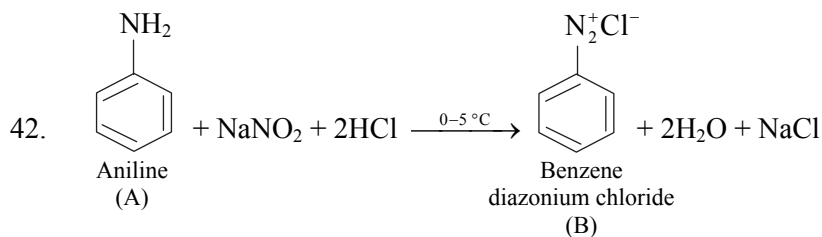
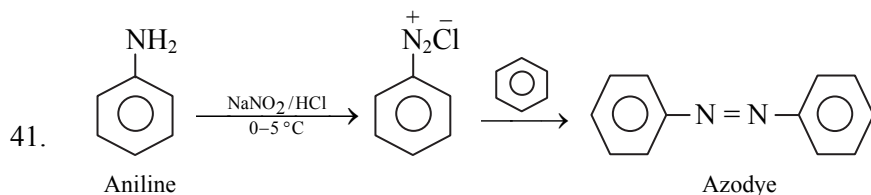
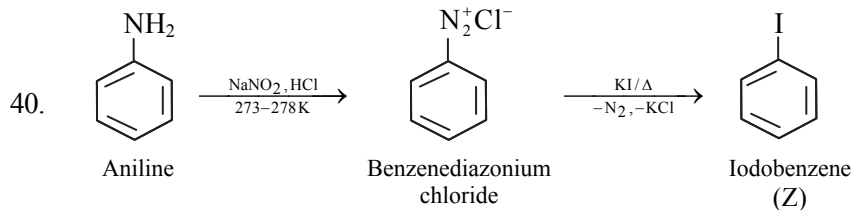
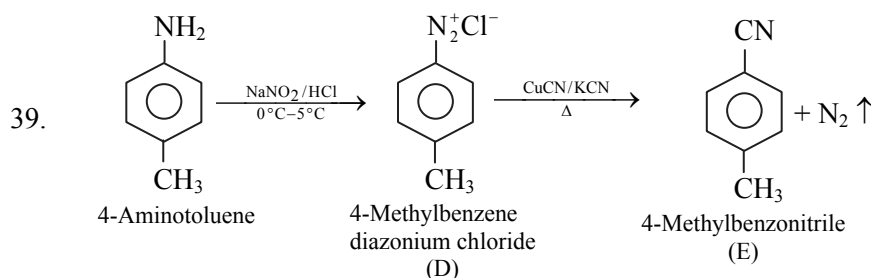
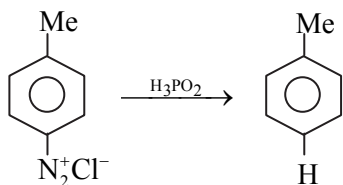


36. In Sandmeyer reaction, copper (I) salts such as cuprous chloride, cuprous bromide or cuprous cyanide are used to replace nitrogen in diazonium salt with  $-\text{Cl}$ ,  $-\text{Br}$  or  $-\text{CN}$  respectively. Hence, among the given options,  $\text{C}_6\text{H}_5\text{I}$  is not formed by Sandmeyer reaction.



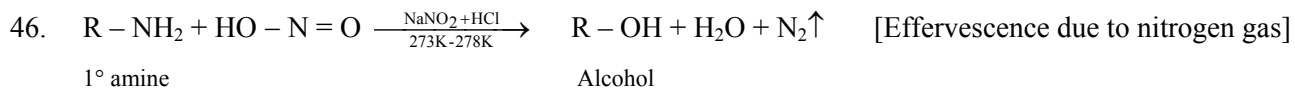
37. Diazotisation [action of nitrous acid ( $\text{NaNO}_2 + \text{HCl}$ )] is given by an aromatic primary amine (having  $-\text{NH}_2$  group directly attached to nucleus), in an inorganic acid, leading to the formation of diazonium salt. In option (B)  $-\text{NH}_2$  is not linked directly to the benzene nucleus hence will not go for diazotisation.

38. Hypophosphorus acid/phosphinic acid ( $\text{H}_3\text{PO}_2$ ) reduces diazonium salts to corresponding arenes.



45.  $\alpha$ -amino acids are capable of forming zwitter ion.

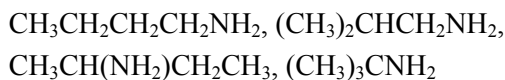




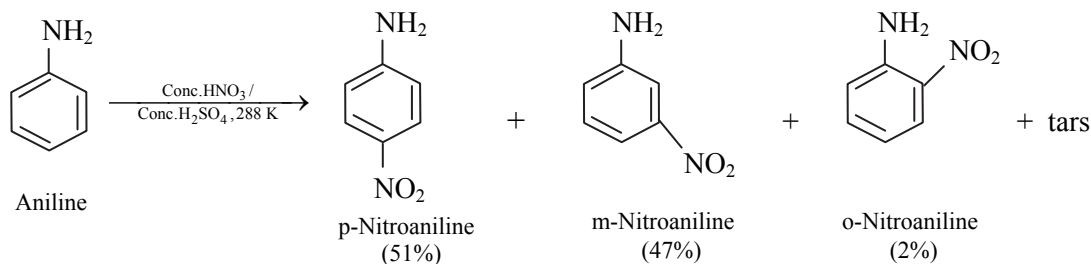
47. The molecular formula of benzonitrile or phenyl cyanide is  $\text{C}_6\text{H}_5\text{CN}$ .

48. Amongst the given options  $\text{C}_6\text{H}_5\text{N}_2^+\text{X}^-$  is the most stable diazonium salt due to resonance stabilization.

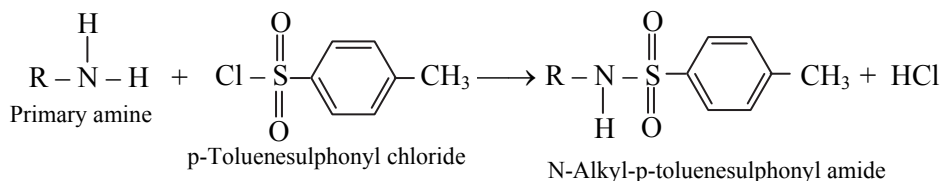
49. Four 1° amines are possible.



50. When aniline is nitrated with nitrating mixture in ice cold condition, the major product obtained is p-nitroaniline

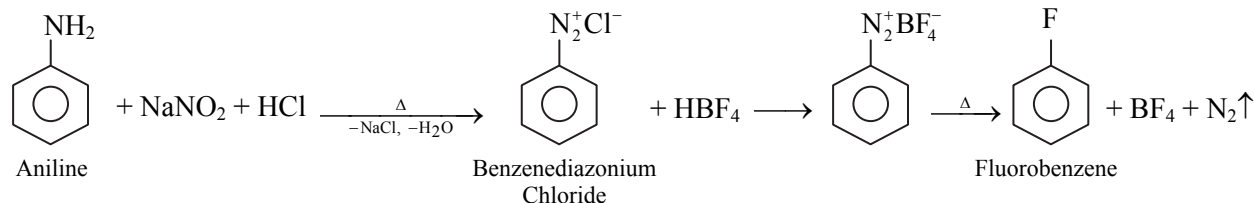


51. Primary amine i.e.,  $\text{C}_2\text{H}_5\text{NH}_2$  react with p-toluenesulphonyl chloride to give N-alkyl-p-toluenesulphonyl amide.

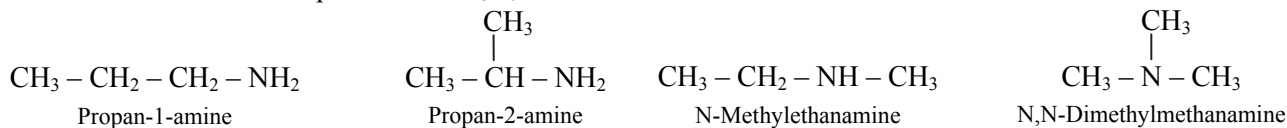


Due to presence of strong electron withdrawing sulphonyl group, hydrogen attached to N atom is strongly acidic and therefore, N-alkyl-p-toluenesulphonyl amide dissolves in aqueous base which upon acidification gives insoluble amide.

52. Reaction of diazonium salt with fluoroboric acid ( $\text{HBF}_4$ ) gives a precipitate of benzenediazonium tetrafluoroborate. After filtration and drying, benzenediazonium tetrafluoroborate is decomposed by heating to obtain corresponding aryl fluoride. This reaction is known as Balz-Schiemann reaction.



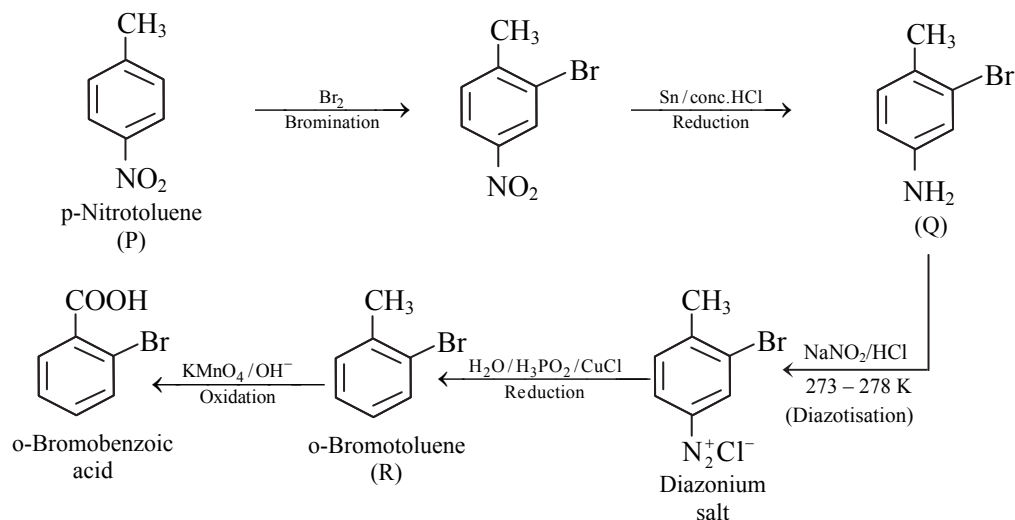
53. Four isomeric amines are possible for  $\text{C}_3\text{H}_9\text{N}$ :



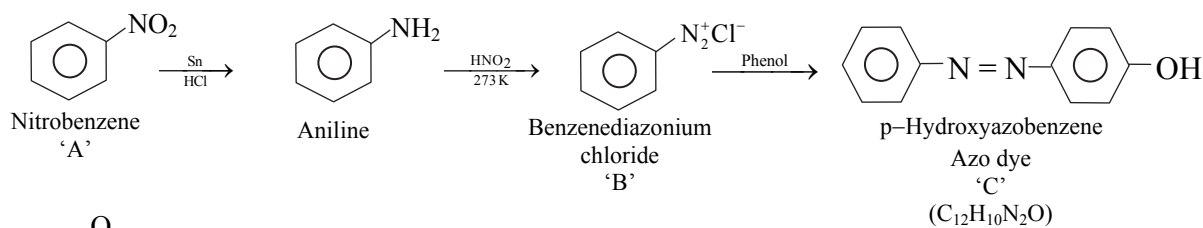
54. Reaction of phthalimide with alkyl or benzyl halides in the presence of alcoholic KOH or aqueous NaOH solution is called as Gabriel phthalimide synthesis. Aromatic primary amines like aniline are not prepared by using this method because nucleophilic substitution of aryl halides with phthalimide anion is not possible.



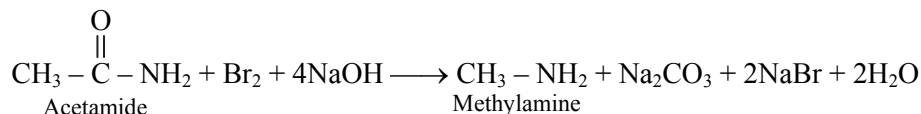
55.



56.

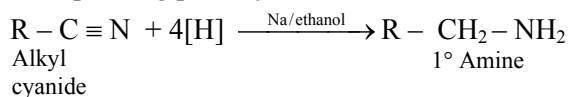


57.



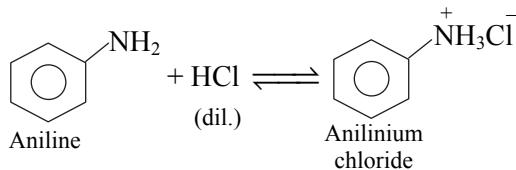
### Evaluation Test

- Mendius reduction: Alkyl cyanides or cyanoalkanes on reduction by sodium and ethanol give corresponding primary amine.

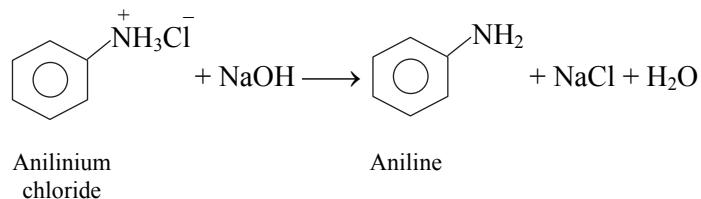


- $\text{CH}_3\text{NO}_2 + 3\text{Cl}_2 + 3\text{NaOH} \longrightarrow \text{CCl}_3 - \text{NO}_2 + 3\text{NaCl} + 3\text{H}_2\text{O}$ .  
Nitromethane  Chloropicrin

- Aniline being an amine, it can be converted to ammonium salt like anilinium chloride.

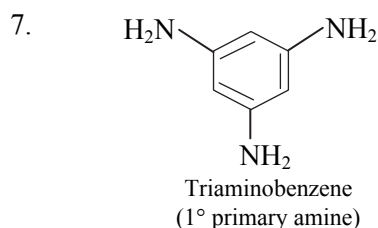


Benzene remains unreacted. Anilinium chloride is soluble in water, while benzene does not dissolve. Benzene being an organic liquid will form an immiscible layer with aqueous anilinium chloride solution and hence the two solutions can be separated. Anilinium chloride dissolved in water can be reacted with NaOH to recover aniline.





4. Stronger the base, lower will be the value of  $pK_b$ . Ammonia is a weaker base than amines. So the value of  $pK_b$  will be higher for  $NH_3$ .
5. As 'Z' gives carbylamine test, it is a primary amine. 'Y' reacts with acetic anhydride and does not give carbylamine, thus; it is secondary. 'X' does not react with acetic anhydride. 'X' is tertiary amine.
- $\therefore$  X, Y and Z are tertiary, secondary and primary amines respectively.
6. Only primary amines give nitrogen gas with nitrous acid. Trimethylamine is a tertiary amine. The other given options are primary amines.

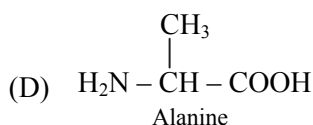
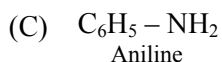
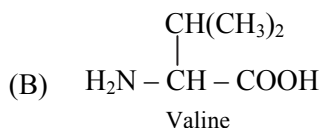
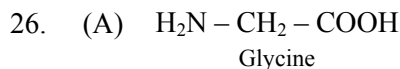


8. Benzene sulphonyl chloride is used in Hinsberg's test to find out acidic hydrogen atom which is soluble in  $H_2O$ .
- Primary  $\longrightarrow$  one acidic H atom  $\longrightarrow$  soluble in  $H_2O$
- Secondary  $\longrightarrow$  no acidic H atom after reacting with one hydrogen atom present in functional group
- Tertiary  $\longrightarrow$  does not react
9. By Gabriel phthalimide method only primary aliphatic amine can be prepared but aniline is aromatic amine.
10. Diazotisation reaction [action of nitrous acid ( $NaNO_2 + HCl$ )] is given by an aromatic primary amine (having  $-NH_2$  group directly attached to nucleus) which leads to the formation of diazonium salt. In option (B),  $C_6H_5 - CH_2 - CH_2 - NH_2$ , amino group is not directly attached to the benzene nucleus hence no diazotisation.



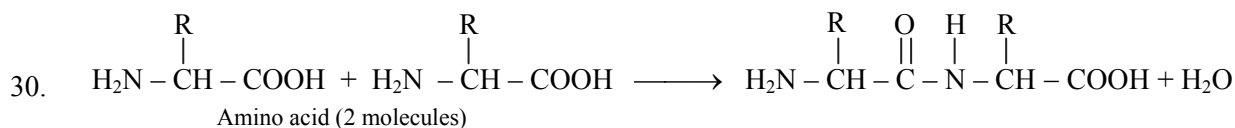


19. In maltose, C-1 of one  $\alpha$ -D-glucopyranose is linked to C-4 of another  $\alpha$ -D-glucopyranose molecule by glycosidic linkage.
21. Lactose is the sugar present in milk which on hydrolysis produces glucose and galactose.
23. In animal body, glucose is stored in the form of glycogen.

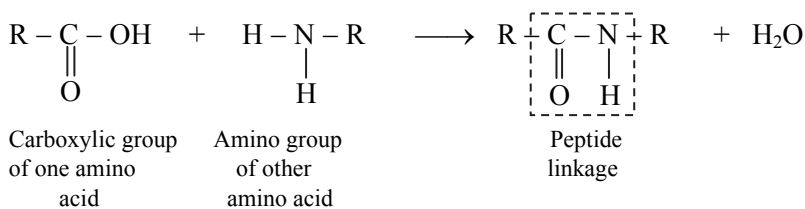


27. Side chain R of amino acids

- (A) Glycine - H-  
(B) Valine -  $(\text{CH}_3)_2\text{CH}-$   
(C) Lysine -  $\text{H}_2\text{N} - (\text{CH}_2)_4-$   
(D) Alanine -  $\text{CH}_3-$

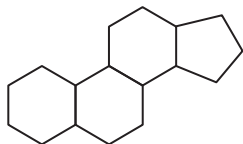


31. During the formation of a protein molecule, carboxyl group of one amino acid and amino group of another amino acid joins together, the bond developed as a result is called peptide linkage/bond.



32. Keratin is a fibrous protein, rest are globular.

34. Denaturation of protein is brought about by heating the protein with alcohol, concentrated inorganic acids or by salts of heavy metals.



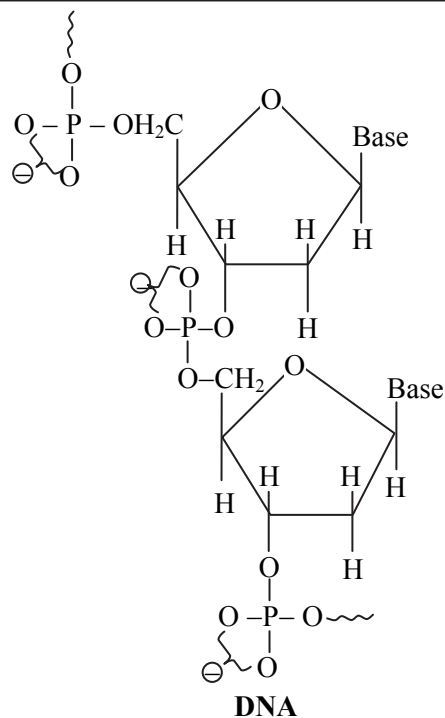
Steroid nucleus (containing 4 rings)

51. Nucleotide contains nitrogenous bases like adenine, guanine, thymine, cytosine and uracil, whereas tyrosine is an amino acid.
53. Glucose is known as dextrose because it occurs in nature as the optically active dextrorotatory isomer.
54. Ribose : Aldopentose    Fructose : Ketohexose    Erythrose : Aldotetrose    Glucose : Aldohehexose

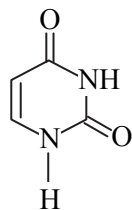




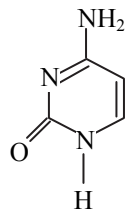
25.



26. Base + sugar = nucleoside  
 Base + sugar + phosphoric acid = nucleotide
27. RNA contains pyrimidine base as uracil and cytosine.

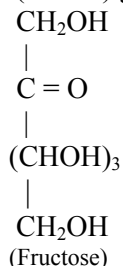
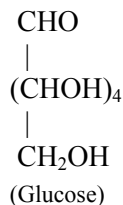


Uracil(U)



Cytosine (C)

28. On hydrolysis of sucrose, glucose and fructose are obtained.  
 Glucose contains an aldehydic ( $-\text{CHO}$ ) group, while fructose contains a ketonic ( $\text{>C}=\text{O}$ ) functional group.



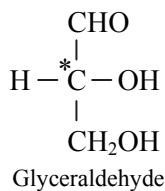
Both have same molecular formula  $\text{C}_6\text{H}_{12}\text{O}_6$ .

29. Carbohydrates that are sugars have sweet taste.
30. Carbohydrates conjugate with lipids to form glycolipids.



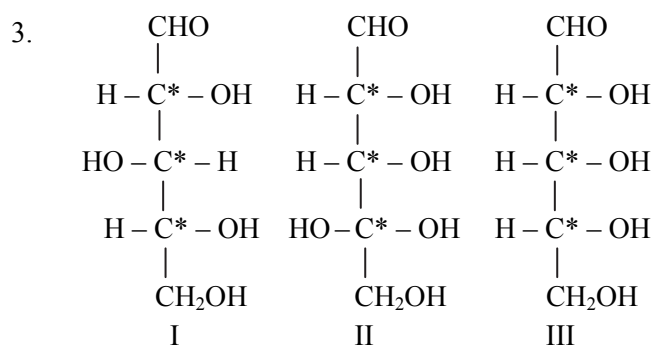
### Competitive Thinking

1.

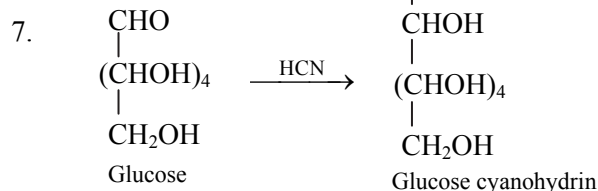
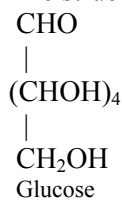




2. Raffinose  $\xrightarrow{\text{Hydrolysis}}$  Glucose + Fructose + Galactose



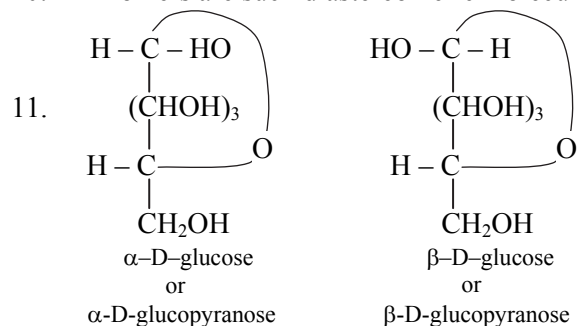
5. The structure of glucose is



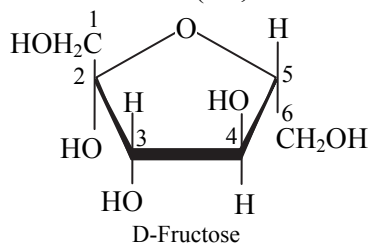
8. Glucose does not react with Schiff's reagent. It neither gives condensation reaction with phenylhydrazine derivatives (such as 2,4-dinitrophenylhydrazine) nor it gives addition reaction with sodium bisulphite ( $\text{NaHSO}_3$ ). However, it reacts with bromine water ( $\text{Br}_2 + \text{H}_2\text{O}$ ) to give gluconic acid.

9. Glucose on reaction with mild oxidising agent like bromine water gets oxidised to six carbon carboxylic acid i.e., gluconic acid. This confirms that the carbonyl group present in glucose is an aldehydic group.

10. Anomers are such diastereomeric molecules which differ in the configuration of C-1 carbon only.



13. There are five atoms (i.e., four carbon and one oxygen atom) present in the ring.



14. Sucrose is a disaccharide of  $\alpha$ -D-glucopyranose and  $\beta$ -D-fructofuranose.

15. Amylopectin is not soluble in water.

16. Starch  $\xrightarrow{\text{Hydrolysis}}$  Monosaccharides  $\longrightarrow$  Glucose.



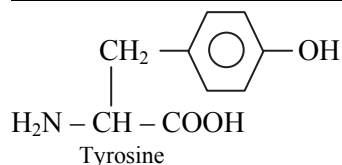


18. In maltose, C-1 of one  $\alpha$ -D-glucopyranose is linked to C-4 of another  $\alpha$ -D-glucopyranose molecule by glycosidic linkage.  
 In cellobiose, C-1 of one  $\beta$ -D-glucopyranose is linked to C-4 of another  $\beta$ -D-glucopyranose molecule by glycosidic linkage.  
 In sucrose, C-1 of  $\alpha$ -D-glucopyranose is linked to C-2 of  $\beta$ -D-fructofuranose by glycosidic linkage.  
 In lactose, C-1 of  $\beta$ -D-galactopyranose is linked to C-4 of  $\beta$ -D-glucopyranose by glycosidic linkage.

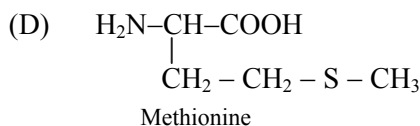
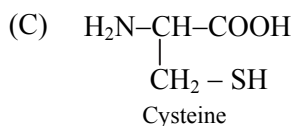
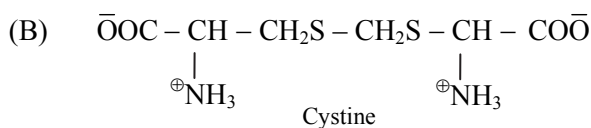
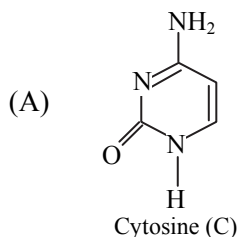
19.

	Carbohydrate	Nature and units linked together
(A)	Maltose	Disaccharide having $\alpha$ -D-glucose units
(B)	Sucrose	Disaccharide having $\alpha$ -D-glucose and $\beta$ -D-fructose units
(C)	Cellulose	Polysaccharide having $\beta$ -D-glucose units
(D)	Lactose	Disaccharide having $\beta$ -D-galactose and $\beta$ -D-glucose units

20.

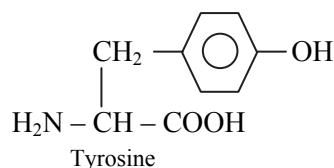
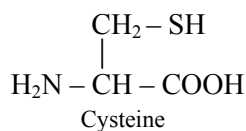
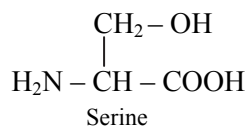
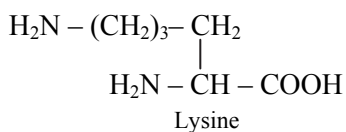


21.

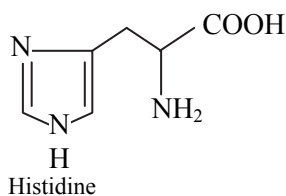


Only cysteine contains thiol i.e., -SH group.

22.



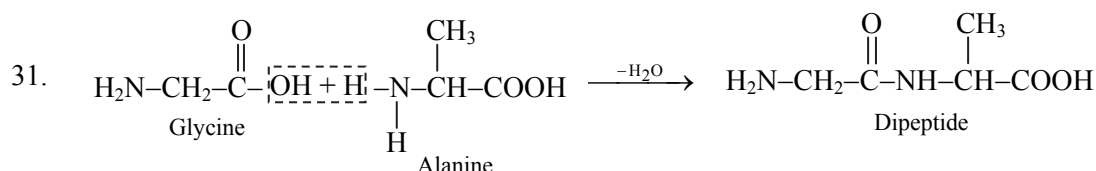
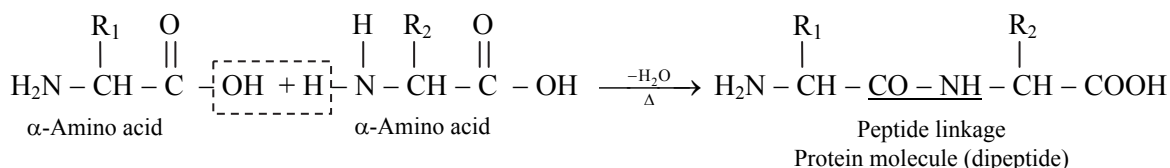
24. Valine, Tyrosine and Leucine are neutral amino acids.  
 25. Histidine is a basic amino acid as it contains basic side chain.



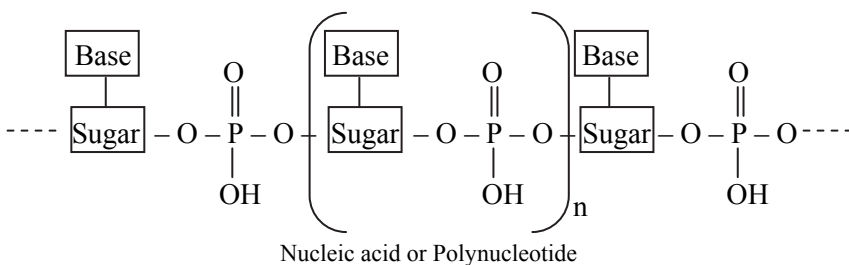
26. Glycine  $\Rightarrow$  Neutral amino acid  
 Aspartic acid  $\Rightarrow$  Acidic amino acid  
 Lysine and arginine  $\Rightarrow$  Basic amino acid



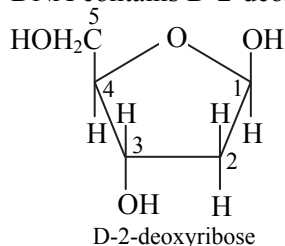
27. Only glycine:  $\begin{array}{c} \text{H} \\ | \\ \text{H} - \text{C} - \text{COOH} \\ | \\ \text{NH}_2 \end{array}$  is an optically inactive amino acid.
28. In the primary structure of a protein, the amino acids are linked by peptide bonds.
30. In peptide linkage i.e.,  $-\text{CONH}-$  group, the carboxyl group of one amino acid molecule forms an amide by combination with the amino group of the next amino acid molecule with the liberation of water molecule.



36.  $\alpha$ -helix structure is formed when the chain of  $\alpha$ -amino acid coil as a right handed screw because of the formation of hydrogen bonds between amide groups of the same peptide chain. This H-bonding is responsible for holding helix in position.
38. Protein can be denatured by heat.
39. Insulin is a peptide hormone, secreted in pancreas and controls carbohydrate metabolism by increasing glycogen in muscles and oxidation of glucose in tissue and also lowers the blood sugar.
41. Vitamin D is a fat soluble vitamin.
43. Vitamin B complex is fat insoluble.
51. A simplified version of nucleic acid chain may be represented as follows:



55. In DNA, two bases adenine (A) and thymine (T) form complementary base pair. Similarly, guanine (G) and cytosine (C) form complementary base pair.
56. DNA contains D-2-deoxyribose sugar and it is present in furanose form.







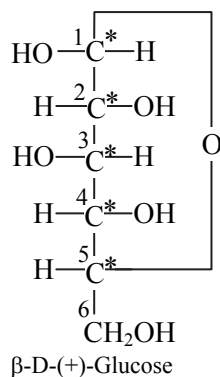
In cellulose, C-1 of one  $\beta$ -D-glucopyranose molecule is linked to C-4 of another  $\beta$ -D-glucopyranose molecule by glycosidic linkage. Thus, in maltose, lactose and cellulose, all the monosaccharide units are joined by C-1 – O – C-4 chain.

Amylopectin is a branched chain polymer. In amylopectin, C-1 of one  $\alpha$ -D-glucopyranose molecule is linked to C-4 of another  $\alpha$ -D-glucopyranose molecule by glycosidic linkage. However, branching occurs due to the formation of a glycosidic linkage between C-1 of one glucopyranose and C-6 of another glucopyranose. Thus, in amylopectin, all the monosaccharide units are not joined by C-1 – O – C-4 chain.

79.

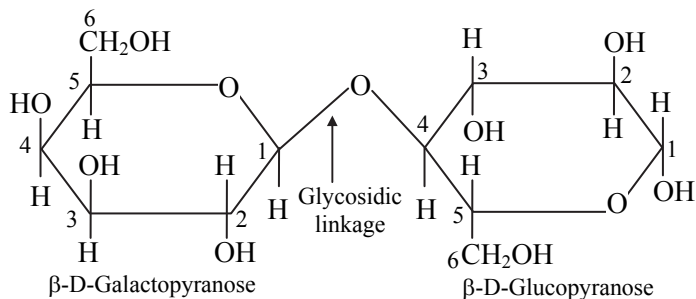
Vitamin	Sources
A	Cod liver oil, shark liver oil, carrots, spinach, papaya, liver, kidney, butter, milk, ghee, curd, etc.
B <sub>12</sub>	Meat, eggs, liver, milk, cheese, fish, etc.
B <sub>2</sub>	Meat, peas, milk, eggs (egg yolk), yeast, green vegetables, liver, kidney, etc.
C	Citrus fruits (like orange, lemon), amla, tomatoes, green vegetables, etc.

From the above table, it is clear that vitamins A, B<sub>2</sub> and C are easily available to vegetarians as these vitamins are present in different vegetables and fruits. However, vitamin B<sub>12</sub> is less available to vegetarians as its sources include fish, meat, eggs and dairy products.

80. There are five chiral carbon atoms (indicated by \*) in  $\beta$ -D-(+)-glucose.

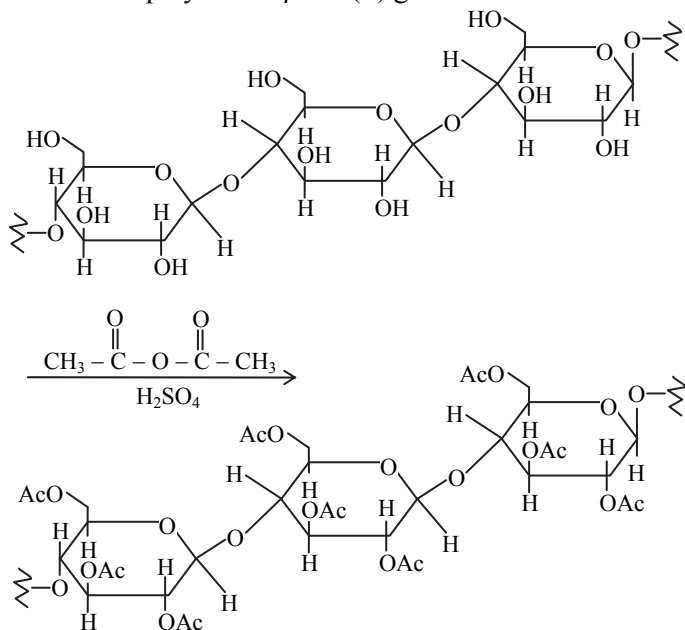
## Evaluation Test

- Co (III) transition metal is present in vitamin B<sub>12</sub>.
- Lactose is obtained by the condensation of one molecule of  $\beta$  – D – galactopyranose (C<sub>1</sub> –  $\beta$ ) unit and one molecule of  $\beta$  – D – glucopyranose (C<sub>4</sub> –  $\beta$ ) unit.

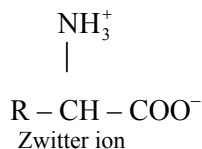




3. Cellulose is polymer of  $\beta$  - D(+) glucose whose structure is:



4. In sucrose, the two monosaccharide units joined by  $\alpha$ -1, 2 glycoside bond. Since, sucrose does not have hemiacetal carbon. Therefore, it is non-reducing sugar.
5. Glucose contains 4 asymmetric carbon atoms.  
 $\therefore$  number of optical isomers are  $2^4 = 16$
7. Zwitter ion is a dipolar ion containing both a positive and negative charge in the following form



The basic group is  $-\text{CO}_2^-$  and acidic group is  $-\text{NH}_3^+$ .

8. General formula of  $\alpha$ -amino acid is  $\text{H}_2\text{N} - \overset{\text{R}}{\underset{|}{\text{CH}}} - \text{COOH}$
9. The carbon atom of  $-\text{CHO}$  group is  $\text{sp}^2$  hybridized while the rest of five carbons in glucose are  $\text{sp}^3$  hybridized.
10. RNA and DNA has ribose and deoxyribose sugars, DNA differs from RNA in absence of hydroxy group at 2<sup>nd</sup> carbon.

# 15 Polymers

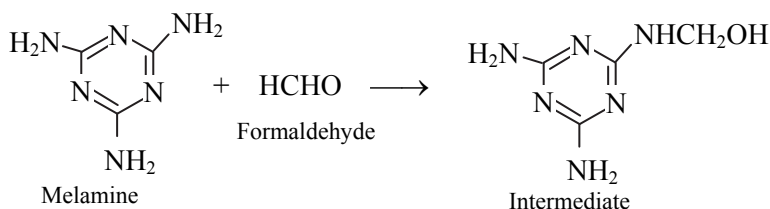


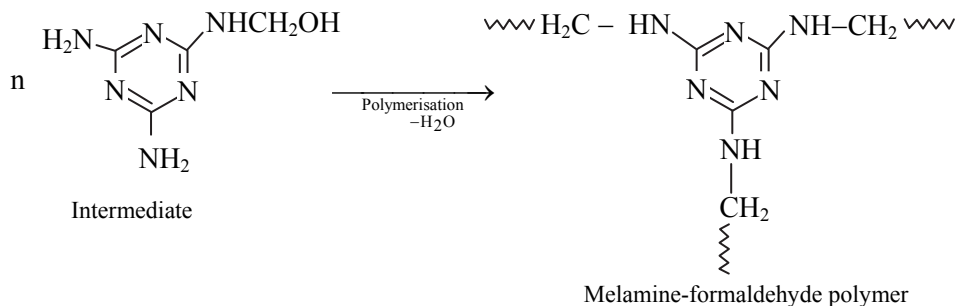
## Hints



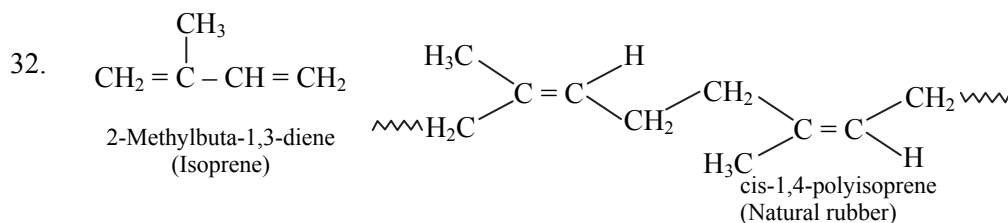
### Classical Thinking

1. Polymers are macromolecules having high molecular weights.
2. The simple molecules which combine to give polymers are called monomers.
3. DDT is an organic compound used as an insecticide and it is not a polymer.
4. Regenerated fibres are semi-synthetic fibres obtained from plant fibres (cellulose/vegetable fibres) after their chemical treatment.
9. Copolymer or heteropolymer is combination of different types of monomers.
11. Peroxides are used in free radical polymerization to generate the free radical which helps in polymerization.
16. Nylon-6,6 is a condensation polymer. It is prepared by polymerization of monomer formed by condensation of hexamethylenediamine and adipic acid.
18. Starting materials used for preparation of nylon-6,6 are,  
Adipic acid  $[\text{HOOC}-(\text{CH}_2)_4-\text{COOH}]$   
Hexamethylenediamine  $[\text{H}_2\text{N}-(\text{CH}_2)_6-\text{NH}_2]$   
Total number of carbon atoms = 12
19. 
$$\text{H}_3\text{N}^+(\text{CH}_2)_6\text{NH}_3^+\text{OOC}^-(\text{CH}_2)_4\text{COO}^-$$
  
Hexamethylene diammonium adipate  
(Nylon salt)
21. Nylon-6 and Nylon-6,6 both are polymers in which 6 and 6,6 represent the number of carbon atoms present in their starting materials. Nylon-6 is a homopolymer and nylon-6,6 is a copolymer.
23. When DMT reacts with ethylene glycol, transesterification takes place and then it polymerizes to give terylene.
26. Terylene fibres are resistant to crease. Also they absorb very little water and hence dry quickly. These fibres are thus used in the manufacturing of wash and wear clothes.
28. When phenol is treated with formaldehyde in the presence of acid or alkali, a high molecular weight substance (copolymer) called bakelite is obtained. It is a condensation polymer.
30. The unbreakable household crockery is made from copolymer of formaldehyde (HCHO) and melamine.

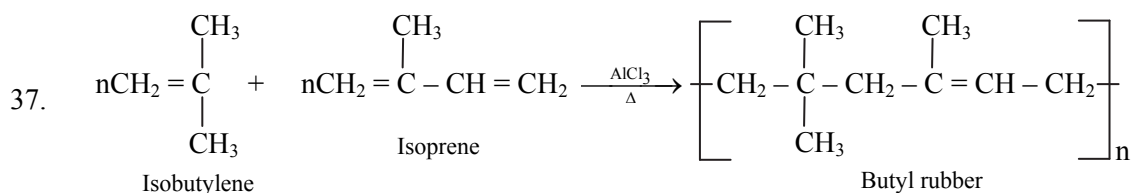
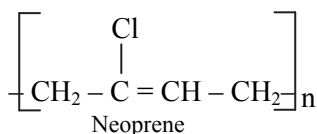




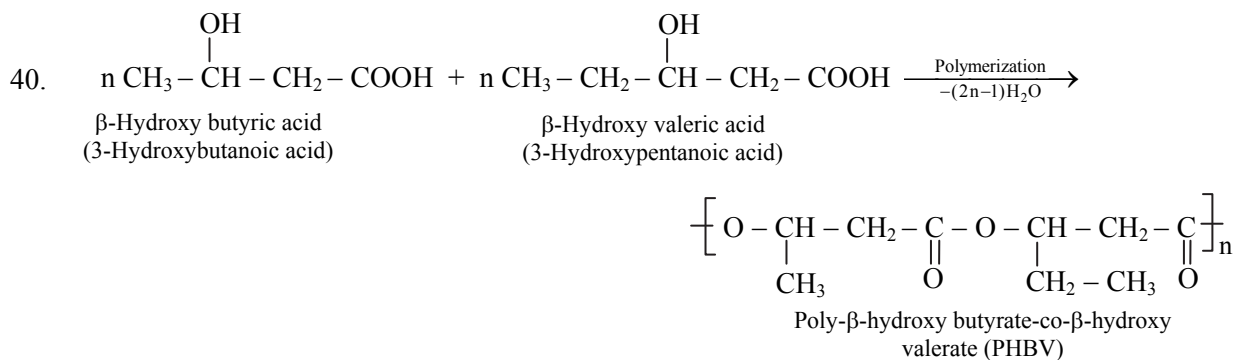
31. Natural rubber (polymer of 2-methylbuta-1,3-diene) is obtained as latex which is a colloidal suspension of rubber in water.



36. Neoprene has the structure,



38. Dacron is a polyester which is not a rubber polymer.
39. Synthetic polymers are resistant to environmental degradation process and do not degrade on their own but accumulate as solid waste materials. Thus, they are called non-biodegradable polymers.

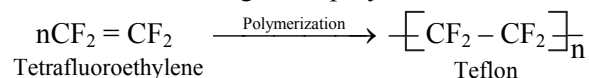


42. Dimethyl terephthalate (DMT) is a monomer.
44. Protein is a natural polymer of  $\alpha$ -amino acids.
48. Nylon-6 is prepared from cyclic monomer i.e.,  $\epsilon$ -caprolactum.

49. Nylon polymer have both acidic group  $\left( \overset{\text{O}}{\parallel} \text{C} \right)$  and basic group  $\left( \text{NH} \right)$ . Hence, nylon polymers are amphoteric.

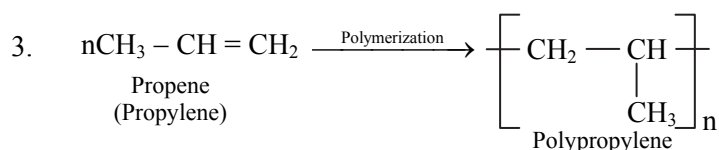
52. Dacron is a condensation polymer and rest are addition polymers.

54. Teflon is a chain growth polymer.



### Critical Thinking

2. Acetate rayon or cellulose acetate is a semisynthetic polymer which is prepared from cellulose, a natural polymer.



6. Elastomers are soft and stretchy and are hence used in making rubber bands.

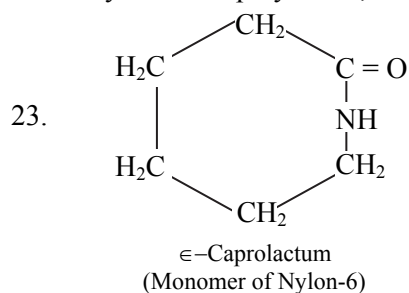
8. Thermosetting polymers are cross linked polymers while thermoplastic polymers are either linear or branched chain polymers.

11. Buna-S rubber and ABS plastic are copolymers whereas polystyrene is a homopolymer.

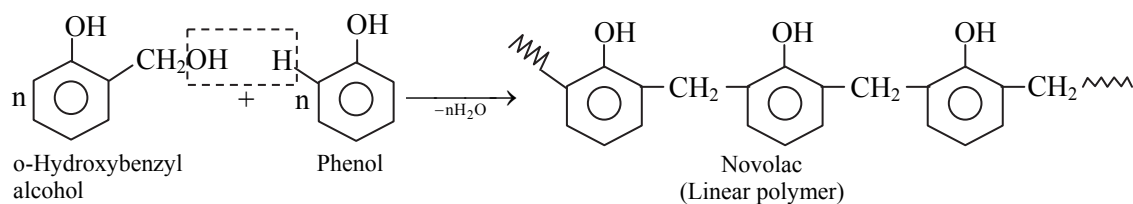
17. Because of branching, the LDPE has low density ( $0.92 \text{ g/cm}^3$ ) and low melting point (384 K).

20. Due to elimination of simple molecules like  $\text{H}_2\text{O}$ ,  $\text{CH}_3\text{OH}$ ,  $\text{HCl}$ ,  $\text{NH}_3$ , etc. during condensation polymerization, all the atoms of monomers are not present in the condensation polymer.

22. Nylon-6 is a polyamide, homopolymer of  $\epsilon$ -caprolactum. It is also called polycaprolactum.



27. Phenol reacts with o-hydroxybenzyl alcohol to give a linear polymer called as novolac having two rings joined by  $-\text{CH}_2-$  linkage.

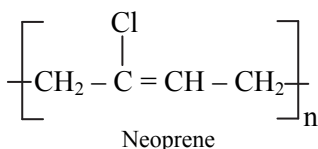






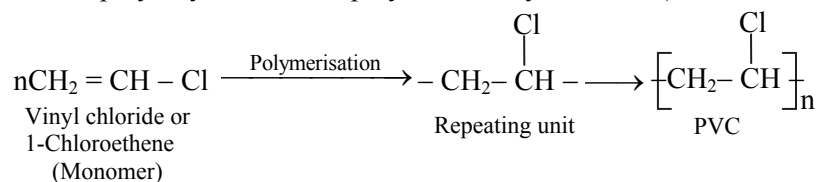


49. Neoprene is a homopolymer i.e., a polymer composed by joining together the monomers of the same structure.



### Competitive Thinking

2. PVC is polyvinyl chloride, a polymer of vinyl chloride (1-Chloroethene)

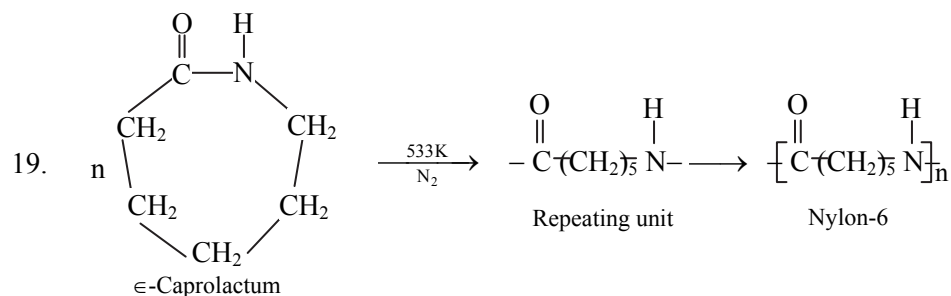


6. Thermoplastic polymers are linear or slightly branched long chain molecules with no cross-linking. Absence of cross-linking enables the polymer to soften on heating and it can be remoulded.

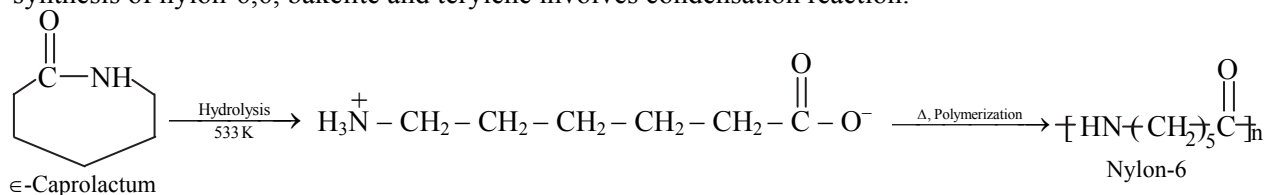
12. Low density polythene is used:

- i. in the manufacturing of flexible pipes, squeeze bottles and toys,
- ii. as insulation for electrical wires and cables,
- iii. as packaging material.

15.  $\text{H}_3\text{N}^+ - (\text{CH}_2)_6 - \text{NH}_3^+ \text{OOC} - (\text{CH}_2)_4 - \text{COO}^-$   
Hexamethylene diammonium adipate (Nylon salt)  
Molecular formula :  $\text{C}_{12}\text{H}_{26}\text{O}_4\text{N}_2$

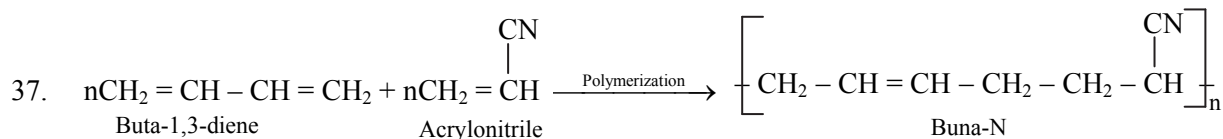


20. Formation of nylon-6 involves hydrolysis of its monomer (caprolactum) in the initial state while the synthesis of nylon-6,6, bakelite and terylene involves condensation reaction.



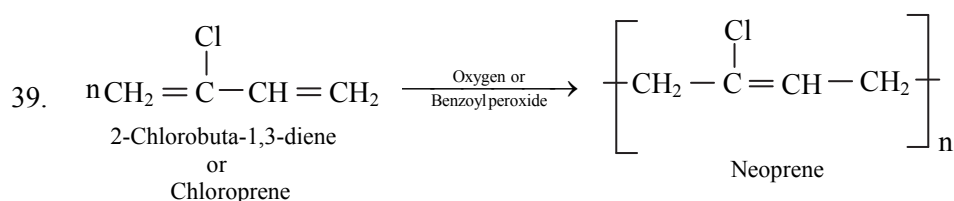
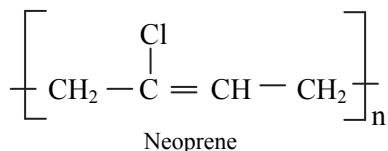
22. Terephthalic acid can be methylated to give dimethyl terephthalate which reacts with ethylene glycol to form dihydroxy diethyl terephthalate which on polymerization gives terylene (dacron).





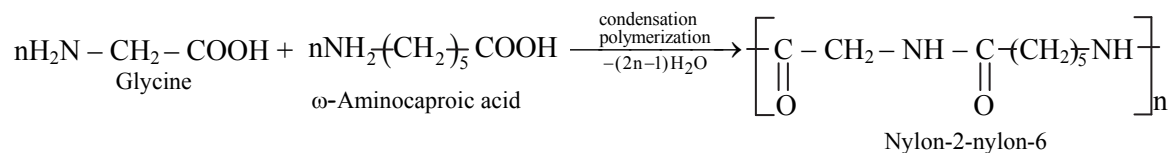
38. Synthetic rubber is poly(halodiene).

eg. Neoprene i.e.,



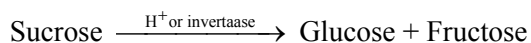
40. Natural rubber has the cis-configuration (cis-1,4-polyisoprene) at every double bond.

42. Glycine and aminocaproic acid are monomers of nylon-2-nylon-6.



45. Silk is a protein fibre. Dacron is a polyester fibre and nylon-6,6 is a polyamide fibre.

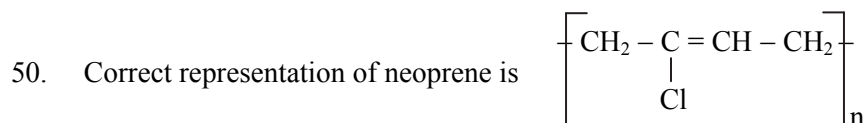
46. Sucrose is a disaccharide which upon acid or enzymatic hydrolysis gives only two molecules of monosaccharides.



All enzymes are proteins which consist of long chains of polypeptides. Starch is a polymer of amylose and amylopectin. Teflon is a polymer of tetrafluoroethene.

47. Dynel is a copolymer of vinyl chloride and acrylonitrile which is used in human hair wigs.

49. Cellulose is a natural polymer and is present in the cell wall of plants.



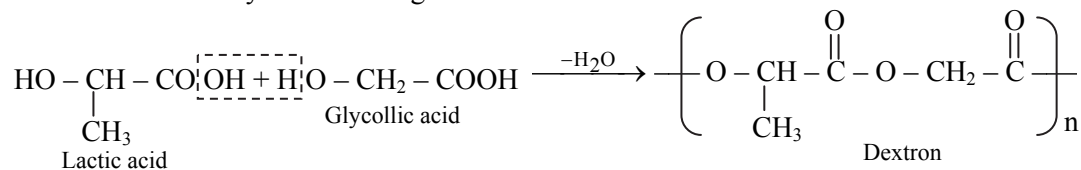
52. The natural rubber has weak intermolecular dispersion forces (van der Waals forces of attraction) and is an example of an elastomer (polymer).

53. Nylon-6,6 is an example of fibre.

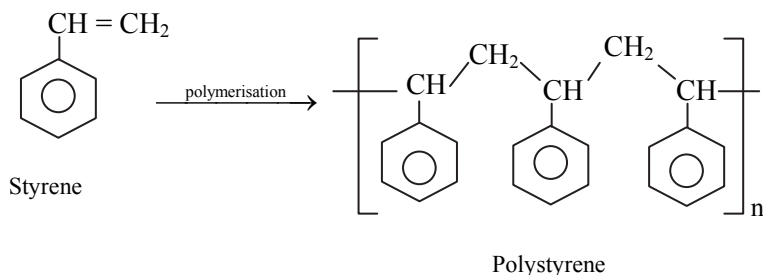
55. Dacron is a condensation polymer formed by polymerisation of DMT (dimethylterephthalate) and ethylene glycol while neoprene and teflon are addition polymers. Acrylonitrile is a monomer of polyacrylonitrile.



56. Dextron is formed by the following reaction:



60. Chain growth polymers involve a series of reaction each of which consume a reactive particles and produces another similar one. The reactive particles may be free radicals or ions (cation or anion) to which monomers get added by a chain reaction. It is an important reaction of alkenes and conjugated dienes or indeed of all kinds of compounds that contain carbon-carbon double bond.

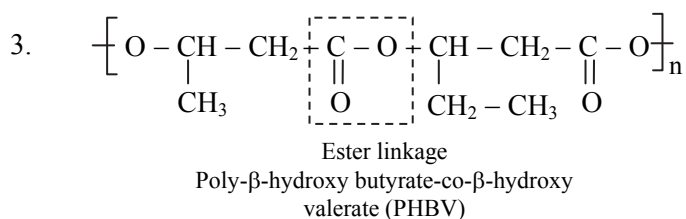
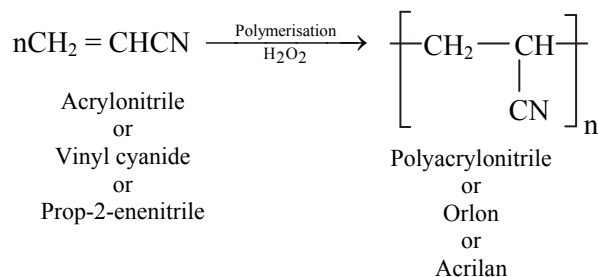


61. Polyurethane or thermocol is a copolymer of toluene diisocyanate and ethylene glycol.
62. Melamine polymer has cross-linked structure that forms a three-dimensional network. Hence, among the given options, the polymer that forms net-like structure is melamine.
65. Polythene, nylon-6 and teflon are homopolymers whereas nylon-6,6 is a heteropolymer.
67. Polypropene, polyacrylonitrile (PAN) and polyvinyl chloride (PVC) are addition polymers. Terylene and nylon-6 are condensation polymers.
68. Homopolymers are polymers containing only one kind of monomer units. Among the given options, only  $\text{[CO-(CH}_2\text{)}_5\text{NH]}_n$  is a homopolymer.



### Evaluation Test

1. Orlon is prepared by polymerization of vinyl cyanide or acrylonitrile in the presence of hydrogen peroxide.







## Hints



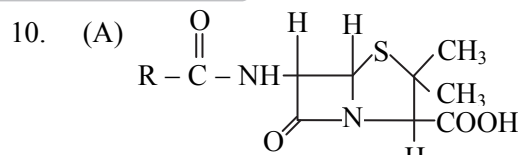
### Classical Thinking

9. Drugs are classified on the basis of:
  - i. pharmacological process
  - ii. action of drugs on a particular biochemical process
  - iii. chemical structure
  - iv. molecular targets
  - v. classification by lay public
10. Heroin is a diacetyl derivative of morphine.
14. Barbiturates are class of tranquilizers (drugs affecting central nervous system).
20. Dilute solution of phenol is used as an antiseptic whereas concentrated phenol is used as a disinfectant.
23. Antacid is a base which neutralizes an excess of acid in the stomach, thus raising the pH value of stomach.
24. Penicillin is a narrow spectrum antibiotic i.e., it is effective against either gram positive or gram negative bacteria.
36. Cationic detergents are quaternary ammonium salts of amines with chlorides, acetates or bromides.
37. Bithional is an antiseptic in medicated soap.

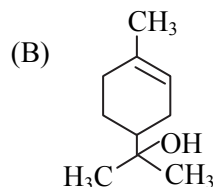


### Critical Thinking

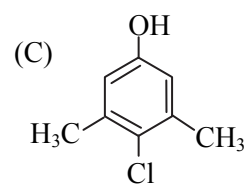
4. When the drug binds at the active site, it blocks the catalytic activity of the enzyme whereas when the drug binds to the allosteric site (i.e., site other than the active site) the shape of the enzyme changes.
9. The drugs which inhibit or check the growth of the organism in the body are called bacteriostatic antibiotics.  
**eg.** Tetracycline, erythromycin and chloramphenicol.



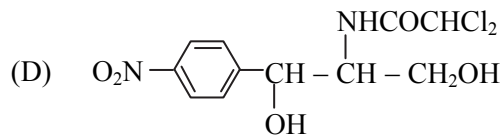
General structure of Penicillin  
( $R-C_9H_{11}N_2O_4S$ )



Terpineol ( $C_{10}H_{18}O$ )

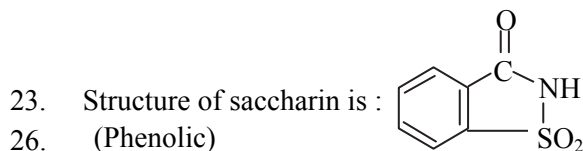


Chloroxylenol ( $C_8H_9ClO$ )

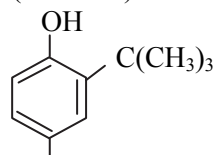


Chloramphenicol  
( $C_{11}H_{12}Cl_2N_2O_5$ )

11. Chloramphenicol is used in treating acute fever, dysentery, typhoid, meningitis, pneumonia, etc.
12. Aspirin and ibuprofen are analgesics whereas equanil is a tranquilizer. Ofloxacin is a bactericidal antibiotic.
14. Chloroxylenol (4-chloro-3,5-dimethylphenol) is used as an antiseptic as well as a disinfectant.
15. Iodoform is used as an antiseptic.
17. Arsphenamine, the drug used to treat syphilis, contain - As = As - linkage.
18. Metal hydroxides of magnesium and aluminium are used as antacids.



26. (Phenolic)

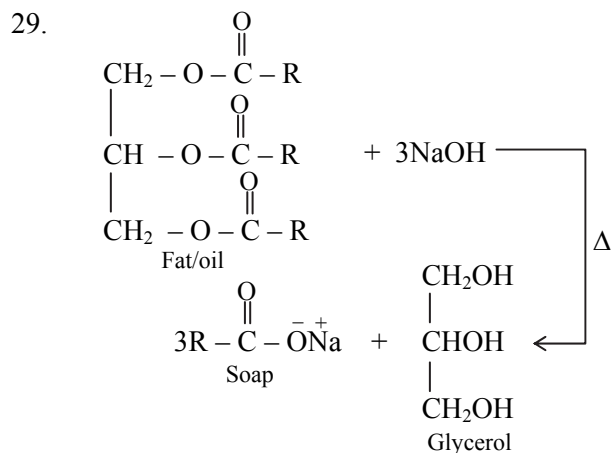


OCH<sub>3</sub> (Methoxy)  
BHA (Butylated Hydroxy Anisole)



28. Soaps are sodium or potassium salts of higher fatty acids.

Eg.  $C_{17}H_{35}COONa$  (Sodium stearate)



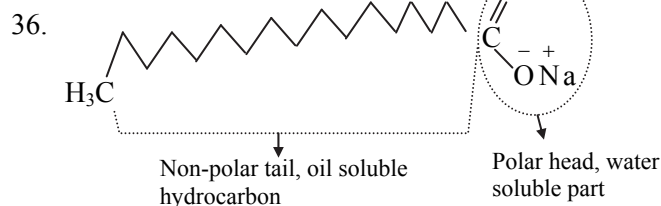
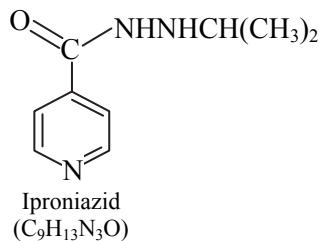
30. The sodium atom (in sodium soaps) or potassium atom (in potassium soaps) is present in polar head part of the soap molecule.

31. Boric acid: antiseptic

Chloramphenicol: antibiotic

Aspirin: analgesic, antipyretic and anti-inflammatory

34. Iproniazid has pyridine ring in its structure.



### Competitive Thinking

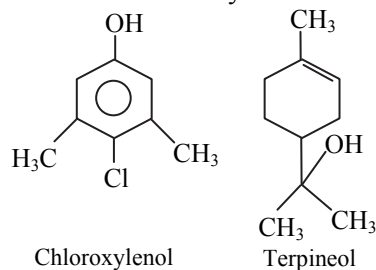
1.

	Compound	Type
(A)	Aspirin	Non-narcotic analgesic
(B)	Valium	Tranquilizer
(C)	Penicillin	Antibiotic
(D)	Sulphanilamide	Antibiotic

2. Ofloxacin, penicillin and aminoglycosides are antibiotics.

3. Mixture of chloroxylenol and terpineol is dettol which acts as an antiseptic.

4. Dettol, which is used as an antiseptic, is a mixture of chloroxylenol and terpineol.



5.

	Compound	Type
(A)	Chloramphenicol	Antibiotic
(B)	Bithional	Antiseptic
(C)	Cimetidine	Antacid
(D)	Chlordiazepoxide	Tranquilizer

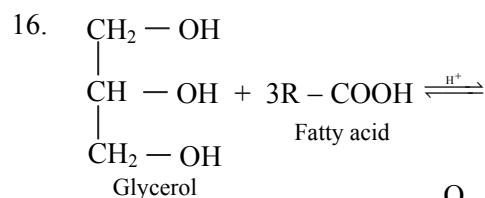
6. Bromopheniramine is an antihistamine.

7. The given drug is iproniazid and it acts as an antidepressant.

8. Phenelzine is a tranquilizer.

9. Salt, sugar, vinegar, sodium benzoate, salts of sorbic acid and propionic acid, etc., are used as food preservatives.

10. Hydration cannot be used to preserve the food as it enhances the growth of microorganisms.

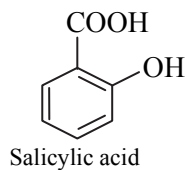


18. Detergents are sodium salts of alkyl hydrogen sulphates or sodium salts of long chain alkyl benzene sulphonic acids.





21. Sodium stearate is a soap. Cetyltrimethyl ammonium bromide is a cationic detergent. Glycerol oleate is a glyceride of oleic acid ( $C_{17}H_{33}COOH$ ) with glycerol.
22. Sodium lauryl sulphate and sodium n-dodecyl benzene sulphonate are anionic detergents while cetyltrimethyl ammonium chloride is a cationic detergent. The non-ionic detergent among the given options is pentaerythrityl stearate.
24. Saponification is defined as a process in which the oils and fats undergo alkaline hydrolysis to produce soaps.
26. Salicylic acid contains both  $-OH$  and  $-COOH$  groups.

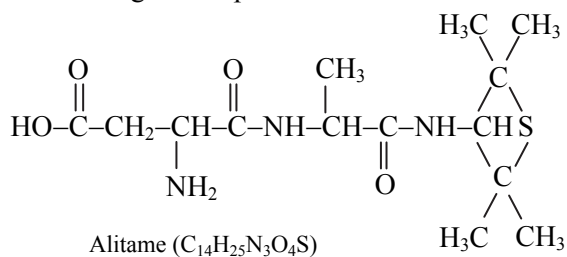


27.   
Sulphanilamide      Sulphapyridine
- Azodye
- Phenelzine (Nardil)
29. The reaction of fat/oil with sodium hydroxide is called saponification reaction.
30. Streptomycin, chloromycetin and penicillin are antibiotics.



### Evaluation Test

1. Aspirin (2-Acetoxybenzoic acid) is an important antipyretic.
2. Alitame is an artificial sweetener and is about 2000 times sweeter than cane sugar. It is very very sweet and stable at higher temperature.

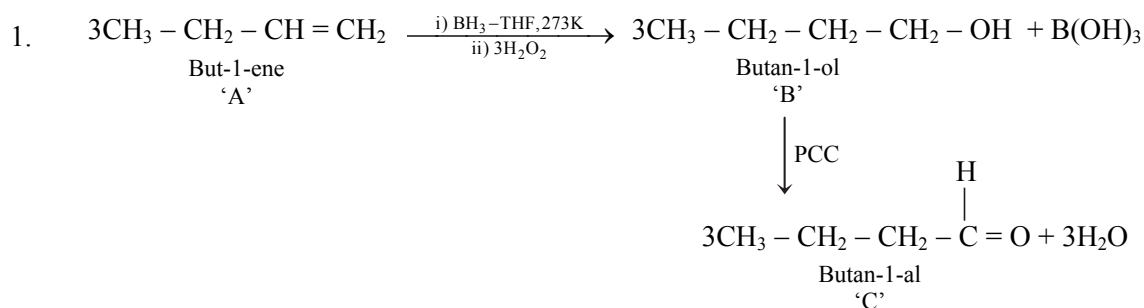


6. Sodium bicarbonate (baking soda) is used as antacid.
7. A molecule of soap has two parts, a long chain of hydrocarbon tail soluble in oil and other part (polar head) soluble in water. When soap is added to an oily or greasy part of the cloth or vessel, the hydrocarbon part of soap dissolves in the oil, keeping the polar head away from the oil. This results in the formation of anions of emulsion (emulsified oil droplets that are negatively charged).

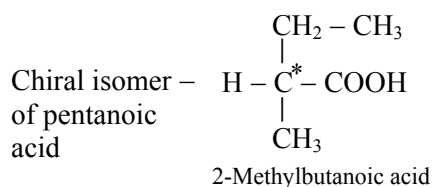
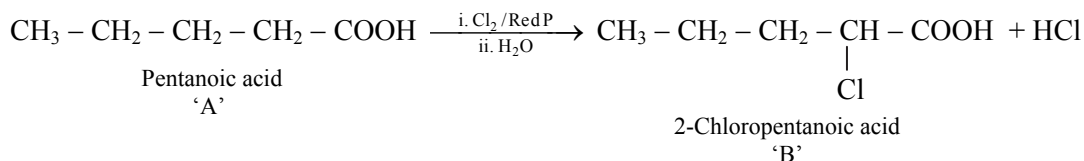
# Organic Reactions



## Hints

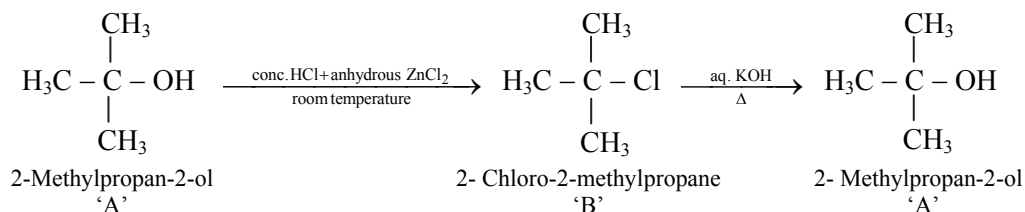


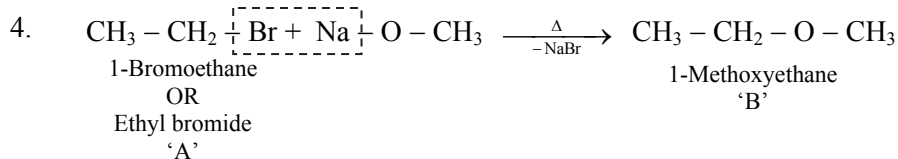
2. As the compound 'A' is a linear chain compound with molecular formula  $\text{C}_5\text{H}_{10}\text{O}_2$  and gives brisk effervescence of  $\text{CO}_2$  when treated with saturated aqueous  $\text{NaHCO}_3$  solution, it is a carboxylic acid with 5 carbons. (i.e.  $\text{CH}_3 - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{COOH}$ , pentanoic acid).



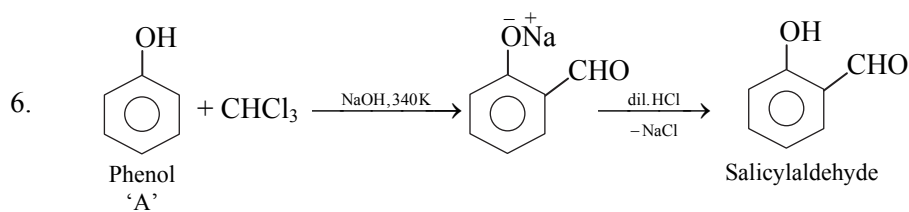
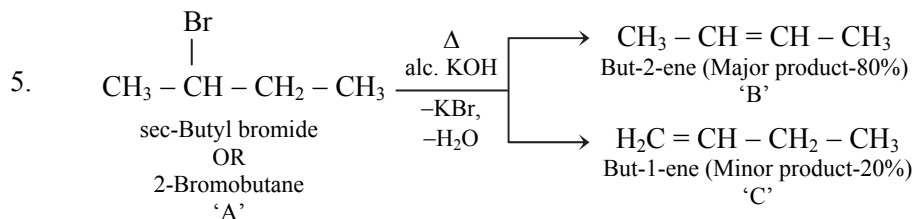
2,2-Dimethylpropanoic acid is the isomer of pentanoic acid but it is achiral. Hence, option (C) is incorrect and option (A) is correct.

3. As the compound 'A' reacts instantaneously with the 'Lucas reagent' (conc.  $\text{HCl}$  + anhydrous  $\text{ZnCl}_2$ ), it is a tertiary alcohol consisting of four carbons [as it gives 'B' ( $\text{C}_4\text{H}_9\text{Cl}$ )].



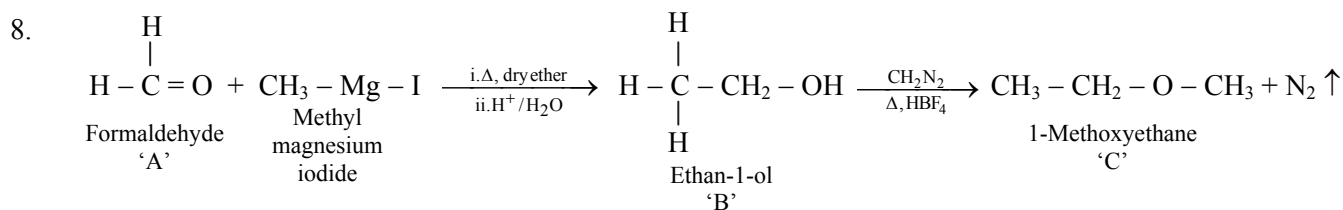
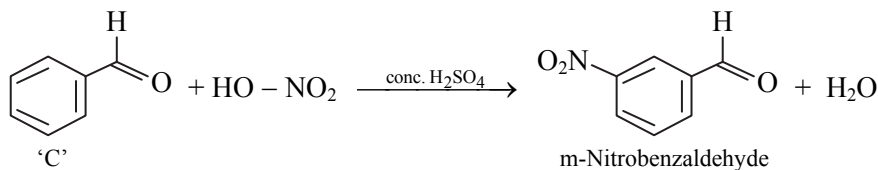
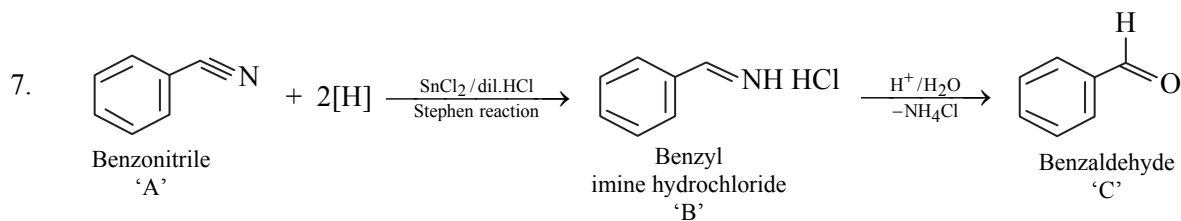
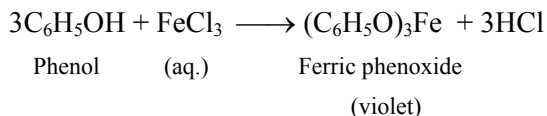


Name of the reaction : Williamson's synthesis



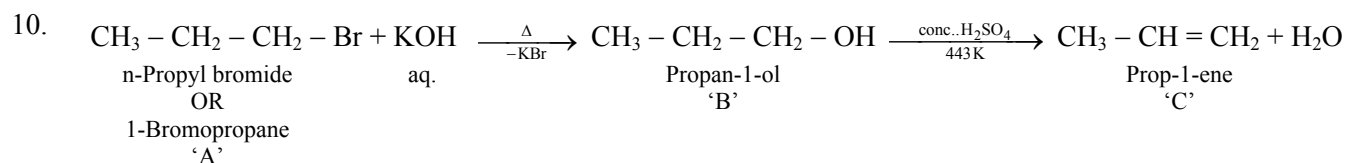
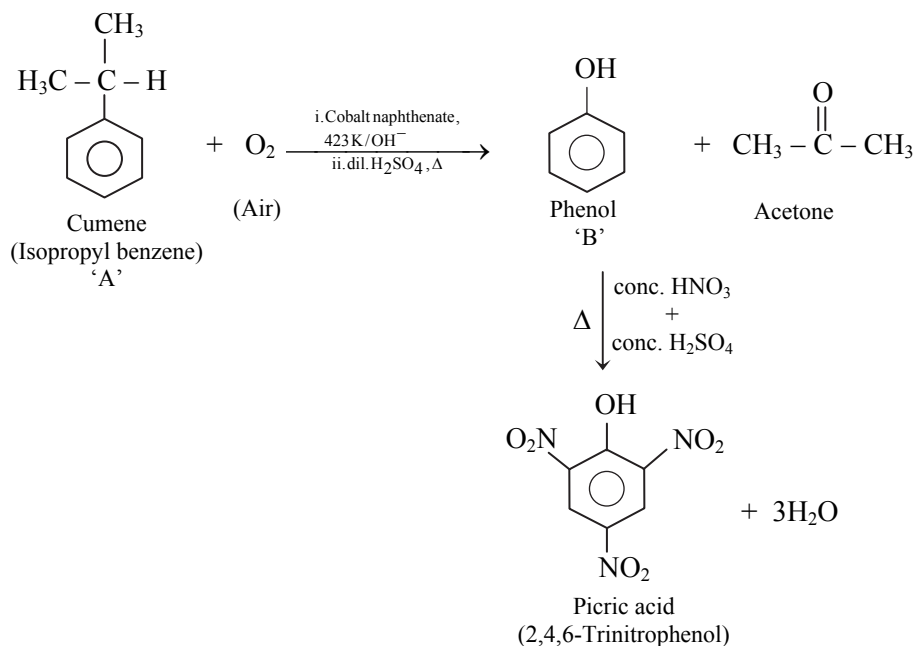
Name of the reaction: Reimer-Tiemann reaction.

Phenol is weak acid. Hence, it turns blue litmus paper red. Phenol forms ferric phenoxide when treated with aq.  $\text{FeCl}_3$  solution. Ferric phenoxide is violet coloured complex.

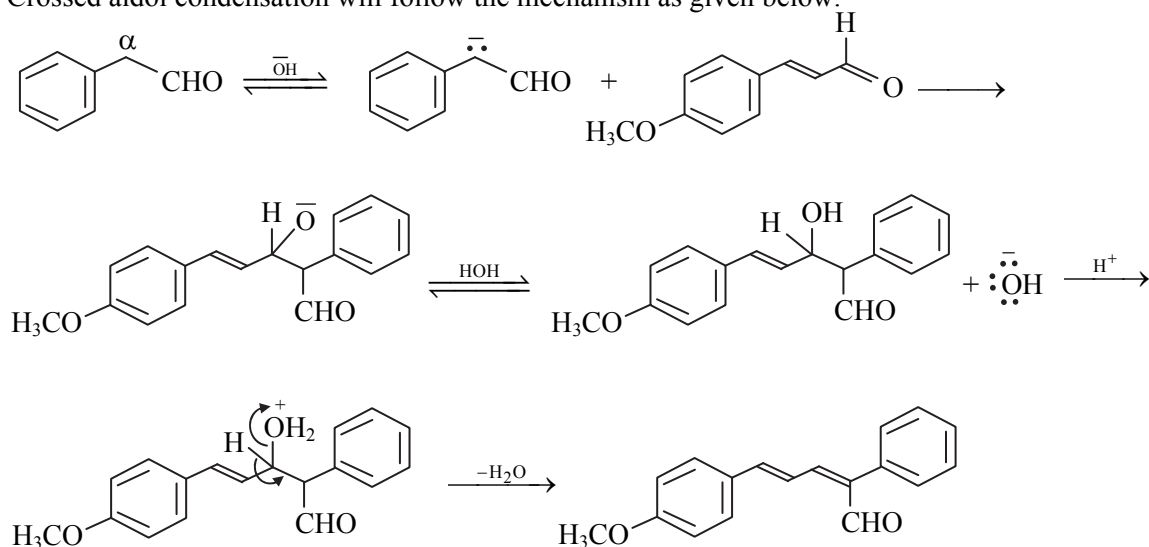
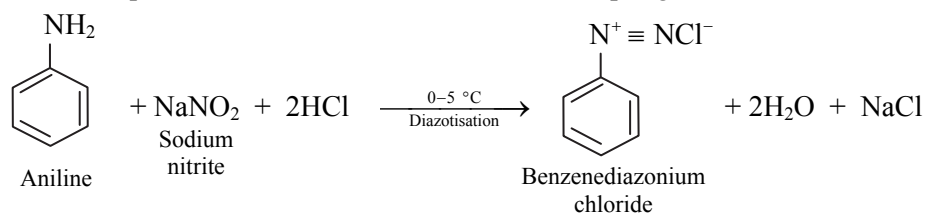


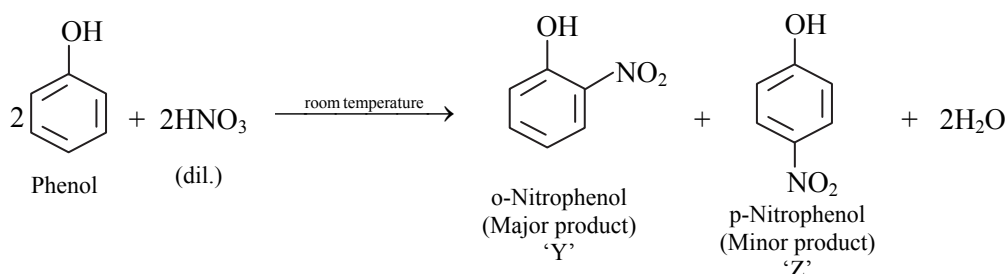
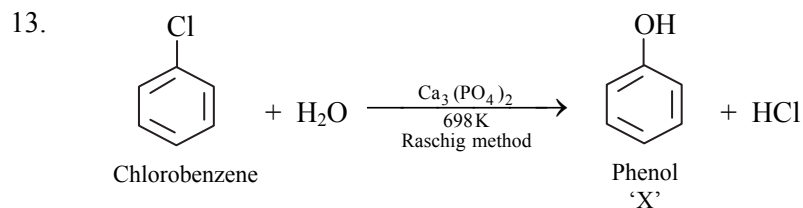
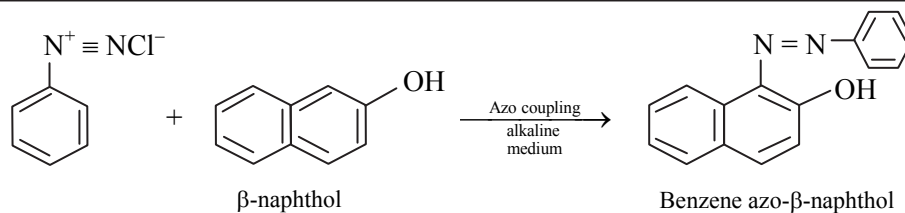


9.

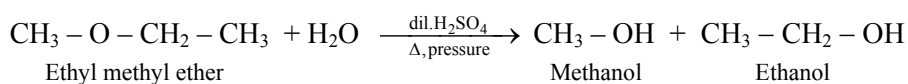


11. Crossed aldol condensation will follow the mechanism as given below.

12. Benzenediazonium chloride (prepared by diazotisation of aniline) is coupled with  $\beta$ -naphthol to give Benzene azo- $\beta$ -naphthol. The reaction is called as 'azo coupling'.



14. i. Wurtz Fittig reaction of two molecules of bromobenzene gives diaryl compound.  
 ii. Bromine is deactivating and ortho-para directing group in case of an electrophilic substitution reaction. The para-substituted product is major product as it is less sterically hindered.
15. As the mixed ether on heating with dil.  $\text{H}_2\text{SO}_4$  gives methanol and ethanol, it is ethyl methyl ether.



Molecular mass of ethyl methyl ether =  $60 \text{ g mol}^{-1}$

Molecular mass of ethanol =  $46 \text{ g mol}^{-1}$

The yield of ethanol obtained =  $80\% = 1.5 \text{ g}$

$$\therefore 100\% \text{ yield of ethanol will be} = 1.5 \times \frac{100}{80} = 1.875 \text{ g}$$

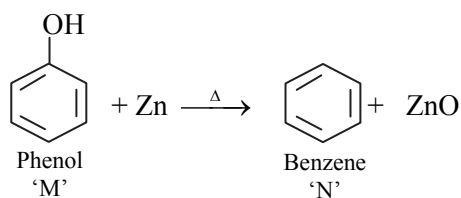
$$\therefore \text{Number of moles of ethanol (100\% yield)} = \frac{1.875\text{g}}{46 \text{ g mol}^{-1}} = 0.04 \text{ mol}$$

Since, 1 mol of ethanol will be formed from 1 mol of ether.

$\therefore$  0.04 mol of ethanol will be formed from 0.04 mol of ether.

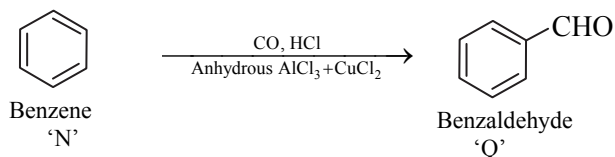
$\therefore$  0.04 mol of ethyl methyl ether =  $0.04 \times 60 = 2.4 \text{ g}$  of ether

16. Phenol gives benzene, when treated with zinc dust.

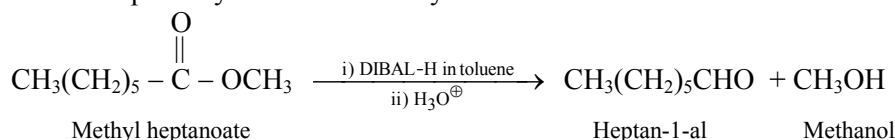




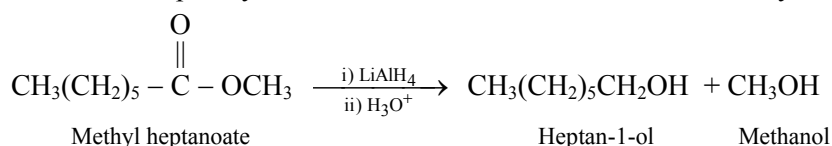
When benzene is treated with CO and HCl under high pressure in the presence of anhydrous  $\text{AlCl}_3$  and  $\text{Cu}_2\text{Cl}_2$ , it gives benzaldehyde and the reaction is called as 'Gatterman-Koch formylation'.



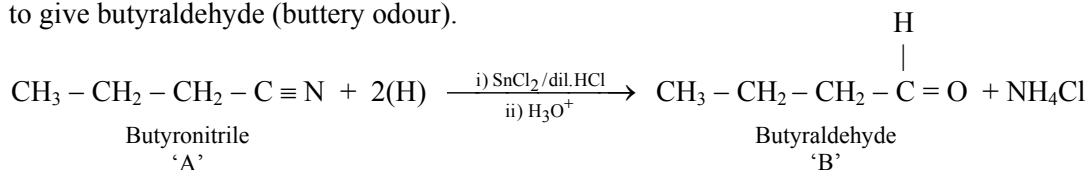
17. Esters are partially reduced to aldehydes with DIBAL-H in toluene followed by acid hydrolysis.



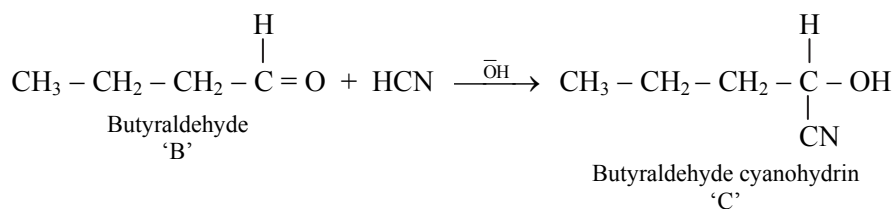
Esters are completely reduced to alcohols with  $\text{LiAlH}_4$  followed by acid hydrolysis.



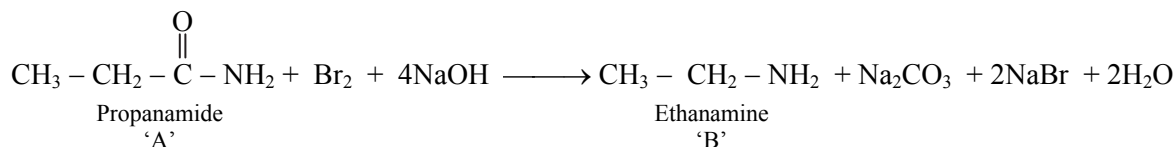
18. Butyronitrile undergoes Stephen reaction in the presence of  $\text{SnCl}_2$  and dil. HCl followed by acid hydrolysis to give butyraldehyde (buttery odour).



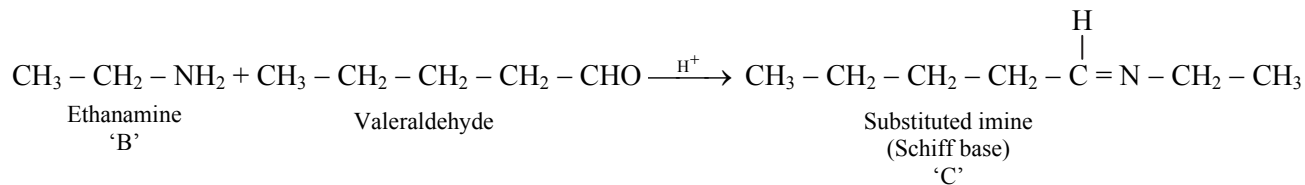
Butyraldehyde on treatment with HCN in the presence of small amount of base gives butyraldehyde cyanohydrin.



19. Propanamide undergoes Hoffmann bromamide degradation in the presence of bromine and alcoholic NaOH to yield ethanamine i.e., compound 'B'.

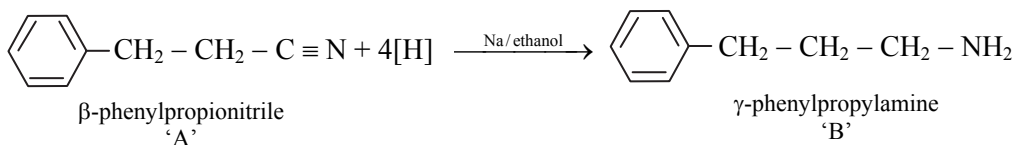


Ethanamine reacts with valeraldehyde in the presence acid catalyst to give corresponding substituted imine i.e., Schiff base.

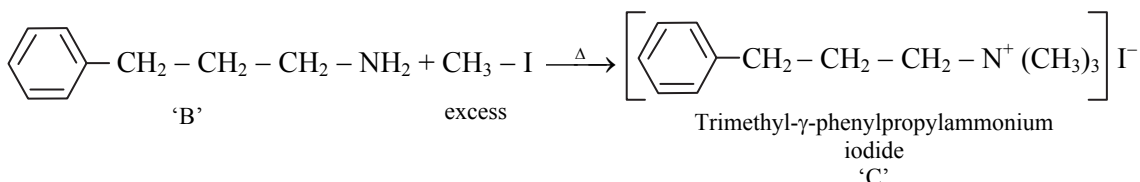




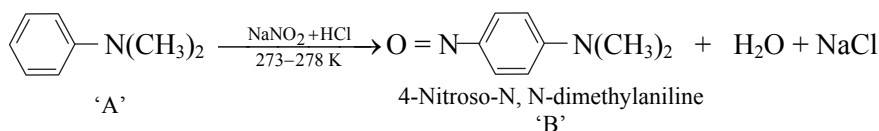
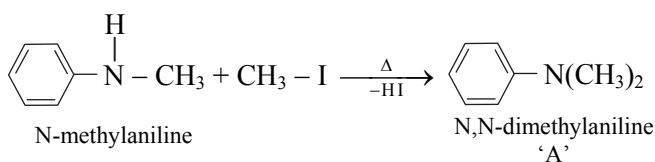
20. Mendius reduction of  $\beta$ -phenylpropionitrile in the presence of sodium and ethanol gives  $\gamma$ -phenylpropylamine ('B').



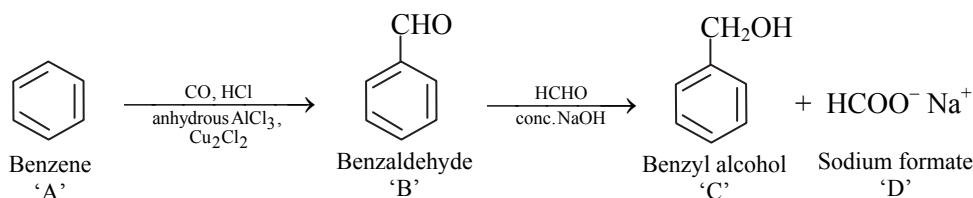
Compound 'B' undergoes Hoffmann's exhaustive methylation when heated with excess of methyl iodide to give tetrasubstituted ammonium iodide.



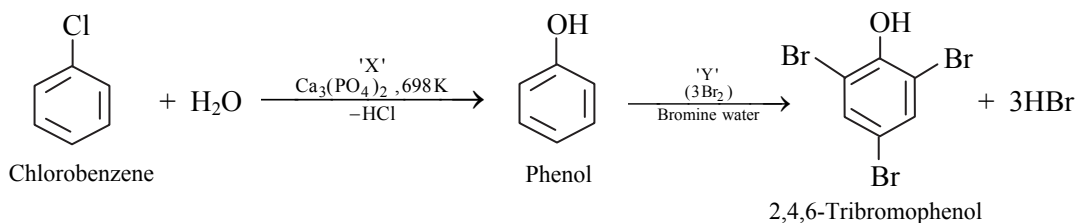
21. Hoffmann methylation of N-methylaniline gives N,N-dimethylaniline i.e., compound 'A'. ( $\text{CH}_3\text{I}$  is not used in excess amount hence, no exhaustive methylation occurs). Nitrosation of 'A' gives compound 'B'.



22. Benzene undergoes Gatterman Koch formylation in the presence of CO, HCl, anhydrous  $\text{AlCl}_3$  and  $\text{Cu}_2\text{Cl}_2$  to give benzaldehyde which on treatment with formaldehyde in the presence of conc. NaOH gives benzyl alcohol and sodium formate. In this crossed Cannizzaro reaction, one of the aldehydes is formaldehyde. Hence the reaction yields exclusively sodium formate.

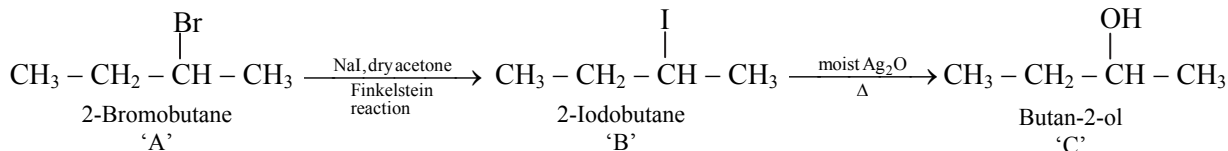


23. Chlorobenzene can be converted into phenol by Raschig method by heating it with steam ( $\text{H}_2\text{O}$ ) at 698 K using  $\text{Ca}_3(\text{PO}_4)_2$  or  $\text{SiO}_2$  as catalyst. Phenol when treated with bromine water gives white precipitate of 2,4,6-tribromophenol.





24. 2-Bromobutane when treated with NaI in the presence of dry acetone gives 2-Iodobutane (Finkelstein reaction). 2-Iodobutane when boiled with moist Ag<sub>2</sub>O (in situ generation of AgOH) gives Butan-2-ol.

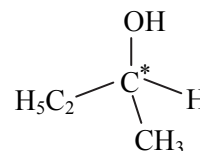


Butan-2-ol (compound 'C') has one chiral carbon atom.

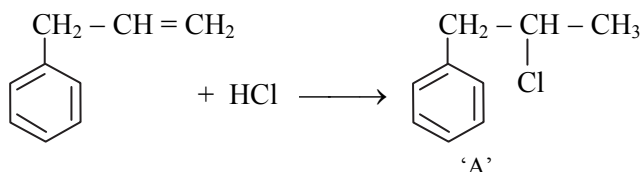
Number of optical isomers = 2<sup>n</sup>

where, n = number of chiral carbon atoms.

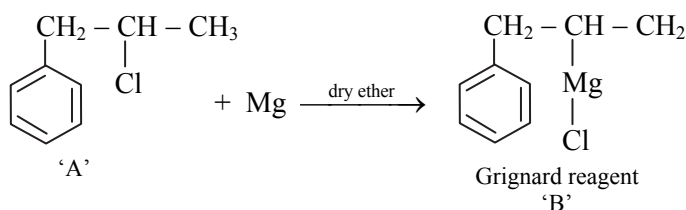
∴ For Butan-2-ol, number of optical isomers = 2<sup>1</sup> = 2



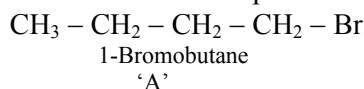
25. In an addition reaction of an unsymmetrical alkene, the negative part of the reagent (Cl<sup>-</sup>) adds to the carbon with less number of hydrogen atoms (Markownikoff's rule).



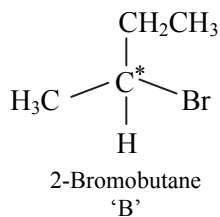
Addition of magnesium metal to the compound 'A' in dry ether gives Grignard reagent i.e., 'B'.



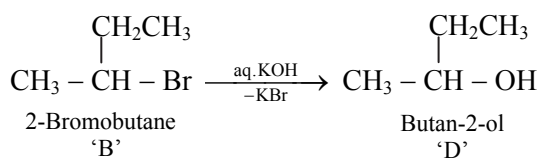
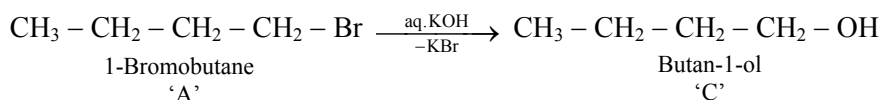
26. The compounds A and B are structural isomers of each other with molecular formula C<sub>4</sub>H<sub>9</sub>Br. Compound A is a linear chain compound and optically inactive. Hence its structure is:



Compound B is optically active isomer of compound A. Hence its structure is as follows:



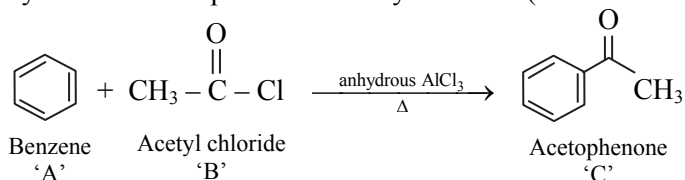
Compounds 'A' and 'B' when treated with aq. KOH solution give butan-1-ol and butan-2-ol respectively.





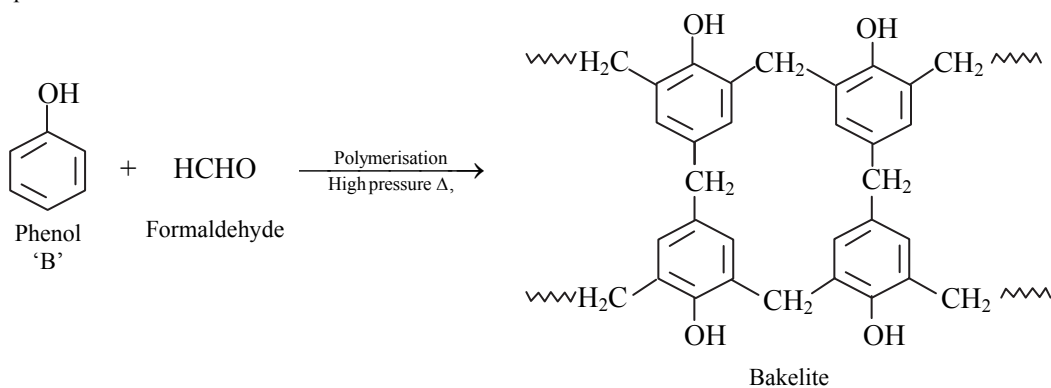
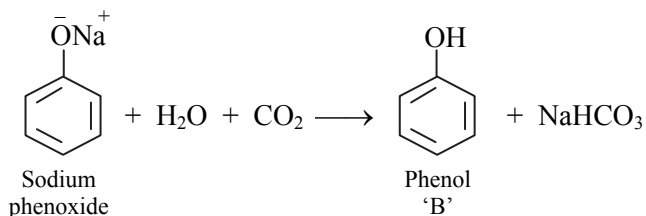


27. Compound 'A' is aromatic hydrocarbon with molecular mass  $78 \text{ g mol}^{-1}$ . Hence it is benzene. Molecular mass of compound B is  $78.5 \text{ g mol}^{-1}$ . When A is treated with B in the presence of anhydrous  $\text{AlCl}_3$ , it gives C which is a methyl ketone (because it gives positive haloform test). The given reaction is Friedel Craft's acylation and compound B is acetyl chloride (molecular mass =  $78.5 \text{ g mol}^{-1}$ ).



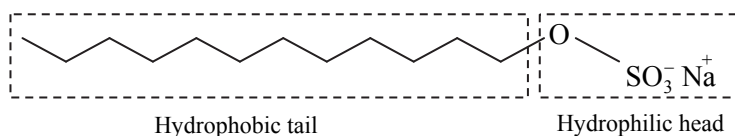
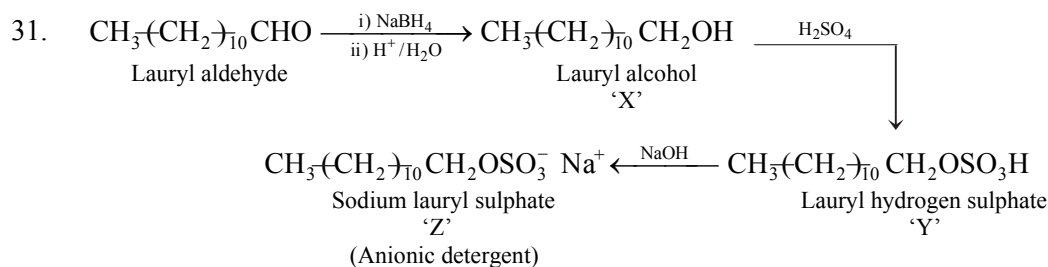
- 28.
- $$\text{Phenol 'A'} \xrightarrow[\text{(Kolbe's reaction)}]{\begin{matrix} \text{i) NaOH} \\ \text{ii) CO}_2 \\ \text{iii) dil. HCl} \end{matrix}} \text{Salicylic acid 'B'} + (\text{CH}_3\text{CO})_2\text{O} \xrightarrow[-\text{CH}_3\text{COOH}]{\text{H}^+} \text{Aspirin (Acetyl salicylic acid)}$$

- 29.
- $$\text{Chlorobenzene 'A'} + 2\text{NaOH} \xrightarrow[300 \text{ atm}]{613 \text{ K (aq.)}} \text{Sodium phenoxide} + \text{NaCl} + \text{H}_2\text{O}$$

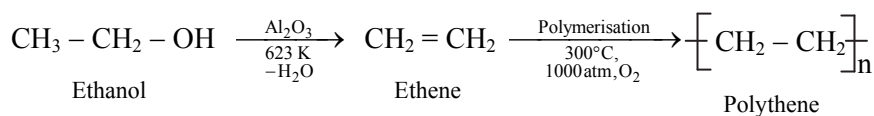


- 30.
- $$\text{CH}_3 - \text{CH}_2 - \text{Br} + \text{NH}_3 (\text{alc.}) \xrightarrow[-\text{CH}_3\text{COOH}]{\text{H}^+} \text{CH}_3 - \text{CH}_2 - \text{NH}_2 + \text{HBr}$$
- Ethanamine 'P'
- $$\downarrow \begin{matrix} \text{HNO}_2 \\ (\text{NaNO}_2 + \text{HCl}) \\ 273 - 278 \text{ K} \end{matrix}$$
- $$\text{CH}_3 - \text{CH}_2 - \text{OH} + \text{N}_2 \uparrow + \text{H}_2\text{O} + \text{NaCl}$$
- Ethanol 'Q'

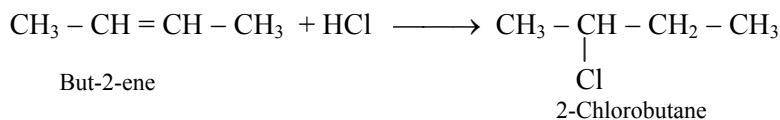
Molecular weight of  $\text{CH}_3 - \text{CH}_2 - \text{OH} = 46 \text{ g mol}^{-1}$ .



32. Polythene can be prepared by polymerisation of ethene which in turn can be prepared by passing vapours of ethanol over heated alumina ( $\text{Al}_2\text{O}_3$ ) at 623 K.



34. When but-2-ene is treated with conc. HCl, 2-chlorobutane is obtained.



Molar mass of But-2-ene =  $56 \text{ g mol}^{-1}$

Molar mass of 2-chlorobutane =  $92.5 \text{ g mol}^{-1}$

Given weight of but-2-ene = 5.6 g

$$\therefore \text{Number of moles of but-2-ene} = \frac{5.6 \text{ g}}{56 \text{ g mol}^{-1}} = 0.1 \text{ mol}$$

0.1 mol of but-2-ene will give 0.1 mol of product i.e. 2-chlorobutane.

$$\therefore \text{Mass of 2-chlorobutane obtained will be} = 0.1 \times 92.5 = 9.25 \text{ g}$$

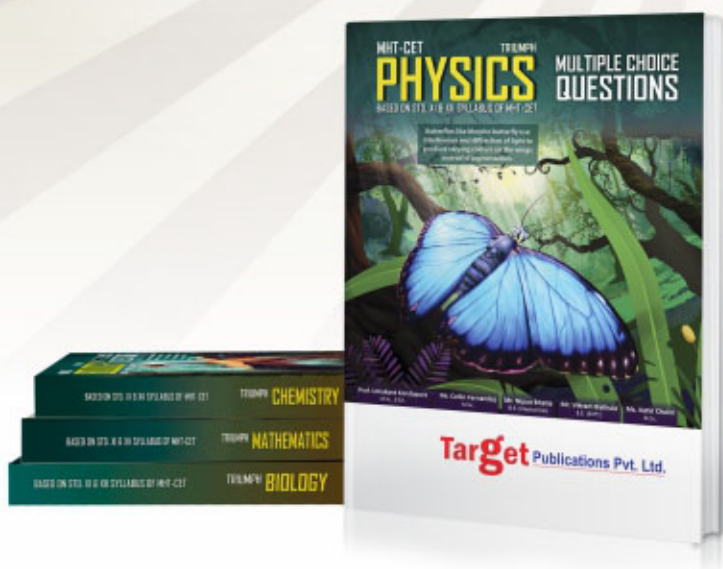
However, yield of the reaction is 50%

$$\therefore \text{Mass of 2-chlorobutane obtained} = 9.25 \times \frac{50}{100} = 4.625 \text{ g}$$



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